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Tertiary Phosphines Containing *Ortho*-carborane as Backbone. Some Palladium(II) Complexes

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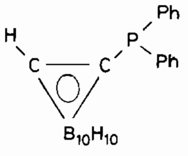
Abstract

Coordination compounds of the type Pd(HPC)$_2$X$_2$, Pd(DPC)X$_2$ and Pd(NPC)X$_2$, where X = Cl or Br and HPC = 1-diphenylphosphino-*o*-carborane; DPC = 1,2-bis(diphenylphoshino)-*o*-carborane; and NPC = 1-bis(dimethylamminophosphino, 2-diphenylphosphino)-*o*-carborane, have been prepared and characterized by IR, Raman and electronic spectroscopy, magnetic and conductivity measurements, and elemental analyses. The compounds containing the monodentate HPC ligand possess a *trans*-planar structure, whereas for those containing the bidentate DPC and NPC ligands a *cis*-planar configuration was found. In all cases, the phosphorus atoms of the tertiary phosphine (HPC) and the ditertiary phosphines (DPC and NPC) are bonded to the palladium atom. The complex [Pd(HPC)Cl$_2$]$_2$ has also been prepared, and a halogen bridge dimeric structure is proposed on the basis of the IR and Raman spectra.

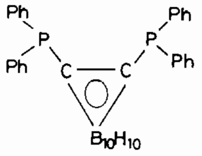
Introduction

Symmetric and asymmetric ditertiary phosphines containing *o*-carborane as backbone have been the subject of a number of studies [1–8]. *o*-carborane is an interesting backbone because its electron-withdrawing power, large size and extensive electronic delocalization confer a rather unusual stability to the molecule. The electron-withdrawing power favors π-back-bonding in the metal–phosphorus bond.

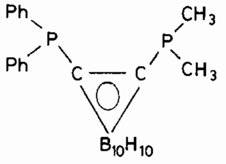
In the present work we have prepared and characterized spectroscopically and analytically a series of complexes of palladium(II) with a tertiary monophosphine (HPC) and two detertiary phosphines (DPC and NPC). The vibrational spectra, magnetic measurements and electronic spectra confirm the planar structure of the complexes reported here. The Pd(HPC)$_2$X$_2$ complexes are *trans*-planar whereas the compound [Pd(HPC)Cl$_2$]$_2$ was found to be dimeric with a halogen bridged structure. The bidentate DPC and NPC ligands produce the expected *cis*-planar complexes.



HPC



DPC



NPC

Experimental

(a) Preparation

The HPC, DPC and NPC ligands were prepared as described elsewhere [7, 8]. The complex compounds were prepared by a general method. To a given amount of Pd(CH$_3$CN)$_2$Cl$_2$ suspended in a small volume of CH$_2$Cl$_2$, the stoichiometric amount of the appropriate ligand was added. The resulting suspension was stirred for 1 h and ethanol was added to precipitate the solid. The solid was filtered off, washed with ethanol and dried. Two recrystallizations from CH$_2$Cl$_2$/CH$_3$OH were carried out. To prepare the corresponding bromide derivative, solid KBr was added to a suspension of the chloride compound. The mixture was heated to *ca.* 50 °C for one hour and the compound extracted with CH$_2$Cl$_2$. The solid was precipitated out with ethanol.

Table I presents the analytical conductivity and magnetic data for the compounds reported here.

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TABLE I. Analytical, Conductivity and Magnetic Data for the HPC, DPC and NPC Complexes of Palladium(II)[a]

Compound[b]	C%	H%	Pd%	Λ_M^{25} [c]	$\chi_M^{Corr} \times 10^6$
$Pd(HPC)_2Cl_2$ (I)	41.7(40.3)	5.4(5.1)	12.4(12.8)	31.2	71
$Pd(HPC)_2Br_2$ (II)	36.2(36.4)	4.9(4.6)	12.1(11.6)	33.6	52
$[Pd(HPC)Cl_2]_2$ (III)	33.3(33.2)	4.1(4.2)	21.0(21.1)	24.1	116
$Pd(DPC)Cl_2$ (IV)	44.2(45.2)	4.7(4.4)	16.6(15.5)	22.4	28
$Pd(DPC)Br_2$ (V)	40.2(40.0)	4.1(3.9)	14.4(13.7)	27.0	42
$Pd(NPC)Cl_2$ (VI)	34.2(34.6)	5.7(5.2)	17.1(17.1)	28.0	56
$Pd(NPC)Br_2$ (VII)	30.9(30.3)	4.5(4.5)	14.0(15.0)	28.5	30

[a] HPC = $C_{14}B_{10}H_{21}P$; NPC = $C_{18}B_{10}H_{32}P_2N_2$; DPC = $C_{26}B_{10}H_{30}P_2$. [b] Calculated values in parentheses. [c] Molar conductivities in dimethylformamide for mM solutions.

TABLE II. Some IR Selected Bands of the HPC, DPC and NPC Complexes of Palladium(II)

Compound	ν(C–H)	Phenyl deformation	ν(N–C)[a]	ν(P–C) Phenyl	Deformation cage
I	3051w	1438s		1098s	740m
					720w
					688s
II	3051w	1438s		1097s	740s
					718w
					690s
III	3053w	1437s		1100s	740m
					712w
					699m
					690s
IV		1440s		1100s	740m
					730m
					690s
V		1435s		1098s	740m
					715w
					700m
					685s
VI	2960sh	1438s	1275w	1095s	740s
	2920m		1185w		713w
	2850m		1162m		690s
VIII	2960sh	1436s	1285m	1097s	740s
	2920m		1183m		714w
	2845w		1160s		688s

[a] N–C stretching mode of the $PN(CH_3)_2$ group.

(b) Physical Measurements

Conductivity and magnetic measurements were performed as described previously [5, 6]. The electronic spectra were obtained on a Beckman DU8 spectrophotometer in dimethylformamide or as nujol mulls. The IR spectra were taken as CsI pellets and recorded on Perkin-Elmer 577 and 237B spectrophotometers. The Raman Spectra were obtained as described elsewhere [9].

Results and Discussion

The magnetic measurements clearly show that the compounds are diamagnetic in the solid state in keeping with a planar d^8 structure for these palladium(II) complexes. The conductivity data show that all compounds behave as non-electrolytes DMF [10].

Table II lists some selected bands and their assignments of the compounds reported here. Compounds **I**, **II** and **III** show a weak band at *ca.* 3050 cm^{-1}, which has been assigned to the C–H stretching mode of the carborane cage. In the free HPC ligand, this mode is observed at the same frequency, showing that the carbon atom of the cage is not involved in coordination. For the complexes **VI** and **VII**, the C–H stretching mode frequencies listed in Table II are due to the methyl groups of the $PN(CH_3)_2$ moiety. The strong bands at *ca.* 1440 cm^{-1} have

TABLE III. Metal–Ligand Vibrations in the HPC, DPC and NPC Complexes of Palladium(II)

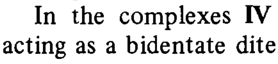
Compound	ν(Pd–P)		ν(Pd–Cl)		ν(Pd–Br)	
	IR	Raman	IR	Raman	IR	Raman
I	420s	423w	3645	343s		
II	400s	398w			274m	279m
III	415s	410m	n.o.	337m		
			300m	311w		
			260m	274m		
IV	410w	423m	390w	393w		
	400w	405m	288w	282w		
V	440m	n.o.[a]			284w	n.o.
	400m	n.o.			230m	n.o.
VI	443m	n.o.	320m	n.o.		
	405m	n.o.	289m	n.o.		
VII	445w	419m			285w	285m
	420w	388m			231m	217m

[a] n.o., not observed.

been assigned to the deformation mode of the phenyl groups. This band shifts 2–4 cm^{-1} in the complexes as consequence of the phosphorus coordination [11]. Sandhu *et al.* [12] have observed the above shift in some PPh_3 complexes and used it as a criterion for phosphorus coordination.

The P–C(phenyl) stretching mode shifts 5–10 cm^{-1}, also implying that the phosphorus atom is bonded to the metal. The P–N stretching modes in the complexes VI and VII are located in the range of 990–980 cm^{-1}. These compounds show two bands in that region which have been assigned to the antisymmetric and symmetric P–N stretching modes in the $PN(CH_3)_2$ groups (VI: 990s, 980m; VII: 985s, 980s). The shifts with respect to the free NPC ligand are 17 and 18 cm^{-1}, respectively. As the phosphorus atom coordinates to the metal, the P–N bond order increases as a result of the increasing pπ–dπ interaction from nitrogen to phosphorus.

The Pd–X (X = Cl or Br) and Pd–P stretching modes are expected to be observed below 480 cm^{-1}, in accordance with the data reported for some triphenylphosphine and 1,2-bis(diphenylphosphine) ethane complexes of palladium(II). The assignment of the bands in this region should be taken as tentative only, since a number of ligand and lattice modes are observed. Table III lists the IR and Raman bands in the Pd–P and Pd–X stretching modes region. If we assume a *trans*-planar configuration for the PdP_2X_2 (X = Cl or Br) skeleton, the nine normal modes are distributed as 2Ag(R) + B_{1g}(R) + $2B_{1u}$(IR) + $2B_{2u}$(IR) + $3B_{3u}$(IR). Accordingly, one Pd–X and one Pd–P stretching should be observed in the IR and Raman spectra. The IR active stretching modes correspond to the antisymmetric vibrations, whereas those that are Raman active are the symmetric ones. Therefore, from Table III it can be inferred that the $Pd(HPC)_2X_2$ complexes possess a *trans*-planar geometry of D_{2h} symmetry. In the $Pd(HPC)Cl_2$ complex, the symmetric and antisymmetric Pd–P stretchings are located at 415 and 410 cm^{-1} whereas the ν(Pd–Cl) show up in the range 340–260 cm^{-1}. The bands at *ca.* 300 and 260 cm^{-1} are clearly bridging Pd–Cl stretching modes. According to group theory and assuming a halogen bridged structure of C_{2h} symmetry such as that shown below, the six ν(Pd–Cl) modes are to be distributed as follows: one terminal and two bridging IR actives and the same number in the Raman. In fact, the Raman spectra shows one terminal ν(Pd–Cl) located at 337 cm^{-1} and two bridging modes located at 310 and 274 cm^{-1}. The IR spectrum shows approximately the same absorptions, although one mode is missing.



In the complexes IV and V, the DPC ligand is acting as a bidentate ditertiary phosphine, and hence a *cis*-planar geometry of C_{2v} symmetry can confidently be assumed for the PdP_2X_2 skeleton. In compound IV, two ν(Pd–P) and two (Pd–Cl) modes are observed in both the IR and Raman spectra, in keeping with the above assumed symmetry. The IR of complex V is also in good agreement with such a model; the Raman spectrum could not be obtained because of fluorescence.

A similar situation was found for the compound VI. The results also agree with a *cis*-planar C_{2v} symmetry, implying that the NPC ligand is coordinated to the metal through the phosphorus atom. From

Table III it can be observed that the frequency of the IR active ν(Pd–P) mode is increased by *ca.* 30 cm^{-1} in the NPC complexes with respect to the HPC and DPC complexes. This effect is probably due to the presence of the more electronegative $N(CH_3)_2$ groups bonded to the phosphorus atom in the NPC ligand.

TABLE IV. Electronic Spectra of the HPC, DPC and NPC Complexes of Palladium(II)

Compound	λ_{max}(nm)[a]	Assignment
I	320(2760)	d–d transition
	277(5826)	phenyl $\pi \rightarrow \pi^*$
II	335(2690)	d–d transition
	275(7070)	phenyl $\pi \rightarrow \pi^*$
III	303(5070)	d–d transition
	287(6425)	phenyl $\pi \rightarrow \pi^*$
IV	339(5585)	d–d transition
	314(3525)	MLCT
	274(3915)	phenyl $\pi \rightarrow \pi^*$
V	340(2685)	d–d transition
	315(3370)	MLCT
	271(5810)	phenyl $\pi \rightarrow \pi^*$
VI	322(3550)	d–d transition
	278(4510)	phenyl $\pi \rightarrow \pi^*$
VII	335(2065)	d–d transition
	295(5340)	phenyl $\pi \rightarrow \pi^*$

[a] Molar absorptivity at band maximum given in parentheses.

The electronic spectra of the compounds reported here show two or three bands in the region of 340–270 nm. Table IV lists the electronic spectra of these compounds and their assignments. The bands have been assigned by comparison with some palladium(II) complexes of 1,2-bis(diethylphosphino) ethane (DEPE) reported in the literature [13]. The Pd(DEPE)Cl_2 shows two bands located at 310 and 260 nm, whereas in the corresponding bromide derivative these absorptions show up at 332 and 298 nm, respectively. The bands at *ca.* 320 nm were assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ electronic transitions, whereas the band at *ca.* 290 nm is clearly a ligand–metal charge transfer band. The electronic spectra of our compounds follow the same pattern, with the exception of **IV** and **V** which show an additional band at *ca.* 310 nm. These bands have been assigned to a metal–ligand charge transfer band. Finally, it is worth noting that the free ligands show a strong band at *ca.* 275 nm, probably due to some $\pi \rightarrow \pi^*$ electronic transition within the phenyl group.

Conclusion

From IR, Raman and electronic spectra, it can be inferred that the compounds **I** and **II** possess a *trans*-planar D_{2h} local symmetry, whereas for the complexes **IV**, **V**, **VI** and **VII**, in which the bidentate phosphines DPC and NPC are involved, a planar C_{2v} symmetry is found. Complex **III** is tentatively formulated as a dimer with halogen bridges.

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References

1 R. Alexander and H. Schroeder, *Inorg. Chem., 2,* 1107 (1963).
2 R. Holm and F. Rohrscheid, *J. Organomet. Chem., 4,* 335 (1965).
3 W. E. Hill, W. Levason and C. A. McAuliffe, *Inorg. Chem., 13,* 244 (1974).
4 W. E. Hill, B. G. Rackley and L. M. Silva-Triviño, *Inorg. Chim. Acta, 75,* 51 (1983).
5 J. G. Contreras, J. P. Peña and L. M. Silva-Triviño, *Bol. Soc. Chil. Quím., 28,* 3 (1983).
6 J. G. Contreras, J. P. Peña and L. M. Silva-Triviño, *Inorg. Chim. Acta, 87,* 181 (1984).
7 W. E. Hill and L. M. Silva-Triviño, *Inorg. Chem., 17,* 2495 (1978).
8 W. E. Hill and L. M. Silva-Triviño, *Inorg. Chem., 18,* 361 (1979).
9 J. G. Contreras, G. V. Seguel, B. Ungerer, W. Maier and D. F. Hollander, *J. Mol. Struct., 102,* 295 (1983).
10 H. D. Smith, Jr., M. A. Robinson and S. Papetti, *Inorg. Chem., 6,* 1014 (1967).
11 D. Corbridge, *Top. Phosphorus Chem., 6,* 235 (1969).
12 S. S. Sandhu and A. Mehta, *J. Organomet. Chem., 77,* 45 (1974).
13 E. Alyea and D. W. Meek, *Inorg. Chem., 11,* 1029 (1972).