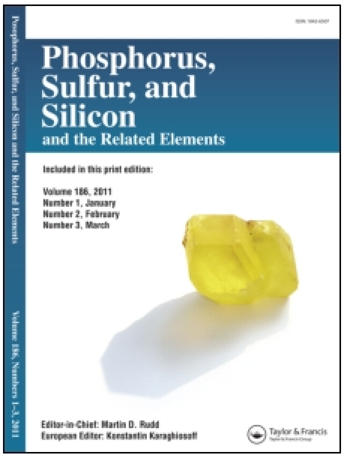

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# Organochalcogenolates of Palladium(II) and Platinum(II): Versatile Molecular Precursors for Metal Chalcogenides

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# Organochalcogenolates of Palladium(II) and Platinum(II): Versatile Molecular Precursors for Metal Chalcogenides

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*This presentation intends to discuss the design and synthesis of low temperature single source molecular precursors for the synthesis of palladium chalcogenides, both in bulk and nano-size regime. Thus a variety of organochalcogenolates of palladium and platinum differing in nuclearity (mono-, bi-, tri- and hexa- nuclear) have been isolated and characterized by uv-vis, NMR ($^1H$, $^{13}C$, $^{31}P$, $^{77}Se$, $^{125}Te$, $^{195}Pt$) spectroscopy and X-ray crystallography. Thermal behavior of several complexes, such as $[Pd(SeCOAr)_2(PR_3)_2]$, $[Pd(OAc)(ECH_2CH_2CH_2NMe_2)]_2$, etc. has been studied by TG analyses. Solvothermal decomposition yields palladium chalcogenides nano-particles (e.g., $Pd_7Te_3$, $Pd_{17}Se_{15}$) which were characterized by XRD, EDAX and SEM method.*

**Keywords** Metal chalcogenides; NMR; organochalcogenolates; palladium; platinum

## INTRODUCTION

Metal chalcogenides constitute an important family of functional inorganic materials, which find several applications in electronic and opto-electronic devices. Platinum group metals form numerous chalcogenides, which differ in stochiometry and structures. Recently they have attracted considerable attention due to their relevance in catalysis and materials science.[1,2] Among other synthetic strategies, molecular precursor route has been quite successful for their preparation. Earlier, we had described the chemistry of N,N-dimethylamino chalcogenolate and pyridine-2-chalcogenolate complexes of palladium and platium.[3,4] Some of our recent results on palladium and platinum complexes derived from selenolate ligands shown in Scheme-1 and their use as molecular precursors are described in this presentation.

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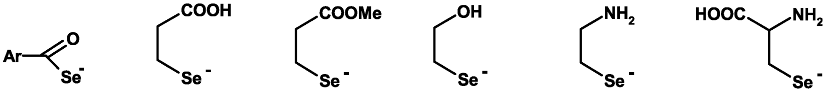


**SCHEME 1**

## RESULTS AND DISCUSSION

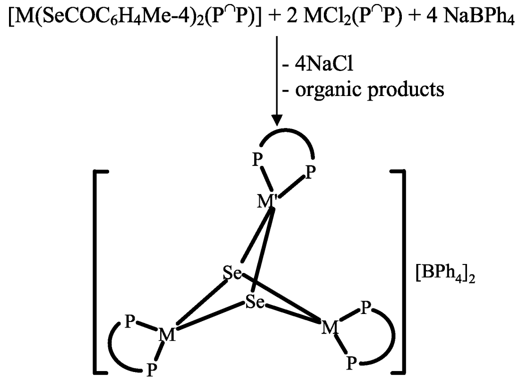
### Selenocarboxylate Complexes

Reaction of $[MCl_2(P^{\cap}P)]$ or $[MCl_2(PPr_3)_2]$ with two equivalents of ArCOSeK in dichloromethane readily yields *cis*-$[M(SeCOAr)_2(P^{\cap}P)]$ or *trans*-$[M(SeCOAr)_2(PPr_3)_2]$ (M = Pd or Pt; Ar = Ph or tol; $P^{\cap}P$ = dppm, dppe, dppp), respectively as yellow (M = Pt) to orange–red (M = Pd) crystalline solids.[5] The IR spectra displayed a carbonyl stretching in the region 1610-1630 $cm^{-1}$ indicative of unidentate ArCOSe ligand. The $^{31}P\{^1H\}$ NMR spectra showed a single resonance suggesting the formation of only one isomeric species. The $^1J(Pt\text{-}P)$ (2726-3030 Hz) is reduced significantly from the values for the corresponding $[PtCl_2(P^{\cap}P)]$ owing to the strong trans influence of Se ligands, which are *trans* to the chelating phosphine. The structure of $[Pt(SeCOPh)_2(dppp)]$, established by X-ray crystallography, revealed a *cis* configuration with unidentate selenobenzoate ligand bonded through selenium atom only.

The mono-nuclear chalcogenolate complexes have been used successfully for the preparation of bi- and tri-nuclear derivatives.[6,7] Thus when $[M(SeCOAr)_2(P^{\cap}P)]$ was treated with $[MCl_2(P^{\cap}P)]$ in the presence of $NaBPh_4$ in methanol, selenido bridged trinuclear complexes, $[M_3(\mu\text{-}Se)_2(P^{\cap}P)_3][BPh_4]_2$ were formed in moderate to high yields via unprecedented cleavage of C-Se bond (Scheme 2). This reaction can be exploited for the preparation of hetero-tri-nuclear complexes. All the complexes have been characterized by uv-vis and NMR ($^1H$, $^{31}P$, $^{77}Se$, $^{195}Pt$) spectroscopy. The $^{77}Se$ NMR spectra exhibited a single resonance, shielding of which depends on the nature of phosphine. For $[Pd_3(\mu\text{-}Se)_2(P^{\cap}P)_3][BPh_4]_2$the signal appeared at $\delta$ -168 (dppm), -132 (dppe) and 48.8 (dppp) ppm. The molecular structure of $[Pd_3(\mu\text{-}Se)_2(dppe)_3][BPh_4]_2$has been established by X-ray crystallography. Coordination around each palladium atom is defined by two P atoms from chelating dppe and two Se atoms.[8]

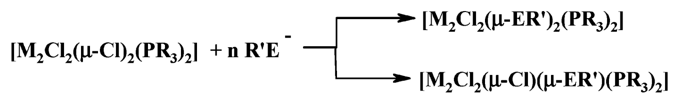
### Complexes from 2-(Methoxycarbonyl)ethyl Selenolate and Related Ligands

Reactions of $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with $NaSeCH_2CH_2COOMe$ (represented here as SeR′) afforded $[M_2Cl_2(\mu\text{-}SeR')_2(PR_3)_2]$ and $[M_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeR')(PR_3)_2]$ depending on the stoichiometry of the



**SCHEME 2** M/M′/P‿P = Pd/Pd/dppm; Pd/Pd/dppe; Pd/Pd/dppp; Pt/Pt/ dppm; Pt/Pt/(PPr$_3$)$_2$; Pd/Pt/dppm; Pt/Pd/dppm.

reactants [Equation (1)]. The latter can also be obtained by treatment of [M$_2$Cl$_2$($\mu$-SeR')$_2$(PR$_3$)$_2$] with [M$_2$Cl$_2$($\mu$-Cl)$_2$(PR$_3$)$_2$]. These complexes have been characterized by IR, NMR ($^1$H, $^{31}$P, $^{77}$Se, $^{195}$Pt) spectroscopy (Figure 1)[9]. The bis selenolato-bridged complexes exist as a mixture of *cis* and *trans* isomers, while chloro/selenolato-bridged derivatives could be isolated in the *cis* form.



(1)

The complex, [Pd$_2$Cl$_2$($\mu$-SeR′)$_2$(PPr$_3$)$_2$], when left in solution for several hours in open atmosphere, red crystalline product, [Pd$_3$Cl$_2$($\mu$-SeR′)$_4$(PPr$_3$)$_2$], characterized by X-ray crystallography,

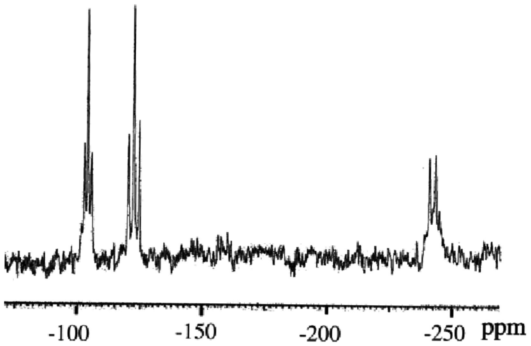
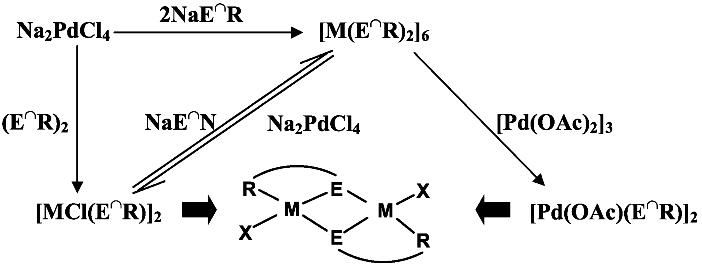


**FIGURE 1** $^{77}$Se$^1$H NMR spectrum of [Pt$_2$Cl$_2$($\mu$-SeCH$_2$CH$_2$COOMe)$_2$(PEt$_3$)$_2$] in CDCl$_3$.

was isolated in poor yield. In this complex, the three distorted palladium atoms are held together by bridging selenolate groups. The three metal planes are tilted towards earch other resulting in a zig-zag shape of the molecule.[9] Other complexes, *trans*-$[Pd_2Cl_2(\mu\text{-}SeR')_2(PPh_3)_2]$, *cis*-$[Pd_2Cl_2(\mu\text{-}SeCH_2CH_2OH)_2(PMePh_2)_2]$, $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeCH_2CH_2COOH)(PPr_3)_2]$ and $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeR')(PPr_3)_2]$ have also been characterized by X-ray crystallography. All of them have bridging selenolate groups.[9–11]

## Palladium and Platinum Complexes without Tertiary Phosphines

The reaction of $Na_2PdCl_4$ with two equivalents of $NaSeCH_2CH_2COOMe$ or $NaSeCH_2CH_2CH_2NMe_2$ in methanol gave homoleptic hexanuclear palladium complexes, $[Pd(SeR)_2]_6$ ($R = CH_2CH_2COOMe$ or $CH_2CH_2CH_2NMe_2$) (Scheme 3). Both the complexes have a centrosysmmetric hexameric structure in which Pd atom has a square planar configuration defined by $PdSe_4$ core.[9,12] Reaction of $Na_2PdCl_4$ with $(Me_2NCH_2CH_2CH_2E)_2$, ($E = S$, Se, Te) afforded binuclear complexes, $[PdCl(ECH_2CH_2CH_2NMe_2)]_2$. The latter is also formed readily when $[Pd(SeR)_2]_6$is treated with $Na_2PdCl_4$.The hexanuclear complex on treatment with $[Pd(OAc)_2]$ gave the acetato derivatives $[Pd(OAc)(ECH_2CH_2CH_2NMe_2)]_2$. All of them have been characterized by X-ray crystallography.[13,14]



SCHEME 2

## Orthopalladated Complexes

Reactions of orthometallated bi-nuclear palladium complexes with NaER, obtained by $NaBH_4$ reduction of $R_2E_2$ in methanol, gave complexes, $[Pd_2(\mu\text{-}ER)_2(C^{\frown}Y)_2]$ ($HC^{\frown}Y$ = N,N-dimethylbenzylamine ($C_6H_5CH_2NMe_2$), N,N-dimethylnaphthylamine ($C_{10}H_7NMe_2$), tri-*o*-tolylphosphine $P(tol\text{-}o)_3$; ER = SePh, $SeC_6H_2Me_3$-2,4,6, TePh,

$TeC_6H_2Me_3$-2,4,6). Similar reactions of $[Pd_2(\mu\text{-}Cl)_2(C_{10}H_6NMe_2\text{-}C,N)_2]$ with $Pb(SMes)_2$or MesSH in the presence of $NaHCO_3$ gave chloro/thiolato-bridged complex $[Pd_2(\mu\text{-}Cl)(\mu\text{-}SMes)(C_{10}H_6NMe_2\text{-}C,N)_2]$ (Mes = 2,4,6-$Me_3C_6H_2$). The complexes $[Pd_2(\mu\text{-}Cl)(\mu\text{-}SMes)(C_{10}H_6NMe_2\text{-}C,N)_2]$ and $[Pd_2(\mu\text{-}SePh)_2(C_{10}H_6NMe_2\text{-}C,N)_2]$ have been structurally characterized.

## Molecular Precursors for Palladium Chalcogenides

The complex, $[Pd(SeCOPh)_2(PPr_3)_2]$ undergoes a single step decomposition (from TG) at 240°C with the formation of $Pd_{17}Se_{15}$ as inferred from weight loss and XRD pattern.[5] Thermolysis in TBP at 200°C gave nano-particles of $Pd_{17}Se_{15}$.

The TG curve of $[Pd_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(PPr_3)_2]$ showed a two-step decomposition with the formation of $Pd_{17}Se_{15}$ as suggested from weight loss and XRD pattern.[8] Solvothermal decomposition in TBP at 195°C gave nanoparticles of $Pd_{17}Se_{15}$, as characterized by XRD, EDAX (calc.: Pd = 60.4%; Se = 39.6%. obs.: Pd = 62.9%; Se = 37.1%) and SEM (Figure 2).

The complexes $[Pd(OAc)(ECH_2CH_2CH_2NMe_2)]_2$ (E = S or Se) on pyrolysis gave $Pd_{16}S_7$ and $Pd_{17}Se_{15}$, respectively. The complex $[Pd_2(\mu\text{-}TeMes)_2(C_{10}H_6NMe_2\text{-}C,N)_2]$ undergoes a two step (TG) decomposition with the formation of $Pd_7Te_3$ as characterized by XRD and EDAX.[15]

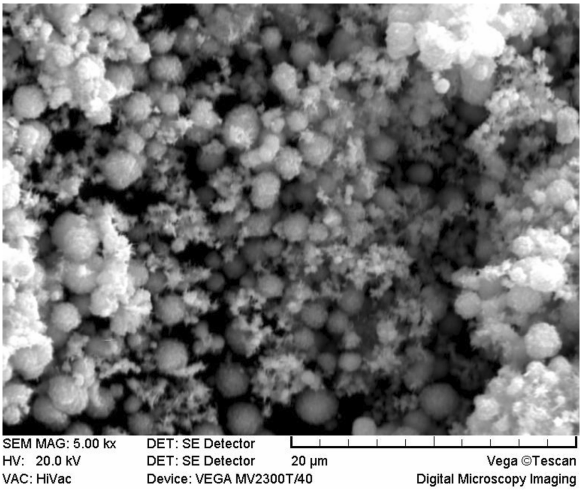


**FIGURE 2** SEM of $Pd_{17}Se_{15}$ obtained from $[Pd_2Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_2(PPr_3)_2]$.

## CONCLUSIONS

A fascinating and rich chemistry of palladium(II) and platinum(II) organochalcogenolate complexes, with or without tertiary phosphines, has been developed. Inter conversion of these complexes is quite facile and proved as a convenient synthetic strategy to isolate complexes differing in nuclearity and structure. Multinuclear NMR ($^{31}$P, $^{77}$Se, $^{125}$Te, $^{195}$Pt) spectroscopy has provided an insight about stereo-chemical aspects of these complexes. It has been demonstrated that several of these complexes are promising candidates for the preparation of metal chalcogenides both as nano-particles and in bulk form at moderately low temperatures.

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