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Emerging trends in organotelluroolate chemistry derived from platinoids

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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 $[\text{Cp}^*\text{Ir}(\text{ppy})(\eta^1\text{-Te}_2\text{Ph}_2)]^+$, $[\text{Cp}^*\text{IrOs}_3(\mu\text{-H})_2(\mu\text{-Tetol})_2(\text{CO})_7]$, $[\text{Pt}(\text{TeC}_5\text{H}_3(3\text{-R})\text{N})_2\text{Te}(\text{PPh}_3)]$, $[\text{Pt}(\text{Ph}_2\text{PCH}(\text{TeC}_5\text{H}_3(3\text{-R})\text{NPPH}_2)_2]$ (R = H, Me), and various other high nuclearity heterometallic $[\text{Cp}^*\text{Ir}(\text{CO})(\mu\text{-TeC}_6\text{H}_4)_2\text{MCp}^*\text{Cl}]\text{Cl}$ (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.

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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.^{6,11–13} Therefore, the reactions of organotellurium ligands with platinum group metal precursors represent an active area for further research.^{14–18} The noteworthy reactivity of platinoids has been utilized in synthetic chemistry to isolate products in quite good yields with great selectivity under normal conditions.¹⁹ 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.²⁰

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 telluroolate 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

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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)tetrahydropyran/dioxane,²⁴ (2-phenyltelluromethyl)tetrahydropyran,²⁴ $\text{Te}(\text{CH}_2\text{CH}_2\text{R})_2$ ($\text{R} = \text{CH}_2\text{NH}_2$, $\text{C}_4\text{H}_8\text{N}$),²⁵ $(4\text{-RC}_6\text{H}_4)_2\text{Te}(\text{CH}_2\text{CH}_2)(2\text{-C}_5\text{H}_4\text{N})$ ($\text{R} = \text{H}, \text{Me}, \text{OMe}$),²⁵ $4\text{-MeOC}_6\text{H}_4\text{Te}(\text{CH}_2)_2\text{N}=\text{C}(\text{CH}_3)(2\text{-HOC}_6\text{H}_4)$,²⁶ $\text{Te}(\text{CH}_2\text{CH}_2\text{N}=\text{C}(\text{CH}_3)\text{C}_6\text{H}_4\text{-2-OH})_2$,²⁶ $2\text{-CH}_3\text{SC}_6\text{H}_4\text{C}=\text{NCH}_2\text{CH}_2\text{TeC}_6\text{H}_4\text{-OMe}$,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 Na_2Te . The second most efficient strategy for the formation of telluroethers is the *in situ* formation of Na_2Te , followed by the addition of the corresponding alkyl halides to isolate the desired product. As an example, the class of cyclic ditelluroether [8]ane Te_2 was synthesized in a similar fashion by the addition of a half equivalent of 1,3 dibromomethane in a THF solution of Na_2Te , followed by the addition of NaBH_4 and a further equivalent of 1,3 dibromomethane.^{29,30} The syntheses of mixed donor thia/tellura [9]ane S_2Te_2 , [11]ane S_2Te_2 , [12]ane S_2Te_2 , [14]ane S_3Te 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 MgCl_2 .

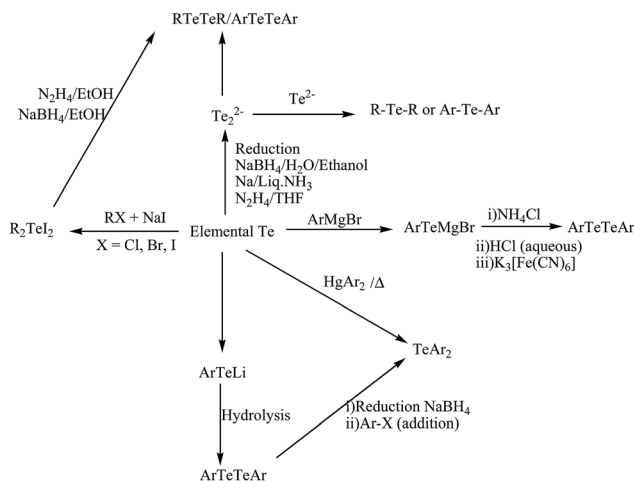
2.2 Diorganotellurides

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 BuLi⁴¹ 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 NaBH_4 , Li metal reaction, Na/NH_3 , and hydrazine.^{42–47} Sodium borohydride reduction of elemental tellurium in ethanol, water, and ethoxy ethanol has been applied for the synthesis for Na_2Te_2 .^{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 Na_2Te_2 , 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 $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, TePh_2 , and CO yields the complex $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{TePh})_2]$, which has also been obtained in moderate yield by the simple addition between $[\text{Ru}\{(\text{CO})_3\text{Cl}_2\}_2]$ and telluroether.^{52,53} The reaction of chelated ditelluroether $\text{RTe}(\text{CH}_2)_3\text{TeR}$; ($\text{R} = \text{Me}$, Ph , or $o\text{-C}_6\text{H}_4(\text{TeMe})_2$) with $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, $[\text{Ru}(\text{dmsO})_4\text{X}_2]$ gave a complex with the general composition $\text{trans-}[\text{RuX}_2(\text{L}\cap\text{L})_2]$ ($\text{X} = \text{Cl}$, Br or I); $\text{L}\cap\text{L} = \text{RTe}(\text{CH}_2)_3\text{TeR}$; ($\text{R} = \text{Me}$, Ph or $o\text{-C}_6\text{H}_4(\text{TeMe})_2$) (Scheme 2).^{54,55} All these products showed poor solubility in organic solvents. To overcome the solubility issues, a bulky phosphine-based ruthenium precursor, $[\text{RuCl}_2(\text{PPh}_3)_3]$, has been used, which on reaction with the same ditelluroether yielded a complex of $[\text{RuCl}(\text{PPh}_3)(\text{L}\cap\text{L})_2]\text{PF}_6$ (Fig. 1) with good solubility in various organic solvents.⁵⁵ In solution, the latter complex is converted to a product with the composition $[\text{RuCl}_2(\text{PPh}_3)\{\text{MeC}(\text{RTeCH}_2)_3\}_3]$, while a longer stay in the solvent results in its decomposition to unknown species;⁵⁶ while this tripodal ligand on reaction with $[\text{Ru}(\text{dmf})_6](\text{SO}_3\text{CF}_3)_3$ in methanol gave a homoleptic compound $[\text{Ru}\{\text{MeC}(\text{CH}_2\text{TeR})_3\}_2](\text{SO}_3\text{CF}_3)_2$ (**I**).^{57,58}

A new class of carbon-backboned ligands $(4\text{-MeO-C}_6\text{H}_4\text{-Te})_2\text{CH}_2$ and $[(\text{CH}_2)_2\text{C}(\text{CH}_2\text{TeMe})_2]$ on reaction with $[\text{RuCl}_4(\text{dmsO})_4]/[\text{RuCl}_2(p\text{-cymene})_2]$ afforded the complex $[\text{RuCl}_2(\text{dmsO})_2(\text{L})][\text{RuCl}_2(p\text{-cymene})_2(\text{L})]$ ($\text{L} = (4\text{-MeO-C}_6\text{H}_4\text{-Te})_2\text{CH}_2$ and $[(\text{CH}_2)_2\text{C}(\text{CH}_2\text{TeMe})_2]$) 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 $[\text{RuCl}_2(p\text{-cymene})_2]$ with two equivalent of homoleptic telluroether $\text{Te}\{\text{CH}_2\text{CH}_2(\text{Ar})\}_2$ ($\text{Ar} = 1,3$ dioxane, thiophene)⁶⁰ or a heteroleptic telluroether like $[(\text{thiophene})\text{Te}\{\text{CH}_2(\text{R})\}]$ ($\text{R} = \text{furan}$, pyrrol),⁶¹ $[\{\text{CH}_2\text{CH}_2(\text{R})\}\text{Te}(\text{C}_6\text{H}_4\text{-}p\text{-OMe})]$ ($\text{R} = \text{thiophene}$, phthalamide , benzotriazole)^{62,63} yielded $[\text{RuCl}_2(p\text{-cymene})\text{L}]$ ($\text{L} = \text{Te}\{\text{CH}_2\text{CH}_2(\text{Ar})\}_2$, $[\{\text{CH}_2\text{CH}_2(\text{R})\}\text{Te}(\text{C}_6\text{H}_4\text{-}p\text{-OMe})]$, $[(\text{thiophene})\text{Te}\{\text{CH}_2(\text{R})\}]$) (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 $\text{OsO}_4\text{-HX}$ or $[\text{OsX}_6]$ with telluroether has not had a successful outcome yet for dithio or diselenoether ligands. In this case, the reaction of $[\text{OsCl}_2(\text{dmsO})_4]$ with carbon-backboned ditelluroether $\text{RTe}(\text{CH}_2)_3\text{TeR}$, $\text{CH}_2(\text{TeMe})_2$, $o\text{-C}_6\text{H}_4(\text{CH}_2\text{TeMe})_2$ led to



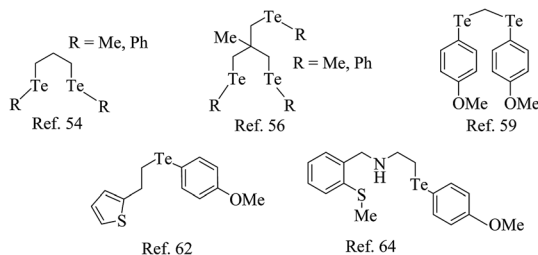
Fig. 1 Crystal structure of $[\text{RuCl}(\text{PPh}_3)\{\text{MeTeCH}_2\}_2]^+$ (redrawn from ref. 55).

a compound with the composition $[\text{OsCl}_2(\text{L}\cap\text{L})_2]$ (**III**) ($\text{L}\cap\text{L} = \text{RTe}(\text{CH}_2)_3\text{TeR}$, $\text{CH}_2(\text{TeMe})_2$, $o\text{-C}_6\text{H}_4(\text{CH}_2\text{TeMe})_2$).^{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 ($\text{R} = \text{Me}$, Et) with metal-cyclohexane $[(\text{C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\text{CF}_3\text{CCF}_3)]$ derived an adduct in which TeR_2 was added to one of the rhodiums attached with bridging carbonyl, which was bonded in a η^1 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 $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and ditelluroethers $\text{Te}(\text{CH}_2)_3\text{TeR}$ ($\text{R} = \text{Me}$, Ph) along with NH_4PF_6 in ethanol solution yielded the complex $[\text{RhCl}_2(\text{L}\cap\text{L})_2]\text{PF}_6$ (Scheme 3). Similarly, various tripodal $\text{Rh}(\text{I})$ and $\text{Ir}(\text{I})$ complexes $[\text{M}\{\text{MeC}(\text{CH}_2\text{TeMe})_3\}(\text{COD})]\text{PF}_6$ ($\text{M} = \text{Rh}$, Ir) were derived from umbrella-like telluroethers, namely with $\text{MeC}(\text{CH}_2\text{TeR})_3$ ($\text{R} = \text{Me}$, Ph).⁵⁵ However, $\text{Rh}(\text{III})$ complexes with the composition $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)\{\text{MeC}(\text{CH}_2\text{ER})_3\}][\text{PF}_6]_2$ with a square pyramidal geometry were isolated by the reaction of $[\{\text{RhCl}_2(\eta^5\text{-C}_5\text{H}_5)\}_2]$ and the corresponding ligand systems.⁵⁶



Scheme 2 Homoleptic and heteroleptic telluroether ligands.





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, CH_2 , 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 $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ is employed in various mole ratios with the ligand system $\text{Te}(\text{CH}_2\text{SiMe}_3)_3$, 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*-{2aryl telluroethyl}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 $\text{M}_2\text{M}'\text{Cl}_4$ (M = Na, K; M' = Pd, Pt)

in a 1 : 2 mole ratio with homoleptic telluroether $\text{Te}(\text{CH}_2\text{CH}_2(\text{Ar}))_2$ **IV** (Ar = 1,3 dioxane, thiophene)^{60,62} or a heteroleptic telluroether, like [(thiophene)Te(CH₂(R))] (R = furan, pyrrol),⁶¹ [$\text{CH}_2\text{CH}_2(\text{R})\text{Te}(\text{C}_6\text{H}_4\text{-}p\text{-Ome})$] (R = thiophene, phthalamide, benzotriazole),^{62,63} led to a complex of the type $[\text{MCl}_2\text{L}_2]$ L = Te{ $\text{CH}_2\text{CH}_2(\text{Ar})_2$, [$\text{CH}_2\text{CH}_2(\text{R})\text{Te}(\text{C}_6\text{H}_4\text{-}p\text{-Ome})$]}, [(thiophene)Te{ $\text{CH}_2(\text{R})$ }]⁶³ while the reaction in 1:1 mole ratio with [$\text{CH}_2\text{CH}_2(\text{R})\text{Te}(\text{C}_6\text{H}_5\text{-}p\text{-Ome})$] (R = 2- $\text{CH}_3\text{SC}_6\text{H}_4\text{CH}=\text{N}$, 2- $\text{CH}_3\text{SC}_6\text{H}_4\text{CHNH}$ **V**, $\{\text{C}_6\text{H}_5\}\{2\text{-HOC}_6\text{H}_4\}\text{C}=\text{N}$ **VI** and a variety of tridentate ligand yielded an expected additive product with the composition $[\text{MCl}(\text{L})]^+$.⁶⁵⁻⁶⁹ Among these cyclic complexes, $[\text{MX}_2\{\text{Te}(\text{CH}_2)_4\}_2]$ (M = Pd, Pt; X = Cl, Br, I) has been isolated from the reaction with cyclic telluroethers, *i.e.*, telluracyclopentane $\text{Te}(\text{CH}_2)_4$.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 RECH_2ER (R = Me, Ph and E = S, Se, Te)⁷⁵ with both metals showed that the thio analogs led to a very stable compound,

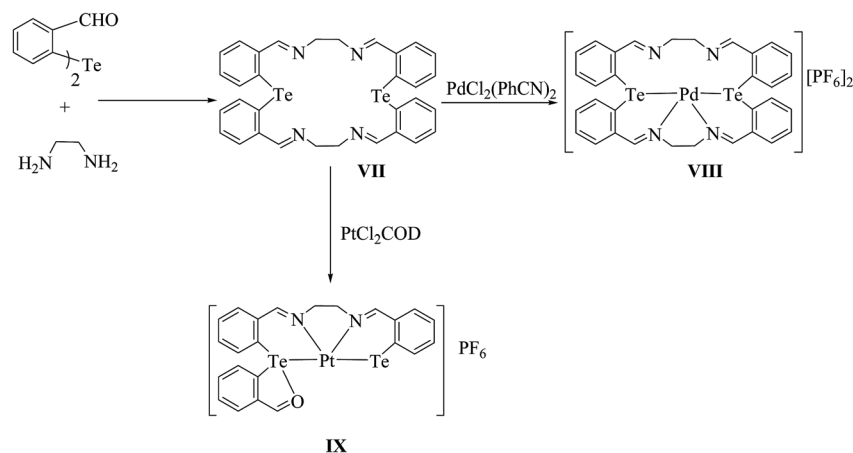
Scheme 4 Schematic representation of the reaction of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with various telluroethers.

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 $[\text{PdL}]^+$ **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 $[\text{PtCl}_2(\text{COD})]$, 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}

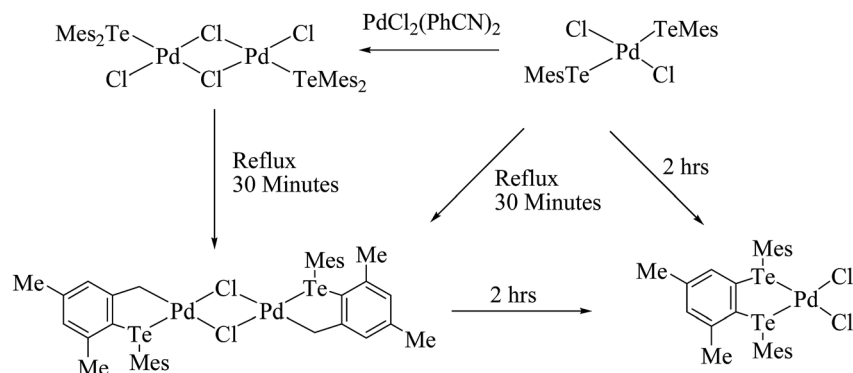
An interesting example of a halobridged complex, $[\text{M}_2\text{X}_2(\mu\text{-X})_2(\text{TeR}_2)_2]$ ($\text{M} = \text{Pd}, \text{Pt}; \text{X} = \text{Cl}, \text{Br}; \text{R} = \text{Mes}, \text{Ph}, o\text{-tol}$), was obtained by the treatment of $[\text{MX}_2(\text{TeR}_2)_2]$ ($\text{R} = \text{Mes}, \text{Ph}, o\text{-tol}$) with MX_2 ($\text{M} = \text{Pd}, \text{Pt}$)/ Na_2PdCl_4 (Scheme 7).^{93–95} These complexes were formed due to the chlorobridged cleavage reaction with the substitution of thio and selenoether 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}Te NMR 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.⁹⁴ An agostic interaction between telluroethers and metal atoms has also been documented in these complexes, where a toluene–methanol solution of $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{TeMes}_2)_2]$ or compound $[\text{PdCl}_2(\text{-TeMes}_2)]$ on refluxing for 30 min yielded a binuclear cyclopalladated complex $[\text{Pd}_2(\mu\text{-Cl})_2\{\text{CH}_2\text{C}_6\text{H}_2(4,6\text{-Me}_2)\text{TeMes}_2\}_2]$ (Scheme 7). However, the latter binuclear compound was converted to the mononuclear compound $[\text{PdCl}_2\{\text{MesTeCH}_2\text{C}_6\text{H}_2(4,6\text{-Me}_2)\text{TeMes}_2\}]$. The formation of the mononuclear compound mainly arose due to nucleophilic attack of mesityl telluroate at the Pd–C bond.⁹³

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.⁹⁶ 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 $[\text{MCl}_2(\text{L})_2]$ ($\text{M} = \text{Pd}, \text{Pt}; \text{L} = \text{PhCN}$ or COD) with a tellurium-ligated macrocyclic Schiff base.



Scheme 7 Cyclometallation of $[\text{PdCl}_2(\text{Mes})_2]$ at different temperatures.



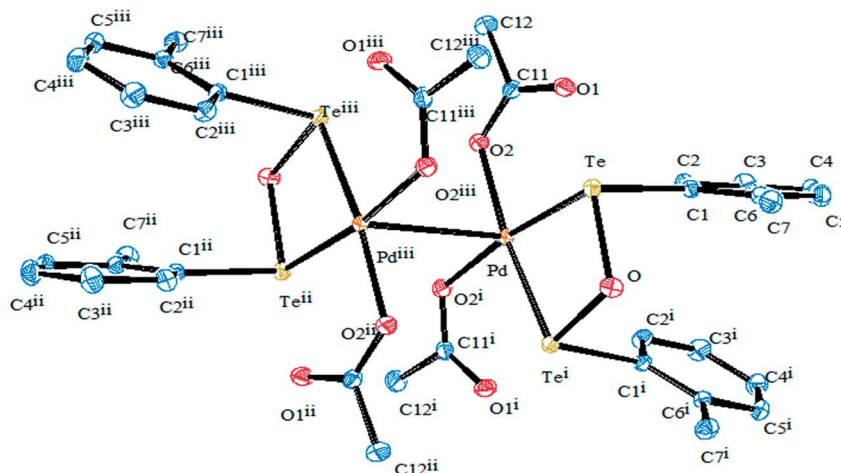


Fig. 5 Crystal structure of [(o-tolyl)Te₂OPd(OAc)₂] (redrawn from ref. 96).

4. Metal tellurolates

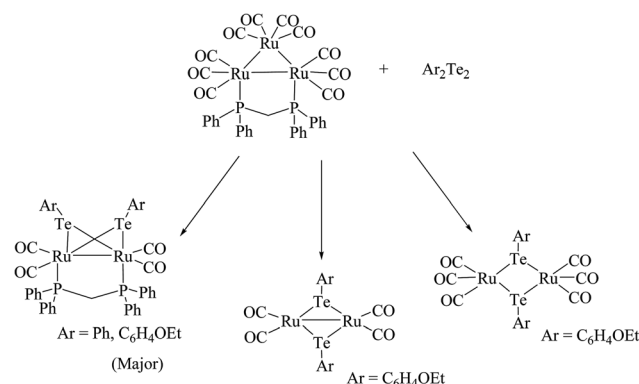
4.1 Ruthenium and osmium

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(Te₂)(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 [Ru₂X₂(CO)₆(μ-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 [Ru₃(CO)₁₀(μ-dppm)] with tetrahydrofuran solution of Ar₂Te₂ (Ar = C₆H₄OEt-4) in a 1 : 2 mole ratio for 6 h yielded a mixture of the products [Ru₂(CO)₄(μ-TeAr)₂(μ-dppm)], [Ru₂(CO)₆(μ-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 [Ru₂(μ₃-Te)(μ-TePh)₃(CO)₆(η¹-COPh)(μ-dppm)].¹⁰²

Heating a solution of [Ru₃(μ-H){(μ₃-η²-C₄H₃O)₂}(CO)₂}(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(μ-dppm)], [Ru₃(μ₃-η²-C₄H₃O){μ-PC₄H₃O₂}(CO)₅(μ-TePh)₂(μ-dppm)] (Fig. 6), [Ru₃(μ-H){(μ₃-η²-C₄H₂O)₂}(CO)₅(μ-TePh)₂(κ²-dppm)], and [Ru₃(μ-H){(μ₃-η²-C₄H₂O){(PC₄H₃O)₃}{μ-P(C₄H₃O)₂}(CO)₄(μ-TePh)₂(κ²-dppm)].¹⁰³ However, the reaction of the tetranuclear ruthenium(II) complex with R₂Te₂ (R =

Me, Et, Fc) yielded the diruthenium complex syn-[Cp*RuCl(μ-TeR)]₂ in quite a good yield.¹⁰⁴ Although the reaction of dialkyliditellurides led to a clean pot synthesis of alkanechalcofenolate 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)₃Ru(Cp*)Cl] were isolated.¹⁰⁴

Treatment of [(η⁶-cymene)Ru(μ-Cl)₃Re(CO)₃] with sodium salt phenyl telluride yielded a yellow heterometallic product [(η⁶-cymene)Ru(μ-TePh)₃][Re₂(CO)₆(μ-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 [Fe₂(μ-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 [Ru₄(CO)₁₂] with [Fe₂(μ-Te)₂(CO)₆] afforded a pentanuclear cluster complex of composition [Fe(CO)₆Ru₃(μ-Te)₂(CO)₁₁].¹⁰⁷ Similar outcome has been obtained by the reaction of [Fe₂(μ-EE)₂(CO)₆] (E = S, Se, Te) with [M₃(CO)₁₂(NCMe)] (M = Ru, Os).^{109,110} These latter complexes are also isolated at room temperature by the precursor [M₃(CO)₁₀(MeCN)₂] (M = Ru, Os).¹¹³ While the reaction with



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



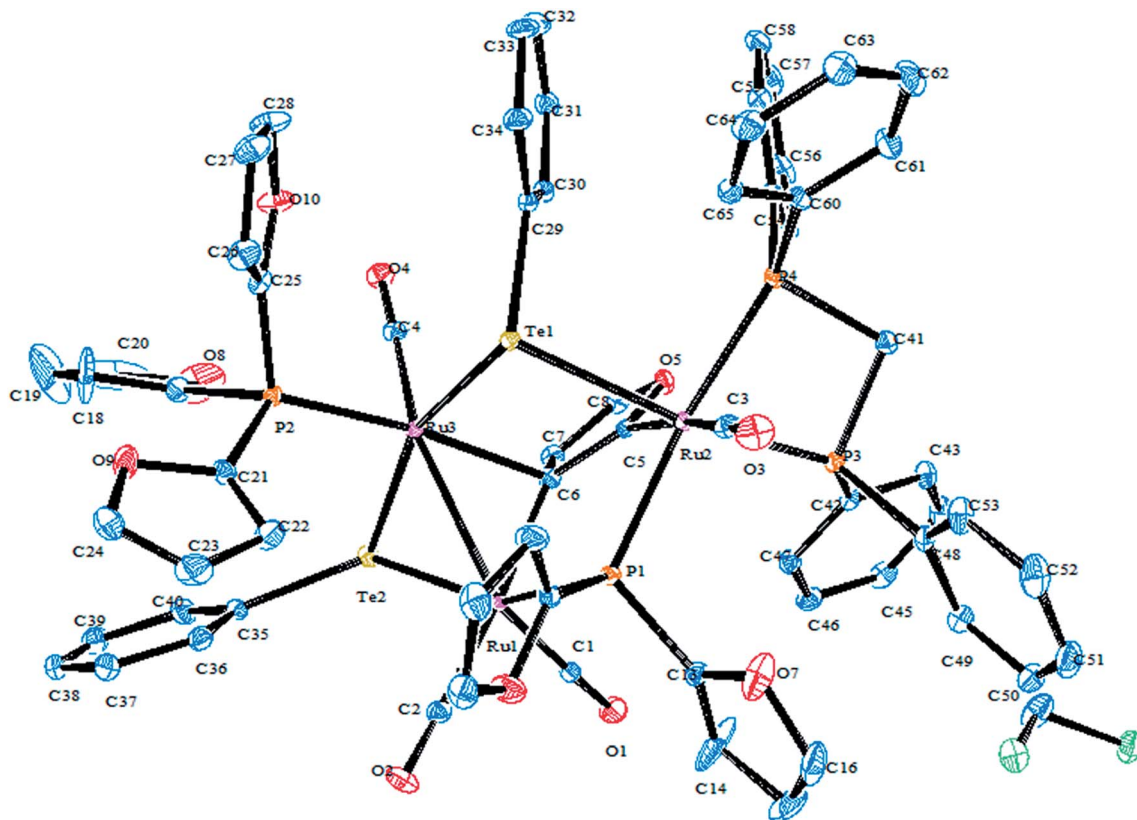
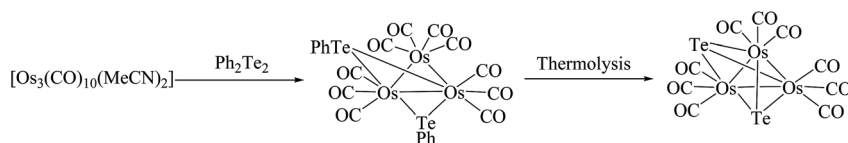


Fig. 6 Crystal structure of $[\text{Ru}_3(\mu_3\text{-}\eta^2\text{-C}_4\text{H}_3\text{O})\{(\mu\text{-PC}_4\text{H}_3\text{O})_2\}(\text{CO})_5(\mu\text{-TePh})_2(\mu\text{-dppm})]$ (redrawn from ref. 103).

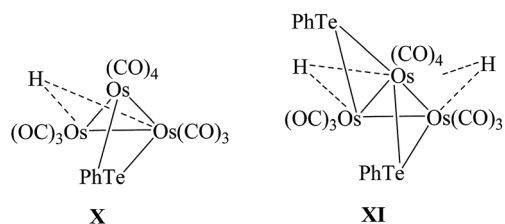


Scheme 9 Synthesis of a trinuclear osmium telluride bridged complex.

trinuclear compound $[\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9]$ results the substitution product $[\text{Ru}_4(\mu_4\text{-Te})_2(\text{CO})_{11}]$.¹¹⁴

In contrast to ruthenium, the reaction of Ph_2Te_2 with the osmium precursor $[\text{Os}_3(\text{CH}_3\text{CN})_2(\text{CO})_{10}]$ under normal conditions yielded the cluster $[\text{Os}_3(\text{CO})_{10}(\mu\text{-TePh})_2]$, 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 $[\text{Os}_3(\text{CO})_9(\mu\text{-Te})_2]$ (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 $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$, are much more complicated. A variety of complexes were formed, out of which three cluster complexes, namely $[\text{Os}_3\text{H}_2(\mu\text{-TePh})_2(\text{CO})_{10}]$ (X), $[\text{Os}_3\text{H}(\mu\text{-TePh})(\text{CO})_{10}]$ (XI), and $[\text{OsH}(\text{CO})_3(\text{TePh})_2]$,¹¹⁵ were isolated. The same ligand upon reaction with phosphine-derived osmium precursors yielded the binuclear product $[\text{Os}_2(\mu\text{-TePh})_2(\text{CO})_4(\mu\text{-dppm})]$ and two isomeric compounds with the composition $[\text{Os}_3(\mu\text{-TePh})_2]$

$(\text{CO})_8(\mu\text{-dppm})]$ (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 $(\text{TeToI})_2$ with the mixed cluster $[\text{Cp}^*\text{IrOs}_3(\mu\text{-H})_2(\text{CO})_{10}]$.¹¹⁷ In this case, three cluster complexes were isolated with the composition $[\text{Cp}^*\text{IrOs}_3(\mu\text{-H})_2(\mu\text{-Tetol})_2(\text{CO})_7]$ (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



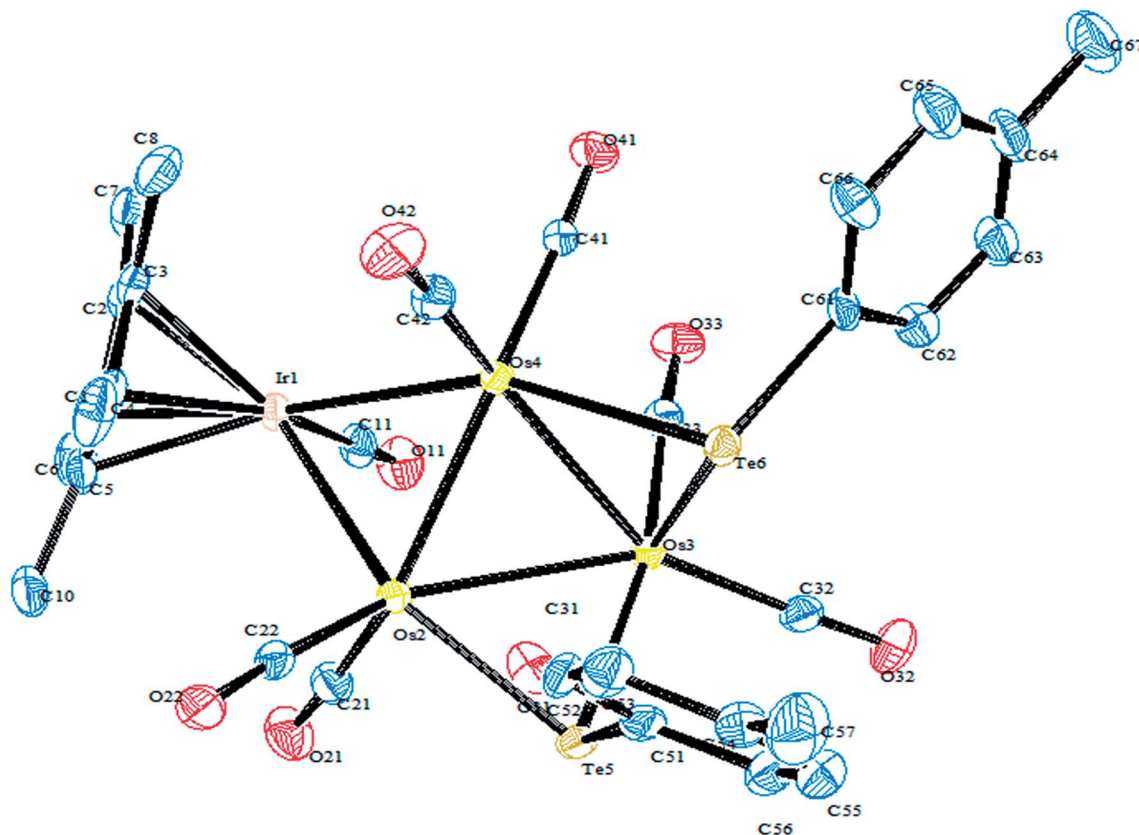


Fig. 8 Crystal structure of $[\text{Cp}^*\text{IrOs}_3(\mu\text{-H})_2(\mu\text{-Tetol})_2(\text{CO})_7]$ (redrawn from ref. 117).



Scheme 10 Reaction of $[(\text{Cp}^*)_2\text{Rh}_2(\mu\text{-CO})\mu\text{-}\eta^2:\eta^2\text{C}_2(\text{CF}_3)_2]$ 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 telluroate ligand system. As an example, the oxidative addition product $[\text{Cp}^*\text{Ir}(\text{CO})(\text{TeTol})_2]$ upon reaction with $[(\text{Cp}^*\text{MCl})_2(\mu\text{-Cl})_2]$ (M = Rh, Ir) yielded a stereoisomer of the binuclear complexes $[\text{Cp}^*\text{Ir}(\text{CO})(\mu\text{-TeTol})_2\text{MCP}^*\text{Cl}]\text{Cl}$ (M = Rh, Ir) bridged with telluride systems (Scheme 12). Interestingly, a similar reaction of $[\text{Cp}^*\text{Ir}(\text{CO})(\text{TeTol})_2]$ with $[\text{Cp}^*\text{RuCl}_4(\mu_3\text{-Cl})_4]$ and

$[\text{RuH}(\text{COD})(\text{CH}_3\text{CN})](\text{BPh}_4)$ resulted in the formation of the tetranuclear $[\text{Cp}^*\text{IrCl}\{\mu\text{-Te}(\eta^6\text{-Tol})\text{RuCp}^*\}_2\text{RuCp}^*(\text{CO})]\text{Cl}_2$ and binuclear $[\text{Cp}^*\text{Ir}(\mu\text{-H})(\mu\text{-TeTol})_2\text{Ru}(\text{CO})(\text{COD})]\text{BPh}_4$ 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.^{127,128} 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.



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



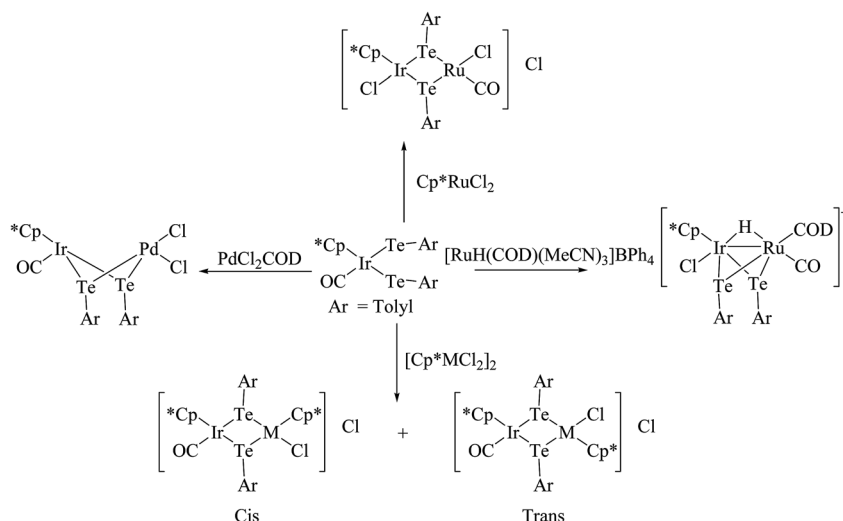


Fig. 9 Crystal structure of $[\text{Cp}^*\text{Ir}(\text{CO})(\mu\text{-TeTol})_2\text{IrCp}^*\text{Cl}]$ (redrawn from ref. 126).

4.3.1. Reactivity of various tellurium systems with palladium and platinum nonchelated phosphine precursors.

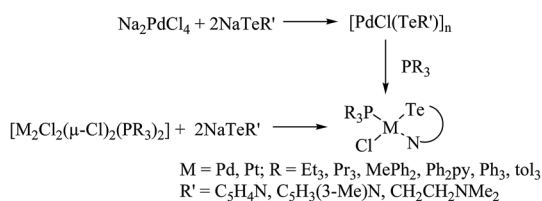
T. B. Rauchfuss and Rheingold synthesized a series of complexes of the type $[\text{Pt}(\text{ETeC}_6\text{H}_4)(\text{PPh}_3)_2]$ ($\text{E} = \text{S}; \text{Se}; \text{Te}$) derived from ligand systems like alkeneditellurides and 1,2 benzeneditellurides,¹²⁹ which represent the first examples of

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



Scheme 12 Synthesis of various heterometallic complexes using $[\text{Cp}^*\text{Ir}(\text{CO})(\text{TeTol})_2]$.





Scheme 13 Reactions of $[\text{M}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PR}_3)_2]$ with various sodium salts of telluroate ligands.

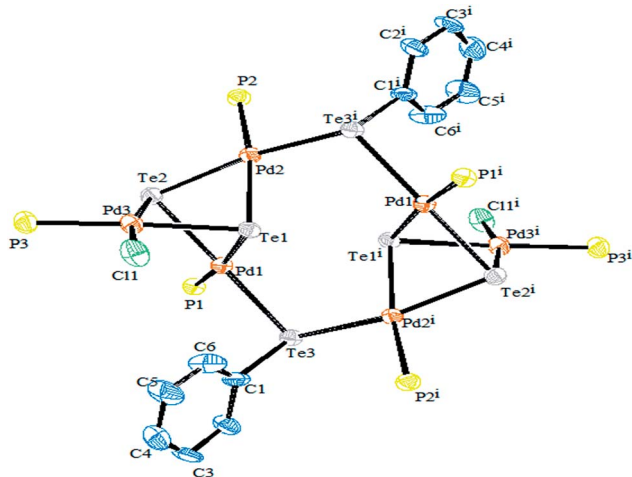
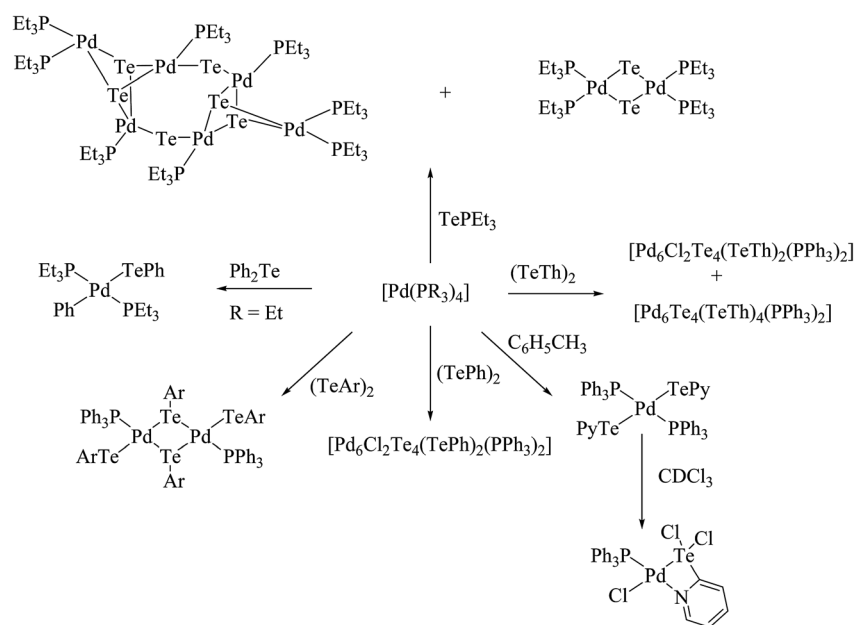


Fig. 10 Crystal structure of $[\text{Pd}_6\text{Te}_6\text{Cl}_2(\text{PET}_3)_6]$ (redrawn from ref. 138).

Performing an oxidative addition reaction between $[\text{Pd}(\text{PPh}_3)_4]$ and various diaryl ditelluride ligand systems yielded binuclear products with the composition $[\text{Pd}_2(\mu\text{-TeAr})_2(\text{TeAr})_2(\text{PPh}_3)_2]$.¹³² In the latter complex, both terminal and bridging positions are occupied with aryl telluroles (Scheme 13).



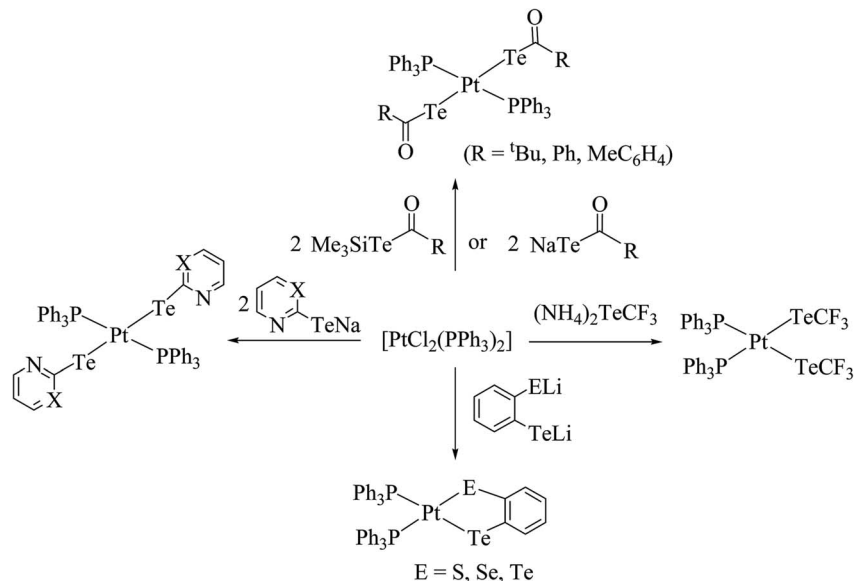
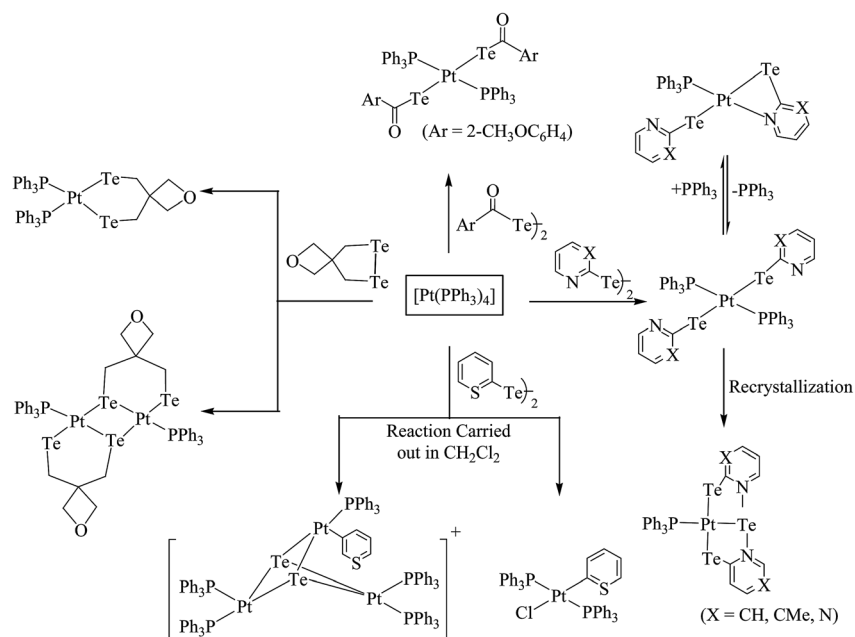
Scheme 14 Oxidative addition of $[\text{Pd}(\text{PR}_3)_4]$ (R = Et, Ph) with various diorganoditellurides.

On the other hand, an alike reaction upon performing with $[\text{M}(\text{PPh}_3)_4]$ (M = Pd, Pt) with various ligand systems, such as CF_3Te_2 , Th_2Te_2 , Ph_2Te_2 , afforded mono-, bi-, tri-, and hexanuclear complexes $[\text{Pd}_6\text{Te}_6\text{Cl}_2(\text{PET}_3)_6]$ (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 $[\text{M}(\text{Ar})(\text{TeAr})(\text{PET}_3)_2]$ (M = Pd, Pt) (Scheme 14).²²

Molecular orbital calculations also concluded that the activation energy barrier for the oxidative addition of dichalcogenides to $[\text{M}(\text{PH}_3)_2]$ decreases in the order $\text{S} > \text{Se} > \text{Te}$ (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 ($\text{S} < \text{Se} < \text{Te}$). 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 $[\text{Pt}(\text{PPh}_3)_4]$ and hemilabile pyridyl ditelluride $(\text{C}_5\text{H}_4\text{N})_2\text{Te}_2$ to isolate novel complexes with the composition $[\text{Pt}\{\text{TeC}_5\text{H}_3(3\text{-R})\text{N}\}_2\text{Te}(\text{PPh}_3)]$ (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 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 2NaTeC₅H₃(3-R)N (R = H, Me) (Scheme 15). The crystal structure of [Pt{TeC₅H₃(3-R)N₂Te(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)C₅H₄N}(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(η²-norbornene)(PPh₃)₂] has also been applied to study oxidative addition with bulky ditellurides of dibenzobarrelenyl and norbornene. The reaction afforded the formation of four- and five-membered telluraplatinacycles compounds [Pt(Te∩C)(PPh₃)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



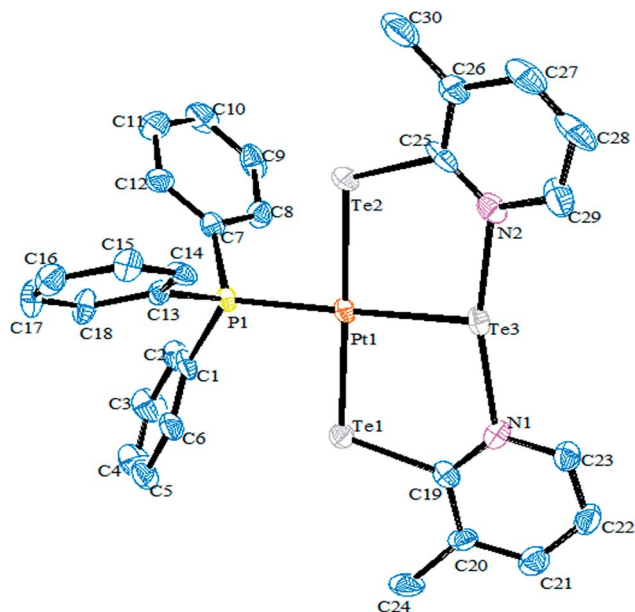
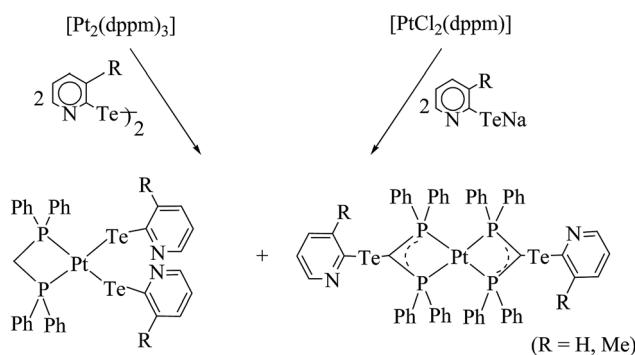


Fig. 11 Crystal structure of [Pt(TeC₅H₃(3-Me)N)₂Te(PPh₃)] (redrawn from ref. 7).



Scheme 17 Reactions of [Pt₂(dppm)₃]/[PtCl₂(dppm)] with dipyriddy ditellurides/pyridyl tellurolytes, respectively.

chelating phosphine diphenylphosphinomethane (dppm) 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 tellurolytes (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{Ph₂PCH(TeC₅H₃(3-R)N)PPh₂}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

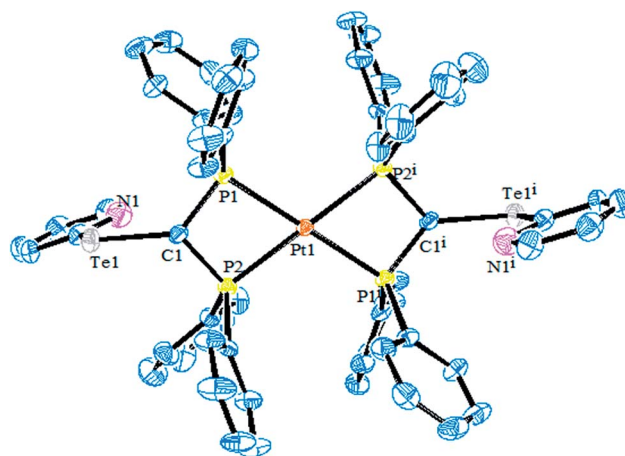


Fig. 12 Crystal structure of [Pt(PPh₂CH(TeC₅H₄N)PPh₂)₂] (redrawn from ref. 8).

the carbon center (Fig. 12). It can be concluded that the reactivity of the same palladium phosphine precursors with 4-pyridyl tellurolytes to lead to the tetranuclear compound [Pd₂(μ-Te)(μ₂-TeC₅H₄N)(4-TeC₅H₄N)(μ-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]/[PtCl₂(dppe)] and the aryl ditellurides/sodium salt of aryl tellurolyte (aryl = py, Ph, tol, Mes, Thienyl), a mononuclear product was isolated.^{8,140,141} Only in the case of the methyl-substituted telluropyridne ligand system was a complex with the composition [PtCl{TeC₅H₃(3-Me)N}(dppe)] isolated, which existed in equilibrium with the moiety [Pt{κ²-

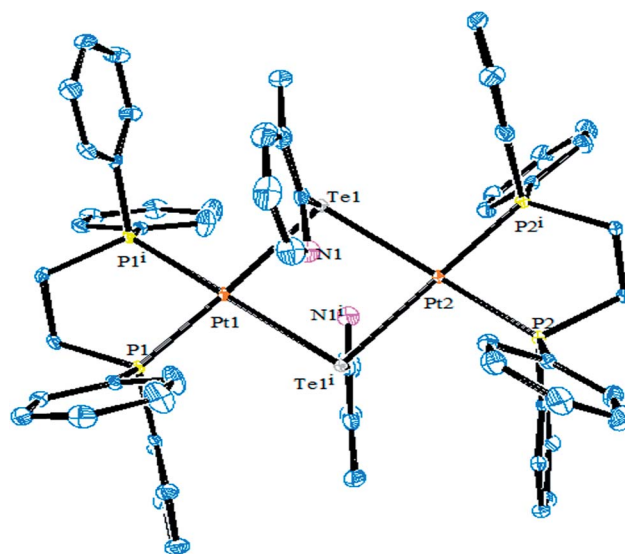
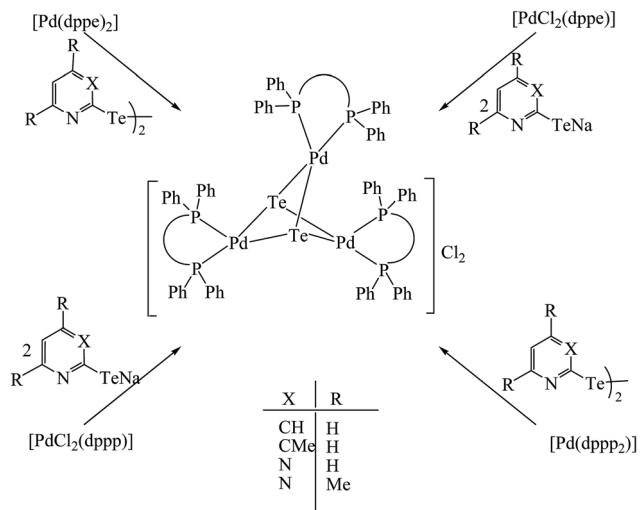


Fig. 13 Crystal structure of [Pd₂(μ-TeC₅H₃(3-Me)N)₂(dppe)] (redrawn from ref. 8).



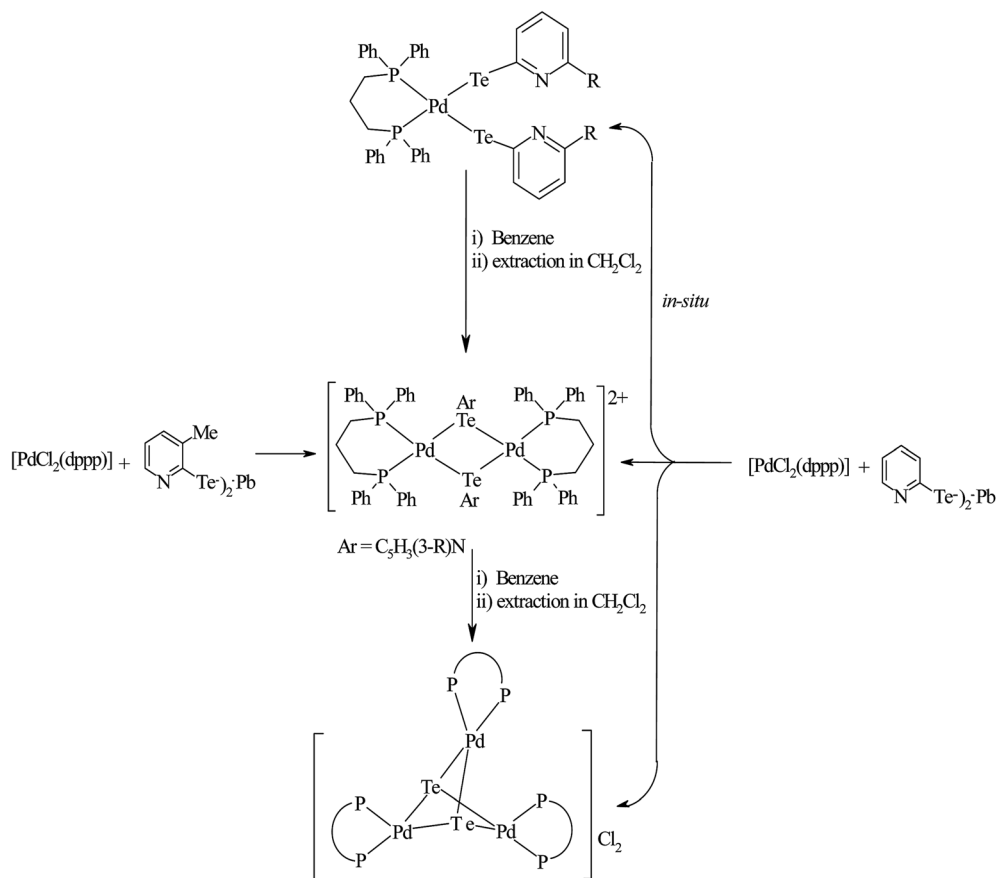
Scheme 18 Reactions of $[\text{Pd}(\text{PNP})_2]$ and $[\text{PdCl}_2(\text{PNP})]$ ($\text{PNP} = \text{dppe}, \text{dppp}$) with Ar_2Te_2 ($\text{Ar} = \{\text{C}_5\text{H}_3(3\text{-R})\text{N}\}, \{\text{C}_5\text{H}_2(4,6\text{-R})\text{N}\}$) ($\text{R} = \text{H}, \text{Me}$) and their corresponding sodium salts.

$\text{TeC}_5\text{H}_3(3\text{-Me})\text{N}\{\text{dppe}\}^+$. 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 $[\text{Pd}(\text{dppe})_2]/[\text{PdCl}_2(\text{dppe})]$ 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.

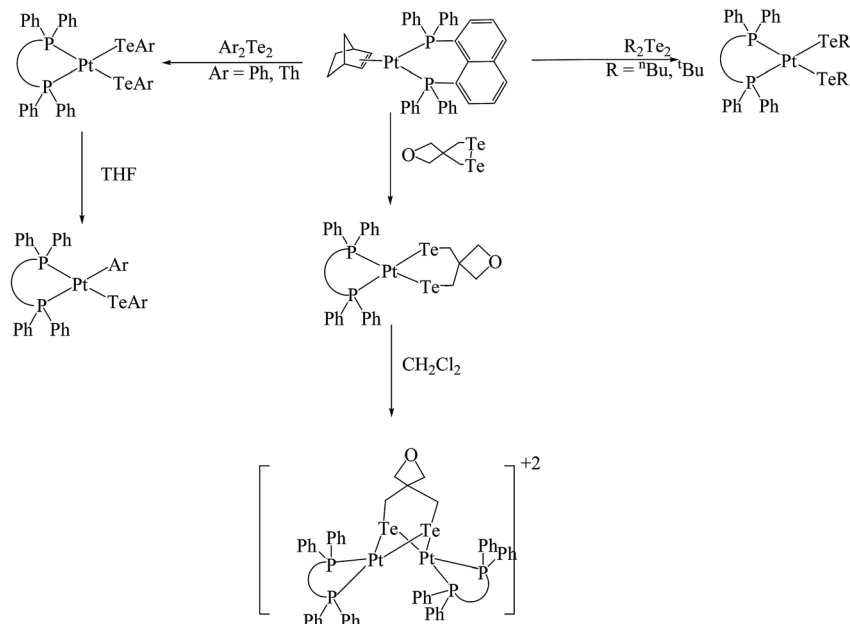
In the case of platinum precursors of diphenylphosphino-propane (dppp), like $[\text{Pt}(\text{dppp})_2]/[\text{PtCl}_2(\text{dppp})]$, performing a similar reaction as mentioned above with various hemilabile ligand systems afforded mono- and trinuclear products.^{8,48} However, the reaction with palladium 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 $[\text{PdCl}_2(\text{dppp})]$ and $[\text{Pb}(\text{TeC}_5\text{H}_4\text{N})_2]$ (Scheme 19).⁸ Upon recording the $^{31}\text{P}\{\text{H}\}$ 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 $[\text{Pt}(\text{dppn})(\text{nb})]$ derived from the chelating phosphine

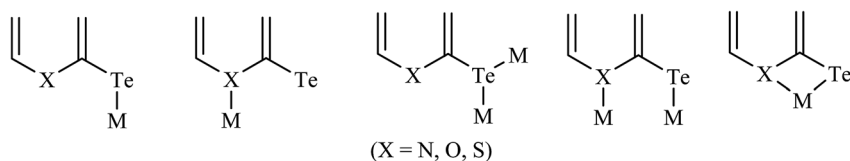


Scheme 19 Reactions of $[\text{PdCl}_2(\text{dppp})]$ with the lead salts of 2-pyridyl chalcogenolate.





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



Scheme 21 Various coordination modes in hemilabile telluroate ligand systems.

diphenylphosphineno naphthalene ($\text{Ph}_2\text{P-naphthyl-PPh}_2$).¹³⁶ These precursors showed a remarkable reactivity toward ditelluride systems. Upon reaction with various cyclic/saturated, acyclic/saturated, and cyclic/unsaturated ditellurides, the mononuclear $[\text{Pt}(\text{Te}_2\text{C}_5\text{H}_8\text{O})(\text{dppn})]$ and binuclear $[\text{Pt}(\text{Te}_2\text{C}_5\text{H}_8\text{O})(\text{dppn})]$ 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).

5. Metal tellurides

The binuclear complexes $[\text{M}_2(\mu\text{-Te})_2(\text{dppe})_2]$ ($\text{M} = \text{Pd}, \text{Pt}$) (Fig. 14) act as a powerful metallophilic ligand to provide a binding site for various transition metals, d^{10} systems, and lanthanide metal centers. The former complexes can be isolated by the reaction between M^{2+} , dppe, and NaTeH in a *N,N*-dimethylformamide and acetonitrile mixture.¹⁴² The reaction of $[\text{Pt}(\text{CH}_3\text{CN})_4(\text{NO}_3)_2]$ with a similar composition to the former complexes led to the formation of pentanuclear complexes $[\text{Pt}\{\text{Pd}_2(\mu\text{-Te})_2(\text{dppe})_2\}_2]^{2+}$ (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+} , PNP, and NaTeH in *N,N*-dimethylformamide for more than 20 h stirring (Scheme 22).¹⁴³ Undoubtedly, strong coordinating solvents, like DMF, CH_3CN , 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 $[\text{Pt}_3\{(\mu\text{-Te})_2(\text{dppe})_2\}_2]^{2+}$ by the oxidative addition of $[\text{Pt}(\text{dppe})_2]$ and vitreous tellurium under refluxing for 5 h.¹⁴⁷ The isolation



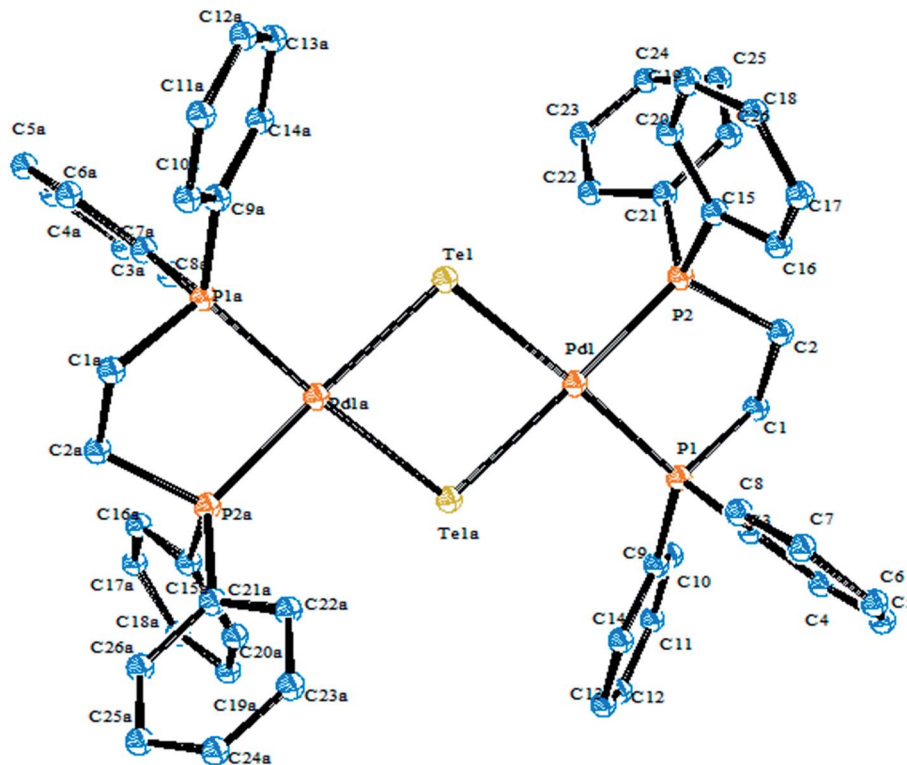


Fig. 14 Crystal structure of $[\text{Pd}_2(\mu\text{-Te})_2(\text{dppe})_2]^{2+}$ (redrawn from ref. 142).

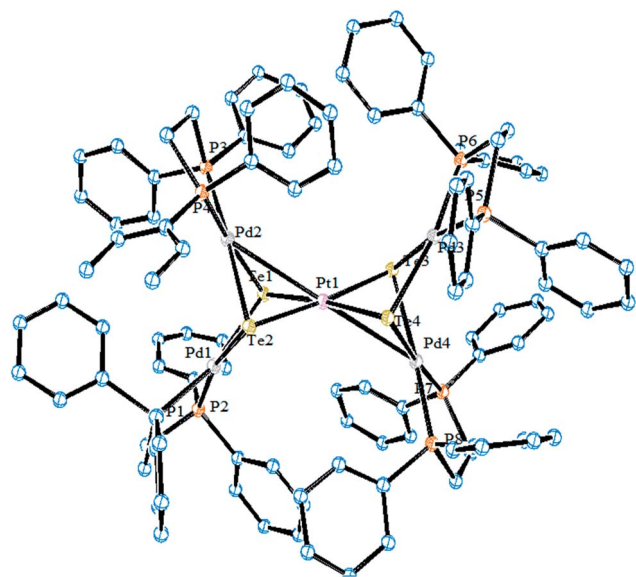


Fig. 15 Crystal structure of $[\text{Pt}\{\text{Pd}_2(\mu\text{-Te})_2(\text{dppe})_2\}_2]^{2+}$ (redrawn from ref. 142).

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 $[\text{PPh}_4]_2[\text{Pd}(\text{Te}_4)_2]$ 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 $[\text{Li}_4(\text{en})_{10}][\text{Pd}_6(\mu_3\text{-Te})_8]$ was formed by the reaction of $[\text{Pb}_2\text{Te}_3]^{2-}$ with $[\text{PdCl}_2(\text{PPh}_3)_2]$.¹⁵¹ Contrary to the palladium precursors, the platinum analog resulted in the cluster complex $[\text{Pt}_4\text{Te}_4(\text{Te}_3)_6]^{4-}$, which was comprised of a Pt_4Te_4 cubane core with a distorted octahedral configuration around the platinum atom.¹⁵² Recently, several platinum group cluster complexes were isolated by refluxing TeCl_4 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 $[\text{CpIr}(\text{CO})(\text{TeTol})_2]$ was subjected to reaction with two equivalents of $[\text{M}(\text{PPh}_3)_4]$ ($\text{M} = \text{Pd}, \text{Pt}$) (Scheme 23), a compound of the type $[\text{CpIr}(\text{CO})(\mu_3\text{-Te})_2\{\text{MTol}(\text{PPh}_3)_2\}]$ was isolated, while the similar reaction with one equivalent of $[\text{Pt}(\text{PPh}_3)_4]$ yielded the intermediate product $[\text{CpIr}(\text{CO})(\mu\text{-Te})(\mu\text{-TeTol})\{\text{PtTol}(\text{PPh}_3)\}]$.¹⁵⁷ The latter complexes upon reaction with $[\text{Pd}(\text{PPh}_3)_4]$ derived the heterometallic complex $[\text{CpIr}(\text{CO})(\mu\text{-Te})_2\{\text{PdTol}(\text{PPh}_3)\}]$





Scheme 22 Various approaches 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 into a Te–Tol bond in the complex [CpIr(CO)(μ-Te)(μ-TeTol){PtTol(PPh₃)}].^{126,157}

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

Fig. 16 Crystal structure of [CpIr(CO)(μ-Te)₂(PdTol(PPh₃)) {PtTol(PPh₃)}] (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-pyrrolidone).^{165,166} Similarly, an attempted reduction of aromatic nitriles serendipitously led to the pharmacologically important product 7-diaza-9H 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 [(η⁶-C₆H₆)Ru(L)](PF₆) (L = 2-





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



Scheme 25 Oxidation of alcohols through ruthenium telluroate complexes.

MeSC₆H₄CH=NCH₂CH₂EC₆H₄-R; R = H, E = S, Se; 2-MeSC₆H₄CH₂NHCH₂CH₂EC₆H₄-R; R = OMe, E = Te),⁶³ 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 × 10⁴. Strikingly, the complex (η⁶-C₆H₆)[Ru(2-MeSC₆H₄CH₂NHCH₂CH₂TeC₆H₄-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 [(η⁶-C₆H₆)



Scheme 26 Transfer of hydrogen reaction catalyzed by ruthenium telluroate 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 telluroate 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



Scheme 27 Representation of palladium–platinum telluroate catalyzed Suzuki and Heck reactions.



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