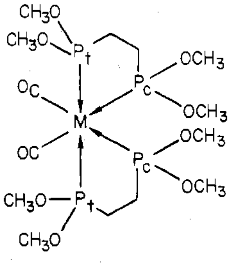
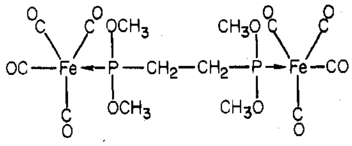
$H_2CH_2P(OCH_3)_2$ support the proposed formulation and exhibit "virtual coupling" patterns[16,17] indicative of significant phosphorus–phosphorus coupling for both the CH_3O (proton and carbon-13) and CH_2CH_2 (proton) resonances.

Ultraviolet irradiations of the metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, and W) with excess of the bidentate ligand $CH_3N(PF_2)_2$ result in complete displacement of all six carbonyl groups to give the corresponding carbonyl-free derivatives $[CH_3N(PF_2)_2]_3M$ (M = Cr, Mo, and W).[5,7] In our hands analogous ultraviolet irradiations of the metal hexacarbonyls with excess $(CH_3O)_2PCH_2CH_2P(OCH_3)_2$ were found to give the dicarbonyls $[(CH_3O)_2PCH_2CH_2P(OCH_3)_2]_2M(CO)_2$ (I: M = Cr, Mo, and W) as the most highly substituted products. The yields of these products I are maximized, however, if the ratio $(CH_3O)_2PCH_2CH_2P(OCH_3)_2/M(CO)_6$ is kept close to the stoichiometric 2/1.



I



II

The infrared spectra of the $[(CH_3O)_2PCH_2CH_2P(OCH_3)_2]_2M(CO)_2$ derivatives exhibit two ν(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 (M = W) the methoxy proton doublet corresponding to four methoxy groups has a significant center peak indicative of some virtual coupling between two phosphorus atoms.[16,17] 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 (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 (P_c in structure I).

The photochemical reaction of $(CH_3O)_2PCH_2CH_2P(OCH_3)_2$ with the hexacarbonyls $M(CO)_6$ (M = Cr, Mo, and W) to give *cis*-$[(CH_3O)_2PCH_2CH_2P(OCH_3)_2]_2M(CO)_2$ (I) derivatives must necessarily proceed through an intermediate *cis*-$[(CH_3O)_2PCH_2CH_2P(OCH_3)_2]M(CO)_4$. In the case of M = Mo this intermediate has been isolated from the ultraviolet irradiation of $(CH_3O)_2PCH_2CH_2P(OCH_3)_2$ with $Mo(CO)_6$ in a 1:1 mole ratio. The chromium analogue *cis*-$[(CH_3O)_2PCH_2CH_2P(OCH_3)_2]Cr(CO)_4$ has been prepared by an alternative but standard method: the displacement of coordinated norbornadiene from *nor*-$C_7H_8Cr(CO)_4$ with $(CH_3O)_2PCH_2CH_2P(OCH_3)_2$.

Some reactions of $(CH_3O)_2PCH_2CH_2P(OCH_3)_2$ with iron carbonyls have also been investigated. Treatment of $Fe(CO)_5$ with $(CH_3O)_2PCH_2CH_2P(OCH_3)_2$ in boiling xylene was found to lead to decomposition. However, reaction of $Fe_2(CO)_9$ with $(CH_3O)_2PCH_2CH_2P(OCH_3)_2$ at room temperature gives the binuclear complex $[(CH_3O)_2PCH_2CH_2P(OCH_3)_2][Fe(CO)_4]_2$ (II) in which the diphosphine functions as a biligate bimetallic ligand. The formation of II relates to the familiar easy dissociation of $Fe_2(CO)_9$ into the stable $Fe(CO)_5$ and the coordinately unsaturated $Fe(CO)_4$ fragment, which can complex with only one phosphorus atom to form the corresponding $R_3PFe(CO)_4$ derivative.

The reaction of $(CH_3O)_2PCH_2CH_2P(OCH_3)_2$ with $Co_2(CO)_8$ in diethyl ether results in rapid CO evolution, even below room temperature. Addition of NH_4PF_6 to the resulting product allows isolation of the $[(CH_3O)_2PCH_2CH_2P(OCH_3)_2]_2CoCO^+$ cation as its hexafluorophosphate salt. The formation of a $(diphos)_2CoCO^+$ cation in this reaction contrasts with the reactions of $Co_2(CO)_8$ with the more usual alkyl and aryl di(tertiary phosphines) $R_2PCH_2CH_2PR_2$ (R = alkyl or aryl) which lead only to $(diphos)Co(CO)_3^+$ derivatives.[3] This is another example of an increase in the π-acceptor strength of an organophosphorus ligand leading to an increased ability to replace carbonyl groups in metal carbonyls.[18]

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 $Cl_2PCH_2CH_2PCl_2$ required for this research.

Registry No. (Pom-Pom)$_2$Cr(CO)$_2$, 67328-83-0; (Pom-Pom)$_2$Mo(CO)$_2$, 67328-84-1; (Pom-Pom)$_2$W(CO)$_2$, 67328-85-2; (Pom-Pom)Cr(CO)$_4$, 67328-86-3; (Pom-Pom)Mo(CO)$_4$, 67328-87-4; (Pom-Pom)[Fe(CO)$_4$]$_2$, 67328-88-5; [(Pom-Pom)$_2$CoCO][PF$_6$], 67328-90-9; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $C_7H_8Cr(CO)_4$, 12146-36-0; $Fe_2(CO)_9$, 15321-51-4; $Co_2(CO)_8$, 10210-68-1; Pom-Pom, 67328-92-1; methanol, 67-56-1; $Cl_2PCH_2CH_2PCl_2$, 28240-69-9; ^{13}C, 14762-74-4.

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

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We recently reported that the interaction of $CpRh(CO)_2$ (Cp = η^5-C_5H_5) and $Me_3NO\cdot 2H_2O$ provides $Cp_2Rh_2(CO)_3$ (**1**) in good yield.[1] In the process of characterizing this compound, we noticed that the cyclopentadienyl ^1H NMR resonance, when recorded under high-resolution conditions, exhibited "virtual" coupling, i.e., second-order effects for the $H_5RhRh'H'_5$ spin system. Harris has discussed $X_nAA'X'_n$ spin

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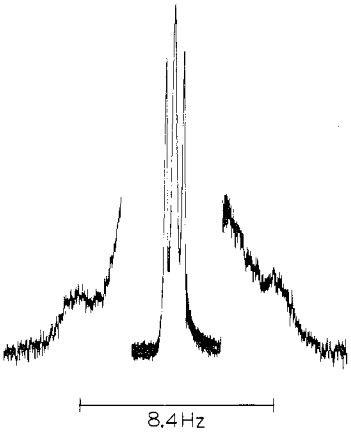

Figure 1. ^1H NMR spectrum of $Cp_2Rh_2(CO)_3$: high resolution, low rf amplitude, center; high rf amplitude, sides.

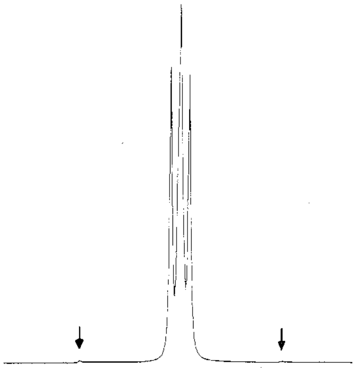

Figure 2. Simulated ^1H NMR spectrum of $Cp_2Rh_2(CO)_3$. Arrows mark the positions of low-probability transitions.

systems in detail.[2,3] In the X spectrum half of the total intensity is present in two lines separated by $N = |J_{AX} + J_{AX'}|$. When $|J_{AA'}| > L = |J_{AX} - J_{AX'}|$, the remaining intensity is largely concentrated near the center of the N doublet, resulting in a pseudotriplet pattern with a broader central peak. The values of N and L determine the relative signs of J_{AX} and $J_{AX'}$, but the sign of $J_{AA'}$ does not affect the spectrum. Simulation of the shape of the central feature provides one way of determining $|J_{AA'}|$, if L can be estimated. An alternative method is to locate the pairs of very weak lines separated by ca. $\pm|J_{AA'}|$ from the $2n$ lines constituting the center peak. Since these outer lines are due to nearly forbidden transitions, they do not saturate as readily as the relatively intense inner lines and hence may become observable at high rf levels. We have utilized both methods in tandem to determine $J_{AA'} = {}^1J_{Rh-Rh}$, together with $J_{AX} = {}^2J_{Rh-H}$ and $J_{AX'} = {}^3J_{Rh-H}$, for $Cp_2Rh_2(CO)_3$. For comparison the spectra of $Cp_2Rh_2(CO)_2CH_2$[4] (**2**) and $Cp_2Rh_2(NO)_2$ (**3**) also have been analyzed.

Experimental Section

^1H NMR spectra were recorded on a Varian HA-100 spectrometer, with an expanded scale (50 Hz) and careful attention to rf power levels, for $CDCl_3$ (10% TMS) solutions of $Cp_2Rh_2(CO)_3$ and $Cp_2Rh_2(NO)_2$ and a C_6H_6 (10% TMS) solution of $Cp_2Rh_2(CO)_2CH_2$. Peak positions were τ 4.50, 4.86, and 4.89, respectively. The experimental spectra were simulated by using the reported formulas[2] for the line positions and intensities in $X_nAA'X'_n$ spectra together with a Lorentzian curve plotting routine. ^{13}C NMR spectra were recorded on a Jeolco FX-60 spectrometer.

$Cp_2Rh_2(CO)_3$ was prepared as previously described,[1] and its IR and ^{13}C NMR spectra agree with data reported earlier.[5] $Cp_2Rh_2(CO)_2(CH_2)$ was prepared by the literature procedure.[4] $Cp_2Rh_2(NO)_2$ was isolated along with other products after treatment of $Rh_2(CO)_2Cl_2$ with nitric oxide and then cyclopentadienylthallium; it has been characterized by elemental analysis and mass spectroscopy and is probably isostructural with $Cp_2Co_2(NO)_2$.[6,7] Details of the synthesis and characterization of $Cp_2Rh_2(NO)_2$ and related products will be reported separately.[8]

Table I. Coupling Constants[a] Determined by Simulation of the Cyclopentadienyl Resonances

compd	$^1J_{Rh-Rh}$	$^2J_{Rh-H}$	$^3J_{Rh-H}$
$Cp_2Rh_2(CO)_3$	4.2	0.7	0.1
$Cp_2Rh_2(CO)_2(CH_2)$	4.4	0.5	0.1
$Cp_2Rh_2(NO)_2$	4.4	1.2	0.2

[a] Values in hertz.

Results and Discussion

The pseudotriplet cyclopentadienyl signal observed at low rf for **1** is shown in Figure 1 and similar patterns are seen for **2** and **3**. At high rf two peaks, displaced to either side of the main signal by ca. 4 Hz, become visible. These peaks saturate much less readily than the main pseudotriplet, and, with respect to the center of the triplet, their positions are symmetrical, reproducible (±0.1 Hz), and not dependent on sample spinning rate. Moreover, the values of $^1J_{Rh-Rh}$ indicated by the peak positions formed a good basis for simulation of the entire pseudotriplet pattern as shown in Figure 2. Initally, we assumed $^3J_{Rh-H} = 0$, i.e., $L = N = {}^2J_{Rh-H}$, but small nonzero values for $^3J_{Rh-H}$ gave closer fits. In these simulations the height of the central peak relative to the N doublet peaks proved to be quite sensitive to the assumed coupling constant values. Changing any one of the three values by even 0.1 Hz from the optimum produced a noticeably poorer fit between the calculated spectrum and the experimental spectrum. The best values determined for $^1J_{Rh-Rh}$, $^2J_{Rh-H}$, and $^3J_{Rh-H}$ in each case are given in Table I.

Values for $^1J_{Rh-Rh}$ have not been reported previously. However, the value of ca. 4 Hz determined in the present work is consistent with the lack of second-order effects in the carbonyl ^{13}C NMR spectrum of $Cp_2Rh_2(CO)_3$[5] or the ^{31}P NMR spectra of Rh_2L_8 ($L = PF_3$,[9] $P(OMe)_3$[10]), in which cases $^1J_{Rh-C}$ or $^1J_{Rh-P}$ is relatively large (83 and ca. 100–200 Hz, respectively). On the other hand $^1J_{Rh-C}$ is relatively small (<10 Hz) for the pairs of C_7H_8 ring carbons in $[Cp_2Rh_2(\mu\text{-}C_7H_8)H]^+$ so that the pseudotriplet ^{13}C NMR patterns observed[11] suggest a comparable value of $^1J_{Rh-Rh}$. Platinum is the only other transition metal for which homonuclear coupling has been observed, with values reported for $Pt_3(t\text{-}BuNC)_6$ (188 Hz),[12] $[Pt_9(CO)_{18}]^{2-}$, (822 Hz),[13] and $Pt_2(1,5\text{-}C_8H_{12})_2(\mu\text{-}(CF_3)_2CO)$ (5355 Hz).[14]

Coupling constants involving different nuclei are best compared in terms of reduced coupling constants $K_{XY} = (2\pi/\hbar\gamma_X\gamma_Y)J_{XY}$.[15] The dominant contribution to $^1K_{XY}$ usually is the Fermi contact term, which is predicted to be fairly large and positive for appreciable s-orbital involvement in the X–Y bond.[15,16] The spectral analysis performed here does not provide the sign of $^1J_{Rh-Rh}$, but the magnitude of $^1K_{Rh-Rh}$ calculated for compounds **1**–**3**, namely, $(3.5\text{–}3.7) \times 10^{22}\ cm^{-3}$, is comparable with values of $^1K_{Rh-C}$ for formally similar rhodium–carbon σ bonds. Thus, the reported values for $^1J_{Rh-C}$ in $CpRh(\eta^3\text{-}C_3H_5)(\eta^1\text{-}C_3H_5)$ (26 Hz)[18] and $Cp_2Rh_2(CO)(CPh_2)_2$ (23 Hz)[19] correspond respectively to $^1K_{Rh-C} = 2.7$ and $2.4 \times 10^{22}\ cm^{-3}$, and we have determined[17] $^1J_{Rh-C}$ for the bridging carbon in **2** to be 29 Hz, or $^1K_{Rh-C} = 3.0 \times 10^{22}\ cm^{-3}$. The signs of $^1K_{Rh-H}$ and $^1K_{Rh-P}$ have been shown to be positive, and the sign of $^1K_{Rh-C}$ for a σ bond is very likely positive also.[20]

These considerations indicate substantial s-orbital participation in the Rh–Rh bonds of compounds **1**–**3**. Of further interest is the fact that the values of $^1J_{Rh-Rh}$ are essentially the same, suggesting that the degree of s-orbital involvement is largely independent of the supplemental bridging group, among the three examined. This lack of variation contrasts with the large range in reported values for $^1J_{Pt-Pt}$ (see above), corresponding to a range for $^1K_{Pt-Pt}$ of $(3.4\text{–}96.6) \times 10^{22}\ cm^{-3}$.

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Registry No. **1**, 12318-88-6; **2**, 62154-28-3; **3**, 67426-08-8.

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(17) ^{13}C NMR of $Cp_2Rh_2(CO)_2CH_2$ ($CDCl_3$, ppm downfield from $SiMe_4$): 89.6 (C_5H_5, $^1J_{Rh-C}$ = ca. 2 Hz), 100.9 (CH_2, $^1J_{Rh-C}$ = 29 Hz, $^1J_{C-H}$ = 148 Hz). The methylene hydrogen atoms form a AA′XX′ spin system with the two rhodium atoms. This observation indicates that racemization of the chiral compound is slow at room temperature. Not enough lines of the spectrum could be resolved for a definitive analysis, but rough calculations indicate that a value of ca. 4 Hz for $^1J_{Rh-Rh}$ is consistent with the pattern observed ($|^2J_{Rh-H} + {}^2J_{Rh'-H}| = 1.65$ Hz).
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Cone Angle and Ligand Profile Calculations for Bulky Phosphine Ligands

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Various studies[1] showing that the chemistry of metal complexes of tertiary phosphines is markedly affected by the steric effects of the substituents on the phosphorus atom have prompted attempts by Tolman[2] and others[3] to gauge quantitatively the steric requirements of such ligands. On the basis of measurements made from CPK models[4] a ligand cone angle θ was defined[2] to express the bulk of a phosphine ligand. Obtaining maximum cone angles from x-ray data involves the calculation of maximum semicone angles, $\theta/2$ (Figure 1), for each organic moiety of the phosphine ligand from coordinates and van der Waals radii data.[5] A mean $\theta/2$ is then obtained leading to a maximum cone angle θ. Our calculations[6-10] have already shown that Tolman's predictions of θ from models are, for the most part, in good agreement with those actually found. It is also very clear that bulky phosphine ligands do not behave as regular solid cones but are better described as irregular conic cogs. To place these ideas on a quantitative basis we have developed the concept of a "ligand profile"[7] which not only yields precise maximum cone angle data but also provides quantitative information about the gaps between moieties in a ligand—the "depth of tooth" of the conic cog. Immirzi and Musco[11] have also attempted to gain information about the bulk of phosphine ligands by evaluating a solid angle Ω from which they obtain an estimate of what they call $\bar{\theta}$. The $\bar{\theta}$ values so obtained are invariably less than those estimated by Tolman, or calculated by us, and the more cog-like the ligand the greater is the discrepancy. The results of our calculations

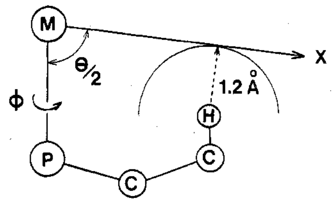

Figure 1. Details of the calculation of the maximum semicone angle, $\theta/2$. The point of contact of the cone-generating vector M → X from the metal, with the van der Waals sphere of the hydrogen atom, is coplanar with the metal, phosphorus, and hydrogen atoms.

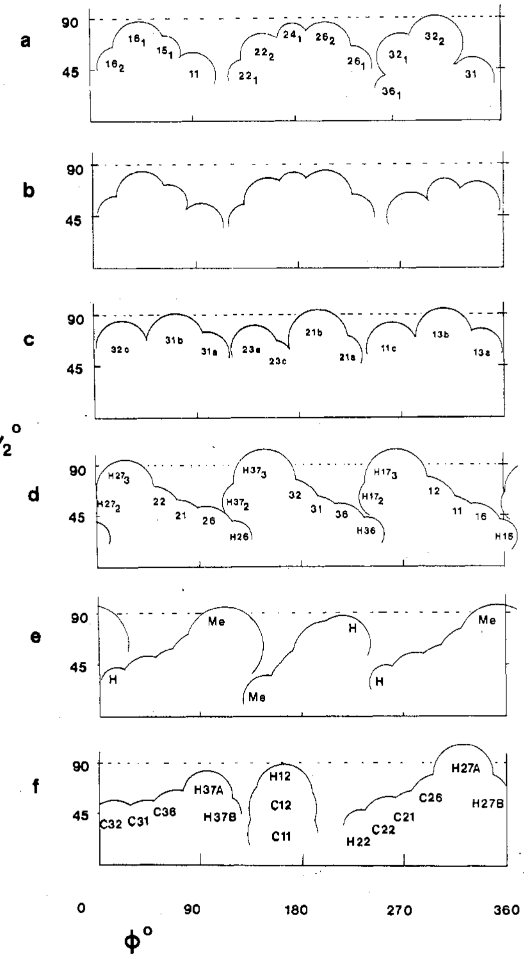

Figure 2. Ligand profiles for (a) Cy_3P in $Cy_3PHg(SCN)_2$; (b) Cy_3P in $(Cy_3P)_3Pt$; (c) t-Bu_3P in t-$Bu_3PHg(OAc)_2$; (d) (o-tol)$_3$P in $[(o\text{-tol})_3P)HgCl{\cdot}ClO_4]_2$; (e) ($o$-tol)$_3$P in $[(o\text{-tol})_3PHg(OAc)_2]_2$; (f) ($o$-tol)$_3$P in $((o\text{-tol})_3P)_2PtI_2$. The ordinate is the maximum semicone angle $\theta/2$. The abscissa is the angle ϕ through which the vector M → X (Figure 1) has been rotated about the M–P bond; the origin of ϕ was arbitrarily chosen. The numbers under some of the curves denote the hydrogen and carbon atoms (Figure 3), whose van der Waals spheres define the ligand profile. For (d), (e), and (f) both carbon and hydrogen atoms define the profile; for (a), (b), and (c) only hydrogen atoms are required.

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