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ESCA Study of Transition Metal Complexes of Secondary Phosphine Chalcogenides: $[M_2(PR_3)_2(\mu\text{-}EPR'_2)_2]$***

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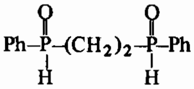
Recently we have reported on synthesis and NMR studies of chalcogenophosphinito bridged metal(I) dimers $[M_2(PR_3)_2(\mu\text{-}EPR'_2)_2]$ (M = Pd, Pt; E = S, Se; R,R′ = alkyl, aryl) [2]. This paper describes X-ray photoelectron measurements of those palladium and platinum complexes as well as of Ni(II) complexes of type *trans*-$NiX_2(\widehat{P\;P})_2$ ($\widehat{P\;P}$ = 1,2-bis[hydroxi-phenyl)phosphino]ethane) [3] which have been carried out in order to support the formal oxidation state of the metal atoms and to get information concerning the charge distribution over the donor atoms and the metal centres.

The binding energies (b.e.) of these complexes as well as those of the sec. phosphine chalcogenides the complexes are derived from are summarized in Table I.

XPS investigations of Pd(I) and Pt(I) complexes are rather scanty [4–6]. Nefedov *et al.* pointed out that metal core level b.e. Pd $3d_{5/2}$ and Pt $4f_{7/2}$ increase with the oxidation number of metal. But whereas there appears to exist a significant difference in b.e. of metal(II) and metal(0) those of metal(I) reported so far fall within the range of the metal(0) values [4, 5].

Metal core b.e. of complexes *1–5*, *7* and *9* fall within the narrow range 336.9–337.3 eV for Pd $3d_{5/2}$ and 71.9–72.1 eV for Pt $4f_{7/2}$. These values are some 1.3 eV lower than those found for metal(II) complexes [4, 5], thus supporting the formulation of these complexes as metal(I) dimers. In accord with an X-ray structure determination [7] both nearly planar coordinated metal(I) atoms are linked by two bridging uninegative chalcogenophosphinito groups

TABLE I. Binding Energy Values [eV].[a,b]

No.	Compound	M[c]	P 2p	E[d]	N 1s or X[e]
1	$[Pd_2(PPh_3)_2(\mu\text{-}SPPh_2)_2]$	377.0	131.2	162.0	–
2	$[Pd_2(PPh_3)_2(\mu\text{-}SPMe_2)_2]$	336.9	131.2	161.8	–
3	$[Pt_2(PPh_3)_2(\mu\text{-}SPPh_2)_2]$	72.0	131.3	162.0	–
4	$[Pt_2(PMePh_2)_2(\mu\text{-}SPPh_2)_2]$	72.1	131.5	162.4	–
5	$[Pt_2(PMePh_2)_2(\mu\text{-}SPEt_2)_2]$	71.9	131.2	162.1	–
6	$Ph_2P(S)H$	–	132.5	162.2	–
7	$[Pd_2(PPh_3)_2(\mu\text{-}SePPh_2)_2]$	337.3	131.2	53.9	–
8	$Ph_2P(Se)H$	–	132.5	54.7	–
9	$[Pd_2(CNMe)_2(\mu\text{-}CNMe)(\mu\text{-}SPPh_2)_2]$	337.2	131.5	162.2	400.3
10	$NiCl_2(\widehat{P\;P})_2$	855.7	132.3	–	198.3
11	$NiBr_2(\widehat{P\;P})_2$	855.7	132.3	–	68.6
12	$NiJ_2(\widehat{P\;P})_2$	855.6	132.2	–	619.3
13	$Ni(NCS)_2(\widehat{P\;P})_2$	855.8	132.5	162.7	398.7
14	 $Ph{-}\underset{H}{\overset{O}{P}}{-}(CH_2)_2{-}\underset{H}{\overset{O}{P}}{-}Ph$	–	132.5	–	–

[a] VARIAN IEE-15, the charging effect was taken into account on the basis of the C 1s binding energy equal to 285.0 eV; the uncertainty corresponds to ±0.1 eV. [b] The M binding energies of *1* and *3* had already been included in [4]. [c] Pd $3d_{5/2}$, Pt $4f_{7/2}$, Ni $2p_{3/2}$. [d] S 2p, Se 3d. [e] Cl 2p, Br 3d, J 3d.

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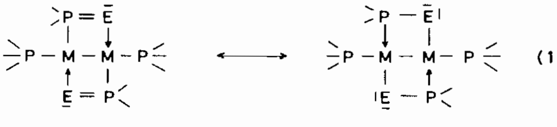
**Secondary Phosphine Chalcogenides. IV. Part III; see ref. [1].

***(M = Pd, Pt; E = S, Se; R,R′ = Alkyl, Aryl) *trans*-$NiX_2(\widehat{P\;P})_2$ (X = Anion; $\widehat{P\;P}$ = 1,2-Bis[hydroxi(phenyl)phosphino]ethane).

and by one M–M single bond, surrounding each metal centre with 16 electrons.

The P 2p b.e. of the terminal and the bridging phosphorus atoms are not resolved, thus, those values are averaged. But comparison of the P 2p b.e. of diphenylphosphine sulfide *6* with complex *9* which contains phosphorus only in bridging position reveals a decrease of 1 eV. Therefore net negative charge must be transferred to phosphorus replacing hydrogen for palladium. The same charge transfer to the bridging phosphorus seems to occur in complexes *1, 3, 4* and *7* since their P 2p b.e. values are generally lower than those of *6* and *8*, respectively. It has been observed for several Pd complexes that P 2p values of the PPh_3 ligand (free PPh_3 130.9 eV) rise by about 0.3–0.8 eV upon coordination [5]. If this is also true for the complexes examined, then the averaged P 2p values have resulted from a decrease of the bridging and an increase of the terminal phosphorus b.e. compared with their precursors *6, 8* and PPh_3, respectively. The S 2p b.e. of complexes *1–5* and *9* remain essentially constant upon coordination compared with that one of *6* showing balanced donor acceptor properties. Contrary, comparing *7* and *8* shows a decrease of the Se 3d energy level upon coordination. The reason might be a weaker P–Se bond and/or different donor acceptor properties of Se compared with S within this type of complexes.

In summary, the results suggest that bonding between the bridging chalcogenophosphinito ligand and the M(I)–M(I) bond of these complexes can be described by resonance structures A and B [eqn. (1)].



(1)

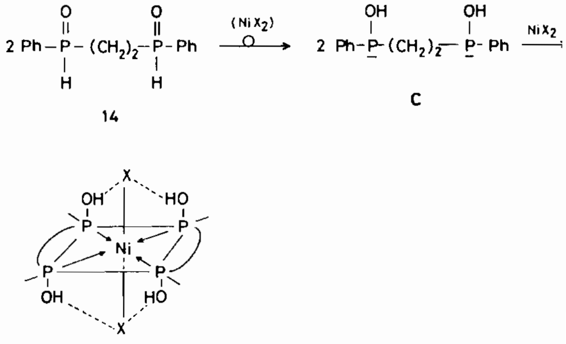
A B

The resulting bond order of 1.5 of the PE bond is in accord with the bond length of 204.6(3) pm of $[Pt_2\{(PhO)_3P\}_2(\mu\text{-}SPEt_2)_2]$ [7] which is in the middle between the expected PS single bond (214 pm) and double bond (194 pm) distances.

Interestingly, b.e. examined of complex *9*, derived from *1* by substitution of both terminal PPh_3 ligands for CNMe and insertion of one CNMe molecule into the Pd–Pd bond, reveal no major changes in the atomic charges accompanied with that process. This is in line with Brant *et al.* who have most recently shown by X-ray photoelectron spectroscopy that insertion into the Pd–Pd bonds of $Pd_2(dpm)_2Cl_2$ and $Pd_2(dam)_2Cl_2$ (dpm = bis(diphenylphosphino)-methane; dam = bis(diphenylarsino)methane) also occurs with minimal changes in the atomic charges [6].

Complexes *10–13* are rather interesting as they present examples of *trans* tetragonal diamagnetic Ni(II) complexes both in the solid state and in solution on the basis of spectroscopic studies (UV–VIS, NMR) as well as magnetic and conductivity measurements. We believe hydrogen bonds between the P–OH groups and the *trans* positioned anions to be of great importance to this particular structure [see structure D in eqn. (2)] [3].

The ESCA spectra do confirm the diamagnetism (since no shake-up satellites are observed [8]) and also the oxidation state. More interesting is the fact, comparing the P 2p values of the ligand precursor *14* with those of *10–13*, that rearrangement of the disecondary phosphine oxide *14* into bis[hydroxi(phenyl)phosphino]ethane [structure C in eqn. (2)] and its coordination on Ni occurs with no major altering of the charge on phosphorus.



14

C

D

(C_2H_4 groups between and C_6H_5 groups on P omitted for clarity in structure D)

Also the effect of anionic ligands in these complexes is negligible on the Ni and P b.e. This can be explained on the basis of the high polarity of the NiX bonding which is proved by the anion b.e. values [9]. Noteworthy, conductivity measurements in nitromethane show these complexes to be non-conducting [3].

References

1 B. Walther and R. Schöps, *Z. Chem.*, in press.

2 B. Walther, B. Messbauer and H. Meyer, *Inorg. Chim. Acta, 37,* L525 (1979).

3 Prepared by reacting the anhydrous Ni(II) salts with *14* in isopropanol; B. Walther, and R. Schöps, unpublished.

4 V. I. Nefedov and Ya. V. Salyn, *Inorg. Chim. Acta, 28,* L135 (1978).

5 V. I. Nefedov, Ya. V. Salyn, I. I. Moiseev, A. P. Sadovskii, A. S. Berenbljum, A. G. Knizhnik and S. L. Mund, *Inorg. Chim. Acta, 35,* L343 (1979).

6 P. Brant, L. S. Benner and A. L. Balch, *Inorg. Chem., 18,* 3422 (1979).

7 K. P. Wagner, R. W. Hess, P. M. Treichel and J. C. Calabrese, *Inorg. Chem., 14,* 1121 (1975).

8 L. J. Matienzo, L. I. Yin, S. O. Grim and W. E. Swartz, *Inorg. Chem., 12,* 2762 (1973).

9 V. I. Nefedov, E. K. Zhumadilov and L. Beyer, *Zh. neorg. Khim. (Russ.), 23,* 2113 (1978).