RSC Advances

REVIEW

View Article Online
View Journal | View Issue

Glymes as versatile solvents for chemical reactions and processes: from the laboratory to industry

Cite this: *RSC Adv.*, 2014, **4**, 11251

Shaokun Tang[a] and Hua Zhao*[b]

Glymes, also known as glycol diethers, are saturated non-cyclic polyethers containing no other functional groups. Most glymes are usually less volatile and less toxic than common laboratory organic solvents; in this context, they are more environmentally benign solvents. However, it is also important to point out that some glymes could cause long-term reproductive and developmental damage despite their low acute toxicities. Glymes have both hydrophilic and hydrophobic characteristics that common organic solvents lack. In addition, they are usually thermally and chemically stable, and can even form complexes with ions. Therefore, glymes are found in a broad range of laboratory applications including organic synthesis, electrochemistry, biocatalysis, materials, Chemical Vapor Deposition (CVD), *etc.* In addition, glymes are used in numerous industrial applications, such as cleaning products, inks, adhesives and coatings, batteries and electronics, absorption refrigeration and heat pumps, as well as pharmaceutical formulations, *etc.* However, there is a lack of a comprehensive and critical review on this attractive subject. This review aims to accomplish this task by providing an in-depth understanding of glymes' physicochemical properties, toxicity and major applications.

Received 6th October 2013
Accepted 9th December 2013

DOI: 10.1039/c3ra47191h

www.rsc.org/advances

1. Introduction

Glymes, *i.e.* glycol diethers, are saturated polyethers containing no other functional groups. When compared with glycols (such as polyethylene glycols, PEGs), glymes do not carry free hydroxyl groups and thus are aprotic polar and chemically inert compounds. There are two major types of glymes: ethylene oxide (EO)-based glymes (also known as PEG-based) and propylene oxide-based glymes (*i.e.* polypropylene glycol (PPG)-based). The general structure of PEG-based glymes and their common names are illustrated in Scheme 1.

Most glymes are completely miscible with both water and hydrocarbon solvents, and could solvate alkali cations. In addition, glymes have many other favorable properties including being liquid at a wide range of temperatures (typically >200 °C, except monoglyme), low viscosity, high chemical and thermal stability, relatively low vapor pressure and low toxicity. Due to these excellent solvent properties, glymes have been widely used in many laboratory and commercial applications including reaction media (*i.e.* organometallic reactions, polymerization, and reactions involving alkali metals, oxidations and reductions), extraction solvents (for metals and organics), gas purification, absorption refrigeration, formulation of adhesives and coatings, textiles, solvents for

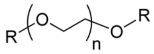
---

[a] Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, China

[b] Department of Chemistry and Forensic Science, Savannah State University, Savannah, GA 31404, USA. E-mail: huazhao98@gmail.com; zhaoh@savannahstate.edu

Shaokun Tang was born in 1974, and graduated from Tianjin University (China) with BS, MS and PhD degrees in Chemical Engineering. She was a research fellow at the National University of Singapore from 2007 to 2008. She is currently an Associate Professor at Tianjin University. She was awarded "Excellent Teacher" of Tianjin University. Her major research interests focus on green chemistry (catalytic preparation of biofuels, supercritical fluid technology for natural compounds extraction, and ionic liquids for renewable energy), as well as functional materials & nanotechnology (controlled synthesis and functionalization of nanostructured materials).

Hua Zhao studied chemistry (BS) and chemical engineering (MS) at Tianjin University (China) before he earned his PhD degree in 2002 from New Jersey Institute of Technology (NJIT) and completed a post-doctoral training at Rutgers University. He is currently an Associate Professor of Chemistry at Savannah State University. He became fascinated with new solvents at graduate school while working on organic synthesis and enzymatic resolution of amino acids in aqueous ionic liquids. His current research interests include biocatalysis in ionic liquids and glymes, preparation of biofuels using ionic liquids and glymes, synthesis of medicinal molecules with anti-cancer and anti-HIV properties, and microwave-assisted enzymatic reactions.



R	n	Common name	Symbol
Me	1	Monoglyme	G1
Me	2	Diglyme	G2
Me	3	Triglyme	G3
Me	4	Tetraglyme	G4
Et	1	Ethyl glyme	G1-Et
Et	2	Ethyl diglyme	G2-Et
Bu	1	Butyl glyme	G1-Bu
Bu	2	Butyl diglyme	G2-Bu
Me	n	Polyglyme	PEG-DME

Scheme 1 Structure of EO-based glymes, and representative common names and symbols.

electronic industry, pharmaceutical formulation, batteries, cleaning solutions, *etc.*

Despite numerous studies on glymes, there is a lack of a comprehensive and critical review on this subject to meet the continuing interest in glymes; in recent years, there has been a strong focus on their applications in electrochemistry, catalysts, Chemical Vapor Deposition (CVD), nanomaterials, and the dissolution of CO_2. This review aims to provide a comprehensive set of physicochemical properties of glymes and a systematic overview of their applications, as well as a critical analysis of their structure–property–application relationships. To be focused on the subject, glycol monoethers and glycol ether esters are not discussed herein as their physical properties, toxicity and applications have been reviewed elsewhere.[1–3]

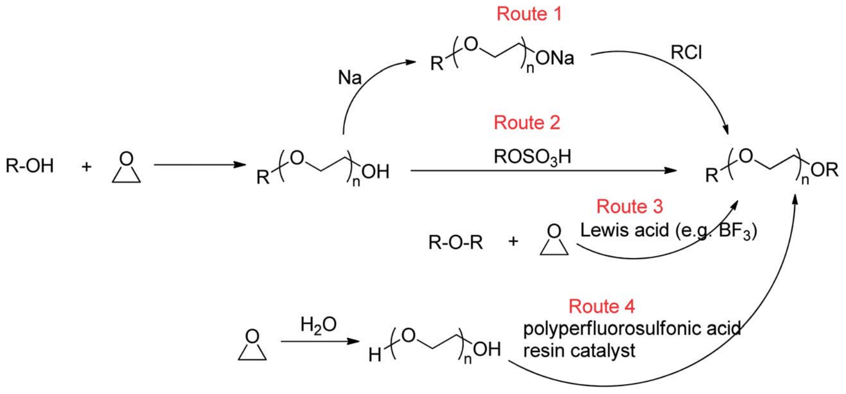
2. Preparations of glymes

Ethylene oxide (EO)-based glymes can be prepared by several common methods on large scales using ethylene epoxide (Scheme 2): Route 1, ethylene oxide reacts with an alcohol to produce glycol monoether, which is further converted to glyme following the Williamson synthesis (*i.e.* glycol ether reacts with sodium to yield sodium alkoxide, which then reacts with alkyl halide to produce the glyme); Route 2, methylation of glycol ether with methyl sulfate; Route 3, Lewis acid-catalyzed cleavage of ethylene oxide by ether, typically resulting in glyme mixtures; Route 4, the reaction of ethylene glycol with alcohol catalyzed polyperfluorosulfonic acid resin at high temperature and pressure. Similarly, propylene oxide-based glymes can be prepared by replacing ethylene oxide with propylene oxide in the above methods.

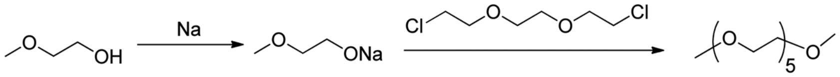
In addition, Haymore *et al.*[4] described a two-step synthesis of pentaglyme (Scheme 3): the reaction of 2-methoxyethanol with sodium metal to yield an alkoxide followed by a nucleophilic substitution of dichloride. Adcock and Lagow[5] prepared perfluoroglyme and perfluorodiglyme as potential high stability fluids and solvents through a direct fluorination method (fluorine gas).

3. Toxicity of glymes

In general, glymes exhibit low to moderate *acute toxicity* (see toxicity data in Tables 1 and 2) when compared with common organic solvents (such as toluene, THF and chloroform). Ethylene glycol dimethyl ether (monoglyme) triggered maternal deaths of pregnant Sprague-Dawley rats at 1000 mg per kg per day and was fetolethal at doses ranging from 120 to 1000 mg per kg per day; a dose of 60 mg per kg per day caused a 7% weight decrease and severe edema in pups surviving to birth.[6] When rats were exposed to 200 ppm diglyme vapor for an extended period of time (15 × 6 h), no toxic effect was observed in terms of normal blood and urine tests and normal organs by autopsy; however, at a higher vapor concentration (600 ppm) for the same period of time, irregular weight gain was observed and



Scheme 2 Common routes for glyme synthesis.



Scheme 3 Synthesis of pentaglyme.

autopsy suggested atrophied thymus and congested adrenals although the blood and urine tests were normal.[7]

However, there is a rising concern that glymes may cause *reproductive and developmental harm* to exposed workers and consumers using paint, carpet cleaners, inkjet cartridges and other products. McGregor *et al.*[8] studied the exposure of male rats to 250 or 1000 ppm diglyme, and found that diglyme was a reproductive toxicant causing increased sperm abnormalities. Schuler *et al.*[9] examined fifteen glycol ethers for their adverse reproductive toxic effects using an *in vivo* mouse screening bioassay; this group found that all mice exposed to glycol ethers with terminal methyl groups, *i.e.*, ethylene glycol monomethyl ether, monoglyme, diethylene glycol monomethyl ether, diglyme and triglyme produced few viable litters (0, 0, 16, 0, and 0%, respectively); similar results were also observed for ethylene glycol monoether ether and ethyl monoglyme (0 and 11% viable litters, respectively). However, two other ethyl ethers (diethylene glycol monoethyl ether and ethyl diglyme), three butyl ethers (ethylene glycol monobutyl ether, diethylene glycol monobutyl ether, butyl diglyme), and three glycol ethers with terminal hydroxyl groups (ethylene glycol, diethylene glycol and triethylene glycol) failed to show this kind of fetotoxicity. They also suggested that: (1) the appending of an alkyl group considerably increased the maternal toxicity of glycols. For example, ethyl glycol monobutyl ether appeared to be more toxic than ethylene glycol monomethyl ether, which was more toxic than ethylene glycol monoethyl ether; but all three showed greater toxicity than ethylene glycol. The diethylene glycol mono-alkyl ethers and (alkyl) diglymes were more toxic than diethylene glycol, and triglyme was more toxic than triethylene glycol. (2) Methyl ethers usually seem more toxic than ethyl or butyl ethers, except for ethylene glycol monobutyl ether. Similarly, Johnson *et al.*[10] found that butyl diglyme was more toxic than diethylene glycol, but did not induce significant developmental toxicity to the hydra.

A review[11] on the genetic toxicology of glycol ethers suggested that diglyme lacks genotoxic potential in some mutagenicity tests, but it was a reproductive toxicant in the mouse sperm test and male rat dominant lethal test. Repeated daily oral doses of diglyme at 684 mg kg^{-1} in a subchronic study of Sprague-Dawley rats suggested the onset of testicular pathology, which was similar to the pathology of equal molar doses of 2-methoxyethanol or 2-ethoxyethanol.[12] Furthermore, it was confirmed that there were two major metabolites of the testicular toxin (*e.g.* diglyme), (2-methoxyethoxy)acetic acid (MEAA) (*ca.* 70%) and methoxyacetic acid (MAA) (*ca.* 6%), along with several other unidentified metabolites, and two major metabolism pathways; however, only MAA is accounted for in the reproductive toxicity of diglyme.[13–15] Hardin and Eisenmann[16] gave time-mated CD-1 mice oral doses of glycol ethers at a dose of 4 mmol kg^{-1} on gestation day 11, and then examined fetuses on gestation day 18 for weight and gross external malformations. All four glycol ethers (ethylene glycol monomethyl ether, monoglyme, diglyme and triglyme) exhibited no treatment-

Table 1 Estimated toxicity for glymes and common organic solvents[a]

Solvent	Oral rat LD_{50} (mg kg^{-1})	Bioaccumulation factor	Developmental toxicity	Mutagenicity
Ethanol	(7055[b])	1.28	(1.00,[c] Toxicant)	−0.10 (+)[e]
Toluene	1083 (636[b])	48.88	0.29 (non)	−0.01 (−)
Benzene	2030 (931[b])	30.78	0.29	0.03 (+)
THF	932 (1652[b])	2.67	0.48	0.05 (−)
Chloroform	1794 (695[b])	5.07 (6.30 (ref. 19))	0.67 (Toxicant)	0.45 (−)
Monoglyme	2997	1.66	0.59 (Toxicant[17])	0.59 (1.00[d]) (+)
Diglyme	3779 (5404[b])	2.04	0.43 (Toxicant[17])	0.38
Triglyme	6496	1.73	0.36	0.18 (1.00[d]) (+)
Tetraglyme	5146 (5140[b])	6.97	−0.10	0.23
Pentaglyme	5604	2.85	−0.10	0.33
Hexaglyme	6112	6.02	−0.06	0.26
Ethyl glyme	3949 (3619[b])	4.60	0.32 (Toxicant[17])	0.20
Butyl glyme	4427 (3253[b])	24.33	0.47	0.05
Ethyl diglyme	6818 (4968[b])	5.82	0.26	0.16
Butyl diglyme	3378 (3901[b])	15.57	0.05	0.23

[a] Toxicity was estimated with the consensus method using Toxicity Estimation Software Tool (TEST) (http://www.epa.gov/nrmrl/std/qsar/qsar.html); disclaimer: these estimated values are for research and evaluation purposes, not for guiding clinical or production applications. [b] Experimental values from the ChemidPlus database (http://chem.sis.nlm.nih.gov/chemidplus/). [c] Experimental values from the CAESAR database (http://www.caesar-project.eu/index.php?page=results&section=endpoint&ne=5). [d] Experimental values from the Toxicity Benchmark database (http://doc.ml.tu-berlin.de/toxbenchmark/). [e] '+' means mutagenicity positive, '−' means mutagenicity negative.

Table 2 Physical and thermodynamic properties of glymes

Glyme	Freezing point (°C)	Boiling point (°C)	Dynamic viscosity (mPa s) at 20 °C	p (mm Hg)[d] at 20 °C	Density (g mL^{-1})[v] at 25 °C	Flash point[e] (°C)	LD_{50}[f] (mg kg^{-1})	Solubility (20 °C)
Monoglyme (G1)	−69.0[b,c,h]	85.2,[b,h] 85,[c] 84.5[mm]	0.4236,[o] 0.432,[q] 0.417,[bb] 0.420,[c] 0.455,[ll] 1.1 (20 °C)[b,h]	54[b,h]	0.86124,[j] 0.86207,[n] 0.86132,[o] 0.8605,[q] 0.8613,[s] 0.86114,[t,u] 0.864,[w] 0.86260,[y] 0.86155,[z] 0.8615,[bb] 0.8626,[cc,dd] 0.8612,[ii] 0.859,[ll] 0.86370,[mm], 0.8683 (20 °C),[b,h] 0.867 (20 °C),[c] 0.86765 (20 °C),[gg]	−6[b,c,h]	5370[b]	Miscible with H_2O
Ethyl glyme (G1-Et)	−74.0[b,h]	121,[b] 121.4,[h] 121.2[mm]	0.593,[bb] 0.7 (20 °C),[b] 0.65 (20 °C)[h]	9,[b] 9.4[h]	0.83607,[z] 0.8362,[aa] 0.8360,[bb] 0.83510,[mm] 0.8417 (20 °C),[b,h]	27[b]	4400[b]	20.4% in H_2O, 3.3% H_2O in[b]
Butyl glyme (G1-Bu)	−69.1[h]	203.6,[h] 206 (dec)[mm]		0.09[h]	0.83189,[mm] 0.8374 (20 °C)[h]	85[h] (open cup)		0.2 wt% in H_2O, 0.6 wt % H_2O in[h]
Diglyme (G2)	−64.0,[a,c] −70,[g] −68[h]	162[a,c,g]	0.981,[m] 1.06,[x] 0.989,[bb] 0.985,[cc] 0.991,[jj] 0.976,[nn] 2.0 (20 °C),[b,h] 1.14(20 °C)[x]	2,[b] 3.0 (100 °C)[h]	0.93873,[j] 0.93882,[k] 0.93924,[l] 0.9394,[m] 0.93892,[n] 0.93871,[t] 0.93935,[u] 0.938,[w] 0.93897,[y] 0.93875,[z] 0.9385,[bb] 0.9389,[cc] 0.9399,[jj] 0.9397,[kk] 0.93961,[nn], 0.9434 (20 °C),[a] 0.944 (20 °C),[c] 0.945 (20 °C),[g,h] 0.94511 (20 °C)[gg]	57,[b] 51[c]	4670[b]	Miscible with H_2O, ethanol, diethyl ether
Ethyl diglyme (G2-Et)	−44.3[b]	189[b]	1.238,[bb] 1.241,[cc] 1.4 (20 °C)[b]	0.5[b]	0.9082 (20 °C),[b] 0.9028,[z] 0.9021,[bb] 0.9035[cc]	90[b]	5000[b]	Miscible with H_2O
Butyl diglyme (G2-Bu)	−60.2,[b] −60[c]	256[b,c]	2.122,[cc] 2.4 (20 °C)[b]	<0.01[b]	0.8814 (20 °C),[b] 0.884 (20 °C),[c] 0.87830,[z] 0.8781[cc]	118,[b] 120[c]	3900[b]	0.3% in H_2O, 1.4% H_2O in[b,c]
Triglyme (G3)	−43.8,[a] −40,[c] −45.0[h]	218,[a] 220,[c] 216[h]	1.96,[nn,r] 2.16,[x] 1.950,[cc] 3.8 (20 °C),[b,h] 2.41 (20 °C)[x]	0.02[b,h]	0.98001,[i] 0.98067,[j] 0.98117,[l] 0.9795,[r] 0.98058,[t,u] 0.981,[w] 0.98071,[y] 0.9807,[cc] 0.98042,[ee] 0.97981,[ff] 0.98023,[nn], 0.986 (20 °C),[a,h] 0.987 (20 °C),[c] 0.98569 (20 °C),[gg] 0.98541 (20 °C)[hh]	111,[b,h] 113[c]	5000[b]	Very soluble in H_2O, benzene
Tetraglyme (G4)	−29.7,[b,h] −30[c]	275[b,c,h]	3.295,[p] 3.67,[x] 3.40,[nn] 4.1 (20 °C),[b,h] 4.18 (20 °C)[x]	<0.01[b,h]	1.00662,[i] 1.00564,[j] 1.00627,[l] 1.0047,[p] 1.00666,[t] 1.00668,[u] 1.00628,[y] 1.00620,[ee] 1.00743,[nn,] 1.0132 (20 °C),[b,h] 1.0 (20 °C),[c] 1.0116 (20 °C),[gg] 1.01115 (20 °C)[hh]	141[b,c,h]	5100[b]	Miscible with H_2O
Proglyme (P2)	−71[b], −80[c]	175[b,c]	1.1 (20 °C)[b]	0.55[b]	0.900 (20 °C)[b,c]	65[b,c]	—	35% in H_2O, 4.5% H_2O in[b,c]
PEG-DME 200	−37[c]	>300[c]	4.3 $mm^2 s^{-1}$ (20 °C)[c]	—	1.01–1.02 (20 °C)[c]	154[c]	—	
PEG-DME 250	−23[c]	>300[c]	7 $mm^2 s^{-1}$ (20 °C),[c] 7.215 $mm^2 s^{-1}$ (20 °C),[gg]	—	1.02–1.04 (20 °C),[c] 1.0355 (20 °C)[gg]	137[c]	—	
Polyglyme (MW = 236)[b]	−28[b]	275[b]	12 (20 °C)[b]	0.01[b]	1.03(20 °C)[b]	135[b]	—	
Polyglyme (MW = 275)[b]	−23[b]	275[b]	12 (20 °C)[b]	<0.01[b]	1.04 (20 °C)[b]	>130[b]	—	Miscible with H_2O
Higlyme (MW > 400)[b]	-5–10[b]	>300[b]	34 (20 °C)[b]	0.1[b]	0.975 (20 °C)[b]	140[b]	—	Miscible with H_2O

Table 2 (*Contd.*)

Glyme	Freezing point (°C)	Boiling point (°C)	Dynamic viscosity (mPa s) at 20 °C	p (mm Hg)[d] at 20 °C	Density (g mL^{-1})[v] at 25 °C	Flash point[e] (°C)	LD$_{50}$[f] (mg kg^{-1})	Solubility (20 °C)
PEG-DME 500	13[c]	>300[c]	25 mm^2 s^{-1} (20 °C)[c]	—	1.05 (50 °C)[c]	220[c]	—	
PEG-DME 1000	36[c]	>300[c]	11 mm^2 s^{-1} (100 °C)[c]	—	1.10 (50 °C)[c]	260[c]	—	
PEG-DME 2000	50[c]	>300[c]	30 mm^2 s^{-1} (100 °C)[c]	—	1.08 (60 °C)[c]	254[c]	—	

[a] Ref. 40. [b] Production specifications from Novolyte Technologies (now a part of BASF). [c] Production specifications from Clariant (viscosity is kinematic viscosity). [d] Vapor pressure. [e] Closed cup. [f] Acute toxicity. [g] Ref. 41. [h] Ref. 42. [i] Ref. 43. [j] Ref. 44. [k] Ref. 45 (this reference also reported other thermodynamic properties of diglyme at 25 °C such as dipole moment $\mu = 1.87$ D, heat capacity $C_\mathrm{p} = 276.9$ J mol^{-1} K^{-1}, *etc.*). [l] Ref. 46. [m] Ref. 47. [n] Ref. 48. [o] Ref. 49 (densities and viscosities of monoglyme at 308.15 K and 318.15 K were also reported). [p] Ref. 50. [q] Ref. 51. [r] Ref. 52 (this reference also reported a dielectric constant of 7.62 as well as refractive index and molar refraction for triglyme). [s] Ref. 53. [t] Ref. 54. [u] Ref. 55. [v] Density data for monoglyme and diglyme were reported at temperatures between 293.15 K and 353.15 K and up to 60 MPa.[56] [w] Ref. 57. [x] Ref. 58. [y] Ref. 59 (density data at 288.18 and 308.15 K were also reported). [z] Ref. 60. [aa] Ref. 61. [bb] Ref. 62 (densities and viscosities were reported for several glymes from 288.15 K to 343.15 K). [cc] Ref. 63. [dd] Ref. 64. [ee] Ref. 65. [ff] Ref. 66. [gg] Ref. 67 (densities, kinematic viscosities and heat capacities were reported for several glymes including pentaethylene glycol dimethyl ether from 283.15 to 423.15 K). [hh] Ref 68 (data on density, isentropic compressibility and isothermal compressibility of triglyme and tetraglyme were reported at 293.15–353.15 K and 0.1–100 MPa). [ii] Ref. 69. [jj] Ref. 70. [kk] Ref. 71. [ll] Ref. 72. [mm] Ref. 73 (densities, refractive indexes, and boiling points of other 1,2-disubstituted ethylene glycol derivatives such as propyl glyme were also reported). [nn] Ref. 74.

related maternal toxicity and no impact on the intrauterine survival; in addition, no treatment-related gross external malformations other than paw defects were reported. Except for triglyme, the other three glycol ethers produced different degrees of paw defects: 87.5% of ethylene glycol monomethyl ether-treated litters (68.5% of fetuses), 86.7% of monoglyme-treated litters (33.8% of fetuses), and 77.8% of diglyme-treated litters (39.7% of fetuses).

In conclusion, although glymes show low to moderate acute toxicity, they have raised concerns regarding chronic exposure and reproductive effects. Therefore, glymes are recommended as benign solvents for industrial applications, not consumer products. The U.S. Environmental Protection Agency (EPA) announced in July 2011 that three glymes pose "high concern to workers, consumers and children" because they may have reproductive or developmental effects: monoglyme and diglyme caused reproductive and developmental damage in rodent studies, and animal studies on ethyl glyme exhibited developmental toxicity and the potential for gene mutation; EPA also plans to restrict new uses of 11 other glymes in the U.S. marketplace.[17] Since lower molecular weight glymes have shown reproductive toxicity in rats and mice, only higher molecular weight glymes should be used in pharmaceutical applications. In the European Union, products containing monoglyme or diglyme have been regulated; their labels must indicate "may impair fertility" or "may cause harm to the unborn child." On the contrary, dipropylene glycol dimethyl ether is known as a very versatile and environmentally friendly solvent. It is not listed as a hazardous air pollutant (HAP), and it has been shown that propylene-based glycol ethers are less toxic than those ethylene-based glycol ethers.[18]

Although toxicity and biodegradability data are not readily available for many glymes, models based on Quantitative Structure Activity Relationships (QSARs) can be used to predict measures of toxicity from physical characteristics of chemical structures. As shown in Table 1, although there are differences between estimated and experimental values, the estimated toxicity may be used as an empirical evaluation of glymes. In general, the estimated toxicity data in Table 1 are consistent with earlier discussions based on experimental data: glymes have low acute toxicity (high oral rat LD$_{50}$ values when compared with common organic solvents), however, there are concerns of their developmental toxicity and mutagenicity. Except for butyl glymes, methyl- and ethyl glymes seems to have relatively low bioaccumulation factors.

4. Physicochemical and metal complexing properties of glymes

4.1. General properties

Glymes are dipolar aprotic solvents with high chemical stability. They are usually stable under neutral and basic conditions, and only undergo pyrolysis under acidic conditions to form methanol and oxycarbonium ions.[20] Some of their common physical and thermodynamic properties are systematically compiled in Table 2. Typically, glymes have high boiling points and a wide range of temperature at which they are liquid (>200 °C, or even >300 °C) except monoglyme. In contrast to some volatile organic solvents, most glymes have very low vapor pressures (<0.5 mmHg at 20 °C) except mono- and diglyme. Many simple glymes have low viscosities in the range 1–4 mPa s at 20 °C. Most glymes are completely miscible with both water and organic solvents (such as ethanol, acetone, benzene, and octane), and tend to solvate cations in the same way as crown ethers. They are also outstanding solvents for many organic materials (including triglycerides[21,22]). Different polarity measures of several glymes are listed in Table 3; dipole moments and dielectric constants increase with the increase in ethylene oxide chain length. The solvatochromic polarity scales in Table 3 also follow the same trend and confirm that glymes

Table 3 Polarity and heat capacity of several glymes

Glyme	Dipole moment (D) at 25 °C	Dielectric constant at 25 °C	Solvatochromic polarity[23]		Heat capacity at 25 °C (J mol^{-1} K^{-1})
			$E_T(30)$, kcal mol^{-1}	E_T^N	
Monoglyme	1.62,[75] 1.61,[57] 1.59,[76] 1.71 (in benzene)[76]	7.18,[77] 7.20,[72] 7.55[78]	38.2	0.231	191.14[79]
Diglyme	1.91,[75] 1.92,[57,76] 1.87,[45] 1.97 (in benzene)[76]	7.4[80]	38.6	0.244	277.76,[79] 276.9,[45] 279.05[81]
Triglyme	2.16,[57,76] 2.22 (in benzene)[76]	7.62[52]	38.9	0.253	367.78,[79] 367.30[66]
Tetraglyme	2.44,[76] 2.45[55,76]	—	—	—	457.10[79]

are generally less polar than methanol ($E_T^N = 0.762$) and acetone (0.355) but more polar than THF (0.207).[23]

Proton affinity (PA) is a direct measure of gas-phase basicities of organic molecules. Meot-Ner[24] calculated the proton affinities (in kcal mol^{-1}) from measurements by pulsed high-pressure mass spectrometry as: monoglyme (205), diglyme (219), triglyme (226), 12-crown-4 (220) and 18-crown-6 (221). Sharma *et al.*[25] determined the proton affinities (in kcal mol^{-1}) of several glymes and crown ethers by measuring proton-transfer equilibria with a pulsed electron beam high ion source pressure mass spectrometer: Me_2O (191), monoglyme (204), diglyme (218), triglyme (224), tetraglyme (227), 12-crown-4 (221), 15-crown-5 (223) and 18-crown-6 (230) [based on PA(NH_3) = 204 kcal mol^{-1}]. The *ab initio* calculations of 12-crown-4, 15-crown-5, 18-crown-6, glymes and protonated species suggest that protonated crown ethers share similar moieties with protonated diglyme; the calculated proton affinities (in kcal mol^{-1}) are: diglyme (222), 12-crown-4 (221), 15-crown-5 (225), and 18-crown-6 (227).[26] Using the B3LYP density functional method, Adötoledo *et al.*[27] found that protonated monoglyme $Gl{\cdot}H^+$ and protonated monoglyme dimer $(Gl)_2H^+$, as well as protonated 12-crown-4-ether ($12c4H^+$), form two internal hydrogen bonds with NH_3, CH_3OH, CH_3NH_2, and $(CH_3)_2NH$ with the exception of $(Gl)_2H^+{\cdot}NH_3$ that bears four O···H bonds. The insertion energy of NH_3, CH_3OH and amines into $12c4H^+$ or $(Gl)_2H^+$ increases with increasing proton affinity of the base, while the association energy of $CH_3OH_2^+$, NH_4^+, *etc.*, with 12c4 or $(Gl)_2$ decreases with increasing proton affinity (of NH_3, CH_3OH, *etc.*). However, in terms of protonation equilibrium constants (K_p), there are considerable differences between macrocyclic polyethers and linear glymes. For example, the K_p constant for the protonation of dicyclohexyl-18-crown-6 (DCC) by HBr at 25 °C is about 10^6 M^{-1}, while the K_p values for diglyme and triglyme are only 0.17 and 0.20 M^{-1}, respectively.[28]

Physical properties of aqueous glymes are important for the understanding of solvent properties of glymes. Meot-Ner *et al.*[29] examined the complexing of H^+ from the formation of intramolecular or intermolecular hydrogen bonds with glymes (monoglyme, diglyme or triglyme) and 0–3 water molecules by pulsed high-pressure mass spectrometry; they found that the bonding of H_3O^+ typically involves two or three hydrogen bonds, and complexes of H^+ and H_3O^+ can be stabilized by interactions with bond dipoles of free ether groups of glymes and crown ethers whilst such a stabilization is enhanced by the decreasing constraints on the geometries of polar groups. Anomalous conformational behaviors of short glymes [$CH_3(OCH_2CH_2)_mOCH_3$ with m = 2–6] in water were studied by FT-IR[30] and Raman spectroscopy;[31] both methods indicate that poly(ethylene oxide) chains progressively prefer the *gauche* (*g*) conformation for the OCH_2–CH_2O segment in the first stage, but this direction of the conformational preference is reversed for concentrations lower than a particular solution composition. Such an anomaly can be attributed to specific interactions and/or structures relevant to the glyme–water system. Furthermore, molecular dynamics simulations of monoglyme and diglyme in aqueous solutions[32] confirmed that the *g* population of the O–C–C–O dihedral increases with the increase in water content; a further examination of the composition dependence of diglyme conformational populations implies that the decrease in the O–C–C–O *g* population in extremely dilute solutions can be attributed to a decrease in the *tgt* population of the C–O–C–C–O–C conformational triad. An atomistic force field for simulations of monoglyme reveals that the binding of monoglyme to water is comparable to water–water binding in water dimers, suggesting strong hydrogen bonding between monoglyme and water.[33] Bedrov and Smith[34] found that the properties of monoglyme–water solutions in a water model depend on the solution composition; in dilute solutions, structural and conformational properties are almost independent of the water model. However, short glymes [$CH_3(OCH_2CH_2)_mOCH_3$ with m = 1–4] in formamide showed a different conformational behavior based on a Raman spectroscopic study:[35] for the solutions with solute mole fractions between 0.5 and 0.01, the population of the *gauche* conformation for the OCH_2–CH_2O segment increases progressively with increasing solvent fraction. Monte Carlo simulations of monoglyme in water at 298 and 398 K indicate that the anti–anti–anti conformer is the only conformer that increases its probability with temperature; the *anti–anti–gauche* conformer is the most populated one among all the types.[36] The Bernal group[37,38] investigated the apparent molar volumes and adiabatic compressibilities of glymes (*e.g.* triglyme and tetraglyme) and crown ethers (*e.g.* 18-crown-6, 15-crown-5 and 12-crown-4) in H_2O and D_2O; their results suggest that the hydration of crown ethers increases with their size and is predominated by the hydrophobic hydration of $-CH_2-$ groups; they also indicate that there is a subtle difference between the hydration of the $-CH_2CH_2O-$ group in crown and straight-chain compounds, and the compressibility data reveal a more negative compressibility due to the addition of a $-CH_2CH_2O-$ group to crown ethers compared to a similar addition to a straight-chain glyme. Douhéret *et al.*[39] measured the densities and ultrasound speeds of aqueous solutions of di-, tri- and tetra-glyme, and determined the excess molar volumes and the excess molar isentropic compressions; the excess molar properties are generally negative values. The standard Gibbs energy changes associated with aggregate formation are negative, implying the aggregation is moderate in aqueous glymes (aggregation number $N = 4–6$), although these aggregates are less stable than those formed from self-assembled species containing hydroxyl groups.

Other experimental or theoretical studies of the physical properties of glymes or glyme-containing mixtures can be found in the literature: optical anisotropies of monoglyme, diglyme, triglyme and tetraglyme,[82] excess heat capacities of liquid mixtures of triglyme and tetraglyme with cyclohexane as well as tetraglyme with *n*-heptane at 288.15, 298.15 and 308.15 K and at atmospheric pressure,[83] weak self-association of glymes based on the evaluation of excess isobaric thermal expansion of glyme and alkane mixtures by an associated mixture model with equation of state contribution,[84] excess molar volumes and excess molar isobaric heat capacities of glymes and ethyl acetate,[44] excess molar volumes and viscosities of glyme and acetonitrile,[85] excess thermodynamic and equilibrium properties of glyme–*n*-alkane mixtures,[45,65,66,71,81] isobaric vapor–liquid equilibrium for the binary systems of monoglymes and alcohols,[53] excess molar volumes of binary mixtures of glymes and 1-propanol,[59,60,63] a calorimetric study of interactions between glyme and alcohol,[61] dynamic viscosities of mixtures of refrigerant (HFC-134a) + glyme at different temperatures and pressures,[86] excess molar enthalpies of mixtures of methanol or trifluoroethanol + glyme,[87,88] static relative permittivities of the ternary system of 2-methoxyethanol + 1,2-dimethoxyethane + water from −10–80 °C,[78] vapor–liquid equilibrium of binary systems consisting of monoglyme with toluene, methylcyclohexane, or (trifluoromethyl)benzene,[69] solubility of HFC-134a refrigerant in glymes,[89] densities, viscosities, and refractive indices of diglyme + cyclohexane or + 1,2,3,4-tetrahydronaphthalene,[70] excess molar heat capacities of mixtures of glymes and various alkanes,[79] and excess heat capacities of glyme–dimethylsiloxane systems at 25 °C,[90] *etc.* López *et al.*[91] estimated the densities, isothermal compressibilities, and isobaric thermal expansion coefficients of glymes in the temperature range 293.15 K–353.15 K at pressures up to 100 MPa from the *PcT* data (*c* is the speed of sound in glyme), and found that the indirect predictions matched the direct experimental values.

4.2. Ion complexing properties

A unique feature of glymes is that they contain multiple ether-type oxygen atoms (similar to crown ethers) and flexible alkoxy chains. Therefore, they often behave like crown ethers in terms of solvating metal ions through oxygen–ion complexation (chelating) properties, which leads to many valuable applications. The chain flexibility was demonstrated by the spin–lattice relaxation of methoxy protons in glymes: the experimental T_1^{-1} values of glymes are significantly lower than those calculated for a rigid molecule although higher than those for completely free motion of methyl groups.[92] This section places special emphasis on the ion chelation properties of glymes while their applications in electrochemistry and chemical reactions are discussed in later sections.

A vivid illustration of the ion–glyme complexation is demonstrated in Fig. 1, where a lithium cation is chelated by a tridentate diglyme molecule. Matsui and Takeyama[93] confirmed that Li^+ is coordinated with six oxygen atoms in either monoglyme or diglyme; however, monoglyme is a bidentate ligand and diglyme is a tridentate ligand. The *trans–cis* isomerization of diglyme is necessary for the coordination to a single cation although it typically has a *trans–trans* conformation of minimum energy.[94] Carvajal *et al.*[72] studied the solvation behaviors of $[Cs^+][BPh_4^-]$, $[Na^+][BPh_4^-]$ and $[Bu(i\text{-}Am)_3^+][BPh_4^-]$ in monoglyme and tetrahydrofuran (THF), and indicated that: (a) free Cs^+ coordinates with monoglyme but not with THF, (b) in both monoglyme and THF, $[Na^+][BPh_4^-]$ primarily yields solvent-separated pairs which dissociate into solvent-coordinated Na^+ ions, (c) however, $[Bu(i\text{-}Am)_3^+][BPh_4^-]$ forms contact ion pairs in both media and dissociates into free $Bu(i\text{-}Am)_3^+$ and BPh_4^- ions not coordinated with the solvent. Using Electron Spin Resonance (ESR) spectroscopy, Hoefelmann *et al.*[95] determined the equilibrium constant of sodium naphthalene and tetraglyme forming a loose ion pair to be 200–300 M^{-1} at 27 °C. Collins *et al.*[96] determined the formation constants of tetraglyme separated ion pairs of bolaform electrolytes Na^+, $^-Fl(CH_2)_nFl^-$, Na^+ (Fl^- is a fluorenyl carbanion; $n = 2, 3, 4,$ or 6) in THF and tetrahydropyran (THP) at 25 °C. They suggested that it is easier to separate the ion-pair with tetraglyme in THP than in THF. For both monoglyme and diglyme, the lithium-ion solvation-shell coordination number is 4 at room temperature and 5 at a lower temperature based on the matrix-solvation FT-IR data.[97] A molecular dynamics simulation study[98,99] on different concentrations of NaI dissolved in dimethyl ether and monoglyme suggests that in diluted solutions, free ions exist as the most common ionic species, followed by ion pairs; with a further increase in salt concentration, ion pairs become the predominant species and many of them are in the form of clusters of 3–6 ions or more ions. Replacing dimethyl ether by monoglyme substantially reduces the ion clustering due to the chelating effect of glyme oxygens with the cation (Na^+). At the highest concentration studied in monoglyme (*i.e.* an oxygen/cation ratio of 16 : 1), free ions constitute ~50% of the total ion concentration and neutral pairs constitute about 20%. For Na^+–

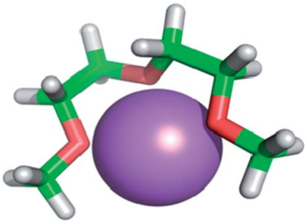


Fig. 1 Lithium cation chelated by a tridentate diglyme molecule (molecular geometry obtained *via* a PM3 semi-empirical method in ArgusLab by Richard Terrett at the Australian National University).

glyme systems, the electric current is mainly due to the movement of free ions and the relative movement of ions within loosely bound ion pairs. Based on the *ab initio* calculations of metal ion–glyme complexes,[100,101] the Lindgren group suggested that the high chain flexibility of glymes enables many stable structures within a narrow energy range with very different geometrical arrangements of the ether oxygens, for example, at least 4 structures of different geometries for M-glyme complexes ($M = Li^+$, Na^+, K^+, Mg^{2+} and Ca^{2+})[100] and 11 structures of different geometries for the Li^+–tetraglyme systems.[101] The coordination numbers of lithium range from 4 to 6 for 1 : 1 complexes of Li^+ with tetra-, penta- and hexaglyme, and the total binding energy increases with the glyme length; the coordination figures mainly consist of the quadratic pyramid, trigonal bipyramid and the trigonal prism type of geometries.[101] Johansson *et al.*[102] performed the *ab initio* calculations of 1 : 1 (cation : molecule) complexes of lithium ions with linear oligomers, $CH_3X(CH_2CH_2X)_nCH_3$, ($n = 0$–5; X = O, NH or S); their results suggest that the total binding energy increases with the increase in glyme chain length and follows the order NH > O > S. Shen *et al.*[103] studied the complexing behavior between alkaline earth cations and crown ethers/triglyme in the gas phase, forming mainly sandwich complexes of doubly charged cations $(12\text{-crown-4})_2M^{2+}$, $(12\text{-crown-4})(\text{triglyme})M^{2+}$, and $(\text{triglyme})_2M^{2+}$; it was also found that triglyme could be easily replaced by 18-crown-6 than 12-crown-4 possibly due to the rate-limiting step disrupting less cation–ligand interactions for the flexible ligand than for the rigid one. Henderson *et al.*[104] indicated that both $[Li_2(CF_3SO_3)_2(\text{diglyme})]$ and $[Li_3(CF_3CO_2)_3(\text{diglyme})]$ contain five-coordinate Li^+ cations coordinated by a tridentate diglyme molecule and two O atoms (each from separate anions) (see Fig. 2). Henderson *et al.*[105] also suggested that the $(\text{monoglyme})_2$:$LiClO_4$ crystals consist of contact ion pairs where the anions have bidentate coordination to the Li^+ cations, whilst the $(\text{diglyme})_2$:$LiClO_4$ crystals consist of fully solvated Li^+ cations where the cations and anions do not directly interact. Grondin *et al.*[106] further studied the Raman spectra of crystalline complexes of $(\text{monoglyme})_2$:$LiClO_4$, $(\text{diglyme})_2$:$LiClO_4$ and $(\text{triglyme})_1$:$LiClO_4$, and established the vibrational assignment for ClO_4^- involved in the solvent-separated ion pair, contact ion pair and aggregate solvates. Dhuaml and Gejji[107] employed *ab initio* Hartree–Fock and density functional calculations to study the electronic structure, charge distribution and vibrational characteristics of $CH_3O(CH_2CH_2O)_nCH_3$ ($n = 3$–7). They found that the *trans*-conformation around C–C and C–O bonds of the backbone of tri- to hexaglymes leads to the lowest energy conformers; however, for heptaglyme ($n = 7$), the *gauche*-conformation around the C–C bonds affords a higher stability to the conformer.

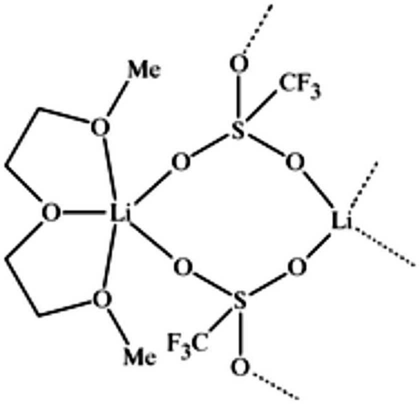


Fig. 2 Li^+ cation coordination in $[Li_2(CF_3SO_3)_2(\text{diglyme})]$.

The Watanabe group[108] prepared an equimolar complex $[Li(\text{glyme})_1][Tf_2N]$ (Tf_2N^- also known as $TFSA^-$ = bis(trifluoromethane)sulfonimide), which maintains a stable liquid state over a wide temperature range and exhibits a high thermal stability and Li^+ ionic conductivity, behaving like a room-temperature ionic liquid (IL). The physicochemical properties (*e.g.* melting point and viscosity) of the glyme–Li salt complex can be manipulated by the glyme structure. The same group[109] further observed a higher oxidative stability of glyme molecules when complexing with Li^+ cations. They found that the electrochemical oxidation of $[Li(\text{glyme})_1][TFSA]$ occurred at the electrode potential of ~5 V *vs.* Li/Li^+, while the oxidation of solutions with excess glyme molecules ($[Li(\text{glyme})_x][TFSA]$, $x > 1$) occurred at a lower potential of ~4 V *vs.* Li/Li^+. Further *ab initio* molecular orbital calculations explained that the increased oxidative stability is due to the donation of lone pairs of ether oxygen atoms to the Li^+ cation, lowering the highest occupied molecular orbital (HOMO) energy level of glyme molecules. The thermal stability of bis(dipivaloylmethanato)strontium [*i.e.* $Sr(dpm)_2$] compounds containing glyme adducts [*i.e.* $Sr(dpm)_2$–triglyme and $Sr(dpm)_2$–tetraglyme] was examined by Cho *et al.*[110] using thermogravimetric analysis, mass spectrometry, and FT-IR spectroscopy. They observed that glyme adducts are decomposed below 200 °C, while the Sr–O and the $C–C(CH_3)_3$ bonds are dissociated at higher temperatures, and the C–O and the C–C bonds are stable up to 400 °C. Glyme molecules in ion complexes weaken the Sr–O bond between the Sr atom and the dpm ligand, leading to the dissociation of the Sr–O bond in $Sr(dpm)_2$–glymes at lower temperatures than the bond in $Sr(dpm)_2$. However, $Sr(dpm)_2$–glymes are less thermally degradable than $Sr(dpm)_2$, resulting in fewer residues at elevated temperatures.

The stability constants (log *K*, *i.e.*, equilibrium constants for complexing) for 18-crown-6 with Na^+, K^+, and Cs^+ are 3–6 in methanol, and are 1.5–2.2 for pentaglyme.[4,112] The stability constants (log *K*) of 1 : 1 complexes of alkali cations M^+ (Na^+, K^+, or Cs^+) with glymes $CH_3O(CH_2CH_2O)_nCH_3$ in methanol increase with *n*, which is different from the complexes between M^+ and crown-ethers $(–CH_2–CH_2–O–)_n$: their stability constants reached the maximum at $n = 6$ (Na^+, K^+) and 6, 7 (Cs^+) (see Table 4).[111,113,114] The stability constants of glymes are slightly lower than those of corresponding PEGs, but both of them are considerably lower than those of crown ethers.[115] The higher stability of the complexes of crown-ethers compared to those of acyclic analogues (such as glymes) can be attributed to the so called "*macrocyclic effect*" (ME), which is a function of the polyether's topology and cation's size.[111,112] The macrocyclic effect is

Table 4 Comparison of stability constants (log K) of glymes [$CH_3O(CH_2CH_2O)_nCH_3$] and crown ethers with alkali ions in methanol at 25 °C[111]

Glyme, $n =$	Na^+	K^+	Cs^+	Crown ether	Na^{+c}	K^{+c}	Cs^{+c}
3	1.18^a	1.38^a	1.17^a	12c4	1.41	1.58	1.6
4	1.28^b	1.72^b	1.45^b	15c5	3.30	3.35	3.58
5	1.47^b	2.20^b	1.85^b	18c6	4.36	6.07	4.79
6	1.60^b	2.55^b	2.17^b	21c7	2.54	4.41	5.01
7	1.67^b	2.87^b	2.41^b	24c8	2.35	3.53	4.15
8	1.83^a	3.28^a	2.77^a	27c9	2.14	3.47	3.95
9	1.96^a	3.66^a	3.09^a	30c10	2.14	3.98	4.15

[a] Calculated value. [b] Experimental value. [c] Selected value from the THECOMAC database.

not only observed in solution, but also in the gas phase formation of alkali metal cation-bound dimers of crown ethers or glymes: the rates for crown ethers were about an order of magnitude higher than those for glymes.[116] Varnek *et al.*[111] demonstrated that the *Substructural Molecular Fragments* method can be used to evaluate the stability constants of these complexes. The Smid group investigated the relative ligand affinities of glymes, crown ethers, polyamines and other cation-binding ligands toward lithium and sodium picrate in toluene[117] and dioxane.[118] The affinity of glymes in binding lithium and sodium picrate dramatically increases with increasing ether chain length up to tetraglyme, and a further increase in the affinity for longer glymes is primarily due to the increase in the number of binding sites. However, crown ethers generally have much higher binding equilibrium constants toward Li^+ and Na^+, which could be over 100 times higher than most glymes. Davidson and Kebarle[119] indicated that monoglyme forms a stronger complex with K^+ than ethylene diamine. Plewa-Marczewska *et al.*[120] determined the formation constants (K_a) of ionic pairs between $Li[CF_3SO_3]$ (or $Li[BF_4]$) and glymes (monoglyme, diglyme or triglyme) using the anion state sensitive ^{19}F NMR and cation ^7Li NMR techniques, and found that the K_a values (log $K_a = 3$–6) are dependent on the salt concentration range used for calculation and are generally a few orders of magnitude lower than those estimated from the conductivity data.

Many studies focus on the ion complexation of glymes in solution. Chan *et al.*[121–123] studied the coordination of fluorenyllithium, -sodium, and -potassium (carbanion pairs) with various glymes: $CH_3O(CH_2CH_2O)_nCH_3$ ($1 \leq n \leq 6$) in dioxane, THF, or tetrahydropyran (THP) using optical and NMR spectroscopy. In the case of fluorenylsodium, 1 : 1 coordination complexes are formed for glyme-separated ion pairs with glyme-5 ($n = 4$), glyme-6 ($n = 5$) and glyme-7 ($n = 6$), but the separated ion pair contains two glyme molecules with glyme-4 and probably glyme-3. In the case of potassium salt, glyme-separated 1 : 1 complexes are observed for glyme-6 and glyme-7, but glyme-4 and glyme-5 yield mainly glymated contact ion pairs and a second glyme molecule is required to convert them to separated ion pairs. Therefore, depending on the cation size and glyme chain length, the chelation of glyme with contact ion pairs results in either glymated contact ion pairs or glyme-separated ion pairs or a mixture of both. A further study on temperature dependence suggests that the reason for glymes being effective complexing agents of alkali ions is mainly due to a small loss in entropy as compared to solvent separated ion-pair formation in THF. Takaki and Smid[124] titrated difluorenylbarium with glymes and crown ethers in THF at 25 °C under vacuum to examine the formation of ion pair–glyme and –crown ether complexes, and found that 1 : 1 complexes are formed for difluorenylbarium with mono- and dibenzo-18-crown-6 as well as with glyme-7 and glyme-9 while a 2 : l crown–ion pair complex is formed for monobenzo-15-crown-5. Canters[58] analyzed the shift and line widths in ^{23}Na NMR spectra of glyme solutions of $NaBPh_4$ and $NaBH_4$ as a function of temperature; it was found that the transition from solvent separated to contact ion pairs and the type of anions show a considerable impact on the position of alkali NMR signals, while the line width is typically a linear function of the viscosity of pure solvent divided by absolute temperature. Detellier and Laszlo[125] observed the tetracoordination of Na^+ when studying the ^{23}Na NMR chemical shifts for $NaClO_4$ in binary mixtures of glyme and tetrahydrofurfuryl alcohol. Although monoglyme tends to form monocyclic intermediates, diglyme and triglyme form bicyclic intermediates. Gilkerson and Jackson[126] noticed that lithium picrate could be dissolved up to 1 mM in a solvent containing 1 equiv. of either triphenylphosphine oxide (TPPO), hexamethylphosphoramide (HMPA), triglyme, or tetraglyme; however, to dissolve 1 mM sodium picrate, at least a tenfold excess of either TPPO, HMPA, or tetraglyme is needed; furthermore, through the conductance and spectrophotometric measurements, they observed a very small extent of dissociation in 1 : 1 ligand–metal picrate complexes and the formation of 2 : 1 and 3 : 1 ligand–cation complexes in the presence of additional ligand. Plewa *et al.*[127] employed ^{19}F NMR spectroscopy and conductivity data to study the ion pair formation of mixtures of salts ($LiBF_4$ and $LiCF_3SO_3$) with 1,4-dioxane and glyme (or water). They suggested that mixtures containing monoglyme or diglyme have similar coordinating properties (in terms of donor and acceptor numbers) to liquid PEG dimethyl ether and solid PEG.

The formation of glyme and salt into a crystal solid has been used to probe the ion complexing properties of glymes. Smid and Grotens[128] reported the crystalline 1 : l complexes of $NaBPh_4$ with glyme-5, glyme-6 and glyme-7, as well as a 2 : l complex with glyme-4. de Boer *et al.*[129] studied alkali biphenyls (NaBp, KBp and RbBp) in triglyme or tetraglyme solutions by NMR and the crystal structures of NaBp·(2 triglyme), KBp·(2 tetraglyme) and RbBp·(2 tetraglyme) by X-ray diffraction; these crystals consist of solvent-separated ion pairs in the solid state. Magnetic experiments were performed for single crystals of these three systems, and the susceptibility measurements suggested a ferromagnetic coupling in NaBp·(2 triglyme) and KBp·(2 tetraglyme) and an antiferromagnetic coupling in RbBp·(2 tetraglyme). The Frech group[130] analyzed the crystal structure of diglyme:$LiCF_3SO_3$ and found that the local environment of Li^+ ions and the torsional angle sequence of bonds in ethylene oxide units are very similar to those in the high molecular weight poly(ethylene oxide)$_3$:$LiCF_3SO_3$. On the other hand, their spectroscopic data of diglyme-$LiCF_3SO_3$ solutions suggest that Li^+ is coordinated by only three oxygen atoms from diglyme and one oxygen atom from a $CF_3SO_3^-$ anion (*i.e.* five-fold coordinated) while triflate anions are two-fold coordinated. The same group[131] further examined the crystal structures of monoglyme:$(LiCF_3SO_3)_2$ and triglyme:$(LiCF_3SO_3)_2$, and indicated in the case of monoglyme:$(LiCF_3SO_3)_2$, that triflate anions are three-fold coordinated and lithium ions are four-fold coordinated whilst in the case of triglyme:$(LiCF_3SO_3)_2$, triflate anions are three-fold coordinated and lithium ions are both four-fold and five-fold coordinated. They also observed the formation of *trans–gauche–trans* conformations for the bond order –O–C–C–O– in adjacent ethylene oxide sequences interacting with a five-coordinate lithium ion. Furthermore, this group[132] characterized the crystalline phases of glyme:$NaCF_3SO_3$ using DSC, X-ray diffraction, and vibrational spectroscopy, and suggested that Na^+ coordinates with 5 to 7 ether and triflate oxygens and more ethylene oxide units lead to higher coordination numbers. They also emphasized that these structures are the result of a convoluted effect of ion–ion interactions, ion-chain heteroatom interactions, and packing constraints from the organic chains. Henderson *et al.*[133] characterized the crystalline phases of $(\text{triglyme})_1$:LiX (X = $CF_3SO_3^-$, BF_4^-, ClO_4^- and AsF_6^-), and found that the phases are isostructural and are different from that of $(\text{triglyme})_1$:$LiBPh_4$. The same group[134] also studied the crystal structures of lithium salt complexes with tetraglyme including $(\text{tetraglyme})_1$:$LiAsF_6$, $(\text{tetraglyme})_{1/2}$:$LiBF_4$, and $(\text{tetraglyme})_{2/5}$:$LiCF_3CO_2$; and found a novel form of six-coordinate Li^+ cation coordination by glyme oxygen atoms resembling double-helix dimers. The ionic association strength of LiX salts was investigated in a variety of aprotic solvents including glymes (see a short review in the Supporting Information of ref. 135), and is correlated with the crystallization kinetics of glyme–LiX and PEO–LiX mixtures.[136,137] The approximate ionic association strength in aprotic solvents is shown below in an increasing order:[135,136]

$$\text{beti}^-, Tf_2N^- < PF_6^- < ClO_4^-, I^- < SCN^- < BF_4^- < CF_3SO_3^- < Br^- < NO_3^- < CF_3COO^- < Cl^-$$

This order implies the strength of an anion interacting with solvated cations through ionic attraction.

In addition to alkali metals, the complexing properties of glymes with other metal and organic cations, or even non-ionic molecules have also been studied. Timko *et al.*[138] compared the complexation of *t*-butylammonium thiocyanate with pentaglyme and 18-crown-6 in chloroform at 24 °C, and found a macrocyclic effect of 18 700. The Bartsch group[139] studied the complexing effect of *p-tert*-butylbenzenediazonium tetrafluoroborate with glymes in 1,2-dichloroethane at 50 °C, and suggested a macrocyclic effect of ~30 when comparing the complexation constants (*K*) for pentaglyme and 18-crown-6 with aryldiazolium ions. They also observed that the *K* value is basically constant (~2) for diglyme, triglyme and tetraglyme, followed by a steady increase for pentaglyme (4.78), hexaglyme (7.71), and heptaglyme (11.8) due to an increasing ability of the glyme to assume a pseudo cyclic structure; however, there is a drastic drop in *K* value for octaglyme (3.81) followed by a gradual increase for nonaglyme (6.32) and decaglyme (13.6). The same group[140] further investigated the complexation of PEG and their dimethyl ethers with *p-tert*-butylbenzenediazonium tetrafluoroborate, and found that complexation constants for PEG 1000 and 1500 and their dimethyl ethers are 12–18% of that for 18-crwon-6. Relying on ^1H NMR spectroscopy, Otera *et al.*[141] suggested the formation of 1 : 1 complexes between glymes, $CH_3O(CH_2CH_2O)_nCH_3$ (n = 2, 3, 4), and dimethyltin dichloride (DMTC) in benzene, as well as both 1 : 1 and 1 : 2 glyme–DMTC complexes for glymes (n = 5, 6) in benzene and with all glymes studied in toluene and 1-chloronaphthalene. Hirashima *et al.*[142] suggested the formation of 1 : 1 complexes between lanthanoid chlorides and triethylene glycol, tetraethylene glycol, pentaethylene glycol, tetraglyme or pentaglyme. The same group[143] found that lanthanoid nitrates [*i.e.* $Ln(NO_3)_3$] form solid complexes with polyethylene glycols and glymes at different compositions: 1 : 1 (Ln : ligand) for triethylene glycol, tetraethylene glycol, pentaethylene glycol and tetraglyme, 1 : 2 (Ln : ligand) for diethylene glycol, 2 : 1 for heptaethylene glycol, and 4 : 3 for pentaglyme and hexaglyme. Inoue and Hakushi[144] found the enthalpy–entropy compensation effect for the complexation of cations with glymes/podands, crown ethers, cryptands, and macrocyclic antibiotics in different solvents (such as water and methanol, *etc.*). Guerra *et al.*[145] observed that bis(trifluorosilyl)cadmium was marginally stable at 20 °C but became very stable in monoglyme by forming alkyl–cadmium–glyme complexes. Markies *et al.*[146] studied the complexation of bis(*p-tert*-butylphenyl)magnesium with 1,3-xylylene crown ethers and glymes, and indicated that in the complex with diglyme, magnesium is pentacoordinated, whilst in the complex with tetraglyme, magnesium is pentacoordinated to three adjacent oxygens of the five available (including the one from the methoxy group). In both cases, coordinative saturation has been reached within the limits of steric restraints. Simple ethers are usually associated with a tetrahedrally coordinated magnesium, but polyethers induce higher coordination states, which could result in improved reactivity of the organomagnesium reagent. Meot-Ner *et al.*[147] determined the binding energies of NH_4^+ to glymes using pulsed high-pressure mass spectrometry, and suggested that binding energies in these complexes increase with the ligand size and the number of available oxygen groups. The *ab initio* calculations of complexing with monoglyme result in the following order of binding energies of ligands: $H_3O^+ > Na^+ > NH_4^+ \approx K^+$. To prepare new inorganic polymers as precursors for thin layer deposition, two different dimensional compounds $[Ca(\text{monoglyme})_n(H_2O)_m]I_2\cdot(\text{monoglyme})_x$ (**1:** $n = 3$, $m = 3$, $x = 1$; **2:** $n = 2$, $m = 4$, $x = 0$) and $[Ca(\text{triglyme})(H_2O)_4]I_2$ were formed through metal ion complexation and hydrogen bonding.[148] Mishra *et al.*[149] prepared hydroxo-bridged, centrosymmetric dimeric yttrium complexes with glymes: $[Y_2L_2(\mu\text{-}OH)_2(H_2O)_x(ROH)_y]I_4$ [**1**: L = triglyme, $x = 2$, $y = 2$, R = iPr; **2**: L = tetraglyme, $x = 2$, $y = 0$; **3**·2EtOH: L = diglyme, $x = 2$, $y = 4$, R = Et; **4**·2EtOH: L = triglyme, $x = 4$, $y = 0$; **5**: L = tetraglyme, $x = 2$, $y = 2$, R = Et]; these ionic derivatives are potential sources of yttrium oxide in high T_c superconductors. Chantooni *et al.*[150] observed two polymorphic forms (*i.e.* triclinic polymorph I and orthorhombic polymorph II) of crystals of the 1 : 2 : 2 pentaglyme : dichloropicric acid : water adduct complex. The IR spectra of the 1 : 2 : 2 tri-, tetra-, and pentaglyme : dichloropicric acid : water complexes indicate that the hydrogen-bonding in the triglyme complex is as strong as or stronger than that in the pentaglyme complex, but the hydrogen-bonding in the tetraglyme complex is weaker than in the pentaglyme complex.

The complexing properties of some glyme analogues have been reported in the literature. Jaycox *et al.*[151] examined the insoluble complexes formed in acidic aqueous media upon mixing poly(acrylic acid) (PAA) and poly(vinylbenzo-18-crown-6) (P18C6) or polyvinylbenzoglymes. The complex formation is a direct result of the hydrogen bonding between carboxyl groups and crown ether- or glyme–oxygen atoms and also from hydrophobic interactions; such a precipitation is pH dependent. Saraswathi and Miller[152] studied the interaction of protons and alkali metal ions with dinucleotide analogs of acyclic polyethers using fast-atom bombardment (FAB) mass spectrometry, and suggested the following order of chelation of alkali metal ions, acyclic glymes < dinucleotide analogs (acyclic glymes substituted with nitrogen bases) < crown ethers.

5. Overview of industrial applications

Glymes have a broad range of industrial applications, such as in cleaning products, inks, adhesives and coatings, batteries and electronics, absorption refrigeration and heat pumps, pharmaceutical formulations, *etc.* For example, mixtures of methanol or trifluoroethanol + PEG-DME 250 or tetraglyme can be used as working fluids for absorption refrigeration machines;[87,88] triglyme and tetraglyme are lubricants for the automotive air-conditioning (A/C) compressor when mixed with refrigerants (such as HFC-134a).[68,86,89] Table 5 summarizes some representative commercial applications of common glymes.

In particular, dipropylene glycol dimethyl ether, known as proglyme (P2), is considered an environmentally friendly solvent and is not listed as a hazardous air pollutant (HAP). Therefore, P2 has versatile applications including the replacement of *N*-methyl pyrrolidone (NMP). NMP is known to have reproductive toxicity whilst much less toxic P2 has similar physical properties including similar solubility behaviors. Thus, P2 is an excellent solvent for coatings (such as waterborne coatings and high solid coatings) and paints (such as electrodeposition coatings, paint strippers, coating- and graffiti-removers), as well as for industrial cleaners for degreasing (such as formulating hard surface cleaners containing bleach).

6. Electrochemical applications

Due to the unique ion complexing properties of glymes (as discussed in 4.2), glymes have been extensively investigated in electrochemistry as electrolyte solvents. Slates and Szwarc[153] suggested that when sodium biphenyl coordinates with diglyme or triglyme in a 1 : 1 stoichiometric ratio, diglyme coordinates with the periphery of the ion pair while two isomeric ion pairs are formed in triglyme (glyme attaching to the periphery of the pair, and glyme separating the ions). Canters *et al.*[154] prepared single crystals of the alkali radical ion pairs of $[Li^+][biphenyl^-]$ in tetrahydropyran (THP), $[Na^+][biphenyl^-]$ in triglyme, and $[K^+][biphenyl^-]$ and $[Rb^+][biphenyl^-]$ in tetraglyme. They found the presence of solvent molecules in stoichiometric quantities in the crystals, acting as the chelating agents of alkali ions. In particular, $Na_2[biphenyl]_2[triglyme]_5$ has shown a strong paramagnetism and electron exchange interaction, and the electron correlation time is in the order of 10^{-11} to 10^{-12} s. Smyrl *et al.*[155] suggested that a spontaneous discharge process for doped polyacetylene in a LiI-monoglyme solution could restrict the reversibility of this and other conductive polymers when used as electrode materials. Foos *et al.*[156] examined the conductivity of LiBr dissolved in glymes (mono- and di-) and their mixtures with other ethers, and found that solution conductivity increases with the salt concentration up to a maximum. Interestingly, they also discovered that the conductivity of 1.0 M LiBr in a 1 : 1 (v/v) mixture of monoglyme and dioxolane increases with the decrease in temperature; this is particularly valuable for battery electrolytes with maximized conductivities at low temperatures.

Sharma and Bhagwat[157] measured the conductivities of alkali metal picrates dissolved in tetraglyme, 18-crown-6 and tetraethylene glycol diquinoline ether at 25 °C in a methanol–water mixture. The formation constants (K_{ML}) of 1 : 1 complexes of alkali metal ions with these ligands in 70% methanol were found to be dependent on the anion; the log K_{ML} values of alkali metal ions with tetraglyme, 18-crown-6 and quinoline ether are in a decreasing order of $K^+ > Na^+ > Rb^+ \approx Cs^+ > Li^+$, $K^+ \gg Na^+ > Rb^+ > Cs^+$, and $Na^+ > K^+ > Rb > CS^+ > Li^+$, respectively. They also observed that the cyclic ligand gives a more stable complex and a higher selectivity than non-cyclic ligands. Pyati and Murray[158] found that the microelectrode voltammetry-derived heterogeneous electron transfer kinetic rates k_{ET} for the redox couple cobalt tris(bipyridine) $[Co(bpy)_3]^{2+/3+}$ in a series of glyme solvents are inversely proportional to the solvent's longitudinal relaxation time and viscosity but directly proportional to the diffusion coefficient of the metal complex. Teeters *et al.*[159] measured the surface tension of a tetraglyme–lithium triflate system, and observed a preferential distribution of the triflate ion between the interface and the bulk. They indicated that the surface concentration increases with the concentration of lithium triflate until a high 'ion aggregation' concentration was reached. These results further stimulated the infrared study of poly(ethylene oxide)–lithium triflate films, and enabled a more mechanistic understanding of polymer electrolyte materials. To provide an aprotic environment for lithium batteries, Choquette *et al.*[160] studied the phase diagrams, potential windows, conductivities and the lithium interfacial resistance of $Li[Tf_2N]$ dissolved in sulfamides and glymes. They suggested that glymes or their mixtures with sulfamides could be useful for batteries whose cathode is not a 2D layer structure. Plewa *et al.*[161] constructed composite electrolytes comprising polyglyme (M_w = 500), LiX (X = I^-, BF_4^- and $CF_3SO_3^-$) and a calix[6]pyrrole derivative (C6P), and focused on the role of C6P as an anion complexing agent. To probe the potential use of tin as an alternative anode material for rechargeable lithium batteries, Katayama *et al.*[162] examined the charge–discharge properties of

Table 5 Major solvent features and industrial applications of glymes[a]

Glyme	Solvent features	Representative industrial applications
Monoglyme (G1)	• Low b.p. (85.2 °C) • High stability	Production of active ingredients, metal–organics, electrolyte solvent for sealed lithium batteries, entrainer, chromium electroplating, cyanoacrylate based adhesives, etching of printed circuit boards, treating aluminum surfaces
Ethyl glyme (G1-Et)		Solvent in paints, adhesives, coatings, shellacs, resins, detergents, dyes and polycarbonate products
Diglyme (G2)	• High solubility for Na/K alloys • Good solvent for Grignard reagents, $LiAlH_4$ and $NaBH_4$ • Chelate ligand for cations • Excellent stability even at high pH values	API production (such as anti-AIDS drug Nevirapine), reaction solvents for organometallic reagents, entrainer for azeotropic distillation, battery electrolyte, conducting thermoplastic paste, solvent for Teflon etchants, a suspension of sodium and naphthalene in G2 used for destruction of polychlorinated biphenyls (PCBs) in transformer oil, solvent in a formulation to improve the bonding of tire cord to rubber, solvent in printing and inkjet inks and inkjet cartridges, brake fluid, paints and other coatings, plastics, adhesives and sealants
Butyl diglyme (G2-Bu)	• Hydrophobic • High b.p. (256 °C)	Selective extraction of gold from hydrochloric solutions containing other metals, used in compositions for production of printed circuits and diode fabrication,
Triglyme (G3)	• High b.p. (218 °C) • Chemically inert	Solvent for Teflon etching, high boiling and inert solvent for organic reactions, a solvent in consumer adhesives and paints, a component of consumer brake fluids and paint/graffiti removers
Tetraglyme (G4)	• High b.p. (275 °C) • High stability • High solubility of inorganic salts	Flue gas cleaning systems, solvent for production of binders for paints, coalescing agent in paint formulations, adhesives production, electrodeposition, manufacture of soldering fluxes/solder pastes, adsorption liquid and gas scrubbing, formulations of paint strippers and adhesive removers, extraction of volatile organic compounds from solid wastes, inert additive for the fixation of methylated methylolmelamine resins in durable-press cotton and cellulosic fabrics, an HFC/CFC lubricant
Proglyme (P2)	• Environmentally friendly • High chemical stability • High b.p. (175 °C) • Replacement for NMP • Replacement for xylene	Excellent replacement for NMP (*N*-methyl pyrrolidone) in many applications, polyurethane dispersion (PUD) formulation and two-pack PU coatings, waterborne coatings and high solid coatings, paint strippers, coatings- and graffiti removers, cleaners for degreasing, electrodeposition coatings, co-solvent in aluminum paste formulations, replacement of xylene for the production of alkyd and polyester resins
Polyglymes (MW 236 or 275)	• Dissolution of gases such as CO_2 and H_2S • High b.p.	Gas purification by removing CO_2, H_2S, COS and water from natural gas or ammonia synthesis gas feed stocks, solvent for manufacturing polyester fibers with improved moisture retention and multiporous hygroscopic fibers, formulation in dyes to dye polyester-cotton textiles, consumer paint strippers
Higlyme (MW > 400)	• High b.p. (>300 °C) • High flash point (140 °C)	Formulations of coatings (urethanes and inks) and agro-chemicals
PEG-DME 200	• High b.p. (>300 °C)	

Table 5 (*Contd.*)

Glyme	Solvent features	Representative industrial applications
		Special solvent, flue gas cleaning systems, delacquing
PEG-DME 250	• High b.p. (>300 °C)	PTC, special solvent, absorption solvent for H_2S, COS, mercaptans and CO_2,
PEG-DME 500	• High b.p. (>300 °C)	PTC, high boiling solvent, electroplating
PEG-DME 1000	• High b.p. (>300 °C)	PTC, high boiling solvent, electrodeposition
PEG-DME 2000	• High b.p. (>300 °C)	PTC, high boiling solvent, electroplating, depolymerization reactions

[a] Polyglymes are polyethylene glycol dimethyl ethers with different molecular weights ranging from 200–2000.

a tin thin film electrode in an ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide containing 0.1 M Li[Tf_2N]. To reduce the interfacial resistance in the ionic liquid electrolyte, a small amount (0.2 M) of glymes (mono-, di-, tri- and tetra-) were added to coordinate with the Li^+ ions.

As discussed in detail in Section 4.2, glymes dissolve alkali salts and form complexes with them; such unique properties have significant electrochemical implications. Izutsu *et al.*[163] studied the complexing of lithium ions in propylene carbonate (PC) with glymes (mono-, di-, tri- and tetra-) using a univalent cation-sensitive glass electrode. An early study by Aurbach and Granot[164] suggested that electrolytes consisting of various lithium salts and glymes (monoglyme, diglyme and ethyl glyme) might not be suitable for rechargeable Li battery systems using Li metal anodes due to a rough morphology of Li upon deposition–dissolution cycling causing a low Li cycling efficiency. However, Brouillette *et al.*[165] indicated that glymes (mono-, di-, tri- and tetra-) are electrochemically stable, possess a good redox window, and are analogs of PEOs used in polymer-electrolyte batteries. Therefore, this group measured the conductance and apparent molar volume and heat capacity of Li[Tf_2N] at various concentrations in glymes; from these data, they concluded that: (a) at low concentrations, Li[Tf_2N] is strongly associated in glymes; (b) at intermediate concentrations, there is a stable solvate of Li[Tf_2N] in glymes in the solution state; (c) at high concentrations, the thermodynamic properties of the lithium salt resemble those of molten salts. Hayamizu *et al.*[166] measured the self-diffusion coefficients of Li^+, Tf_2N^-, and the solvent (including glymes) in Li[Tf_2N]–solvent systems using a pulse-gradient spin-echo (PGSE) NMR method. They observed that the ionic conductivity and the diffusion coefficients increase with the increase in glyme chain length (monoglyme → diglyme → triglyme), and the degree of dissociation at 30 °C is in the range of 31–38%. To further understand the role of PEO in electrolyte systems, the same group[167] employed pulsed-field gradient spin-echo (PGSE) ^1H, ^{19}F, and ^7Li NMR to study electrolytes of glymes $CH_3O(CH_2CH_2O)_nCH_3$ (n = 3–50) mixed with Li[Tf_2N]. They suggested that the segmental motions of the PEO moiety in glymes induce high chain flexibility and enable high solubility and transport of doped Li^+ ions; the rate of segmental motion decreases with the increase in PEO chain length. To probe the molecular interactions of lithium salts in glymes used for solid polymer and liquid electrolytes, Henderson *et al.*[168] determined the phase behavior and solvate structures of glyme complexes with Li[Tf_2N] and Li[beti] (beti = bis(perfluoroethanesulfonyl) imide) to be (monoglyme)$_1$:Li[beti], (diglyme)$_2$:Li[Tf_2N], (diglyme)$_{1/2}$:Li[Tf_2N], and low-temperature (triglyme)$_1$:Li[beti]; most solvates undergo order–disorder solid phase transitions. Kolosnitsyn *et al.*[169,170] studied the cycling of a sulfur electrode in a mixture of 3-methoxysulfolane and sulfolane with glymes (mono-, di- and tetra-) and lithium triflate (Li[OTf]) as the supporting electrolyte. They found a decrease in the electrode capacity with the increase in PEO units of glymes and in the number of donor centers in sulfone molecules, which is due to the variation of the form taken by lithium polysulfides in solutions and the increase in electrolyte viscosity. Tobishima *et al.*[171] investigated the conductivity, lithium ion solvation state and charge–discharge cycling efficiency of lithium metal anodes in glyme-based electrolytes for rechargeable lithium cells; ethylene carbonate (EC) and methylethylcarbonate (MEC) were added to glymes in order to dissolve 1.0 M $LiPF_6$. They found that the conductivity increases with the decrease in PEO chain length and the solution viscosity; they also indicated that di- and tri-glyme exhibit a better performance than mono- and tetra-glyme in terms of conductivities at low temperature (below 0 °C) and the charge–discharge cycling at a high current. The same group[172] further demonstrated the use of such tertiary electrolyte systems (mixing glymes with 1 M $LiPF_6$–EC/MEC) in rechargeable lithium cells with Si-based anodes: for both Li/Si + C and Li/Si–C + C cells, the discharge capacity appears to be larger than the system without glyme, and the cycling life of the latter cells is also improved. Kaulgud *et al.*[173] carried out *ab initio* Hartree–Fock calculations to determine the electronic structure and vibrational frequencies of $CH_3(OCH_2CH_2)_nOCH_3$–M^+–OTf^- (n = 2–4, M = Li, Na, and K) complexes. They suggested that the metal ion has various coordinations from 5 to 7 in these complexes, and Li^+ ions bind to one of the oxygen atoms of OTf^- in tetraglyme–lithium triflate while Na^+ or K^+ ions show bidentate coordination. In addition, the metal ion tends to bind more strongly to ether oxygens of tetraglyme than its di- or triglyme analogues. The Watanabe group[174] determined the physicochemical properties of triglyme and tetraglyme solutions of Li[Tf_2N] and observed the formation of complexes ([Li(glyme)][Tf_2N]) in concentrated solutions. The ionic conductivity is concentration-dependent and reaches its maximum at ~1 M. The viscosity increases with the salt concentration while the self-diffusion coefficient of each species in the solutions decreases with the salt concentration. [Li(glyme)][Tf_2N] may be considered as a quasi-ionic liquid in terms of similar ionicity. Orita *et al.*[175] observed that a higher amount of tetraglyme in tetraglyme–Li[Tf_2N] complexes decreases the viscosity and increases the ionic conductivity of the mixture; in addition, the mixture has a higher thermal stability than conventional organic electrolytes when the molar ratio of tetraglyme is more than 40 mol%. They further demonstrated the potential of [Li(tetraglyme)][Tf_2N] as a replacement of organic electrolytes in lithium ion batteries with appropriate electrode-active materials. Tamura *et al.*[176] prepared glyme–cyclic imide lithium salt (Li[CTFSI]) complexes as thermally stable electrolytes for lithium batteries, *i.e.* [Li(G3)][CTFSI] (solid) and [Li(G4)][CTFSI] (liquid). The latter complex shows a much higher thermal stability than pure G4, and a high ionic conductivity of 0.8 mS cm^{-1} at 30 °C despite its high viscosity. They also observed a stable charge–discharge cycling behavior of a [$LiCoO_2$|[Li(G4)][CTFSI]|Li metal] cell during 50 cycles, implying the applicability of the [Li(G4)][CTFSI] complex in a 4 V class lithium secondary battery. The Watanabe group[177] investigated the physicochemical and electrochemical properties of a 1 : 1 complexing mixture of triglyme and $Li[N(SO_2F)_2]$ (lithium bis(fluorosulfonyl)amide) as a safe lithium-ion secondary battery electrolyte. This new electrolyte has a relatively high thermal stability, and enabled a stable charge–discharge of Li^+ ions with both $LiFePO_4$ positive electrode and graphite negative electrode leading to high coulombic efficiency and long cycle. In addition, they achieved 82% of capacity retention after 100 cycles of charge–discharge operations of a [$LiFePO_4$ positive electrode|G3-LiFSI electrolyte|graphite negative electrode] cell. The same group[178] further examined the use of a 1 : 1 equimolar complex electrolyte of triglyme:Li[Tf_2N] in lithium secondary batteries using lithium metal and two positive electrode materials ($LiFePO_4$ and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$). They observed a relatively favorable surface formed at the electrolyte/lithium metal electrode interface; and they also found an excellent capacity retention with low degradation for both 3V-class [$LiFePO_4$|Li metal] and 4V-class [$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$|Li metal] cells.

The lithium/sulfur (Li/S) battery has become a promising electrochemical system because of its high theoretical capacity of 1675 mA h g^{-1}.[179] However, the present Li/S system has a number of obstacles to overcome, such as its poor active material conductivity, active material dissolution, and the highly reactive lithium metal electrode. The Watanabe group[180] examined the redox reaction of sulfur supported on inverse opal carbon (IOC) in a [Li(tetraglyme)][Tf_2N] molten complex electrolyte. They found that the Li|[Li(tetraglyme)][Tf_2N]|sulfur/100 nm IOC cell maintained a large discharge capacity of *ca.* 800 mA h g^{-1}-sulfur and a high coulombic efficiency of >97% after 50 cycles. They suggested that the [Li(tetraglyme)][Tf_2N] molten salt could be a promising electrolyte enabling a high coulombic efficiency of charge–discharge in Li–S batteries. Barchasz *et al.*[181] found that conventional carbonate-based electrolytes cannot be used in Li/S cells and then suggested that Li/S cell electrolytes require solvents with high solvation power such as tetraglyme and ethyl diglyme, but not those solvents (*e.g.* monoglyme, butyl diglyme and 1,3-dioxolane) with low polysulfide solubility. Polyglyme (average $M_n = 250$) plays a vital role in Li/S electrolytes, and could prevent fast electrode passivation and extend the length of a second discharge plateau, resulting in a discharge capacity of about 1100 mA h g^{-1} for the first discharge and over 550 mA h g^{-1} remaining after 10 cycles.

In addition to the alkaline battery system, other metal battery systems have also been explored using glyme-based electrolytes. Aurbach *et al.*[182] prepared new electrolyte solutions based on glymes (such as mono-, di- and tetra-) and magnesium aluminates, giving an electrochemical window of 2.5 V and >99% efficiency of Mg deposition–dissolution cycles. They further developed new rechargeable Mg batteries (1–1.5 V) using these electrolyte solutions and cathodes of the Mg_xMoS_y type (Chevrel phase) for delivering over 1000 charge–discharge cycles. This group[183] further constructed rechargeable Mg battery systems by using $Mg(AX_{4-n}R_n)_2$ complexes (A = Al, B, Sb, P, As, Fe, and Ta; X = Cl, Br, and F; and R = butyl, ethyl, phenyl, and benzyl) in several ether solvents and glymes (mono-, di- and tetra-). They found some of these Mg complexes in THF or glymes gave a wide electrochemical window (>2 V) and allowed the reversible deposition of magnesium. This group[184] further developed new magnesium batteries comprising Mg metal anodes, an electrolyte with a general structure of $Mg(AlX_{3-n}R_nR')_2$ (R, R′ = alkyl groups, X = halide) in ethereal solutions (such as THF and tetraglyme), and Chevrel phases of $MgMo_3S_4$ stoichiometry as highly reversible cathodes. The magnesium battery systems could be cycled thousands of times with little loss in capacity; in addition, they are environmentally benign alternatives to lead–acid and nickel–cadmium batteries and are constructed from abundant, inexpensive, and nonpoisonous materials.

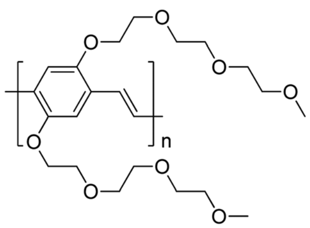
Solid-state electrolytes consisting of poly(ethylene oxide) (PEO) doped with salts have promising applications in batteries, capacitors and fuel cells because these electrolytes exhibit high ionic conductivity. In addition, they are soft solids, and if small glyme molecules are used, they are monodispersed and do not entangle like polymers. Rao and Klemann[185] investigated the behavior of Li/TiS_2 cells in a low-temperature melt comprising LiI:glyme solvate, and suggested the cells could be discharged at high rates in the low temperature melt and could be stored in solid electrolyte long-term. Zhang *et al.*[186] measured the ionic conductivities of several solid electrolytes comprising lithium salts with glymes, and indicated that the $(tetraglyme)_{0.5}$:$LiBF_4$ electrolyte has the highest conductivity among those small-molecule electrolytes with a lithium transport number of 0.65. The same group[187] further observed an increase in conductivity (from around 10^{-7} to 10^{-4} S cm^{-1}) by substituting PEO molecules in conducting crystalline complexes PEO_6:$LiXF_6$ (X = P or As) with glymes (tri- and tetra-). Since the stoichiometric compositions of glyme–salt complexes are lower than 6 : 1 (4 : 1 for G3 : $LiXF_6$ and 5 : 1 for G4 : $LiXF_6$), there are three phases present, the 6 : 1 phase, the glyme complex and a liquid containing some salt; and it is believed that the liquid is primarily responsible for the conductivity. This group[188] also evaluated two glyme-based solid electrolytes: G3 : $LiAsP_6$ and G4 : $LiAsP_6$, and reported that they have quite different transport numbers ($t_+ = 0.8$ and 0.1 respectively). This is due to two factors: (a) there are tunnels in the crystal structure of the G3 complex for Li^+ migration, but not in the G4 complex; (b) there is a weaker binding of AsF_6^- in the structure of G4 than in G3. The Bruce group[189] further determined the crystal structures of complexes $[CH_3O(CH_2CH_2O)_nCH_3]$:$LiAsF_6$ ($n = 8–12$), and indicated that Li^+ ions are six coordinated if only ether oxygens are involved in coordination and the coordination number becomes five if a fluorine from the AsF_6^- anion is involved in coordination. They also observed low lithium transport numbers ($t_+ < 0.3$) and lower conductivities in these complexes compared with complexes formed with lower glymes ($n = 3, 4$). Xia and Smid[190] conducted the differential thermal analysis of solid polymer electrolyte complexes of lithium (or sodium) triflate and homopolymers derived from three methacrylate monomers $CH_2{=}C(CH_3)COO(CH_2CH_2O)_nCH_3$ (n = 4, 8 or 22 on average), and found that the conductivities of these complexes were comparable to those known for alkali complexes of poly(ethylene oxide). Holzer *et al.*[191] described a different type of solid electrolyte containing a glyme motif, poly[1,4-(2,5-bis(1,4,7,10-tetraoxaundecyl))phenylene vinylene] (BTEM-PPV, see Scheme 4), for constructing red-orange light-emitting electrochemical cells (LECs). The high electronic conductivity and ionic conductivity of BTEM-PPV could be attributed to its conjugated backbone and glyme-containing side chains. LECs based on this polymer are relatively bright light emitting devices with low response times. Because of the covalent linkage of PEO chains to the PPV backbone, an ionochromic effect was also observed in both absorption spectrum and electroluminescence spectrum when BTEM–PPV is complexed with metal ions; this indicates its potential application in chemical sensors.

7. Uses In organic reactions

Glymes play various vital roles in organic synthesis. The most common role is acting as the reaction media (solvent role). Other important roles include reaction additives/metal chelators, catalysts and reagents. The following sections discuss some representative examples in each of these categories.

7.1. Reaction solvents

Glymes are liquid over a wide temperature range (Table 2) and are suitable for reactions at low temperatures (low freezing points). For example, monoglyme has a freezing point of −69 °C and has been widely used in low-temperature reactions, but it can also be removed easily during the workup (boiling point 85 °C). In addition, glymes have a strong solvating power and can dissolve a variety of compounds, particularly chelating with metal ions. For example, the solvating power of the ether-type solvents increases in the order 2-methyltetrahydrofuran < THF < monoglyme < diglyme < triglyme < tetraglyme; in particular, triglyme and tetraglyme are strong chelating agents for Na^+ ions.[58] Therefore, glymes (especially monoglyme) have been explored in numerous organic reactions since the 1960s, such as reduction, oxidation, substitution, C–C coupling, borane chemistry, and other reactions.

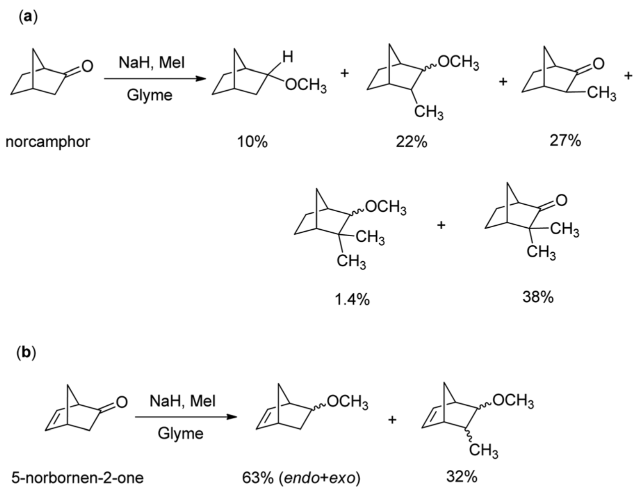


Scheme 4 Structure of BTEM-PPV.

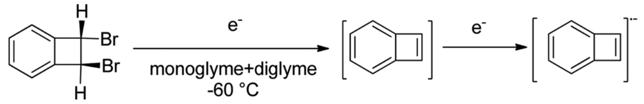
Reduction reactions. When norcamphor and 5-norbornen-2-one were treated with NaH and MeI in monoglyme, reduction products (methyl ethers) were obtained (Scheme 5); it is the carbonyl group that is reduced and not the *O*-alkylation products, 2-methoxynorbornene and 2-methoxynorbornadiene.[192]

The benzocyclobutadiene radical anion was produced by the addition of *trans*-1,2-dibromobenzocyclobutene to an excess of solvated electrons in a mixture of monoglyme and diglyme at −60 °C (Scheme 6).[193] Similarly, treating cyclooctatetraene with potassium mirror in monoglyme at −90 °C (or −80 °C) yielded an anion radical.[194,195] Miller *et al.*[196] treated dibenzonorcaradiene with different electron-transfer reducing agents in anhydrous monoglyme to form a dibenzonorcaradiene anion radical, whose cyclopropane isomerization led to various reduction products; for example, the Na-reduction after 12 h at r.t. produced 9-methylphenanthrene (25.4%), 9-methyl-9,10-dihydrophenanthrene (47.9%), and 6,7-dihydro-5*H*-dibenzo[*a*,*c*]-cycloheptene (26.6%).

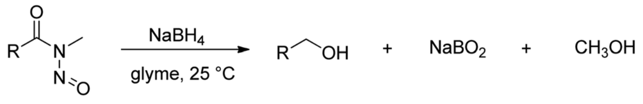
Walborsky *et al.*[197] studied the reductive cleavage of 1,1-biphenylene-2-methylcyclopropane using sodium and lithium in liquid ammonia, sodium in monoglyme, sodium naphthalide in monoglyme, and by controlled potential electrolysis in acetonitrile at a mercury cathode (Scheme 7). The isomer ratio of two products 9-propylfluorene and 9-isopropylfluorene ranged from 96 : 4 to 81 : 19. However, the use of monoglyme as the solvent gave a lower product ratio. In the synthesis of



Scheme 5 Reduction of norcamphor and 5-norbornen-2-one in monoglyme.



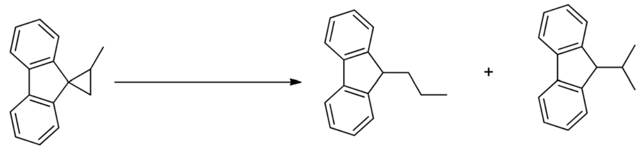
Scheme 6 Preparation of benzocyclobutadiene radical anion.



Scheme 8 Reduction of nitrosoamides to alcohols.

asymmetric phosphine macrocycles, Wei *et al.*[198] eliminated the protecting tosyl groups at −78 °C by sodium naphthalenide in monoglyme containing *t*-butyl alcohol (as a proton source); this method was used by the same group in an earlier detosylation study.[199]

Partial reduction of a lactam to produce the indole alkaloid roxburghine D was achieved by using di-isobutyl aluminium hydride in monoglyme at −70 °C.[200] Dahl *et al.*[201] prepared $CH_3Ge(PH_2)_2H$ and $CH_3Ge(PH_2)_3$ by the reaction of CH_3GeCl_3 with $LiAl(PH_2)_4$ in triglyme at −23 °C. Saavedra[202] carried out the reduction of nitrosoamides to alcohols using $NaBH_4$ in dry monoglyme at room temperature for 2–8 h, achieving 50–82% yields (Scheme 8). Ohsawa *et al.*[203] found that the potassium metal–crown ether–diglyme system could be effective for the reductive removal of sulfonyl group from *O*-sulfonates or sulfonamides. The Rieke group[204,205] prepared highly reactive metal powders of Fe, Co, Ni, Pd and Pt from the reduction of anhydrous metal halides in monoglyme or THF by lithium in the presence of a small amount of naphthalene. Inaba *et al.*[206] prepared highly reactive metallic nickel by reducing nickel halides with lithium in monoglyme using naphthalene as an electron carrier, and further investigated it as a reductive homocoupling reagent for benzylic mono- and polyhalides (Scheme 9) to produce 1,2-diarylethanes. Specifically, the coupling of benzylic monohalides at room temperature yielded the corresponding ethane derivatives, and the coupling of benzylic di- and trihalides gave mixtures of *cis* and *trans* isomers of substituted ethenes. Carbonyl-substituted *closo* polyhedral boranes with B_{10} and B_{12} cages are important derivatives that can be converted to other functional groups such as cyanide, amide, keto, ester, amine, *etc.* The same group[207] further demonstrated that metallic nickel could be a versatile coupling reagent for ketone preparation by the reaction of benzylic, allylic, vinylic, and pentafluorophenyl halides with acid halides at 85 °C in monoglyme. Reduction of the B_{12} 1,12-dicarbonyl to 1,12-bis(hydroxymethyl)decahydrododecaborate salts was achieved by using $LiAlH_4$ in anhydrous monoglyme at room temperature.[208]

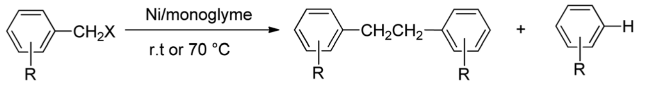


Condition	Conversion (%)	%	%
Na/NH_3 (-28°C)	90	95	5
Na/NH_3-*t*-BuOH (-28°C)	90	96	4
Li/NH_3 (-78°C)	100	96	4
Electrolysis/ acetonitrile (25°C)	100	93	7
Na/glyme (25°C)	22	82	18
Na naphthalide/ glyme (25°C)	100	81	19
Na naphthalide/ glyme (-78°C)	21	83	17

Scheme 7 Reductive cleavage of cyclopropane ring.

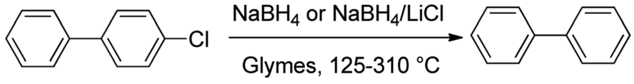
Bianconi *et al.*[209] described a general method for the reductive coupling of carbonyl ligands in $[M(CO)_2(dmpe)_2Cl]$ complexes, M = Nb or Ta and dmpe = 1,2-bis(dimethylphosphino)ethane: the reaction of $[M(CO)_2(dmpe)_2Cl]$ with 40% sodium amalgam in THF or monoglyme, after the filtration, the addition of Me_3SiY, Y = Cl or CF_3SO_3 (triflate), and the recrystallization from pentane results in $[M(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2Y]$ with 40–70% isolated yields. The Walton group[210,211] developed a general method for synthesizing dirhenium octahydrides $Re_2H_8(PR_3)_4$ [PR_3 = PMe_3, PEt_3, P-*n*-Pr_3, PMe_2Ph, PEt_2Ph, $PMePh_2$, $Ph_2PCH_2PPh_2$ (dppm), and $Ph_2PCH_2CH_2PPh_2$ (dppe)], *via* the reduction of triply bonded complexes $Re_2Cl_4(PR_3)_4$ using $LiAlH_4$ in monoglyme and the subsequent hydrolysis step. Taking the advantage of glymes as high-boiling inert solvents, Yang and Pittman[212] studied the dechlorination of 4-chlorobiphenyl with $NaBH_4$ in glymes at 120–310 °C (Scheme 10). At comparable reaction conditions, the dechlorination rates decreased in the order of tetraglyme > triglyme > diglyme, and a complete dechlorination was observed in $NaBH_4$/tetraglyme at 310 °C in 1 h. The addition of LiCl to $NaBH_4$ could enhance the dechlorination rate in di-, tri-, and tetraglyme respectively at 120–135 °C. On the other hand, the dechlorination of 4-chlorobiphenyl was not successful in the $NaBH_4$/diphenyl ether system. Based on the same methodology, this group[213] also accomplished the dechlorination of pentachlorophenol and 1,2,4-trichlorobenzene using $NaBH_4$ in tetraglyme at 290–315 °C or by $NaBH_4$/LiCl at 125–135 °C in diglyme, triglyme or tetraglyme after premixing at room temperature. Furthermore, this group[214] achieved a quantitative dechlorination of a polychlorinated biphenyl (PCB) mixture (Aroclor 1016) using $NaBH_4$ in tetraglyme at 290–310 °C in 2 h in a sealed tube, or using $NaBH_4$/LiCl/glyme solvents (di-, tri-, or tetraglyme) at 125–135 °C.

Kanth and Brown[215] noted that $NaBH_4$ and $NaBF_4$ have reasonably high solubilities in glymes (particularly triglyme and

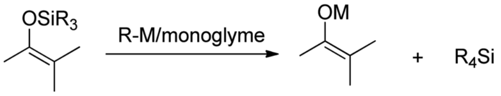


X = Cl, Br, or I
R = H, 4-CH_3, 3-CH_3O, 3-CF_3, 4-Cl, 4-Br, 4-NO_2, 4-CN, 4-CH_3OCO

Scheme 9 Ni-catalyzed reductive homocoupling of benzylic halides.



Scheme 10 Dechlorination of 4-chlorobiphenyl.



Scheme 13 Preparation of metal enolates from trialkylsilyl enol ethers.

tetraglyme). As illustrated in Scheme 11, they developed an improved procedure for the generation of diborane (B_2H_6) by the reaction of $NaBH_4$ in triglyme or tetraglyme, followed by the generation of diborane through a reaction of $NaBF_4$ with $NaBH_4$ in triglyme (or tetraglyme) in the presence of Lewis acids such as $AlCl_3$ and BCl_3. Triglyme (or tetraglyme) could be easily recovered and recycled.

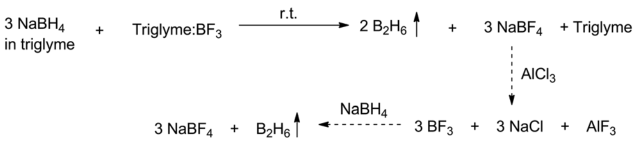
Oxidation reactions. Ouellette and Levin[216] conducted the oxidation of phenylcyclopropane by Na_2PdCl_4 in 2 : 1 (v/v) monoglyme–water, and found that the product distribution is dependent on the ratio of phenylcyclopropane to Na_2PdCl_4 (Scheme 12). At a low ratio of phenylcyclopropane/Pd(II), propiophenone is the major oxidation product; however, at a high ratio, an isomerization to *trans*-propenylbenzene occurs, which is further oxidized to phenylacetone.

Ochiai and Fujita[217,218] synthesized allylic nitrates *via* the reaction of *ent*-16-kaurene or *ent*-15-kaurene with thallium(III) trinitrate in monoglyme. McKillop *et al.*[219] found that thallium(III) nitrate is capable of oxidizing chalcones, deoxybenzoins and benzoins in aqueous glyme–perchloric acid; the same group[220] also oxidized diarylacetylenes to benzils in good yields in aqueous acidic glyme or in methanol.

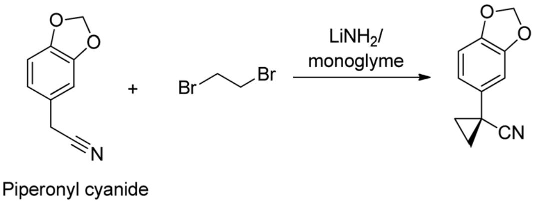
Substitution reactions. Stork and Hudrlik[221] synthesized different metal enolates from trialkylsilyl enol ethers using organometallic reagents in monoglyme (Scheme 13). For example, at room temperature, methyllithium completely converts trimethylsilyl enol ether of 2-methylcyclohexanone into lithium enolate in 6 min in monoglyme but in ~1 h in ether. In another study, Stork and Hudrlik[222] described the preparation of trialkylsilyl enol ethers from ketone and NaH in monoglyme under reflux conditions followed by the addition of triethylamine and trimethylsilyl chloride and subsequent workups. In the preparation of racemic alkaloid 3-*epi*-elwesine, piperonyl cyanide was converted to cyclopropane carbonitrile *via* a two-step substitution reaction using $LiNH_2$ in monoglyme at room temperature with 65–75% yield (Scheme 14),[223] although the use of $NaNH_2$/glyme only afforded low yields of the cyclopropane.[224]

Kice and Kasperek[225] examined the hydrolysis of aryl α-disulfones in various $Et_3N–Et_3NH^+$ buffers in 60% dioxane and 60% monoglyme as solvents; they found that the triethylamine-catalyzed reaction is a general base catalysis (by triethylamine) rather than nucleophilic catalysis (Scheme 15a). The same group[226] further investigated the hydrolysis of *p*-nitrophenyl *p*-toluenesulfonate in $Et_3N–Et_3NH^+$ buffer in both 20% acetonitrile and 60% aqueous monoglyme, and found no significant catalysis by triethylamine in this case. However, they observed that *N*-ethylpyrrolidine (NEP) could catalyze the hydrolysis in 60% monoglyme, which is shown to be *via* nucleophilic catalysis (Scheme 15b).

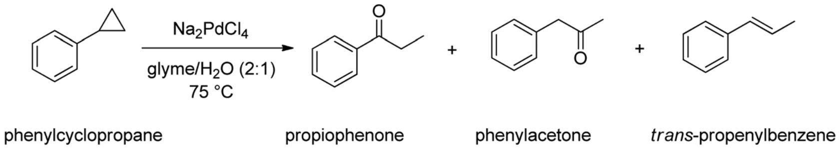
The nucleophilic aromatic substitution of haloaryl sulfones with alkali phenoxides was studied in glymes at 160 °C (Scheme 16).[227] The reaction was found to be first order in halo sulfone and of fractional (~0.5) order in phenoxide ion. The longer glyme chain length promoted a faster reaction, and when $n \approx 20$ the reaction rate was about 25 times faster than when $n = 2$ (diglyme). The likely reason for the rate enhancement is that polyglyme is a better cation solvating solvent than diglyme. Pastor and Hessell[228] studied the aromatic substitution of hexa-, tetra-, tri-, di-, and monochlorobenzenes with sodium alkanethiolates in several glymes, and found that the product yield decreased in the order: tetraglyme > triglyme > diglyme > monoglyme. It was explained that tetraglyme is more effective in solvating the sodium cation, generating a more nucleophilic unsolvated thiolate anion.



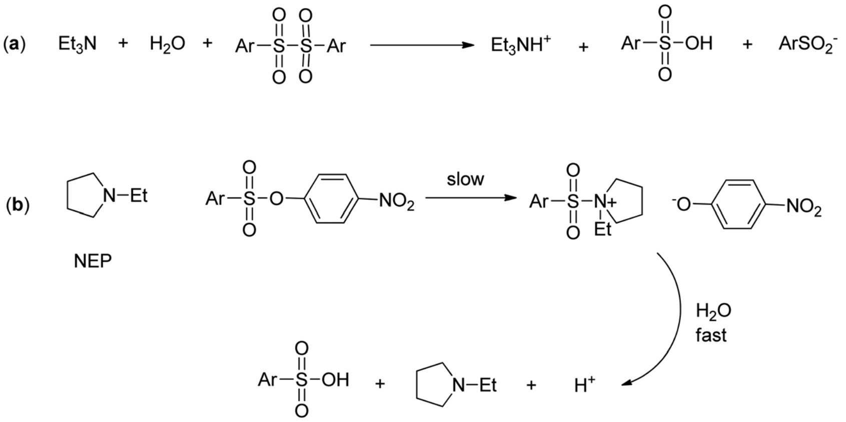
Scheme 11 Improved procedure for diborane generation.



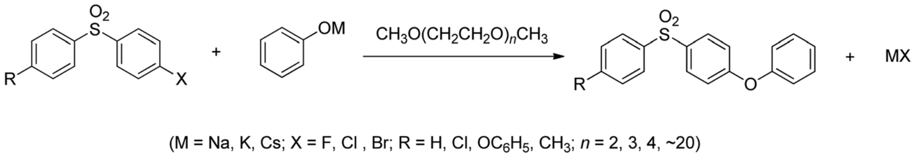
Scheme 14 Conversion of piperonyl cyanide to cyclopropane carbonitrile.



Scheme 12 Oxidation of phenylcyclopropane by Na_2PdCl_4 in aqueous monoglyme.



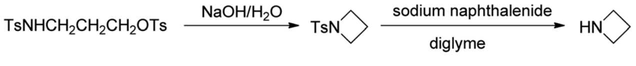
Scheme 15 Hydrolysis of (a) aryl α-disulfones and (b) *p*-nitrophenyl *p*-toluenesulfonate.



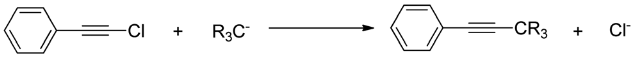
Scheme 16 Nucleophilic substitution of haloaryl sulfones with alkali phenoxides.

Bis(h^5-cyclopentadienyl)tungsten dichloromethide hydride, $Cp_2WH(CHCl_2)$, was synthesized as the insertion product from the reaction of bis(h^5-cyclopentadieny1)tungsten dihydride and sodium trichloroacetate in monoglyme (Scheme 17); however, in a chlorobenzene–diglyme mixture, the thermal decomposition of sodium chlorodifluoroacetate in the presence of bis(h^5-cyclopentadieny1)tungsten dihydride yielded the substitution product, bis(h^5-cyclopentadienyl)tungsten bis(chlorodifluoroacetate), $Cp_2W(O_2C_2ClF_2)_2$.[229]

White and McGillivray[230] reported an effective method for azetidine preparation (Scheme 18) *via* reductive detosylation using sodium naphthalenide in diglyme, which afforded improved yields and simple procedures (superior to monoglyme and THF). The azetidine–diglyme solution could be further converted to *N*-aroylazetidines by adding different aroyl chlorides. 6-(Arylalkylamino)uracils and 6-anilinouracils, potent inhibitors of *Bacillus subtilis* DNA polymerase III, were prepared by the reactions between 6-chlorouracil and appropriate amines in monoglyme instead of aqueous solutions, which considerably reduced the reaction time.[231] Izumi and Miller[232] examined the nucleophilic attack of carbanions (R_3C^-) to displace the chloride ion from phenylchloroacetylene (Scheme 19); they suggested that reactions in DMSO–KOH are mainly those of ions, however, in aprotic monoglyme, reactions of $R_3C–Na^+$ are those of its aggregates. The DMSO–KOH medium is only suitable for relatively strong carbon acids, while the Na–glyme conditions have broader applications.



Scheme 18 Preparation of azetidine.

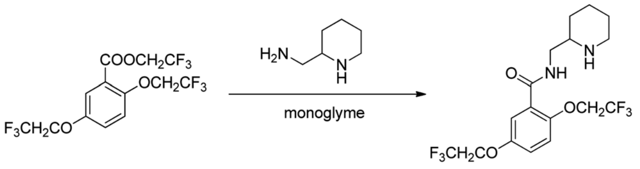


Scheme 19 Nucleophilic attack of a carbanion.

Banitt *et al.*[233] carried out the nucleophilic acyl substitution of 2,2,2-trifluoroethyl 2,5-bis(2,2,2-trifluoroethoxy)benzoate with 2-aminomethylpiperidine in monoglyme (Scheme 20), achieving 76.5% isolated yield. Okamoto *et al.*[234] investigated the reaction of 5-dimethylamino-1-naphthalenesulfonyl chloride with butylamine in chloroform with glymes as oligomer co-solvents, and determined the second-order rate constants by fluorometry. The addition of glymes imposed an acceleration effect especially when their concentrations were lower than 20% (v/v), and such an effect became more pronounced for glymes with longer chain length (tetraglyme > triglyme > diglyme > monoglyme). In addition, the rate acceleration seems to

$$Cp_2WH_2 + CCl_3COONa \xrightarrow[84\ °C,\ 5\ h]{\text{monoglyme}} Cp_2WH(CHCl_2) + NaCl + CO_2$$

Scheme 17 Insertion reaction of bis(h^5-cyclopentadieny1)tungsten dihydride.



Scheme 20 Synthesis of *N*-(2-piperidylmethyl)-2,5-bis(2,2,2-trifluoroethoxy)benzamide.

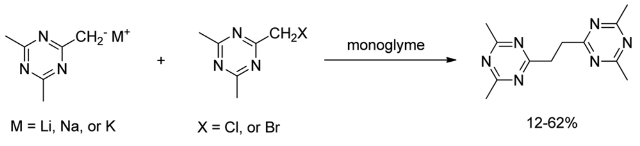
correlate with the volume fraction of the co-solvent, which can be attributed to the polymer effects of glymes and is explained by the thermodynamics of polymer solutions.

Reactions of Li^+, Na^+, and K^+ salts of 2,4,6-trimethyl-*s*-triazine with 2-halomethyl-4,6-dimethyl-*s*-triazine ($X = Cl$, Br) in monoglyme yielded 1,2-bis(4,6-dimethyl-*s*-triazin-2-yl)ethane (Scheme 21), and other compounds including 1,2-bis(4,6-dimethyl-*s*-triazin-2-yl)ethene, 1,2,3-tris(4,6-dimethyl-*s*-triazin-2-yl)cyclopropane, 1,2,3-tris(4,6-dimethyl-*s*-triazin-2-yl)propane and 1,2,3,4-tetrakis(4,6-dimethyl-*s*-triazin-2-yl)butane.[235] It is suggested that 1,2-bis(4,6-dimethyl-*s*-triazin-2-yl)ethane is produced through an S_N2 mechanism, while other products are formed through carbenoid reactions.

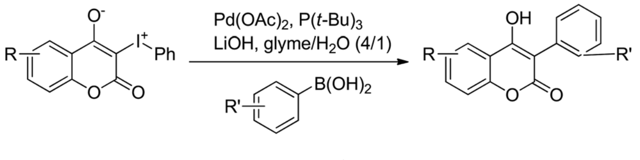
Carbon–carbon coupling reactions. Zhu *et al.*[236] employed a phenyliodonium zwitterion as an efficient electrophile in the palladium-catalyzed Suzuki-type reaction with aryl boronic acids in monoglyme–water (4/1) (Scheme 22). The mild reaction conditions and commercial accessibility of 4-hydroxycoumarins and boronic acids make this method a versatile tool for the synthesis of 3-aryl-4-hydroxycoumarins.

Kim *et al.*[237] indicated that Ni nanoparticles (5.7 ± 3.8 nm) exhibited a moderate catalytic activity in the oxidative addition reaction of benzylchloride and bromoacetonitrile in monoglyme under reflux conditions to prepare 3-arylpropanenitrile (Scheme 23), whereas larger Ni particles (3 μm and 100 mesh) showed no activity.

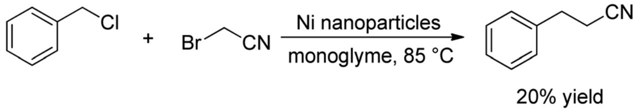
Smith and Fu[238] developed a stereoconvergent method for the catalytic asymmetric Negishi cross-coupling of various racemic secondary propargylic halides with arylzinc reagents in monoglyme catalyzed by a chiral Ni/pybox complex (Scheme 24). In most cases, they achieved 70–80% yields and ee (enantiomeric excess) near or above 90%. It is important to point out that the catalyst components ($NiCl_2 \cdot$glyme and pybox ligand) are commercially available.[238,239]



Scheme 21 Reactions of 2,4,6-trimethyl-*s*-triazine salts with 2-halomethyl-4,6-dimethyl-*s*-triazine.



Scheme 22 Pd-catalyzed coupling of phenyliodonium zwitterion with aryl boronic acid.

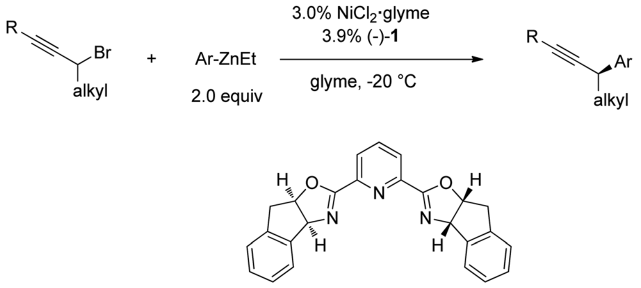


Scheme 23 Catalytic activity of Ni nanoparticles in an oxidative addition reaction.

Organometallic compounds are common reagents for C–C coupling reactions. However, Fitt and Gschwend[240] pointed out that monoglyme (and perhaps other glymes) should not be used in metalation reactions including those using *t*-butyllithium (*t*-BuLi). In the presence of *t*-BuLi, monoglyme undergoes deprotonation and β-elimination steps even at −70 °C to form lithium methoxide (Scheme 25), which is characteristic of 1,2-diheterosubstituted ethanes. Thus, there is no complex formed between monoglyme and *t*-BuLi. The reaction rates of different butyllithiums with monoglyme decrease in the order of *t*-BuLi > *sec*-BuLi ≫ *n*-BuLi.

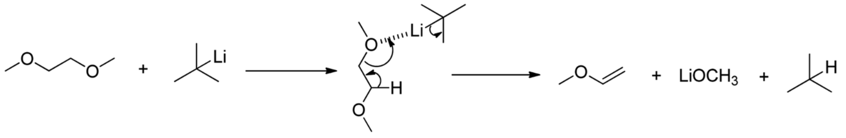
The Delia group[241,242] reported the synthesis of mono-, di- and tri-substituted phenylpyrimidines *via* Suzuki coupling reactions in various solvents (Scheme 26). They found that the monoglyme–water mixture, *t*-butanol and polar aprotic solvents (such as acetonitrile, acetone, THF, $CHCl_3$ and CH_2Cl_2) gave the best results; polar protic solvents (such as methanol and ethanol) induced ether byproducts under basic conditions while nonpolar solvents (such as hexane) gave more byproducts and a 2-substituted isomer.

Borane chemistry. Geanangel and Shore[243] firstly prepared NaB_5H_8 and KB_5H_8 by reacting B_5H_9 and metal hydride in monoglyme at room temperature, and then produced B_6H_{10} by the reaction of alkali metal $B_5H_8^-$ salts with diborane (B_2H_6) at −78 °C in monoglyme; finally, refluxing glyme solutions of B_6H_{10} led to decaborane $B_{10}H_{14}$ in 20–30% yields. Hosmane *et al.*[244] quantitatively prepared boron hydride species $[B_{11}H_{14}]^-$ by reacting $K[B_9H_{14}]$ with 0.4 equiv. of B_5H_9 (or directly from B_5H_9 and metal hydride such as *t*-BuLi) in monoglyme at 85 °C

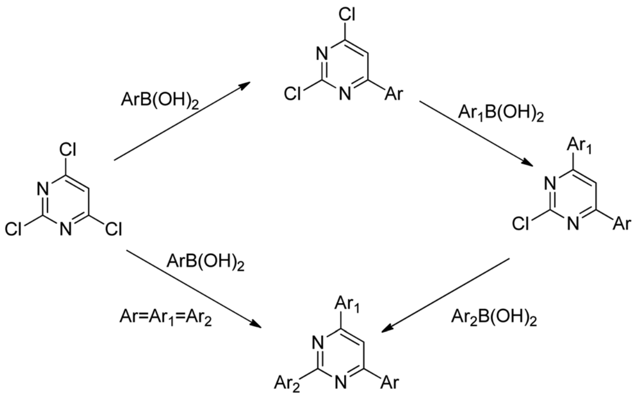


(-)-**1**

Scheme 24 Cross-coupling of racemic propargylic halides with arylzinc reagents.



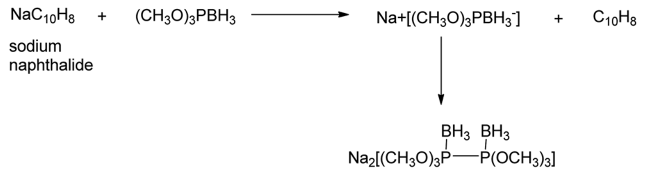
Scheme 25 Reactivity of monoglyme with *t*-butyllithium.



Scheme 26 Mono-, di-, and triarylation of the pyrimidine ring.

for 20 h. Lawrence *et al.*[245] synthesized the tetradecahydrononaborate(1−) anion $[B_9H_{14}]^-$ by the reaction of B_5H_9 with NaH (or KH) in THF or monoglyme.

Pelter *et al.*[246] prepared a thioester by the reaction of trisethylthioborane and benzoic acid in refluxing monoglyme for 7 h to give 78% isolated yield. Peacock and Geanangel[247] conducted the reduction of trimethyl phosphite-borane by sodium naphthalide (which was prepared in monoglyme) to a new type of diphosphine derivative (Scheme 27). Leyden *et al.*[248] carried out the reaction of $[(\eta^5\text{-}C_5H_5)_2Ni]$ with *nido*-$(B_{11}H_{13})^{2-}$, $(B_{10}H_{13})^-$, or $(B_9H_{12})^-$ catalyzed by Na/Hg amalgam in monoglyme to produce *closo*-$[(\eta^5\text{-}C_5H_5Ni)B_{11}H_{11}]^-$, *nido*-$[(\eta^5\text{-}C_5H_5Ni)B_{10}H_{12}]^-$, as well as isomeric *closo*-1- and $[2\text{-}(\eta^5\text{-}C_5H_5Ni)B_9H_9]^-$ anions, respectively; they also performed the reaction of $[(\eta^5\text{-}C_5H_5)_2Ni]$ or $[(\eta^5\text{-}C_5H_5NiCO)_2]$ with *closo*-$(B_{11}H_{11})^{2-}$, $(B_{10}H_{10})^{2-}$, or $(B_9H_9)^{2-}$ in monoglyme to yield *closo*-$[(\eta^5\text{-}C_5H_5Ni)B_{11}H_{11}]^-$, $[(\eta^5\text{-}C_5H_5Ni)_2B_{10}H_{10}]$, and isomeric 1- and $[2\text{-}(\eta^5\text{-}C_5H_5Ni)B_9H_9]^-$, respectively. Wermer and Shore[249] suggested that pentaborane (B_5H_9) could be reduced by alkali metal naphthalide in THF or monoglyme to produce the nonahydropentaborate(2−) dianion $[B_5H_9]^{2-}$, which could be further protonated to form B_5H_{11} with yields up to 38% (Scheme 28).

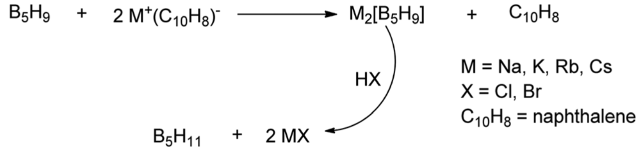


Scheme 27 Reduction of trimethyl phosphite-borane by sodium naphthalide.

Getman *et al.*[250] synthesized *arachno*-$[B_9H_{13}]^{2-}$ as K^+ and Na^+ salts *via* the deprotonation of $K[B_9H_{14}]$ by KH in monoglyme and the deprotonation of $Na[B_9H_{14}]$ by $NaNH_2$ in liquid ammonia respectively. Kang *et al.*[251] suggested that monoglyme was the best refluxing solvent for converting *arachno*-$S_2B_7H_8^-$ to *hypho*-$S_2B_7H_{10}^-$; they further carried out the synthesis of new metalladithiaborane clusters, derived from *hypho*-$S_2B_7H_{10}^-$ in refluxing monoglyme, such as the treatment of *hypho*-$S_2B_7H_{10}^-$ with $Cp(CO)_2FeCl$ to form of $C_5H_5FeS_2B_7H_8$, with $(CO)_5MnBr$ to form *hypho*-l-$(CO)_4Mn$-2,5-$S_2B_6H_9$, and with $[Cp^*RhCl_2]_2$ to form *arachno*-7-Cp*Rh-6,8-$S_2B_6H_8$. Holub *et al.*[252] carried out the reaction between Na_2[*nido*-6,9-$C_2B_8H_{10}$] and PCl_3 in monoglyme at room temperature for 24 h to prepare phosphadicarbaborane *nido*-7,8,11-$PC_2B_8H_{11}$ (35%), which was converted to a [7,8,11-*nido*-$PC_2B_8H_{10}]^-$ anion by deprotonation; following the same strategy by using $PhPCl_2$ as the phosphorus source, they also synthesized the isomeric compound 7-Ph-7,8,10-*nido*-$PC_2B_8H_{10}$ (64%), and *nido*-7,8,11-$PC_2B_8H_{11}$ (14%) (from an accompanying dephenylation reaction).

Miscellaneous reactions. Rosen and Sworm[253] synthesized iodine isocyanate (INCO) in 0.4 to 0.5 N at −30 °C in the dark in ether, THF or monoglyme *via* the reaction of an excess of pure silver cyanate with iodine. The reaction rate was fastest in monoglyme, followed by THF and then ether. The decomposition of INCO at −11 °C was also the highest in glyme (75% decomposition in 24 h) but much slower in THF and ether (15 to 25% decomposition in 24 h). INCO is a reactive pseudohalogen used for forming C–N bonds from many unsaturated compounds. Gassman *et al.*[254] developed a method for the cleavage of nonenolizable ketones by a mild cleavage reagent: a 10 : 3 ratio of potassium *t*-butoxide and water in aprotic solvents including DMSO, monoglyme, hexamethylphosphoramide, hexane, or diethyl ether. A 90% yield was obtained after 4 h at 30 °C in the cleavage of benzophenone to give benzoic acid using potassium *t*-butoxide–water–monoglyme.

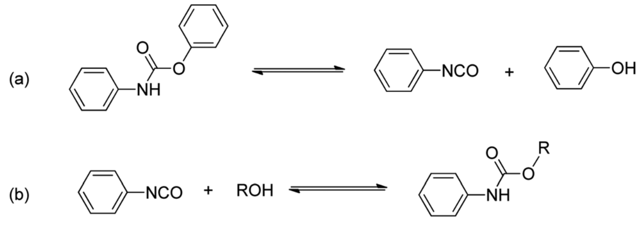
Finucane and Thomson[255] oxidized triterpene 12-enes with various substituents in ring A (*e.g.* taraxeryl acetate and cholesteryl acetate) to their corresponding αβ-unsaturated ketones by treating them with *N*-bromosuccinimide in moist solvents (dioxane, THF, monoglyme, or diglyme) under the irradiation of visible light. Lateef *et al.*[256] suggested that a series of *meta*- and *para*-substituted phenyl carbanilates undergo a rapid reversible dissociation in monoglyme (Scheme 29). They also indicated that the reaction followed the Hammett equation with positive ρ values of 1.49–1.66. As a precursor for preparing 2,5-dihydroxy-3,6-diphenyl-5,6-dihydropyrazine-1,4-dioxide, phenylglyoxal 2-oxime was synthesized by the acid hydrolysis of an α-oximino acetal (Scheme 30) in a mixture of monoglyme and pH 3.5 buffer.[257] The oxime substrate is insoluble in the buffer alone or



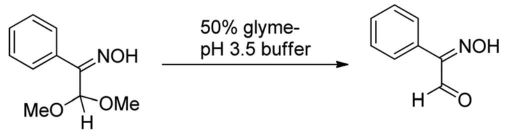
Scheme 28 Preparation of dianion $(B_5H_9)^{2-}$ and B_5H_{11}.

in aqueous methanol, but is soluble in a mixture of glyme and buffer. Pittman *et al.*[258] dissolved polystyrene in a mixture of monoglyme and diglyme (2/1, v/v) for a reaction with $Cr(CO)_6$ to prepare styrenetricarbonylchromiumstyrene copolymers.

Monoglyme was used as the solvent in the multi-step synthesis of D,L-muscone from cyclododecanone:[259] cyclotetradecenone and triethylsilane were refluxed in monoglyme catalyzed by chloroplatinic acid to afford 1-triethylsiloxycyclotetradecene, which was converted to 2-chloro-2-cyclopentadecenone after adding dichlorocarbene in refluxing glyme-tetrachloroethylene (1 : 4); the final product was obtained by a conjugate addition of dimethylcopper lithium in ether, followed by a workup using saturated NH_4Cl and then chromium(II) perchlorate reduction of α-chloro ketone in dimethyl formamide. Wilt and Rasmussen[260] carried out the Favorskii reaction of bromo ketones in methanol and monoglyme (sodium methoxide as the base) to prepare epimeric methyl benzonorbornene-2-carboxylate, and found that more polar methanol led to more exo ester (exo : endo 80 : 20) while the less polar solvent monoglyme increased the endo ester (exo : endo 58.5 : 41.5). In addition, higher ester yields were reported in monoglyme than in methanol. Stang and Mangum[261] prepared alkyl methylenecyclopropenes by the addition of unsaturated carbenes to alkynes in monoglyme with *t*-BuOK at −55 °C. The same group[262] also synthesized 2-indazoles by the reaction of triflate $(CH_3)_2C{=}CHOTf$ with azobenzene and *tert*-butylazobenzene in monoglyme with *t*-BuOK at −20 °C *via* unsaturated carbene additions to azo compounds. To encapsulate chalcogen atoms by transition-metal carbonyl clusters, Vidal *et al.*[263] synthesized the $[PhCH_2N(C_2H_5)_3]_3[Rh_{17}(S)_2(CO)_{32}]$ complex through reacting $Rh(CO)_2$acac and alkali carboxylates in tetraglyme, with H_2S or SO_2 under ∼300 atm of CO and H_2 at 140–160 °C. Similarly, as an example of the encapsulation of arsenic by transition-metal carbonyl clusters, $[PhCH_2N(C_2H_5)_3]_3[Rh_{10}As(CO)_{22}]\cdot C_4H_8O$ was prepared by the reaction of $Rh(CO)_2$acac and alkali carboxylates in tetraglyme with Ph_3As under *ca.* 300 atm of CO and H_2.[264]



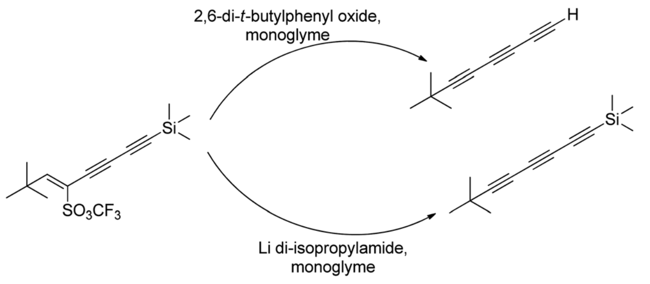
Scheme 29 Thermal dissociation of aryl carbanilates in monoglyme.



Scheme 30 Hydrolysis of phenylglyoxal dimethyl acetal oxime.

Collins *et al.*[265] demonstrated that the repeated action of a sodium–potassium alloy in glyme–triglyme and the subsequent quenching with CH_3I or with water could be an efficient low-temperature method to degrade coal by the cleavage of aliphatic and aromatic–aliphatic carbon–carbon bonds. Ladika and Stang[266] carried out the elimination of trifluoromethanesulfonic aid (CF_3SO_3H) from $RCH{=}C(OSO_2CF_3)C{\equiv}C{-}C{\equiv}CSiMe_3$ promoted by different bases in monoglyme to yield unsymmetrical trialkynes $R[C{\equiv}C]_3SiMe_3$ or $R[C{\equiv}C]_3H$ (Scheme 31).

Paxson *et al.*[267] performed cobalt carbonyl-catalyzed reactions of syn gas by using a CO–H_2 mixture at about 200–250 °C and 200 bar in glymes: in diglyme, the product selectivity for ethanol was 68% while in ethyl diglyme the selectivity for *n*-propanol increased to 40% (ethanol 28%). It is suggested that the solvent cleavage occurs and the terminal methoxy moieties supply the methyl group of ethanol. van Tamelen and Seeley[268] carried out the catalytic N_2-fixation by electrolytic and chemical reduction using monoglyme. Pez *et al.*[269] found that the reaction of a titanium metallocene complex, μ-($\eta^1 : \eta^5$-cyclopentadienyl)-tris(η-cyclopentadienyl)dititanium, with N_2 (∼10 atm) in monoglyme formed a complex giving a characteristic ν(N–N) peak at 1222 cm^{-1}; it was further treated with THF/monoglyme and diglyme to yield a crystalline N_2 complex with $\nu(N{-}N) = 1282\ cm^{-1}$. These complex systems could have potential applications in N_2-fixation. Budt *et al.*[270] achieved the regioselective NBS-epoxidation of farnesate attached to helical peptides in monoglyme–water (5 : 1) mixture at 0 °C. Hayward and Shapley[271] reacted $Re_2(CO)_{10}$ with sodium dispersion in glymes (diglyme and triglyme) to prepare the rhenium carbonyl clusters $Re_4(CO)_{16}{}^{2-}$, $H_2Re_6C(CO)_{18}{}^{2-}$, $Re_7C(CO)_{21}{}^{3-}$, and $Re_8C(CO)_{24}{}^{2-}$, as Et_4N^+ and $(PPh_3)_2N^+$ salts. Tee and Enos[272] examined the kinetics of hydrolysis of six *p*-nitrophenyl alkanoates in basic aqueous solutions containing up to 80% (v/v) of the co-solvents: ethylene glycol, 2-methoxyethanol, monoglyme, diglyme, or DMSO; they suggested that the ether-type solvents

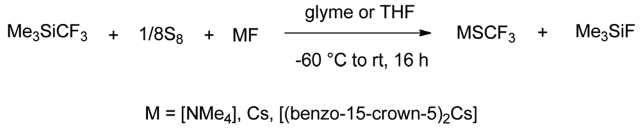


Scheme 31 Preparation of unsymmetrical trialkynes *via* elimination in monoglyme.

(2-methoxyethanol, monoglyme and diglyme) are more effective than ethylene glycol or DMSO in reducing and eliminating the hydrophobic aggregation and coiling of longer chain alkanoates. Briggs[273] carried out the trimerization of ethylene to hex-1-ene using a homogeneous three-component catalyst of chromium, hydrolyzed alkylaluminium and monoglyme with 74% selectivity; the replacements (such as diglyme, triglyme, THF, and *o*-dimethoxybenzene) for monoglyme gave less desirable results. A tricyclic ring/cage system of $RC_6H_5\cdot 5BNR'_2$ products were formed by reactions between dehalogenation products of $F_2BN(i\text{-}Pr)_2$ with monoalkylbenzenes using monoglyme as the co-solvent.[274] Hung *et al.*[275] prepared linear and cyclic perfluorinated polyethers through the ionic polymerization of a trifluorovinyl ether alcohol ($CF_2{=}CFOR_fCH_2OH$, $R_f = CF_2CF(CF_3)OCF_2CF_2$) and the subsequent fluorination of the polyfluorinated polyethers (Scheme 32). They found that without a solvent, linear polymers with M_n values up to 29 000 were produced, while in glyme solution, cyclic oligomers were the major products and a cyclic dimer was obtained in yields up to 60%. The reaction of arylcalcium iodides and nitrous oxide (N_2O) in monoglyme favored the formation of azobenzenes due to the insertion with N_2O into diphenylcalcium.[276]

Kirij *et al.*[277] prepared $[(CH_3)_4N][Te(CF_3)_3]$ and $[(CH_3)_4N][I(CF_3)_2]$ by the reactions of $(CH_3)_3SiCF_3/[(CH_3)_4N]F$ with $Te(CF_3)_2$ and CF_3I respectively in THF or monoglyme at −60 °C. Yagupolskii *et al.*[278] carried out an aza Curtius rearrangement by reacting *N*-(trifluoromethylsulfonyl)carboximidoyl chlorides with sodium azide in monoglyme or acetonitrile at −5 to +10 °C to form carbodiimides ($RN{=}C{=}NSO_2CF_3$). Israelsohn *et al.*[279] reported that a $PtCl_4$–CO catalyst could promote the hydration of internal and terminal alkynes in aqueous monoglyme or diglyme to afford aldehyde-free ketones between 80 and 120 °C. The reaction was found to be strongly dependent on the electronic and steric nature of the alkynes. Monoglyme or THF was used to dissolve elemental sulfur, Me_3SiCF_3, and fluoride salts for the preparation of trifluoromethanethiolates, $[NMe_4]SCF_3$, $CsSCF_3$ and $[(benzo\text{-}15\text{-}crown\text{-}5)_2Cs]SCF_3$ (Scheme 33).[280] It is known that SCF_3 salts are versatile nucleophilic reagents for synthesizing a variety of organic, organometallic and inorganic molecules. Tyrra *et al.*[281] prepared tetramethylammonium trifluoromethyltellurate(0), $[NMe_4]TeCF_3$, with 60% yield from Me_3SiCF_3, elemental tellurium and $[NMe_4]F$ in monoglyme; they further carried out the cation exchange of $[NMe_4]TeCF_3$ with [PNP]Br ([PNP] = bis(triphenylphosphoranylidene)ammonium) and [(dibenzo-18-crown-6)K]Br and demonstrated the high nucleophilicity of $TeCF_3^-$ when coupled with these low coordinating cations.

It is also important to know that glymes may be inferior to other organic solvents in some reactions. For example, the alkylation rates of alkali enolates in DMSO were found to be 1000-fold faster than that in glymes (mono- and di-) although the same reaction was even slower in diethyl ether.[282]



$$Me_3SiCF_3 + 1/8S_8 + MF \xrightarrow[\text{-60 °C to rt, 16 h}]{\text{glyme or THF}} MSCF_3 + Me_3SiF$$

M = [NMe4], Cs, [(benzo-15-crown-5)2Cs]

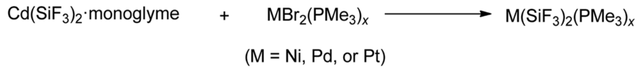
Scheme 33 Preparation of trifluoromethanethiolates.

7.2. Reaction additives/metal chelators

The second important role of glymes in reactions is acting as additives or metal chelators. Shinohara *et al.*[283] observed highly reactive agent-separated ion pairs formed *via* complexing sodium polystyryl ion pairs with tri- or tetraglyme; by adding glyme to solutions of sodium polystyryl in THF at 25 °C, they found propagation constants of the polymerization of living polymers increasing with the glyme concentration. Trifluorosilyl substituted dialkyl compounds including *trans*-$Pt(SiF_3)_2(PMe_3)_2$, $Pd(SiF_3)_2(PMe_3)_2$, and $Ni(SiF_3)_2(PMe_3)_3$ were synthesized by reacting an excess amount of $Cd(SiF_3)_2\cdot$monoglyme with trimethylphosphine metal dibromides of platinum, palladium, and nickel (Scheme 34).[284]

Liang and Ying[285] studied the kinetics and mechanism of the anionic equilibrium polymerization of α-methylstyrene in cyclohexane with butyllithium as the initiator and monoglyme or diglyme as the polar additive; kinetic equations of the equilibrium polymerization is dependent on the mole ratio of glyme/butyllithium; the stability of complexes formed by poly(α-methylstyryl)lithium (P_nLi) and the ether additive is in a decreasing order of [P_nLi (diglyme)] > [P_nLi (monoglyme)] > [P_nLi (THF)]. Wang *et al.*[286] employed ^7Li and/or ^{13}C NMR spectroscopy to investigate the aggregation equilibrium and electronic structure of methyl α-lithioisobutyrate (MIBLi) in THF with the co-existence of various Li^+-binding ligands; they found that the addition of ligands to coexisting tetrameric and dimeric MIBLi in THF increases the dimeric population in the order monoglyme < diglyme < 12-crown-4 < hexamethylphosphoric triamide, which is in agreement with the increasing strength of complexation between MIBLi (lithium cation) and the ligands.

Bis(trifluoromethy1)cadmium·glyme [$(CF_3)_2Cd\cdot$monoglyme] is a convenient reagent used in the preparation of trifluoromethyl substituted metal compounds.[287] For example, $(CF_3)_2Cd\cdot$monoglyme exchanges ligands with GeI_4, SnI_4, or PI_3 to form $(CF_3)_4Ge$, $(CF_3)_4Sn$, or $(CF_3)_3P$ respectively at room



$$Cd(SiF_3)_2\cdot \text{monoglyme} + MBr_2(PMe_3)_x \longrightarrow M(SiF_3)_2(PMe_3)_x$$

(M = Ni, Pd, or Pt)

Scheme 34 Synthesis of trifluorosilyl substituted dialkyl compounds.

$$CF_2{=}CFOR_fCH_2OH \longrightarrow \left(CF_2CHFOR_fCH_2O\right)_n \longrightarrow \left(CF_2CF_2OR_fCF_2O\right)_n$$

Scheme 32 Preparation of perfluorinated polyethers.

temperature. The reaction of $(CF_3)_2Cd\cdot$monoglyme with acyl halides such as $CH_3C(O)Br$ formed the acyl fluorides $CH_3C(O)F$ in 95% yield at −25 °C. Krause and Morrison[288] prepared Lewis base adducts of bis(trifluoromethyl)cadmium $(CF_3)_2Cd$ by mixing $(CF_3)_2Hg$ with dimethylcadmium in THF, monoglyme, diglyme, or pyridine; Lewis base exchange is achieved when the glyme adduct is dissolved in a base, for example, $(CF_3)_2Cd\cdot$monoglyme in pyridine. They suggested that $(CF_3)_2Cd\cdot$base species are more reactive than $(CF_3)_2Hg$: $(CF_3)_4Sn$ (66% yield) and $(CF_3)_4Ge$ (43% yield) were synthesized by ligand exchanges between $SnBr_4$ and GeI_4 with $(CF_3)_2Cd\cdot$monoglyme respectively at room temperature; the reaction of acyl halides with $(CF_3)_2Cd\cdot$monoglyme at subambient temperature produced the acyl fluoride with ∼90% yield, and stereospecific difluorocarbene *cis*-2-butene at −30 °C. This group[289] used the same method to prepare monosubstituted compounds $(CF_3)BrNi(PEt_3)_2$, $(CF_3)BrPd(PEt_3)_2$, and $(CF_3)IPt(PBu^n{}_3)_2$ in 60–70% yields by the reaction of $(CF_3)_2Cd\cdot$monoglyme with bis(trialkylphosphine) group 8B dihalides such as $Br_2Ni(PEt_3)_2$ within 0.5–5 h; however, when an excess amount of $(CF_3)_2Cd\cdot$monoglyme was present, disubstituted compounds $(CF_3)_2M(PEt_3)_2$ (M = Ni, Pd, or Pt) were found over an extended reaction period. The Morrison group[290] also conducted the synthesis of $(\eta^5\text{-}C_5H_5)Co(CO)(CF_3)_2$ (63% yield) *via* the reaction of $(CF_3)_2Cd\cdot$monoglyme with $(\eta^5\text{-}C_5H_5)Co(CO)I_2$. This group[291] further investigated the ligand exchange reactions of $Cd(CF_3)_2\cdot$monoglyme with various aryl-containing Pb, Sn, and Ge halides, acetates, and thioethers in THF or $CHCl_3$; they found that when an excess of trifluoromethylating agent was used, these new compounds $PbPh(CF_3)_3$ (51%), $PbPh_2(CF_3)_2$ (61%), $PbPh_3CF_3$ (81%), $SnPh_2(CF_3)_2$ (55%), $SnPh_3CF_3$ (80%), and $GePh_3CF_3$ (72%) were obtained, and when the trifluoromethylating agent was the limiting reactant, partially substituted compounds $PbPh_2(Cl)CF_3$ (78%), $PbPh_2(O_2CCH_3)CF_3$ (89%), $PbPh(O_2CCH_3)_2CF_3$ (63%), and $PbPh(O_2CCH_3)(CF_3)_2$ (64%) were isolated. Murray *et al.*[292] performed the reaction of $[Au(CH_2)_2PPh_2]_2Br_2$ with $Cd(CF_3)_2$(monoglyme) in CH_2Cl_2 to synthesize a dialkyl Au(II) phosphorus ylide dimer $[Au(CH_2)_2PPh_2]_2(CF_3)_2$, whose X-ray crystal structure was also determined. Nair and Morrison[293] prepared $TlPh(CF_3)_2$ with 87% yield by reacting $Cd(CF_3)_2\cdot$monoglyme with $TlPhCl_2$ after 72 h, and $Tl(CF_3)_2OAc$ with 46% yield by reacting $Cd(CF_3)_2\cdot$monoglyme with $Tl(OAc)_3$ after 45 min. Loizou *et al.*[294] prepared cyclopentadienyldinitrosyl(trifluoromethyl)chromium(0) $CpCr(NO)_2CF_3$ (71%), and cyclopentadienyldinitrosyl-(trifluoromethyl)molybdenum(0) $CpMo(NO)_2CF_3$ (44%) *via* the reaction of $Cd(CF_3)_2\cdot$monoglyme with the corresponding chlorides at 65 °C. Ludovici *et al.*[295] achieved nearly quantitative yields of $C_nF_{2n+1}NO$ ($n = 1, 2, 3, 6$) by the reaction of NOCl with $Cd(C_nF_{2n+1})_2\cdot$monoglyme. Daniele *et al.*[296] synthesized $La(OTf)(OC_6H_3\text{-}2,6\text{-}Me_2)_2$(glyme) [glyme = triglyme or tetraglyme] derivatives through reactions between lanthanum triflate adducts $La(OTf)_3$(glyme) and 2 equiv. LiOAr ($Ar{=}C_6H_3\text{-}2,6\text{-}Me_2$) in THF. The grafting of $La(OTf)(OC_6H_3\text{-}2,6\text{-}Me_2)_2$(triglyme) onto silica produced a hybrid material, which was used as a catalyst for the activation of formaldehyde in water for hydroxymethylation of silyl enol ether in mild conditions. The Fu group at MIT has demonstrated that the $NiCl_2\cdot$glyme/pybox ligand is an effective chiral catalyst for the asymmetric Negishi cross-coupling of racemic secondary propargylic halides with alkylzinc[239] or arylzinc reagents.[238]

7.3. Catalysts

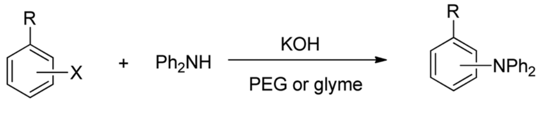
Glymes contain multiple ethylene oxide units, which define many glymes as amphiphiles (with both hydrophilic and lipophilic properties). Ideally, these glymes can be used as direct phase-transfer catalysts. The second case for glymes acting as catalysts is that glymes can form complexes with alkali cations like crown ethers. The third category is that glyme oxygens can form hydrogen-bonds with reaction intermediates and thus promote the reaction by stabilizing these intermediates. The fourth category is where glymes are ligands of metal salt catalysts.

Direct phase-transfer catalysts. Gokel *et al.*[115] suggested that shorter-chain PEGs and their ether derivatives are more effective catalysts than longer-chain analogues in phase-transfer reactions such as the nucleophilic substitution of 1-chlorooctane in *n*-decane with aqueous sodium cyanide to synthesize 1-cyanooctane. Sukata[297] synthesized alkyl *p*-tolyl sulfones (80–95% yields) from sodium *p*-toluensulfinate monohydrate and different alkyl halides in PEG-400 or PEG-400 diethyl ether, or in methanol containing PEG-1000 or PEG-1000 diethyl ether as a catalyst.

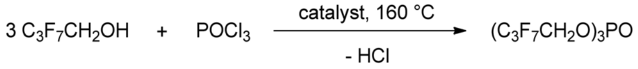
Complexing with alkali cations. Lee and Chang[298] found that a mixture of PEG dimethyl ethers could be used as phase-transfer agents to move $KMnO_4$ from aqueous solution into benzene or CH_2Cl_2; such a system was shown to be effective for the oxidation of terminal alkenes to corresponding carboxylic acids with one less carbon, and nonterminal alkenes to diones, diols, ketols and carboxylic acids. Paradisi *et al.*[299] carried out the nucleophilic substitution reaction of 1-chloro-4-nitrobenzene with KOH in 2-propanol to synthesize 1-isopropoxy-4-nitrobenzene catalyzed by Bu_4NBr or alkali ion complexing agents such as 18-crown-6, Carbowax 20M, MPEG 5000, and Triton X-100; however, tetraglyme was less effective and monoglyme showed no effect. Bergbreiter and Blanton[300] reduced alkyl and aryl halides to hydrocarbons by suspensions of $NaBH_4$ in toluene co-catalyzed by tri-*n*-butyltin chloride and polyether phase-transfer catalysts (PTCs); among the three PTCs studied, benzo-15-crown-5, polyethylene-bound benzo-15-crown-5 and poly(ethylene glycol) dimethyl ether (MW 1000), the crown ether is generally more active. Sukata and Akagawa[301] conducted the phase-transfer reaction of inactivated aryl halides with diphenylamine catalyzed by a series of PEGs and glymes (such as PEG-3000, PEG-400 dimethyl ether and PEG-6000 dimethyl ether) (Scheme 35). Their results suggest that one molecule of high molecular weight PEG or glyme could bind with more than one K^+; also, ∼9 ethylene oxide units are typically needed to form a crown-shape complex, and PEGs and glymes with 4–9 ethylene oxide units are most effective in complexing with a K^+ cation. It was found[302,303] that cyclophosphazenic polypodands are stronger complexing agents of alkali metal salts than glymes, and thus become highly efficient catalysts for solid–liquid and liquid–liquid phase-transfer reactions including nucleophilic substitution, alkylation, reduction and oxidation reactions. The stronger ability of polypodands in binding ion pair aggregates and thus activating the anion by increasing the interionic distance in the single ion pair attributes to the higher catalytic activities of polypodands.[304] Lazrek *et al.*[305] achieved the regioselective phase-transfer reaction of *N*-alkylation with acyclic side chains of pyrimidine and purine heterocycles at *N*-1 and *N*-9 respectively catalyzed by 18-crown-6 or tetraglyme in the presence of potassium *tert*-butoxide at 0 °C.

Kudryavtsev and Zakharov[306] investigated the phosphorylation of heptafluorobutanol with phosphorus(V) oxychloride (Scheme 36) catalyzed by complex catalysts based on Li^+, Na^+, K^+, or Cs^+ chlorides and polydentate ligands (such as dibenzo-18-crown-6, mono-, di-, and tetraglymes, and PEG-600 and PEG-1000); the addition of polydentate ligands improved the solubility of inorganic salts and increased the reaction rates by a factor of 1.3–2.8. Although the LiCl and PEG systems were shown to be most efficient, the use of glymes with LiCl led to 91–92% yields in 1.9–2.7 h (*vs.* 94% yield in 3.6 h without the addition of any ligand). Kochergina and Anufriev[307] carried out the nucleophilic substitution of 6,7-dichloro-3-ethyl-2-ethoxynaphthazarine to prepare echinochrome trimethyl ether (Scheme 37). The reaction was accelerated by the use of monoglyme and diglyme as both catalysts and solvents; in particular, the reaction in diglyme produced up to 72% yield *vs.* 52% without adding any glyme. It was explained that glymes effectively solvate the potassium cation to form ion pairs.

Stabilizing reaction intermediates. Koh *et al.*[308] studied the aminolysis of thiophenyl 4-nitrobenzoate with deuterated 4-chlorobenzylamine in acetonitrile catalyzed by glymes, and found that the k_{cat}/Oxy values (Oxy is the number of oxygens in glymes) increase with the chain length up to triglyme and only up to four oxygens per glyme molecule are used to catalyze the aminolysis (see the interaction between zwitterionic tetrahedral intermediate and triglyme in Scheme 38). They further indicated that this reaction has primary deuterium kinetic isotope effects (PKIEs), $k_{H(cat)}/k_{D(cat)} = 1.28–1.62$.

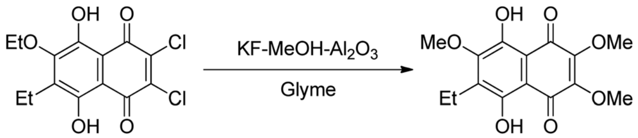


Scheme 35 Phase-transfer reaction of aryl halides with diphenylamine.

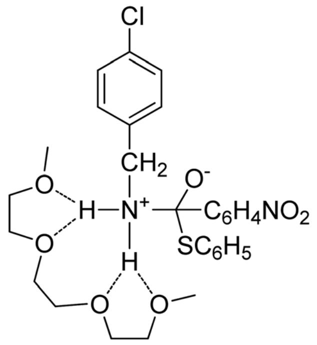


$$3\,C_3F_7CH_2OH + POCl_3 \xrightarrow[\text{- HCl}]{\text{catalyst, 160 °C}} (C_3F_7CH_2O)_3PO$$

Scheme 36 Phosphorylation of heptafluorobutanol with phosphorus oxychloride.

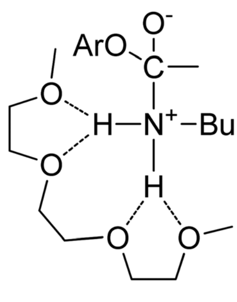


Scheme 37 Conversion of 6,7-dichloro-3-ethyl-2-ethoxynaphthazarine into echinochrome trimethyl ether.

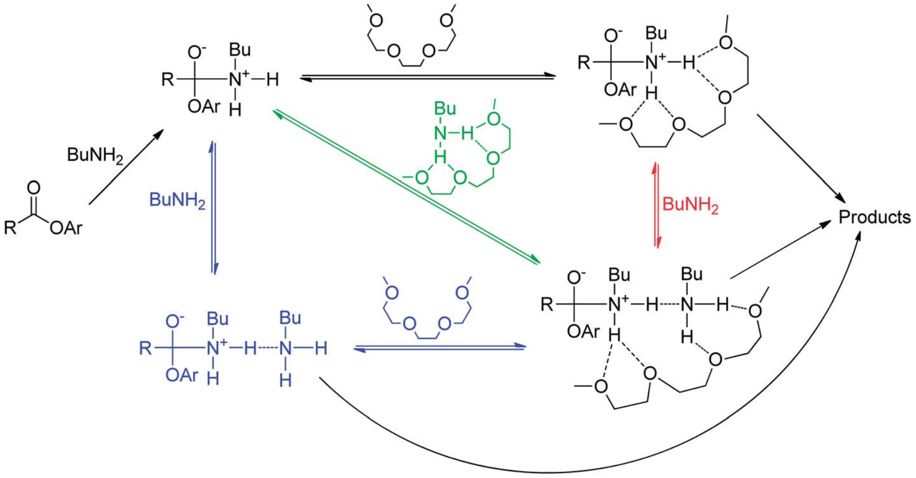


Scheme 38 Binding interaction between glyme and intermediate during aminolysis of thiophenyl 4-nitrobenzoate with 4-chlorobenzylamine.

Hogan and Gandour[309] suggested that glymes are more effective catalysts than crown ethers (an inverse macrocyclic effect) in the butylaminolysis of *p*-nitrophenyl acetate in chlorobenzene; this group[310] further observed a break in a plot of the catalytic rate constant *vs.* chain length of catalyst, indicating triglyme gives the optimum catalysis. The same group[311] further examined the transition structure complexes for the glyme- and α,ω-dimethoxyalkane-catalyzed butylaminolysis of 4-nitrophenyl acetate in chlorobenzene. They confirmed that the k_{cat}/Oxy values increase with oligomer length up to triglyme and then plateau. The ester aminolysis in aprotic solvents involves a rate-limiting breakdown of a zwitterionic tetrahedral intermediate, which forms a complex with a glyme molecule (Scheme 39). They further concluded that the number of polyether oxygens required for optimum catalysis and the best spacing (in α,ω-dimethoxyalkanes) among these oxygens are strongly dependent on the number of ammonium protons in the transition structure. More recently, Basilio *et al.*[312,313] studied the butylaminolysis of *p*-nitrophenyl acetate in chlorobenzene catalyzed by crown ethers or glymes as phase-transfer catalysts, and proposed a reaction pathway to reflect a 1st-order dependence on the catalyst concentration and a 2nd-order dependence on butylamine concentration (Scheme 40). The new pathway (red arrows) involves the complexing of ether-TI (ether-



Scheme 39 Complexing between zwitterionic tetrahedral intermediate and triglyme.



Scheme 40 Mechanisms of glyme-catalyzed ester aminolysis.

tetrahedral intermediate) with an amine molecule, which is an addition to the mechanisms (green and blue arrows) traditionally accepted for the catalysis by phase-transfer agents of aminolysis reactions in aprotic solvents. The green arrows indictate butylamine attacking the ester to form the tetrahedral intermediate (TI), and the amine complexing with the ether catalyst before binding to TI; the blue arrows indicate butylamine attacking the ester to form the TI and a second butylamine forming hydrogen bonds with the TI followed by glyme binding to both butylamine components. The same group[314] further examined a more complex reaction system of butylaminolysis of 4-nitrophenylcaprate in water–AOT–chlorobenzene microemulsions catalyzed by triglyme (Scheme 41), and discussed four simultaneous reaction pathways.

Ligands of metal salt catalysts. The Fu group[315] developed a nickel ($NiCl_2 \cdot$monoglyme)–diamine catalyst (diamine = (*S*,*S*)-*N*,*N*′-dimethyl-1,2-diamino-1,2-diphenylethane) to carry out asymmetric Hiyama reactions of α-bromo esters with aryl silanes to yield α-aryl esters in satisfactory ees (Scheme 42).

It is also interesting to note in some cases that glymes are inactive or less active than PEGs as phase-transfer catalysts, *i.e.*, reactions of aryldiazonium salts with $CBrCl_3$ or CH_3I initiated by potassium acetate,[316] dehydrohalogenation of 2-bromooctane with aqueous KOH.[317]

7.4. Reagents

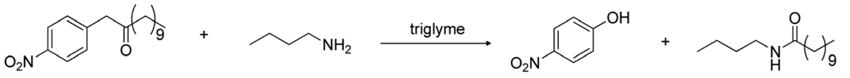
Typically, glymes are chemically inert; however, they could become reactive under certain conditions. Newman and Liang[318] observed that when 3-nitroso-5-methyl-5-*tert*-butyl-2-oxazolidone was treated with sodium phenoxide, the stereospecific cleavage of monoglyme occurred to form 2-methoxyethyl *trans*-2,2,3-trimethyl-l-butenyl ether in 46% yield. Ishii *et al.*[319] studied the anodic fluorination of monoglyme and diglyme (Scheme 43) in acetonitrile using a fluoride salt as a supporting electrolyte and a fluoride ion source with an undivided cell; they observed that corresponding monofluoromethyl ethers were obtained as the main products in satisfactory yields. However, the anodic fluorination of crown ethers caused C–C bond cleavage, producing selective α,ω-difluoro products with high yields.

Grabovskiy *et al.*[320] studied the oxidation of a series of ethers including monoglyme by dimethyldioxirane (DMDO), and suggested a second-order reaction kinetics $r = k[\mathrm{DMDO}][\mathrm{ether}]$. They also determined the rate constants at 5–50 °C, as well as the activation parameters of the reaction. The main oxidation products of monoglyme with DMDO (10 : 1 molar ratio) in acetone at 25 °C include methanol (32%), 2-methoxyethanal (4%) and methoxyacetic acid (3%). Boron-based compounds including sodium borohydride ($NaBH_4$) and ammonia borane (NH_3BH_3) have been studied as chemical hydrogen storage materials. Yoon *et al.*[321] developed a safe and efficient method for preparing NH_3BH_3: iodine oxidation of $Bu_4N^+B_3H_8^-$ in monoglyme solution yielded (glyme)B_3H_7, which was converted to NH_3BH_3 by displacement of the coordinated glyme with anhydrous ammonia.

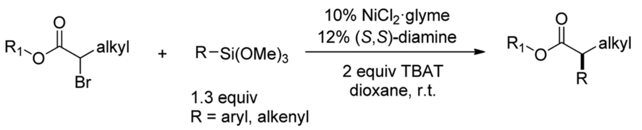
In addition, there are some reactive glymes (such as polyglycol allyl methyl ether, polyglycol diallyl ether and PEG methyl ether methacrylate) commercially available. As a typical application, the allyl-containing glymes can react with siloxanes through a Pt-catalyzed hydrosilylation reaction to produce polyether modified silicones, which have applications as silicone surfactants and polyurethane foam stabilizers.

8. (Co-)solvents for biocatalysis

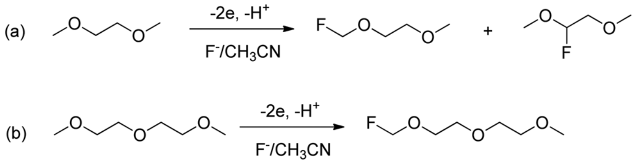
Surprisingly, glymes and their aqueous solutions are not commonly used as solvents for enzymatic processes. There have been some conflicting results on the enzyme activity and stability in aqueous solutions of glymes. Some studies suggest the high enzyme activity and/or stability in aqueous glymes. Yoshpe-Besancon *et al.*[322] observed that a 55% triglyme solution could shift the equilibrium of aminopeptidase A from amide bond hydrolysis to peptide bond formation, which allowed a selective α-amino protection of derivatives of many amino acids (except glycine and proline) by the malyl group. Rosell *et al.*[323] found that 50% (v/v) aqueous solutions of diglyme (G2) or



Scheme 41 Butylaminolysis of 4-nitrophenylcaprate.



Scheme 42 Hiyama reactions of α-bromo esters with aryl silanes.



Scheme 43 Anodic fluorination of (a) monoglyme and (b) diglyme.

tetraglyme (G4) depressed the hydrolytic activity of penicillin acylase by roughly 65%, but boosted its synthetic activity by ~4.8 times. In addition, these two solutions showed negligible impact on the enzyme stability. Berkowitz *et al.*[324] suggested that 10% triglyme in aqueous buffer solution enabled the optimal efficiency for a PPL-catalyzed hydrolysis of a drug intermediate at both lower enzyme loading and higher temperature. Schroën *et al.*[325] studied the enzymatic synthesis of antibiotic cephalexin catalyzed by penicillin G acylase (Scheme 44), and found the enzyme retained 90% activity after incubation in 30–36% (v/v) glymes (mono-, di- and tri-) at 30 °C for 24 h; compared with the direct synthesis in water, the addition of methanol and triglyme could increase the equilibrium concentration of cephalexin by a factor of 2–3. However, Illanes and Fajardo[326] found that in 50/50 (v/v) mixtures of organic solvents and aqueous buffer, *Escherichia coli* penicillin acylase maintained a high stability in polyols (such as ethylene glycol and glycerol), a low stability in glyme and diglyme, and no activity after 24 h in methanol, DMF and DMSO.

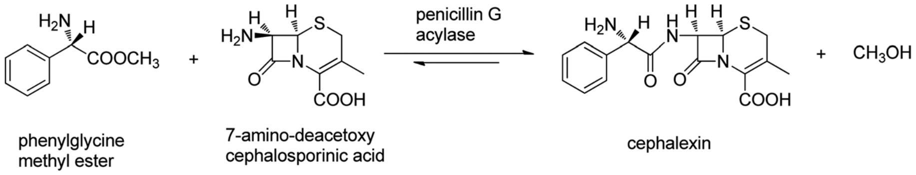
On the other hand, there are even limited studies on the enzymatic reactions in neat glymes although PEGs[327–329] and PEG-based aqueous biphasic systems (ABS)[330] are known media for enzymatic reactions. The Sheldon group[331] indicated that cross-linked enzyme aggregates (CLEAs) of penicillin G acylase was not quite active in a mixture of glyme–water (95 : 5, v/v), resulting in low conversions [10% in monoglyme (log $P = -0.8$) and 5% in triglyme (log $P = -1.8$) after 1 h] for the synthesis of ampicillin. The Zhao group[21] found that long-chain glymes are highly compatible with immobilized *Candida antarctica* lipase B (Novozym 435), resulting in higher enzyme activities and stabilities than *t*-butanol and some ionic liquids. Furthermore, this group noticed that soybean oil is fully miscible with glymes, which enables a homogeneous reaction mixture for enzymatic preparation of biodiesel; in the presence of glymes, the immobilized lipase showed a very high tolerance to high methanol concentrations (up to 60–70% v/v), and nearly quantitative triglyceride conversions could be obtained under mild reaction conditions.

9. Materials

This section focuses on the applications of glymes as materials or as media to prepare new materials.

9.1. Nanomaterials

A series of metal or nonmetal nanoparticles with functionalized surfaces were synthesized in glyme solvents by the Kauzlarich group. They demonstrated a straightforward and versatile technique to control both crystal size and surface termination of the nanomaterials. Methyl-terminated Ge nanocrystals with an average particle size of around 3.5 nm were produced by the metathesis reaction between the Zintl salt NaGe and $GeCl_4$ in degassed monoglyme or diglyme.[332] The Kauzlarich and Taylor group[333,334] further extended this method to prepare alkyl-terminated crystalline Ge nanoparticles by the reactions between $GeCl_4$ and NaGe, KGe, or Mg_2Ge followed by surface termination with alkyl Li and Grignard reagents in glymes. It was observed that diglyme and triglyme seemed to support the reaction better than monoglyme and the reactions in triglyme were much faster than in diglyme. Moreover, the largest particles (8–10 nm) of Ge nanoparticles were produced in monoglyme while the smallest particles of 4.5 nm mean size were synthesized in triglyme. Furthermore, alkyl-terminated silicon nanoclusters were also prepared by the reaction of $SiCl_4$ with Mg_2Si in monoglyme and surface-terminated with various alkyl groups, R-*n*-Si (R = methyl, ethyl, *n*-butyl, and *n*-octyl).[335] Based



Scheme 44 Enzymatic synthesis of antibiotic cephalexin.

on the same technique, this group[336] further synthesized the surface-capped and organic-functionalized tin nanoparticles of Sn/R, Sn/Si–R (R = *n*-C_4H_9), and Sn/SiO_2 core–shell particles *via* the reaction of Mg_2Sn with $SnCl_4$ or $SiCl_4$ in monoglyme.[336]

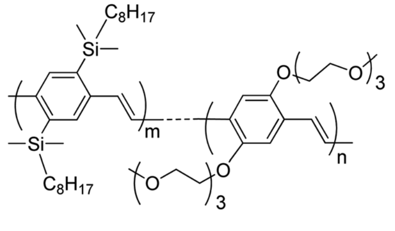
Plasma-deposited PEG-like films have become emerging materials as 'non-stick' surfaces toward protein and bacteria. Ratner and co-workers[337] designed PEG-like coatings *via* radio-frequency plasma deposition of short-chain oligoglymes, dioxane, and crown ethers onto glass cover slips; the films were characterized by X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), dynamic contact angle goniometry, and radiolabeled fibrinogen adsorption. The Brétagnol group[338,339] constructed new micro-structured surfaces through a spatial arrangement of different functional domains by a combination of the plasma polymerization of diglyme (leading to coatings with a high concentration of ethylene oxide groups (>70%)) and photolithography. The high stability of these films in acetone suggests that these coatings could be used in classical lift-off processes involving washing in acetone for designing patterned surfaces.[339] The same group[340] further developed a straightforward nanoscale writing technique, enabling the fabrication of bio-adhesive patterns directly in a non-bio-adhesive matrix. This method involves two major steps: (a) plasma polymerization of diglyme to form a protein-repelling PEO-like coating, (b) direct electron beam lithography inside the matrix by tuning the ether bond concentration of the coating to produce nanoscale bio-adhesive patterns.

The Stucky group[341] developed a time evolution kinetic-dependent crystal growth model to examine the nanocrystal growth of CdS from cadmium acetate and sodium sulfide in different solvents (*e.g.* ethylene glycol, monoglyme, diglyme, and trioctylphosphine), using trialkylphosphine oxide (alkyl = ethyl or octyl) as a surfactant. They observed that the size of nanoparticles is controllable by the reaction time and temperature; the nanoparticle sizes are suitable for spectroscopic analysis of electron quantum confinement. The same group[342] also prepared CdS nanorods through the reaction of cadmium acetate and sodium sulfide at low temperature (25–65 °C) in an aqueous phase using nonionic pluronic amphiphilic triblock copolymers, $(EO)_x(PO)_y(EO)_x$, as structure-directing agents. However, when the same reaction is refluxed in ethylene glycol and monoglyme without surfactant, a new morphology of microrods with flat ends, dumbbell-shaped microrods, and cotton-ball-like microparticles is produced. Chiu and Kauzlarich[343] synthesized crystalline germanium nanoparticles by the reduction of $GeCl_4$ with sodium naphthalide in monoglyme within 10 min. Pickering *et al.*[344] prepared octyloxy-capped boron nanoparticles through a reduction of BBr_3 with sodium naphthalenide in dry monoglyme followed by the addition of excess octanol at room temperature. The size distribution of the nanoparticles can be controlled by tuning the reaction conditions, such as concentration and reducing agent. Similarly, Cho[345] performed the reaction of $SnCl_4$ and $GeCl_4$ with sodium naphthalide in monoglyme and RLi (R = butyl, ethyl, methyl) to prepare $Sn_{70}Ge_{30}$@carbon core–shell nanoparticles. The core sizes and shell thicknesses of these nanoparticles are dependent on the alkyl terminator. Electrochemical studies suggest that nanoparticles synthesized with butyl terminators exhibit the highest capacity retention after 40 cycles (95%) and a first charge capacity of 1040 mA h g^{-1}. Shirahata and Sakka[346] synthesized highly luminescent Si nanoparticles (NPs) terminated with alkoxy monolayers through the reduction $SiCl_4$ by sodium biphenylide in a toluene–monoglyme mixture using an inverse micelle method; they also observed the size-dependent UV photoluminescence (PL) properties for non-oxidized Si NPs at room temperature, as well as a high quantum efficiency of the UV fluorescence. Mishra *et al.*[347] prepared heterometal–organic complexes including $NaY(TFA)_4$(diglyme), $[Na(triglyme)_2]$ $[Y_2(TFA)_7(THF)_2]$, $Na_2Y(TFA)_5$(tetraglyme), $NaLn(TFA)_4$(diglyme), [Ln = Er, Tm, or Yb], and $Na_2Ln(TFA)_5$(tetraglyme) [Ln = Er, or Yb] (TFA = trifluoroacetate), and used them as precursors for up-converting $NaY(Ln)F_4$ (Ln = Yb, Er, Tm) nanocrystals and thin films, which have potential applications as lanthanide-doped up-conversion (UC) emission materials.

9.2. Polymeric materials

Shirai *et al.*[348] carried out radical polymerization to prepare polymers carrying glyme units as alkali cation binding sites and photodimerizable cinnamoyl units. They found that the photodimerization of the cinnamoyl groups with relatively short glyme chains could improve their cation binding ability, and the addition of alkali metal cations as templates enforced the effect of photodimerization on the cation binding properties. Morgado *et al.*[349] found that an orange-emitting PPV-based statistical copolymer with glyme-like side groups (Scheme 45) has a photoluminescence efficiency of ~17%. The presence of glyme units enables the solvation of salts and the ion mobility under the applied electric field, thus this copolymer carries both ion-coordinating and luminescence moieties.

Moore *et al.*[350] dissolved poly(enaminonitrile) (PEAN) or miscible blends of PEAN with poly(ethylene oxide) in a number of glymes, and observed the cloud points of these solutions when the temperature increases. The Sneddon and Remsen groups[351,352] found that polyborazylene could be dissolved in monoglyme or THF, and could be further precipitated by the addition of pentane. Monoglyme was used as a solvent for dissolving and mixing two polymeric precursors, namely allylhydridopolycarbosilane (AHPCS) ($[Si(CH_2CH{=}CH_2)_2CH_2]_{0.05}$ $[SiH_2CH_2]_{0.95}$) and polyborazylene (PBz) $[B_3N_3H_{4-x}]_n$, which serve as the sources for the SiC and BN phases respectively.[353] Following the removal of solvent, the co-pyrolysis of these two



Scheme 45 PPV-based statistical copolymer with glyme-like side groups.

precursors at 1000 °C affords a two-phase SiC–BN ceramic composite whose highly unusual microstructure resembles that of certain polymer blends.

López and Ratner[354] reported weakly ionized, radio-frequency and glow-discharge plasmas from the vapor of glyme precursors (mono-, di- and tri-), and then used them to deposit organic thin films on polytetrafluoroethylene (PTFE). Sandner *et al.*[355] performed the free-radical photopolymerization of an oligo(ethylene glycol) dimethacrylate ($(EG)_{23}DMA$) in two glymes ($(EG)_3DME$ and $(EG)_{11}DME$) as plasticizers in the presence of $LiCF_3SO_3$, which was analyzed by differential scanning calorimetry (DSC), FT-Raman spectroscopy and sol–gel analysis. The addition of $LiCF_3SO_3$ increased the polymerization rate.

9.3. Inorganic materials

Baker *et al.*[356] prepared homoleptic dicyclohexylphosphide (PCy_2) complexes of early transition metals using monoglyme (G1) as the complexing agent for Li^+; these new complexes include $[Li(G1)][Zr(PCy_2)_5]$, $[Li(G1)][Hf(PCy_2)_5]$, $[Li(G1)][Ti(PCy_2)_4]$, $[Li(G1)][V(PCy_2)_4]$, $[Li(G1)][Re(PCy_2)_4]$, $[Li(G1)_2][Nb(PCy_2)_4]$, $Mo(PCy_2)_4$, $[Li(G1)_3][Cr_2(PCy_2)_5]$, $[Li(G1)_3][W_2(PCy_2)_5]$ and $[Li(G1)][Mn_2(PCy_2)_5]$. Baxter *et al.*[357] synthesized the adducts of [Gd-(tmhd)$_3$] (tmhd-H = 2,2,6,6-tetramethylheptane-3,5-dione) with a series of glyme ligands from monoglyme to heptaglyme. These complexes were evaluated as precursors for Atmospheric Pressure Chemical Vapor Deposition (APCVD) coatings of $Ce_{0.9}Gd_{0.1}O_{1.95}$ thick electrolyte films for solid oxide fuel cells (SOFCs). The advantages of using these complexes for metal organic chemical vapor deposition (MOCVD) include: (1) readily available in crystalline solids of fixed stoichiometry; (2) soluble in hydrocarbons (both aliphatic or aromatic) and air stable; and (3) better mass transport properties of more stable complexes can be prepared from longer chain glymes. Drake *et al.*[358] synthesized the monomeric materials [M(β-diketonate)$_2$(L–L)] by reacting oligomeric alkaline earth metal β-diketonate complexes, [M(β-diketonate)$_2$] with a glyme (tri- and tetra-) ligand (L). The same group[359] further prepared eight-coordinate triglyme-bridged dimeric complexes, $[(Ln(tmhd)_3)_2L^1]$ (Ln = Eu or Tb, L^1 = triglyme, and tmhd = $Bu^tCOCHCOBu^t$) through the reaction of hydrated β-diketonate complexes $[Ln(tmhd)_3(H_2O)]$ with triglyme in hexane. They also prepared the nine-coordinate monomeric compound $[La(tmhd)_3L^2]$ *via* the reaction of $[La(tmhd)_3(H_2O)]$ with tetraglyme (L^2) in hexane. These complexes are stable in air with moisture and also have a good volatility and thermal stability. Arunasalam *et al.*[360] used carbonate and hydroxide compounds to prepare a number of Group 2 β-diketonate complexes supported by multidentate glyme ligands (tri-, tetra- or heptaglyme), including a single-crystal structure of a calcium complex of [(Ca(hfpd)$_2$)$_2$(heptaglyme)] where [H-hfpd = 1,1,1,5,5,5-hexafluoropentane-2,4-dione]. These β-diketonate and carboxylate compounds have potential applications as CVD precursors for both MO and MF_2 thin films. Arnáiz *et al.*[361] synthesized outer-sphere addition compounds of $MoO_2Br_2(H_2O)_2$ with diethyl ether, dioxane, glyme, diglyme, triglyme and tetraglyme by crystallizing diethyl ether extracts of a solution of sodium molybdate in concentrated hydrobromic acid and the respective ether. They also suggested that the polyether interacts with the $MoO_2Br_2(H_2O)_2$ units through hydrogen bonds based on the X-ray structure analysis of diglyme and tetraglyme adducts. Crochet and Fromm[362] prepared and characterized crystalline cobalt, nickel, zinc, and mercury halide adducts with polyethers as ligands including [Co(μ-Cl)$_2$CoCl$_2$(monoglyme)$_2$], *cis*-[CoI$_2$(H$_2$O)$_2$(monoglyme)$_2$]$^{2+}$-[CoI$_4$]$^{2-}$, [NiI$_2$(monoglyme)$_2$], [ZnI$_2$(monoglyme)], [HgCl$_2$-(monoglyme)], [CoI$_2$(diglyme)], [ZnI$_2$(diglyme)], [HgI$_2$(diglyme)], [CoCl(μ-Cl)(diglyme)]$_2$, [NiI(μ-I)(diglyme)]$_2$, [Co(μ-Cl)(triglyme)]$_2^{2+}$[CoCl$_2$(μ-Cl)]$_2^{2-}$, and *cis*-[(NiI$_2$)(triglyme)]$_n$. Some of these adducts exhibit unusual coordination numbers and arrangements.

10. Other applications

10.1. Chemical Vapor Deposition (CVD)

CVD is an important method for producing new materials. When preparing f-element oxides by the CVD procedure, the reproducibility becomes a challenge because regular precursors often self-associate, form a hydrate and undergo hydrolysis or cleavage of the ligands on storage. As an effort to design new lanthanide complexes with suitable mass transport properties for metal–organic chemical vapor deposition (MOCVD) applications, the Fragalà group[363,364] have developed new adducts La(hfac)·monoglyme·H_2O, La(hfac)·diglyme and La(hfac)·triglyme (hfac = $CF_3COCHCOCF_3$), which possess better volatility and thermal stability than conventional lanthanum CVD precursors. Pollard *et al.*[365] found that monoglyme and diglyme formed neutral complexes of [Y(hfac)$_3$(glyme)], whilst triglyme and tetraglyme produced ionic complexes [Y(hfac)$_2$(glyme)]$^+$ [Y(hfac)$_4$]$^-$; upon CVD at 250–350 °C using oxygen as a carrier gas, these complexes yielded mixed yttrium oxide–fluoride ceramics. The Fragalà group[366] prepared and characterized [Y(hfac)$_3$·monoglyme], [Y(hfac)$_3$·diglyme], [Y(hfac)$_3$·(H$_2$O)$_2$·triglyme] and [Y(hfac)$_2$·tetraglyme]$^+$[Y(hfa)$_4$]$^-$; they found these adducts were suitable for MOCVD applications due to their high volatility and high thermal stabilities with a residue lower than 2–4%. In particular, a YBaCuO HTc superconductor was produced from the low-pressure MOCVD process of a [Y(hfa)$_3$·monoglyme] complex using a multimetal molten single source. Kang *et al.*[367] synthesized thermally stable Ln(hfac)$_3$·monoglyme (Ln = Ho or Y) complexes and indicated their high potential as MOCVD precursors. Pollard *et al.*[368] designed new glyme-adduct precursors of [Ce(hfac)$_3$(glyme)] (glyme = mono-, di-, or tri-) and [(Ce(hfac)$_3$)$_2$(μ-tetraglyme)] and used them in the CVD formation of films of cerium oxides on substrates Si, Pt, and TiN. The Fragalà group[369] also prepared Ce(hfac)$_3$·diglyme, Ce(hfac)$_3$·diethyldiglyme and Ce(hfac)$_3$·dibutyldiglyme, and found that these complexes are ideal for CeO_2 film deposition due to their high volatility and high thermal stability with low residue. Malandrino *et al.*[370] synthesized novel complex precursors Eu(hfac)$_3$·glyme (glyme = mono- or di-) and found that both complexes are thermally stable and could be evaporated with <4% residue. Another study by this group[371] suggested that La(hfac)$_3$·diglyme could be evaporated from the melt up to 130 °C without side decomposition processes. The Malandrino group[372] further prepared and characterized Nd(hfac)$_3$·monoglyme·H$_2$O and Nd(hfac)$_3$·diglyme, which exhibit high volatility and good thermal stability with a remaining residue lower than 3%. In particular, Nd(hfa)$_3$·diglyme was used in a low-pressure MOCVD preparation of $NdBa_2Cu_3O_{7-\delta}$ thin films.

In addition to these lanthanide adducts using glymes, other metal complexes have also been investigated. In an attempt to prepare precursors for Supercritical Fluid Transport (SFT) CVD, Blake *et al.*[373] synthesized new S-donor tetraphenyldithioimidodiphosphinate compounds [Na(Ph$_2$P(S)NP(S)Ph$_2$)(L)] (where L = triglyme or tetraglyme); however, these complexes are not quite soluble in supercritical CO$_2$. The Winter group[374] prepared calcium complexes with η^2-pyrazolato ligands including those adducts containing glymes [*e.g.* Ca(*t*Bu$_2$pz)$_2$(triglyme), and Ca(*t*Bu$_2$pz)$_2$(tetraglyme) Ca(Me$_2$pz)$_2$(triglyme), and Ca(Me$_2$pz)$_2$(tetraglyme)], resulting in volatile, thermally stable precursors for CVD applications.

10.2. NMR solvents

Deuterated monoglyme can be used as a co-solvent for low-temperature reactions monitored by a direct NMR analysis to probe the underlying reaction mechanism, as pioneered by the Buncel group. This group[375] performed low-temperature (−40 °C) NMR studies using a new solvent mixture of CD$_3$CN–monoglyme-d$_{10}$ (1 : 1, v/v) as the medium for a reaction of 2,4,6-trinitroanisole (TNA) with phenoxide; their results suggest the 1,1 adduct is the only species produced and no 1,3 *O*-adduct of phenoxide formed either prior to the 1,1 species or later. A further study of this reaction system by this group[376] revealed both O- and C-bonded phenoxide σ-complex adducts, implying the formation of the former *via* kinetic control and of the latter through thermodynamic control. This group[377] also used the same solvent system at −40 °C to room temperature to investigate the regioselectivity in Meisenheimer complexation of the reaction of 2,4,6-trimethylphenoxide ion (MesO$^-$) with 2,4,6-trinitroanisole (TNA) *via* ^{1}H and ^{13}C NMR, and suggest a kinetic preference for C-1 attachment and the σ-adduct from C-3 attack being more thermodynamically stable. The same deuterated solvent system was also employed by this group to examine the reactivity of 4-nitrobenzofuroxan (NBF) with several aryloxide nucleophiles; they observed the formation of a C-7 *O*-adduct with the ambident (O– and C–) nucleophile phenoxide ion at −40 °C.[378]

10.3. Chromatography

Rouse *et al.*[379] synthesized new glyme-substituted polysiloxane (Scheme 46) and 18-crown-6-substituted polysiloxane and applied them as the stationary phase for gas chromatography. The glyme polysiloxane has an operational temperature range of 20–280 °C and a selectivity comparable to that of Carbowax 20 M. Schuetz *et al.*[380] found that an eluent of hexane/monoglyme/formic acid (85%) (150 : 50 : 3) could be used to purify *p*-biphenyl-*n*-hexanoic acid in silica-based column chromatography, achieving 98% purity.

10.4. Dissolution of CO$_2$ and other gases

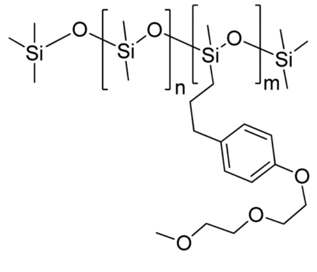
Sciamanna and Lynn[381] determined the gas solubilities of H$_2$S, SO$_2$, CO$_2$, propane and *n*-butane in glymes (di-, tri- and tetra-) and PEG monoethers at the partial pressure of gas solute between 3 and 100 kPa. The temperature dependence of gas solubility was described by Henry's law coefficients. The presence of a small amount of water (<6 wt %) decreases the gas solubility in glymes; the hydrogen-bonding properties of PEG monoethers also reduces the gas solubility. Henni *et al.*[382] reported the solubilities of CO$_2$ in 14 solvents including glymes, PEG monoethers, selexol® and sulfolane at 25, 40 and 60 °C; they suggested that glymes (particularly diglyme, triglyme and tetraglyme) are outstanding solvents for CO$_2$ removal. Kodama *et al.*[74] measured the solubilities and saturated densities of CO$_2$ in glymes (di-, tri- and tetra-) at 313.15 K as a function of pressure (at high pressures, CO$_2$ mole fraction is 0.857 at 7.126 MPa in diglyme, 0.827 at 7.202 MPa in triglyme and 0.822 at 7.316 MPa in tetraglyme). These data of CO$_2$ solubilities and saturated densities were further correlated with a three parameter pseudo-cubic equation of state.

10.5. Other applications

Monoglyme was used in aqueous solutions to improve the solubility of oxiranes in order to determine their nanomole quantities spectrophotometrically.[383] Interestingly, Dasilva-Carbalhal *et al.*[384] studied the effect of glymes on the conductance percolation of AOT/isooctane/water microemulsions. The addition of glymes (mono-, di-, tri-, and tetra-) to the microemulsion led to a decrease in the percolation threshold. This modification promotes the exchange of matter between droplets in the AOT film. More recently, various glymes were used to dissolve triglycerides, and thus were investigated as co-solvents for the CaO-catalyzed transesterification of soybean oil (>50% v/v loading) into biodiesel; under the optimum conditions, a >98% conversion of triglycerides could be achieved in 4 h using dipropylene glycol dimethyl ether (P2) as the co-solvent.[22]

11. Perspectives

Recent active research on glymes seems to focus on their applications in electrochemistry, catalysis, CVD, nanomaterials, and the dissolution of CO$_2$. However, there could be renewed interest in exploring their solvent role in organic reactions, biocatalysis and biofuel production. Glymes can also be derived



Scheme 46 Glyme-substituted polysiloxane stationary phase.

to contain functional groups such as double bonds, and thus become precursors for other applications. Many glymes are less volatile and less toxic than some common laboratory organic solvents; however, there is still lack of a systematic database on their acute and long-term toxicity as well as biodegradability. In addition, despite their versatile roles in industrial and consumer products, glymes have not been well studied in terms of their physicochemical properties such as dielectric constant, polarity, hydrophobicity (log *P*), heat capacity, phase equilibrium, *etc.*

In addition to glymes, other solvents carrying polyether or polyol moieties have also been extensively studied; these solvents include glycol monoethers and glycol ether esters,[1–3] polyethylene glycol (PEG) and aqueous solutions,[330] and glycerol and its derivatives.[385–387] New solvents can also be developed to carry the functionality of these moieties, for example, ionic liquids can be functionalized with various glycol groups to become tailored-made solvents.[388] As another example, a new family of glycerol derivatives including 1,3-dialkoxy-2-propanols and 1,2,3-trialkoxypropanes were prepared by García *et al.*;[389] these new solvents share some structural features with glymes and have a wide range of polarity properties, implying their high potential for solvent substitution.

Acknowledgements

HZ acknowledges the supports by the Henry Dreyfus Teacher-Scholar Award (2012), NIH MBRS-RISE grant (1R25GM096956), NIH NIBIB contract award (HHSN268201200011C), and the National Natural Science Foundation of China (21328601).

References

1 S. T. Cragg, in *Patty's Toxicology*, ed. E. Bingham and B. Cohrssen, John Wiley & Sons, Hoboken, NJ, 6th edn, 2012, vol. 4, pp. 641–787.

2 S. T. Cragg, in *Patty's Toxicology*, ed. E. Bingham and B. Cohrssen, John Wiley & Sons, Hoboken, NJ, 6th edn, 2012, vol. 4.

3 R. L. Smith, *Environ. Health Perspect.*, 1984, **57**, 1–4.

4 B. L. Haymore, J. D. Lamb, R. M. Izatt and J. J. Christensen, *Inorg. Chem.*, 1982, **21**, 1598–1602.

5 J. L. Adcock and R. J. Lagow, *J. Org. Chem.*, 1973, **38**, 3617–3618.

6 D. E. Leonhardt, L. W. Coleman and W. S. Bradshaw, *Reprod. Toxicol.*, 1991, **5**, 157–162.

7 J. C. Gage, *Br. J. Ind. Med.*, 1970, **27**, 1–18.

8 D. B. McGregor, M. J. Willins, P. McDonald, M. Holmström, D. McDonald and R. W. Niemeier, *Toxicol. Appl. Pharmacol.*, 1983, **70**, 303–316.

9 R. L. Schuler, B. D. Hardin, R. W. Niemeier, G. Booth, K. Hazelden, V. Piccirillo and K. Smith, *Environ. Health Perspect.*, 1984, **57**, 141–146.

10 E. M. Johnson, B. E. Gabel and J. Larson, *Environ. Health Perspect.*, 1984, **57**, 135–139.

11 D. B. McGregor, *Environ. Health Perspect.*, 1984, **57**, 97–103.

12 K. L. Cheever, W. W. Weigel, D. E. Richards, J. B. Lal and H. B. Plotnick, *Toxicologist*, 1985, **5**, 140.

13 K. L. Cheever, D. E. Richards, W. W. Weigel, J. B. Lal, A. M. Dinsmore and F. B. Daniel, *Toxicologist*, 1986, **6**, 32.

14 K. L. Cheever, D. E. Richards, W. W. Weigel, J. B. Lal, A. M. Dinsmore and F. B. Daniel, *Toxicol. Appl. Pharmacol.*, 1988, **94**, 150–159.

15 K. P. Lee, L. A. Kinney and R. Valentine, *Toxicology*, 1989, **59**, 239–258.

16 B. D. Hardin and C. J. Eisenmann, *Teratology*, 1987, **35**, 321–328.

17 http://www.environmentalhealthnews.org/ehs/news/2011/epa-takes-on-glymes.

18 P. J. Spencer, *Toxicol. Lett.*, 2005, **156**, 181–188.

19 J. A. Arnot and F. A. P. C. Gobas, *Environ. Rev.*, 2006, **14**, 257–297.

20 L. W. Sieck and M. Meot-Ner, *J. Phys. Chem.*, 1984, **88**, 5324–5327.

21 S. Tang, C. L. Jones and H. Zhao, *Bioresour. Technol.*, 2013, **129**, 667–671.

22 S. Tang, H. Zhao, Z. Song and O. Olubajo, *Bioresour. Technol.*, 2013, **139**, 107–112.

23 C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319–2358.

24 M. Meot-Ner, *J. Am. Chem. Soc.*, 1983, **105**, 4906–4911.

25 R. B. Sharma, A. T. Blades and P. Kebarle, *J. Am. Chem. Soc.*, 1984, **106**, 510–516.

26 H. Wasada, Y. Tsutsui and S. Yamabe, *J. Phys. Chem.*, 1996, **100**, 7367–7371.

27 D. Adötoledo, V. Aviyente, J. M. L. Martin and C. Lifshitz, *J. Phys. Chem. A*, 1998, **102**, 6357–6365.

28 E. Shchori and J. Jagur-Grodzinski, *J. Am. Chem. Soc.*, 1972, **94**, 7957–7962.

29 M. Meot-Ner, L. W. Sieck, S. Scheiner and X. Duan, *J. Am. Chem. Soc.*, 1994, **116**, 7848–7856.

30 H. Matsuura and T. Sagawa, *J. Mol. Liq.*, 1995, **65–66**, 313–316.

31 S. Masatoki, M. Takamura, H. Matsuura, K. Kamogawa and T. Kitagawa, *Chem. Lett.*, 1995, **24**, 991–992.

32 D. Bedrov and G. D. Smith, *J. Chem. Phys.*, 1998, **109**, 8118.

33 D. Bedrov, M. Pekny and G. D. Smith, *J. Phys. Chem. B*, 1998, **102**, 996–1001.

34 D. Bedrov and G. D. Smith, *J. Phys. Chem. B*, 1999, **103**, 3791–3796.

35 R. Begum, S. Masatoki and H. Matsuura, *J. Mol. Struct.*, 1996, **384**, 115–120.

36 O. Engkvist and G. Karlström, *J. Chem. Phys.*, 1997, **106**, 2411–2417.

37 P. Bernal, A. Bunn, J. Logan and J. McCluan, *J. Solution Chem.*, 2000, **29**, 651–665.

38 P. Bernal and J. McCluan, *J. Solution Chem.*, 2001, **30**, 119–131.

39 G. Douhéret, J. C. R. Reis, M. I. Davis, I. J. Fjellanger and H. Høiland, *Phys. Chem. Chem. Phys.*, 2004, **6**, 784–792.

40 *CRC Handbook of Chemistry and Physics*, ed. W. M. Haynes, CRC Press, Boca Raton, 2012.

41 N. P. Cheremisinoff, *Industrial Solvents Handbook*, Marcel Dekker, Inc., New York, 2003.

42 *Industrial solvents handbook*, ed. E. W. Flick, Noyes Data Corporation, Westwood, NJ, 1998.

43 T. Treszczanowicz, G. C. Benson and B. C.-Y. Lu, *Thermochim. Acta*, 1990, **168**, 95–102.

44 C. A. Tovar, E. Carballo, C. A. Cerdeiriña and L. Romanı, *J. Chem. Eng. Data*, 1997, **42**, 1085–1089.

45 H. Nakai, H. Soejima, K. Tamura, H. Ogawa, S. Murakami and Y. Toshiyasu, *Thermochim. Acta*, 1991, **183**, 15–27.

46 C. Dethlefsen and A. Hvidt, *J. Chem. Thermodyn.*, 1985, **17**, 193–199.

47 M. E. de Ruiz Holgado, C. R. de Schaefer, E. L. Arancibia and M. Katz, *Fluid Phase Equilib.*, 1994, **95**, 299–312.

48 A. Spanedda, L. Lepori and E. Matteoli, *Fluid Phase Equilib.*, 1991, **69**, 209–222.

49 P. K. Muhuri and D. K. Hazra, *J. Chem. Eng. Data*, 1994, **39**, 375–377.

50 R. L. McGee, W. J. Wallace and R. D. Rataiczak, *J. Chem. Eng. Data*, 1983, **28**, 305–307.

51 W. J. Wallace and A. L. Mathews, *J. Chem. Eng. Data*, 1963, **8**, 496–498.

52 W. J. Wallace, C. S. Shephard and C. Underwood, *J. Chem. Eng. Data*, 1968, **13**, 11–13.

53 J. L. Cabezas, S. Beltran and J. Coca, *J. Chem. Eng. Data*, 1991, **36**, 184–188.

54 J. C. R. Reis and T. P. Iglesias, *Phys. Chem. Chem. Phys.*, 2011, **13**, 10670–10680.

55 C. F. Riadigos, R. Iglesias, M. A. Rivas and T. P. Iglesias, *J. Chem. Thermodyn.*, 2011, **43**, 275–283.

56 M. J. P. Comuñas, A. Baylaucq, C. Boned and J. Fernández, *J. Chem. Eng. Data*, 2003, **48**, 1044–1049.

57 J.-L. M. Abboud and R. Notari, *Pure Appl. Chem.*, 1999, **71**, 645–718.

58 G. W. Canters, *J. Am. Chem. Soc.*, 1972, **94**, 5230–5235.

59 A. Pal and A. Kumar, *Int. J. Thermophys.*, 2003, **24**, 1073–1087.

60 A. Serna, I. García de la Fuente, J. A. González and J. C. Cobos, *Fluid Phase Equilib.*, 1997, **133**, 187–192.

61 M. A. Villamañan, C. Casanova, A. H. Roux and J.-P. E. Grolier, *J. Chem. Thermodyn.*, 1982, **14**, 251–258.

62 H.-C. Ku and C.-H. Tu, *J. Chem. Eng. Data*, 2000, **45**, 391–394.

63 A. Pal and S. Sharma, *J. Chem. Eng. Data*, 1998, **43**, 532–536.

64 A. Pal and S. Sharma, *J. Chem. Eng. Data*, 1999, **44**, 212–215.

65 T. Treszczanowicz and D. Cieślak, *J. Chem. Thermodyn.*, 1993, **25**, 661–665.

66 G. C. Benson, M. K. Kumaran, T. Treszczanowicz, P. J. D'arcy and C. J. Halpin, *Thermochim. Acta*, 1985, **95**, 59–66.

67 A. Conesa, S. Shen and A. Coronas, *Int. J. Thermophys.*, 1998, **19**, 1343–1358.

68 E. R. López, J. L. Daridon, A. Baylaucq and J. Fernández, *J. Chem. Eng. Data*, 2003, **48**, 1208–1213.

69 K. Aizawa and M. Kato, *J. Chem. Eng. Data*, 1991, **36**, 159–161.

70 T. M. Aminabhavi and B. Gopalakrishna, *J. Chem. Eng. Data*, 1995, **40**, 462–467.

71 A. J. Treszczanowicz, C. J. Halpin and G. C. Benson, *J. Chem. Eng. Data*, 1982, **27**, 321–324.

72 C. Carvajal, K. J. Tölle, J. Smid and M. Szwarc, *J. Am. Chem. Soc.*, 1965, **87**, 5548–5553.

73 K. Kusano, *J. Chem. Eng. Data*, 1978, **23**, 141–143.

74 D. Kodama, M. Kanakubo, M. Kokubo, S. Hashimoto, H. Nanjo and M. Kato, *Fluid Phase Equilib.*, 2011, **302**, 103–108.

75 A. Lago, M. A. Rivas, J. Legido and T. P. Iglesias, *J. Chem. Thermodyn.*, 2009, **41**, 257–264.

76 K. Kimura and R. Fujishiro, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 608–610.

77 J.-F. Côté, D. Brouillette, J. E. Desnoyers, J.-F. Rouleau, J.-M. St-Arnaud and G. Perron, *J. Solution Chem.*, 1996, **25**, 1163–1173.

78 M. Cocchi, P. De Benedetti, A. Marchetti, M. C. Menziani, R. Seeber, L. Tassi and A. Ulrici, *J. Solution Chem.*, 2001, **30**, 149–169.

79 L. M. Trejo, M. Costas and D. Patterson, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 3001–3008.

80 G. T. Hefter and M. Salomon, *J. Solution Chem.*, 1994, **23**, 579–593.

81 F. Kimura, P. J. D'arcy, M. E. Sugamori and G. C. Benson, *Thermochim. Acta*, 1983, **64**, 149–154.

82 G. D. Patterson and P. J. Flory, *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 1111–1116.

83 C. A. Tovar, E. Carballo, C. A. Cerdeiriña, M. I. Paz Andrade and L. Romaní, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 3505–3509.

84 A. J. Treszczanowicz and T. Treszczanowicz, *Fluid Phase Equilib.*, 1998, **148**, 209–220.

85 A. Pal and H. Kumar, *J. Chem. Eng. Data*, 1999, **44**, 1330–1334.

86 M. J. P. Comuñas, A. Baylaucq, C. Boned and J. Fernández, *Ind. Eng. Chem. Res.*, 2004, **43**, 804–814.

87 E. R. López, J. García, A. Coronas and J. Fernández, *Fluid Phase Equilib.*, 1997, **133**, 229–238.

88 E. R. López, J.-Y. Coxam, J. Fernández and J.-P. E. Grolier, *J. Chem. Eng. Data*, 1999, **44**, 1409–1413.

89 S. I. Tseregounis and M. J. Riley, *AIChE J.*, 1994, **40**, 726–737.

90 J. Smith, L. Andreoli-Ball and D. Patterson, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 2875–2881.

91 E. R. López, J. L. Daridon, F. Plantier, C. Boned and J. Fernández, *Int. J. Thermophys.*, 2006, **27**, 1354–1372.

92 T. Nogrady and A. S. V. Burgen, *J. Am. Chem. Soc.*, 1969, **91**, 3890–3893.

93 T. Matsui and K. Takeyama, *Electrochim. Acta*, 1998, **43**, 1355–1360.

94 M. Andersson and G. Karlstrom, *J. Phys. Chem.*, 1985, **89**, 4957–4962.

95 K. Hoefelmann, J. Jagur-Grodzinski and M. Szwarc, *J. Am. Chem. Soc.*, 1969, **91**, 4645–4651.

96 G. L. Collins, T. E. H. Esch and J. Smid, *J. Solution Chem.*, 1978, **7**, 9–18.

97 G. Ritzhaupt and J. P. Devlin, *J. Phys. Chem.*, 1986, **90**, 1143–1147.

98 V. A. Payne, J.-H. Xu, M. Forsyth, M. A. Ratner, D. F. Shriver and S. W. de Leeuw, *Electrochim. Acta*, 1995, **40**, 2087–2091.

99 V. A. Payne, J. Xu, M. Forsyth, M. A. Ratner and D. F. Shriver, *J. Chem. Phys.*, 1995, **103**, 8746–8755.

100 P. Johansson, S. P. Gejji, J. Tegenfeldt and J. Lindgren, *Solid State Ionics*, 1996, **86-88**, 297–302.

101 P. Johansson, J. Tegenfeldt and J. Lindgren, *Polymer*, 1999, **40**, 4399–4406.

102 P. Johansson, *Polymer*, 2001, **42**, 4367–4373.

103 N. Shen, R. M. Pope and D. V. Dearden, *Int. J. Mass Spectrom.*, 2000, **195/196**, 639–652.

104 W. A. Henderson, V. G. Young, Jr, N. R. Brooks and W. H. Smyrl, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2002, **58**, m501–m503.

105 W. A. Henderson, N. R. Brooks, W. W. Brennessel and V. G. Young, Jr, *J. Phys. Chem. A*, 2004, **108**, 225–229.

106 J. Grondin, D. Talaga, J.-C. Lassègues and W. A. Henderson, *Phys. Chem. Chem. Phys.*, 2004, **6**, 938–944.

107 N. R. Dhuaml and S. P. Gejji, *Theor. Chem. Acc.*, 2006, **115**, 308–321.

108 T. Tamura, K. Yoshida, T. Hachida, M. Tsuchiya, M. Nakamura, Y. Kazue, N. Tachikawa, K. Dokko and M. Watanabe, *Chem. Lett.*, 2010, **39**, 753–755.

109 K. Yoshida, M. Nakamura, Y. Kazue, N. Tachikawa, S. Tsuzuki, S. Seki, K. Dokko and M. Watanabe, *J. Am. Chem. Soc.*, 2011, **133**, 13121–13129.

110 Y. S. Cho, S.-I. Cho, H.-K. Ryua, J. S. Heo, D. H. Lee and S. H. Moon, *J. Electrochem. Soc.*, 2003, **150**, F11–F19.

111 A. Varnek, G. Wipff, V. P. Solov'ev and A. F. Solotnov, *J. Chem. Inf. Model.*, 2002, **42**, 812–829.

112 H. K. Frensdorff, *J. Am. Chem. Soc.*, 1971, **93**, 600–606.

113 R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen and D. Sen, *Chem. Rev.*, 1985, **85**, 271–339.

114 R. M. Izatt, K. Pawlak, J. S. Bradshaw and R. L. Bruening, *Chem. Rev.*, 1991, **91**, 1721–2085.

115 G. W. Gokel, D. M. Goli and R. A. Schultz, *J. Org. Chem.*, 1983, **48**, 2837–2842.

116 H. Zhang and D. V. Dearden, *J. Am. Chem. Soc.*, 1992, **114**, 2754–2755.

117 W.-Y. Xu and J. Smid, *J. Am. Chem. Soc.*, 1984, **106**, 3790–3796.

118 C. B. Tsvetanov, E. B. Petrova, D. K. Dimov, I. M. Panayotov and J. Smid, *J. Solution Chem.*, 1990, **19**, 425–436.

119 W. R. Davidson and P. Kebarle, *Can. J. Chem.*, 1976, **54**, 2594–2599.

120 A. Plewa-Marczewska, M. Kalita, M. Marczewski and M. Siekierski, *Electrochim. Acta*, 2010, **55**, 1389–1395.

121 L. L. Chan and J. Smid, *J. Am. Chem. Soc.*, 1967, **89**, 4547–4549.

122 L. L. Chan and J. Smid, *J. Am. Chem. Soc.*, 1968, **90**, 4654–4661.

123 L. L. Chan, K. H. Wong and J. Smid, *J. Am. Chem. Soc.*, 1970, **92**, 1955–1963.

124 U. Takaki and J. Smid, *J. Am. Chem. Soc.*, 1974, **96**, 2588–2593.

125 C. Detellier and P. Laszlo, *Helv. Chim. Acta*, 1976, **59**, 1333–1345.

126 W. R. Gilkerson and M. D. Jackson, *J. Am. Chem. Soc.*, 1982, **104**, 1218–1223.

127 A. Plewa, M. Kalita and M. Siekierski, *Electrochim. Acta*, 2007, **53**, 1527–1534.

128 J. Smid and A. M. Grotens, *J. Phys. Chem.*, 1973, **77**, 2377–2382.

129 E. de Boer, A. A. K. Klaassen, J. J. Mooij and J. H. Noordik, *Pure Appl. Chem.*, 1979, **51**, 73–83.

130 C. P. Rhodes and R. Frech, *Macromolecules*, 2001, **34**, 2660–2666.

131 R. Frech, C. P. Rhodes and M. Khan, *Macromol. Symp.*, 2002, **186**, 41–49.

132 C. P. Rhodes, M. Khan and R. Frech, *J. Phys. Chem. B*, 2002, **106**, 10330–10337.

133 W. A. Henderson, N. R. Brooks, W. W. Brennessel and V. G. J. Young, *Chem. Mater.*, 2003, **15**, 4679–4684.

134 W. A. Henderson, N. R. Brooks and V. G. J. Young, *Chem. Mater.*, 2003, **15**, 4685–4690.

135 W. A. Henderson, *J. Phys. Chem. B*, 2006, **110**, 13177–13183.

136 W. A. Henderson, *Macromolecules*, 2007, **40**, 4963–4971.

137 W. A. Henderson and N. R. Brooks, *Inorg. Chem.*, 2003, **42**, 4522–4524.

138 J. M. Timko, R. C. Helgeson, M. Newcomb, G. W. Gokel and D. J. Cram, *J. Am. Chem. Soc.*, 1974, **96**, 7097–7099.

139 R. A. Bartsch and P. N. Juri, *Tetrahedron Lett.*, 1979, **20**, 407–410.

140 R. A. Bartsch, P. N. Juri and M. A. Mills, *Tetrahedron Lett.*, 1979, **20**, 2499–2502.

141 J. Otera, T. Shiomi, K. Murakami and Y. Kawasaki, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2964–2967.

142 Y. Hirashima, K. Ito and J. Shiokawa, *Chem. Lett.*, 1983, **12**, 9–10.

143 Y. Hirashima, K. Kanetsuki, I. Yonezu, K. Kamakura and J. Shiokawa, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 738–743.

144 Y. Inoue and T. Hakushi, *J. Chem. Soc., Perkin Trans. 2*, 1985, 935–946.

145 M. A. Guerra, T. R. Bierschenk and R. J. Lagow, *J. Am. Chem. Soc.*, 1986, **108**, 4103–4105.

146 P. R. Markies, O. S. Akkerman, F. Bickelhaupt, W. J. J. Smeets and A. L. Spek, *Organometallics*, 1994, **13**, 2616–2627.

147 M. Meot-Ner, L. W. Sieck, J. F. Liebman and S. Scheiner, *J. Phys. Chem.*, 1996, **100**, 6445–6450.

148 K. M. Fromm, H. Goesmann and G. Bernardinelli, *Polyhedron*, 2000, **19**, 1783–1789.

149 S. Mishra, S. Daniele, L. G. Hubert-Pfalzgraf and E. Jeanneau, *Eur. J. Inorg. Chem.*, 2007, 2208–2215.

150 M. K. J. Chantooni, D. Britton and I. M. Kolthoff, *J. Crystallogr. Spectrosc. Res.*, 1993, **23**, 497–503.

151 G. D. Jaycox, R. Sinta and J. Smid, *J. Polym. Sci., Polym. Chem. Ed.*, 1982, **20**, 1629–1638.

152 M. Saraswathi and J. M. Miller, *J. Am. Soc. Mass Spectrom.*, 1996, **7**, 42–49.

153 R. V. Slates and M. Szwarc, *J. Am. Chem. Soc.*, 1967, **89**, 6043–6050.

154 G. W. Canters, A. A. K. Klassen and E. de Boer, *J. Phys. Chem.*, 1970, **74**, 3299–3302.

155 W. H. Smyrl, S. R. Kurtz, J. M. Zeigler and D. S. Ginley, *J. Chem. Soc., Chem. Commun.*, 1983, 1155–1156.

156 J. S. Foos, T. S. Stolki and X. Beebe, *J. Electrochem. Soc.*, 1989, **136**, 2748–2749.

157 U. Sharma and V. K. Bhagwat, *Asian J. Chem.*, 1992, **4**, 758–763.

158 R. Pyati and R. W. Murray, *J. Am. Chem. Soc.*, 1996, **118**, 1743–1749.

159 D. Teeters, R. G. Neuman and B. D. Tate, *Solid State Ionics*, 1996, **85**, 239–245.

160 Y. Choquette, G. Brisard, M. Parent, D. Brouillette, G. Perron, J. E. Desnoyers, M. Armand, D. Gravel and N. Slougui, *J. Electrochem. Soc.*, 1998, **145**, 3500–3507.

161 A. Plewa, F. Chyliński, M. Kalita, M. Bukat, P. Parzuchowski, R. Borkowska, M. Siekierski, G. Z. Żukowska and W. Wieczorek, *J. Power Sources*, 2006, **159**, 431–437.

162 Y. Katayama, S. Miyashita and T. Miura, *J. Power Sources*, 2010, **195**, 6162–6166.

163 K. Izutsu, T. Nakamura, K. Miyoshi and K. Kurita, *Electrochim. Acta*, 1996, **41**, 2523–2527.

164 D. Aurbach and E. Granot, *Electrochim. Acta*, 1997, **42**, 697–718.

165 D. Brouillette, G. Perron and J. E. Desnoyers, *J. Solution Chem.*, 1998, **27**, 151–182.

166 K. Hayamizu, Y. Aihara, S. Arai and C. G. Martinez, *J. Phys. Chem. B*, 1999, **103**, 519–524.

167 K. Hayamizu, E. Akiba, T. Bando and Y. Aihara, *J. Chem. Phys.*, 2002, **117**, 5929–5939.

168 W. A. Henderson, F. McKenna, M. A. Khan, N. R. Brooks, V. G. J. Young and R. Frech, *Chem. Mater.*, 2005, **17**, 2284–2289.

169 V. S. Kolosnitsyn, E. V. Karaseva, D. Y. Seung and M. D. Cho, *Russ. J. Electrochem.*, 2003, **39**, 1089–1093.

170 V. S. Kolosnitsyn, E. V. Karaseva, N. V. Shakirova, D. Y. Seung and M. D. Cho, *Russ. J. Electrochem.*, 2002, **38**, 1360–1363.

171 S. Tobishima, H. Morimoto, M. Aoki, Y. Saito, T. Inose, T. Fukumoto and T. Kuryu, *Electrochim. Acta*, 2004, **49**, 979–987.

172 T. Inose, D. Watanabe, H. Morimoto and S. Tobishima, *J. Power Sources*, 2006, **162**, 1297–1303.

173 T. V. Kaulgud, N. R. Dhumal and S. P. Gejji, *J. Phys. Chem. A*, 2006, **110**, 9231–9239.

174 K. Yoshida, M. Tsuchiya, N. Tachikawa, K. Dokko and M. Watanabe, *J. Phys. Chem. C*, 2011, **115**, 18384–18394.

175 A. Orita, K. Kamijima, M. Yoshida, K. Dokko and M. Watanabe, *J. Power Sources*, 2011, **196**, 3874–3880.

176 T. Tamura, T. Hachida, K. Yoshida, N. Tachikawa, K. Dokko and M. Watanabe, *J. Power Sources*, 2010, **195**, 6095–6100.

177 S. Seki, K. Takei, H. Miyashiro and M. Watanabe, *J. Electrochem. Soc.*, 2011, **158**, A769–A774.

178 S. Seki, N. Serizawa, K. Takei, K. Dokko and M. Watanabe, *J. Power Sources*, 2013, **243**, 323–327.

179 B. L. Ellis, K. T. Lee and L. F. Nazar, *Chem. Mater.*, 2010, **22**, 691–714.

180 N. Tachikawa, K. Yamauchi, E. Takashima, J.-W. Park, K. Dokko and M. Watanabe, *Chem. Commun.*, 2011, **47**, 8157–8159.

181 C. Barchasz, J.-C. Leprêtre, S. Patoux and F. Alloin, *Electrochim. Acta*, 2013, **89**, 737–743.

182 D. Aurbach, Y. Gofer, Z. Lu, A. Schechter, O. Chusid, H. Gizbar, Y. Cohen, V. Ashkenazi, M. Moshkovich, R. Turgeman and E. Levi, *J. Power Sources*, 2001, **97–98**, 28–32.

183 D. Aurbach, H. Gizbar, A. Schechter, O. Chusid, H. E. Gottlieb, Y. Gofer and I. Goldberg, *J. Electrochem. Soc.*, 2002, **149**, A115–A121.

184 D. Aurbach, I. Weissman, Y. Gofer and E. Levi, *Chem. Rec.*, 2003, **3**, 61–73.

185 B. M. L. Rao and L. P. Klemann, *J. Electrochem. Soc.*, 1980, **127**, 761–762.

186 C. Zhang, Y. G. Andreev and P. G. Bruce, *Angew. Chem., Int. Ed.*, 2007, **46**, 2848–2850.

187 C. Zhang, E. Staunton, Y. G. Andreev and P. G. Bruce, *J. Mater. Chem.*, 2007, **17**, 3222–3228.

188 C. Zhang, D. Ainsworth, Y. G. Andreev and P. G. Bruce, *J. Am. Chem. Soc.*, 2007, **129**, 8700–8701.

189 C. Zhang, S. J. Lilley, D. Ainsworth, E. Staunton, Y. G. Andreev, A. M. Z. Slawin and P. G. Bruce, *Chem. Mater.*, 2008, **20**, 4039–4044.

190 D. W. Xia and J. Smid, *J. Polym. Sci., Polym. Lett. Ed.*, 1984, **22**, 617–621.

191 L. Holzer, F. P. Wenzl, S. Tasch, G. Leising, B. Winkler, L. Dai and A. W. H. Mau, *Appl. Phys. Lett.*, 1999, **75**, 2014–2016.

192 J. S. J. McConaghy and J. J. Bloomfield, *J. Org. Chem.*, 1968, **33**, 3425–3428.

193 R. D. Rieke and P. M. Hudnall, *J. Am. Chem. Soc.*, 1969, **91**, 3678–3679.

194 G. Moshuk, G. Petrowski and S. Winstein, *J. Am. Chem. Soc.*, 1968, **90**, 2179–2181.

195 R. Rieke, M. Ogliaruso, R. McClung and S. Winstein, *J. Am. Chem. Soc.*, 1966, **88**, 4729–4730.

196 L. L. Miller and L. J. Jacoby, *J. Am. Chem. Soc.*, 1969, **91**, 1130–1134.

197 H. M. Walborsky, M. S. Aronoff and M. F. Schulman, *J. Org. Chem.*, 1971, **36**, 1036–1040.

198 L. Wei, A. Bell, K. H. Ahn, M. M. Holl, S. Warner, I. D. Williams and S. J. Lippard, *Inorg. Chem.*, 1990, **29**, 825–837.

199 L. Wei, A. Bell, S. Warner, I. D. Williams and S. J. Lippard, *J. Am. Chem. Soc.*, 1986, **108**, 8302–8303.

200 H. Riesner and E. Winterfeldt, *J. Chem. Soc., Chem. Commun.*, 1972, 786–787.

201 A. R. Dahl, C. A. Heil and A. D. Norman, *Inorg. Chem.*, 1975, **14**, 1095–1098.

202 J. E. Saavedra, *J. Org. Chem.*, 1979, **44**, 860–861.

203 T. Ohsawa, T. Takagaki, F. Ikehara, Y. Takahashi and T. Oishi, *Chem. Pharm. Bull.*, 1982, **30**, 3178–3186.

204 A. V. Kavaliunas, A. Taylor and R. D. Rieke, *Organometallics*, 1983, **2**, 377–383.

205 G. L. Rochfort and R. D. Rieke, *Inorg. Chem.*, 1986, **25**, 348–355.

206 S. Inaba, H. Matsumoto and R. D. Rieke, *J. Org. Chem.*, 1984, **49**, 2093–2098.

207 S. Inaba and R. D. Rieke, *J. Org. Chem.*, 1985, **50**, 1373–1381.

208 G. T. King and N. E. Miller, *Inorg. Chem.*, 1986, **25**, 4309–4311.

209 P. A. Bianconi, R. N. Vrtis, C. P. Rao, I. D. Williams, M. P. Engeler and S. J. Lippard, *Organometallics*, 1987, **6**, 1968–1977.

210 P. E. Fanwick, D. R. Root and R. A. Walton, *Inorg. Chem.*, 1989, **28**, 395–397.

211 P. E. Fanwick, D. R. Root and R. A. Walton, *Inorg. Chem.*, 1989, **28**, 3203–3209.

212 C. Yang and C. U. J. Pittman, *Tetrahedron Lett.*, 1997, **38**, 6561–6564.

213 C. Yang and C. U. J. Pittman, *Synth. Commun.*, 1998, **28**, 517–525.

214 C. U. J. Pittman and C. Yang, *J. Hazard. Mater.*, 2001, **82**, 299–311.

215 J. V. B. Kanth and H. C. Brown, *Inorg. Chem.*, 2000, **39**, 1795–1802.

216 R. J. Ouellette and C. Levin, *J. Am. Chem. Soc.*, 1971, **93**, 471–476.

217 M. Ochiai and E. Fujita, *J. Chem. Soc., Chem. Commun.*, 1975, 967–968.

218 E. Fujita and M. Ochiai, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1948–1953.

219 A. McKillop, B. P. Swann, M. E. Ford and E. C. Taylor, *J. Am. Chem. Soc.*, 1973, **95**, 3641–3645.

220 A. McKillop, O. H. Oldenziel, B. P. Swann, E. C. Taylor and R. L. Robey, *J. Am. Chem. Soc.*, 1973, **95**, 1296–1301.

221 G. Stork and P. F. Hudrlik, *J. Am. Chem. Soc.*, 1968, **90**, 4464–4465.

222 G. Stork and P. F. Hudrlik, *J. Am. Chem. Soc.*, 1968, **90**, 4462–4464.

223 R. V. Stevens and L. E. DuPree, *J. Chem. Soc. D*, 1970, 1585–1586.

224 R. V. Stevens and M. P. Wentland, *J. Am. Chem. Soc.*, 1968, **90**, 5580–5583.

225 J. L. Kice and G. J. Kasperek, *J. Am. Chem. Soc.*, 1970, **92**, 3393–3397.

226 J. L. Kice, C. A. Walters and S. B. Burton, *J. Org. Chem.*, 1974, **39**, 346–351.

227 W. T. Reichle, *J. Org. Chem.*, 1972, **37**, 4254–4257.

228 S. D. Pastor and E. T. Hessell, *J. Org. Chem.*, 1985, **50**, 4812–4815.

229 K. S. Chen, J. Kleinberg and J. A. Landgrebe, *Inorg. Chem.*, 1973, **12**, 2826–2828.

230 J. White and G. McGillivray, *J. Org. Chem.*, 1974, **39**, 1973–1974.

231 N. C. Brown, J. Gambino and G. E. Wright, *J. Med. Chem.*, 1977, **20**, 1186–1189.

232 T. Izumi and S. I. Miller, *J. Org. Chem.*, 1978, **43**, 871–875.

233 E. H. Banitt and G. J. Conard, *J. Labelled Compd. Radiopharm.*, 1981, **18**, 713–720.

234 A. Okamoto, T. Hayashi and I. Mita, *Polym. J.*, 1983, **15**, 423–427.

235 C. L. Stephens, H. L. Nyquist and K. I. Hardcastle, *J. Org. Chem.*, 2002, **67**, 3051–3056.

236 Q. Zhu, J. Wu, R. Fathi and Z. Yang, *Org. Lett.*, 2002, **4**, 3333–3336.

237 S. Kim, B. K. Yoo, K. Chun, W. Kang, J. Choo, M.-S. Gong and S.-W. Joo, *J. Mol. Catal. A: Chem.*, 2005, **226**, 231–234.

238 S. W. Smith and G. C. Fu, *J. Am. Chem. Soc.*, 2008, **130**, 12645–12647.

239 S. W. Smith and G. C. Fu, *Angew. Chem., Int. Ed.*, 2008, **47**, 9334–9336.

240 J. J. Fitt and H. W. Gschwend, *J. Org. Chem.*, 1984, **49**, 209–210.

241 J. M. Schomaker and T. J. Delia, *J. Org. Chem.*, 2001, **66**, 7125–7128.

242 T. J. Delia, J. M. Schomaker and A. S. Kalinda, *J. Heterocycl. Chem.*, 2006, **43**, 127–131.

243 R. A. Geanangel and S. G. Shore, *J. Am. Chem. Soc.*, 1967, **89**, 6771–6772.

244 N. S. Hosmane, J. R. Wermer, Z. Hong, T. D. Getman and S. G. Shore, *Inorg. Chem.*, 1987, **26**, 3638–3639.

245 S. H. Lawrence, J. R. Wermer, S. K. Boocock, M. A. Banks, P. C. Keller and S. G. Shore, *Inorg. Chem.*, 1986, **25**, 367–372.

246 A. Pelter, T. Levitt and K. Smith, *J. Chem. Soc. D*, 1969, 435–436.

247 L. A. Peacock and R. A. Geanangel, *Inorg. Chem.*, 1976, **15**, 244–246.

248 R. N. Leyden, B. P. Sullivan, R. T. Baker and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1978, **100**, 3758–3765.

249 J. R. Wermer and S. G. Shore, *Inorg. Chem.*, 1987, **26**, 1644–1645.

250 T. D. Getman, J. A. Krause, P. M. Niedenzu and S. G. Shore, *Inorg. Chem.*, 1989, **28**, 1507–1510.

251 C.-H. Kang, S.-J. Kim, J.-J. Ko, K.-B. Lee and S. O. Kang, *Bull. Korean Chem. Soc.*, 1993, **14**, 537–539.

252 J. Holub, D. L. Ormsby, J. D. Kennedy, R. Greatrex and B. Štíbr, *Inorg. Chem. Commun.*, 2000, **3**, 178–181.

253 S. Rosen and D. Sworm, *Anal. Chem.*, 1966, **38**, 1392–1397.

254 P. G. Gassman, J. T. Lumb and F. V. Zalar, *J. Am. Chem. Soc.*, 1967, **89**, 946–952.

255 B. W. Finucane and J. B. Thomson, *J. Chem. Soc. D*, 1969, 1220.

256 A. B. Lateef, J. A. Reeder and L. Rand, *J. Org. Chem.*, 1971, **36**, 2295–2298.

257 T. P. Karpetsky and E. H. White, *J. Org. Chem.*, 1972, **37**, 339–341.

258 C. U. J. Pittman, P. L. Grube, O. E. Ayers, S. P. McManus, M. D. Rausch and G. A. Moser, *J. Polym. Sci., Part A-1*, 1972, **10**, 379–386.

259 G. Stork and T. L. MacDonald, *J. Am. Chem. Soc.*, 1975, **97**, 1264–1265.

260 J. W. Wilt and R. R. Rasmussen, *J. Org. Chem.*, 1975, **40**, 1031–1036.

261 P. J. Stang and M. G. Mangum, *J. Am. Chem. Soc.*, 1975, **97**, 3854–3856.

262 P. J. Stang and M. G. Mangum, *J. Am. Chem. Soc.*, 1977, **99**, 2597–2601.

263 J. L. Vidal, R. A. Fiato, L. A. Cosby and R. L. Pruett, *Inorg. Chem.*, 1978, **17**, 2574–2582.

264 J. L. Vidal, *Inorg. Chem.*, 1981, **20**, 243–249.

265 C. J. Collins, H. P. Hombach, B. Maxwell, M. C. Woody and B. M. Benjamin, *J. Am. Chem. Soc.*, 1980, **102**, 851–853.
266 M. Ladika and P. J. Stang, *J. Chem. Soc., Chem. Commun.*, 1981, 459–460.
267 T. E. Paxson, C. A. Reilly and D. R. Holecek, *J. Chem. Soc., Chem. Commun.*, 1981, 618–619.
268 E. E. van Tamelen and D. A. Seeley, *J. Am. Chem. Soc.*, 1969, **91**, 5194.
269 G. P. Pez, P. Apgar and R. K. Crissey, *J. Am. Chem. Soc.*, 1982, **104**, 482–490.
270 K.-H. Budt, J.-M. Vatele and Y. Kishi, *J. Am. Chem. Soc.*, 1986, **108**, 6080–6082.
271 C.-M. T. Hayward and J. R. Shapley, *Organometallics*, 1988, **7**, 448–452.
272 O. S. Tee and J. A. Enos, *Can. J. Chem.*, 1988, **66**, 3027–3030.
273 J. R. Briggs, *J. Chem. Soc., Chem. Commun.*, 1989, 674–675.
274 W. Maringgele, U. Seebold, A. Heine, D. Stalke, M. Noltemeyer, G. M. Sheldrick and A. Meller, *Organometallics*, 1991, **10**, 2097–2098.
275 M.-H. Hung, W. B. Farnham, A. E. Feiring and S. Rozen, *J. Am. Chem. Soc.*, 1993, **115**, 8954–8959.
276 M. L. Hays and T. P. Hanusa, *Tetrahedron Lett.*, 1995, **36**, 2435–2436.
277 N. V. Kirij, Y. L. Yagupolskii, N. Maggiarosa, W. Tyrra and D. Naumann, *J. Fluorine Chem.*, 2001, **112**, 213–218.
278 L. M. Yagupolskii, S. V. Shelyazhenko, I. I. Maletina, V. N. Petrik, E. B. Rusanov and A. N. Chernega, *Eur. J. Org. Chem.*, 2001, 1225–1233.
279 O. Israelsohn, K. P. C. Vollhardt and J. Blum, *J. Mol. Catal. A: Chem.*, 2002, **184**, 1–10.
280 W. Tyrra, D. Naumann, B. Hoge and Y. L. Yagupolskii, *J. Fluorine Chem.*, 2003, **119**, 101–107.
281 W. Tyrra, N. V. Kirij, D. Naumann and Y. L. Yagupolskii, *J. Fluorine Chem.*, 2004, **125**, 1437–1440.
282 H. Zook and J. Miller, *J. Org. Chem.*, 1971, **36**, 1112–1116.
283 M. Shinohara, J. Smid and M. Szwarc, *J. Am. Chem. Soc.*, 1968, **90**, 2175–2177.
284 M. A. Guerra and R. J. Lagow, *J. Chem. Soc., Chem. Commun.*, 1990, 65–66.
285 L. Liang and S. Ying, *Makromol. Chem.*, 1993, **194**, 581–600.
286 J. S. Wang, R. Jerome, R. Warin, H. Zhang and P. Teyssie, *Macromolecules*, 1994, **27**, 3376–3382.
287 L. J. Krause and J. A. Morrison, *J. Chem. Soc., Chem. Commun.*, 1980, 671–672.
288 L. J. Krause and J. A. Morrison, *J. Am. Chem. Soc.*, 1981, **103**, 2995–3001.
289 L. J. Krause and J. A. Morrison, *J. Chem. Soc., Chem. Commun.*, 1981, 1282–1283.
290 C. D. Ontiveros and J. A. Morrison, *Organometallics*, 1986, **5**, 1446–1448.
291 J. K. Galiotos and J. A. Morrison, *Organometallics*, 2000, **19**, 2603–2607.
292 H. H. Murray, J. P. J. Fackler, L. C. Porter, D. A. Briggs, M. A. Guerra and R. J. Lagow, *Inorg. Chem.*, 1987, **26**, 357–363.
293 H. K. Nair and J. A. Morrison, *Inorg. Chem.*, 1989, **28**, 2816–2820.
294 D. C. Loizou, J. Castillo, A. R. Oki, N. S. Hosmane and J. A. Morrison, *Organometallics*, 1992, **11**, 4189–4193.
295 K. Ludovici, D. Naumann, G. Siegemund, W. Tyrra, H.-G. Varbelow and H. Wrubel, *J. Fluorine Chem.*, 1995, **73**, 273–274.
296 S. Daniele, L. G. Hubert-Pfalzgraf and J. Vaissermann, *Polyhedron*, 2003, **22**, 127–132.
297 K. Sukata, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 613–614.
298 D. G. Lee and V. S. Chang, *J. Org. Chem.*, 1978, **43**, 1532–1536.
299 C. Paradisi, U. Quintily and G. Scorrano, *J. Org. Chem.*, 1983, **48**, 3022–3026.
300 D. E. Bergbreiter and J. R. Blanton, *J. Org. Chem.*, 1987, **52**, 472–473.
301 K. Sukata and T. Akagawa, *J. Org. Chem.*, 1989, **54**, 1476–1479.
302 D. Landini, A. Maia, L. Corda, A. Maccioni and G. Podda, *Tetrahedron Lett.*, 1989, **30**, 5781–5784.
303 D. Landini, A. Maia, L. Corda, A. Maccioni and G. Podda, *Tetrahedron*, 1991, **47**, 7477–7488.
304 A. A. Varnek, A. Maia, D. Landini, A. Gamba, G. Morosi and G. Podda, *J. Phys. Org. Chem.*, 1993, **6**, 113–121.
305 H. B. Lazrek, M. Taourirte, J.-L. Barascut and J.-L. Imbach, *Nucleosides Nucleotides*, 1991, **10**, 1285–1293.
306 I. Y. Kudryavtsev and L. S. Zakharov, *Russ. Chem. Bull.*, 2001, **50**, 1457–1460.
307 T. Y. Kochergina and V. F. Anufriev, *Russ. J. Org. Chem.*, 2002, **38**, 534–537.
308 H. J. Koh, K. L. Han and I. Lee, *J. Org. Chem.*, 1999, **64**, 4783–4789.
309 J. C. Hogan and R. D. Gandour, *J. Am. Chem. Soc.*, 1980, **102**, 2865–2866.
310 J. C. Hogan and R. D. Gandour, *J. Org. Chem.*, 1991, **56**, 2821–2826.
311 J. C. Hogan and R. D. Gandour, *J. Org. Chem.*, 1992, **57**, 55–61.
312 N. Basilio, L. García-Río, J. R. Leis, J. C. Mejuto and M. Pérez-Lorenzo, *Chem. Commun.*, 2005, 3817–3819.
313 N. Basilio, L. García-Río, J. C. Mejuto and M. Pérez-Lorenzo, *J. Org. Chem.*, 2006, **71**, 4280–4285.
314 L. García-Río, J. C. Mejuto and M. Pérez-Lorenzo, *J. Phys. Chem. B*, 2007, **111**, 11149–11156.
315 X. Dai, N. A. Strotman and G. C. Fu, *J. Am. Chem. Soc.*, 2008, **130**, 3302–3303.
316 R. A. Bartsch and I. W. Yang, *Tetrahedron Lett.*, 1979, **20**, 2503–2504.
317 Y. Kimura and S. L. Regen, *J. Org. Chem.*, 1982, **47**, 2493–2494.
318 M. S. Newman and W. C. Liang, *J. Org. Chem.*, 1973, **38**, 2438–2441.
319 H. Ishii, Y. Hou and T. Fuchigami, *Tetrahedron*, 2000, **56**, 8877–8881.
320 S. A. Grabovskiy, Q. K. Timerghazin and N. N. Kabal'nova, *Russ. Chem. Bull.*, 2005, **54**, 2384–2393.
321 C. W. Yoon, P. J. Carroll and L. G. Sneddon, *J. Am. Chem. Soc.*, 2009, **131**, 855–864.

322 I. Yoshpe-Besancon, D. Auriol, F. Paul, P. Monsan, J. C. Gripon and B. Ribadeau-Dumas, *Biotechnol. Appl. Biochem.*, 1993, **18**, 93–102.
323 C. M. Rosell, M. Terreni, R. Fernandez-Lafuente and J. M. Guisan, *Enzyme Microb. Technol.*, 1998, **23**, 64–69.
324 D. B. Berkowitz, R. E. Hartung and S. Choi, *Tetrahedron: Asymmetry*, 1999, **10**, 4513–4520.
325 C. G. P. H. Schroën, V. A. Nierstrasz, P. J. Kroon, R. Bosma, A. E. M. Janssen, H. H. Beeftink and J. Tramper, *Enzyme Microb. Technol.*, 1999, **24**, 498–506.
326 A. Illanes and A. Fajardo, *J. Mol. Catal. B: Enzym.*, 2001, **11**, 587–595.
327 H. Ohno and N. Yamaguchi, *Bioconjugate Chem.*, 1994, **5**, 379–381.
328 N. Y. Kawahara and H. Ohno, *Bioconjugate Chem.*, 1997, **8**, 643–648.
329 F. Kurusu and H. Ohno, *Electrochim. Acta*, 2000, **45**, 2911–2915.
330 J. Chen, S. K. Spear, J. G. Huddleston and R. D. Rogers, *Green Chem.*, 2005, **7**, 64–82.
331 L. Cao, F. van Rantwijk and R. A. Sheldon, *Org. Lett.*, 2000, **2**, 1361–1364.
332 B. R. Taylor and S. M. Kauzlarich, *Chem. Mater.*, 1998, **10**, 22–24.
333 B. R. Taylor and S. M. Kauzlarich, *Chem. Mater.*, 1999, **11**, 2493–2500.
334 B. R. Taylor, G. A. Fox, L. J. Hope-Weeks, R. S. Maxwell, S. M. Kauzlarich and H. W. H. Lee, *Mater. Sci. Eng., B*, 2002, **96**, 90–93.
335 C.-S. Yang, R. A. Bley, S. M. Kauzlarich, H. W. H. Lee and G. R. Delgado, *J. Am. Chem. Soc.*, 1999, **121**, 5191–5195.
336 C.-S. Yang, Q. Liu and S. M. Kauzlarich, *Chem. Mater.*, 2000, **12**, 983–988.
337 E. E. Johnston, J. D. Bryers and B. D. Ratner, *Langmuir*, 2005, **21**, 870–881.
338 F. Brétagnol, L. Ceriotti, M. Lejeune, A. Papadopoulou-Bouraoui, M. Hasiwa, D. Gilliland, G. Ceccone, P. Colpo and F. Rossi, *Plasma Processes Polym.*, 2006, **3**, 30–38.
339 F. Brétagnol, M. Lejeune, A. Papadopoulou-Bouraoui, M. Hasiwa, H. Rauscher, G. Ceccone, P. Colpo and F. Rossi, *Acta Biomater.*, 2006, **2**, 165–172.
340 F. Brétagnol, L. Sirghi, S. Mornet, T. Sasaki, D. Gilliland, P. Colpo and F. Rossi, *Nanotechnology*, 2008, **19**, 125306.
341 C.-S. Yang, D. D. Awschalom and G. D. Stucky, *Chem. Mater.*, 2001, **13**, 594–598.
342 C.-S. Yang, D. D. Awschalom and G. D. Stucky, *Chem. Mater.*, 2002, **14**, 1277–1284.
343 H. W. Chiu and S. M. Kauzlarich, *Chem. Mater.*, 2006, **18**, 1023–1028.
344 A. L. Pickering, C. Mitterbauer, N. D. Browning, S. M. Kauzlarich and P. P. Power, *Chem. Commun.*, 2007, 580–582.
345 J. Cho, *Electrochim. Acta*, 2008, **54**, 461–466.
346 N. Shirahata and Y. Sakka, *J. Ceram. Soc. Jpn.*, 2010, **118**, 932–939.
347 S. Mishra, G. Ledoux, E. Jeanneau, S. Daniele and M.-F. Joubert, *Dalton Trans.*, 2012, **41**, 1490–1502.
348 M. Shirai, H. Ishida and M. Tanaka, *J. Polym. Sci., Part B: Polym. Phys.*, 1988, **26**, 2075–2091.
349 J. Morgado, F. Cacialli, R. H. Friend, B. S. Chuah, H. Rost, S. C. Moratti and A. B. Holmes, *Synth. Met.*, 2001, **119**, 595–596.
350 J. A. Moore, J.-H. Kim and P. R. Seidel, *Chem. Mater.*, 1991, **3**, 742–745.
351 P. J. Fazen, E. E. Remsen, J. S. Beck, P. J. Carroll, A. R. McGhie and L. G. Sneddon, *Chem. Mater.*, 1995, **7**, 1942–1956.
352 P. J. Fazen, J. S. Beck, A. T. Lynch, E. E. Remsen and L. G. Sneddon, *Chem. Mater.*, 1990, **2**, 96–97.
353 K. Moraes, J. Vosburg, D. Wark and L. V. Interrante, *Chem. Mater.*, 2004, **16**, 125–132.
354 G. P. López and B. D. Ratner, *Plasmas Polym.*, 1996, **1**, 127–151.
355 B. Sandner, N. Kotzian, J. Tubke, S. Wartewig and O. Lange, *Macromol. Chem. Phys.*, 1997, **198**, 2715–2727.
356 R. T. Baker, P. J. Krusic, T. H. Tulip, J. C. Calabrese and S. S. Wreford, *J. Am. Chem. Soc.*, 1983, **105**, 6763–6765.
357 I. Baxter, S. R. Drake, M. B. Hursthouse, K. M. A. Malik, J. McAleese, D. J. Otway and J. C. Plakatouras, *Inorg. Chem.*, 1995, **34**, 1384–1394.
358 S. R. Drake, S. A. S. Miller and D. J. Williams, *Inorg. Chem.*, 1993, **32**, 3227–3235.
359 S. R. Drake, A. Lyons, D. J. Otway, A. M. Z. Slawin and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1993, 2379–2386.
360 V.-C. Arunasalam, I. Baxter, S. R. Drake, M. B. Hursthouse, K. M. A. Malik, S. A. S. Miller, D. M. P. Mingos and D. J. Otway, *J. Chem. Soc., Dalton Trans.*, 1997, 1331–1336.
361 F. J. Arnáiz, R. Aguado, M. R. Pedrosa, J. Mahía and M. A. Maestro, *Polyhedron*, 2001, **20**, 2781–2785.
362 A. Crochet and K. M. Fromm, *Z. Anorg. Allg. Chem.*, 2010, **636**, 1484–1496.
363 G. Malandrino, R. Licata, F. Castelli, I. L. Fragalà and C. Benelli, *Inorg. Chem.*, 1995, **34**, 6233–6234.
364 G. Malandrino, C. Benelli, F. Castelli and I. L. Fragalà, *Chem. Mater.*, 1998, **10**, 3434–3444.
365 K. D. Pollard, J. J. Vittal, G. P. A. Yap and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 1998, 1265–1268.
366 G. Malandrino, R. Lo Nigro, I. L. Fragalà and C. Benelli, *Eur. J. Inorg. Chem.*, 2004, 500–509.
367 S.-J. Kang, Y. S. Jung and I.-H. Suh, *Bull. Korean Chem. Soc.*, 1999, **20**, 95–98.
368 K. D. Pollard, H. A. Jenkins and R. J. Puddephatt, *Chem. Mater.*, 2000, **12**, 701–710.
369 G. Malandrino, R. Lo Nigro, C. Benelli, F. Castelli and I. L. Fragalà, *Chem. Vap. Deposition*, 2000, **6**, 233–238.
370 G. Malandrino, M. Bettinelli, A. Speghini and I. L. Fragalà, *Eur. J. Inorg. Chem.*, 2001, 1039–1044.
371 G. G. Condorelli, S. Gennaro and I. L. Fragalà, *Chem. Vap. Deposition*, 2000, **6**, 185–192.
372 R. Lo Nigro, R. G. Toro, M. E. Fragalà, P. Rossi, P. Dapporto and G. Malandrino, *Inorg. Chim. Acta*, 2009, **362**, 4623–4629.

373 A. J. Blake, J. A. Darr, S. M. Howdle, M. Poliakoff, W.-S. Li and P. B. Webb, *J. Chem. Crystallogr.*, 1999, **29**, 547–554.
374 D. Pfeiffer, M. J. Heeg and C. H. Winter, *Inorg. Chem.*, 2000, **39**, 2377–2384.
375 E. Buncel, J. M. Dust, A. Jonczyk, R. A. Manderville and I. Onyido, *J. Am. Chem. Soc.*, 1992, **114**, 5610–5619.
376 E. Buncel and R. A. Manderville, *J. Phys. Org. Chem.*, 1993, **6**, 71–82.
377 R. A. Manderville and E. Buncel, *J. Am. Chem. Soc.*, 1993, **115**, 8985–8989.
378 R. A. Manderville and E. Buncel, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1887–1894.
379 C. A. Rouse, A. C. Finlinson, B. J. Tarbet, J. C. Pixton, N. M. Djordjevic, K. E. Markides, J. S. Bradshaw and M. L. Lee, *Anal. Chem.*, 1988, **60**, 901–905.
380 A. J. Schuetz, M. G. Weller and R. Niessner, *Fresenius' J. Anal. Chem.*, 1999, **363**, 777–782.
381 S. F. Sciamanna and S. Lynn, *Ind. Eng. Chem. Res.*, 1988, **27**, 492–499.
382 A. Henni, P. Tontiwachwuthikul and A. Chakma, *Can. J. Chem. Eng.*, 2005, **83**, 358–361.
383 H. E. Mishmash and C. E. Meloan, *Anal. Chem.*, 1972, **44**, 835–836.
384 J. Dasilva-Carbalhal, L. García-Río, D. Gómez-Díaz, J. C. Mejuto and M. Pérez-Lorenzo, *J. Colloid Interface Sci.*, 2005, **292**, 591–594.
385 Y. Gu and F. Jérôme, *Green Chem.*, 2010, **12**, 1127–1138.
386 A. Wolfson, C. Dlugy and Y. Shotland, *Environ. Chem. Lett.*, 2007, **5**, 67–71.
387 A. Behr, J. Eilting, K. Irawadi, J. Leschinski and F. Lindner, *Green Chem.*, 2008, **10**, 13–30.
388 S. Tang, G. A. Baker and H. Zhao, *Chem. Soc. Rev.*, 2012, **41**, 4030–4066.
389 J. I. García, H. García-Marín, J. A. Mayoral and P. Pérez, *Green Chem.*, 2010, **12**, 426–434.