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Controlled Syntheses and Structures of Bimetallic Complexes of Two Bidentate Phosphine–Phosphido Ligands

DEVON W. MEEK*, ROBERT WAID, KWOLIANG D. TAU

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, U.S.A.

RICHARD M. KIRCHNER*

Department of Chemistry, Manhattan College, Bronx, N.Y. 10471, U.S.A.

and CARL N. MORIMOTO

Professional Services Division, Control Data Corporation, Sunnyvale, Calif. 94086, U.S.A.

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As recent as four years ago, bridging organophosphorus groups (*e.g.*, R_2P^-) in coordination compounds were relatively rare; however, now that paucity is rapidly disappearing through the rational syntheses of bimetallic and cluster compounds that contain bridging μ_2-PR_2, μ_3-PR, and μ_4-PR groups [1]. To our knowledge, all of these bridging organophosphido groups function as independent units, *i.e.*, they are not a part of a chelate ring to another ligand atom. Thus, we report herein the first examples of bimetallic complexes that contain bridging phosphido groups resulting from one of the novel chelating phosphine–phosphido ligands $Ph_2PCH_2CH_2CH_2PPh^-$ or $Cy_2PCH_2CH_2CH_2PPh^-$ (Ph = C_6H_5 and Cy = cyclo-C_6H_{11}).

Treatment of either of the tertiary-secondary biphosphines $Ph_2PCH_2CH_2CH_2P(H)Ph$(PPH) [2] or $Cy_2PCH_2CH_2CH_2P(H)Ph$(CyPPH) with either Pd(II) or Pt(II) halides, in the presence of a base [3], leads to bimetallic complexes of the types $M_2X_2(PP)_2$† or $M_2X_2(CyPP)_2$ (X = halide, PP and CyPP are the anionic forms of PPH and CyPPH, respectively). In the case of more robust Pt–L bonds (*e.g.*, Pt–CH_3), treatment of *cis*-$Pt(CH_3)_2(COD)$† with either of the ligands PPH or CyPPH in benzene or toluene at 25 °C readily yields the monomeric, planar complexes $Pt(CH_3)_2$(ligand) in 80–90% yields. However, if the solutions are refluxed for 1 hour, methane is evolved and the bimetallic phosphido-bridged complexes $Pt_2(CH_3)_2(PP)_2$ and $Pt_2(CH_3)_2(CyPP)_2$ result. Owing to the presence of two different types of phosphorus atoms (phosphine and phosphido) and the 33.8% natural abundance of ^{195}Pt (I = 1/2), these Pt_2X_2-(phosphine–phosphido)$_2$ complexes produce a complicated $^{31}P\{^1H\}$ NMR spectrum (*e.g.*, Fig. 1). The central portion of the spectrum consists of two ten-line multiplets, consistent with an AA′XX′ spin system, which would represent the four phosphorus nuclei of a dimeric structure. The satellites result from ^{31}P–^{195}Pt coupling.

To confirm the nature of the bridging phosphido groups and the bimetallic structure of the complex $Pt_2(CH_3)_2(Ph_2PCH_2CH_2CH_2P(Ph))_2$ in the solid state, an X-ray structure determination was undertaken. Preliminary examination of the crystal and data collection were performed on a Syntex $P2_1$ diffractometer. Space group: $P2_1/n$; $a = 15.285(5)$, $b = 16.874(3)$, $c = 18.419(7)$ Å, $\beta = 110.98(2)°$; V = 4435.7 Å^3; D = 1.63 g/cm^3; and Z = 4. The structure was solved by the heavy atom method using a Patterson map and difference Fouriers. The final cycle of full-matrix, least-squares refinement gave the conventional agreement factor R = 0.066, using 4648 reflections with $I > 3\sigma \cdot I$.

The crystal structure consists of the packing of discrete bimetallic molecules of formula $Pt_2(CH_3)_2$-$[(C_6H_5)_2P(CH_2)_3P(C_6H_5)]_2$. The closest intermolecular contacts, ranging from 3.50 to 3.67 Å, are between the phenyl rings of different bimetallic molecules. Each molecule consists of two platinum atoms bridged only by the phosphido moiety of two identical anionic ligands, 1-diphenylphosphino-3-phenylphosphido-propane (PP). In addition to the two phosphido bridges, each platinum atom achieves a four-coordinate, approximately planar geometry by bonding to a methyl group and a diphenylphosphino

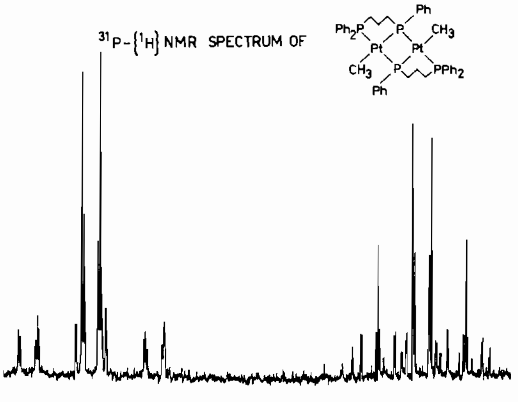

Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of $Pt_2(CH_3)_2(PP)_2$ in benzene at room temperature. The principal multiplets are centered at −155.1 and 2.28 ppm, relative to external 85% H_3PO_4. The positive chemical shifts are downfield from the standard. The P–P coupling constants are +8.9, −23.7, +134.4, and +337.8 Hz.

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*Authors to whom all correspondence should be addressed.

†The designation PP is used here to denote the anion that results from loss of a P–H proton from $Ph_2PCH_2CH_2CH_2P$-(H)Ph(PPH).

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group, thereby creating a chelate ring with the corresponding phenylalkylphosphido bridge.

A drawing which gives the important bond distances of the inner coordination sphere of each platinum is shown in Fig. 2. The dihedral angle between the approximately square-planar coordination spheres of the platinum atoms of 37 ℃ gives a folded configuration to the bimetallic molecule in which the methyls and the diphenylphosphino groups are in a *trans* arrangement. A perspective view showing the nonplanarity of the bridging phosphido linkage is given in Fig. 3. This view also shows the bulky phenyl groups attached to each bridging phosphide bending away from each other due to steric repulsions. The closest intramolecular contact between these two phenyl rings is 3.37 Å between C(9) and C(28). In addition, the methyl groups tend to bend away from all of the bulky phenyl rings in a bend away from all of the bulky phenyl rings in a direction toward unfilled space in the coordination sphere.

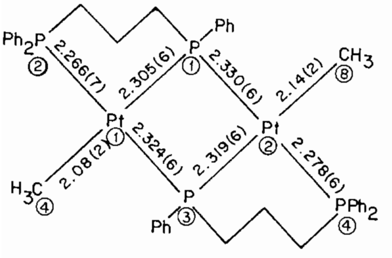

Fig. 2. A drawing of the inner coordination sphere of each platinum for Pt$_2$(CH$_3$)$_2$(PP)$_2$, giving the important bond distances. Angles within the coordination sphere are: Pt(1)–P(1)–Pt(2) = 98.9(2), Pt(1)–P(3)–Pt(2) = 98.6(2), P(1)–Pt(1)–P(2) = 95.9(1), P(1)–Pt(2)–C(8) = 95.9(7), P(1)–Pt(1)–P(3) = 74.9(2), P(1)–Pt(2)–P(3) = 74.5(2), P(1)–Pt(1)–C(4) = 170.4(6), P(1)–Pt(2)–P(4) = 170.1(2), P(3)–Pt(1)–C(4) = 96.0(6), P(3)–Pt(2)–P(4) = 96.1(2), P(3)–Pt(1)–P(2) = 169.8(2), P(3)–Pt(2)–C(8) = 169.9(7).

The Pt(1) to Pt(2) distance of 3.521(1) Å indicates no significant metal-to-metal bonding. The four Pt–P distances to the bridging phosphido groups are longer (mean = 2.320(3) Å) than the two Pt–P distances to the terminal phosphino groups (mean = 2.272(5) Å). Bridging ligand–metal distances are usually longer than terminal ligand–metal distances, and this effect is presumably more important in this complex than the effect that might result from the differences, mainly thc attachment of one phenyl group, between a phosphido and a phosphino ligand. Also, the four Pt–P distances of the bridging phosphido groups are slightly asymmetric; the two Pt–P bonds *trans* to CH$_3$ are slightly shorter (mean = 2.312(6) Å) than those *trans* to phosphorus (mean = 2.327(6) Å). Nevertheless, all of the Pt–P distances fall within the range of known Pt–P bonding distances (*ca.* 2.24 to 2.33 Å) [5–7].

The Pt–C distances of 2.082(22) and 2.141(24) Å are not significantly different and compare well with the sum of the atomic radii, Pt–C(sp^3) 2.09 Å [8], and with the Pt–C distances of 2.05(2) and 2.12(2) Å in Pt(CH$_2$CH$_2$CH$_2$CH$_2$)(PPh$_3$)$_2$ [9]. In addition, the Pt–C distance *trans* to a halide ion in several platinum(II) phosphine complexes (*e.g.*, 2.086(7) Å in *trans*-PtBr(η^1-C$_3$H$_5$)(PEt$_3$)$_2$ [10], 2.090(4) Å in *trans*-PtCl(η^1-C$_3$H$_5$)(PPh$_3$)$_2$ [11], 2.079(14) Å in *trans*-Pt(CH$_2$SiMe$_3$)Cl(PMe$_2$Ph)$_2$ [12], 2.071(1) Å in *trans*-PtCl(Me)(PMePh$_2$)$_2$ [13], 2.120(7) Å in *trans*-Pt(I·SO$_2$)Me(PPh$_3$)$_2$ [14], and 2.08(1) Å in *trans*-PtCl(CH$_2$CN)(PPh$_3$)$_2$ [15] are similar to the values found in this investigation.

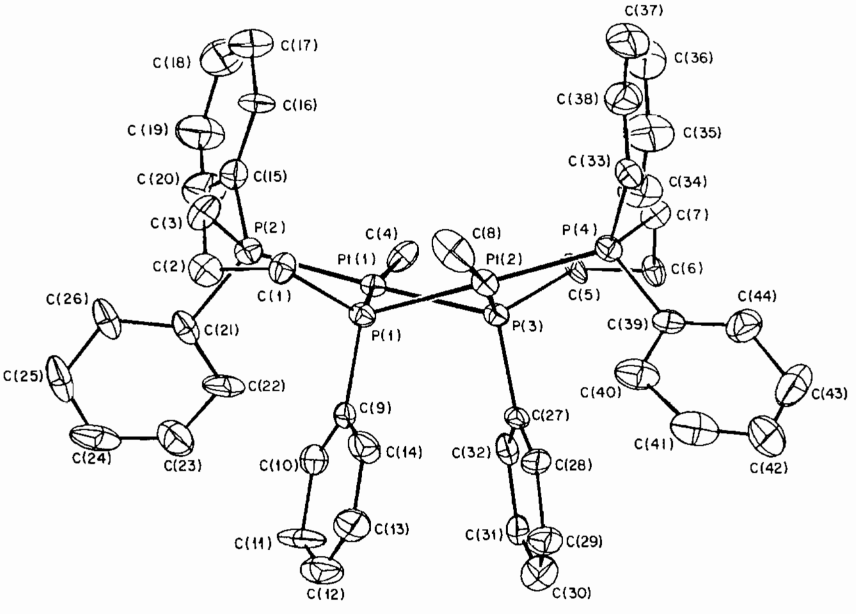

Fig. 3. An ORTEP drawing that illustrates the folded nature of the bridging phosphido linkages.

Acknowledgements

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References

1 For example, recent papers that provide leading references on organophosphido bridging ligands are: K. Fischer and H. Vahrenkamp, *Z. Anorg. Allgem. Chem., 475*, 109–15 (1981); H. Schumann and H. Neumann, *Z. Naturforsch., 36b*, 708–712 (1981); P. Braunstein, D. Matt, O. Bars, M. Louer, D. Grandjean, J. Fischer and A. Mitschler, *J. Organometal. Chem., 213*, 79–107 (1981); A. J. Carty, S. A. Maclaughlin and N. J. Taylor, *J. Organometal. Chem., 204*, C27–C32 (1981); F. Iwasaki, M. J. Mays, P. R. Raithby, P. L. Taylor and P. J. Wheatley, *J. Organometal. Chem., 213*, 185–206 (1981); R. J. Haines, N. D. C. T. Steen and R. B. English, *J. Organometal. Chem., 209,* C34 (1981); and M. J. Mays, P. R. Raithby and P. L. Taylor, submitted for publication in *J. Organometal. Chem.*, (1981).

2 R. J. Uriarte, T. J. Mazanec, K. T. Tau and D. W. Meek, *Inorg. Chem., 19*, 79 (1980).

3 J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 2433 (1964).

4 R. G. Hayter, 'Preparative Inorganic Reactions', Vol. 2, W. L. Jolly, Ed., 1965, pp. 211–236, and references cited therein; R. G. Hayter, *J. Am. Chem. Soc., 86*, 823 (1964).

5 S. Otsuka, T. Yoshida, M. Matsumoto and K. Nakatsu, *J. Am. Chem. Soc., 98*, 5850 (1976).

6 C. J. Cardin, D. J. Cardin, M. F. Lappert and K. W. Muir, *J. C. S. Dalton Trans.*, 46 (1978).

7 A. Del Pra, E. Forsellini, G. Bombieri, R. A. Michelin and R. Ros, *J. C. S. Dalton Trans.*, 1862 (1979).

8 L. Pauling, 'Nature of the Chemical Bond', 3rd edit., Cornell Univ. Press, Ithaca, N.Y., 1960.

9 C. G. Biefeld, H. A. Eick and R. H. Grubbs, *Inorg. Chem., 12*, 2166 (1973).

10 J. C. Huffman, M. P. Laurent and J. K. Kochi, *Inorg. Chem., 16*, 2639 (1977).

11 J. A. Kuduk and J. A. Ibers, *J. Organometal. Chem., 139*, 199 (1977).

12 B. Jovanovic, L. Manojlovic-Muir and K. W. Muir, *J. Chem. Soc. Dalton*, 195 (1974).

13 M. A. Bennett, G. B. Roberson, P. O. Whimp and T. Yoshida, *J. Am. Chem. Soc., 95*, 3028 (1973).

14 M. R. Snow and J. A. Ibers, *Inorg. Chem., 12*, 224 (1973).

15 R. Ros, R. A. Michelin, U. Belluco, G. Zanotti, A. Del Pra and G. Bombieri, *Inorg. Chim. Acta, 29*, L187 (1978).