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Stereochemical Consequences of Chelated, Bridging Phosphino-Phosphido Ligands in Bimetallic Complexes.

The Molecular Structure of Both *Meso*- and S_n,S_n-$[PtCl\{C_6H_5P(CH_2)_3P(C_6H_{11})_2\}]_2$

ROBERT GLASER*, DENNIS J. KOUNTZ, JUDITH C. GALLUCCI and DEVON W. MEEK*

Department of Chemistry and the Materials Research Laboratory, The Ohio State University, Columbus, Ohio 43210, U.S.A.

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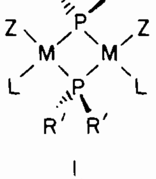
Phosphido- and arsenido-bridged complexes of transition metals have attracted considerable attention recently on the reasonable assumption that the R_2As^-, RAs^{2-}, R_2P^-, and RP^{2-} groups would reduce undesirable fragmentation of bimetallic and cluster complexes [1, 2]. Our results [3], as well as recent reports by Carty [4], Collman [5], and Geoffroy [6] indicate that organophosphido bridges of the types $M{-}(\mu\text{-}PR_2)_2{-}M$ may be more reactive than generally assumed. One might increase the stability of the μ-PR_2 linkage by incorporating it into a chelate ring; however in contrast to the numerous examples of bis-PR_2-bridged bimetallic complexes of the general structure *1*, only two reports (besides ours) of an organophosphido group attached to a chelate chain have appeared [7].

Phosphido-bridged complexes of planar metals (*e.g.*, platinum, palladium, iridium, and rhodium) of the general type $[MZ(L)(\mu\text{-}PR_2)]_2$ can be envisioned such that two Z ligands exhibit *cis*- and *trans*-dispositions (*1* and *2*, respectively) *vis-a-vis* the $M_2(\mu\text{-}PR_2)_2$ core. Of the two isomeric forms, only the *trans*-isomer (*2*) is possible when the bridging phosphido group is linked to a terminal ligand *via* a chelate chain. We now report an important stereochemical consequence of a linked, bridging-phosphido group, compared to an analogous complex of structural type *2*.



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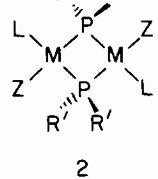

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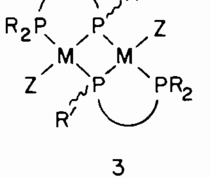

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Tertiary-secondary diphosphine ligands of the type $R_2PCH_2CH_2CH_2P(Ph)H$ provide rational and controlled routes to phoshido-bridged bimetallic complexes [8]. The compound $[PtCl\{PhP(CH_2)_3P(C_6H_{11})_2\}]_2$ was synthesized from $PtCl_2\{(Ph(H)PCH_2CH_2CH_2P(C_6H_{11})_2\}$ in THF in the presence of NEt_3; single crystals of both the *meso*- and the *dl*,-isomers were obtained by allowing absolute ethanol (layered over a dichloromethane solution of the complex) to diffuse slowly into the CH_2Cl_2.

Crystal Data for (*4*): (148 K) for R_n,S_n-$[PtCl\{(C_6H_5)P(CH_2)_3P(C_6H_{11})_2\}]_2$: monoclinic, space group $P2_1/n$, a = 11.1177(7), b = 12.466(1), c = 16.371(1) Å, β = 99.751(1)°, U = 2236 Å^3, and Z = 2. The structure of (*4*) was solved by the Patterson method and refined by full-matrix least squares (SHELX-76) [9] using 4365 unique reflections (with $F_o^2 \geqslant 3\sigma(F_o^2)$) that were collected on a Syntex P$\bar{1}$ diffractometer (MoK$_\alpha$ radiation for $4.0° \leqslant 2\theta \leqslant 57.0°$). The final refinement included anisotropic thermal parameters for the non-hydrogen atoms, hydrogen atoms at idealized positions (C–H = 0.95 Å and $B(H) = B_{iso}(C) + 1.0$ Å^2), and an isotropic extinction coefficient. The final discrepancy indices are $R(F)$ = 0.026 and $R_w(F)$ = 0.027 for 227 variables.

Crystal Data for (*5*): (148 K) for S_n,S_n-$[PtCl\{(C_6H_5)P(CH_2)_3P(C_6H_{11})_2\}]_2$: orthorhombic, space group $P2_12_12_1$, a = 15.269(1), b = 17.119(2), c = 16.605(1) Å, U = 4340 Å^3, and Z = 4. The structure was solved using 'Multan 80' [10] and refined on 4667 unique reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$ (MoK$_\alpha$ radiation for $4.0° \leqslant 2\theta \leqslant 55.0°$). The absolute configuration of the data crystal was determined by the Bijvoet method [11]. The final refinement paralleled that of (*4*), except that the phenyl rings of (*5*) were constrained as rigid bodies (D_{6h} symmetry with r_{C-C} = 1.395 Å); at convergence $R(F)$ = 0.027 and $R_w(F)$ = 0.027 for 368 variables.

Drawings of (*4*) and (*5*) are given in Figs. 1 and 2, respectively. Both structures contain two nonbonded platinum atoms bridged by two organophosphido groups that are linked to chelating dicyclohexylphosphino groups. The most important structural difference between (*4*) and (*5*) is the location of the phenyl rings with respect to the $\overline{\mathrm{Pt{-}P{-}Pt{-}P}}$ core: in (*4*) one phenyl is on each side of the core, whereas in (*5*) both phenyls lie on the same side of the $\overline{\mathrm{Pt{-}P{-}Pt{-}P}}$ core. In the *meso*-isomer (*4*), the $\overline{\mathrm{Pt{-}P{-}Pt{-}P}}$ core is rigorously planar (imposed by a crystallographic $\bar{1}$), whereas, the Pt–P–Pt–P core is bent (19.1°) in the chiral complex (*5*).

As a consequence of the bent $\overline{\mathrm{Pt{-}P{-}Pt{-}P}}$ core, the nonbonding Pt···Pt distance (3.5454(5) Å) in (*5*) is slightly shorter than the Pt···Pt distance in (*4*). These Pt–Pt distances, as well as the Pt–P and

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*Authors to whom correspondence should be addressed.

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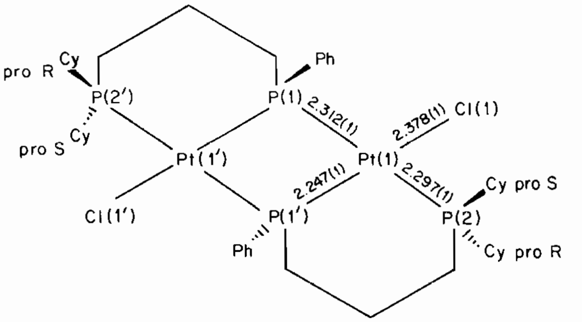

Fig. 1. A drawing of the inner coordination sphere of the platinum atoms in R_n,S_n-[$Pt_2Cl_2\{C_6H_5P(CH_2)_3P(C_6H_{11})_2\})_2$], (*4*), giving the important bond distances. Angles within the coordination sphere are: Pt′–P(1)–Pt = 103.37(4)°, P(1)–Pt–P(2) = 93.02(4)°, P(1)–Pt–Cl(1) = 169.93(4)°, P(1′)–Pt–P(1) = 76.33(3)°, P(2)–Pt–P(1′) = 166.30(4)°, P(1′)–Pt–Cl(1) = 94.04(3)°, and P(2)–Pt–Cl(1) = 96.78(3)°. The primed atoms are related to the unprimed atoms by the inversion center.

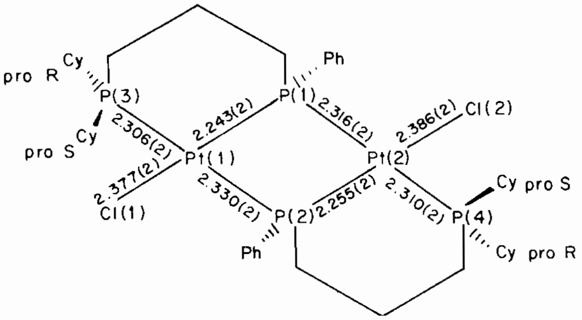

Fig. 2. A drawing of the inner coordination sphere of the platinum atoms in S_n,S_n-[$Pt_2Cl_2\{C_6H_5P(CH_2)_3P(C_6H_{11})_2\}_2$], (*5*), giving the important bond distances. Angles within the coordination sphere are: Pt(1)–P(1)–Pt(2) = 102.1(1), Pt(1)–P(3)–Pt(2) = 101.3(1), P(1)–Pt(1)–P(2) = 92.5(1), P(3)–Pt(2)–P(4) = 97.3(1), P(1)–Pt(2)–Cl(2) = 93.6(1), P(1)–Pt(1)–P(3) = 76.3(1), P(1)–Pt(2)–P(3) = 76.4(1), P(1)–Pt(1)–Cl(1) = 170.5(1), P(1)–Pt(2)–P(4) = 166.4(1), P(3)–Pt(1)–Cl(1) = 94.6(1), P(3)–Pt(1)–P(2) = 168.4(1), P(3)–Pt(2)–Cl(2) = 169.9(1), P(2)–Pt(1)–Cl(1) = 96.7(1), P(4)–Pt(2)–Cl(2) = 92.7(1).

Pt–Cl distances in (*4*) and (*5*) are similar to those found in the diplatinum complexes *trans*-[PtCl(μ-PPh_2)(Ph_2PH)]$_2$ and [Pt(μ-PPh_2)(dppe)]$_2Cl_2$ [12]. The Pt–Pt distances are much longer than a single bond (*cf.*, Pt–Pt = 2.628(1) Å in [Pt(dppe)]$_2$ [13]). The difference in the *trans* influence of the terminal phosphino group and the chloro ligand is evident from the asymmetry of the Pt–μ-P distances, *ca.* 2.25 Å (μ-P *trans* to Cl) *vs. ca.* 2.31 Å (μ-P *trans* to PCy_2).

The coordination geometry about each platinum atom is essentially planar except for the slight tetrahedral deviations from the mean plane through the platinum atom and its four substitutents. The heterocyclic six-membered rings (Pt–P–C–C–C–P) exhibit chair conformations with one cyclohexyl ring (pro R) on the terminal phosphino phosphorus atom in a 1,3-*cis*-diaxial orientation to the phenyl ring on the bridging phosphido phosphorus atom. In (*4*) and on P(3) in (*5*) the pro-R cyclohexyl substituent adopts the more sterically demanding orientation, which has the tertiary proton facing the phenyl ring at *ca.* 2.7 Å. A less demanding steric orientation is observed on P(4) or (*5*) where the tertiary proton is turned away from the neighboring phenyl ring, which results in a slight flattening of the heterocyclic six-membered ring in the Pt(2) region. Otherwise, the cyclohexyl rings (pro R and pro S) in both (*4*) and (*5*) exhibit the classical cyclohexane chair geometry with normal van der Waals intermolecular contacts.

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