RSC Advances



REVIEW

View Article Online

View Journal | View Issue



Cite this: RSC Adv., 2017, 7, 55175

Emerging trends in organotellurolate chemistry derived from platinoids

Rohit Singh Chauhan (1)** and Neelam Shivran b

This perspective begins with the discussion of various basic synthetic approaches applied for the synthesis of several organotellurium ligands, their chemistry derived from platinum group metals, and the reactivity difference among them. It also gives an overview on the development of various bi, tri, and high nuclearity complexes syntheses. Investigations targeting the organotellurium ligand systems revealed a remarkable reactivity due to the dynamic nature of the lone pair available on the tellurium metal, which has led to a serendipitous isolation of the complexes $[Cp*Ir(ppy)(\eta^1-Te_2Ph_2)]^+$, $[Cp*IrOs_3(\mu-H)_2(\mu-Tetol)_2(CO)_7]$, $[Pt{TeC_5H_3(3-R)N}_2Te(PPh_3)]$, $[Pt{Ph_2PCH(TeC_5H_3(3-R)NPPh_2)}_2]$ (R = H, Me), and various other high nuclearity heterometallic $[Cp*Ir(CO)(\mu-TeC_6H_4)_2MCp*Cl]Cl$ (M = Rh, Ir) complexes. Studies of the various complexes investigated the various binding modes of coordination and the facile cleavage of the Te-C and Te-Te bonds of tellurium-based ligand systems. Attempts have been made to present a comprehensive account of the subject matter. Various promising aspects of these complexes, such as their synthesis, reactivity, structures, and applications, are covered in this review.

Received 26th August 2017 Accepted 20th November 2017

DOI: 10.1039/c7ra09480a

rsc.li/rsc-advances

1. Introduction

Organosulphur and selenium derived metal complexes have been well documented for more than several decades.¹⁻⁴ When one considers its homologues analog involving tellurium elements, it is clear that tellurium chemistry is still relatively uncharted. Due to their high reactivity, air sensitivity, and diffusive sets of orbitals, tellurium complexes are unstable and hence unexplored. Thus, the prompt reactivity and rich coordination of organotellurium ligand systems has drawn substantial interest over the last few years.⁵⁻¹⁰

The metalloid character of tellurium makes it amphoteric (acid as well as base) in nature depending upon the nature of the reactive substrate. Therefore, the reactions of organotellurium ligands with platinum group metal precursors represent an active area for further research. The noteworthy reactivity of platinoids has been utilized in synthetic chemistry to isolate products in quite good yields with great selectivity under normal conditions. These complexes are not only used as precursors but are also envisaged as an active species in various catalytic reactions. In particular, the superior stability of the platinum family complexes endow them with an opportunity to be utilized to comprehend the mechanistic details as well as the nature of complexes involved in particular catalytic cycles.

Renewed interest in the field of coordination chemistry derived from organotellurium ligand systems has been stimulated by a number of recent publications^{7,8,21–23} dealing with the oxidative addition reactions of platinum group metal precursors with various diarylditelluride ligand systems. The outcomes of these reactions depend upon the nature of the solvent, especially in chlorinated solvents, which yield multinuclear complexes together with several unidentified products;^{21–23} whereas, the similar reaction in solvents like benzene and toluene affords different multinuclear complex. The formation of several products mainly results from the bond cleavage of Te–C bonds rather than Te–Te bonds.^{22,23} The comparable bond energies of Te–Te and Te–C bonds and the increased metallic character of Te may be the reason for the unexpected reactivity of organotellurium ligands.

Thus, this perspective aims to cover the various synthetic approaches for organotellurium ligands, different aspects and versatility of platinum group metal complexes derived from these ligand systems, with a particular emphasis on hemilabile tellurolate ligand systems since the subject was recently explored.

2. Synthetic strategy of various organo-tellurium ligands

2.1 Telluroethers

The synthetic approaches applied for the synthesis of various monodentate, bidentate, and hybrid telluroethers have been reviewed previously by various groups.^{6,24–28} However, there have been no significant recent developments reported. The

^aDepartment of Chemistry, K. J. Somaiya College of Science and Commerce, Vidyavihar, Mumbai-400 077, India. E-mail: rohit.chauhan@somaiya.edu

^bDepartment of Chemistry, Indian Institute of Science Education and Research, Pune-411008, India

RSC Advances

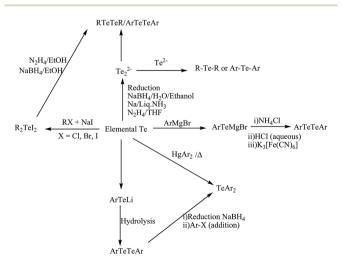
common synthetic methods applied for the synthesis of telluroethers are highlighted in the following.

- 2.1.1. Reduction of ditellurides. This is one of the most effective methods used, in which the reduction of ditellurides takes place accompanied with the addition of organic halides compounds. The molar quantity of organic halides is usually double with respect to ditellurides. This method has also been used in the preparation of various asymmetrical telluroethers, but there are some issues around the poor yield due to the formation of symmetrical telluroethers. Most recently Prof. A. K. Singh et al. recently developed various telluroethers, such as (2-phenyltelluromethyl)tetrhydropyran/dioxane,24 (2-phenyltelluromethyl)tetrhydropyran,24 Te(CH2CH2R)2 (R = CH2NH2, C_4H_8N), 25 (4-RC₆H₄)Te(CH₂CH₂){2-C₅H₄N} (R = H, Me, OMe), 25 $4-MeOC_6H_4Te(CH_2)_2N=C(CH_3)(2-HOC_6H_4)_{,26}$ $Te(CH_2CH_2N=$ $C(CH_3)C_6H_4-2-OH)_2$, ²⁶ 2- $CH_3SC_6H_4C=NCH_2CH_2TeC_6H_4-OMe$, ²⁷ $4-\text{MeOC}_6\text{H}_4\text{Te}(\text{CH}_2)_n\text{C}=\text{N}(2-\text{HOC}_6\text{H}_4)(\text{C}_6\text{H}_5)^{28}$ applying the same strategy.
- 2.1.2. In situ generation of Na₂Te. The second most efficient strategy for the formation of telluroethers is the *in situ* formation of Na2Te, followed by the addition of the corresponding alkyl halides to isolate the desired product. As an example, the class of cyclic ditelluroether [8]aneTe2 was synthesized in a similar fashion by the addition of a half equivalent of 1,3 dibromomethane in a THF solution of Na₂Te, followed by the addition of NaBH₄ and a further equivalent of 1,3 dibromomethane.29,30 The syntheses of mixed donor thia/tellura [9]aneS₂Te₂, [11]aneS₂Te₂, [12] aneS2Te2, [14]aneS3Te macrocyclic ligands and tripodal telluroether were also carried out based on the same strategy.31-35
- 2.1.3. Applying a Grignard reagent. Currently, Grignard reagent is also used as a promising methodology for the formation of telluroethers, especially for the isolation of heteroaromatic analogs and for unsymmetrical telluroether synthesis. In this case, the insertion of tellurium metal in to the Grignard reagent of the organic moiety corresponding to the expected telluroether is performed first. Subsequently, the addition of halo aryl or alkyl is followed in freezing conditions. Recently, an unsymmetrical 1-naphthyl-based telluroether and symmetrical pyridyl telluroethers have been isolated with the same strategy.36-38 In order to justify the mechanistic details, we performed the following process: (i) halopyridine underwent a complete metal-halogen exchange reaction with i-prMgCl to give pyridyl magnesium chloride, (ii) the latter compound was reacted with an equivalent of tellurium metal via an insertion mode, (iii) followed by the addition of alkyl/ aryl halide to yield the desired telluroether with the elimination of MgCl2.

2.2 Diorganotellurides

The majority of synthetic approaches have been applied to the synthesis of various ditelluride ligand systems. Among these, the insertion of elemental tellurium in to reactive M-C bonds is a quite common methodology. Various approaches are described below.

- 2.2.1. Insertion of chalcogen in to Li-Aryl bond. The insertion of elemental tellurium in to the Li-aryl bond followed by oxidation has been performed for the synthesis of various ditelluride ligand systems. The lithiation of bromoaryl compounds has been accomplished by the substitution of the bromo group through lithium metal with reagents like n-BuLi^{39,40} or Bu^tLi⁴¹ in polar solvents like THF and petroleum ether at a temperature of -78 °C. The resulting lithiated aryl group reacts with active elemental tellurium metal to yield a lithiated chalcogenolate ion, which on hydrolysis gives the corresponding diaryl ditelluride ligand systems.
- 2.2.2. Reaction of E^{2-} with haloaryl compounds. The reaction of heteroaromatic and aromatic halocompounds with ditellurido dianions in different solvents is another important synthetic pathway to synthesize a class of various ditelluride ligand systems. In most of the reactions, reducing reagents are generated through an in situ mode by a variety of reducing agents, like NaBH4, Li metal reaction, Na/NH3, and hydrazine.42-47 Sodium borohydride reduction of elemental tellurium in ethanol, water, and ethoxy ethanol has been applied for the synthesis for Na₂Te₂. 45-48 The latter has been synthesized by an in situ and dropwise addition of haloaryl compounds, yielding the corresponding diaryl ditelluride; while hydrazine hydrate in the presence of NaOH in DMF has also been used to prepare Na₂Te₂, which on reaction with bromopyridine and chloropyrimidines, affords their corresponding ditellurides (Scheme 1).49
- 2.2.3. Insertion of tellurium in to aryl magnesium halide. The lithiation of haloaryl compounds takes place at -78 °C, but this cryogenic condition and the instability of the lithiated products results in a poor yield, which makes this method really an inconvenient route for the synthesis of ditellurides. In contrast, the stability and ease of handling of aryl magnesium bromide compounds makes this synthetic strategy quite trendy. Normally for all cases, a Grignard reagent of the corresponding alkyl or arylhalo compounds is first synthesized, 36,37,50,51 followed by the insertion of elemental tellurium, which on acid hydrolysis yields the corresponding ditellurides in a moderate yield.



Scheme 1 Synthetic approaches for the synthesis of various ditellurides and monotellurides.

3. Metal complexes with telluroether ligands

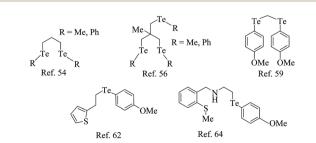
3.1 Ruthenium and osmium

The reaction of $RuCl_3 \cdot nH_2O$, $TePh_2$, and CO yields the complex [Ru(CO)₂Cl₂(TePh)₂], which has also been obtained in moderate yield by the simple addition between [Ru{(CO)₃Cl₂}₂] and telluroether. 52,53 The reaction of chelated ditelluroether RTe(CH₂)₃TeR; (R = Me, Ph, or o-C₆H₄(TeMe)₂) with RuCl₃-·nH2O, [Ru(dmso)4X2] gave a complex with the general composition trans- $[RuX_2(L\cap L)_2]$ (X = Cl, Br or I); $L\cap L$ = RTe(CH₂)₃TeR; (R = Me, Ph or o-C₆H₄(TeMe)₂) (Scheme 2).^{54,55} All these products showed poor solubility in organic solvents. To overcome the solubility issues, a bulky phosphine-based ruthenium precursor, [RuCl₂(PPh₃)₃], has been used, which on reaction with the same ditelluroether yielded a complex of $[RuCl(PPh_3)(L\cap L)_2]PF_6$ (Fig. 1) with good solubility in various organic solvents.55 In solution, the latter complex is converted to a product with the composition [RuCl₂(PPh₃){MeC(RTeCH₂)}₃], while a longer stay in the solvent results in its decomposition to unknown species;56 while this tripodal ligand on reaction with [Ru(dmf)₆](SO₃CF₃)₃ in methanol gave a homoleptic compound $[Ru\{MeC(CH_2TeR)_3\}_2](SO_3CF_3)_2 (I).^{57,58}$

A new class of carbon-backboned ligands (4-MeO– C_6H_4 – $Te)_2CH_2$ and $[(CH_2)_2C(CH_2TeMe)_2]$ on reaction with $[RuCl_4(dmso)_4]/[RuCl_2(p\text{-cymene})]_2$ afforded the complex $[RuCl_2(dmso)_2(L)]/[RuCl_2(p\text{-cymene})_2(L)]$ (L= (4-MeO– C_6H_4 – $Te)_2CH_2$ and $[(CH_2)_2C(CH_2TeMe)_2]$) which contains a telluroether in a chelating fashion with the formation of a strained four-membered ring. These complexes were configured in a distorted octahedral geometry around the Ru metal center.⁵⁹

The reaction of $[RuCl_2(p\text{-cymene})]_2$ with two equivalent of homoleptic telluroether $Te\{CH_2CH_2(Ar)\}_2$ (Ar = 1,3 dioxane, thiophene) 60 or a heteroleptic telluroether like [(thiophene)Te $\{CH_2(R)\}$] (R = furan, pyrol), 61 [$\{CH_2CH_2(R)\}$ Te($C_6H_4\text{-}p\text{-OMe}$)] (R = thiophene, phthalamide, benzotriazole) 62,63 yielded [RuCl_2(p-cymene)L] (L = Te{CH_2CH_2(Ar)}_2, [{CH_2CH_2(R)} Te($C_6H_4\text{-}p\text{-OMe}$)], [(thiophene)Te{CH_2(R)}]) (Scheme 2). The same type of composition (II) has also been derived with various tridentate hybrid ligand systems. $^{64-67}$

The chemistry of halo osmium precursors OsO_4 -HX or $[OsX_6]$ with telluroether has not had a successful outcome yet for dithio or diselenoether ligands. In this case, the reaction of $[OsCl_2(dmso)_4]$ with carbon-backboned ditelluroether $RTe(CH_2)_3TeR$, $CH_2(TeMe)_2$, $o-C_6H_4(CH_2TeMe)_2$ led to



Scheme 2 Homoleptic and heteroleptic telluroether ligands.

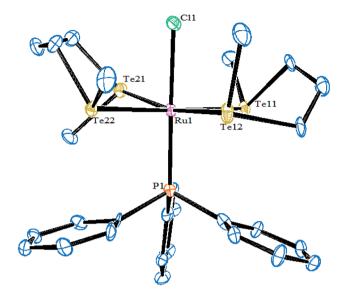


Fig. 1 Crystal structure of $[RuCl(PPh_3)\{MeTeCH_2\}_2]^+$ (redrawn from ref. 55).

a compound with the composition $[OsCl_2(L\cap L)_2]$ (III) $(L\cap L = RTe(CH_2)_3TeR, CH_2(TeMe)_2, o-C_6H_4(CH_2TeMe)_2)$. ^{54,68} Unlike for thio and selenoether ligands, a very clean route to the final product has been achieved in the case of telluroethers. Compared to the ruthenium analogs, very few examples of telluroether-based osmium complexes are known so far.

3.2 Rhodium and iridium

Very little work on rhodium and iridium complexes derived from organotellurium ligand systems, i.e., telluroethers, has been documented so far. Compared to ruthenium, the related references for rhodium and iridium complexes are less significant in number. The reaction of TeR_2 (R = Me, Et) with metallocyclic [(C₅H₅)₂Rh₂(μ-CO)(CF₃CCF₃)] derived an adduct in which TeR2 was added to one of the rhodiums attached with bridging carbonyl, which was boned in a η¹ fashion.⁶⁹ Such a type of insertion followed by the addition of tellurium can be particularized due to diffusive sets of lone pairs and their ease of availability to coordination. While the reaction of RhCl3- $\cdot 3H_2O$ and ditelluroethers $Te(CH_2)_3TeR$ (R = Me, Ph) along with NH_4PF_6 in ethanol solution yielded the complex $[RhCl_2(L \cap L)_2]$ PF₆ (Scheme 3). Similarly, various tripodal Rh(1) and Ir(1) complexes $[M{MeC(CH_2TeMe)_3}(COD)]PF_6$ (M = Rh, Ir) were derived from umbrella-like telluroethers, namely with MeC(CH₂TeR)₃ (R = Me, Ph).⁵⁵ However, Rh(III) complexes with the composition $[Rh(\eta^5-C_5H_5)\{MeC(CH_2ER)_3\}][PF_6]_2$ with a square pyramidal geometry were isolated by the reaction of [$\{RhCl_2(\eta^5-C_5H_5)\}_2$] and the corresponding ligand systems.⁵⁶

RSC Advances Review

$$[M(COD)Cl]_2 + 2MeC(CH_2TeR)_3 + 2NH_4PF_6$$

$$[Rh(C_5H_5)Cl_2\}_2] + Te(CH_2CH_2CH_2TeR)_2$$

$$[Rh(C_5H_5)Cl_2\}_2] + Te(CH_2CH_2CH_2TeR)_2$$

$$[M(COD)(MeC\{CH_2TeR\}]PF_6$$

$$[Rh(C_5H_5)\{Te(CH_2CH_2CH_2TeR)_2\}]$$

$$(M = Rh, Ir; R = Me, Ph)$$

Scheme 3 Reaction of rhodium and iridium precursors with tripodal telluroether.

The fluxional behavior of the latter complex was established by its ¹H NMR spectrum, which showed a single resonance for TeMe, CH₂, and COD (Scheme 3). It was concluded, during a dynamic process, that a flip on and off movement takes place through the arm of the tripod around the metal center.

Similarly, when the reaction with RhCl₃·3H₂O is employed in various mole ratios with the ligand system Te(CH₂SiMe₃), a variety of products has been isolated (Scheme 4) depending upon the mole ratio of the ligand (Fig. 2).70 Most of these complexes have shown issues with their solubility in common organic solvents. The solubility issues have been overcome with the development of a new class of telluroether in which the backbone consists of a morpholine group. Rh(III) complexes derived from the same ligand N-{2aryltelluroethyl}morpholine (Scheme 4)71 have shown ready solubility in all organic solvents other than diethyl ether and hexane, in which the complexes are sparingly soluble. Their high solubility makes them promising catalysts in the hydrogenation reactions of ketones.

3.3 Palladium and platinum

Compared to other platinoids, a significant amount of work has been documented on Pd(II) and Pt(II) complexes derived from telluroethers. The reaction of $M_2M'Cl_4$ (M = Na, K; M' = Pd, Pt)

in a 1:2 mole ratio with homoleptic telluroether Te{CH₂CH₂ (Ar)₂ IV $(Ar = 1,3 \text{ dioxane, thiophene})^{60,62}$ or a heteroleptic telluroether, like [(thiophene)Te{ $CH_2(R)$ }] (R = furan, pyrol), 61 $[\{CH_2CH_2(R)\}Te(C_6H_4-p-OMe)]$ (R = thiophene, phthalamide, benzotriazole), 62,63 led to a complex of the type [MCl₂L₂] L = Te $\{CH_2CH_2(Ar)\}_2$, $[\{CH_2CH_2(R)\}Te(C_6H_4-p-OMe)]$, $[\{thiophene\}Te]$ $\{CH_2(R)\}$; while the reaction in 1:1 mole ratio with $[\{CH_2CH_2(R)\}Te(C_6H_5-p-OMe)]$ (R = 2-CH₃SC₆H₄CH=N, 2-CH₃SC₆H₄CHNH V, $\{C_6H_5\}\{2\text{-HOC}_6H_4\}C=N\}$ VI and a variety of tridentate ligand yielded an expected additive product with the composition [MCl(L)]⁺.65-69 Among these cyclic complexes, $[MX_2\{Te(CH_2)_4\}_2]$ (M = Pd, Pt; X = Cl, Br, I) has been isolated from the reaction with cyclic telluroethers, i.e., telluracyclopentane Te(CH₂)₄.⁷² In the case of the platinum metal system, both cis- and trans-configured complexes have been reported. However, only a trans isomer has been isolated in the case of palladium, which was also supported by its X-ray structure results (Fig. 3).72 The trans configuration was also obtained by ligand systems like 4 oxatellurane,73 1,3 dihydrobenzotellurophene, and 2,7-dihydro-1*H*-dibenzotellurophene ligands.74 A comparative study of bidentate ligand RECH₂ER (R = Me, Ph and E = S, Se, Te)⁷⁵ with both metals showed that the thio analogs led to a very stable compound,

Scheme 4 Schematic representation of the reaction of RhCl₃·3H₂O with various telluroethers

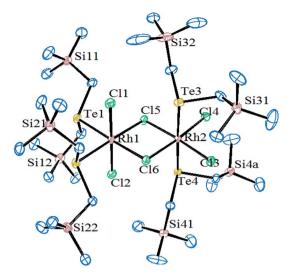


Fig. 2 Crystal structure of $[Rh_2Cl_4(\mu-Cl)_2\{Te(CH_2SiMe_3)_2\}_4]$ (redrawn from ref. 70).

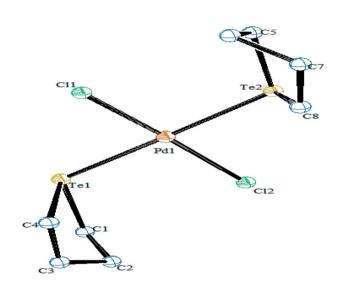


Fig. 3 Crystal structure of $[PdCl\{Te(CH_2)_4\}_2]$ (redrawn from ref. 72).

namely [MCl₂(η^1 -PhSCH₂SPh)₂], while selenium complexes are slowly decomposed into their polymeric form with the composition [{MCl₂(RECH₂ER)₂}n] and a free ligand; while tellurium analogs of the same ligand, *i.e.*, RTeCH₂TeR (R = Me, Ph), only gave the polymeric [{MCl₂(RECH₂ER)₂}n] (M = Pd, Pt) compounds. The similar ligand system (4-MeOC₆H₄Te)₂CH₂ formed a monomeric structure [MCl₂(L \cap L)] compound comprised of a four-membered strained ring with an acute angle of 81° between Te–Pd–Te (Fig. 4).^{76,77}

Platinum(w) complexes with the composition $[{PtMe_3I}_2{(4-RTe)_2CH_2}]$, $(R = Ph, 4-MeOC_6H_4)$ and $[{PtMe_3I}_2{(PhTeCH_2TePh)_2}]$, containing bridging, chelating, and

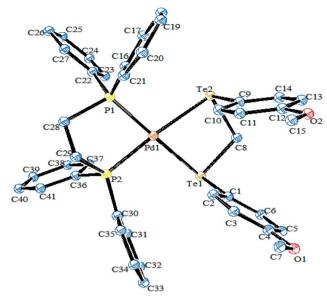


Fig. 4 Crystal structure of [Pd{(4MeO- $C_6H_4Te_2$)CH $_2$ }(dppe)] (redrawn from ref. 77).

monodentate ditelluroethers, respectively, have also been isolated. The homoleptic complexes $[M(L \cap L)_2](PF_6)_2$ (M = Pd,Pt); $L \cap L = RTe(CH_2)_3 TeR$, R = Me, Ph; o-CH₂(TeMe)₂, o-C₆-H₄(CH₂TeMe)₂, MeC(CH₂TeMe)₃, and MeC(CH₂TePh)₃ have been prepared from [MCl₂(MeCN)₂], TlPF₆, and the corresponding ligands in acetonitrile solution.54,55 The 1{H}NMR spectra of the above-mentioned complexes show broad resonance due to an inversion process. Prof. A. K. Singh et al. developed a series of telluroethers, namely 1,3-(4-MeOC₆H₄-TeCH₂)₂CHOH,⁷⁹ 4-MeOC₆H₄TeCH₂CH(OH)CH₂OH, 4-MeOC₆- $H_4Te(CH_2)_nC=N(2-HOC_6H_4)(C_6H_5)$, (2-phenyltelluromethyl) tetrhydropyran,81 (2-phenyltelluromethyl)tetrhydropyran,82 $Te(CH_2CH_2R)_2$ (R = CH_2NH_2 , C_5H_4N), (4-RC₆H₄) $Te(CH_2CH_2\{2-1\})$ C_5H_4N) (R = H, Me, OMe), 83-88 N-{2-(4-MeOC₆H₄Te)CH₂CH₂}phthalimide, 89 with a possible one or more donor atoms, like oxygen and nitrogen, other than just the available tellurium atom (Scheme 5). Obviously, both metals (Pd, Pt) are directly bonded to tellurium with weak interactions through the donor atoms.

Tellurium has also been ligated into a macrocyclic Schiff base, and the resulting ligand **VII** upon reaction with [PdCl₂ (PhCN)₂] yielded the complex [{PdCl₂}₂L]. In this complex,

Scheme 5 Tridentate hybrid telluroether ligands.

palladium is coordinated with each tellurium as well as the nitrogen of the Schiff base. However, the same reaction in a 1:1 ratio of palladium precursor to the ligand gave the product $[PdL]^+$ **VIII**, ⁹⁰ in which palladium is coordinated to the Te_2N_2 core of the ligand, leaving the two nitrogen atoms uncoordinated (Scheme 6); ⁹¹ while in the case of $[PtCl_2(COD)]$, a symmetrical ring opening of the ligand took place to give the product **IX**, where platinum is coordinated to the TeN_2C core. Surprisingly, the complexation mode of the tellurium ligand

system was totally different from the similar selenium analogs.

In the case of the latter ligand system, palladium is directly

coordinated to all four nitrogen atoms. 92,93

An interesting example of a halobridged complex, $[M_2X_2(\mu X)_2(TeR_2)_2]$ (M=Pd, Pt; X=Cl, Br; R=Mes, Ph, o-tol), was obtained by the treatment of $[MX_2(TeR_2)_2]$ (R=Mes, Ph, o-tol) with MX_2 (M=Pd, Pt)/ Na_2PdCl_4 (Scheme 7). $^{93-95}$ These complexes were formed due to the chlorobridged cleavage reaction with the substitution of thio and seleoether through monotellurides. Usually, telluroether complexes are oriented in the cis form, which is slowly transformed to the trans isomer in solution. The conversion of the cis to the trans form was encountered in the $^{125}TeNMR$ spectrum of the latter complexes, which exhibited a single resonance first, but in the longer acquisition results two prominent resonances were observed,

attributed to the *cis* as well as *trans* forms. An agostic interaction between telluroethers and metal atoms has also been documented in these complexes, where a toluene–methanol solution of $[Pd_2Cl_2(\mu\text{-}Cl)_2(TeMes_2)_2]$ or compound $[PdCl_2(TeMes)_2]$ on refluxing for 30 min yielded a binuclear cyclopalladated complex $[Pd_2(\mu\text{-}Cl)_2\{CH_2C_6H_2(4,6\text{-}Me_2)\text{TeMes}_2\}_2]$ (Scheme 7). However, the latter binuclear compound was converted to the mononuclear compound $[PdCl_2\{MesTeCH_2C_6-H_2(4,6\text{-}Me_2)\text{TeMes}\}_2]$. The formation of the mononuclear compound mainly arose due to nucleophilic attack of mesityl tellurolate at the Pd–C bond.

Recently, an intricate palladacycle was synthesized by the reaction between ditolyl telluride and palladium acetate in toluene solution, which yielded two complexes with the composition $[(o\text{-tolylTe})_2\text{OPd}(\text{OAc})_2]$ (Fig. 5) and trinuclear $[\text{Pd}(o\text{-tolyl})\{\text{di-}o\text{-tolyltelluride}\}]_2\text{Pd}(\mu\text{-OAc})_2$. The former complex was a bidentate tellurinic acid anhydride, while the latter was coordinated to tolyl and telluride. The formation of both binuclear $[(o\text{-tolylTe})_2\text{OPd}(\text{OAc})_2]$ and trinuclear $[\text{Pd}(o\text{-tolyl})\{\text{di-}o\text{-tolyltelluride}\}]_2\text{Pd}(\mu\text{-OAc})_2$ complexes can be encountered by intramolecular cyclopalladation via the bond formation between palladium metal centers and tolyl carbon.

Scheme 6 Reaction of $[MCl_2(L)_2]$ (M = Pd, Pt; L = PhCN or COD) with a tellurium-ligated macrocyclic Schiff base.

Scheme 7 Cyclometallation of [PdCl₂(Mes)₂] at different temperatures.

Crystal structure of [(o-tolylTe)₂OPd(OAc)₂] (redrawn from ref. 96).

Metal tellurolates

4.1 Ruthenium and osmium

The coordination chemistry of ruthenium cluster complexes toward the highly reactive organotellurium ligand is very rich in the literature, but still various aspects of its reactivity pattern are uncultivated. With this prospect, the refluxing of Ru₃(CO)₁₂ with Na₂Te₂ and PPh₄PBr at 80-130 °C for 8 h yielded the cluster complex [Ru₄(Te)₂(Te)₂(TeMe)₂(CO)₈](PPh₄)₂.⁹⁷ The crystal structure of the latter complex consisted of four rectangles with a center of inversion in the midst. While the oxidative addition of diorganoditelluride to [Ru₃(CO)₁₂] yielded a variety of compounds. In particular, the reaction of diphenyl ditelluride resulted in the formation of a binuclear complex bridged by phenyl tellurolate along with the polymeric form of [Ru(CO)₂(μ-TePh)]_n. 98,99 Performing the same reaction with the addition of halogen yielded the complex $[Ru_2X_2(CO)_6(\mu\text{-TePh})_2]$ (X = Br, I), which was isolated by breaking of the Ru-Ru bond.99 Similarly, on refluxing a phosphine precursor of the ruthenium complex $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ with tetrahydrofuran solution of Ar_2Te_2 $(Ar = C_6H_4OEt-4)$ in a 1 : 2 mole ratio for 6 h yielded a mixture of the products $[Ru_2(CO)_4(\mu\text{-TeAr})_2(\mu\text{-dppm})]$, $[Ru_2(CO)_6(\mu\text{-TeAr})_2]$ and [Ru(CO)₄(TeAr)₂] (Scheme 8).¹⁰⁰ However in toluene solution, other than [Ru₂(CO)₄(μ-TeAr)₂(μ-dppm)], several products101 have been afforded due to the competitive cleavage of Te-Te and Te-C bonds. At room temperature in CH₂Cl₂, reaction with a diphenyl ditelluride ligand system yielded the binuclear compound [Ru₂(μ-TePh)₂(CO)₄(μ-dppm)] as well as the trinuclear unsaturated clusters [Ru₃(μ₃-Te)₂(μ-TePh)₂(CO)₆(μ-dppm)] and $[Ru_2(\mu_3\text{-Te})(\mu\text{-TePh})_3(CO)_6(\eta^1\text{-COPh})(\mu\text{-dppm})]$. ¹⁰²

Heating a solution of $[Ru_3(\mu-H)\{(\mu_3-\eta^2-C_4H_2O)(\mu-PC_4H_3-\eta^2-C_4H_2O)(\mu-PC_4H_3-\eta^2-C_4H_2O)(\mu-PC_4H_3-\eta^2-C_4H_2O)(\mu-PC_4H_3-\eta^2-C_4H_2O)(\mu-PC_4H_3-\eta^2-C_4H_2O)(\mu-PC_4H_3-\eta^2-C_4H_2O)(\mu-PC_4H_3-\eta^2-C_4H_2O)(\mu-PC_4H_3-\eta^2-C_4H_2O)(\mu-PC_4H_3-\eta^2-C_4H_2O)(\mu-PC_4H_3-\eta^2-C_4H_2O)(\mu-PC_4H_3-\eta^2-C_4H_2O)(\mu-PC_4H_3-\eta^2-C_4H_2O)(\mu-PC_4H_3-\eta^2-C_4H_2O)(\mu-PC_4H_3-\eta^2-C_4H_3O)(\mu-PC_4H_3-\eta^2-C_4H_3O)(\mu-PC_4H_3-\eta^2-C_4H_3O)(\mu-PC_4H_3-\eta^2-C_4H_3O)(\mu-PC_4H_3-\eta^2-C_4H_3O)(\mu-PC_4H_3-\eta^2-C_4H_3O)(\mu-PC_4H_$ O)₂}(CO)₇(μ-dppm)] with Ph₂Te₂ at 110 °C for 2 h resulted in various cluster complexes, mainly [Ru₃(μ₃-Te)₂(μ-TePh)₂ $(CO)_6(\mu\text{-dppm})], [Ru_3(\mu_3-\eta^2-C_4H_3O)\{\mu-PC_4H_3O_2\}(CO)_5(\mu-TePh)_2$ $(\mu\text{-dppm})$] (Fig. 6), $[Ru_3(\mu\text{-H})(\mu_3-\eta^2-C_4H_2O)\{\mu\text{-}C_4H_3O_2\}(CO)_5$ $(\mu\text{-TePh})2(\kappa^2\text{-dppm})$, and $[Ru_3(\mu\text{-H})(\mu_3-\eta^2\text{-}C_4H_2O)\{(PC_4H_3O)_3\}$ $\{\mu-P(C_4H_3O)_2\}(CO)_4(\mu-TePh)_2(\kappa^2-dppm)\}$. However, the reaction of the tetranuclear ruthenium(π) complex with R_2Te_2 (R=

Me, Et, Fc) yielded the diruthenium complex syn-[Cp*RuCl (μ-TeR)]2 in quite a good yield. 104 Although the reaction of dialkylditellurides led to a clean pot synthesis of alkanechalcogenolate diruthenium complex, in the case of phenyl derivatives of the tellurium-ligated system, two products [Cp*RuCl(µ-TePh)]₂ and [Cp*Ru(μ-TePh)₃RuCp*]Cl isolated.104

Treatment of $[(\eta^6\text{-cymene})\text{Ru}(\mu\text{-Cl})_3\text{Re}(\text{CO})_3]$ with sodium salt phenyl telluride yielded a yellow heterometallic product $[(\eta^6\text{-cymene})\text{Ru}(\mu\text{-TePh})_3][\text{Re}_2(\text{CO})_6(\mu\text{-TePh})_3].^{105}$ Half sandwich complex [(Cp*Ru)₂B₂H₆(μ-TePh)] has been obtained by the thermolysis of [(Cp*Ru)₂B₂H₆S₂] in the presence of Ph₂Te₂.¹⁰⁶ The reactions of $[Fe_2(\mu\text{-Te})_2(CO)_6]$ with low valent precursor of ruthenium metal derive heteronuclear telluride bridged cluster compound by the insertion between the Te-Te bond.107-112 Therefore the treatment of $[Ru_4(CO)_{12}]$ with $[Fe_2(\mu-Te)_2(CO)_6]$ afforded a pentanuclear cluster complex of composition [Fe(CO)₆Ru₃(μ-Te)₂(CO)₁₁]. Similar outcome has been obtained by the reaction of $[Fe_2(\mu-EE')_2(CO)_6]$ (E = S, Se, Te) with $[M_3(CO)_{12}(NCMe)]$ (M = Ru, Os). These latter complexes are also isolated at room temperature by the precursor $[M_3(CO)_{10}(MeCN)_2]$ (M = Ru, Os). While the reaction with

Oxidative addition of [Ru₃(CO)₁₀(μ-dppm)] with diaryl Scheme 8 ditelluride.

Fig. 6 Crystal structure of
$$[Ru_3(\mu_3-\eta^2-C_4H_3O)\{(\mu-PC_4H_3O)_2\}(CO)_5(\mu-TePh)_2(\mu-dppm)]$$
 (redrawn from ref. 103)

$$[Os_3(CO)_{10}(MeCN)_2] \xrightarrow{Ph_2Te_2} \begin{array}{c} PhTe & OC & CO \\ OC & Os & CO \\ OC & O$$

Scheme 9 Synthesis of a trinuclear osmium telluride bridged complex.

trinuclear compound [Fe₃(μ_3 -Te)₂(CO)₉] results the substitution product [Ru₄(μ_4 -Te)₂(CO)₁₁].¹¹⁴

In contrast to ruthenium, the reaction of Ph2Te2 with the osmium precursor [Os₃(CH₃CN)₂(CO)₁₀] under normal conditions yielded the cluster [Os₃(CO)₁₀(μ-TePh)₂], in which both tellurium linkages were at opposite Os-Os edges.115 Thermolysis of the latter complex resulted in the cleavage of Te-C bonds and yielded the product [Os₃(CO)₉(μ-Te)₂] (Scheme 9). ¹¹⁶ Different to the selenium analog, in this case there was no evidence of intact REER bonds in these complexes, but the conversion from one isomer to other isomer is much more facile; while the reaction with unsaturated osmium cluster compounds, like [Os₃ $(\mu-H)_2(CO)_{10}$, are much more complicated. A variety of complexes were formed, out of which three cluster complexes, namely $[Os_3H_2(\mu\text{-TePh})_2(CO)_{10}]$ (X), $[Os_3H(\mu\text{-TePh})(CO)_{10}]$ (XI), and [OsH(CO)₃(TePh)]₂, 115 were isolated. The same ligand upon reaction with phosphine-derived osmium precursors yielded the binuclear product $[Os_2(\mu\text{-TePh})_2(CO)_4(\mu\text{-dppm})]$ and two isomeric compounds with the composition $[Os_3(\mu\text{-TePh})_2$

 $(CO)_8(\mu\text{-dppm})]$ (Fig. 7), which mainly differ from the phenyl orientation attached to the telluride metal center.¹¹⁶

A very close output was obtained when performing the oxidative addition reaction of $(TeTol)_2$ with the mixed cluster $[Cp*IrOs_3(\mu-H)_2(CO)_{10}]$.¹¹⁷ In this case, three cluster complexes were isolated with the composition $[Cp*IrOs_3(\mu-H)_2(\mu-Tetol)_2(CO)_7]$ (Fig. 8). These clusters had relatively different orientations of the tolyl group around the tellurium center, with two of them being stereoisomers having the tolyl group orientation away from the cluster core, *i.e.*, *exo*, or inward toward the core, *i.e.*, *endo*. These possibilities of obtaining various stereoisomers

RSC Advances Review

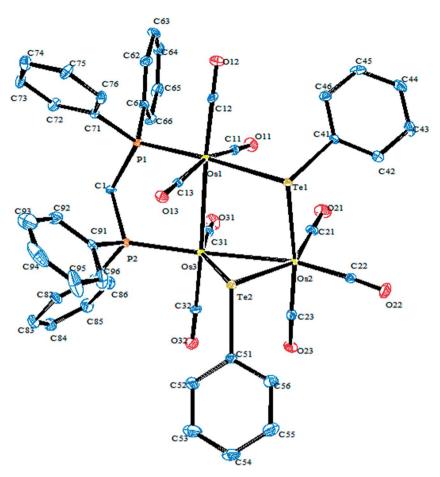


Fig. 7 Crystal structure of $[Os_3(\mu-TePh)_2(CO)_8(\mu-dppm)]$ (redrawn from ref. 116).

have only been reported in ditellurides systems, and can be encountered due to the dynamic nature of tellurium lone pairs.117

Rhodium and iridium

A new class of rhodium precursors, like [Tp*Rh(COE)(MeCN)] (Tp* = hydrotris(3,5 dimethylpyrazol-1-yl)borate; COE = cyclooctene), were explored to study the oxidative addition reaction with diphenyl ditelluride. 118 The latter reaction mixture resulted in an oxidative additive product, namely [Tp*Rh(TePh)₂ (MeCN)], which was allowed to react further with a small amount of [(Cp*Ru)₄(µ₃-Cl)₄] to yield the mixed binuclear compound [Tp*RhCl(μ-TePh)₂RuCp*(CH₃CN)]. However, on stirring the reaction mixture in an open atmosphere, it binds with oxygen to result in the complex [(Tp*RhCl(μ-TePh)₂-RuCp*O₂)]. The reaction of $[(Cp*)_2Rh_2(\mu-CO)\mu-\eta^2:\eta^2C_2(CF_3)_2]$ with R_2Te_2 (R = Me, Et, ⁱpr, Ph, Fc) yielded the product $[(Cp^*)_2Rh(\mu\text{-TeR})_2\{\mu\text{-}C_2(CF_3)_2\}]^{\text{119,120}} \ (Scheme \ 10) \ along \ with$ some of the product $[(Cp^*)_2Rh(\mu\text{-TeR})_2\{\mu\text{-CO}(CCF_3)_2\}]$ formed via the insertion process. A new class of internally functionalized dianion ligands [Te(^tBuN)P(μ^tBuN)2P(NtBu)Te]²⁻ upon reaction with [Cp*Rh₂(µ-Cl)₂Cl₂] afforded a cyclic compound with the composition $[Cp*Rh\{^tBuN(Te)P(\mu-N^tBu)_2P(Te)NBu^t\}_2(\mu-Te)]$. ¹²¹

The reaction of iridium carbonyl clusters with diphenyl ditelluride is very selective with a very sluggish rate, requiring 20 h of continuous stirring to complete the reaction. The refluxing of PhTeTePh and [Ir₆(CO)₁₅]²⁻ gave the anionic cluster [Ir₆(CO)₁₄(µ-TePh)] in tetrahydrofuran solution. ¹²² By applying the same experimental conditions with a 2:1.5 mole ratio of PhTeTePh with $\left[\text{Ir}_6(\text{CO})_{15}\right]^{2-}$ yielded exclusively the neutral product [Ir₆(CO)₁₃(μ-TePh)₂]; however, similar reactions with other chalcogenides yielded a mixture of products in which a similar neutral product was isolated in very poor yield via a solvent extraction methodology. The best strategy applied to isolate the above neutral complex was the reaction of [Ir₆(CO)₁₆] with PhTeTePh in refluxing toluene. The same reaction with other chalcogenides was much less effective in terms of isolation of the cluster compound (Scheme 11).122

In an attempt to synthesize hyper-valent iridium complexes, organotellurium compounds have played a key role to isolate such complexes. In this context, an oxidative addition of Ph2Te2 with the Ir(1) compound [Cp*Ir(ppy)(solv)]+ was applied. 123 Surprisingly the reaction led to the formation of the Ir(III) η^1 -ditelluride complex [Cp*Ir(ppy)(η^1 -Te₂Ph₂)](OTf). It is noteworthy that isolation of a complex with the coordination η^{1} -REER is very much less common, e.g. $[Cp*Mn(CO)_2]_2(\mu-\eta^1-REER)$, ¹²⁴ but it is strongly believed that these coordination modes derived compounds take part as an intermediate in the oxidative addition of R_2E_2 (E = S, Se, Te) to give the Pd(0) and Pt(0) precursors. 125 The proven potency from the dynamic nature of tellurium metal can be encountered with

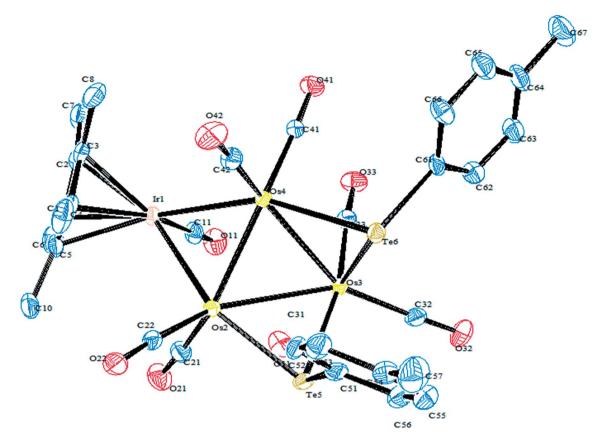


Fig. 8 Crystal structure of $[Cp*IrOs_3(\mu-H)_2(\mu-Tetol)_2(CO)_7]$ (redrawn from ref. 117)

Scheme 10 Reaction of $[(Cp^*)_2Rh_2(\mu-CO)\mu-\eta^2:\eta^2C_2(CF_3)_2]$ with R_2Te_2 (R = Me, Et, i pr, Ph, Fc).

the ease of synthesis of homo- and heterometallic complexes with iridium compounds derived from the tellurolate ligand system. As an example, the oxidative addition product $[Cp*Ir(CO)(TeTol)_2]$ upon reaction with $[(Cp*MCl)_2(\mu-Cl)_2]$ (M=Rh, Ir) yielded a stereoisomer of the binuclear complexes $[Cp*Ir(CO)(\mu-TeTol)_2MCp*Cl]Cl$ (M=Rh, Ir) (Fig. 9) bridged with telluride systems (Scheme 12). Interestingly, a similar reaction of $[Cp*Ir(CO)(TeTol)_2]$ with $[Cp*RuCl_4(\mu_3-Cl)_4]$ and

Scheme 11 Oxidative addition reactions of diphenylditellurides with iridium carbonyl clusters.

[RuH(COD)(CH₃CN)](BPh₄) resulted in the formation of the tetranuclear [Cp*IrCl{ μ -Te(η ⁶-Tol)RuCp*]₂RuCp*(CO)]Cl₂ and binuclear [Cp*Ir(μ -H)(μ -TeTol)₂Ru(CO)(COD)]BPh₄ complexes, respectively (Scheme 12). ¹²⁶

4.3 Palladium and platinum

Tellurium complexes with palladium and platinum phosphine precursors are comparatively more stable than any other precursors. The main stability factor is the π bonding involving d_{xy} orbitals of the palladium and platinum metals with the available empty orbitals of phosphine, which results in the extent of σ overlapping being stronger in the phosphine complexes. Hence, these complexes play a crucial role in a reduction of the electron density around the metal center, which is enhanced due to the ease of donation of the lone pair available on the tellurium center.

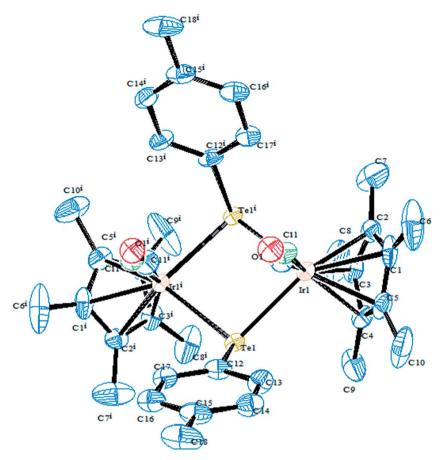


Fig. 9 Crystal structure of [Cp*Ir(CO)(μ-TeTol)₂IrCp*Cl] (redrawn from ref. 126).

4.3.1. Reactivity of various tellurium systems with palladium and platinum nonchelated phosphine precursors. T. B. Rauchfuss and Rheingold synthesized a series of complexes of the type $[Pt(ETeC_6H_4)(PPh_3)_2]$ (E = S; Se; Te) derived from ligand systems like alkeneditellurides and 1,2 benezeneditellurides, ¹²⁹ which represent the first examples of

mixed chalcogenides ligand systems (Scheme 15). Various complexes of the type [MCl{TeC $_5$ H $_3$ (3-R')N}(PR $_3$)] (M = Pd, Pt; R = PEt $_3$, Ph $_2$ Me) have been derived by cleaving of the bond between metal bridged chlorides, *e.g.*, the reaction of [M $_2$ Cl $_2$ (μ -Cl $_2$ (PR $_3$) $_2$] (M = Pd, Pt; R = PEt $_3$, Ph $_2$ Me) with two equivalent of NaTe(R'C $_5$ H $_3$ N) (R' = H, Me) (Scheme 13). ^{130,131}

Scheme 12 Synthesis of various heterometallic complexes using [Cp*Ir(CO)(TeTol)₂].

This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

Open Access Article. Published on 05 dhjetor 2017. Downloaded on 4.11.2025 5:11:00 e paradites.

RSC Advances

$$\begin{aligned} Na_2PdCl_4 + 2NaTeR' & \longrightarrow & [PdCl(TeR')]_n \\ & & \downarrow & PR_3 \\ & & & PR_3 \\ & & \downarrow & PR_3 \\ & & \downarrow$$

Scheme 13 Reactions of $[M_2Cl_2(\mu-Cl)_2(PR_3)_2]$ with various sodium salts of tellurolate ligands

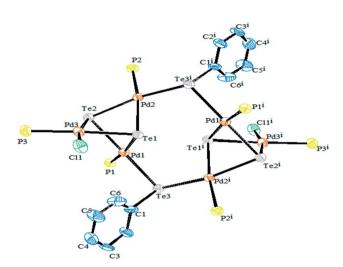


Fig. 10 Crystal structure of [Pd₆Te₆Cl₂(PEt₃)₆] (redrawn from ref. 138).

Performing an oxidative addition reaction between [Pd(PPh₃)₄] and various diaryl ditelluride ligand systems yielded binuclear products with the composition [Pd₂(μ-TeAr)₂ (TeAr)₂(PPh₃)₂].¹³² In the latter complex, both terminal and bridging positions are occupied with aryl tellurols (Scheme 13).

On the other hand, an alike reaction upon performing with $[M(PPh_3)_4]$ (M = Pd, Pt) with various ligand systems, such as CF₃Te₂ Th₂Te₂, Ph₂Te₂, afforded mono-, bi-, tri-, and hexanuclear complexes [Pd₆Te₆Cl₂(PEt₃)₆] (Fig. 10) depending on the nature of the solvent (Schemes 14 and 16).21,133-138 It has been well established that the bonding energy between C-Te and Te-Te is quite comparable compared to other analogs of the chalcogen family, and therefore the reaction with tellurium ligands afforded polynuclear compounds. Tanaka et al. found that upon performing an oxidative addition between Pd(0) or Pt(0) species with various telluroethers, cleavage of the C-Te bonds take place, leading to isolation of a compound with the composition $[M(Ar)(TeAr)(PEt_3)_2]$ (M = Pd, Pt)(Scheme 14).22

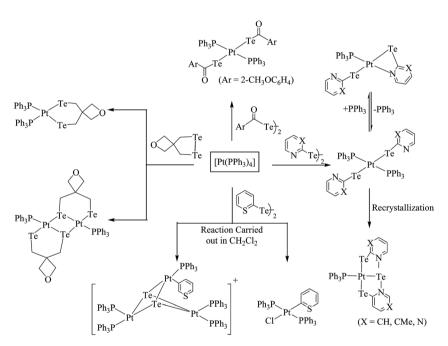
Molecular orbital calculations also concluded that the activation energy barrier for the oxidative addition of dichlacogenides to $[M(PH_3)_2]$ decreases in the order S > Se > Te (in terms of the addition of E-E bonds). 125 Hence, the exothermicity of the reaction is also decreased with respect to the M-E-R bond strength. This statement quantifies that the oxidative addition of Te-Te bonds to low valent metal precursors is very simplistic compared to with the rest of the other dichalcogenides analogs and results in a complex (mononuclear) that is less stable compared to thiolato and selenolato complexes. However, the tendency for isolation of the dimerized product follows the reverse trend (S < Se < Te). Therefore, it can easily be concluded that binuclear complexes are higher in tellurium system compared to the other analogs.

Recently, Jain et al. performed an oxidative addition among [Pt(PPh₃)₄] and hemilabile pyridyl ditelluride (C₅H₄N)₂Te₂ to isolate novel complexes with the composition [Pt{TeC₅H₃(3-R) N_{2} Te(PPh₃)] (R = H, Me) (Scheme 16) along with an expected oxidative addition product.7 The former complex was the first example of its own type of tellurium (0) acting as a ligand system

Scheme 14 Oxidative addition of $[Pd(PR_3)_4]$ (R = Et, Ph) with various diorganoditellurides.

$$\begin{array}{c} Ph_{3}P \\ PTe \\ PPh_{3} \\ Ph_{3}P \\ PPh_{3} \\ Ph_{3}P \\ Ph_$$

Scheme 15 Reactions of [PtCl₂(PPh₃)₂] with various sodium/lithium salts of aryl tellurolates



Scheme 16 Oxidative addition reactions of [Pt(PPh₃)₄] with various diaryl ditellurides.

(Fig. 11). The serendipitous isolation of the latter one was also justified by the substitution reaction of [PtCl₂(PPh₃)₂] with the $2NaTeC_5H_3(3-R)N$ (R = H, Me) (Scheme 15). The crystal structure of [Pt{TeC₅H₃(3-R)N}₂Te(PPh₃)] showed that the bare tellurium was directly coordinated to the metal center and flanked by the two pyridyl rings (Fig. 5). Density function calculations highlighted that the extra stability of this complex was due to the aromatic nature of the five-membered ring formed by Pt-Te-C-N-Te. While similar reactions in the case of palladium led to isolation of an expected oxidative addition product,8 which on keeping for a longer time period in CDCl3

solution, yielded a green product, [PdCl{Te(Cl)₂C₅H₄N}(PPh₃)], in which tellurium is oxidized from a +2 to a +4 oxidation state by the attachment of two chlorine atoms (Scheme 7).

A new class of platinum(0) phosphine precursors $[Pt(\eta^2 - \eta^2 - \eta^2)]$ norborene)(PPh₃)₂] has also been applied to study oxidative addition with bulky ditellurides of dibenzobarrelenyl and norborene. The reaction afforded the formation of four- and fivemembered telluraplatinacycles compounds $[Pt(Te \cap C)(PPh_3)_3]$ in the presence of excess triphenyl phosphine. 139

4.3.2. Reactivity of various tellurolates with palladium and platinum chelated phosphine precursors. The reactivity of the RSC Advances Review

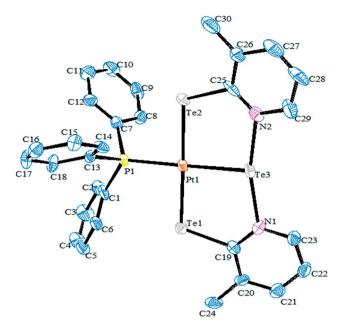


Fig. 11 Crystal structure of $[Pt{TeC_5H_3(3-Me)N}_2Te(PPh_3)]$ (redrawn from ref. 7).

Scheme 17 Reactions of $[Pt_2(dppm)_3]/[PtCl_2(dppm)]$ with dipyridyl ditellurides/pyridyl tellurolates, respectively.

chelating phosphine diphenylphosphinomethane ligand is comparatively higher than that of other chelating phosphines. The main striking factor of the reactivity is strain, caused by the projection of the four-membered ring. The cone angle drawn on P-M-P ranges from 70-72°, which means it is highly acute. To overcome the acuteness, the complementary angle is widened in space to provide the space to react with the incoming ligand. In the case of the substitution reaction between [PtCl₂(dppm)] and the sodium salt of aryl tellurolates (aryl = Ph, Tol, Mes), cis configured mononuclear complexes were obtained. 133,140,141 However, a similar substitution and an oxidative addition with hemilabile ligand systems, like derivatives of 2 and 4-dipyridylditelluride, yielded an expected mononuclear complex as well as C-H activated [Pt{Ph2- $PCH(TeC_5H_3(3-R)NPPh_2_{2})]$ (R = H, Me) (Scheme 17).^{8,131} The latter complexes had a distorted square planer geometry around the metal, with the angle around the activated carbon center varying from 100-126°, which shows an allylic configuration of

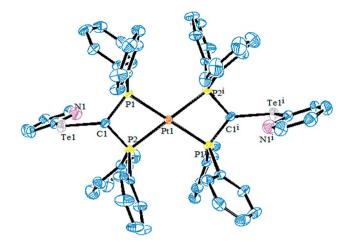


Fig. 12 Crystal structure of $[Pt{PPh_2CH(TeC_5H_4N)PPh_2}_2]$ (redrawn from ref. 8).

the carbon center (Fig. 12). It can be concluded that the reactivity of the same palladium phosphine precursors with 4-pyridyl tellurolates to lead to the tetranuclear compound $[Pd_2(\mu-Te)(\mu_2-TeC_5H_4N)(4-TeC_5H_4N)(\mu-dppm)]_2$ (ref. 131) can be rationalized by the high reactivity of the palladium phosphine precursor and tellurium-based ligand.

However, the chemistry related to diphenylphosphinoethane with tellurium systems seemed to be as expected. This may be due to the strainless five-membered ring project by "dppe" ligand. On performing an oxidative addition/substitution reaction between $[Pt(dppe)_2]/[PtCl_2(dppe)]$ and the aryl ditellurides/ sodium salt of aryl tellurolate (aryl = py, Ph, tol, Mes, Thienyl), a mononuclear product was isolated. Ph, tol, in the case of the methyl-substituted telluropyridne ligand system was a complex with the composition $[PtCl\{TeC_5H_3(3-Me)N\}(dppe)]$ isolated, which existed in equilibrium with the moiety $[Ptf(\kappa^2-mem)]$

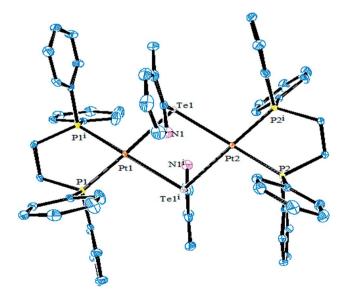


Fig. 13 Crystal structure of [Pd $_2\{\mu TeC_5H_3(3-Me)N\}_2(dppe)$] (redrawn from ref. 8).

Scheme 18 Reactions of $[Pd(P\cap P)_2]$ and $[PdCl_2(P\cap P)]$ $(P\cap P=dppe,dppp)$ with Ar_2Te_2 $(Ar=\{C_5H_3(3-R)N\},\{C_5H_2(4,6-R)N\}$ (R=H,Me)) and their corresponding sodium salts.

 $TeC_5H_3(3-Me)N$ {(dppe)] $^+$. Conductometric measurements were performed to correlate the nature of the complex in solution and it was reported that in the case of highly polar solvents, like methanol and acetonitrile, the nature of the complex was a 1:1 electrolyte. Surprisingly, the palladium chemistry is totally

different from their platinum analogs. On performing a similar reaction between palladium phosphine precursors [Pd(dppe)₂]/[PdCl₂(dppe)] with hemilabile ligand systems, like pyridyl (Fig. 13) and pyrimidyl ditelluride, 8,48,141 resulted the rapid conversion of mono- to trinuclear complex in a chlorinated solvent (Scheme 18). This result shows the high susceptibility of tellurium ligands toward the chlorinated solvents.

In the case of platinum precursors of diphenylphosphinopropane (dppp), like [Pt(dppp)₂]/[PtCl₂(dppp)], performing a similar reaction as mentioned above with various hemilabile ligand systems afforded mono- and trinuclear products.8,48 However, the reaction with palladium phosphine precursors yielded only trinuclear products in a moderately good yield. A mechanistic study was performed to isolate the trinuclear product by the mild reaction between [PdCl₂(dppp)] and [Pb(TeC₅H₄N)₂] (Scheme 19).8 Upon recording the ³¹P{¹H} NMR within 2 h stirring of the reaction, there was a single resonance corresponding to mononuclear complexes, which again on further stirring for up to 4-5 h at the same temperature showed two quite shielded resonances, corresponding to bi- and trinuclear products. By the extraction of the product in dichloromethane, the trinuclear product was exclusively isolated. The formation of bi- and trinuclear products was also characterized with single crystal X-ray analysis.

Weigand et al. had applied a new class of Pt(0) precursors [Pt(dppn)(nb)] derived from the chelating phosphine

Scheme 19 Reactions of [PdCl₂(dppp)] with the lead salts of 2-pyridine chalcogenolate.

Scheme 20 Oxidative addition reaction between [Pt(dppn)(nb)] with various cyclic and acyclic diorgano ditellurides.

Scheme 21 Various coordination modes in hemilabile tellurolate ligand systems

diphenylphosphineno naphthalene (Ph $_2$ P-napthyl-PPh $_2$). These precursors showed a remarkable reactivity toward ditelluride systems. Upon reaction with various cyclic/saturated, acyclic/saturated, and cyclic/unsaturated ditellurides, the momonuclear [Pt(Te $_2$ C $_5$ H $_8$ O)(dppn)] and binuclear [Pt(Te $_2$ C $_5$ H $_8$ O)(dppn)] products were isolated, which on keeping for a prolonged time period in the solvent decomposed into several products (Scheme 20). It was noticed that alkyl tellurides result in the products by the cleavage of Te–Te bonds, however aryl telluride derives the products not only by the Te–Te bond cleavage but also by Te–C bond cleavage. 136

Notable attention^{7,8} has been drawn by the outcome of the above-mentioned document conclusion on hemilabile ligands. The discussion focused on complexes derived by hemilabile organochalcogens, which have been the subject of considerable interest due to their rich coordination chemistry. In fact, as a concluding remark, the coordination potential of hemilabile ligand systems, especially those that possess α heteroatoms as well as their corresponding anions, referred to as chalcogenolates, is immense.^{1,9,10} There is indeed a considerable versatility in the various coordination modes of these molecules, which may include monodentate binding through E or through heteroatoms, bridging through a single E, bridging through both E and N, or chelating *via* the E to N backbone.^{48,134} All these coordination modes, either alone or in combination, have been

observed or assigned on the basis of spectroscopic and/or crystallographic evidence of both homo- and heteroleptic metal complexes (Scheme 21).

Metal tellurides

The binuclear complexes $[M_2(\mu-Te)_2(dppe)_2]$ (M = Pd, Pt) (Fig. 14) act as a powerful metallophilic ligand to provide a binding site for various transition metals, d10 systems, and lanthanide metal centers. The former complexes can be isolated by the reaction between M2+, dppe, and NaTeH in a N,N-dimethylformamide and acetonitrile mixture.142 The reaction of [Pt(CH₃CN)₄(NO₃)₂] with a similar composition to the former complexes led to the formation of pentanuclear complexes [Pt ${Pd_2(\mu-Te)_2(dppe)_2}_2]^{2+}$ (ref. 142) (Fig. 15) in which the platinum metal center was coordinated with all four bridging tellurido linkages. Similarly, various trinuclear products have been isolated by the reaction between M^{2+} , $P \cap P$, and NaTeH in N,Ndimethylformamide for more than 20 h stirring (Scheme 22).143 Undoubtedly, strong coordinating solvents, like DMF, CH₃CN, may enable the coordination of tellurium to further platinum moieties with ease, resulting in tri- to pentanuclear products. 143-146 Morley et al. also isolated the trinuclear product $[Pt_3{(\mu-Te)_2(dppe)_2}_2]^{2+}$ by the oxidative addition of $[Pt(dppe)_2]$ and vitreous tellurium under refluxing for 5 h.147 The isolation

Review

Fig. 14 Crystal structure of $[Pd_2(\mu-Te)_2(dppe)_2]^{2+}$ (redrawn from ref. 142).

C25

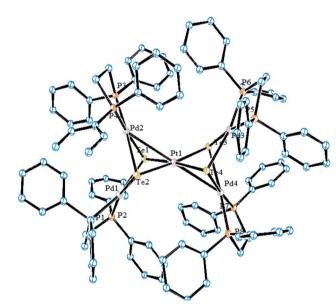


Fig. 15 Crystal structure of $[Pt{Pd_2(\mu-Te)_2(dppe)_2}_2]^{2+}$ (redrawn from ref. 142).

of the trinuclear product *via* an oxidative addition mode is unprecedented and could be rationalized by the fact that the higher nucleophilicity of tellurium makes it highly susceptible to the nucleophilic attack of chlorinated solvents.

Redox studies of these complexes were studied by cyclic voltammetry. 142,144,145 In the case of telluride bridged cluster

complexes, it all depends upon the nature of the phosphine and metal center. The cyclic voltammograms of dppe-derived complexes showed a reversible nature, whereas it was irreversible in other cases. The order of chemical reversibility followed the trend: dppe > dppp > dppm.

Cluster compounds like $[PPh_4]_2[Pd(Te_4)_2]$ were synthesized by refluxing the palladium precursor with tellurium powder.¹⁴⁸ This intriguing complex exists in two crystallographic forms: the α and β forms. The triclinic α and orthorhombic β forms were separated using ethylene diamine and ether solvents, respectively. ^{148–150} Similarly, the complex $[Li_4(en)_{10}][Pd_6(\mu_3-Te)_8]$ was formed by the reaction of [Pb₂Te₃]²⁻ with [PdCl₂(PPh₃)₂].¹⁵¹ Contrary to the palladium precursors, the platinum analog resulted in the cluster complex [Pt4Te4(Te3)6]4-, which was comprised of a Pt₄Te₄ cubane core with a distorted octahedral configuration around the platinum atom. 152 Recently, several platinum group cluster complexes were isolated by refluxing TeCl₄ with the corresponding metal precursors. ^{153–156} The high nucleophilicity of the terminal telluride in mononuclear complexes makes them highly susceptible for further reaction with coordinative unsaturated complexes like the Pt(0) and Pd(0) precursors. Thus, when the oxidative addition product [CpIr(CO)(TeTol)₂] was subjected to reaction with two equivalent of $[M(PPh_3)_4]$ (M = Pd, Pt) (Scheme 23), a compound of the type $[CpIr(CO)(\mu_3-Te)_2\{MTol(PPh_3)\}_2]$ was isolated, while the similar reaction with one equivalent of [Pt(PPh₃)₄] yielded the intermediate product [CpIr(CO)(μ-Te)(μ-TeTol){PtTol(PPh₃)}]. 157 The latter complexes upon reaction with [Pd(PPh₃)₄] derived the heterometallic complex [CpIr(CO)(μ-Te)₂{PdTol(PPh₃)}

RSC Advances Review

$$K_{2}PtCl_{4} + PP + 2NaTeH \xrightarrow{CH_{3}CN + C_{2}H_{5}OH} Pt_{3}(\mu_{3}-Te)_{2}(PP)_{3}]^{2+}$$

$$[Pd(NO_{3})_{2}] + PP + 2NaTeH \xrightarrow{CH_{3}CN + C_{2}H_{5}OH} Pt_{3}(\mu_{3}-Te)_{2}(PP)_{3}]^{2+}$$

$$2M_{2}(\mu_{2}-Te)_{2}(PP)_{2}\}_{2} + [M(CH_{3}CN)_{4}](NO_{3})_{2} \xrightarrow{DMF} [M\{M_{2}(\mu_{2}-Te)_{2}(PP)_{2}\}_{2}]^{2+}$$

$$(M = Pd, Pt) (P^{O}P = dppe, dppb)$$

Scheme 22 Various approached used for the synthesis of high nuclearity complexes.

Scheme 23 Synthesis of various heterometallic complexes bridged with telluride systems.

{PtTol(PPh₃)}] (Fig. 16), which was formed by the facile inversion of the Pd(0) center in to a Te–Tol bond in the complex [CpIr(CO)(μ -TeTol){PtTol(PPh₃)}].^{126,157}

Similarly, [Pt(TeR)₂(dppe)] (R = Ph, Fc) upon reaction with a rhenium carbonyl cluster yielded heterometallic tellurolato bridged complexes [(dppe)Pt(μ -TeR)₂ReCl(CO)₃] (R = Ph, Fc). ^{158,159}

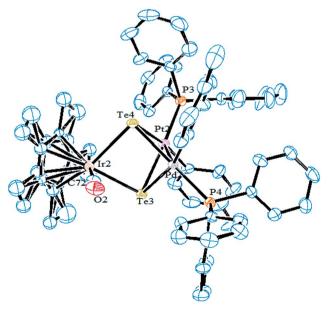


Fig. 16 Crystal structure of $[CpIr(CO)(\mu-Te)_2{PdTol(PPh_3)} {PtTol(PPh_3)}]$ (redrawn from ref. 157).

6. Applications

6.1 Catalysis

The efficient and selective transformation of various functional groups have taken place with sodium hydrogen telluride (NaHTe) and Na₂Te, which have been reported in further applications in recent years. $^{160-164}$ In particular, the reduction of aromatic aldehydes to alcohols is the most important transformation by Na₂Te in NMP (*N*-methyl-2-pyrorolidone). 165,166 Similarly, an attempted reduction of aromatic nitriles serendipitously led to the pharmacologically important product 7-diaza-9*H* purines in low yields (Scheme 24). $^{166-168}$

One more striking example of the conversion by debromination of vic-dibromides to alkenes is that catalyzed by *p*-methoxyphenyltelluride. Again on reinvestigation, it was found that the more electron-rich diorganoditellurides associated with reducing agents, like glutathione (GSH) or sodium ascorbate, are better debrominating agents than the previous reaction (Scheme 24).¹⁶⁹⁻¹⁷¹

Recently, it was found that ruthenium complexes derived by various telluroethers, like $[(\eta^6\text{-}C_6H_6)Ru(L)](PF_6)$ (L = 2-

R
$$R'$$
 CHO
 Na_2Te
 $NMP, 80^0$
 R'
 CH_2OH
 $R = R' = H$
 $R = H, R' = Me, ^iC_3H_7$
 $R = Me, R' = H$

$$Ar-C=N \xrightarrow{Na_{2}Te} NMP, 100^{\circ}C \xrightarrow{N} N$$

$$Ar=Ph, tolyl$$

$$Ar = N \xrightarrow{Na_{2}Te} N$$

$$Me$$

Scheme 24 Schematic representation of various reactions catalyzed by organotellurium analogs.

Scheme 25 Oxidation of alcohols through ruthenium tellurolate complexes.

MeSC₆H₄CH=NCH₂CH₂EC₆H₄-R; R = H, E = S, Se; 2-MeSC₆-H₄CH₂NHCH₂CH₂EC₆H₄-R; R = OMe, E = Te), have proven potential as an excellent catalyst in the oxidation of primary and secondary alcohols. The TON values for the oxidation of various alcohols, like cyclic, acyclic, and benzylic, ranged from 7.8–9.6 \times 10⁴. Strikingly, the complex (η^6 -C₆H₆)[Ru(2-MeSC₆H₄CH₂-NHCH₂CH₂TeC₆H₄-OMe)](PF₆) appeared to be the most efficient in this process with the highest % conversion (98%). A comparative study of all the ruthenium complexes derived by various chalcogen analogs showed that the catalytic efficiency varies in the order of Te > Se > S. This fact can be rationalized by the softer ligand making it easier to form the intermediate oxy species Ru=O, which plays a pivotal role in any oxidation reaction (Scheme 25).

The second important class of reaction, *i.e.*, transfer of hydrogen reaction, is also catalyzed by the complexes $[(\eta^6-C_6H_6)$

$$\begin{array}{ccc} O & & \underbrace{[(n^6\text{-}C_6H_6)Ru(L)^{2^+}]} & OH \\ 2\text{-propanol, KOH} & & & R' \\ & & & L = 2\text{-MeSC}_6H_4CH=NCH}_{2})_2Te \\ & & & & 2\text{MeSC}_6H_4CH_2NH_2CH}_{2})_2Te \end{array}$$

Scheme 26 Transfer of hydrogen reaction catalyzed by ruthenium tellurolate complexes.

Ru(L)](PF₆) (L = 2-MeSC₆H₄CH=NCH₂CH₂EC₆H₄-R; R = H, E = S, Se; 2-MeSC₆H₄CH₂NHCH₂CH₂EC₆H₄-R; R = OMe, E = Te) (Scheme 26). In the case of acetophenone, the conversion efficiency was up to 98%, while in various other aliphatic secondary ketones, it ranged up to 90%. Similarly as an oxidation reaction, the catalytic efficiency of these reactions also varies in the same order. An earlier well-established catalyst for this reaction was Ru(II) complexes of 2-(aminomethyl)pyridine phosphine with a TOF of 10^{-5} h⁻¹ and up to 97% conversion in 2-propanol using NaOH as a base. Comparatively, a half sandwich ruthenium complex of the above-mentioned composition derived with various telluroethers of pyrrolidine, morpholine, and benzotriazole moieties^{62,172,173} also showed a similar efficiency rate with a short reaction time.

6.2 Suzuki and Heck reaction

Due to the air and moisture sensitivity of phosphorus-derived complexes, there is increasing interest in phosphine-free ligands¹⁷⁴⁻¹⁷⁷ for the Suzuki–Miyaura reaction. With this prospect, palladium chalcogenolate¹⁷⁸ complexes are considered as existing substituents for C–C coupling reactions. Various coupling reactions are primarily catalyzed by palladium selenated and tellurated compounds. An early study performed by Prof. A. K. Singh *et al.* showed that palladium tellurolate complexes are as efficient as their selenium analogs.¹⁷⁹ The conversion was found to be up to 85%, particularly for activated 1-bromo-4-nitrobenzene (Scheme 27).

It is well documented that Pd–Se bonded compounds have promise for the Heck reaction.¹⁷⁸ Within this continuation, a Schiff base-derived telluroether palladium complex showed good selectivity for the isolation of a *trans*-alkene product. The catalytic activity depended on the nature of the halide, while the electron-withdrawing groups on the aryl ring increased the reaction rate. For aryl bromides, a very small amount of complex (0.001 mmole) was sufficient to catalyze the Heck reaction (Scheme 27).¹⁷⁹

6.3 Material science

Binary systems of Pt and Te (as a combination of metal and semiconductor) are important precursors for their application in the field of sensors and magnetic memories. ^{180–182} In

$$R \xrightarrow{\qquad \qquad } X + (HO)_2 B \xrightarrow{\qquad \qquad } \frac{PtCl(L1-H)/[PdCl_2L2)_2]}{K_2CO_3, 24h, 100^0 C} R \xrightarrow{\qquad \qquad } Y$$

$$R \xrightarrow{\qquad \qquad } X + \underbrace{\qquad \qquad } Y \xrightarrow{\qquad \qquad } \frac{PtCl(L1-H)/[PdCl_2L2)_2]}{K_2CO_3, 24h, 100^0 C} \xrightarrow{\qquad \qquad } Y$$

$$X = Br, I \qquad Y = COOH, Ph, COOMe \qquad \qquad R = H, Me, CN, CHO, NO_2, Cl$$

$$\begin{split} L1 &= p\text{-}OMeC_6H_4(TeCH_2CH_2N = C\{2\text{-}CH_3\}C_{10}H_6OH)\\ L2 &= p\text{-}OMeC_6H_4(Te\text{-}benzotriazole) \end{split}$$

Scheme 27 Representation of palladium-platinum tellurolate catalyzed Suzuki and Heck reactions.

RSC Advances Review

particular, the composites of PtTe2 are known to enhance the Seebeck coefficient of PbTe bulk particles. 183 Similarly, multicomponent rod-shaped mixed composites FePt-PtTe2 have exhibited high coercivity (Hc > 500).184 Pt3Te4 also has shown a catalytic ability in the transformation of nitrophenol to aminophenol. 185 Platinum group metal chalcogen materials are also prominently used for low resistance ohmic contacts. These thermodynamically stable contacts are very crucial for device durability. At the interface of Pt/CdTe diffusion couples, a non planner reaction layer of intermetallic CdPt and Pt-Te is formed.186

Platinum group metal chalcogenides comprise various binary and ternary chalcogenide materials. Undoubtedly, the preparatory methods dealing with platinum group metal sulfide and selenide materials applying single source molecular precursor's methods are greater in number with respect to their tellurium precursors. 187 The complex [PdCl{Te(3-MeC₅H₃-N) $\{(PR_3)\}$ (R = propyl, Ph) upon heating in a furnace at 340 °C under an argon atmosphere yielded a molecular precursor of the binary composition PdTe. 130 The latter compositions supported on carbon have relevance in various catalytic reactions used at an industrial scale. 188 However, complexes like [PdCl2(4-MeOC₆H₄TeCH₂CH₂N(CH₂CH₂)₂O)] also result in the formation of Pd-Te nanoparticles of 5 nm diameter. 189 A similar composition has also been documented by heating the hexanuclear complex at >250 °C.138 Thiolate- and selenolate-derived palladium complexes with the composition $[Pd_2(\mu-ER)_2(\eta^3-C_4H_7)]$ (E = S, Se) upon refluxing in xylene solution afforded Pd_4E (E =S, Se); however, the tellurolate analogs resulted in the formation of Pd₃Te₂ composites at room temperature. 190 Recently, a composition of Pd₇Te₃ has been isolated upon refluxing the complex [PdCl₂(TeMes₂)₂] in xylene solution.⁹³

6.4 Biological importance

Upon evaluating the biological activity of tellurium-derived ruthenium complexes, it has been found that the complexes are quite potent as anticancer agents. Recently, a biological study of the complexes $[(\eta^6-p-Me\ C_6H_4Pr^i)_2Ru_2(\mu-TeC_6H_5)_3]PF_6$ and $[(\eta^5-C_5H_5)_2Ru_2(\mu-TeC_6H_5)_3]PF_6$ (ref. 96) showed their good biological activity on normal and human cancer cell lines. The former complexes are even cyto-toxic in nature, which revealed their strong selectivity to cancer cells compared to normal ones. These promising outcomes of ruthenium complexes as anticancer agents deserves more exploration toward various other biological activities.

Conclusions

The versatile reactivity of organotellurolate ligands is quite evident from the ongoing discussions and reports in the literature. Their remarkable reactivity is derived due to presence of soft (tellurium) and hard donor atoms (N, O, S) in various ligands derived from organic moieties, like thinyl, pyridyl, furan, and pyrimidyl. In the meantime, one in particular cannot be declined: that the notable reactivity may also arise due to the comparable bond energies of Te-Te and Te-C bonds, which

facilitates a competitive cleavage among them. Furthermore, among all the other chalcogens, the easy availability of lone pairs and high polarizability makes them great building block synthons for various heterometallic and high nuclearity metal complexes. It is hoped that this perspective will support further enthusiasm in this field and provide momentum for further research in this field to help establish their potential application in various fields.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

One of the authors (RSC) is grateful to DST for the financial support under the DST young scientist scheme YSS/2014/ 000797. We thank Dr V. K. Jain for his encouragement with this work and for his valuable suggestions for the preparation of this article.

References

- 1 (a) P. D. Akrivos, H. J. Katsikis and A. Koumoutsi, Coord. Chem. Rev., 1997, 167, 95; (b) P. D. Akrivos, Coord. Chem. Rev., 2001, 213, 181.
- 2 P. J. Blower and J. R. Dilworth, Coord. Chem. Rev., 1987, 76,
- 3 J. R. Dilworth and N. Wheatley, Coord. Chem. Rev., 2000,
- 4 W. Levason, S. D. Orchid and G. Reid, Coord. Chem. Rev., 2002, 225, 159.
- 5 (a) S. Dey, V. K. Jain, A. Knoedler, A. Klein, W. Kaim and S. Zalis, Inorg. Chem., 2002, 41, 2864; (b) S. Dey, L. B. Kumbhare, V. K. Jain, T. Schurr, W. Kaim, A. Klein and F. Belaj, Eur. J. Inorg. Chem., 2004, 4510.
- 6 A. K. Singh and S. Sharma, Coord. Chem. Rev., 2000, 209, 49.
- 7 (a) G. Kedarnath and V. K. Jain, Coord. Chem. Rev., 2013, 257, 1409; (b) R. S. Chauhan, G. Kedarnath, A. Wadawale, A. Munoz-Castro, R. Arratia-Perez, V. K. Jain and W. Kaim, Inorg. Chem., 2010, 49, 4179.
- 8 (a) R. S. Chauhan, G. Kedarnath, A. Wadawale, A. L. Rheingold, A. Munoz-Castro, R. Arratia-Perez and V. K. Jain, Organometallics, 2012, 31, 1743; (b) R. S. Chauhan, G. Wadawale, A. M. Z. Slawin and V. K. Jain, Dalton Trans., 2013, 42, 259.
- 9 T. Wirth, Organoselenium Chemistry: Modern Developments in Organic Synthesis, in Topics in Current Chemistry, Springer-Verlag, Berlin, 2000, vol. 208.
- 10 S. Narayan, V. K. Jain and B. Varghese, J. Chem. Soc., Dalton Trans., 1998, 2359.
- 11 (a) D. Dakternieks, R. D. Giacomo, R. W. Gable and B. F. Hoskins, J. Am. Chem. Soc., 1988, 110, 6541; (b) D. Dakternieks, R. D. Giacomo, R. W. Gable and B. F. Hoskins, J. Organomet. Chem., 1989, 377, 43.
- 12 (a) A. K. Singh, V. Srivastava, J. K. Basumatary, T. P. Singh and A. K. Saxena, Phosphorus, Sulfur Silicon Relat. Elem.,

Review

1994, **89**, 31; (*b*) A. K. Singh, V. Srivastava, J. K. Basumatary, T. P. Singh and A. K. Saxena, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1993, **85**, 175.

- 13 J. E. Drake, R. J. Drake, L. N. Khasrou and R. Ratnani, *Inorg. Chem.*, 1996, 35, 2831.
- 14 V. P. Ananikov and I. P. Beletskaya, Org. Biomol. Chem., 2004, 2, 284.
- (a) V. P. Ananikov, M. A. Kabeshov, I. P. Beletskaya,
 V. N. Khrustalev and M. Y. Antipin, *Organometallics*, 2005,
 24, 1275; (b) I. P. Beletskaya and V. P. Ananikov, *Eur. J. Org. Chem.*, 2007, 3431.
- 16 L. B. Han, N. Choi and M. Tanaka, J. Am. Chem. Soc., 1997, 119, 1795.
- 17 (a) N. Nakata, R. Uchiumi, T. Yoshino, T. Ikeda, H. Kamon and A. Ishii, Organometallics, 2009, 28, 1981; (b) A. Ishii, Y. Yamaguchi and N. Nakata, Dalton Trans., 2010, 39, 6181; (c) A. Ishii, N. Nakata, R. Uchiumi and K. Murakami, Angew. Chem., Int. Ed., 2008, 47, 2661.
- 18 Comprehensive Organometallic Chemistry II, ed. R. J. Puddephatt, E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1st edn, 1995, vol. 9, p. 1.
- 19 Catalytic Heterofunctionalization, ed. A. Togni and H. Grützmacher, Wiley-VCH: Weinheim, 2001, p. 1.
- 20 M. E. Cucciolito, V. De Felice, G. Roviello and F. Ruffo, *Eur. J. Inorg. Chem.*, 2011, 457.
- 21 R. Oilunkaniemi, R. S. Laitinen and M. J. Ahlgren, J. Organomet. Chem., 2001, 623, 168.
- 22 L. B. Han, N. Choi and M. Tanaka, J. Am. Chem. Soc., 1997, 119, 1795.
- 23 A. Khanna, B. L. Khandelwal, A. K. Saxena and T. P. Singh, *Polyhedron*, 1995, 14, 2705.
- 24 A. K. Singh, M. Kadarkaraisamy, M. Mishra, J. Sooriyakumar, J. E. Drake, M. B. Hursthouse, M. E. Light and J. P. Jasinski, *Inorg. Chim. Acta*, 2008, 361, 1426–1436.
- 25 G. Singh, A. K. Singh, P. Sharma, J. E. Drake, M. B. Hursthous and M. E. Light, J. Organomet. Chem., 2003, 688, 20–26.
- 26 P. R. Kumar, A. K. Singh, R. J. Butcher, P. S. Shrama and R. A. Toscano, *Eur. J. Inorg. Chem.*, 2004, 1107–1114.
- 27 P. R. Kumar, S. Upreti and A. K. Singh, *Inorg. Chim. Acta*, 2008, 361, 1426–1436.
- 28 A. Kumar, M. Agarwal, A. K. Singh and R. J. Butcher, *Inorg. Chim. Acta*, 2009, 362, 3208; A. Kumar, M. Agarwal and A. K. Singh, *J. Organomet. Chem.*, 2008, 693, 3533.
- 29 Y. Takaguchi, E. Horn and N. Furukawa, *Organometallics*, 1996, 15, 5112.
- 30 W. Levason, G. Reid and V. A. Tolhurst, J. Chem. Soc., Dalton Trans., 1998, 3411.
- 31 W. Levason, S. D. Orchard and G. Reid, *Chem. Commun.*, 2001, 427.
- 32 S. C. Menon, H. B. Singh, R. P. Patel and S. K. Kulshreshtha, J. Chem. Soc., Dalton Trans., 1996, 1203.
- 33 E. G. Hope, T. Kemmit and W. Levason, *Organometallics*, 1988, 7, 78.

- 34 J. Conolly, A. R. J. Genge, W. Levason, S. D. Orchard, S. J. A. Pope and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1999, 2343.
- 35 A. J. Barton, W. Levason, G. Reid and A. J. Ward, Organometallics, 2001, 20, 3644.
- 36 K. K. Bhasin, V. Arora, T. Klapotke and M. J. Crawford, *Eur. J. Inorg. Chem.*, 2004, 4781.
- 37 K. K. Bhasin, N. Singh, R. Dhiman, G. Ram, Shivani, S. K. Mehta and R. J. Butcher, *J. Organomet. Chem.*, 2006, **691**, 628.
- 38 K. K. Bhasin, Rishu, S. Singh, H. Kumar and S. K. Mehta, *J. Organomet. Chem.*, 2010, **695**, 648.
- 39 A. Rodriguez, J. Romero, J. A. Garcia-Vazuez, M. L. Duran, A. Sousa Pedrares, A. Sousa and J. Zubieta, *Inorg. Chim. Acta*, 1999, 284, 133.
- 40 K. K. Bhasin, P. Venugopalan and J. Singh, *Phosphorus*, *Sulfur Silicon Relat. Elem.*, 2002, **177**, 2579.
- 41 L. Engman and M. P. Cava, Organometallics, 1982, 1, 470.
- 42 F. P. Colonna, G. Distfano, V. Galasso, K. J. Irgolic, G. C. Pappalardo and L. Pope, J. Chem. Soc., Perkin Trans. 2, 1981, 281.
- 43 L. A. Summers, J. Heterocycl. Chem., 1987, 24, 533.
- 44 L. Syper and J. Mlochowski, Tetrahedron, 1988, 44, 6119.
- 45 K. K. Bhasin, N. Singh, V. Trehan, P. K. Jain and J. Singh, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2003, **178**, 753.
- 46 K. K. Bhasin, E. Arora, K. Kaur, S. K. Kang, M. Gobel, T. M. Klapoetke and S. K. Mehta, *Tetrahedron*, 2009, **65**, 247.
- 47 K. K. Bhasin, E. Arora, S. K. Mehta and T. M. Klapoetke, J. Organomet. Chem., 2011, 696, 835.
- 48 R. S. Chauhan, R. K. Sahrma, G. Kedarnath, D. B. Cordes, A. M. Z. Slawin and V. K. Jain, *J. Organomet. Chem.*, 2012, 717, 180.
- 49 K. K. Bhasin and J. Singh, *J. Organomet. Chem.*, 2002, **658**, 71.
- 50 K. K. Bhasin and V. Arora, Appl. Organomet. Chem., 2004, 18, 359.
- 51 K. K. Bhasin, V. Arora, S. K. Sharma and P. Venugopalan, *Appl. Organomet. Chem.*, 2005, **19**, 161.
- 52 R. Oilunkaniemi, R. S. Laitenen and M. Ahlgren, *Inorg. Chem. Commun.*, 2000, 3, 8.
- 53 A. K. Singh, M. Misra and M. Kadarkaraisamy, *Phosphorus*, *Sulfur Silicon Relat. Elem.*, 1998, **143**, 101.
- 54 W. Levason, B. Patel, G. Reid and A. J. Ward, *J. Organomet. Chem.*, 2001, **619**, 218.
- 55 W. Levason, S. D. Orchard, G. Reid and V.-A. Tolhurst, I. Chem. Soc., Dalton Trans., 1999, 2071–2076.
- 56 W. Levason, S. D. Orchard and G. Reid, *J. Chem. Soc., Dalton Trans.*, 2000, 4551.
- 57 W. Levason, S. D. Orchard and G. Reid, *J. Chem. Soc., Chem. Commun.*, 1999, 1071.
- 58 W. Levason, S. D. Orchard and G. Reid, *Inorg. Chem.*, 2000, **39**, 3853.
- 59 A. K. Singh, M. Kadarkaraisamy, J. E. Drake and R. J. Butcher, *Inorg. Chim. Acta*, 2000, **304**, 45.
- 60 A. K. Singh, J. Sooriyakumar, J. E. Drake, M. B. Hursthouse and M. E. Light, *J. Organomet. Chem.*, 2000, **631**, 244.

61 S. Bali, A. K. Singh, J. E. Drake, M. B. Hursthouse and

RSC Advances

- M. E. Light, J. Organomet. Chem., 2006, 3788.
- 62 S. Bali, A. K. Singh, P. Sharma, R. A. Toscaro, J. E. Drake, M. B. Hursthouse and M. E. Light, *J. Organomet. Chem.*, 2004, 689, 2346.
- 63 D. Das, P. Singh and A. K. Singh, J. Organomet. Chem., 2010, 695, 955.
- 64 K. N. Sharma, H. Joshi, A. K. Sharma, O. Prakash and A. K. Singh, *Chem. Commun.*, 2013, 49, 9344.
- 65 S. Kumar, G. K. Rao, A. Kumar, M. P. Singh and A. K. Singh, *Dalton Trans.*, 2013, **42**, 16939.
- 66 T. P. Lin and F. P. Gabbai, J. Am. Chem. Soc., 2012, 134, 12230.
- 67 P. Singh and A. K. Singh, Organometallics, 2010, 29, 6433.
- 68 A. J. Barton, W. Levason, G. Reid and V.-A. Tolhurst, *Polyhedron*, 2000, **19**, 235.
- 69 M. Devery, R. S. Dickson, B. W. Skelton and A. H. White, *Organometallics*, 1999, **18**, 5292.
- 70 L. Vigo, M. J. Poropudas, P. Salin, R. Oilunkaniemi and R. S. Laitinen, *J. Organomet. Chem.*, 2009, **694**, 2053.
- 71 P. Singh, D. Das, M. Singh and A. K. Singh, *Inorg. Chem. Commun.*, 2010, 13, 988.
- 72 T. Kemmitt, W. Levason, R. D. Oldroyd and M. Webster, *Polyhedron*, 1992, **11**, 2165.
- 73 A. K. Singh, M. Kadarkaraisamy, S. Husebye and K. W. Tornroos, J. Chem. Res., 2000, 64.
- 74 A. Z. Al-Rubaie, A. Al-Marzook and S. A. N. Al-Jadaan, *Recl. Trav. Chim. Pays-Bas*, 1996, **115**, 427.
- 75 A. F. Chiffey, J. Evans, W. Levason and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1994, 2835.
- 76 B. L. Khandelwal, A. Khalid, A. K. Singh, T. P. Singh and S. Karthikeyan, J. Organomet. Chem., 1996, 507, 65.
- 77 J. E. Drake, J. Yang, A. Khalid, V. Srivastava and A. K. Singh, *Inorg. Chim. Acta*, 1997, 254, 57.
- 78 H. B. Singh, A. Regini, J. P. Jasinski, E. S. Paight and R. J. Butcher, *J. Organomet. Chem.*, 1994, **466**, 283.
- 79 A. K. Singh and V. Singh, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1993, **80**, 95.
- 80 R. Batheja, S. Katiyar, V. Singh and A. K. Singh, *Polyhedron*, 1994, **13**, 777.
- 81 R. Batheja and A. K. Singh, *Polyhedron*, 1997, 16, 2509.
- 82 R. Batheja and A. K. Singh, Polyhedron, 1997, 16, 4337.
- 83 A. Khanna and B. L. Khandelwal, *Indian J. Chem.*, 1996, **35A**, 236.
- 84 J. E. Drake, J. H. E. Bailey, A. K. Singh and V. Srivastava, *Acta Crystallogr.*, 1993, (49), 684; A. K. Singh, V. Srivastava and B. L. Khandelwal, *Polyhedron*, 1990, **9**, 851–857.
- 85 A. Khalid, B. L. Khandelwal, A. K. Singh, T. P. Singh and B. Padmanabhan, *J. Coord. Chem.*, 1994, 31, 19.
- 86 A. Khaled and A. K. Singh, Polyhedron, 1996, 16, 33.
- 87 B. L. Khandelwal, A. Khalid and A. K. Singh, *Indian J. Chem.*, 1996, 35A, 438.
- 88 A. Regini, R. Kaur, N. Sudha, S. C. Menon and H. B. Singh, Proc. - Indian Acad. Sci., Math. Sci., 1995, 107, 431.
- 89 R. Batheja, S. K. Dhingra and A. K. Singh, *J. Organomet. Chem.*, 1995, **487**, 173.

- 90 S. C. Menon, H. B. Singh, R. P. Patel and S. K. Kulshreshtha, I. Chem. Soc., Dalton Trans., 1996, 1203.
- 91 S. C. Menon, A. Panda, H. B. Singh and R. J. Butcher, J. Chem. Soc., Chem. Commun., 2000, 143.
- 92 A. Panda, S. S. Zade, H. B. Singh and R. J. Butcher, *Eur. J. Inorg. Chem.*, 2006, 172.
- 93 S. Kolay, M. Kumar, A. Wadawale, D. Das and V. K. Jain, *Dalton Trans.*, 2014, 43, 16056.
- 94 S. Kolay, M. Kumar, A. Wadawale, D. Das and V. K. Jain, I. Organomet. Chem., 2015, 794, 40.
- S. Kolay, A. Wadawale, S. Nigam, M. Kumar, C. Majumder,
 D. Das and V. K. Jain, *Inorg. Chem.*, 2015, 54, 11741.
- 96 T. Chakraborty, S. Sharma, H. B. Singh and R. J. Butcher, *Organometallics*, 2011, **30**, 2525.
- 97 B. K. Das and M. G. Kanatzidis, Inorg. Chem., 1995, 34, 1011.
- 98 E. D. Schermer and W. H. Baddley, *J. Organomet. Chem.*, 1971, 30, 67.
- 99 R. Nagarajaprakash, B. Ramakrishna, K. Mahesh, S. M. Mobin and B. Manimaran, *Organometallics*, 2013, 32, 7292.
- 100 N. Begum, M. I. Hyder, S. Islam, S. E. Kabir, K. Kundu and K. M. Abdul Malik, *Indian J. Chem.*, 2005, 44A, 516.
- 101 K. A. Azam, M. Bhowmick, G. M. G. Hossain, S. E. Kabir, K. Kundu, K. M. A. Malik and S. Pervin, *J. Chem. Crystallogr.*, 2001, 31, 63.
- 102 N. Begun, M. I. Hyder, M. R. Hassan, S. E. Kabir, D. W. Bennet, D. T. Haworth, T. A. Sidhiquee, D. Rokhsana, A. Sharmin and E. Rosenberg, Organometallics, 2008, 27, 1550.
- 103 S. Ghosh, G. Hogarth, S. E. Kabir, E. Nordlander, L. Salassa and D. A. Tocher, *J. Organomet. Chem.*, 2011, **696**, 1982.
- 104 Y. Nishibayashi, H. Imajima, G. Onodera, Y. Inade, M. Hidai and S. Uemura, *Organometallics*, 2004, 23, 5100.
- 105 A. A. Pasynskii, S. S. Shapovalov, I. V. Skabitsky, O. G. Tikhonova and T. A. Krishtop, *Russ. J. Coord. Chem.*, 2015, 41, 234.
- 106 C. E. Rao, K. Yuvaraj and S. Ghosh, J. Organomet. Chem., 2015, 776, 123.
- 107 P. Mathur, I. J. Mavunkal and A. L. Rheingold, *J. Chem. Soc., Chem. Commun.*, 1989, 382.
- 108 P. Mathur and I. J. Mavunkal, J. Organomet. Chem., 1988, 350, 251.
- 109 S. Chatterjee, S. K. Patel and S. M. Mobin, *J. Organomet. Chem.*, 2011, **696**, 1782.
- 110 P. Mathur, P. Payra, S. Ghosh, M. M. Hossain, C. V. V. Satyanarayana, F. O. Chicote and R. K. Chadha, J. Organomet. Chem., 2000, 606, 176.
- 111 P. Mathur, P. Sekar, C. V. V. Satyanarayana and M. F. Mahon, *J. Chem. Soc., Dalton Trans.*, 1996, 2173.
- 112 P. Mathur, I. J. Mavunkal, V. Rugmini and M. F. Mahon, *Inorg. Chem.*, 1990, 29, 4838.
- 113 P. Mathur, I. J. Mavunkal and V. Rugmini, *Inorg. Chem.*, 1989, 28, 3616.
- 114 P. Mathur, B. H. S. Thimappa and A. L. Rheingold, *Inorg. Chem.*, 1990, **29**, 4658.
- 115 J. Zhang and W. K. Long, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 1249–1253.

- 116 S. E. Kabir, M. S. Saha, D. Tocher, G. M. G. Hossain and E. Rosenberg, *J. Organomet. Chem.*, 2006, 691, 97;
 E. D. Schermer and W. H. Baddley, *J. Organomet. Chem.*, 1971, 30, 67.
- 117 P. Srinivasan, M. E. Tai and W. K. Leong, *J. Organomet. Chem.*, 2006, **691**, 941–951.
- 118 S. Nagao, H. Seino, M. Hiddai and Y. Mizobe, *Dalton Trans.*, 2005, 3166–3172.
- 119 M. P. Devery, R. S. Dickson, G. D. Fallon, G. A. Koutsantonis, B. W. Skelton and A. H. White, *Z. Anorg. Allg. Chem.*, 2008, **634**, 675.
- 120 M. P. Devery, R. S. Dickson, B. W. Skelton and A. H. White, *Organometallics*, 1999, **18**, 5292.
- 121 A. Nordheider, K. S. A. Arachchige, A. M. Z. Slawin, J. D. Woollins and T. Chivers, *Dalton Trans.*, 2015, 44, 8781.
- 122 R. D. Pergola, A. Ceriotti, A. F. de Biani, L. Garlaschelli, M. Manassero, R. Piacentini, M. Sansoni and P. Zanello, Organometallics, 1998, 17, 802.
- 123 Y.-K. Sau, X. Yi Yi, K.-W. Chan, C.-S. Lai, I. D. Williams and W.-H. Leung, *J. Organomet. Chem.*, 2010, **695**, 1399.
- 124 R. D. Adams, J. W. Long and J. L. Perrin, *J. Am. Chem. Soc.*, 1998, **120**, 1922.
- 125 J. M. Gonzales, D. G. Musaev and K. Morokuma, *Organometallics*, 2005, 24, 4908.
- 126 T. Nakagawa, H. Seino and Y. Mizobe, *J. Organomet. Chem.*, 2010, **695**, 137.
- 127 L. M. Venanzi, Chem. Ber., 1968, 4, 162.
- 128 E. Shustorovich and P. A. Dobosh, *J. Am. Chem. Soc.*, 1979, **101**, 4090.
- 129 D. M. Giolando, T. B. Rauchfuss and A. L. Rheingold, *Inorg. Chem.*, 1987, 26, 1636.
- 130 S. Dey, V. K. Jain, J. Singh, V. Trehan, K. K. Bhasin and B. Varghese, *Eur. J. Inorg. Chem.*, 2003, 744.
- 131 S. Dey, K. Vivekananda, A. P. Wadawale, V. K. Jain and N. Bhuvanesh, *ChemistrySelect*, 2017, 2, 5073.
- 132 L. Y. Chia and W. R. McWhinnie, *J. Organomet. Chem.*, 1978, 148, 165.
- 133 (a) M. Risto, E. M. Jahr, M. S. Hannu-Kurre, R. Oilunkaniemi and R. S. Laitinen, *J. Organomet. Chem.*, 2007, **692**, 2193; (b) R. Oilunkaniemi, R. S. Laitinen and M. Ahlgren, *J. Organomet. Chem.*, 2000, **595**, 232.
- 134 N. V. Kirji, W. Tyrra, I. Pantenburg, D. Naumann, H. Scherer and Y. L. Yagupolskii, *J. Organomet. Chem.*, 2006, **691**, 2679.
- 135 S. Kato, O. Niyomura, Y. Kawahara and T. Kanda, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 1677.
- 136 A. Wagner, L. Vigo, R. Oilukaniemi, R. S. Laitinen and W. Weigand, *Dalton Trans.*, 2008, 3535;
 M. M. Karjalainen, T. Wiegand, J. M. Rautiainen, A. Wagner, H. Görls, W. Weigand, R. Oilunkaniemi and R. S. Laitinen, *J. Organomet. Chem.*, 2017, 836, 17.
- 137 A. Singhal, V. K. Jain, B. Varghese and E. R. T. Tiekink, *Inorg. Chim. Acta*, 1999, **285**, 190.
- 138 J. G. Brennam, T. Siegrist, S. M. Stuczynski and M. L. Steigerwald, *J. Am. Chem. Soc.*, 1990, 112, 9233.
- 139 Y. Yamaguchi, N. Nakata and A. Ishii, Eur. J. Inorg. Chem., 2013, 5233.

- 140 R. S. Chauhan, G. Kedarnath, A. Wadawale, J. A. Golen, A. L. Rheingold and V. K. Jain, *J. Organomet. Chem.*, 2013, 737, 40.
- 141 R. S. Chauhan, G. Kedarnath, J. A. Golen, A. L. Rheingold and V. K. Jain, *Indian J. Chem.*, 2013, **52 A**, 42.
- 142 C. Nishitani, T. Shizuka, K. Matsumoto, S. Okeya and H. Kioto, *Inorg. Chem. Commun.*, 1998, 1, 325.
- 143 K. Matsumoto, K. Takahashi, M. Ikuzawa and H. Kimoto, *Inorg. Chim. Acta*, 1998, **281**, 174.
- 144 A. L. Ma, J. B. Thoden and L. B. Dahl, *J. Chem. Soc., Chem. Commun.*, 1992, 1516.
- 145 K. Matsumoto, M. Ikuzawa, M. Kamibuko and S. Ooi, *Inorg. Chim. Acta*, 1994, 129.
- 146 K. Matsumoto, C. Nishitani, M. Tadokoro and S. Okey, I. Chem. Soc., Dalton Trans., 1996, 3335.
- 147 M. R. Lewtas, C. P. Morley and M. Divaira, *Polyhedron*, 2000, 19, 751.
- 148 R. D. Adams, T. A. Wolfe, B. W. Eichhorn and R. C. Haushalter, *Polyhedron*, 1989, **8**, 701.
- 149 H. Wolkers, K. Dehnicke, D. Fenske, J. Magull, C. Oliver and S. Weigerber, *Z. Naturforsch.*, 1994, **64B**, 4004.
- 150 M. G. Kanatzidis, Comments Inorg. Chem., 1990, 10, 161; Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 1991, 47, 1193.
- 151 G. Thiele, G. You and S. Dehnen, *Inorg. Chem.*, 2015, 54, 2491.
- 152 J. M. McConnachie, J. Bollinger and J. A. Ibers, *Inorg. Chem.*, 1993, 32, 3923.
- 153 A. Gunther, A. Isaeva, A. I. Baranov and M. Ruck, *Chem.*–*Eur. J.*, 2011, **17**, 6382.
- 154 A. Gunther, M. Heise, F. R. Wagner and M. Ruck, *Angew. Chem., Int. Ed.*, 2011, **50**, 9987.
- 155 A. Gunther, A. Isaeva and M. Ruck, *Z. Anorg. Allg. Chem.*, 2013, **639**, 254.
- 156 A. Gunther and M. Ruck, Z. Anorg. Allg. Chem., 2012, 638, 317.
- 157 T. Nakagawa, H. Seino, S. Nagao and Y. Mizobe, *Angew. Chem., Int. Ed.*, 2006, **45**, 7758.
- 158 A. A. Y. Pasynskii, V. Torubaev, A. Palova, I. V. Skanitsky, G. Denisov and V. Grinberg, *J. Cluster Sci.*, 2015, **26**, 247.
- 159 A. A. Pasynskii, Y. V. Torubaev, A. Pavlova, S. S. Shapovalov, I. V. Skabitskii and G. Denisov, *Russ. J. Coord. Chem.*, 2014, 40, 611.
- 160 N. Petragnani and J. V. Comasseto, Synthesis, 1986, 1.
- 161 N. Petragnani and J. V. Comasseto, *Synthesis*, 1991, 793, 897.
- 162 J. V. Comasseto, L. W. Ling, N. Petragnani and H. A. Stefani, *Synthesis*, 1997, 373.
- 163 N. Petragnani, in *Tellurium in Organic Synthesis—Best Synthetic Methods*, ed. O. Meth-Cohn, Academic, 1994.
- 164 N. Petragnani and A. McKillop, Tellurium, in Comprehensive Organometallic Chemistry, Pergamon, NewYork, 1995, vol. 11.
- 165 H. Suzuki and T. Nakamura, J. Org. Chem., 1993, 58, 241.
- 166 N. Petragani and H. A. Stefani, Tetrahedron, 2005, 61, 1613.
- 167 G. Blay, L. Cardona, B. Garcia, L. Lahoz and J. R. Pedro, *Tetrahedron*, 1996, **52**, 8611.

168 A. S. Pepito and D. C. Dittmer, J. Org. Chem., 1997, 62, 7920.

RSC Advances

- 169 W. Li, X. J. Zhou and Q. Ma, Synth. Commun., 1995, 25, 553.
- 170 C. C. Silveira, E. J. Lenardao and J. V. Comasseto, *Synth. Commun.*, 1994, **24**, 575.
- 171 V. Bargues, G. Blay, J. Fernandez and J. R. Pedro, *Synlett*, 1996, 655.
- 172 P. Singh, M. Singh and A. K. Singh, J. Organomet. Chem., 2009, 694, 3872.
- 173 P. Singh and A. K. Singh, Eur. J. Inorg. Chem., 2010, 4187.
- 174 I. G. Jung, S. U. Son, K. H. Park, K.-C. Chung, J. W. Lee and Y. K. Chung, *Organometallics*, 2003, **22**, 4715.
- 175 E. Diez-Barra, J. Guerra, V. Hornillos, S. Merino and J. Tejeda, J. Organomet. Chem., 2003, 22, 4610;
 C. S. Consorti, M. L. Zanini, S. Leal, G. Ebeling and J. Dupont, Org. Lett., 2003, 5, 83.
- 176 J. Masllorens, M. Moreno-Manas, A. Pla-Quintana and A. Roglans, *Org. Lett.*, 2003, 5, 1559.
- 177 S. B. Park and H. Alper, Org. Lett., 2003, 5, 3209; C. Mazet, L. H. Gade, Eur. J. Inorg. Chem., 2003, 1161.
- 178 Q. Yao, E. P. Kinney and C. Zheng, Org. Lett., 2004, 6, 2999.

- 179 A. Kumar, M. Agarwal and A. K. Singh, *J. Organomet. Chem.*, 2008, **693**, 3533.
- 180 D. H. Cobden, Nature, 2001, 409, 32.
- 181 Y. Cui, Q. Wei, H. Park and C. M. Lieber, Science, 2001, 293, 1289.
- 182 G. A. Prinz, Science, 1998, 282, 1660.
- 183 W. Zhou, J. Zhu, D. Li, H. H. Hng, F. Y. C. Boey, J. Ma, H. Zhang and Q. Yan, *Adv. Mater.*, 2009, **21**, 3196.
- 184 Q. Yan, M. S. Raghuveer, H. Li, B. Singh, T. Kim, M. Shima, A. Bose and G. Ramanath, *Adv. Mater.*, 2007, **19**, 3.
- 185 A. K. Samal and T. Pradeep, Langmuir, 2010, 26, 19136.
- 186 H. Cordes and R. Schmid-Fetzer, Semicond. Sci. Technol., 1994, 9, 2085.
- 187 S. Dey and V. K. Jain, Platinum Met. Rev., 2004, 48, 16.
- 188 (a) L. Y. Chiang, J. W. Swirczewski, R. Kastrup, C. S. Hsu and R. B. Upasani, J. Am. Chem. Soc., 1991, 113, 6574; (b) M. Misono and N. Nojiri, Appl. Catal., 1990, 64, 1.
- 189 P. Singh, D. Das, M. Singh and A. K. Singh, *Inorg. Chem. Commun.*, 2010, **13**, 988.
- 190 A. Singhal, V. K. Jain, R. Mishra and B. Varghese, J. Mater. Chem., 2000, 10, 1121.