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Synthesis and Solution Structure of $\{Hg[PPh_2(CH_2)_nPPh_2]_2\}(O_3SCF_3)_2$, $n = 1, 2$

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There are several modes of coordination open to bidentate phosphines: (i) monodentate, (ii) chelating bidentate, or (iii) bridging bidentate.[1,2] Examples of all bonding modes have been described mainly for square-planar or octahedral transition-metal complexes.[1,2] Tetracoordinate mercury prefers a tetrahedral coordination geometry.[3] This geometry should be associated with a greater ring strain in 4- and 5-membered chelate complexes.[2] In this context this work deals with a study of the structure and the ^{31}P and ^{199}Hg NMR parameters of the potentially tetracoordinate and hence tetrahedral title compounds.

Results and Discussion

Mercury(II) trifluoromethanesulfonate and the bidentate ligands L = $PPh_2(CH_2)_nPPh_2$, $n = 1, 2$ (dppm and dppe), form isolatable complexes of stoichiometry $[HgL_2](O_3SCF_3)_2$. The new cationic complexes are readily soluble in polar organic solvents such as methanol, pyridine, Me_2SO, DMF, or dichloromethane. Mercury(II) coordinates up to four monodentate tertiary phosphine ligands[3,4] (e.g. $[Hg(PPh_2Me)_4]^{2+}$; vide infra), suggesting mercury to be tetracoordinate in the title compounds. The mercury-199 NMR spectra (^{199}Hg: $I = 1/2$; abundance 16.8%) of the $[HgL_2]^{2+}$ complexes consist of 1:4:6:4:1 quintets, indicating four equivalent phosphorus atoms to be coordinated to mercury. This is confirmed by the phosphorus-31 NMR spectra, showing only one kind of phosphorus, and ^{199}Hg satellite patterns of appropriate intensities. ^{199}Hg and ^{31}P NMR patterns thus would be in keeping with mononuclear complexes involving chelating bidentate ligands. The ^{199}Hg and ^{31}P NMR parameters are summarized in Table I.

Phosphorus-31 NMR parameters of transition-metal phosphorus chelate complexes proved to be a valuable tool in the assignment of the ring sizes involved.[5] This is exemplified in Table II, listing data for $Pt(\eta^2\text{-}L)Me_2$,[6] which are representative of transition-metal phosphorus chelate complexes. The ^{31}P chemical shifts and $^1J(^{195}Pt,^{31}P)$ coupling constants of $[Pt(\eta^2\text{-}L)_2]Cl_2$ were measured to ensure that the trends of the complexes containing one and two chelate ligands were the same; they are included in Table II. The coordination shift Δ of four-membered transition-metal phosphorus chelate rings (e.g. L = dppm) is negative, corresponding to a strongly negative ring contribution Δ_R (Table II), while Δ_R is strongly positive for the 5-membered ring (L = dppe). (Δ = coordination chemical shift: change in $\delta(^{31}P)$ of the ligand upon coordination to a metal center. Δ_R = ring contribution: coordination shift of a chelated phosphine complex minus the coordination shift of an equivalent phosphorus in a nonchelated analogue.)

In contrast, no such correlation appears to be present in the series $[HgL_2]^{2+}$, the ring contributions being comparatively small and virtually independent of the ligand L (Table I; the Δ_R values have been obtained by comparison to $[Hg(PPh_2Me)_4]^{2+}$). This implies that the Δ_R values of $[Hg(dppm)_2]^{2+}$ and $[Hg(dppe)_2]^{2+}$ starkly fall outside the range predicted. For dppe this agrees however with recent measurements of $[HgX_2(\eta^2\text{-}cis\text{-}PPh_2CH{=}CHPPh_2)]$ involving a 5-membered chelate ring, where unexpectedly low $\delta(^{31}P)$ values were noted.[7]

Table I. NMR Parameters of $[HgL_2]^{2+\,a}$ and $[Hg(MePh_2P)_4]^{2+\,b}$

	$\delta(^{31}P)$	Δ	Δ_R	$\delta(^{199}Hg)$	$^1J(^{199}Hg,^{31}P)$
$[Hg(\eta^1\text{-dppm})_2]^{2+}$	13.3	35.9	1.9	1311^c	2952
$[Hg(\eta^2\text{-dppe})_2]^{2+}$	21.0	34.3	0.3	2018^c	2295
$[Hg(MePh_2P)_4]^{2+}$	6.0	34.0		2093^c	2150

[a] 0.1 mmol/mL Me_2SO; 303 K. [b] 0.1 mmol/mL MeOH; 203 K. [c] Quintet.

Table II. NMR Parameters of $Me_2Pt(chelate)^a$ and $[Pt(chelate)_2]Cl_2{}^b$

	$\delta(^{31}P)$	Δ	Δ_R	$^1J(^{195}Pt,^{31}P)$
$Me_2Pt(\eta^2\text{-dppm})$	−40.0	−17.7	−51.9	1434
$Me_2Pt(\eta^2\text{-dppe})$	54.5	67.7	33.3	1794
$[Pt(\eta^2\text{-dppm})_2]Cl_2$	−41.7	−19.1	−53.5	2075
$[Pt(\eta^2\text{-dppe})_2]Cl_2$	47.8	61.1	26.7	2315

[a] Taken from ref 6. [b] This work: saturated solutions in methanol; 303 K.

The one-bond mercury-phosphorus coupling constant of $[Hg(dppm)_2]^{2+}$ also behaves in an unexpected manner. The value of 2952 Hz (Table I) approaches the range usually observed for cationic mercury complexes coordinated by three tertiary phosphine ligands.[4] The ^{199}Hg chemical shift can be regarded as normal for $[Hg(dppe)_2]^{2+}$, a range of 2000–2200 ppm being typical for HgP_4 configurations.[4] On the other hand there is a shift of 800 ppm to low frequency for $[Hg(dppm)_2]^{2+}$ (Table I). This is in the region usually observed for complexes of the type $[Hg(PR_3)_2]^{2+}$. A similar effect has been reported for the platinum-195 resonance of the compound $Pt(\eta^2\text{-dppm})Me_2$, which was found shifted by 700 ppm to low frequency relative to the resonance of $Pt(\eta^2\text{-dppe})Me_2$.[8]

The anomalous data of $[Hg(dppm)_2]^{2+}$ can be explained on the assumption of a $[Hg(\eta^1\text{-dppm})_2]^{2+}$ structure being fluxional on the NMR time scale as a result of an *intra*molecular displacement of coordinated and free phosphorus in the η^1-dppm ligands in the fast-exchange limit.

This would account for (i) the multiplicities of the ^{199}Hg and ^{31}P NMR spectra, since the expected AA′MM′X pattern becomes an A_4X pattern in the fast-exchange limit, (ii) the phosphorus-31 chemical shift being the mean of the chemical shifts of the coordinated and the free phosphorus in the η^1-dppm ligands, (iii) the coupling constant $J(^{199}Hg,^{31}P)$ being the mean of $^1J(^{199}Hg,^{31}P)$ and $^3J(^{199}Hg,^{31}P)$, and (iv) the position of the mercury-199 resonance being actually that of a $[Hg(PR_3)_2]^{2+}$ species.

The fast-exchange limit is retained down to 253 K in methanol. In favorable cases (supercooling of a methanol solution), the slow-exchange limit is nearly attained at 173 K, and separate features of coordinated ($\delta(^{31}P)$ 42.0) and free phosphorus ($\delta(^{31}P)$ −20.5) in the η^1-dppm ligands can be discerned in ^{31}P NMR spectra. The coupling constant $^1J(^{199}Hg,^{31}P)$ equals 6036 Hz.

The existence of $[Hg(\eta^1\text{-dppm})_2]^{2+}$ in contrast to $[Hg(\eta^2\text{-dppe})_2]^{2+}$ appears to be due to the ring strain of a 4-membered ring formed by dppm in a tetrahedrally coordinated metal complex.[2] Mercury achieves tetracoordination in $[Hg(\eta^2\text{-dppe})_2]^{2+}$, while it is coordinated to only two phosphorus atoms in $[Hg(\eta^1\text{-dppm})_2]^{2+}$. This could be interpreted to mean that the ring strain causes rejection of the coordination of a third and fourth phosphorus atom to mercury. It is, however, interesting to note that mercury prefers the η^1-dppm ligand associated with intramolecular exchange instead of an increase in the number of co-

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(1) McAuliffe, C. A.; Levason, W. "Phosphine, Arsine and Stibine Complexes of the Transition Elements"; Elsevier: Amsterdam, 1979.

(2) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, 99.

(3) McAuliffe, C. A. "The Chemistry of Mercury"; Macmillan: London, 1977.

(4) Colton, R.; Dakternieks, D. *Aust. J. Chem.* **1981**, *34*, 323.

(5) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(6) Appleton, T. G.; Bennett, M. A.; Tomkins, I. B. *J. Chem. Soc., Dalton Trans.* **1979**, 439.

(7) Buergi, H. B.; Fischer, E.; Kunz, R. W.; Parvez, M.; Pregosin, P. S. *Inorg. Chem.* **1982**, *21*, 1246.

(8) Hietkamp, S.; Stuffken, D. J.; Vrieze, K. *J. Organomet. Chem.* **1979**, *169*, 107.

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ordinated phosphorus atoms in a structure involving bridging bidentate dppm ligands.

Experimental Section

NMR spectra were recorded on a multinuclear Bruker WP-80 spectrometer operating in the FT mode. Chemical shifts are given in ppm relative to the high frequency of 85% H_3PO_4 or aqueous $Hg(ClO_4)_2$ (2 mmol of HgO/cm^3 of 60% $HClO_4$); coupling constants are in hertz. Elemental analyses were obtained on a Heraeus EA 415 apparatus.

Literature methods were used to prepare $[Hg(Me_2SO)_6](O_3SCF_3)_2$,[9] $[Pt(\eta^2\text{-dppm})_2]Cl_2$, and $[Pt(\eta^2\text{-dppe})_2]Cl_2$.[10]

Preparation of $[Hg(\eta^1\text{-dppm})_2](O_3SCF_3)_2$. $[Hg(Me_2SO)_6](O_3SCF_3)_2$ (96.7 mg, 0.1 mmol) and dppm (96 mg, 0.2 mmol) were mixed together in a Schlenk tube under dinitrogen in 1 cm^3 of CH_2Cl_2, and the mixture was stirred at room temperature for 15 min. The CH_2Cl_2 was evaporated, and the product was precipitated from the oily residue as a colorless microcrystalline powder by adding 1 cm^3 of H_2O. The precipitate was filtered, washed with 1 cm^3 of H_2O, and vacuum-dried, giving an almost quantitative yield; mp 105 °C.[11]

Preparation of $[Hg(\eta^2\text{-dppe})_2](O_3SCF_3)_2$ by the above method gave the product, recrystallized from toluene/ethanol/petroleum ether as colorless crystals. The yield was about 80%; mp 227 °C.[11]

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Registry No. $[HgL_2](O_3SCF_3)_2$ (L = dppm), 93503-32-3; $[HgL_2](O_3SCF_3)_2$ (L = dppe), 93503-34-5; $[Hg(Me_2SO)_6](O_3SCF_3)_2$, 76703-09-8.

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[9] Peringer, P. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1501.

[10] Brown, M. P.; Fisher, J. R.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Thomson, M. A.; Seddon, K. R. *J. Chem. Soc., Chem. Commun.* **1979**, 931. Westland, A. D. *J. Chem. Soc.* **1965**, 3060.

[11] Satisfactory elemental analyses were obtained.

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Copper(I) Complexes with Unsaturated Small Molecules. Synthesis and Properties of Monoolefin and Carbonyl Complexes

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In this contribution, we present the synthesis and properties of monoolefin and carbonyl complexes that establish the similarities and differences in the copper(I) coordination chemistry with these small molecules. Our recently reported study of Cu(I)–di-2-pyridylamine complexes with monoolefins, acetylene, and carbon monoxide demonstrates some of the features of cuprous complexes with these small molecules.[1,2] In particular, this study suggests that the structural chemistry is comparable to that of Ni(0) and other d^{10} metals.[5,6] Monoolefin complexes generally have trigonal-planar geometries, but tetrahedral complexes can be prepared with the proper choice of ligands.[1-4] Carbonyl complexes tend toward four-coordinate geometries,[6,7] although higher coordination numbers are also known.[8] However, our studies also show that some significant differences exist in the coordination chemistry of the two types of d^{10} metal ions. Olefin and acetylene bonds are not significantly lengthened on coordination to Cu(I) ions, unlike the significant increases in bond lengths of these molecules on coordination to Ni(0) ions.[5,6] This lack of effect on coordination may be a manifestation of the poor π-back-bonding ability of the cuprous ion. Similarly, cuprous ion does not appear to coordinate more than one carbonyl group, whereas Ni(0) complexes with two, three, and four carbonyl groups are well-known.[6] Other species, including counterions such as perchlorate and tetraphenylborate, occupy the fourth site.[1,9]

The complexes described here were prepared to determine whether the properties suggested in our previous studies[1-4] are general features of copper coordination chemistry with these molecules. A series of nitrogen-donating ligands is used to prepare ethylene, propylene, cyclohexene, and carbonyl complexes. The type of coordinated nitrogen atom varies from tertiary amines to aromatic heterocyclic nitrogen donors. Our Cu(I)–monoolefin complexes reported here and elsewhere[1-3] are the only ones that are both *stable* to loss of olefin and *soluble* in common solvents and can thus be spectrally characterized. We assign structures to these complexes on the basis of the similarities of their spectral parameters to those of complexes of known structure.

Experimental Section

General Methods. All chemicals were reagent grade and were used as received unless otherwise noted. The solvents methanol, diethyl ether, and cyclohexene were deaerated with prepurified nitrogen and stored over molecular sieves (4A), which were activated prior to use by heating at approximately 250 °C under high vacuum and then stored under nitrogen. *N,N,N′,N′*-Tetramethylethylenediamine (TMEN) and *N,N,N′,-N′*-tetraethylethylenediamine (TEEN) were thoroughly degassed and then stored over activated molecular sieves under nitrogen. Standard glovebox and Schlenkware techniques were used to handle air-sensitive compounds. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, and by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer 283-B infrared spectrophotometer. NMR spectra were obtained in deuterioacetone with a Perkin-Elmer EM-390 spectrometer; all reported peak positions are relative to external tetramethylsilane.

General Methods for Preparation of Copper(I) Complexes. Copper perchlorate hexahydrate (0.25 g, 0.67 mmol) and copper dust (0.20 g, 3.1 mmol) were stirred in 10 mL of methanol overnight under an atmosphere of the appropriate gas (ethylene, propylene, or carbon monoxide). *Caution! The Cu(I) complexes produced in this step are unstable and can explode if taken to dryness.*[10] The ligand (0.16 g of TMEN, 0.23 g of TEEN, 0.21 g of 2,2′-bipyridine, or 0.24 g of 1,10-phenanthroline, 1.3 mmol) was then added, TMEN and TEEN as methanol solutions and 2,2′-bipyridine (bpy) and 1,10-phenanthroline (OP) as powders. After complete addition, the reaction mixture was stirred for approximately 0.5 h and then filtered under nitrogen pressure. The volume of the filtrate was reduced with a stream of the appropriate gas. White, slightly yellow, or gray microcrystalline products were obtained by adding diethyl ether and collected by filtration under nitrogen.

The above procedure with the following changes was used to prepare the cyclohexene complexes: use of an initial reaction mixture of 5 mL of methanol and 5 mL of cyclohexene and elimination of the concentration step. In addition to the ligands indicated above, the ligand di-2-pyridylamine $(NH(py)_2)$ (0.23 g, 1.3 mmol) was also used.

(Ethylene)(tetramethylethylenediamine)copper(I) Perchlorate (1). Anal. Calcd for $C_8H_{20}ClCuN_2O_4$: C, 31.27; H, 6.56; N, 9.12. Found:

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[1] Thompson, J. S.; Whitney, J. F. *Inorg. Chem.* **1984**, *23*, 2813–2819.

[2] Thompson, J. S.; Whitney, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 5488–5490.

[3] Thompson, J. S.; Harlow, R. L.; Whitney, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3522–3527.

[4] Thompson, J. S.; Whitney, J. F. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 756–759.

[5] (a) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33–61. (b) Mingos, D. M. P. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds; Pergamon Press: New York, 1982; Vol. 3, pp 1–88. (c) Jolly, P. W. *Ibid.*, Vol. 6, pp 101–143. (d) Hartley, F. R. *Ibid.*, Vol. 6, pp 471–762.

[6] Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1974; Vol. I, pp 1–93.

[7] (a) Sorrell, T. N.; Jameson, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 6013–6018. (b) Sorrell, T. N.; Malachowski, M. R. *Inorg. Chem.* **1983**, *22*, 1883–1887.

[8] McCool, M. W.; Marsh, R. E.; Ingle, D. M.; Gagne, R. R. *Acta Crystallogr., Sect. B* **1981**, *B37*, 935–937.

[9] Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1980**, *19*, 1191–1197.

[10] Ogura, T. *Inorg. Chem.* **1976**, *15*, 2301–2303.

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