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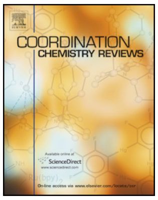

Review

New vistas in the chemistry of platinum group metals with tellurium ligands

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ABSTRACT

This article focuses on recent developments in the chemistry of platinum group metals (Ru, Os, Rh, Ir, Pd and Pt) with tellurium ligands. Attempts have been made to present a comprehensive account of the subject matter. Platinum group metal complexes with different kinds of tellurium ligands, such as diorganoditellurides, tellurolates, telluroethers, tellurides, polytellurides and tellurium(IV), are described. Various aspects of these complexes like synthesis, reactivity, structures and applications are covered in this review.

Abbreviations: ppy, metalated 2-phenylpyridine; OTf, trifluoromethanesulfonate; Fc, ferrocenyl ($C_5H_5FeC_5H_4^-$); Tp*, hydrotris(3,5-dimethylpyrazol-1-yl)borate; Coe, cyclooctene; Cp, cyclopentadienyl; Cp*, pentamethylcyclopentadienyl; Th, 2-thienyl (C_4H_3S); py, pyridine (C_5H_5N); dppm, bis(diphenylphosphino)methane; dppe, bis(diphenylphosphino)ethane; dppp, 1,3-bis(diphenylphosphino)propane; dpae, 1,2-bis(diphenylarsino)ethane; np, $N(CH_2CH_2PPh_2)_3$; pp3, tris {2-(diphenylphosphino)ethyl}phosphine; c-Hx, cyclohexyl; TMNO, trimethylamine N-oxide; dba, dibenzylidenacetone; tht, tetrahydrothiophene; dmf, dimethylformamide.

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1. Introduction

Tellurium was discovered by an Austrian Chemist F. J. Müller von Reichenstein in 1782, and several years later (in 1798), it was named from the Latin tellus meaning earth by another Austrian Chemist M. H. Klaproth. Although the first organotellurium compound, diethyltelluride (Et_2Te) was prepared by Wöhler in 1840, the chemistry of tellurium compounds remained dormant for a long time as evident from the fact that only about 50 papers were published between 1910 and 1950 while on an average 100 papers per year appeared between 1950 and 1990 [1]. This slow development and inhibition to persue organotellurium chemistry can be traced historically. There has been a general belief that these compounds have obnoxious smell and are air and light sensitive, difficult to handle and are toxic to humans [1]. Additionally, it was generally perceived that the chemistry of tellurium derivatives would be more or less similar to that of sulfur or selenium. However, several dissimilarities in the properties of tellurium compounds and those of lighter congeners as well as historical misconceptions have been recognized with time. During the last two decades or so organotellurium chemistry has witnessed a rapid development encompassing diverse areas. These include (i) applications of organotellurium compounds in organic synthesis [2–4], (ii) chalcogenides as organocatalysts [5], intramolecular coordination in organotellurium compounds [6], macrocyclic tellurium compounds [7], ligand chemistry of organotellurium compounds [7–12], tellurium compounds of main group elements [13,14], metal complexes in catalysis [15], molecular precursors for metal chemical vapor deposition [16,17], polychalcogenides [$Q^{2-}{}_x$ (Q = S, Se, Te)] [18–21], pharmacological and glutathione peroxidase like catalytic activity [21–26] and biomethylation of selenium and tellurium [27].

Tellurium exhibits a wide range of integral and fractional formal oxidation states. The common oxidation states are −2 (Te^{2-}), −1 ($Te_2{}^{2-}$, Te^-), +2, +4 and +6 while the factional oxidation states are reported in poly nuclear cations ($Te_x{}^{2+}$) and anions ($Te^{2-}{}_x$). Redox cycling of tellurium between +II and +IV oxidation states occurs readily. Compounds in these oxidation states can function as both electron donors (Lewis base) as well as electron acceptors (Lewis acid) primarily depending on the nature of the substituent on tellurium atom. Hypervalent nature of tellurium based on 3c–4e interaction similar to selenium is also encountered in its compounds.

The increased nucleophilicity, low electronegativity, diffused orbitals, increased metallic character, larger size than that of the lighter congeners (S or Se), cumulatively results in weakening of the Te—C bond. The weaker nature of Te—C bond of tellurium endow properties, structures and reactivities of metal complexes derived from tellurium ligands which are quite often distinct from those of the corresponding sulfur or selenium derivatives. For example, while the lighter chalcogenoethers (R_2S or R_2Se) generally act as neutral donor ligand towards gold(I), the corresponding telluroether complex of gold(I) are hardly isolated as gold(I) (e.g., (tht)AuCl) readily oxidizes Ph_2Te to Ph_2TeCl_2 with concomitant formation of metallic gold [28]. Gabbai and co-workers have, however, recently isolated an internally functionalized telluroether complex, $[AuCl\{PPh_2{-}C_6H_4)_2Te\}]$ [28]. The chemistry of platinum group metals with sulfur, and to some extent selenium, ligands has been extensively explored, whereas tellurium ligands have received attention only during the past two decades or so. The past decade has witnessed a rapid growth in the chemistry of platinum group metals with tellurium ligands with several unprecedented results. Thus it was considered worthwhile to review the subject area in a comprehensive manner so as to give further impetus to the progress of this field.

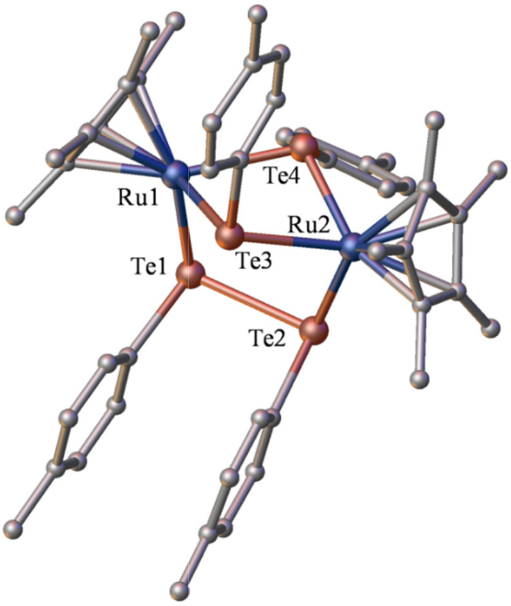
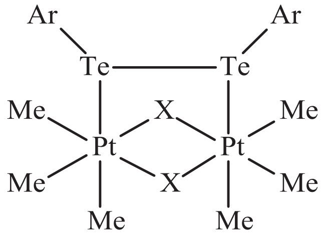


Fig. 1. Structure of $[\{Cp^*Ru(\mu\text{-Tetol-}p)\}_2(p\text{-tol}_2Te_2)]$ (redrawn from Ref. [30]).

2. Metal complexes with diorganoditellurides

Diorganoditellurides generally undergo Te—Te bond cleavage to give tellurolate complexes, but as a ligand with intact coordinated diorganoditelluride are scanty. Trimethylplatinum halides, except chloride, react rapidly with diarylditelluride in chloroform to yield μ-η^1,η^1-ditelluride bridged binuclear complexes, $[\{PtMe_3X\}_2(Ar_2Te_2)]$ (X = Br or I; Ar = Ph or p-tol) (**I**) as orange-red crystalline solids [29]. These complexes are fluxional at room temperature. The ^{125}Te NMR resonances are shielded with respect to the corresponding free ditelluride and show coupling with ^{195}Pt nucleus ($^1J(^{195}Pt{-}^{125}Te)$ of ~900 Hz) [29].



(X = Br or I; Ar = Ph or *p*-tol)

(**I**)

The complex, $[\{Cp^*Ru(\mu\text{-TeAr})\}_2(Ar_2Te_2)]$ (Ar = Ph or tol) represents another example of μ-η^1, η^1-ditelluride bridged species [30]. The complex is isolated from a reaction between $[Cp^*RuCl_2]_2$ and $Me_3SiTeAr$ in THF at room temperature. The coordinated ditelluride is believed to be formed by coupling of tellurolate ligands at the diruthenium center. The Te-Te distance (2.902 (3) Å) (R = p-tol) is slightly elongated from the one observed in free ditelluride (Te—Te = 2.696 Å in tol_2Te_2). The Ru—Te (tellurolate) bond is longer (av Ru—Te = 2.68 Å) than the one with ditelluride ligand (Ru—Te = 2.540 (3) Å (Fig. 1) [30].

Treatment of $[\{Cp^*Ir(ppy)(H_2O)][OTf]$ with diphenylditelluride results in the formation of η^1-bonded ditelluride complex, $[Cp^*Ir(ppy)(PhTeTePh)][OTf]$ rather than the oxidative addition product formed by cleavage of Te—Te bond [31]. The Te—Te distance