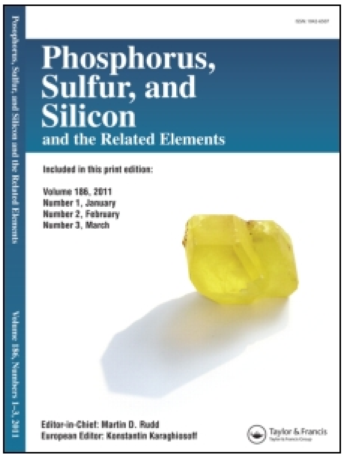

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CHEMISTRY OF PALLADIUM AND PLATINUM WITH SELENIUM AND TELLURIUM LIGANDS

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Reactions of NaER (E = Se, Te; R = Ph, substituted Ph or 2-pyridyl) with a number of mono- and bi-nuclear palladium and platinum complexes have been investigated. Complexes of the type $[M(Sepy)_2]$, $[M(ER)_2(PR_3)_2]$, $[M_2Cl_2(\mu\text{-}ER)_2(PR_3)_2]$ and $[M_2Cl_2(\mu\text{-}Cl)(\mu\text{-}ER)(PR_3)_2]$ (M = Pd, Pt) were isolated. They were characterized by elemental analysis, NMR (^{1}H, ^{13}C, ^{31}P, ^{77}Se, ^{125}Te, ^{195}Pt) data and in a few cases by X-ray diffraction studies. The $[M(Sepy)_2(PPh_3)_2]$ dissociates into PPh_3 and $[M(Sepy)(\eta^2\text{-}Sepy)(PPh_3)]$ in solution. 2-Selenopyridine in its complexes acts in a monodentate (bonding through selenium) as well as in chelating ($Se\frown N$) or bridging fashion. The mononuclear complexes $[M(ER)_2(PR_3)_2]$ are useful precursors for stepwise synthesis of cationic bi- and tri-nuclear derivatives.

Keywords: palladium; platinum; organochalcogenide; NMR

INTRODUCTION

Over the last few decades the chemistry of transition metal complexes with organochalcogenide ligands is dominated by metal thiolates[1] with little emphasis on higher homologs (selenolates and tellurolates).[2] The high propensity of organochalcogenides to bridge metal atoms makes them unsuitable for isolation of mononuclear complexes. Monomeric complexes are attractive due to their utility as precursors for semiconductor materials,[2,3] catalytic reactions[4] and for stepwise synthesis of homo- and hetro-, bi- and high-nuclearity complexes. This presentation deals with the synthesis and characterization of palladium and platinum complexes with organo-selenolates and -tellurolate ligands.

RESULTS AND DISCUSSION

Reactions of $[MCl_2(P^\frown P)]$ with NaER readily gave mononuclear complexes (Eq. 1).

$$[MCl_2(P^\frown P)] + 2\,NaER \rightarrow \underset{\textbf{I}}{[M(ER)_2(P^\frown P)]} + 2NaCl \quad ......(1)$$

[where M = Pd, Pt; ER = SePh, TePh or Sepy; $P^\frown P$ = $2PBu_3$, $2PMe_2Ph$, $2PMePh_2$, $2PPh_3$, $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH_2CH_2PPh_2$ (dppe), $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp)]

With chelating phosphines (dppm, dppe, dppp), **I** adopts a *cis* configuration. However, in the case of monodentate phosphines a *cis* complex (I) was formed initially which slowly isomerized to the *trans* product. The ^{31}P NMR spectra of **I** showed single resonances. The resonances for the platinum complexes were flanked with platinum satellites. The magnitude of $^{1}J(^{195}Pt-^{31}P)$ was reduced significantly from the corresponding values for $[MCl_2(P^\frown P)]$ due to the strong *trans* influence of the ER group. Since the *trans* influence for tertiary phosphines and RE^- are comparable, the $^{1}J(Pt-P)$ are expected to have similar values for the *cis* and *trans* isomers of I containing monodentate PR_3 ligands. This was indeed the case. However, both ^{77}Se and ^{125}Te nuclie have naturally occurring NMR active isotopes (I = ½) and hence the magnitude of $^{2}J(^{77}Se/\ ^{125}Te-^{31}P)$ would enable the identification of isomers. The ^{31}P NMR spectra of I showing such couplings ($^{2}J \sim 45$ Hz) have been assigned as *cis* complexes, while vanishingly small couplings indicate the formation of *trans* product. Both $^{2}J(^{77}Se-^{31}P)$ and $^{2}J(^{125}Te-^{31}P)$ are of comparable magnitude.

The $[M(Sepy)_2(PPh_3)_2]$ (M = Pd, Pt) dissociates in $CDCl_3$ solution and establishes an equilibrium between $[M(Sepy)(\eta^2\text{-}Sepy)(PPh_3)]$ (II) (nitrogen *trans* to chelating phosphine) and PPh_3. Repeated recrystalisation of $[Pd(Sepy)_2(PPh_3)_2]$ gave pure II (M = Pd). The variable temperature ^{31}P NMR spectroscopy revealed that II and PPh_3 predominantes at room temperature, but at -30 ^{0}C *trans*-$[M(Sepy)_2(PPh_3)_2]$ [M = Pt; δ ^{31}P, 23.1 ppm, $^{1}J(Pt\text{-}P)$ 2805 Hz] is the primary product.

The $^{77}Se\{^{1}H\}$ NMR spectrum of $[Pt(SePh)_2(PBu_3)_2]$ showed a triplet of triplets at δ -1219 ppm [$^{2}J(^{77}Se\ -^{31}P)_{cis}$ 7 Hz; $^{1}J(^{195}Pt\ -^{31}P)_{cis}$ 100 Hz] indicating the *trans* configuration of the complex. However, the *cis* complexes, I showed a doublet of $^{2}J(^{77}Se\ -^{31}P)_{trans} \sim 80$ Hz; $^{2}J(^{77}Se\ -^{31}P)_{cis} \sim 10$ Hz, $^{1}J(^{195}Pt-^{77}Se)_{cis}$ 160 - 208 Hz) (Figure 1). The ^{195}Pt NMR spectra exhibited a triplet due to coupling with two phosphorus nuclei. The ^{195}Pt resonances are shielded on substituting dppm by dppe. The observed shielding may be attributed to the ring size effects of the phosphine ligands. The ^{195}Pt NMR chemical shifts showed pronounced dependence of the chalcogen atom. The signal is shielded as one decends down the group (S, Se, Te) (*e.g.* $[Pt(EPh)_2(dppe)]$: E = S, ^{195}Pt δ -4733 ppm; Se, -4947 ppm; Te, -5310 ppm). The observed trend is in accord with the binding ability of organochalcogenide group (SR < SeR < TeR). Such a trend has been reported in $[Pt(CNS)_3L]^-$ complexes (L = SMe_2, $SeMe_2$, $TeMe_2$).[5] Structures of some of these complexes have been established by X-ray diffraction analysis (Table 1).[6-9]

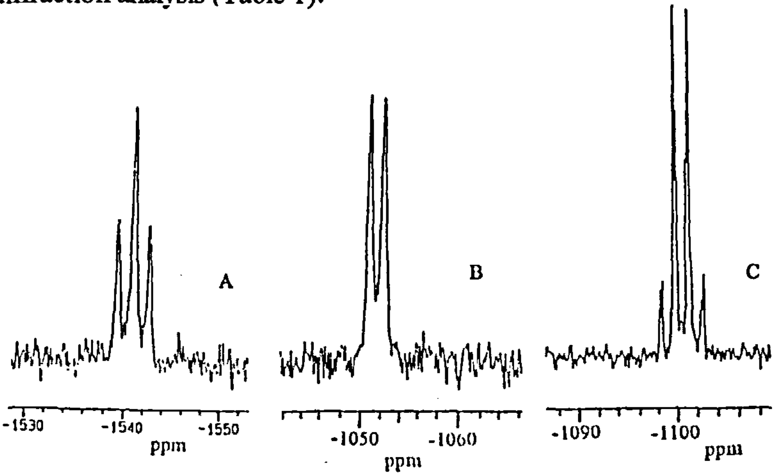


Figure 1 $^{77}Se\{^1H\}$ NMR spectra of (A) $[Pd_2(\mu\text{-}SePh)_2(dppe)_2][ClO_4]_2$ (B) $[Pd(SePh)_2(dppe)]$; (C) $[Pt(SePh)_2(dppe)]$ in $CDCl_3$.

Table 1: M-E and M-P bond distances for I

Complex	av. M-E	av.M-P	Ref.
trans-$[Pt(SePh)_2(PPh_3)_2]$	2.418	2.293	6
cis-$[Pd(SC_6F_5)_2(dppe)]$	2.357	2.263	7
cis-$[Pd(SePh)_2(dppe)]$	2.462	2.279	7
cis-$[Pt(SePh)_2(dppm)]$	2.447	2.255	8
cis-$[Pt(Sepy)_2(dppe)]$	2.466	2.257	9

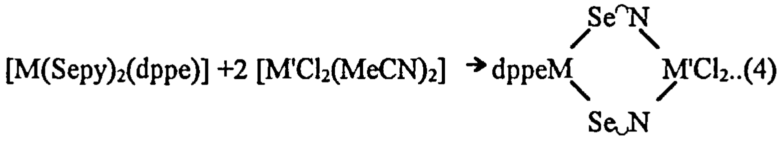
The mononuclear complexes I are useful precursors for the synthesis of bi- and tri-nuclear complexes (Eq. 2-4).

$$[M(ER)_2(P^\frown P)] + [M(solvent)_2(P^\frown P)]X_2 \rightarrow [M_2(\mu\text{-}ER)_2(P^\frown P)_2]X_2 \quad (2)$$

III

$$2\,[Pt(SR')_2(dppm)] + PtCl_2(PhCN)_2 + 2\,NaBF_4 \longrightarrow [(dppm)Pt(\mu\text{-}SR')_2Pt(\mu\text{-}SR')_2Pt(dppm)][BF_4]_2 \quad ...(3)$$

IV



$$[M(Sepy)_2(dppe)] + 2\,[M'Cl_2(MeCN)_2] \rightarrow dppeM(Se^\frown N)_2M'Cl_2 \quad ..(4)$$

V

The ^{31}P NMR spectra of binuclear complexes (III) exhibited a single resonance which is deshielded from the corresponding signal for mononuclear complexes. Similar deshielding was observed for ^{195}Pt signals. The ^{195}Pt NMR spectra of III (M = Pt) also showed $^{2}J(^{195}Pt\text{-}^{195}Pt)$ couplings (~ 650 Hz) further indicating their binuclear formulation. The $^{2}J(Pt\text{-}Pt)$ coupling in binuclear platinum(II) complexes stabilized by single atom bridging ligand vary between 200-900 Hz.[5] The magnitude of $^{1}J(Pt\text{-}P)$ increases (140-180 Hz) from values for the corresponding mononuclear complexes. The elemental analysis of IV were consistent with trinuclear formulation. The ^{31}P NMR spectra were similar to the binuclear complexes with the marginal increase in $^{1}J(Pt\text{-}P)$ values.

The uncoordinated nitrogen atoms in $[M(Sepy)_2(dppe)]$ can also be employed for ligation. Thus the reaction of $[M(Sepy)_2(dppe)]$ with $[M'Cl_2(MeCN)_2]$ gave insoluble orange to brown coloured solids, $[dppeM(Sepy)_2M'Cl_2]$ (M/ M = Pd, Pt) (V). The IR spectra displyed bands in the region 280 - 313 cm^{-1} assignable to νM-Cl absorptions which were absent in $[M(Sepy)_2(dppe)]$.

A number of reactions of NaER with $[M_2Cl_2(\mu\text{-}Cl)_2(PR'_3)_2]$ were investigated. With simple R groups binuclear complexes of the type $[M_2Cl_2(\mu\text{-}X)(\mu\text{-}ER)(PR'_3)_2]$ and $[M_2Cl_2(\mu\text{-}ER)_2(PR'_3)_2]$ were isolated depending on the stoichiometry of the reactants. The former were isolated exclusively in the *cis* form (phosphine *trans* to the bridging chloride) while the later gave a mixture of *cis* and *trans* isomers. When R is py, both mono- $[MCl(\eta^2\text{-}Epy)(PR'_3)_2]$ and bi- nuclear $[M_2Cl_2(\mu\text{-}Epy)_2(PR'_3)_2]$ (E = S or Se) were formed, and the two existed in a dynamic equilibrium in solution. The equilibrium can be shifted in either direction with a suitable choice of phosphine ligand. Thus, with PPh_3 only mononuclear complex formed.

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