

Table II. Infrared Bands and Assignments (in  $\text{cm}^{-1}$ )<sup>a</sup>

absorption	assignment
3200 br, s	$\nu(\text{OH})(\text{H}_2\text{O})$
1815 sh, m	Sq, $\nu(\text{C}=\text{O})$
1640 sh, m	Sq, $\nu(\text{C}=\text{C})$
1500 br, s	Sq, $\nu(\text{C}-\text{C}) + \nu(\text{C}-\text{O})$
1110, 1085 sh, w	Sq, $\nu_{1,3}, E_u^b$
850, 750 br, w	$\nu(\text{Fe}-\text{O}-\text{H}) + \rho_r(\text{H}_2\text{O})$
660, 460 br, w	$\rho_w(\text{H}_2\text{O})$
420 sh, w	unassigned
390 sh, w	$\nu(\text{Fe}-\text{O})$
350 sh, vw	Sq, $\nu_2, A_{1g}^b$

<sup>a</sup> Abbreviations: br, broad; s, strong; sh, sharp; m, moderate; w, weak; v, very. <sup>b</sup> Reference 18.

Infrared spectra of squarate-containing compounds are quite characteristic of the mode of coordination.<sup>2</sup> Thus it is possible to distinguish the terminal form of squarate as in II from the bridging form by virtue of the lower symmetry of the former. Polymeric divalent metal squarates, which contain the squarate ion in approximately  $D_{4h}$  symmetry, have as the most prominent feature in their infrared spectra a broad band near  $1500 \text{ cm}^{-1}$  assigned to a mixture of C–O and C–C stretching modes.<sup>1,2,12</sup> The infrared spectrum of  $[\text{Fe}(\text{Sq})(\text{OH})(\text{H}_2\text{O})_2]_2 \cdot 2\text{H}_2\text{O}$ , however, shows not only this absorption but also moderate bands at 1640 and  $1815 \text{ cm}^{-1}$ . The former absorption may be assigned to a C=C stretching mode and the latter to a C=O stretching mode. The infrared spectrum of this complex thus suggests nominal  $C_{2v}$  symmetry for the squarate ion, as in squaric acid and metal squarates involving bidentate coordination of the squarate ion. A number of other infrared absorptions are present in the spectrum of  $[\text{Fe}(\text{Sq})(\text{OH})(\text{H}_2\text{O})_2]_2 \cdot 2\text{H}_2\text{O}$ , all of which are consistent with structure II.<sup>17</sup> These bands and appropriate assignments are listed in Table II. We have assigned a weak absorption at  $850 \text{ cm}^{-1}$  to the Fe–O–H deformation mode associated with bridging hydroxo groups.<sup>15</sup> This assignment is supported by the observation that this band decreases in intensity upon partial deuteration.

The thermal weight loss curve of  $[\text{Fe}(\text{Sq})(\text{OH})(\text{H}_2\text{O})_2]_2 \cdot 2\text{H}_2\text{O}$  obtained in a nitrogen atmosphere shows two inflections. The first, at  $160^\circ\text{C}$ , corresponds to a 17.3% weight loss and the second, at  $290^\circ\text{C}$ , corresponds to a 64.8% total weight loss. If the first step corresponds only to dehydration then 4.6 mol of water/mol of dimer is lost. This suggests that the hydrogen bonding between squarate and water is sufficiently strong that water coordinated to the metal, rather than water which is nominally "lattice" water, is lost first upon thermal decomposition. An X-ray powder pattern of the final residue shows the presence of iron metal. The total theoretical weight loss is 66.6% if iron metal is the only product of the decomposition. The thermal behavior of this material contrasts markedly with that of the vanadium analogue.<sup>2</sup> The vanadium complex loses 2 mol of water/mol of dimer at  $80^\circ\text{C}$  under vacuum and 6 mol of water in either air or argon at ca.  $150^\circ\text{C}$  and, ultimately, decomposes to vanadium oxides, rather than the metal, at higher temperatures. The complexity of the final decomposition step in these complexes has been previously noted for both divalent<sup>18,19</sup> and trivalent<sup>2</sup> metal squarates.

**Acknowledgment.** The authors acknowledge support of this work by the Office of Naval Research.

**Registry No.** II, 66540-74-7.

**Supplementary Material Available:** A listing of observed magnetic susceptibilities, Table I (1 page). Ordering information is given on any current masthead page.

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## Poly(tertiary phosphines and arsines). 16. Some Metal Carbonyl Complexes of 1,2-Bis(dimethoxyphosphino)ethane<sup>1</sup>

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Received March 7, 1978

This paper presents a survey of some of the metal carbonyl chemistry of the ligand  $(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2$ . This ligand is a much stronger  $\pi$  acceptor than the extensively studied<sup>3</sup> ligands  $\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2$  (R = alkyl or aryl) because of the greater electronegativity of the terminal methoxy groups. Other chelating strong  $\pi$ -accepting trivalent phosphorus ligands include  $\text{CH}_3\text{N}(\text{PF}_2)_2$ ,<sup>4-7</sup>  $\text{F}_2\text{PCH}_2\text{CH}_2\text{PF}_2$  and its homologues,<sup>8,9,10</sup>  $(\text{CF}_3)_2\text{PCF}_2\text{CF}_2\text{P}(\text{CF}_3)_2$ ,<sup>11</sup> and  $(\text{CF}_3)_2\text{PC}-\text{H}_2\text{CH}_2\text{P}(\text{CF}_3)_2$ .<sup>12,13</sup>

## Experimental Section

Carbon and hydrogen analyses (Table I) were performed by the Atlantic Microanalytical Laboratory, Atlanta, Ga. Other analytical determinations (Table I) were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Melting and decomposition points (Table I) were taken in capillaries and are uncorrected.

Infrared spectra in the  $\nu(\text{CO})$  region (Table I) were taken in pentane, hexane, or dichloromethane solutions and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Each spectrum was calibrated against the  $1601\text{-cm}^{-1}$  band of polystyrene film. Proton NMR spectra (Table I) were taken in  $\text{CDCl}_3$  solutions and recorded on a Varian T-60 spectrometer at 60 MHz.

All solvents including triethylamine used in reactions were freshly distilled under nitrogen from appropriate drying agents ( $\text{Na}/\text{C}_6\text{H}_5)_2\text{CO}$ ,  $\text{LiAlH}_4$ , etc.). All reactions were run under nitrogen. The air-sensitive  $(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2$  was handled in a nitrogen-filled glovebox (Vacuum Atmospheres).

The  $\text{Cl}_2\text{PCH}_2\text{CH}_2\text{PCl}_2$  was obtained from white phosphorus, phosphorus trichloride, and ethylene according to the patented procedure.<sup>14</sup>

**Preparation of  $(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2$  (abbreviated as Pom-Pom).** A mixture of 16.7 mL (12.1 g, 120 mmol) of tri-

**Table I.** Properties of the Metal Carbonyl Complexes of 1,2-Bis(dimethoxyphosphino)ethane

complex	color	mp, °C	analyses			infrared $\nu(\text{CO})$ , cm <sup>-1</sup>	proton NMR, <sup>a</sup> ppm		
			% C	% H	% other		CH <sub>3</sub> O <sup>b</sup>	CH <sub>2</sub> CH <sub>2</sub>	
(Pom-Pom) <sub>2</sub> Cr(CO) <sub>2</sub>	white	295-298 dec	calcd found	31.4 31.3	6.0 6.1	536 (mol wt) 527 (mol wt in C <sub>6</sub> H <sub>6</sub> )	1880 s, 1820 s	6.32 d (11) 6.16 d (14) 6.51 d (8)	8.4 br
(Pom-Pom) <sub>2</sub> Mo(CO) <sub>2</sub>	white	118 dec	calcd found	29.0 29.2	5.6 5.6		1900 s, 1830 s	6.41 t (11) 6.24 t (12) 6.59 t (10)	~8.3 br
(Pom-Pom) <sub>2</sub> W(CO) <sub>2</sub>	white	118 dec	calcd found	25.2 25.2	4.8 4.9		1890 s, 1830 s	6.40 t (10) 6.25 d (12) 6.60 d (9)	8.30 br
(Pom-Pom)Cr(CO) <sub>4</sub>	white	92-93	calcd found	31.8 31.7	4.3 4.3		2025 m, 1935 s, 1912 vs	6.27 d (11)	8.06 d (20)
(Pom-Pom)Mo(CO) <sub>4</sub>	white	65	calcd found	28.4 28.6	3.8 3.9		2033 m, 1941 s, 1916 vs	6.26 d (12)	8.08 d (21)
(Pom-Pom)[Fe(CO) <sub>4</sub> ] <sub>2</sub>	white	111	calcd found	30.6 30.6	2.9 3.0	550 (mol wt) 551 (mol wt in C <sub>6</sub> H <sub>10</sub> O)	2058 m, 1982 s, 1931 vs	6.24 t (13)	7.65 s
[(Pom-Pom) <sub>2</sub> CoCO]- [PF <sub>6</sub> ]	pale yellow	230-231 dec	calcd found	23.6 23.7	4.9 4.9	8.9 (Co), 17.3 (F) 8.8 (Co), 17.5 (F)	1982 s	6.20	7.95 br

<sup>a</sup> Key: s = singlet, d = doublet, t = apparent triplet (generally from virtual coupling), br = broad; coupling constants in Hz are given in parentheses. <sup>b</sup> In the (Pom-Pom)<sub>2</sub>M(CO)<sub>2</sub> derivatives the first of the three listed CH<sub>3</sub>O resonances has approximately twice the relative intensity of each of the other two.

**Table II.** Reactions of Metal Carbonyls with 1,2-Bis(dimethoxyphosphino)ethane

metal carbonyl (g, mmol)	Amt of Pom-Pom, g (mmol)	Amt of solvent, mL	reaction temp, °C	reaction time, h	product	isolated yield, <sup>f</sup> %
Cr(CO) <sub>6</sub> (0.66, 3.0)	1.28 (6.0)	C <sub>6</sub> H <sub>6</sub> (300)	25	7 (UV)	(Pom-Pom) <sub>2</sub> Cr(CO) <sub>2</sub> <sup>a</sup>	54
Mo(CO) <sub>6</sub> (0.53, 2.0)	1.28 (6.0)	C <sub>6</sub> H <sub>6</sub> (350)	25	4 (UV)	(Pom-Pom) <sub>2</sub> Mo(CO) <sub>2</sub> <sup>b</sup>	9
Mo(CO) <sub>6</sub> (0.53, 2.0)	0.43 (2.0)	C <sub>6</sub> H <sub>6</sub> (350)	25	2 (UV)	(Pom-Pom)Mo(CO) <sub>4</sub> <sup>b</sup>	17
W(CO) <sub>6</sub> (0.9, 2.8)	1.2 (5.6)	C <sub>6</sub> H <sub>6</sub> (350)	25	6 (UV)	(Pom-Pom) <sub>2</sub> W(CO) <sub>2</sub> <sup>a</sup>	44
C <sub>7</sub> H <sub>8</sub> Cr(CO) <sub>4</sub> (0.35, 1.37)	0.32 (1.5)	hexane (25)	40	4	(Pom-Pom)Cr(CO) <sub>4</sub> <sup>c</sup>	15
Fe <sub>2</sub> (CO) <sub>9</sub> (0.8, 2.2)	0.46 (2.0)	THF (25)	25	20	(Pom-Pom)[Fe(CO) <sub>4</sub> ] <sub>2</sub> <sup>d</sup>	8
Co <sub>2</sub> (CO) <sub>8</sub> (0.34, 1.0)	0.64 (3.0)	Et <sub>2</sub> O (15)	25 <sup>e</sup>	1	[(Pom-Pom) <sub>2</sub> CoCO][PF <sub>6</sub> ] <sup>e</sup>	24

<sup>a</sup> After removal of solvent from the reaction mixture the residue was crystallized from a mixture of dichloromethane and pentane at -15 °C. <sup>b</sup> After removal of solvent from the filtered reaction mixture the residue was crystallized from pentane at -15 °C. <sup>c</sup> After removal of solvent from the filtered reaction mixture the residue was crystallized from pentane at -78 °C. <sup>d</sup> Solvent was removed at 25 °C (25 mm). A concentrated dichloromethane solution of the residue was chromatographed on a Florisil column. The product was eluted with hexane. After evaporation of the hexane eluate the product was crystallized from a mixture of dichloromethane and hexane. <sup>e</sup> The (CH<sub>3</sub>O)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(OCH<sub>3</sub>)<sub>2</sub> was added to the diethyl ether solution of Co<sub>2</sub>(CO)<sub>8</sub> at -40 °C and the reaction mixture was then allowed to warm to room temperature over 2 h. After the reaction period was over solvent was removed at 25 °C (25 mm). A concentrated acetone solution of the orange oily residue was treated with excess saturated ethanolic NH<sub>4</sub>PF<sub>6</sub>. The pale yellow precipitate was filtered and then recrystallized from ethanol at -15 °C. <sup>f</sup> These isolated yields are undoubtedly much lower than the yields of product actually formed owing to large losses in the crystallization steps.

ethylamine, 4.85 mL (3.8 g, 120 mmol) of methanol, and 190 mL of diethyl ether was treated at -78 °C with 4.9 mL (7.0 g, 30 mmol) of Cl<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PCl<sub>2</sub> over a period of 30 min. The reaction mixture was then allowed to warm slowly to room temperature. After adding an additional 40 mL of diethyl ether to facilitate stirring, it was stirred at room temperature for 2 h. The reaction mixture was then filtered from the precipitated triethylamine hydrochloride. Additional diethyl ether was used to wash the precipitate. The diethyl ether was distilled from the combined filtrates and washings under nitrogen at atmospheric pressure. Vacuum distillation of the liquid residue gave a 60 to 70% yield of colorless liquid (CH<sub>3</sub>O)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(OCH<sub>3</sub>)<sub>2</sub>: bp 60-64 °C (0.07 mm); proton NMR (CDCl<sub>3</sub>)  $\tau$  6.40 (CH<sub>3</sub>O, doublet, 12 Hz separation with a minimum of three additional center peaks), 8.47 (CH<sub>2</sub>CH<sub>2</sub>, apparent triplet, 7 Hz separation); phosphorus-31 NMR (CH<sub>2</sub>CH<sub>2</sub>) -185.6 ppm relative to 85% H<sub>3</sub>PO<sub>4</sub>. The (CH<sub>3</sub>O)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(OCH<sub>3</sub>)<sub>2</sub> was unexpectedly air-sensitive and therefore was handled in a nitrogen-filled glovebox.

Anal. Calcd for C<sub>6</sub>H<sub>16</sub>O<sub>4</sub>P<sub>2</sub>: C, 33.6; H, 7.5. Found: C, 33.5; H, 7.5.

**Reactions of (CH<sub>3</sub>O)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(OCH<sub>3</sub>)<sub>2</sub> with Metal Carbonyls (Table II).** The indicated quantities of the metal carbonyl, (CH<sub>3</sub>O)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(OCH<sub>3</sub>)<sub>2</sub>, and solvent were heated or irradiated for the indicated period of time (Table II). After filtration of any precipitate and removal of the solvent at ~25 °C (25 mm), the product was isolated by the procedure indicated in Table II.

The metal carbonyls used for these experiments either were commercial products or were prepared by standard procedures.<sup>15</sup>

Ultraviolet irradiations were performed using a 125-W mercury lamp with a Pyrex jacket.

**Carbon-13 NMR Spectra.** The indicated carbon-13 NMR spectra were recorded on a Jeolco PFT-100 spectrometer operating at 25.0349 MHz with proton noise decoupling and a deuterium lock using CDCl<sub>3</sub> solutions; chemical shifts ( $\delta$ ) are given in parts per million downfield from internal tetramethylsilane:

**A.** (CH<sub>3</sub>O)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(OCH<sub>3</sub>)<sub>2</sub>: CH<sub>3</sub>O at  $\delta$  53.7 (triplet, *J* = 6 Hz); CH<sub>2</sub>CH<sub>2</sub> at  $\delta$  25.1.

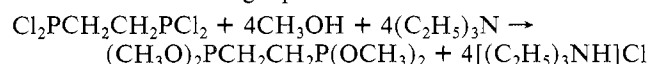
**B.** [(CH<sub>3</sub>O)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(OCH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Cr(CO)<sub>2</sub>: CO at  $\delta$  ~233 (broad); CH<sub>3</sub>O at  $\delta$  52.4,  $\delta$  50.7, and  $\delta$  50.5 of approximate relative intensities 2:1:1; CH<sub>2</sub>CH<sub>2</sub> at  $\delta$  ~29 (broad).

**C.** [(CH<sub>3</sub>O)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(OCH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>W(CO)<sub>2</sub>: CO at  $\delta$  ~214 (broad); CH<sub>3</sub>O at  $\delta$  54.0,  $\delta$  53.0, and  $\delta$  51.2 of approximate relative intensities 1:1:2; CH<sub>2</sub>CH<sub>2</sub> at  $\delta$  ~32.5 (broad).

**D.** [(CH<sub>3</sub>O)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(OCH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>CoCO[PF<sub>6</sub>]: CO not observed; CH<sub>3</sub>O at  $\delta$  53.5; CH<sub>2</sub>CH<sub>2</sub> at  $\delta$  27.5 (broad).

### Results and Discussion

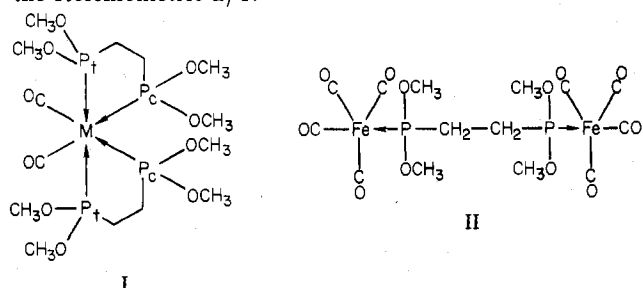
The bidentate ligand (CH<sub>3</sub>O)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(OCH<sub>3</sub>)<sub>2</sub> was prepared from Cl<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PCl<sub>2</sub> by conventional methods based on the following equation:



The product is a very air-sensitive liquid which can be purified by vacuum distillation. The NMR spectra of (CH<sub>3</sub>O)<sub>2</sub>PC-

$\text{H}_2\text{CH}_2\text{P}(\text{OCH}_3)_2$  support the proposed formulation and exhibit "virtual coupling" patterns<sup>16,17</sup> indicative of significant phosphorus-phosphorus coupling for both the  $\text{CH}_3\text{O}$  (proton and carbon-13) and  $\text{CH}_2\text{CH}_2$  (proton) resonances.

Ultraviolet irradiations of the metal hexacarbonyls  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{and W}$ ) with excess of the bidentate ligand  $\text{CH}_3\text{N}(\text{PF}_2)_2$  result in complete displacement of all six carbonyl groups to give the corresponding carbonyl-free derivatives  $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{M}$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{and W}$ ).<sup>5,7</sup> In our hands analogous ultraviolet irradiations of the metal hexacarbonyls with excess  $(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2$  were found to give the dicarbonyls  $[(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2]_2\text{M}(\text{CO})_2$  (I:  $\text{M} = \text{Cr}, \text{Mo}, \text{and W}$ ) as the most highly substituted products. The yields of these products I are maximized, however, if the ratio  $(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2/\text{M}(\text{CO})_6$  is kept close to the stoichiometric 2/1.



The infrared spectra of the  $[(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2]_2\text{M}(\text{CO})_2$  derivatives exhibit two  $\nu(\text{CO})$  frequencies of approximately equal relative intensities in accord with the indicated cis rather than the generally less stable trans isomers. Both the proton and carbon-13 NMR spectra of the eight methoxy groups indicate that four methoxy groups are nearly magnetically equivalent whereas the remaining four methoxy groups form two nonequivalent pairs. In the case of the tungsten derivative I ( $\text{M} = \text{W}$ ) the methoxy proton doublet corresponding to four methoxy groups has a significant center peak indicative of some virtual coupling between two phosphorus atoms.<sup>16,17</sup> Since in octahedral metal complexes the phosphorus-phosphorus coupling involving trans phosphorus atoms is generally larger than that involving cis phosphorus atoms, the four approximately magnetically equivalent methoxy groups may tentatively be assigned to those bonded to the mutually trans pair of phosphorus atoms ( $\text{P}_t$  in structure I). The remaining four methoxy groups, which appear as two magnetically nonequivalent pairs, would then be those attached to phosphorus atoms trans to carbonyl groups ( $\text{P}_c$  in structure I).

The photochemical reaction of  $(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2$  with the hexacarbonyls  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{and W}$ ) to give *cis*- $[(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2]_2\text{M}(\text{CO})_2$  (I) derivatives must necessarily proceed through an intermediate *cis*- $[(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2]\text{M}(\text{CO})_4$ . In the case of  $\text{M} = \text{Mo}$  this intermediate has been isolated from the ultraviolet irradiation of  $(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2$  with  $\text{Mo}(\text{CO})_6$  in a 1:1 mole ratio. The chromium analogue *cis*- $[(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2]\text{Cr}(\text{CO})_4$  has been prepared by an alternative but standard method: the displacement of coordinated norbornadiene from *nor*- $\text{C}_7\text{H}_8\text{Cr}(\text{CO})_4$  with  $(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2$ .

Some reactions of  $(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2$  with iron carbonyls have also been investigated. Treatment of  $\text{Fe}(\text{CO})_5$  with  $(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2$  in boiling xylene was found to lead to decomposition. However, reaction of  $\text{Fe}_2(\text{CO})_9$  with  $(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2$  at room temperature gives the binuclear complex  $[(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2]_2[\text{Fe}(\text{CO})_4]_2$  (II) in which the diphosphine functions as a bidentate bimetallic ligand. The formation of II relates to the familiar easy dissociation of  $\text{Fe}_2(\text{CO})_9$  into the stable  $\text{Fe}(\text{CO})_5$  and the

coordinate unsaturated  $\text{Fe}(\text{CO})_4$  fragment, which can complex with only one phosphorus atom to form the corresponding  $\text{R}_3\text{PFe}(\text{CO})_4$  derivative.

The reaction of  $(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2$  with  $\text{Co}_2(\text{CO})_8$  in diethyl ether results in rapid CO evolution, even below room temperature. Addition of  $\text{NH}_4\text{PF}_6$  to the resulting product allows isolation of the  $[(\text{CH}_3\text{O})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2]_2\text{CoCO}^+$  cation as its hexafluorophosphate salt. The formation of a (diphos) $_2\text{CoCO}^+$  cation in this reaction contrasts with the reactions of  $\text{Co}_2(\text{CO})_8$  with the more usual alkyl and aryl di(tertiary phosphines)  $\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2$  ( $\text{R} = \text{alkyl or aryl}$ ) which lead only to (diphos) $\text{Co}(\text{CO})_3^+$  derivatives.<sup>3</sup> This is another example of an increase in the  $\pi$ -acceptor strength of an organophosphorus ligand leading to an increased ability to replace carbonyl groups in metal carbonyls.<sup>18</sup>

**Acknowledgment.** We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AFOSR-75-2869. We also thank Dr. Edward Weil of the Stauffer Chemical Co. and Dr. W. F. Masler of B. F. Goodrich Co. for helpful discussions and assistance in obtaining the quantities of  $\text{Cl}_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2$  required for this research.

**Registry No.** (Pom-Pom) $_2\text{Cr}(\text{CO})_2$ , 67328-83-0; (Pom-Pom) $_2\text{Mo}(\text{CO})_2$ , 67328-84-1; (Pom-Pom) $_2\text{W}(\text{CO})_2$ , 67328-85-2; (Pom-Pom) $\text{Cr}(\text{CO})_4$ , 67328-86-3; (Pom-Pom) $\text{Mo}(\text{CO})_4$ , 67328-87-4; (Pom-Pom) $[\text{Fe}(\text{CO})_4]_2$ , 67328-88-5;  $[(\text{Pom-Pom})_2\text{CoCO}][\text{PF}_6]$ , 67328-90-9;  $\text{Cr}(\text{CO})_6$ , 13007-92-6;  $\text{Mo}(\text{CO})_6$ , 13939-06-5;  $\text{W}(\text{CO})_6$ , 14040-11-0;  $\text{C}_7\text{H}_8\text{Cr}(\text{CO})_4$ , 12146-36-0;  $\text{Fe}_2(\text{CO})_9$ , 15321-51-4;  $\text{Co}_2(\text{CO})_8$ , 10210-68-1; Pom-Pom, 67328-92-1; methanol, 67-56-1;  $\text{Cl}_2\text{PCH}_2\text{CH}_2\text{P}(\text{OCH}_3)_2$ , 28240-69-9;  $^{13}\text{C}$ , 14762-74-4.

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## Determination of the Magnitude of $^1J_{\text{Rh-Rh}}$ in Three Dirhodium Complexes

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Received February 14, 1978

We recently reported that the interaction of  $\text{CpRh}(\text{CO})_2$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) and  $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$  provides  $\text{Cp}_2\text{Rh}_2(\text{CO})_3$  (I) in good yield.<sup>1</sup> In the process of characterizing this compound, we noticed that the cyclopentadienyl  $^1\text{H}$  NMR resonance, when recorded under high-resolution conditions, exhibited "virtual" coupling, i.e., second-order effects for the  $\text{H}_3\text{RhRh}'\text{H}'_3$  spin system. Harris has discussed  $\text{X}_n\text{AA}'\text{X}'_n$  spin