

Secondary Phosphine Chalcogenides. II*. The Reaction of Diorganophosphine Sulfides and Selenides with Palladium(0) and Platinum(0) Complexes. A Convenient Synthesis of Chalcogenophosphinito Bridged Metal(I) Dimers $[(R_3P)M(XPR'_2)]_2$ (M = Pd, Pt; X = S, Se)

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The coordination chemistry of secondary phosphine oxides has recently been reviewed [2]. The knowledge of the behaviour of secondary phosphine sulfides and selenides towards transition metal complexes is essentially confined to carbonyl systems of group VI and VII metals to data [3].

Marsala, Faraone and Piraino [4] have recently shown that $Ph_2P(S)H$ reacts with the d^8 complex $Ir(CO)(PPh_3)_2Cl$ to form $Ir(CO)H(PPh_3)_2(SPPH_2)Cl$ containing a S-linked thiophosphinito group. In the case of $Rh(CO)(PPh_3)Cl$ the oxidative addition reaction forming a rhodium(III) hydrido complex seems to be followed by reductive elimination of HCl resulting $Rh(CO)(PPh_3)(SPPH_2)$.

We now wish to describe reactions of secondary phosphine chalcogenides $R'_2P(X)H$ (X = S, Se) with the d^{10} complexes $M(PR_3)_4$ (M = Pd, Pt) as well as the first results of NMR measurements of the platinum complexes obtained.

*Part I: see reference [1].

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Experimental

All preparations were performed under argon atmosphere using standard Schlenk techniques. Solvents were dried and freshly distilled before use. The starting materials $R_2P(X)H$ [5], $M(PR_3)_4$ (M = Pd [6], Pt [7]) were prepared by published methods.

$[(R_3P)M(XPR'_2)]_2$

An equimolar amount of solid $R'_2P(X)H$ was added at room temperature to a benzene solution of $M(PR_3)_4$ (ca. 2.5 mmol, 50 ml). After the H_2 evolution ceased the mixture was stirred for 10 h. Compounds II and III (see Table I) were collected by filtration. Partial removal of benzene under vacuum and addition of hexane yielded I, V, VII–IX. Addition of ether followed by hexane caused the other complexes IV, VI, X to precipitate. The complexes were washed twice with diethyl ether, vacuum dried, and recrystallized from the solvents given in Table I. The yields were about 95% in cases I–V and about 85% in cases VI–X. Melting points and IR data are listed in Table I. Correct elemental analysis has been obtained for all of these compounds (e.g. I: $C_{25}H_{23}P_2PtS$, Calculated: C, 49.02; H, 3.78; P, 10.11; Pt, 31.84%. Found: C, 48.83; H, 3.75; P, 9.9; Pt, 32.1%).

Results

Treatment of benzene solutions of $M(PR_3)_4$ (M = Pd, Pt) with secondary phosphine sulfides and selenides at room temperature has been found to give chalcogenophosphinito bridged metal(I) complexes in high yields according to eq. 1 (Table I):

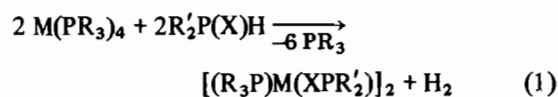


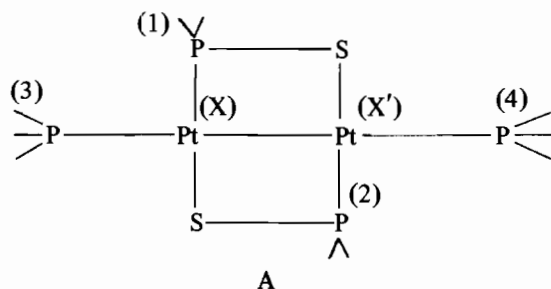
TABLE I. $[(R_3P)M(XPR'_2)]_2$ Complexes.

	Compound	M.p. (dec.) [°C]	$\nu(PS)(KBr [cm^{-1}])$
I	$[(MePh_2P)Pt(SPPH_2)]_2$	212–13 (C_6H_6/C_6H_{14})	577
II	$[(MePh_2P)Pt(SPEt_2)]_2$ [8]	234–35 ($CHCl_3/C_6H_{14}$)	545
III	$\{(Ph_3P)Pt(SPPH_2)\}_2$	302–03 ($CHCl_3/C_6H_6$)	575
IV	$[(Ph_3P)Pt(SPCyc_2)]_2$	340–41 ($C_6H_6/Ae, C_7H_{16}$)	571
V	$[(Ph_3P)Pt(SPMe_2)]_2$ [8]	296–98 ($CHCl_3/C_7H_{16}$)	553
VI	$[(Ph_3P)Pt(SePPH_2)]_2$	261–62 ($CH_2Cl_2/Ae, C_6H_{14}$)	–
VII	$[(MePh_2^P)Pd(SPPH_2)]_2$	173–74 (C_6H_6/C_6H_{14})	576
VIII	$[(Ph_3P)Pd(SPPH_2)]_2$	214–15 (C_6H_6/Ae)	575
IX	$[(Ph_3P)Pd(SPMe_2)]_2$	194–95 ($CH_2Cl_2/Ae, C_7H_{16}$)	555
X	$[(Ph_3P)Pd(SePPH_2)]_2$	157–60 (Acetone/Ae, C_6H_{14})	–

The reaction is accompanied by evolution of dihydrogen which is essentially complete within an hour. Also III has been obtained from $(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_4)$ and $\text{Ph}_2\text{P}(\text{S})\text{H}$ using the same conditions.

A possible reaction mechanism is proposed which involves the initial coordination of $\text{R}'_2\text{P}(\text{X})\text{H}$ to the metal(0) complex with its subsequent oxidative addition to the coordinatively unsaturated metal species to form an intermediate metal(II) hydrido compound which is reduced by H_2 extrusion resulting in the final dimeric metal(I) complex. The formation of at least one intermediate is supported by the observed change in colour of the $\text{Pd}(\text{PR}_3)_4$ solution from yellow to red immediately after addition of $\text{R}'_2\text{P}(\text{S})\text{H}$ which then slowly brightens. Clearly, this mechanism deserves further experiments.

The diamagnetic pale yellow-green (I–V), yellow (VII–IX) or red (VI, X) complexes are indefinitely stable under argon but decompose smoothly in air. Generally complexes with the MePh_2P ligand are soluble in C_6H_6 , CH_2Cl_2 and CHCl_3 (but VII is only stable for a short period in CH_2Cl_2 and CHCl_3) whereas those with Ph_3P are less soluble. The PS stretching vibrations are easily assigned from the IR spectra (Table I). The lower PS bond order of the complexes compared with the secondary phosphine chalcogenides gives rise to a pronounced shift to lower waves for the remarkably constant amount of 60 cm^{-1} if $\text{R}' = \text{Ph}$ and 40 cm^{-1} if $\text{R}' = \text{Me, Et}$. This reflects a very small influence of the metal atom as well as the ligand R_3P on the PS bonding. Some platinum complexes of this type have already been described by Treichel and coworkers [8] (prepared by oxidative addition of $\text{R}'_2\text{P}(\text{S})-\text{P}(\text{S})\text{R}'_2$ to $\text{Pt}(\text{PR}_3)_4$). $[(\text{PhO})_3\text{P}(\text{S})\text{Pt}(\text{SPeEt}_2)]_2$ has been shown by X-ray structure determination to have a centrosymmetric structure as shown in A [8].



Within it both nearly planar coordinated platinum(I) centers are linked by two bridging thiophosphinito groups and by one Pt–Pt single bond. The oxidation number, +1, of the metal atoms or complexes III and VIII has recently been confirmed by ESCA studies [9].

It might be expected that the coupling constants in these complexes will be very sensitive to the Pt–Pt

TABLE II. ^{31}P ^1H N.m.r. Data.^a

Compound	$\delta(\text{P}^1, \text{P}^2)$	$\delta(\text{P}^3, \text{P}^4)$	$^1\text{J}(\text{PtPt})$	$^1\text{J}(\text{P}^1\text{Pt})$	$^2\text{J}(\text{P}^2\text{Pt})$	$^3\text{J}(\text{P}^1\text{P}^2)$	$^1\text{J}(\text{P}^3\text{Pt})$	$^2\text{J}(\text{P}^4\text{Pt})$	$^3\text{J}(\text{P}^3\text{P}^4)$	$^2\text{J}(\text{P}^1\text{P}^3)$	$^3\text{J}(\text{P}^1\text{P}^4)$
I	10.98	2.12	100.6	+3654.4	-202.3	11.3	+2769.0	+413.0	208.4	7.2	5.0
II	20.6	-0.9	125.7	+3522.7	-103.5	7.1	+2488.8	+526.1	239.3	6.7	3.1
$[(\text{PhO})_3\text{P}(\text{S})\text{Pt}(\text{SPeEt}_2)]_2$	17.36	108.57	464.7	+3266.9	-53.0	6.8	+4420.2	+915.4	621.6	15.6	7.8
$[(\text{MeO})_3\text{P}(\text{S})\text{Pt}(\text{SPMe})]_2$ [10]	23.0	128.2	410	+3286	-96	9	+4339	+673	+513	14	12

^a CDCl_3 , δ given in ppm relative to external 85% H_3PO_4 , positive values are to lower field, sign $\{^1\text{J}(\text{P}^1-\text{P}^2-\text{Pt})\} > 0$, $\Delta\text{J} = \pm 0.8\text{ Hz}$.

bond strength and the influence of the ligands on it. Table II gives the NMR data of I, II and $[(\text{PhO})_3\text{PPt}(\text{SPeEt}_2)]_2$ (prepared by ligand exchange of I and $(\text{PhO})_3\text{P}$ [8]). The data for $[(\text{MeO})_3\text{PPt}(\text{SPMe}_2)]_2$ also are reported in Table II [10]. Using the nomenclature shown in structure A the spectral analysis has been performed in terms of the three isotopomers, which are present due to the natural abundance of ^{195}Pt ($J = \frac{1}{2}$) and the ^{31}P atoms, having no (i, 43.8%), one (ii, 44.8%) and two (iii, 11.4%) ^{195}Pt atoms. i gives rise to a deceptively simple AA'XX' spectrum ($\text{AA}' = \text{P}^1\text{P}^2$; $\text{XX}' = \text{P}^3\text{P}^4$) [11], whereas ii and iii are analyzed in terms of ABXMN ($\text{A} = \text{P}^1$, $\text{B} = \text{P}^2$, $\text{X} = ^{195}\text{Pt}$, $\text{M} = \text{P}_3$, $\text{N} = \text{P}_4$) and AA'XX'MM' ($\text{AA}' = \text{P}^1\text{P}^2$; $\text{XX}' = ^{195}\text{Pt}^{195}\text{Pt}$; $\text{MM}' = \text{P}^3\text{P}^4$) spin systems [12, 13] respectively. The calculated data has been confirmed by computer simulation using a LAOC-2D computer programs.

The most striking feature of Table II is the exceptional sensitivity of $J(\text{PtPt})$ to the ligands *trans* to the metal-metal bond and the correlation of $^1J(\text{PtPt})$ and $^3J(\text{P}_3\text{P}_4)$. Further NMR measurements are in progress to study the influence of the ligands on the platinum bond in more detail.

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