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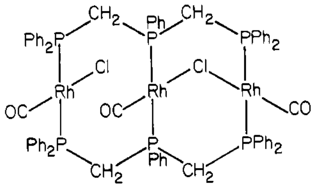
Characterization of Chelating Bis((diphenylphosphino)methyl)phenylphosphine as a Bridging Ligand in Bi- and Trinuclear Complexes

Sir:

Recently there has been significant interest in the use of polydentate phosphine ligands in the building of bi- and polynuclear metal complexes.[1-7] We have recently reported that the triphosphine bis((diphenylphosphino)methyl)phenylphosphine (dpmp)[8] is capable of functioning as a bridging or a chelating ligand as shown in **1** and **2**, respectively.[1] Chelate ring formation selectively ties up the two end phosphorus atoms and leaves the central phosphorus atom available for coordination to another metal center. Here we report on the use of this method of differentiation between the phosphorus atoms to form a variety of bi- and trinuclear complexes in which the basic chelate structure remains an integral structural unit but displays considerable flexibility in its conformation.



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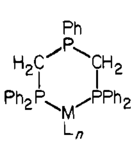
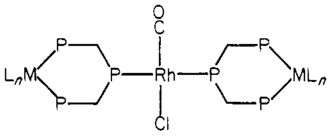


2, $ML_n = PdCl_2$
3, $ML_n = Mo(CO)_4$

Colorless crystals of $(dpmp)Mo(CO)_4$ (**3**)[9] are readily isolated from the reaction between dpmp and (norbornadiene)$Mo(CO)_4$ in dichloromethane solution at 25 °C followed by precipitation by ether. Spectroscopic data characterizing this and other new compounds are given in Table I. While the ^{31}P chemical shift of the terminal phosphorus atoms of the ligand experiences a high-frequency (low-field) displacement relative to the free ligand, as is usual for a coordinated phosphine,[10] the chemical shift for the internal phosphorus atom occurs at a lower frequency than that of the free ligand. This is indicative of chelating of the triphosphine in a manner that leaves the central phosphorus atom uncoordinated. The $^{31}P\{^1H\}$ NMR spectrum of $dpmpPdCl_2$ shows similar features.[1]

Reaction of a dichloromethane solution of **2** or **3** with a dichloromethane solution of $(CO)_4Rh_2(\mu\text{-}Cl)_2$ followed by precipitation yields **4** or **5**, respectively, in good yields (>75%).



4a, $ML_n = PdCl_2$
b, $ML_n = PtCl_2$
5, $ML_n = Mo(CO)_4$

The platinum analogue of **4a** is prepared similarly. The yellow color and carbonyl stretching frequencies of the rhodium-bound carbonyl group indicate that these substances are physically similar to the well-known *trans*-$(Ph_3P)_2Rh(CO)Cl$. Coordination of the central phosphorus atom (and only that phosphorus atom) to the rhodium atom in **4** and **5** is clearly shown by the presence of Rh–P coupling in the $^{31}P\{^1H\}$ NMR spectrum. Notice that the triangular complexes **4** and **5** have the same 3/2 metal/triphosphine stoichiometry as the complex **1** but have drastically different arrangements of the bridging phosphines. In view of the extensive ligand exchange and rearrangements noted earlier[1,11] in the reactions between complexes of 2-(diphenylphosphino)pyridine, it is significant that the chelated units retain their integrity in the formation of **4** and **5**.

The physical properties of these complexes suggest that there is little direct interaction between the individual metal centers. How this can be is not readily apparent from the structure of **2**, in which the boat conformation of the chelate ring directs the central phosphorus lone pair to a position directly over the chelated palladium.[1] In order to explore this point, an X-ray crystallographic study of a related species, $(CH_3CN)PdCl_2(\mu\text{-dpmp})PdCl_2$, has been undertaken. This binuclear complex was obtained from the reaction between **2** and $(PhCN)_2PdCl_2$ in dichloromethane solution followed by recrystallization of

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Table I. Spectroscopic Parameters

compd	$^{31}P\{^1H\}$ NMR spectra[a] δ	$^{31}P\{^1H\}$ NMR spectra[a] *J*, Hz	IR spectra[b] ν(CO), cm^{-1}
(dpmp)$PdCl_2$	18.8 (d)	57 (*J*(P–P))	. . .
	−40.7 (t)		
(dpmp)$Mo(CO)_4$	23.3 (d)	79 (*J*(P–P))	2010, 1923, 1900, 1885 sh
	−37.3 (t)		
$Cl_2Pd(\mu$-dpmp)$PdCl_2(NCCH_3)$	22.4 (s)		
	5.6 (s)		
$[Cl_2Pd(\mu$-dpmp)$]_2Rh(CO)Cl$	19.3 (s)		1986 sh, 1975
	9.3 (d)	128 (^1J(Rh–P))	
$[Cl_2Pt(\mu$-dpmp)$]_2Rh(CO)Cl$	5.9 (d)	128 (^1J(Rh–P))	1980
	0.0 (s)	3525 (^1J(Pt–P))	
$[(OC)_4Mo(\mu$-dpmp)$]_2Rh(CO)Cl$	23.8 (s)		2020, 1980, 1930 sh, 1900
	9.8 (d)	125 (^1J(Rh–P))	
dpmp	−33.0[c]	115 (*J*(P–P))	
	−22.5[c]		
	−33.8[d]		

[a] Recorded at 81 MHz with 85% H_3PO_4 external standard in dichloromethane solution at 25 °C. Abbreviations: s, singlet; d, doublet; t, triplet. [b] From Nujol mulls. [c] Second-order spectrum, chemical shift of terminal phosphorus atoms. [d] Chemical shift of internal phosphorus atom.

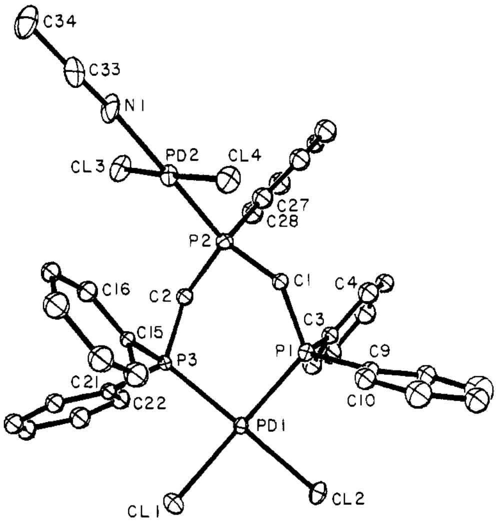

Figure 1. Perspective drawing of $(CH_3CN)PdCl_2(\mu$-dpmp)$PdCl_2 \cdot CH_3CN$. Some selected bond distances (Å) and angles (deg) are as follows: Pd(1)–P(1), 2.239 (4); Pd(1)–P(3), 2.241 (4); Pd(1)–Cl(1), 2.324 (3); Pd(1)–Cl(2), 2.348 (4); Pd(2)–Cl(3), 2.300 (4); Pd(2)–Cl(4), 2.288 (4); Pd(2)–P(2), 2.230 (4); Pd(2)–N(1), 2.065 (14); Cl(1)–Pd(1)–Cl(2), 91.8 (1); P(1)–Pd(1)–P(3), 93.8 (1); Cl(3)–Pd(2)–Cl(4), 176.5 (2); Cl(3)–Pd(2)–N(1), 89.9 (4); Cl(4)–Pd(2)–N(1), 91.5 (4).

the yellow precipitate from acetonitrile. The structural results are shown in Figure 1.[12] The triphosphine ligand has assumed a skew-boat conformation, which allows the two palladium ions to be quite remote from one another (Pd···Pd = 5.854 Å).

The spectroscopic results in Table I suggest that phosphorus–phosphorus coupling in these complexes may be a useful indicator of structure. While the P–P coupling in the chelated complexes is less than in the free ligand, it is still substantial. In **1** and related species it it also sizable, generally ca. 50 Hz. However, in the last four examples in the table where chelated dpmp is acting as a bridge (probably with a skew-boat ring conformation), the P–P coupling is too small to be resolved and the natural line widths indicate that it must be less than 15 Hz.

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Registry No. **2**, 84751-00-8; **3**, 86217-32-5; **4a**, 86217-34-7; **4b**, 86217-35-8; **5**, 86217-36-9; $Cl_2Pd(\mu$-dpmp)$PdCl_2(NCCH_3)$, 86217-33-6; (dpmp)$PtCl_2$, 86217-37-0; $BMo(CO)_4$ (B = norbornadiene), 12146-37-1; $(CO)_4Rh_2(\mu$-$Cl)_2$, 14523-22-9; $(PhCN)_2PdCl_2$, 14220-64-5.

Supplementary Material Available: Listings of atomic fractional coordinates, thermal parameters, and bond lengths and distances for $(CH_3CN)PdCl_2(\mu$-dpmp)$PdCl_2 \cdot CH_3CN$ (5 pages). Ordering information is given on any current masthead page.

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(12) Orange crystals of $(CH_3CN)PdCl_2(\mu$-dpmp)$PdCl_2 \cdot CH_3CN$ were obtained from gradual cooling of a saturated acetonitrile solution of the complex. Crystal data and details of refinement: space group $P2_12_12_1$ (No. 19); T = 140 K; a = 12.302 (4), b = 12.483 (3), c = 24.316 (5) Å; Z = 4; Mo Kα, λ = 0.710 69 Å; P2 diffractometer; ω scans; 2θ(max) 50°; blocked-cascade least squares; R = 0.069; 3193 reflections, $I > 3\sigma(I)$; 234 parameters.

Heterogeneous Electron Transfer as a Pathway in the Dissolution of Magnetite in Oxalic Acid Solutions

Sir:

The dissolution of metal oxides is a process of importance in several fields such as hydrometallurgy, passivity of metals, and cleaning of boilers and metal surfaces in general. The basic ideas concerning the process of dissolution of metal oxides were put forward by Engell,[1] Wagner and Valverde,[2,3] and Vermilyea,[4] and the subject was reviewed by Diggle[5] some years ago. For the specific case of dissolution of iron oxides by acidic solutions containing complexing agents, our recent review[6] and references therein may be consulted. In the case

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