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Contribution from the Department of Chemistry, City of London Polytechnic, London EC3N 2EY, England,
Department of Chemistry, University of Maryland, College Park, Maryland 20742,
and Technical Services Division, U.S. Customs Service, Washington, D.C. 20229

Multinuclear Magnetic Resonance Studies of Group 6 Metal Carbonyl Complexes of Unsymmetrical Bisphosphorus Ligands[1]

IAN J. COLQUHOUN,[2a] SAMUEL O. GRIM,*[2a,b] WILLIAM McFARLANE,[2a] J. DALE MITCHELL,[2c] and PATRICIA H. SMITH[2b]

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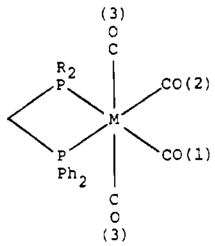
Carbon-13 nuclear magnetic resonance data are presented for the compounds $[Ph_2PCH_2PR^1R^2]M(CO)_4$, where $R^1 = R^2$ = *t*-Bu or *i*-Pr and R^1 = Ph and R^2 = *i*-Pr and M = Cr, Mo, or W, and $[Ph_2P(S)CH_2PR^1R^2]M(CO)_4$ where $R^1 = R^2$ = *i*-Pr or Ph and R^1 = *i*-Pr and R^2 = Ph and M = Cr, Mo, or W. Multiple resonance selective decoupling and spin-tickling experiments have been used to determine the signs of the carbonyl carbon-13 to phosphorus-31, phosphorus-31 to phosphorus-31, and phosphorus-31 to tungsten-183 coupling constants and have also been used to aid the chemical shift assignments of the carbonyl carbon-13 resonances. Carbon-13 data are also reported for many of the ligand carbons in these complexes.

Carbon-13 nuclear magnetic resonance (NMR) measurements are extremely useful in the study of metal carbonyls and in particular of metal carbonyl complexes of phosphorus ligands.[3-8] In the case of the group 6 metal carbonyls, well-documented generalities[9,10] have been established for the ^{13}C chemical shifts of the carbonyl groups and for the magnitudes of the corresponding two-bond phosphorus–carbon coupling constants in compounds with simple phosphorus donor ligands such as tertiary phosphines, triorganophosphites, and chelating ligands including bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe). Most of the cases reported so far have had relatively simple ^{13}C spectra for the carbonyl groups, being either of the type *trans*-$L_2M(CO)_4$ or *fac*-$L_3M(CO)_3$ (containing only one kind of CO group) or the type $LM(CO)_5$ or *cis*-$L_2M(CO)_4$ (containing two kinds of CO group). Exceptions are compounds such as $(dppm)M(CO)_4$ in which the equatorial carbonyl groups are part of an AA′X spin system (A, A′ = ^{31}P; X = ^{13}C) and can give a pseudo triplet ^{13}C resonance when $^2J_{PP'}$ is sufficiently large.



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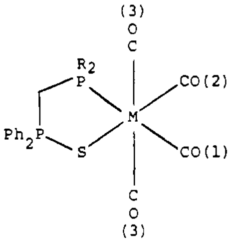

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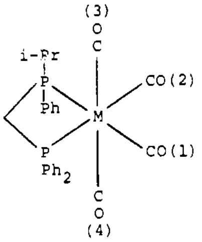

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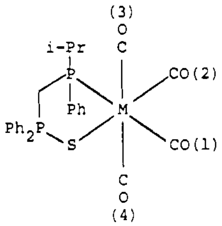

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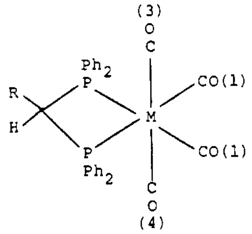

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However, for the compounds reported here, which contain unsymmetrical chelating phosphorus ligands, the ^{13}C NMR spectra of the carbonyl region are much more complicated. Thus complexes of the ligand $Ph_2PCH_2PR_2$ [R = *i*-Pr or *t*-Bu (Ia)] have nonequivalent equatorial and equivalent axial carbonyl groups, as do the complexes of $Ph_2P(S)CH_2PR_2$ [R = Ph or *i*-Pr (Ib)]. Complexes of $Ph_2PCH_2PPh(i\text{-}Pr)$ and $Ph_2P(S)CH_2PPh(i\text{-}Pr)$ on the other hand have four unique carbonyl groups (Ic and Id), and for the bis(tertiary phosphine) complex each carbonyl ^{13}C resonance is expected to be a doublet of doublets owing to coupling to two nonequivalent phosphorus nuclei provided that $\delta_{PP'}$ is large enough. Thus the entire carbonyl spectrum should consist of 16 lines, although accidental overlapping may reduce this number in any particular case, and the assignment of the coupling constants and chemical shifts is very difficult or impossible without recourse to the selective phosphorus decoupling experiments used here.

Experimental Section

The ligands and their complexes were prepared as described previously.[1,11,12] Proton-decoupled FT ^{13}C NMR spectra were recorded on a Varian FT 80 instrument at 20.1 MHz from samples (in 10-mm o.d. tubes) dissolved in CH_2Cl_2 with added $CDCl_3$ to provide an internal lock. A pulse width of 20 μs, corresponding approximately to a 90° pulse and a pulse delay of 10 s were used. Satisfactory signal-to-noise ratios were obtained from 5000 accumulations in most cases, although the sparingly soluble complex $[Ph_2P(S)CH_2PPh_2]W(CO)_4$ required 21 000 accumulations, corresponding to about $2^1/_2$ days.

$^{13}C\{^{31}P, {}^1H\}$ and $^{31}P\{^{183}W, {}^1H\}$ decoupling experiments were carried out on a JEOL FX-60 spectrometer at observing frequencies of 15.0

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* To whom correspondence should be addressed at the University of Maryland.

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Table I

^{13}C NMR Data for the Carbonyl Groups of $[Ph_2PCH_2P(R^1R^2)]M(CO)_4$[a]

M	R^1, R^2	CO(1) δ	CO(1) $J_{\mathrm{Ph_2P}}$[f]	CO(1) $J_{\mathrm{R^1R^2P}}$[g]	CO(2) δ	CO(2) $J_{\mathrm{Ph_2P}}$[g]	CO(2) $J_{\mathrm{R^1R^2P}}$[f]	CO(3) δ	CO(3) $J_{\mathrm{Ph_2P}}$[f]	CO(3) $J_{\mathrm{R^1R^2P}}$[f]	CO(4) δ	CO(4) $J_{\mathrm{Ph_2P}}$[f]	CO(4) $J_{\mathrm{R^1R^2P}}$[f]
Cr	$(t\text{-Bu})_2$	17.8	(–)8.1	(–)4.7	17.8	(–)5.4	(–)8.8	13.9	–13.7	–10.6			
Cr	$(i\text{-Pr})_2$	17.7	–14.4	–5.2	17.9	–5.2	–14.0	11.8	–12.7	–12.7			
Cr	Ph, *i*-Pr	17.5	–14.1	–5.2	18.3	–5.5	–13.9	11.3	–12.8	–12.8	10.2	–13.3	–13.3
Cr	Ph_2	17.8	*b*								10.5	(–)12.8	
Mo	$(t\text{-Bu})_2$	18.6	–9.3	+25.9	18.1	+24.9	–9.8	13.0	–8.8	–7.4			
Mo	$(i\text{-Pr})_2$	18.3	–9.8	+22.6	18.5	+24.9	–9.3	11.3	–8.6	–8.6			
Mo	Ph, *i*-Pr	18.0	(–)10.1	(+)24.1	18.7	(+)24.8	(–)9.6	10.8	(–)8.7	(–)8.7	9.5	(–)8.5	(–)8.5
Mo	Ph_2	18.1	*c*								9.7	(–)8.6	
W	$(t\text{-Bu})_2$	18.7	–7.9	+23.2	19.4	+23.8	–8.4	15.1	–6.9	–5.9			
W	$(i\text{-Pr})_2$	18.9	–8.3	+21.5	19.1	+23.2	–7.9	12.6	–6.9	–6.9			
W	Ph, *i*-Pr	18.9	–8.2	+22.1	19.5	+22.5	–7.8	12.3	–7.1	–7.1	11.0	–6.6	–6.6
W	Ph_2	19.0	*d*								11.5	(–)6.6	

^{13}C NMR Data for the Carbonyl Groups of $[Ph_2P(S)CH_2PR^1R^2]M(CO)_4$[a]

M	R^1, R^2	CO(1) δ	CO(1) $^3J_{\mathrm{PS}}$[f]	CO(1) $^2J_{\mathrm{P}}$[g]	CO(2) δ	CO(2) $^3J_{\mathrm{PS}}$[g]	CO(2) $^2J_{\mathrm{P}}$[f]	CO(3) δ	CO(3) $^3J_{\mathrm{PS}}$[f]	CO(3) $^2J_{\mathrm{P}}$[f]	CO(4) δ	CO(4) $^3J_{\mathrm{PS}}$[f]	CO(4) $^2J_{\mathrm{P}}$[f]
Cr	$(i\text{-Pr})_2$	16.1	+11.2	+1.8	17.6	0	(–)12.2	8.7	+2.0	–13.2			
Cr	Ph, *i*-Pr	16.1	(+)13.1	1.4	17.9	0	(–)12.0	8.4	0	(–)12.8	7.0	0	(–)14.1
Cr	Ph_2	16.4	(+)11.5	1.2	17.0	0	(–)12.3				7.9	0	(–)12.6
Mo	$(i\text{-Pr})_2$	15.3	+9.6	+31.7	17.8	0	(–)8.2	8.5	+1.2	–8.7			
Mo	Ph, *i*-Pr	15.2	(+)10.0	(+)32.6	17.8	0	(–)8.7	8.2	0	(–)9.6	7.0	0	(–)9.0
Mo	Ph_2		*e*			*e*					7.5	0	(–)9.1
W	$(i\text{-Pr})_2$	16.9	+9.8	+31.6	16.4	0	(–)4.4	11.8	+2.1	–6.7			
W	Ph, *i*-Pr	16.8	(+)10.6	(+)10.6	16.5	0	(–)6.1	11.6	0	(–)6.9	10.4	1.2	(–)7.8
W	Ph_2	17.5	(+)10.3	(+)10.3	15.9	0	(–)5.5				11.5	1.1	(–)6.4

[a] Chemical shifts are in ppm (±0.1 ppm) to high frequency of $M(CO)_6$, whose shifts relative to tetramethylsilane are[10] 211.3, 200.8, and 191.4 ppm for M = Cr, Mo, and W, respectively. Coupling constants are in Hz (±0.2 Hz). Parentheses indicate that the sign of a coupling constant has been obtained by analogy with a similar compound; the absence of parentheses indicates that the sign was determined experimentally by double resonance and/or spectral analysis. [b] $J(\mathrm{cis}) + J(\mathrm{trans}) = 9.6$ Hz. [c] $J(\mathrm{cis}) + J(\mathrm{trans}) = 15.3$ Hz. [d] $J(\mathrm{cis}) + J(\mathrm{trans}) = 11.6$ Hz. [e] Poor solubility and impurity peaks prevented reliable determination of these parameters. [f] Cis. [g] Trans.

and 24.2 MHz, respectively. The carbon–phosphorus double resonance experiments were performed by applying the phosphorus frequency to the proton-decoupling coil as described previously.[13] An extra coil tuned to the ^{183}W resonance frequency (2.48 MHz, $I = {}^1/_2$, abundance = 14.3%) was wound in the probe for the phosphorus–tungsten experiments. The ^{31}P and ^{183}W irradiating frequencies were provided by a Gen Rad 1061 frequency synthesizer. For the ^{13}C experiments all samples were ca. 0.07 M in $Cr(acac)_3$ to permit a pulse repetition interval of 1 s for observation of the carbonyl resonances.

Resonance peaks are described in the Discussion as being at high or low frequency relative to other resonances. High-frequency, low-field, or "deshielded" chemical shifts all have the same sense; i.e., in the usual convention they are to the left side of the spectrum. Low-frequency, high-field, and "shielded" chemical shifts have the opposite sense.

All the compounds examined had first-order or very nearly first-order AX-type proton-decoupled ^{31}P spectra. ^{13}C spectra were simplified for the purposes of assignment by (a) complete phosphorus decoupling, effected by frequency modulation of the phosphorus rf carrier frequency $[{}^1/_2(\nu_P + \nu_{P'})]$ with an audio frequency equal to ${}^1/_2(\nu_P - \nu_{P'})$, and (b) removal of coupling to either P or P′ by irradiation at ν_P or $\nu_{P'}$. Figure 1 illustrates these experiments, showing the carbonyl region of the ^{13}C spectrum of $[Ph_2PCH_2(i\text{-}Pr)_2]Cr(CO)_4$. From these decoupling experiments the chemical shift of each carbon and the associated couplings to phosphorus were readily determined. In order to assign the equatorial carbonyl groups as cis or trans to the diphenylphosphino group, it was necessary to compare the observed coupling constants with those already found[9,10] in $LM(CO)_5$ complexes for which no ambiguity of interpretation arises.

Sign determinations were done by selective decoupling experiments with the irradiation frequency set to, e.g., $\nu_P + {}^1/_2J_{PP'}$ ($\gamma B_2/2\pi$ was about 10 Hz, although this varied, depending upon the magnitude of $J_{PP'}$). Note that this frequency does not correspond to an actual transition but to the midpoint of a doublet since it is the ^{13}C satellites in the ^{31}P spectrum which must be considered. The effect of this irradiation was to sharpen *half* of the lines of the decoupled spectrum produced by high-power ($\gamma B_2/2\pi \approx 50$ Hz) irradiation at ν_P. This type of experiment gave the sign of $J_{CP'}$, relative to that of $J_{PP'}$. The sign of $J_{PP'}$ in the tungsten series of compounds was determined relative to that of $^1J_{WP}$ (which is known to be positive[14]) by means of $^{31}P\{^{183}W, {}^1H\}$ experiments. Spin-tickling experiments[15] were used in the case of the $[Ph_2PCH_2PR_2]W(CO)_4$ compounds, but selective decoupling was used for the $[Ph_2P(S)CH_2PR_2]W(CO)_4$ series since $^2J_{PW}$ was small (<10 Hz). It is not permissible, however, to assume that the sign of $^2J_{PMP'}$ for the Cr and Mo complexes, is the same as that in the W complexes. Indeed it is known that sign changes do occur.[16] In the $[Ph_2PCH_2PR_2]M(CO)_4$ series it was observed that C(1) of the aromatic group was coupled in all cases to both phosphorus nuclei, thus permitting sign determinations relative to $J_{PP'}$. In addition it was found that the magnitudes of the two couplings remained almost invariant in all the compounds ($^1J_{PC}$ = ca. 25–30 Hz, $^3J_{P'C}$ = ca. 8 Hz). The odds were against any sign change occurring here, so the sign of $^1J_{PC}$ was determined relative to that of $J_{PP'}$ (already known from the $^{31}P\{^{183}W\}$ experiments) for the tungsten compounds. $^{13}C\{^{31}P\}$ selective decoupling experiments were then performed on the Cr and the Mo complexes, and the sign of $J_{PP'}$ was determined relative to that of $^1J_{PC}$ (now taken to be positive, from results on the W complexes). For all three ligands it was found that $^2J_{PMP'}$ was negative for M = Cr and positive for M = Mo or W.

In the $[Ph_2P(S)CH_2PR_2]M(CO)_4$ series $J_{PP'}$ had similar magnitude (ca. 70 Hz) throughout, irrespective of M. $^{31}P\{^{183}W\}$ selective decoupling experiments showed this to be positive for the tungsten compounds, and $^{13}C\{^{31}P\}$ work showed that $J_{PP'}$ had the same sign as $^1J_{CP(S)}$ in the Mo and Cr compounds and is therefore again positive.

Results and Discussion

The carbon-13 NMR results for the carbonyl groups are given in Table I. For the $[Ph_2PCH_2P(t\text{-}Bu)_2]M(CO)_4$ and

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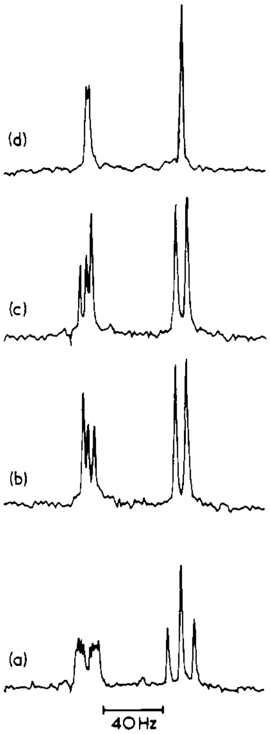

Figure 1. Carbon-13 spectra at 15.0 MHz of the carbonyl groups of $[Ph_2PCH_2P(i\text{-}Pr)_2]Cr(CO)_4$: (a) normal spectrum; (b) spectrum with selective decoupling of the $(i\text{-}Pr)_2P$ group by irradiation at $\delta_{^{31}P}$ 43.1; (c) spectrum with selective decoupling of the Ph_2P group by irradiation at $\delta_{^{31}P}$ 24.9; (d) spectrum with simultaneous decoupling of the $(i\text{-}Pr)_2P$ and Ph_2P groups by irradiation at $\delta_{^{31}P}$ 43.1 and 24.9.

$[Ph_2PCH_2P(i\text{-}Pr_2)]M(CO)_4$ compounds, the CO region generally consists of eight lines of equal intensity at high frequency due to the nonequivalent equatorial carbonyls (1 and 2 of Ia) and four lines of equal intensity at lower frequency due to the equivalent axial carbonyls. In the case of $[Ph_2PCH_2P(t\text{-}Bu)_2]Cr(CO)_4$ the equatorial CO's have the same chemical shift so the number of lines is correspondingly reduced. This was clearly shown by simultaneous double irradiation at both phosphorus frequencies in the compound. This collapsed the CO resonances to two peaks, one in the axial and one in the equatorial region of the spectrum. The width at half-height of the equatorial CO peak (1.7 Hz) was only marginally larger than that of the axial CO peak (1.3 Hz), confirming the very near coincidence of the two equatorial CO resonances. The $[Ph_2PCH_2P(i\text{-}Pr)_2]M(CO)_4$ compounds generally exhibit the same pattern as the *t*-Bu compounds in the equatorial CO region, but the axial CO region is a 1:2:1 triplet due to identical or nearly identical coupling constants between each phosphino group and the axial carbons. The equatorial CO region of the spectra of $[Ph_2PCH_2PPh(i\text{-}Pr)]M(CO)_4$ is again composed of eight lines of approximately equal intensity, and the axial CO region, which now represents nonequivalent CO's, is a pair of 1:2:1 triplets, since each CO fortuitously has couplings of equal magnitude to the different phosphorus nuclei. For the $[Ph_2P(S)CH_2P(i\text{-}Pr)_2]M(CO)_4$ complexes, the axial region of the CO spectrum is a doublet of doublets. The equatorial CO region appears as six lines with intensities of 1:1:1:1:2:2, except in the W case where some of these lines are superimposed. The axial CO spectral region of $[Ph_2P(S)CH_2PPh(i\text{-}Pr)]M(CO)_4$ is likewise a doublet of doublets, and the equatorial CO's exhibit a pattern much like the $[Ph_2P(S)CH_2P(i\text{-}Pr)_2M(CO)_4$ compounds. $[Ph_2P(S)CH_2PPh_2]Cr(CO)_4$ displays a doublet in the axial ^{13}CO region and a triplet (with slight additional splitting of two of the lines) in the equatorial region. The ^{13}CO NMR spectrum of $[Ph_2P(S)CH_2PPh_2]W(CO)_4$ is similar to the spectra of the other phosphine–phosphine sulfide metal carbonyl derivatives reported above. $[Ph_2P(S)CH_2Ph_2]Mo(CO)_4$ decomposed somewhat in solution during acquistion of the spectrum, and the equatorial region of the spectrum was not decipherable, but the axial region was a doublet of doublets.

The ^{13}C chemical shifts of carbonyl groups in metal carbonyl derivatives generally occur at higher frequency as the electron density on the metal increases.[3] Thus, since most ligands, and in particular phosphorus ligands, have a larger σ-donor/π-acceptor ratio than carbon monoxide, the ^{13}C chemical shifts in substituted metal carbonyls will be at higher frequency than in the corresponding unsubstituted metal carbonyls. Furthermore, with octahedral stereochemistry, in the group 6 metal carbonyls and their derivatives, the CO's trans to phosphorus are always shifted to higher frequency than the CO's cis to phosphorus.[9,10] These generalities are also applicable to this work, and for convenience, the ^{13}C chemical shifts listed in Table I for the carbonyl groups are given in ppm relative to those in the corresponding unsubstituted metal carbonyls. These are 211.3, 200.8, and 191.4 ppm from tetramethylsilane (Me_4Si), for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$, respectively. In addition, the following observations can be made.

(a) In the $Ph_2PCH_2PR^1R^2$ derivatives, the chemical shift of CO(2), trans to the diphenylphosphino groups, is marginally shifted to higher frequency relative to that of CO(1) which is trans to the isopropylphenylphosphino or dialkylphosphino group, except in the case of $[Ph_2PCH_2P(t\text{-}Bu)_2]Cr(CO)_4$, for which the CO(1) and CO(2) resonances are coincident, and in the case of $[Ph_2PCH_2P(t\text{-}Bu)_2]Mo(CO)_4$, for which the CO(1) and CO(2) resonances are reversed. However, because of small differences (<1 ppm) in these chemical shifts and because of a significant steric effect which large groups on phosphorus cause in the chemical shifts of CO's cis to that phosphorus (vide infra), it is probably inappropriate to attempt to explain these differences on the basis of σ-donor/π-acceptor properties of the separate phosphino groups.

(b) The chemical shifts of the axial CO groups, e.g., CO(3) in Ia, increase in frequency in the order $Ph_2PCH_2PPh_2$ < $Ph_2PCH_2P(i\text{-}Pr)_2$ < $Ph_2PCH_2P(t\text{-}Bu)_2$ with the difference between the *i*-Pr and *t*-Bu compounds being remarkably large, about 2 ppm for each series of Cr, Mo, and W complexes. We ascribe this to a 1,2-cis steric influence in the four-membered chelate ring, in the expected steric order of *t*-Bu > *i*-Pr > Ph. It should be noted that a bulky group attached to the methylene carbon of bis(diphenylphosphino)methane (R is, for example, neopentyl or diphenylphosphino in Ie) causes a similar large shift to higher frequency for CO(3).[17] This would be a 1,3-cis interaction in the four-membered chelate ring, but its effect on the chemical shift of CO(3) is in the same direction as that caused by the 1,2-cis interaction. The chemical shift assignments of the axial CO's (3 and 4) of compounds represented by Ic cannot be made with absolute certainty, but the trends indicated by the 1,2-cis interaction discussed above allow tentative assignments for these CO's. For example, the two unique axial CO's in $[Ph_2PCH_2PPh(i\text{-}Pr)]Cr(CO)_4$ have ^{13}C chemical shifts of 11.3 and 10.2 ppm from those in $Cr(CO)_6$, whereas the axial CO chemical shift in $[Ph_2PCH_2P(i\text{-}Pr)_2]Cr(CO)_4$ is 11.8 ppm and that in $[Ph_2PCH_2PPh_2]Cr(CO)_4$ is 10.5 ppm. Since the steric environment of CO(3) in the $[Ph_2PCH_2PPh(i\text{-}Pr)]Cr(CO)_4$ compound (Ic) is similar to CO(3) in $[Ph_2PCH_2P(i\text{-}Pr)_2]Cr(CO)_4$ (Ia), i.e., cis to one isopropyl group and one phenyl group, and since CO(4) in $[Ph_2PCH_2PPh(i\text{-}Pr)]Cr(CO)_4$ is in a similar environment to the axial CO's in $[Ph_2PCH_2PPh_2]Cr(CO)_4$, i.e., cis to two phenyl groups, CO(3) and CO(4) in Ic for the chromium

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Table II. ^{13}C NMR Data for the Ligand Resonances of $[Ph_2PCH_2P(R^1R^2)]M(CO)_4$[a]

		C(1)			C(o)		C(m)		C(p)		C(B)			C(α)			C(β)	
M	R^1, R^2	δ	J_1[b]	J_2[b]	δ	J_1	δ	J_1	δ	J_1	δ	J_1	J_2	δ	J_1	J_2	δ	J_2
Cr	$(t\text{-Bu})_2$	137.0	+25.0	+8.2	130.4	12.8	128.5	9.8	129.6	1	34.8	17.1	+8.6	35.6	7.3	+1.8	29.1	5.5
Mo	$(t\text{-Bu})_2$	136.8	+25.6	+7.9	130.9	14.6	128.6	9.8	129.8	1	36.2	+20.1	+9.2	34.2	+7.3	+3.1	29.1	6.7
W	$(t\text{-Bu})_2$	135.8	+30.8	+8.2	130.7	14.1	128.5	9.8	129.9	1	38.7	+23.8	+13.4	34.6	+7.3	+7.3	29.0	5.8
Cr	$(i\text{-Pr})_2$	136.8	+25.4	+7.8	130.7	12.7	128.6	9.8	129.9	1	38.9	+18.6	+13.7	27.9	+7.8	+10.7	18.5 18.2	3.9 1.5 [d]
Mo	$(i\text{-Pr})_2$	136.5	+25.6	+8.5	131.2	14.6	128.6	9.8	130.0	1	39.7	+20.8	+13.4	27.1	+7.3	+12.2	18.7 18.6	8.5 <1 [d]
W	$(i\text{-Pr})_2$	135.8	+30.5	+8.5	131.0	14.9	128.6	10.4	130.2	1	42.5	+25.6	+18.3	27.5	+8.5	+14.6	18.7 18.7	6.1 <1 [d]
Cr	Ph, *i*-Pr[c]										42.7	17.8	16.1	32.6	6.6	14.2	17.3 16.8	6.8 4.8 [d]
Mo	Ph, *i*-Pr[c]										43.7	19.1	16.9	32.2	7.2	14.4	17.8 17.0	8.0 0 [d]
W	Ph, *i*-Pr[c]										46.8	23.9	21.5	32.6	7.8	18.1	17.9 17.0	7.0 0 [d]

[a] Chemical shifts are in ppm (±0.1 ppm) to high frequency of tetramethylsilane. Coupling constants are in Hz (±0.2 Hz). [b] J_1 refers to J_{Ph_2P-C} and J_2 refers to $J_{R^1R^2P-C}$. [c] Where there is no entry the three phenyl groups are all different in these complexes, and it was not possible to make individual assignments. [d] Chirality or prochirality at phosphorus leads to anisochronicity of the methyl resonances of the isopropyl groups.

compound are assigned ^{13}C chemical shifts of 11.3 and 10.2 ppm, respectively. Similar reasoning was used to make the tentative chemical shift assignment for the axial CO's in the molybdenum and tungsten compounds of $Ph_2PCH_2PPh(i\text{-}Pr)$ and also in the phosphine sulfide compounds $[Ph_2P(S)CH_2PPh(i\text{-}Pr)]M(CO)_4$, where M is Cr, Mo, or W (Id).

In general, the ^{13}C nuclei of the CO's in the group 6 metal carbonyl derivatives of the phosphine–phosphine sulfide ligands are not as deshielded as those of the corresponding complexes of bis(tertiary phosphine) chelating ligands. According to previous observations and discussion,[3,9,10] this implies that the metal carries less electronic charge in the case of the sulfide ligands compared to the phosphine ligands and that the phosphine–phosphine-sulfide ligands have therefore a lower σ-donor/π-acceptor bonding ability than the bis(tertiary phosphines). The chemical shifts of the equatorial CO's, CO(1) and CO(2) in Ib and Id, in the molybdenum complexes seem unusual compared to those in the Cr and W analogues. Specifically, CO(2) which is trans to S occurs at considerably higher frequency than CO(1) which is trans to P in the Mo compounds, but this order is opposite in the W compounds, and the difference is not as pronounced as in the Cr compounds. If the trans influence is a predominant factor in the CO chemical shift, this would imply that the σ-donor/π-acceptor ratio for a phosphine sulfide is smaller than that of a phosphine when bonded to molybdenum, but the opposite is observed for tungsten.

Phosphorus-31–carbon-13 coupling constants for the carbonyl groups of $[Ph_2PCH_2P(R^1R^2)]M(CO)_4$ are given in Table IA in which experimentally determined absolute signs of the cis and trans coupling $^2J_{PMC}$ are presented for the first time. The results bear out predictions,[9,10,18] made on the basis of the correspondence which was apparent between the *magnitudes* of $^2J_{PMC}$ and $^2J_{PMP}$, sign information being available[16] for the latter coupling constant only. It is now found that cis $^2J_{PMC}$ is negative for M = Cr, Mo, and W but trans $^2J_{PMC}$ is negative only for M = Cr, being positive for M = Mo and W. This pattern of signs is identical with that found[16] for $^2J_{PMP}$ in $(R_3P)_2M(CO)_4$ complexes. It is believed that changes in the mutual polarizability of the ligand lone-pair orbitals are responsible for these sign variations,[16,19,20] but theoretical prediction of the sign in specific cases is not yet possible.

Phosphorus–phosphorus coupling constants for the $[Ph_2PCH_2P(R^1R^2)]M(CO)_4$ series of compounds are presented in Table IVA. Signs are given for this coupling in a complete series (Cr, Mo, W) containing the four-membered chelate ring. The only previous sign determination[21] of this type was for the molybdenum complex $EtN(PF_2)_2Mo(CO)_4$ in which J_{PP} is +120 Hz. In the present series $^2J_{PMP'}$ is found to be positive for the Mo and W complexes, and negative for M = Cr. I.e., in comparison with the *cis*-$(R_3P)_2M(CO)_4$ series there has been a sign change in the cases of M = Mo and (vide supra). Two of us have proposed[22] a straightforward approach to the question of J_{PP} values in complexes of chelating ligands in which the total coupling constant is divided into two contributions, one ($J_{PP'}{}^M$) transmitted via the metal center and the other ($J_{PP'}{}^B$) via the ligand backbone. By analogy with the nonchelated *cis*-$(R_3P)_2M(CO)_4$ compounds $J_{PP'}{}^M$ may be taken to be negative,[16] and since the total coupling $J_{PP'}$ is always algebraically more positive in the chelates, it follows that $J_{PP'}{}^B$ itself must be positive. In the Mo and W compounds this coupling is numerically larger than $J_{PP'}{}^M$, but not in the Cr derivatives. In support of this view it may be noted that for the *cis*-$(Me_3P)_2M(CO)_4$ series the *magnitude* of $^2J_{PMP}$ follows[16] the order Cr > Mo > W. This positive contribution $J_{PP'}{}^B$ is interesting in that $^2J_{PCP}$ in compounds where both phosphorus atoms are quadruply connected is generally small and negative,[23] e.g., 17.3 Hz in $[Ph_2P(Se)]_2CH_2$. The differnce could arise from the fact that rotation about the P–C bond is not possible in the chelate compound or from the serious distortion of the P–C–P angle from the tetrahedral value necessitated by the geometry of the four membered ring.

The signs and magnitudes of $^2J_{PMC}$ and $^3J_{PSMC}$ in the complexes derived from the bis(phosphine) monosulfides are also given in Table IB. In all cases the trans coupling $^2J_{PMC}$ involving the coordinated phosphino group is some 5–10 Hz more positive than the corresponding coupling in the diphosphine complexes themselves. This may reflect the reduction of strain achieved by having a five-membered ring. The various cis $^2J_{PMC}$ couplings are very similar in the two kinds of complex. The three bond couplings $^3J_{P(S)MC}$ are generally close to zero

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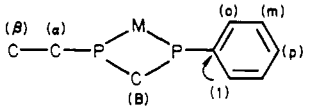
Table III. ^{13}C NMR Data for the Ligand Resonances of $[Ph_2P(S)CH_2P(R^1R^2)]M(CO)_4$[a]

	C(1)			C(o)		C(m)		C(p)		C(B)			C(α)			C(β)	
	δ	J_P	J_{PS}	δ	J	δ	J	δ	J	δ	J_P	J_{PS}	δ	J_P	J_{PS}	δ	J
$Ph_2P(S)CH_2P(i\text{-}Pr)_2$				131.7	9.9	128.6	12.2	131.4	<2	27.1	−36.6	+57.4	24.2	−14.6	+8.6	19.3	*b*
Cr complex	129.2	2.6	79.3	131.4	9.9	129.2	12.2	132.8	2.8	29.6	<1	(+)63.6	28.7	(+)14.8	(+)4.6	19.1	*b*
Mo complex	128.4	5.2	77.3	131.4	9.8	129.2	12.1	132.9	2.8	28.0	1.8	(+)62.1	28.1	(+)14.4	(+)4.8	19.2	*b*
W complex	128.2	3	79.4	131.8	9.8	128.6	12.2	133.3	2.5	28.4	+6.1	+63.4	29.2	+18.9	+4.3	19.3	*b*
$Ph_2P(S)CH_2P(i\text{-}Pr)Ph$	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	31.5	(−)33.5	(+)55.1	27.5	(−)11.7	(+)9.8	19.4	*b*
Cr complex	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*d*	*d*	*d*				18.0	*b*
Mo complex	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	31.4	ca. 4	61.5	32.5	18.0	ca. 5	18.2	*b*
W complex	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	32.1	8.5	62.9	33.2	22.7	4.3	18.2	*b*
$Ph_2P(S)CH_2PPh_2$	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	35.1	(−)31.9	(+)54.4					
Cr complex	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	37.5	4.9	(+)61.2					
Mo complex	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	35.7	6.0	62.8					
W complex	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*	36.6	9.6	63.5					

[a] Chemical shifts are in ppm (±0.1 ppm) to high frequency of tetramethylsilane. Coupling constants are in Hz (±0.2 Hz). [b] These carbons are diastereotopic, and full analysis was not possible. [c] The presence of several types of phenyl group produced much overlapping and prevented full analysis. [d] This region of the spectrum was complex and contained impurity lines.

with the exception of those to CO(1) for which there is a planar "Z-path" relationship between the coupled nuclei. That is, the phosphorus nucleus and the coupled CO group are mutually trans with respect to rotation about the S–M bond (even though the SMC configuration is cis), suggesting an angular dependence, perhaps of the Karplus type,[24] for this coupling. The values of $^3J_{PP'}$ in the bis(phosphine) monosulfide complexes given in Table IVB differ only slightly from those in the free ligands and are clearly sensitive to minor conformational changes brought about by differences in the phosphorus substituents. It seems likely that $^3J_{PP'}{}^M$ is considerably smaller than $^2J_{PP'}{}^B$ which therefore dominates the observed coupling constant.

^{13}C NMR data for the ligand resonances (labeling scheme given below) for $[Ph_2PCH_2PR^1R^2]M(CO)_4$, where R^1R^2 is *t*-Bu$_2$, *i*-Pr$_2$, or *i*-PrPh and M is Cr, Mo, and W are given in Table II. The labeling scheme is given by



. The chemical shifts of the carbons of the phenyl groups are in good agreement with those of the dppm and dppe complexes of the group 6 metal carbonyls reported earlier.[9] The chemical shift of the ligand backbone methylene carbon moves to higher frequency in the order Cr < Mo < W for each of the three series of $[Ph_2PCH_2PR^1R^2]M(CO)_4$ compounds examined. For C(1) of the phenyl groups the signs (both positive) and magnitude of $^1J_{PC}$ and $^3J_{PC}$ have been determined. Likewise, the signs (again both positive) and magnitudes have been determined of the two one-bond P–CH_2 couplings for the ligand backbone carbon. In each case the coupling constant for the diphenylphosphino group is larger than that of the R^1R^2P group and the discrepancy is largest when the R^1R^2 groups are bulkiest.

Table III gives the ^{13}C NMR data for the methylene carbons of the $Ph_2P(S)CH_2PR^1R^2$, where R^1R^2 is *i*-Pr$_2$, Ph(*i*-Pr), or Ph$_2$ and their complexes. It is interesting to note, that unlike the situation just discussed for the bis(tertiary phosphine) complexes, the chemical shift of the methylene carbon is least in all the molybdenum complexes, although in all cases the chemical shift of the free ligand methylene is to lower frequency relative to those in the complexes. Other peculiarities of the molybdenum complexes of the phosphine–phosphine sulfide ligands have been noted, viz.: (a) they seem to decompose more readily than their chromium and tungsten analogues when in solution;[11] (b) the ^{31}P coordination shift of the thiophosphoryl group is the least (compared to Cr and W) for the Mo case;[1,11] (c) the high-frequency shift of ^{13}CO (relative to the uncomplexed metal carbonyl) of CO(1) (Ib and Id) in the Mo complexes is considerably less then expected relative to the Cr and W complexes (vide supra).

Table IV

^{31}P NMR Data for $[Ph_2PCH_2P(R^1R^2)]M(CO)_4$

M	R^1R^2	δ_{Ph_2P}[a]	$\delta_{PR^1R^2}$[a]	J_{PP}[b]
Cr	(*t*-Bu)$_2$	26.6	61.5	−12.5
Cr	(*i*-Pr)$_2$	24.9	43.1	−20.8
Cr	Ph, *i*-Pr	26.1	34.7	−17.4
Cr	Ph$_2$	25.4		
Mo	(*t*-Bu)$_2$	2.8	43.0	+22.8
Mo	(*i*-Pr)$_2$	1.9	23.9	+15.3
Mo	Ph, *i*-Pr	1.6	12.2	+19.7
Mo	Ph$_2$	0.0		
W	(*t*-Bu)$_2$	−22.0	23.6	+25.6
W	(*i*-Pr)$_2$	−23.6	1.4	+20.8
W	Ph, *i*-Pr	−24.0	−11.6	+25.2
W	Ph$_2$	−23.6		

^{31}P NMR Data for $[Ph_2P(S)CH_2P(R^1R^2)]M(CO)_4$ and Ligands

M	R^1R^2	$\delta_{Ph_2P(S)}$[a]	$\delta_{PR^1R^2}$[a]	J_{PP}[b]
Cr	(*i*-Pr)$_2$	57.9	82.3	+69.9
Cr	Ph, *i*-Pr	57.2	68.7	(+)77
Cr	Ph$_2$	57.5	63.9	(+)83
Mo	(*i*-Pr)$_2$	55.5	60.5	+64.5
Mo	Ph, *i*-Pr	55.3	45.7	(+)70
Mo	Ph$_2$	55.5	37.9	(+)78
W	(*i*-Pr)$_2$	60.4	49.0	+62.0
W	Ph, *i*-Pr	59.8	32.9	+68.8
W	Ph$_2$	59.7	25.3	+75.7
	(*i*-Pr)$_2$	41.8	−9.2	+76.9
	Ph, *i*-Pr	40.5	−19.3	(+)71
	Ph$_2$	40.1	−28.0	+76

[a] In ppm (±0.1 ppm) to high frequency of 85% H_3PO_4. [b] In Hz (±0.2 Hz). For derivation of signs see text.

All these observations seem to be internally consistent and probably indicate a lower stability of the tertiary phosphine–phosphine sulfide complexes of molybdenum.

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Registry No. $[Ph_2PCH_2P(t\text{-}Bu)_2]Cr(CO)_4$, 74525-14-7; $[Ph_2PCH_2P(i\text{-}Pr)_2]Cr(CO)_4$, 62264-12-4; $[Ph_2PCH_2PPh(i\text{-}Pr)]Cr(CO)_4$, 62264-09-9; $[Ph_2PCH_2PPh_2]Cr(CO)_4$, 16743-46-7; $[Ph_2PCH_2P(t\text{-}Bu)_2]Mo(CO)_4$, 74525-15-8; $[Ph_2PCH_2P(i\text{-}Pr)_2]$Mo-

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(CO)$_4$, 62264-13-5; [Ph$_2$PCH$_2$PPh(*i*-Pr)]Mo(CO)$_4$, 62264-10-2; [Ph$_2$PCH$_2$PPh$_2$]Mo(CO)$_4$, 26743-81-7; [Ph$_2$PCH$_2$P(*t*-Bu)$_2$]W(CO)$_4$, 74525-16-9; [Ph$_2$PCH$_2$P(*i*-Pr)$_2$]W(CO)$_4$, 62264-14-6; [Ph$_2$PCH$_2$PPh(*i*-Pr)]W(CO)$_4$, 62264-11-3; [Ph$_2$PCH$_2$PPh$_2$]W(CO)$_4$, 41830-14-2; [Ph$_2$P(S)CH$_2$P(*i*-Pr)$_2$]Cr(CO)$_4$, 62264-23-7; [Ph$_2$P(S)CH$_2$PPh(*i*-Pr)]Cr(CO)$_4$, 62263-99-4; [Ph$_2$P(S)CH$_2$PPh$_2$]Cr(CO)$_4$, 62264-01-1; [Ph$_2$P(S)CH$_2$P(*i*-Pr)$_2$]Mo(CO)$_4$, 62264-22-6; [Ph$_2$P(S)CH$_2$PPh(*i*-Pr)]Mo(CO)$_4$, 62264-28-2; [Ph$_2$P(S)CH$_2$PPh$_2$]Mo(CO)$_4$, 54340-52-2; [Ph$_2$P(S)CH$_2$P(*i*-Pr)$_2$]W(CO)$_4$, 62264-21-5; [Ph$_2$P(S)CH$_2$PPh(*i*-Pr)]W(CO)$_4$, 62264-27-1; [Ph$_2$P(S)CH$_2$PPh$_2$]W(CO)$_4$, 62264-00-0; Ph$_2$P(S)CH$_2$P(*i*-Pr)$_2$, 54006-31-4; Ph$_2$P(S)CH$_2$PPh(*i*-Pr), 54006-27-8; Ph$_2$P(S)CH$_2$PPh$_2$, 54006-28-9.

Contribution from the Chemical Physics Program,
Washington State University, Pullman, Washington 99164

Structure and Magnetic Properties of the Ferromagnetically Coupled Nickel Dimer $(C_3H_6N_2H_6)_2[Ni_2Cl_8(H_2O)_2]$

C. P. LANDEE and R. D. WILLETT*

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The crystal structure of dimeric $(C_3H_6N_2H_6)_2[Ni_2Cl_8(H_2O)_2]$ $[(PDANiCl_4{\cdot}H_2O)_2]$ has been determined at room temperature. Crystal data are as follows: $C2/c$; $Z = 4$; $a = 18.892$ (8) Å, $b = 7.354$ (2) Å, $c = 19.009$ (9) Å; $\beta = 129.15$ (3)°; $R = 0.055$ for 2314 reflections. The salt consists of symmetrical bibridged chloride dimers, with bridging Ni–Cl distances of 2.430 and 2.459 Å. The Ni–Cl–Ni bridging angle is 95.05°. Each Ni atom has a distorted octahedral Cl_5OH_2 coordination sphere. The water molecules are trans axial within each dimer. Powder susceptibility data, determined between 2 and 240 K, show the existence of ferromagnetic exchange between Ni centers. The magnetic parameters determined are $J/k = 11.7$ K, $D/k = -4.9$ K, $z'J'/k = -0.76$ K, and $g = 2.297$. The existence of ferromagnetic coupling is consistent with predictions of modern superexchange arguments, in particular with the presence of octahedral coordination and a bridging angle near 90°.

Introduction

Magnetic exchange interactions between metal ions in binuclear transition-metal salts continue to be a subject of wide interest, with particular emphasis on determining magnetic–structural correlations. These correlations are manifestations of rather intricate details of the nature of the interactions between the unpaired electrons in the magnetic orbitals of the metal atoms. Thus, their elucidation and understanding present fundamental experimental and theoretical challenges to inorganic and theoretical chemists. In addition, the understanding of these relations is of considerable practical importance in the area of solid-state physics for the design and synthesis of new low-dimensional magnetic systems with specific types of magnetic properties.

A prime example of this type of magnetic–structural correlation has been the linear relationship found between the exchange constant, J, and the bridging Cu–O–Cu angle in bibridged copper dimers containing symmetric Cu–OH–Cu bridges.[1] Theoretical arguments predict that the exchange energy should be dependent upon such a geometrical variation. It has been shown by Hay, Thibeault, and Hoffmann[2] for two spin $^1/_2$ ions that $2J$ (the singlet–triplet energy separation) can be expressed by the combination of two terms

$$2J = 2K_{ab} - 2(\epsilon_1 - \epsilon_2)^2/(J_{aa} - J_{bb}) \qquad (1)$$

where the exchange and Coulomb integrals are slowly varying functions of the molecular parameters and ϵ_1 and ϵ_2 are the energies of the molecular orbitals formed from the magnetic orbitals on the two metal ions. The first term gives a ferromagnetic contribution; the second gives an antiferromagnetic contribution. Semiempirical techniques were used to show that $\epsilon_1 - \epsilon_2$ was 0 (e.g., the antiferromagnetic contribution was zero) at an angle slightly larger than 90°. This copper series was particularly straightforward because of the simplicity of the system: a single half-filled d orbital ($d_{x^2-y^2}$), planar coordination geometry, lack of axial perturbation. Hence, the only structural parameter of magnetic significance was the bridging Cu–O–Cuangle (or, alternatively, the Cu–Cu distance since the Cu–O distances are essentially constant).

Another series which has received considerable study, recently, has been the bibridged nickel chloride dimers.[4] Structurally, the dimers may contain either five-coordinate Ni^{2+} ions such as the $Ni_2Cl_8^{2-}$ ion in $[HN(C_2H_4)_3NCH_3]_2$-Ni_2Cl_8[3a] or six-coordinate Ni^{2+} ions such as the $Ni_2(en)_4Cl_2$ ion in $[Ni_2(en)_4Cl_2]Cl_2$.[3b] The dimers with square-pyramidal coordination are generally antiferromagnetic, while the trigonal-bipyramidal or six-coordinate systems are ferromagnetic.[4] Theoretically, the expression for the exchange energy now becomes eq 2 where m is the number of unpaired electrons

$$2J = (1/m^2)\sum_{i=1}^{m}\sum_{j=1}^{m}K_{ij} - (1/m^2)\sum_{i=1}^{m}(\epsilon_{2i} - \epsilon_{2i-1})^2/(J_{ai,ai} - J_{ai,bi}) \qquad (2)$$

on each metal ion, the first sum runs over all m^2 combinations of electron i on metal a and electron j on metal b, and the second sum is over all distinct pairs of MO's formed from equivalent pairs of localized orbitals on the two metal sites. Again, the first term gives a ferromagnetic contribution; the second, an antiferromagnetic interaction. For Ni^{2+}, the localized orbitals are essentially metal d_{z^2} and $d_{x^2-y^2}$ orbitals. Because of the axially symmetric nature of the d_{z^2} orbital, the difference in energy between the MO's formed from that pair will be quite insensitive to small geometrical changes for octahedral or square-pyramidal complexes. Thus, the antiferromagnetic contributions in eq 2 will be dominated by the $d_{x^2-y^2}$ orbital contributions just as for the Cu^{2+} dimers but reduced

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