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Cationic rhenium complexes ligated with N-heterocyclic carbenes – an overview

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This review provides an overview of the currently known cationic rhenium NHC complexes. Synthesis, structures and properties are described. The title compounds are potential candidates for both catalytic and medical applications. Besides the variety of ancillary ligands, which are in some cases easily substituted, functionalization can be carried out in the side chain or at the backbone of the carbene ligand as well as – in the case of biscarbene ligands – at the bridging moiety. Cationic Re NHC complexes are promising precursors for radiopharmaceuticals and diagnostics – not only because of the possibility to radiolabel the metal (steps in this direction have been made and described already) – but rather the opportunity to link the complexes to biomolecules *via* the different possibilities provided by the ligands. The development of OLEDs based on luminescent Re(I) carbene complexes renders another potential application.

1. Introduction

In recent years several overview articles and reviews concerning the metal rhenium and NHCs – including their applications in catalysis and radiochemistry – as well as group 7 metal–NHC complexes have been published.[1]

The profound interest in this research area is due to the fact that rhenium is cheaper than most of the noble metals which are commonly used in catalysis, and it can bear a variety of different ligand systems[1h] and has two isotopes, which can be easily produced – even directly in hospitals – which are therefore suitable for radiotherapeutic purposes.[2] Rhenium further provides an almost unrivalled variety of oxidation states that are accessible under "non-exotic" reaction conditions.[3]

1.1 Pharmaceuticals

The reactor-produced radionuclide ^{186}Re with a half-life of 89.2 h and moderate emission energy ($E_\beta^{max/average}$ = 1.1/0.36 MeV; E_γ = 137 keV) can be received in analogy to ^{188}Re ($E_\beta^{max/average}$ = 2.1/0.8 MeV; E_γ = 155 keV), which is produced by using a ^{188}W/^{188}Re generator system in the form of Na[^{188}ReO$_4$].[2a,b] Although both isotopes are able to transfer energy to cancer tissue and can be identified by single photon emission computed tomography imaging, ^{188}Re features a more convenient half-life time ($t_{1/2}$ = 16.9 h).[1d,2c,4]

The application of radioactive rhenium complexes is variegated – not only for treatment of cancer (bone, liver, ovarian, breast *etc.*) but also for inflammable joint diseases (*e.g.* arthritis).[5] For nuclear medicine therapies like radiation synovectomy $^{186/188}$Re sulfur colloids have been applied and ^{188}Re–tin colloids are already in clinical trials.[5c,s–u] ^{188}Re-HEDP therapy for bone pain palliation proved to be effective[5e] and Lipiodol with radiolabelled rhenium is in clinical trials for the metabolic radiotherapy of heptacellular carcinoma.[5d,f] For this most common type of liver cancer several complexes with a $^{186/188}$rhenium(V) oxo scaffold are known.[5h–k] The design of radio labeled antibodies with rhenium is popular with respect to radio immunotherapy.[5a,l,m,6] Labeling of MAG3 peptide conjugates with rhenium oxo cores as the chelate site – for instance ^{186}Re-MAG3-HBP is expected to be a useful radiopharmaceutical for the palliation of metastatic bone pain[5n] or $^{186/188}$Re-(CO)$_3$-A7 showed high uptake in tumor-bearing mice.[5p] Besides the conventional cancer therapy, Re(I)(CO)$_3$ derivatives showing anticancer activity are promising candidates as organometallic therapeutic and diagnostic agents.[7]

1.2 Catalysis

Although rhenium complexes are known in different oxidation states (–III to +VII) and with a variety of ligand systems, particularly rhenium oxo and carbonyl complexes are established in catalysis.[1h,8] Besides the oxygen atom transfer reaction – for instance deoxygenation reactions as well as dehydration or deoxydehydration reactions can be catalyzed by Re(VII) complexes,[8a,i] rhenium carbonyl complexes can act as catalysts in quite a number of different reactions *e.g.* hydroarylations, transfer-hydrogenation reactions and formation of carbon–

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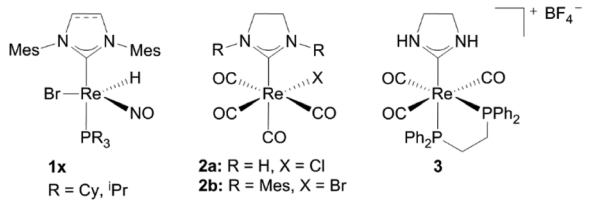


Fig. 1 Re(I) hydride (**1x**)[11a] and carbonyl catalysts (**2**, **3**).[11b]

carbon or carbon–heteroatom bonds, which were summarized by Kuninobu and Takai in 2011.[1h,8k,l]

NHC complexes with almost every metal in the periodic table are known as homogeneous as well as heterogeneous catalysts.[9] In addition to the "classical" catalysis in organic solvents the field of catalysis in aqueous media or water became more interesting in the past few years.[1g,10] However, only two groups have reported on rhenium carbene complexes as catalysts so far.[11] Rhenium(I) hydride complexes **1x** catalyze the dehydro coupling of $Me_2NH{\cdot}BH_3$ and ammonia borane $NH_3{\cdot}BH_3$ as well as the transfer hydrogenation of several olefins, where $Me_2NH{\cdot}BH_3$ donates hydrogen to produce the corresponding alkanes.[11a] Liu *et al.* tested the catalytic activity of several rhenium carbonyl complexes in the insertion reaction of terminal alkynes into β keto esters. Complexes **2**, **3** and [(NHC)$Re_2(CO)_9$] (NHC = 1,3-bis(hydro)-4,5-dihydroimidazol-2-ylidene) are able to catalyze the formation of ethyl(2*E*)-2-methyl-5-oxo-3-phenyl-2-hexenoate but need the support of photoirradiation and show only moderate activities (Fig. 1).[11b]

Although the metal rhenium is known since 1925, significant amounts were accessible only since the 1950s.[12] Synthesis routes of a broad variety of rhenium complexes are well established since then and some general reviews were published, this review focuses on the synthesis and properties of cationic rhenium NHC complexes – particularly with regard to their potential application in medicine.

2. Cationic rhenium mono-NHC complexes

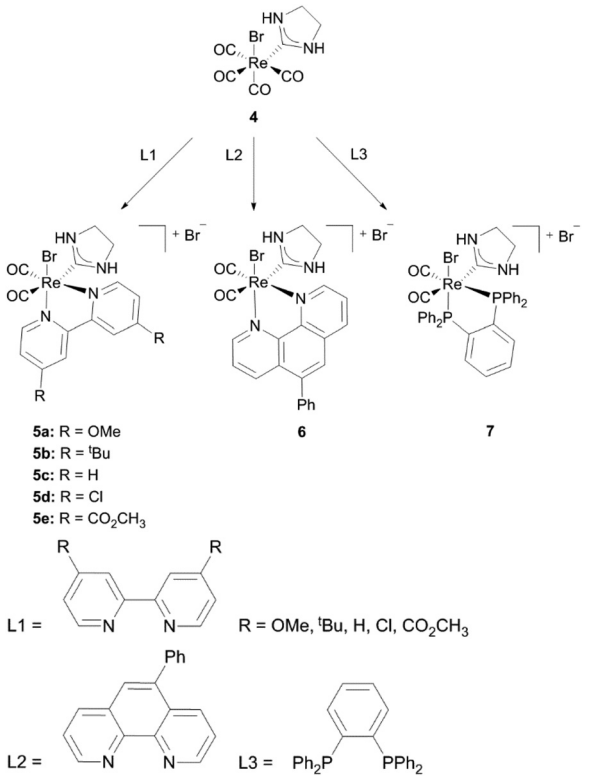
2.1 Re(I) complexes bearing saturated mono-NHC ligands

The $Re(CO)_3$ fragment, which can be found in the majority of cationic Re(I) NHC complexes, has attracted attention concerning luminescence for potential application in light emitting diodes (LEDs), organic light emitting diodes (OLEDs) and biological labelling markers.[1a,13]

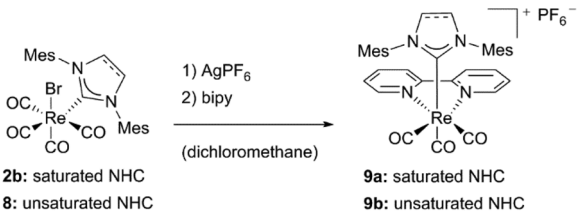
The first cationic Re(I) NHC complexes were isolated by Che and coworkers.[14] These compounds contain bidentate diimine or phosphine ligands and could be obtained by the reaction of the corresponding diimines (**L1**, **L2**) or chelating phosphines (**L3**) with the literature known complex **4**.[15] All complexes (**5–7**) are assumed to display a pseudo-octahedral geometry, although only the molecular structures of **5c**, **5e** and **7** have been determined by X-ray analysis. Based on molecular orbital calculations and photophysical studies it is found out that changing the electron-donating/accepting ability of the bidentate diimine ligand *via* modification of the electron withdrawing character of the R group leads to reasonable emission lifetimes, quantum yields and well defined redox potentials. The metal to ligand charge transfer (MLCT) excited stage energy is strongly influenced by the R group of complexes **5** and can only be altered by changing the polarity of the solvent at room temperature. However a change to intra-ligand (IL) charge transfer occurs at 77 K in the case of the Phphen ligand. At this temperature all complexes were found to be emitting, nevertheless only complexes **5** and **6** maintained this behaviour at room temperature.[14]

Related to complex **5c**, bipyridine NHC Re(I) complexes bearing mesityl substituted ligands could be isolated by the same group.[16] In order to achieve substitution with bipyridine, addition of a silver salt has been necessary. Liu *et al.* ascribe this to the steric bulkiness of the ligands, which may exacerbate the replacement of the CO ligands. Both the saturated and unsaturated compounds **9a** and **9b** have been characterized by NMR, IR and mass spectrometry, but no crystal structures are reported (Schemes 1 and 2).[16]

A cationic macrocycle substituted Re(I) complex with a coordinated PCC ligand was achieved *via* template (controlled) synthesis in 2007.[17] Starting from Re(I) template **2a** and a fluorinated diphosphine (1,2-bis(di(*o*-fluorophenyl)phosphine)-



Scheme 1 Luminescent cationic Re(I) monocarbene complexes synthesized by Che and coworkers.[14]



Scheme 2 Synthesis of bipyridine NHC Re(I) complexes by Liu and coworkers.[16]

benzene) a bidentate phosphine complex **10a** could be formed selectively in acetonitrile. Efforts to carry out this synthesis according to the literature-known conditions[14] with similar diphosphine resulted in mixtures of complexes **10a**, **11** and **12**. This formation of mixtures was ascribed to the simultaneously activation of NH and CF, respectively the insolubility of the products in solvents of low polarity (Scheme 3).[18]

The air and water stable macrocyclic [11]ane-P2C^{NHC} Re(I) complex **12** was obtained *via* the template controlled ring formation reaction *via* the isolatable neutral intermediate **13**.[17,18] Deprotonation of **10a** and a S_N2_{Ar} type attack of the deprotonated nitrogen atoms at the C–F bond of the *o*-fluorenyl diphosphine connects it to the carbene ligand, resulting in a macrocyclic and polydentate NHC complex **12** (Scheme 4).[17–19]

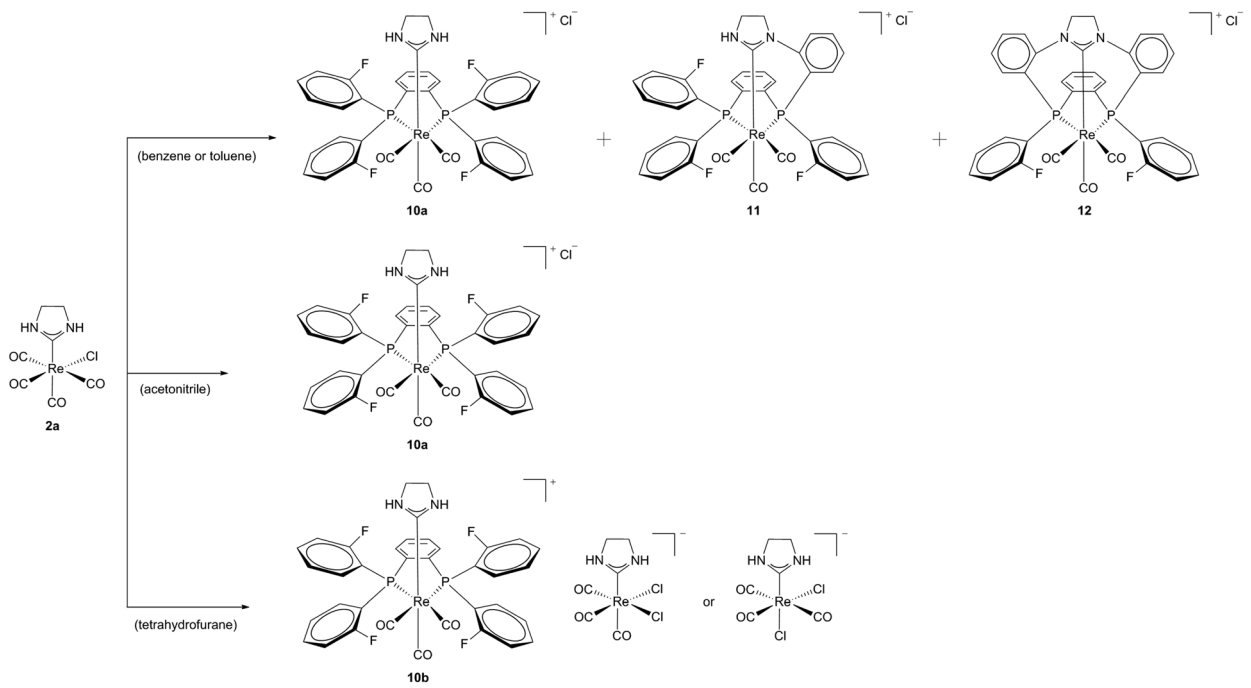
In addition, cationic Re(I) macrocycles with a mixed NHC/phosphine donor set (**14**, **15**) could be obtained by the same group. Using the same method of template synthesis ethylene bridged diphosphines and NHC ligands could be facially coordinated to the metal. No intermediates have been reported (Scheme 5).[20]

As a comparatively easy method, to generate carbene complexes of different metals, is known since a couple of years.[1i] Using functionalized isocyanides, which contain – beside the isocyanide moiety – a nucleophilic part, leads *via* intramolecular 1,2 addition usually to imidazolidin-2-ylidenes.[17,21]

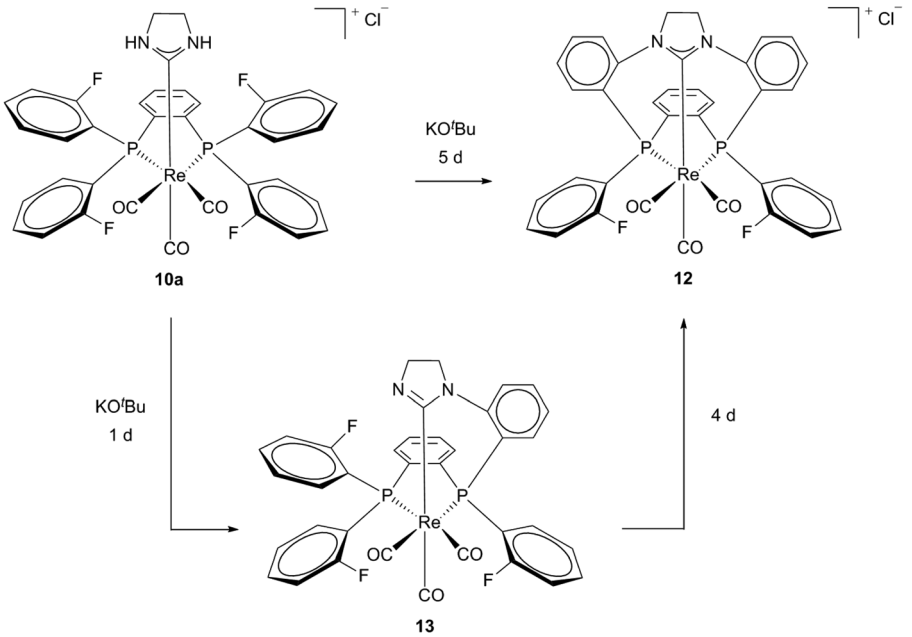
Hahn and coworkers established a cationic tris-NHC–Re(I) by template controlled cyclization of a β-azido functionalized isocyanide.[22] As the metal template they used complex **17**,[15] which contains besides strong π-acceptor CO-ligands two strong σ-donor NHCs and one bromide ligand, so that the abstraction of the halide followed by attaching 2-azidoethyl isocyanide at the 'free coordination site' yields complex **18**. IR spectroscopy revealed that the functionalized isocyanide is activated for a nucleophilic attack upon coordination to the rhenium core. As a result the formation of tris(NHC) complex **19** could be achieved by reduction and of the azido function and ensuing intramolecular cyclization (Scheme 6).[22]

2.2 Re(I) complexes bearing unsaturated mono-NHC-ligands

Formation of cationic agostic and solvent stabilized 16 electron complexes *via* halide abstraction was achieved by Whittlesey *et al.*[23] By reacting neutral mono-Re NHC precursors (**20**, **23**) with $NaBAr_4^F$ salts, complexes **21** and **24** are generated. Attempts to isolate agostic product **21** failed leading to an undefined rhenium carbonyl species and the additionally appearing tetracarbonyl compound $[Re(I^iPr_2Me_2)_2(CO)_4]BAr_4^F$ (**22**). Directly bubbling of CO into the reaction mixture of **20** and $NaBAr_4^F$ leads to selective formation of an 18 electron



Scheme 3 Products of the reaction of **2a** with a fluorinated diphosphine in various solvents.[18]



Scheme 4 Generation of macrocyclic polydentate Re(I) NHC complex **12** *via* neutral intermediate **13**.[17–19]

complex *cis*-**22**. Addition of acetonitrile to the reaction mixture instead of CO results in the formation of $[Re(I^iPr_2Me_2)_2(CO)_3(MeCN)]BAr_4^F$. These observations suggest that even less weakly coordinating ligands are able to displace the agostic interactions in complex **21**. As a less electrophilic bis-NHC species **21** is stabilized *via* the agnostic bond of one NHC, monocarbene complex **24**, which contains a less nucleophilic ligand, and binds a less strongly coordinating solvent molecule to become stable. Preparation of this complex is achieved by reacting the neutral triflate rhenium precursor **23** with the sodium salt of the non-coordinating anion BAr_4^F in dichloromethane. After halide abstraction subsequent monodentate binding of the solvent takes place, whereas in the presence of CO the carbonylated cationic rhenium complex **25** is formed (Schemes 7 and 8).[23]

Another literature known synthetic route to NHC complexes with different metals is the transformation of coordinated imidazoles to NHC ligands.[24]

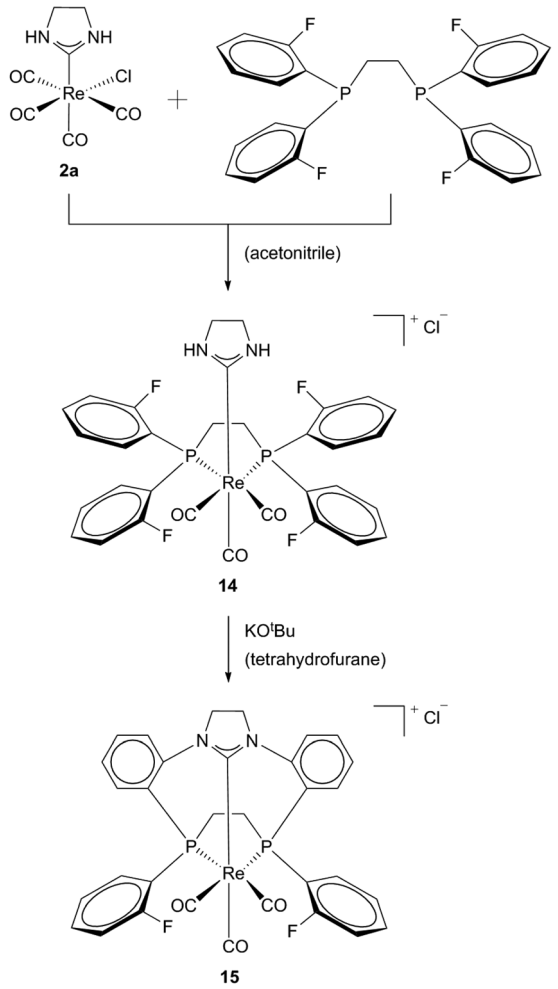
Pérez, Riera, López and coworkers described the formation of cationic rhenium(I) carbonyl complexes containing both NHC and *N*-alkylimidazole ligands as a pseudo-tautomerisation.[24a,c,e,25] Starting from a highly stable cationic *N*-alkylimidazole containing *fac*-Re[$(CO)_3$] complex **26**, one of the imidazole ligands is deprotonated by a strong base resulting in a stable neutral but not isolable intermediate **27**, which features an imidazole-2-yl ligand. The non-substituted nitrogen atom at the NHC of the highly reactive compound **27** can be protonated or methylated easily by electrophiles. Using methyltrifluoro-methanesulfonic acid affords the cationic complex **29** and trifluoromethanesulfonic acid leads to **28**, which contains a NH–NHC ligand, respectively (Scheme 9).[24a–c]

In addition, the group discovered that besides the nature of the imidazole ligands, the ancillary substituents at the metal influence the resulting product.[26]

Starting from $[Re(OTf)(CO)_3(N\text{-MeIm})_2]$ (**30**) the triflate ligand was substituted, supported by $NaBAr'_4$ to obtain complex **31a**.[24a] The subsequent change of the coordination mode of one imidazole ligand by deprotonation with $KN(SiMe_3)_2$ led to the imidazole-2-yl complex **32**. From the latter, the cationic Re–NHC complex **33** could be generated *via* methylation at the non-coordinated nitrogen atom. The influence of the substituent on the phosphane ligand becomes apparent when complexes **31b** and **31c**, which can be synthesized analogously to complex **31a**, were treated under similar conditions as described for complex **31a**. In the case of PMe_3 (in complex **31a**) a cationic Re(I)–NHC complex **33** is created whereas arylphosphane ligands lead to binuclear Re(I)–Re(I) complexes (**35**) bearing abnormal NHC ligands obtained *via* double activation of the *N*-methylimidazole (Scheme 10).

A methoxycarbene ligand is generated by the formation of a four-membered cycle including one rhenium atom and methylation of the oxygen atom of the *cis*-carbon-monoxide ligand. The bridging and build-up of the abnormal NHC moiety is achieved *via* deprotonation of the backbone of the *N*-methylimidazole and coordination to a second rhenium atom. This leads to a formal intramolecular ligand coupling resulting in an *N*,*N*-bidentate ligand coordinated at rhenium-2. *cis*/*trans*-Rhenium complexes featuring *N*,*N*-bidentate chelate ligands (**36**) formed as side products here.[27]

Various benzoxazol-2-ylidene-substituted Re(I) phenanthroline complexes can be obtained starting from acetonitrile con-



Scheme 5 Synthesis of Re(I)-[11]-ane-P_2C^{NHC} macrocycles by Hahn *et al.*[20]

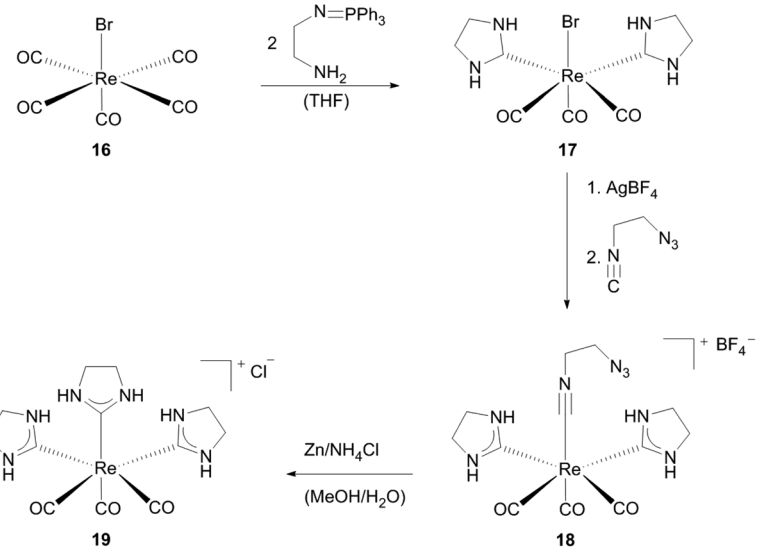
taining rhenium carbonyl complexes (**37**, **42x**).[28] As previously reported, N,O-heterogenocarbene complexes can be built *via* intramolecular cyclization, if the isocyanide C atom is not deactivated by strong (d → p)π-back-bonding from the metal core.[1i,29] Contrary to similar rhenium complexes published by Hahn *et al.*,[29a] the strong π-accepting carbonyl ligands coordinated to the rhenium precursor support the formation of the reported luminescent rhenium complexes **38**, **39** and **43a–c** (Scheme 11).

Complex **39**, which may be considered as the N-protonated form of the neutral rhenium complex **38** bearing an anionic N-deprotonated carbene ligand, could be generated *via* acidification and subsequent metathesis. This complex as well as the methylated equivalent **40** adopts a distorted octahedral geometry with a facial arrangement of the three carbonyl ligands.

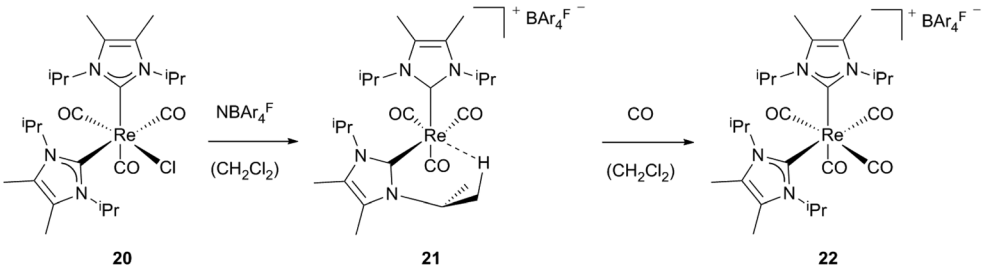
Similar reactions with several phosphines bearing rhenium phenanthroline precursors **41x** lead to carbene complexes **43x** where both carbonyl ligands are arranged in the *cis* conformation (Scheme 12).[28] Furthermore, the same group reported – based on their previous work[28] – in 2014 luminescent N,S-, N,N-, and N,O-NHC rhenium(I) complexes *via* a ligand substitution reaction.[13b]

Starting from $Re(CO)_5Br$ (**16**) *via* a neutral bis(N,O-carbene) rhenium precursor **44** several cationic mono carbene rhenium compounds (**45x**, **46**), could be obtained. X-Ray analysis shows that complex **46** bears two unsymmetrical *cis* carbonyl ligands, one is located *trans* to the carbene ligand, the other, as well as the isocyanide ligand are *trans* to the diimine ligand (Scheme 13).

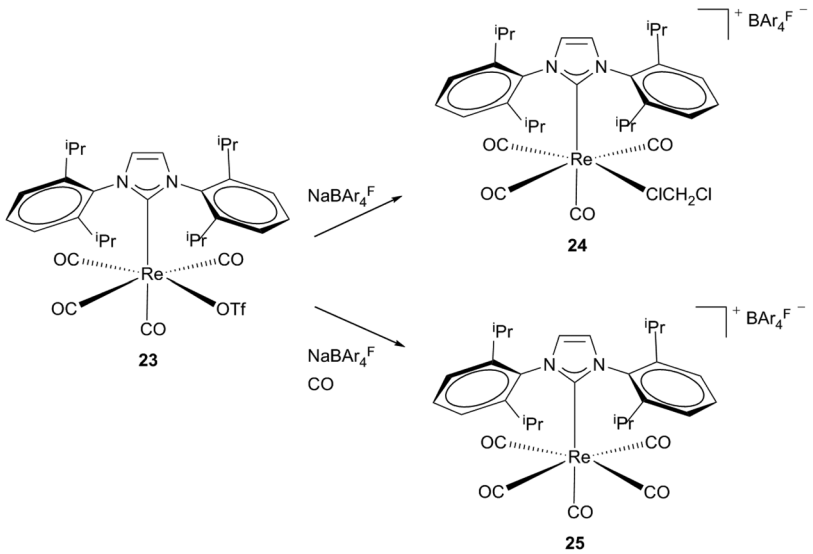
The opening of one NHC ligand in complex **44** and thus the formation of an isocyanide moiety are favoured by the substitution of the CO ligand, positioned *trans* to the carbene by a diimine, as a consequence of the weakening of the pπ



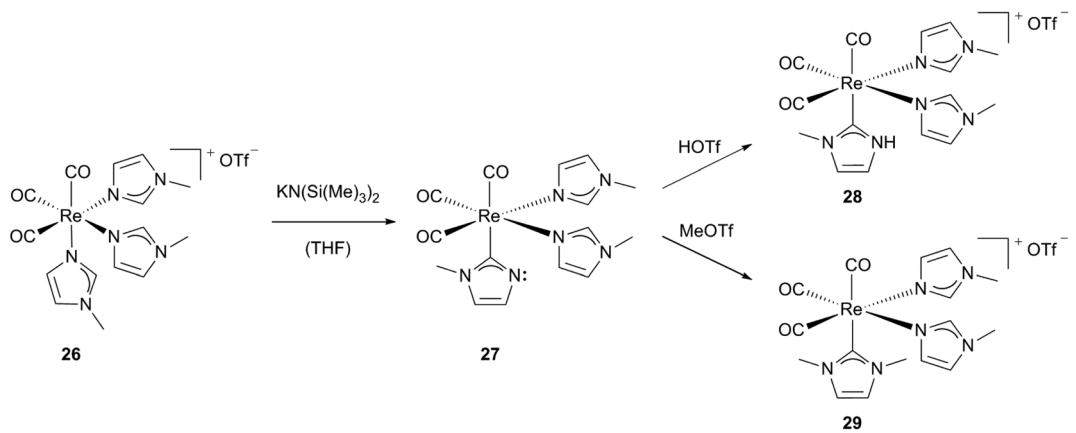
Scheme 6 Synthesis of Re(I) monocarbene complexes *via* cyclization reactions.[22]



Scheme 7 Generation of cationic Re(I) compounds bearing two unsaturated NHCs.[23]



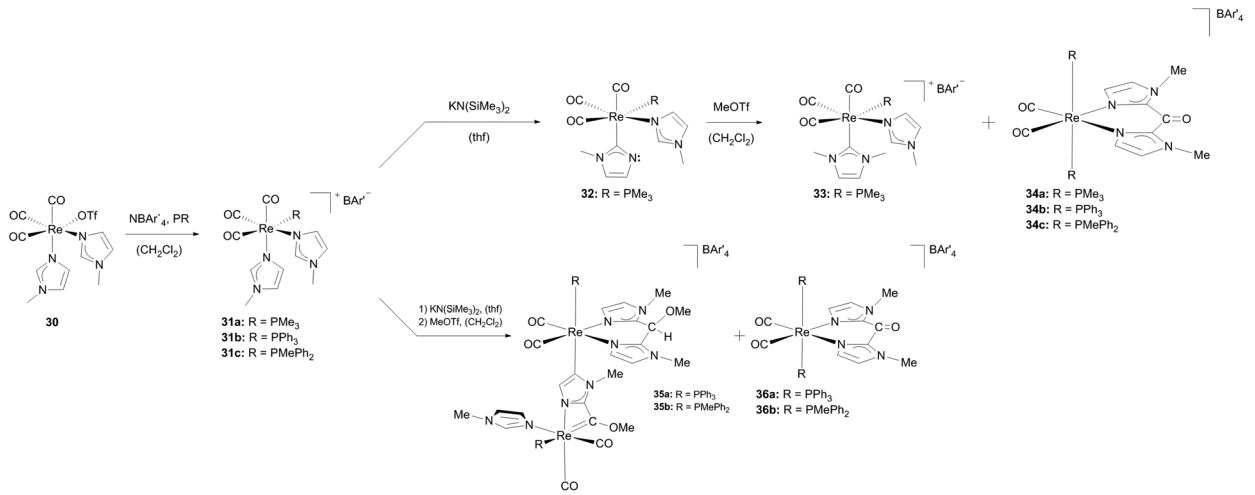
Scheme 8 Pathways by Whittlesey *et al.* for cationic unsaturated Re(I) monocarbene complexes.[23]



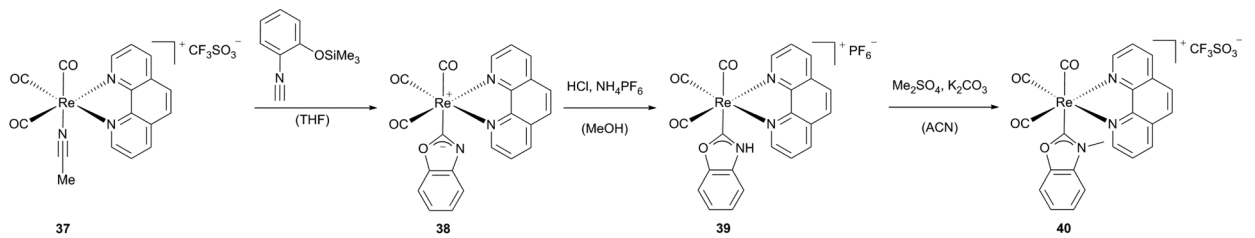
Scheme 9 Synthesis of Re(I) carbonyl complexes bearing one NHC and two *N*-alkylimidazole ligands.[24a,b]

(carbene)–pπ (O) interaction resulting from enhanced π-(rhenium → carbene)-back-donation.

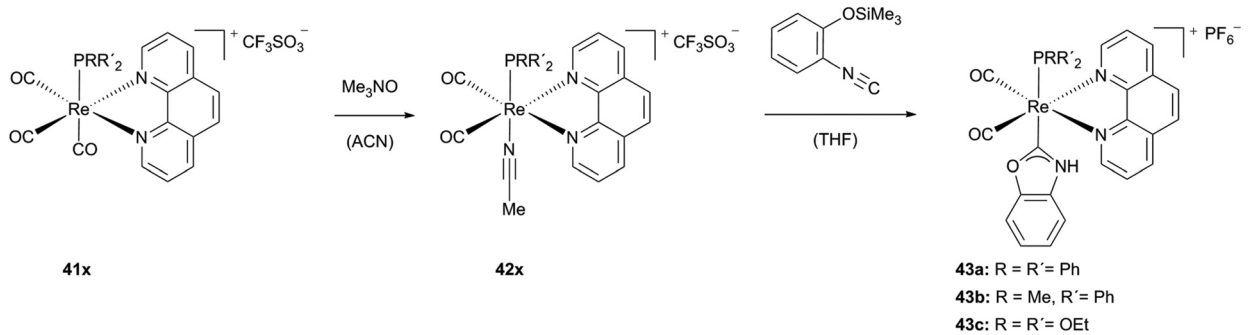
For complexes **45x** and **46** an interconversion between the isocyanide and the N,O-heterocyclic carbene form occurs, while complexes **48x** and **49** are generated by the conversion of one coordinated isocyanide ligand to a carbene ligand. The formation of only one carbene ligand – even with a large excess of nucleophiles – results from the different reactivities of the coordinated isocyanide ligands in precursor complex **47**. While the isocyanide ligand, standing in the *trans* position to



Scheme 10 Formation of different cationic Re(I) NHC complexes influenced by ancillary ligands at the metal core.[24a,26]



Scheme 11 Synthesis of luminescent $Re(CO)_3$ phenanthroline complexes.[28]

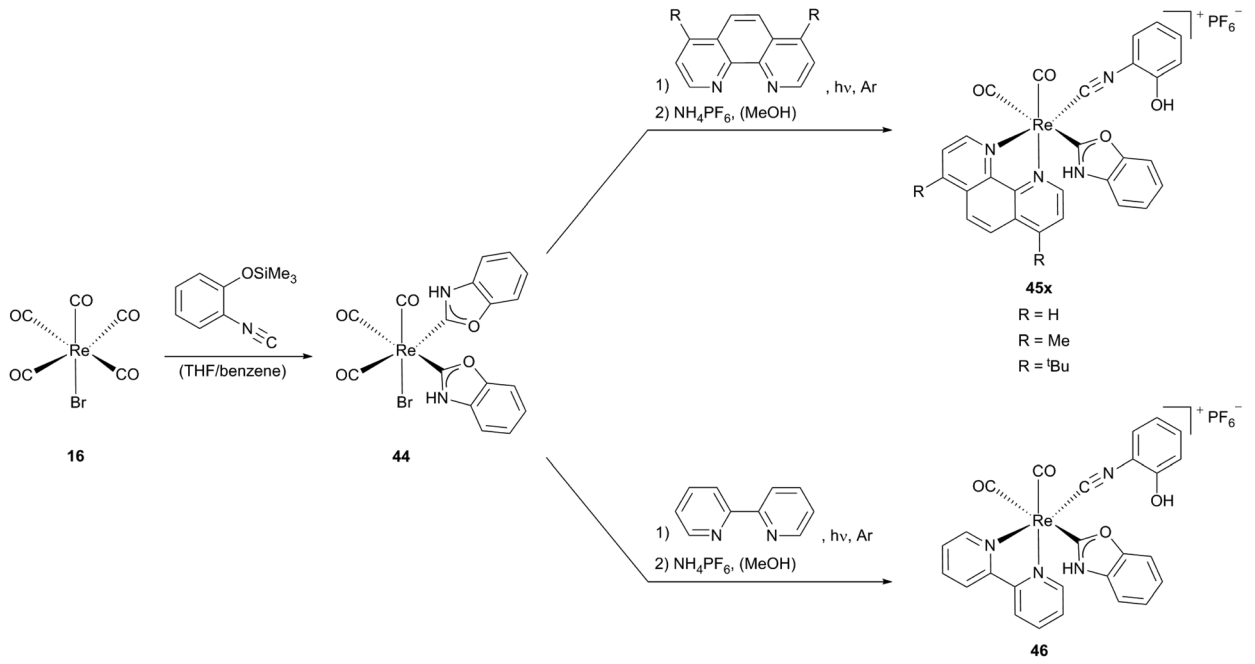


Scheme 12 Generation of benzoxazol-2-ylidene-substituted phenanthroline complexes by Ko and coworkers.[28]

the carbonyl ligand is susceptible to the nucleophilic attack, the isocyanide C atom positioned *trans* to the diimine receives a stronger π-back bonding from the metal and hence is more electron rich, consistent with the observations for complexes **45x** and **46**. Reacting complex **50b** with concentrated sulfuric acid leads to the distorted octahedral target NHC complex **51** (Scheme 14).[13b]

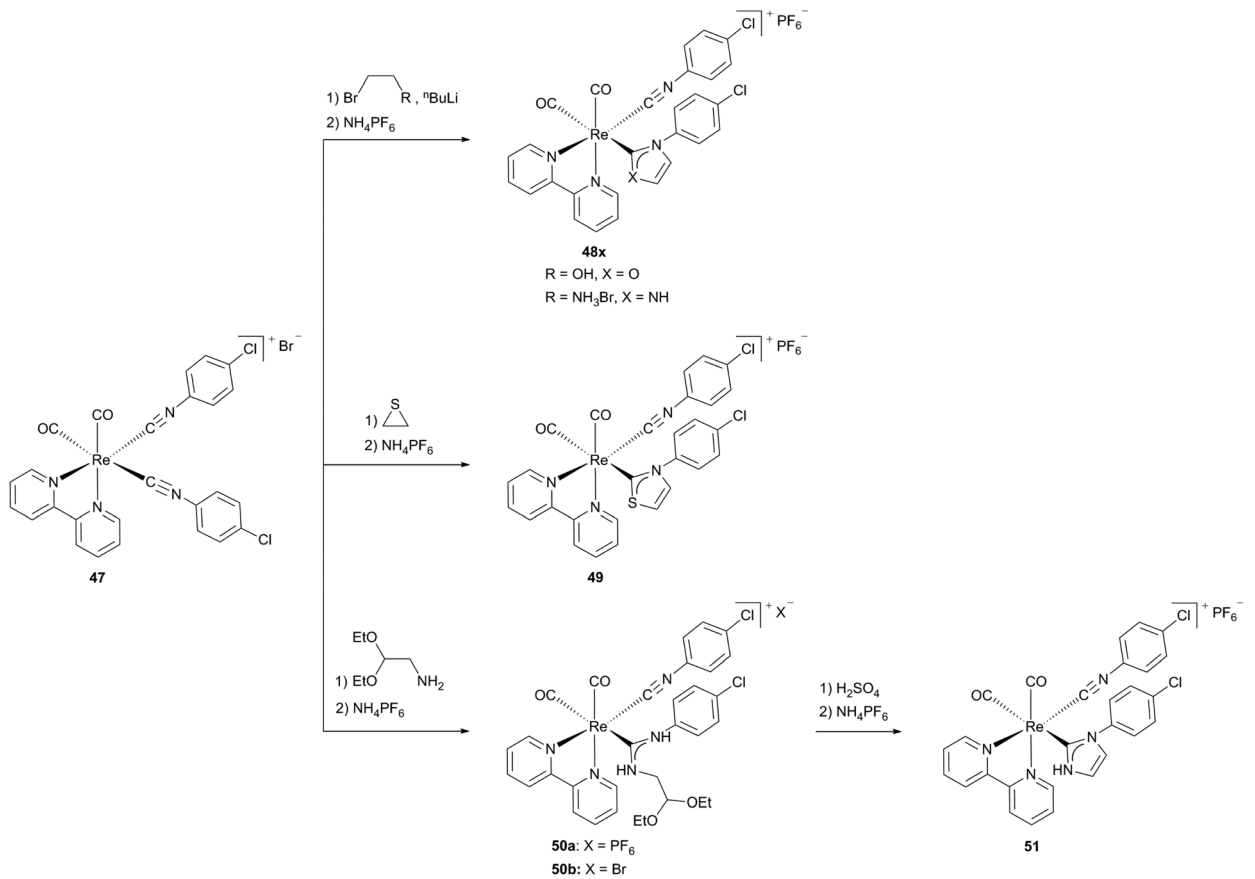
As the first investigations of luminescence of N-heterocyclic rhenium(I) complexes were reported by Che *et al.*[14] (see before), Ko and coworkers studied the photophysical and electrochemical properties of rhenium diimine complexes bearing N,N-, N,S- and N,O-NHC ligands.[13b,28]

The knowledge about the influence of the relatively strong π-acceptor ability of almost every modification of or at a ligand (complexes **38–40**, **43**, **45**, **46**, **48x–51**) can be used for the development of further luminescent NHC complexes for various applications (*e.g.* photocatalysis of CO_2 reduction) by tuning the emission properties.[13b,28]



16 44

Scheme 13 Oxazole–Re(I) complexes containing phenol substituted isocyanides.[13b,28]



47 49 51

Scheme 14 Generation of cationic N,S-, N,N- and N,O-NHC Re(I) diimine complexes.[13b]

2.3 Unsaturated Re(v) complexes bearing mono-NHC ligands

Various cationic Re(v) complexes with unsaturated mono-NHC ligands have been prepared.[4,30]

Royo, Romão *et al.*[30a] and Abram *et al.*[30b] were the first to obtain cationic Re(v) oxo complexes bearing four unsaturated carbene ligands, by reacting strong Lewis basic NHCs with various rhenium precursors.

Dicationic monooxo-complex **53** is the reaction product of $[ReOCl_3(PPh_3)_2]$ with an excess of free carbene **52**. The triphenylphosphane- and two of the chloride-ligands are displaced by four monocarbene ligands.[30a] The green complex **53** is described as moisture-sensitive in solution – traces of water lead to the formation of a dioxo species[30b] (see below) – and air-stable for a short time as a solid.

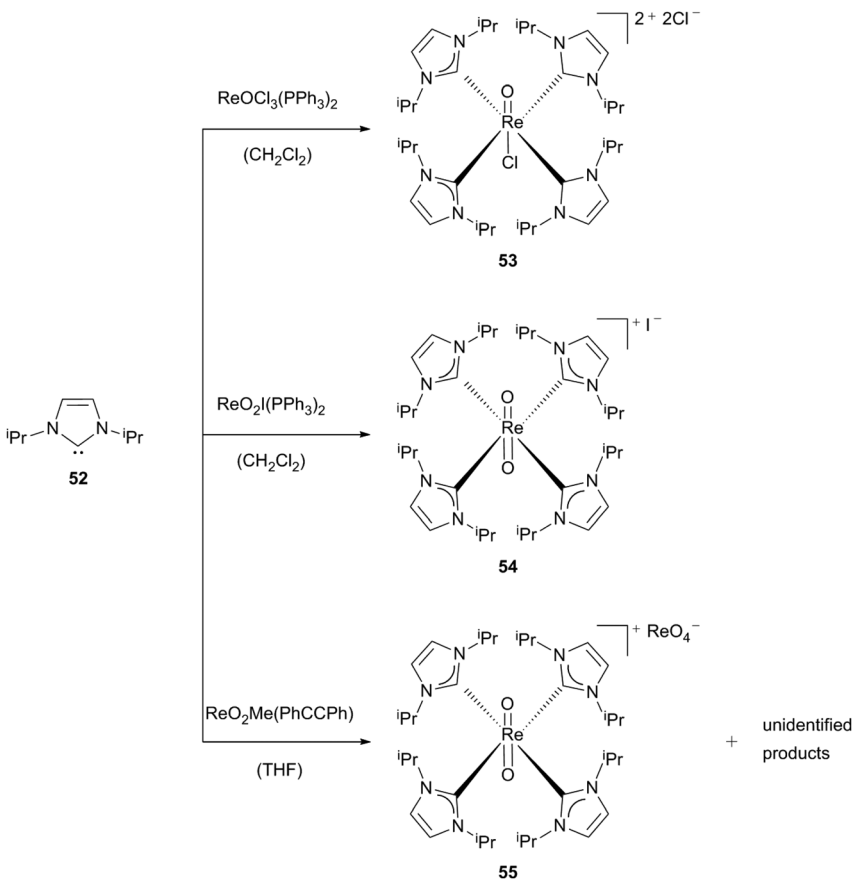
By using the same ligand (**52**) with different rhenium compounds and reaction conditions, monocationic tetrakis-(carbene)dioxorhenium complexes **54** and **55** can be formed. The brown solid (**54**) can be generated starting from $[ReO_2I(PPh_3)_2]$. $[ReO_2Me(PhCCPh)]$ yields yellow crystals (**55**) featuring an approximate D_4 symmetry with perrhenate as an anion and one thf-solvent molecule. Royo, Romão *et al.* assumed that the formation of complex **55** is caused by adventitious water in the reaction mixture, with some unidentified products additionally found (Scheme 15).[30a]

Starting from three different rhenium precursors **57–59** Abram *et al.* reported a cationic dioxorhenium(v) complex bearing four carbene ligands, which are methyl-substituted at the backbone.[30b,d]

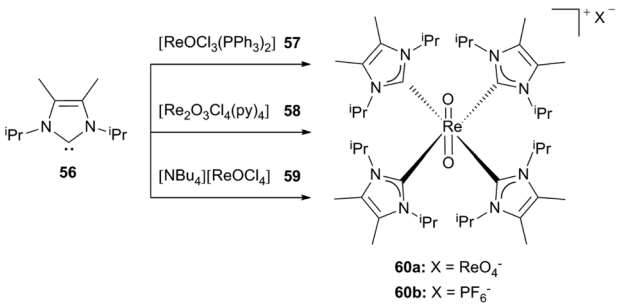
Depending on the reaction conditions hexafluorophosphate (**60b**) or perrhenate salts (**60a**) of the complex could be isolated. Performing the reaction of $[ReOCl_3(PPh_3)_2]$ with an excess of the free carbene **56** in air in combination with traces of water in the solvent leads to **60a** and HL^{iPr} as a side product, whereas the addition of ammonium hexafluorophosphate yields the stable **60b** (Scheme 16).[30b]

Using the free carbenes **61**/**65** under the same reaction conditions as applied for the synthesis of compound **60**, the monooxo species **62**/**68** can be isolated as green powders. By solving complexes **62** and **68** in methanol and adding hexafluorophosphate salts in the presence of L^{Me} (**61**), an exchange of the chloro ligand for a methoxy ligand takes place whereas for L^{Et} (**65**) crystals of the composition $[ReOCl(L^{Et})_4]$-$[PF_6]\cdot 2KPF_6$ (**68b**) are obtained (Scheme 17).[30d]

Another synthetic approach *via* NHC transfer reagents for compounds considered for radiopharmaceutical applications was shown for **65**. By reacting silver tetrafluoroborate with an



Scheme 15 Synthesis of the first cationic Re(v) NHC oxo complexes.[30a]



Scheme 16 Tetrakis(1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene) rhenium(v) dioxo complexes.[30b]

excess of free carbene (**56**, **65**) the corresponding silver(I)NHC complexes could be obtained, which then can be used as transmetallation agents. The known precursors for Re(v) carbene complexes, such as $[ReOCl_3(PPh_3)_2]$ and $[NBu_4][ReOCl_4]$ form the orange-red product **67** with an excess of the silver carbene (**66**) and addition of $(NH_4)(CF_3SO_3)$ (Scheme 18).[30c]

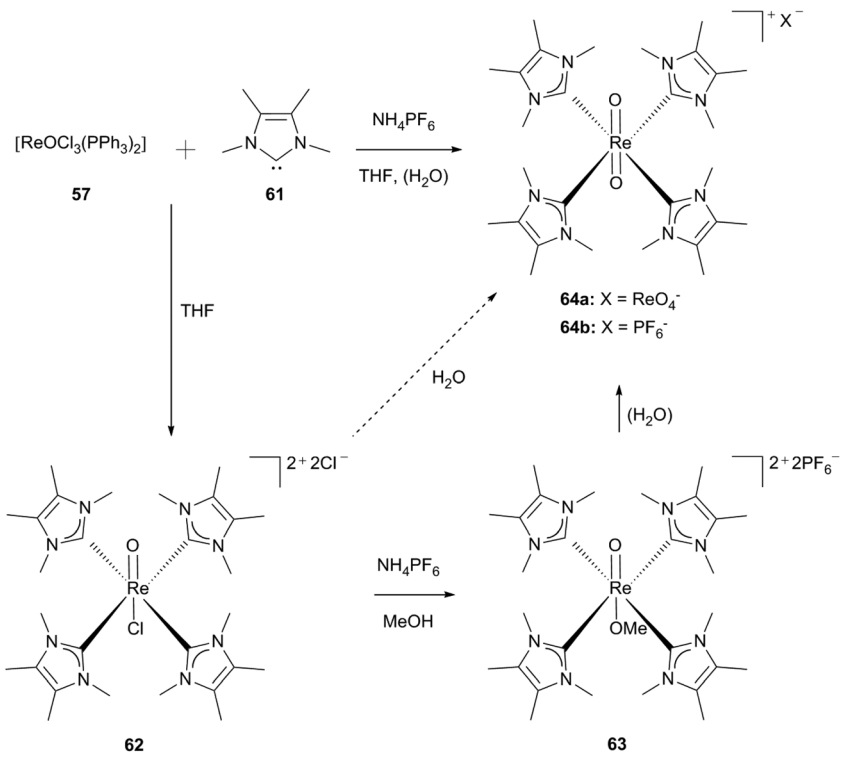
The dioxo species (**60**, **64**, **67**) as well as complexes **62**, **63**, **66** and **68** feature planar coordination spheres with equatorially bonded NHC ligands.[30b–d] Although the steric demand of the ligands does not affect the paddle-wheel type ligand arrangement, it influences the stabilities as well as the structures of the complexes depending on the nature of the alkyl substituents at the NHC ligands. Isopropyl substituted imidazolylidene ligands seem to be more basic than the methyl substituted analogues, which signifies a higher nucleophilicity at the carbene C-atom. Consequently dioxo rhenium complexes (**60**, **64**, **67**) more stable due to their ability to (better) stabilize the augmented electron density.[1k,31]

Furthermore nitridorhenium(v) as well as phenyl-imidorhenium(v) complexes with ligands L^{Me} (**61**) and L^{Et} (**65**) were published by the same group.[30e,f]

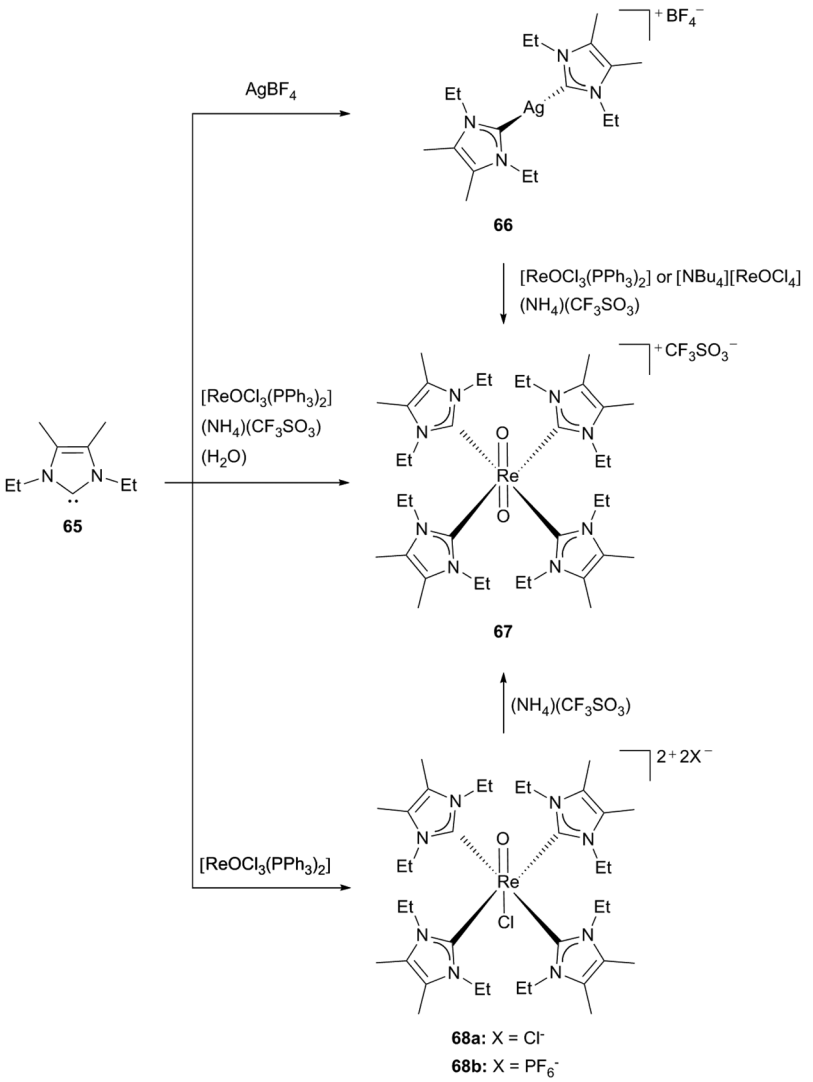
They used $[ReNCl_2(PR'_2Ph)_3]$ (R′ = Me, Et) as the rhenium precursor to yield **69a,b** as stable solids by application of an excess of the corresponding carbenes (**61**, **65**) in dry solvents. Attempts to generate the analogous isopropyl complex have failed so far. Due to the different steric bulkiness of the NHC ligands, caused by the alkyl side chains, hydrolysis induced by moisture is favoured for $[ReNCl(\mathbf{61})_4]Cl$ (**69a**); whereas $[ReO_2(\mathbf{65})_4][ReO_4]$ (**70**) is formed in hot methanol (Scheme 19).[30f]

Compared to the hydrolysis susceptibility of nitridorhenium carbene complexes (**69**), using the formally dianionic ligand "PhN^{2-}", isoelectronic with an oxo ligand and thus able to stabilize rhenium in higher oxidation states, leads to "hydrolysis-inert" phenylimidorhenium(v) carbene complex **71**.[30e]

Matching the analogous nitrido complex **69b**, the phenylimido ligand is able to generate a conjugated π-system and hence can compensate for the electron density that is donated by the carbene ligands to the rhenium centre. Again, by performing the reaction in dry solvents Abram and coworkers obtained $[Re(NPh)X(\mathbf{65})_4]^{2+}$ (**71x**; X: Br, Cl), whereas the traces of water in the reaction mixture resulted in the hydroxo derivative (**72**). Purple crystals of **72c** could be obtained *via* recrystal-



Scheme 17 Tetrakis(1,3-dimethyl-4,5-dimethyl-imidazol-2-ylidene)rhenium(v) oxo complexes.[30d]



Scheme 18 Synthesis of Re(v) NHC complexes starting from **65**.[30c,d]

lization in methanol, which is mandatory to get rid of the carbenium salt that is formed as a side product. Coordination of a hydroxo instead of a methoxo ligand can be explained by the steric shielding of the NHC ligands, which allow less free space in the *trans* position to the imido ligand.[30e] This behaviour was observed before for rhenium oxo complex **63**.[30d] The fact that only stable phenylimido rhenium complexes with carbene **65** can be prepared to date, whereas efforts to generate analogous complexes with **56**/**61** lead to dioxo complexes may be explained by the matched shielding of the ethyl substituted carbene caused by its fitting steric demand (Scheme 20).[30e]

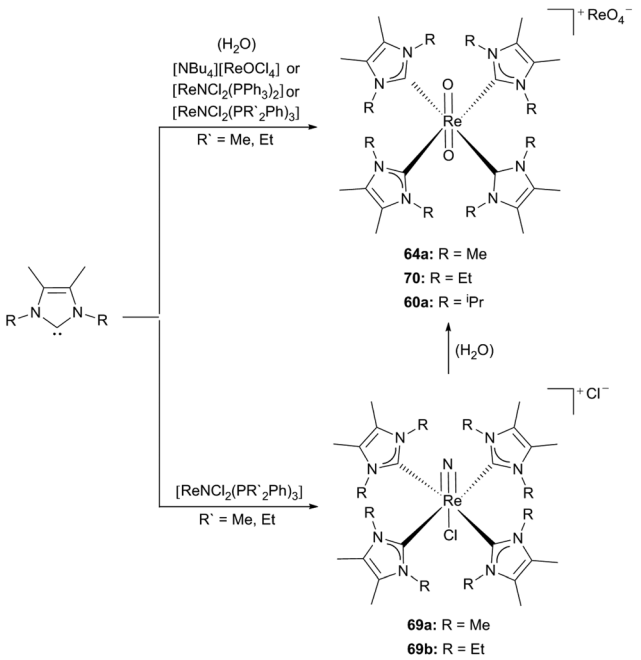
3. Cationic rhenium bis-NHC complexes

3.1 Cationic rhenium(I) bis-NHC complexes

Based on the previous work,[32] Herrmann, Kühn and coworkers reported the synthesis of chelated NHC cationic Re(I) carbonyl complexes with weakly coordinating anions (WCA).[33]

The uncharged rhenium precursors *fac*-bromotricarbonyl (NHC)Re(I) (**75x**) were synthesized by treatment of $[NEt_4]_2[ReBr_3(CO)_3]$ with free carbenes (**74x**), which were obtained starting from *N* substituted imidazoles (**73x**) *via* the S_N2 reaction and subsequent deprotonation with a base.[32] These stable bis(NHC) complexes (**75x**) are able to react with silver WCA salts ($AgPF_6$, $Ag[Al(OC(CF_3)_3)_4]$ in acetonitrile at room temperature to give the corresponding rhenium(I) bis(NHC) acetonitrile WCA complexes (**76**, **77**) (Scheme 21).

All obtained complexes were characterized by mass spectrometry and spectroscopic methods. Interestingly, the variation of the bridge length and the substituents as well as the WCA anions did not strongly influence both the yield and the IR resonances. All the $Re(CO)_3$ moieties display a distorted C_{3v} local symmetry. This asymmetry results in a degenerate CO stretching mode, where one of the CO groups differs from the



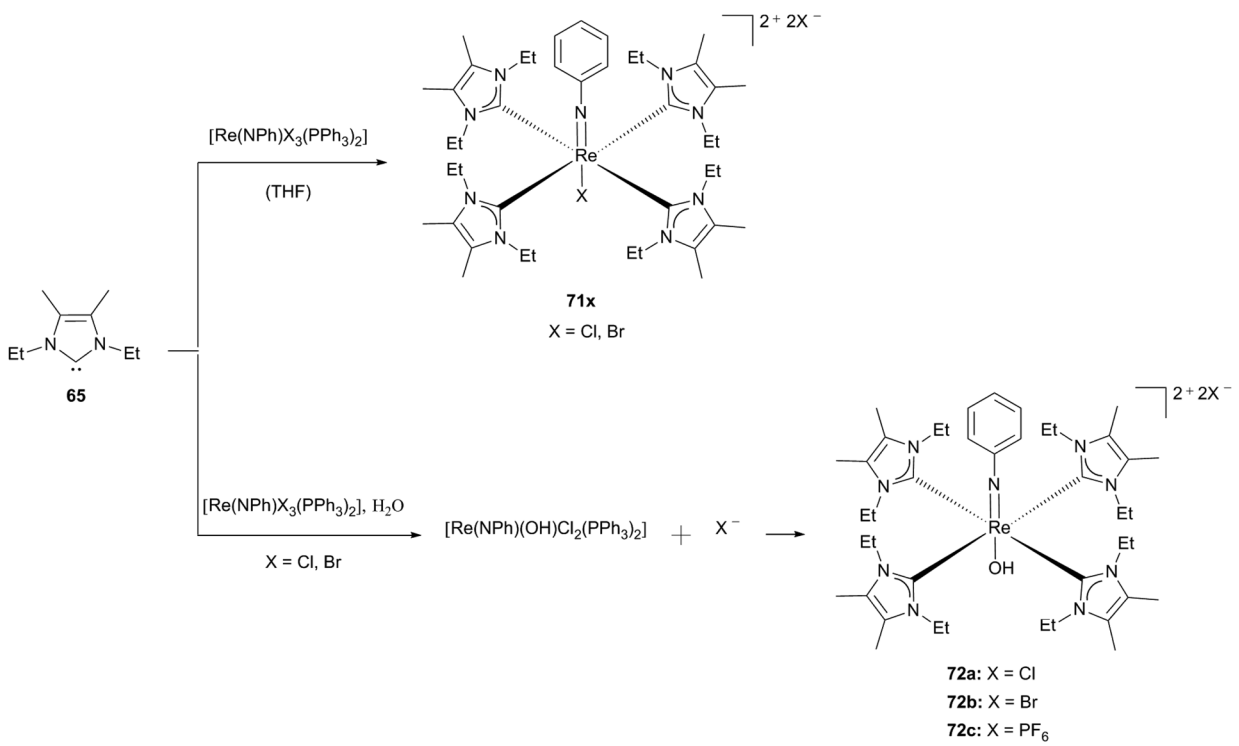
Scheme 19 Formation of cationic Re(v) nitride or oxo complexes due to the reaction conditions.[30f]

other two. Though, despite the observed little resonance variance no general trend relating to the influence of the different bridge length could be determined.

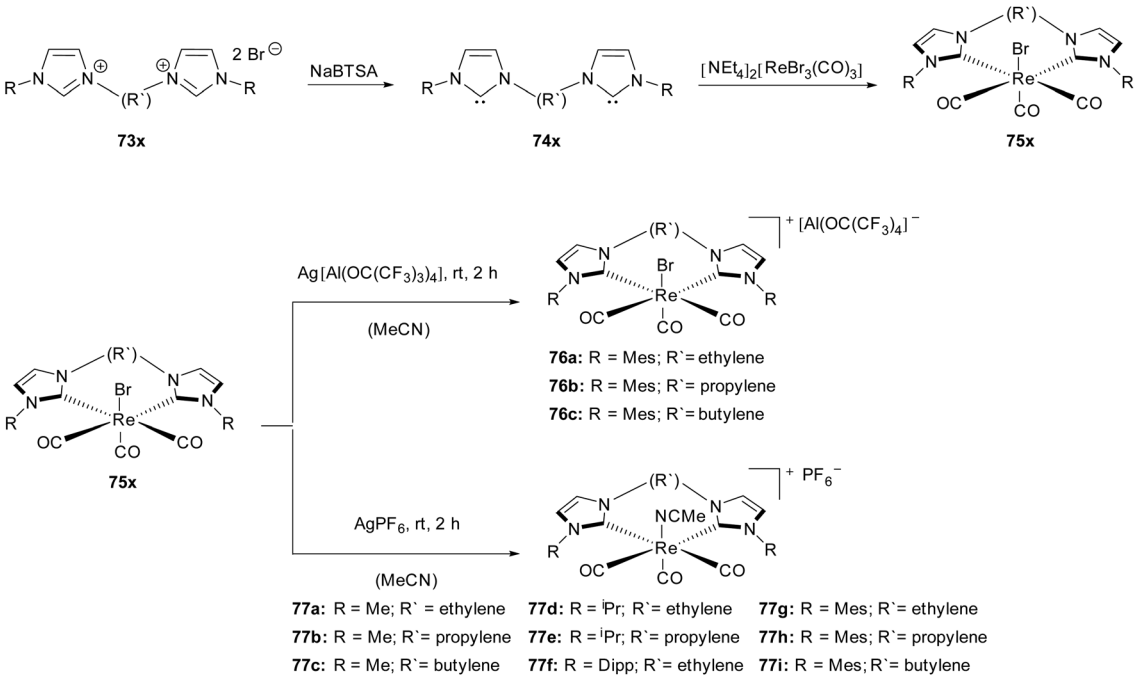
The distorted octahedral symmetry is confirmed by X-ray structure analysis for complexes **77a**, **77b**, **77h** and **77i**. In comparison with their uncharged Re(I) NHC analogues fairly similar bond distances between the metal and the *trans*-carbonyl group have been found.[32] However, the steric demand of the acetonitrile ligand, being different from the bromo ligand, influences the position of the bulky mesitylene ligands independent of the length of the bridging moiety in complexes **77h** and **77i**. The increasing bridge length between the NHC moieties is, however, responsible for a higher torsion angle between the imidazole rings. In the case of a large WCA ligand as a counterion (**76a**), only a minor change of the bond length compared to the uncharged derivative appears. All attempts to obtain single crystals of the complexes (**77c–f**) as well as **76b** have failed so far, whereas the crystallisation of **76c** has led to the first Re(I) NHC CCC pincer complex.[33]

With regard to potential application in catalysis or pharmaceutical chemistry the stability of the Re(I) NHC compounds was examined by temperature dependent NMR experiments. The labile acetonitrile ligand can be easily exchanged by DMSO, changing also the geometry of complex **77h**. The compound remains stable up to 93 °C for several minutes. This allows for potential use as a homogeneous transition metal catalyst, for *e.g.* hydroamination reactions.

Catalytic applications in the hydroamination of 4-pentyn-1-amine as examined by Müller, Yan *et al.*[34] have failed so far, so that the focus should be laid on other catalytic reactions or on modification of the complex. Replacing one of the strongly



Scheme 20 Phenylimidorhenium(v) carbene complexes synthesised by Abram and coworkers.[30e]



Scheme 21 Cationic Re(I)(CO)$_3$bis(NHC)(WCA) by Herrmann, Kühn and coworkers.[33]

binding NHC ligands – in combination with an WCA – for example pyridine containing Re(I) carbonyl complexes as reported by Stagni, Massi, Brown *et al.*[35] and Yang *et al.*[36] – could create efficient catalysts.[37]

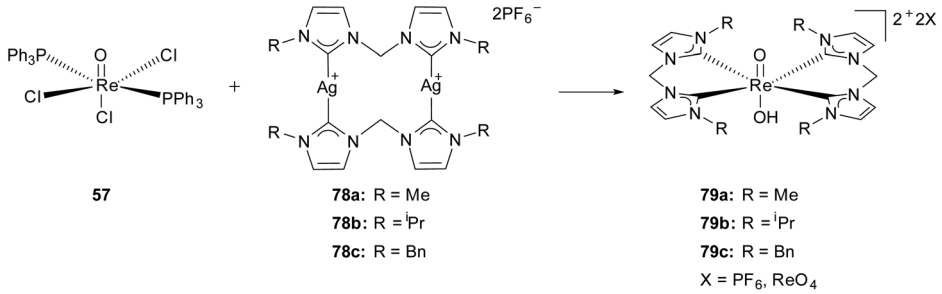
3.2 Cationic rhenium(V) bis-NHC complexes

The group of Hor reported the first Re(V) complexes in which the *trans* oxo-hydroxo core is stabilized by two chelating N-heterocyclic dicarbene ligands.[30g] The air and moisture stable complexes **79** were obtained *via* transmetalation from a silver(I) carbene precursor **78**[38] with the commercially available complex $ReOCl_3(PPh_3)_2$ (**57**) in good yields. For **79a/b** the characterization of the complexes was carried out *via* NMR, MS, EA, FTIR and single crystal XRD. All three cationic mononuclear complexes (**79**) occur in an octahedral geometry with the two NHC ligands orthogonal to the *trans* oxo-rhenium-hydroxo axis. The asymmetric units ($[ReO(OH)(L^R)_2]^{2+}$) (**79**) contain in all cases two disordered anions in the ratios of PF_6^- : ReO_4^- = 0.7 : 0.3 (**79a**); 0.74 : 0.26 and 0.66 : 0.34 (**79b**); 0.65 : 0.35 (**79c**). The presence of an oxo-rhenium-hydroxo motif is explained as the most likely one. On the one hand the observed length of the rhenium oxo bonds do not fit in the typically literature known range of rhenium oxo bonds in a stable $[O{=}Re{=}O]^{2+}$ rhenium dioxo core with monodentate NHC ligands,[30a,b,d] on the other hand the di-hydroxy rhenium motif is excluded due to incongruence regarding charge neutrality and the lower probability of the occurring of a trication (Scheme 22).[30g]

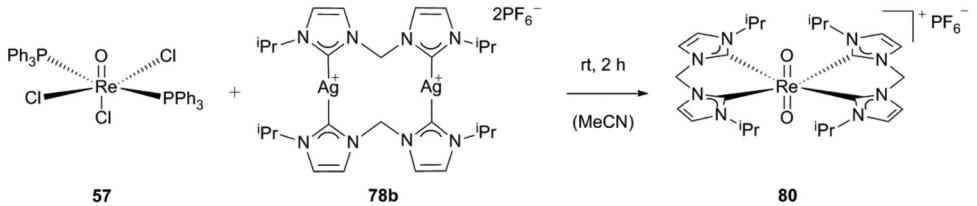
Based on this work, the groups of Reiner and Kühn developed a route towards a radiolabeled ^{188}Re N-heterocyclic carbene complex (**^{188}Re-80**).[4] The cold *trans*-dioxobis(1,1′-methylene-bis(3,3′-diisopropylimidazolium-2-ylidene))rhenium(V)-hexa-fluorophosphate (**80**) was synthesized following a previously published procedure.[4,30g] By reacting $ReOCl_3(PPh_3)_2$ with one equivalent of the corresponding silver carbene (**78b**) in acetonitrile, the *trans*-dioxorhenium biscarbene complex (**80**) is obtained. The synthesis can be carried out under an aerobic atmosphere due to the relative inertness of rhenium(V) NHC complexes with *trans*-dioxo-rhenium cores towards oxidation, moisture, thermal stress and even nucleophilic attack-caused by the steric shielding of the metal centre owing to the pseudo-octahedral coordination and the closed shell electronic structure (Scheme 23).[1f,4,30b,d,f,39]

The synthesis of the generator-produced ^{188}Re–NHC complex (**^{188}Re-80**) starts with $^{188}ReO_4^-$, which can be produced by using a ^{188}W/^{188}Re-generator. After transformation to the $^{188}ReOCl_3(PPh_3)_2$ intermediate (**^{188}Re-57**), adding cold $ReOCl_3(PPh_3)_2$, transmetallation *via* silver carbene (**78b**) and purification by HPLC, the ^{188}Re-labeled counterpart (**^{188}Re-80**) can be obtained (Scheme 24).

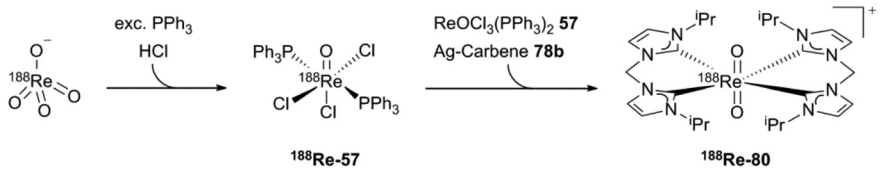
The carried out stability tests revealed that indeed the unlabelled rhenium complex (**80**) is stable for 24 h at room temperature in a solution of acetonitrile and water, nevertheless undesirable decomposition occurred by testing the ^{188}Re-labelled counterpart (**^{188}Re-80**). Under the applied conditions, starting with water at 37 °C in a pH range from 5 to 8, with phosphate buffered saline solutions (37 °C; pH: 5, 6 & 7) as well as bovine serum, which is reasonably similar to the *in vivo* environment, the decomposition took place more quickly. The authors ascribe this to the bulkiness of the ligands at the



Scheme 22 Generation of cationic Re(v) oxo-hydroxo biscarbene complexes by Hor *et al.*[30g]



Scheme 23 Synthesis of *trans*-dioxobis(1,1′-methylene-bis(3,3′-diisopropylimidazolium-2-ylidene))rhenium(v) hexafluorophosphate.[4]



Scheme 24 The first generator produced cationic ^{188}Re NHC complex.[4]

rhenium centre and to the presence of potentially coordinating anions in the used environmental media.[4]

In contrast to the similar water stable ^{99}Tc NHC complex (dioxobis(1,1′-methylene-bis(3,3′-dimethylimidazolium-2-ylidene))-technecium(v)) published by Braband and coworkers,[40] which differs from the metal only by its less bulky methyl substituents, the bulkiness of the isopropyl ligands and the terminal oxo ligands may promote the de-coordination of the NHC ligand as the primary decomposition pathway in aqueous medium instead of reoxidation to free ^{188}perrhenate. The rapid decomposition in phosphate buffered saline solutions is due to the higher ionic strength of buffered solutions – especially chloride anions can compete with the carbenes at the rhenium – hence imidazolium salts are generated, that do not have the ability to bind to the metal again. Furthermore, biomacromolecules that are abundant in the fetal bovine serum may facilitate the decomposition of the complex (**^{188}Re-80**) by undergoing nucleophilic reactions with rhenium. The formed adducts of biomacromolecules with the metal leads to the formation of $^{188}ReO_4^-$.

Despite the unfitness of this particular complex for use in radiopharmaceutical applications, due to its reduced stability under physiological conditions, a new approach for carrier-free and carrier-added radiolabeled rhenium NHC complexes has been opened.[4] These investigations done by Reiner and Kühn *et al.*[4] illustrate that although several radiopharmaceuticals based on the $Re^{I}(CO)_3$-fragment[5o–r,41] as well as Re(v)-complexes[5h–j,l] are known, only estimations based on steric, kinetic and electronic considerations can be done. Whether Re(i) or Re(v) in combination with different types of ligands are more stable under physiological relevant conditions can only be figured out by testing these compounds.

4. Conclusion and perspectives

In this review, synthetic routes to cationic rhenium NHC complexes and their properties have been summarized. Since the first cationic Re(i) carbene complex was isolated in 1998[14] a variety of different approaches such as template synthesis or intramolecular cyclization have been reported. Beside the $Re(CO)_3$ core, bearing varying auxiliary ligands rhenium(v) mono- or bis-NHC compounds comprising nitrido, imido and oxo units arouse interest with respect to their potential appli-

cations, particularly in medicine. Apart from the direct coordination of a free NHC moiety to the metal, the synthetic approach *via* transmetalation of stable silver NHC precursors looks quite promising for future clinical applications. With respect to nuclear medicine, creating diagnostic or therapeutic radiopharmaceuticals for instance can be carried out by radiolabelling of rhenium,[4] or by linking the complexes bearing potential coupling groups (organoimido, alkylamido or alkylcarboxyl) to biomolecules *via* the N- or C-terminus of peptides.[30e] Investigations of high valent Re(v) biscarbene (O, OH) complexes as oxidation catalysts[30g] or Re(i) complexes bearing NHCs in hydroamination reactions[33] or as photocatalysts[13b] are still ongoing. It also appears to be rather straightforward that in this field further research concerning luminescence, toxicity, air and water stability as well as solubility has to be executed with regard to further development of applications of these complexes.

Acknowledgements

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