Carbon-13 Nuclear Magnetic Resonance Spectra of Tungsten and Molybdenum Carbonyl Derivatives

By **Paul S. Braterman** * and **David W. Milne,** Department of Chemistry, The University, Glasgow W.1
Edward W. Randall * and **Edward Rosenberg,** Department of Chemistry, Queen Mary College, London E1 4NS

^{13}C N.m.r. data are presented for the series of complexes $(CO)_{6-n}ML_n$ (where M = Mo or W; L = alkylphosphine, alkyl phosphite, bisdiphenylphosphinoethane, bisdiphenylphosphinomethane, and n = 1 or 2) and for the corresponding free ligands. Chemical shifts and coupling constants for the co-ordinated carbon monoxide and ligand carbons are compared with results from other spectroscopic techniques. The chemical shift of co-ordinated carbon monoxide is found to reflect the charge donor ability of L. The phosphorus to carbon monoxide coupling constants vary in a similar way to phosphorus–phosphorus coupling constants in this class of compounds and a dependence of ^1J M–^{13}CO on s-electron density at the metal atom is suggested.

THE Group VIA metal carbonyls and their substituted derivatives have been the subject of numerous bonding studies using ^{31}P n.m.r.,[1,2] i.r.,[3] and u.v. spectroscopies.[4,5] The recent developments in instrumentation[6] now make this class of compounds amenable to study by ^{13}C n.m.r. spectroscopy. Recent reports on the ^{13}C n.m.r. of transition-metal carbonyl complexes have shown that the ^{13}C chemical shifts, δCO, in co-ordinated carbon monoxide are sensitive to changes in its stereochemistry and electronic environment.[7-9] We have examined a range of phosphine and phosphite derivatives of molybdenum and tungsten carbonyls and compare our results with those of other workers.[8,9]

Carbonyl ^{13}*C-Shifts*.—There are four obvious trends in δCO (see Table 1): (1) δCO increases (*i.e.* there is a downfield shift) if CO is replaced by any ligand L (L =

---

[1] E. G. Finer and R. K. Harris, *Progr. Nuclear. Magnetic Resonance Spectroscopy*, 1971, **6**, 61, and references therein.

[2] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 346.

[3] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

[4] (*a*) P. S. Braterman and A. P. Walker, *Discuss. Faraday Soc.*, 1969, **47**, 121; (*b*) D. W. Milne, Ph.D. Thesis, Glasgow, 1972; P. S. Braterman, D. W. Milne, and A. P. Walker, unpublished work.

[5] N. A. Beach and H. B. Gray, *J. Amer. Chem. Soc.*, 1968, **90**, 5713.

[6] E. W. Randall, *Chem. in Britain*, 1971, **7**, 371.

[7] L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Comm.*, 1971, 1078.

[8] B. E. Mann, unpublished results.

[9] (*a*) O. A. Gansow, B. Y. Kimura, G. R. Dobson, and R. A. Brown, *J. Amer. Chem. Soc.*, 1971, **93**, 5922; (*b*) O. A. Gansow, D. A. Schexnayder, and B. Y. Kimura, *J. Amer. Chem. Soc.*, 1972, **94**, 3406.

phosphine, phosphite, amine, or arsine); (2) δCO increases with successive replacement of CO by L; (3) δCO (*trans*) > δCO (*cis*); and (4) there is an essentially constant difference in δCO with change of metal for any particular type of complex.

These empirical trends may be discussed in the light of current theory. Carbon chemical shifts are dominated by the paramagnetic term of the screening constant arising from mixing of ground and excited states of carbon in the magnetic field according, in the Pople MO treatment,[10] to the equation

$$\delta_p = -\frac{K}{\Delta E}\langle r^{-3}\rangle_{2p}\{Q_{AA} + Q_{AB}\} \qquad (1)$$

where ΔE is an average excitation energy, $\langle r^{-3}\rangle_{2p}$ is the inverse cubed radius of the $2p$-orbitals, and the Q terms contain elements of the charge density, bond-order matrix. Both $\langle r^{-3}\rangle_{2p}$ and Q_{AA} depend on the local charge density with Q_{AA} remaining essentially constant for most carbon nuclei.[10] Q_{AB} Arises essentially because of a second-order paramagnetic term on the neighbouring atom B inducing currents on A. Q_{AB} Requires σ- and π-bonding between A and B and may be considered to be an indirect field effect of B on A. Direct field effects of circulations on B are not included in the Pople treatment. It is pertinent to suggest here that the Buckingham–Stephens model for ^1H shifts[11] in metal hydrides, which is essentially a direct field model in one limit, is also relevant to the metal–carbon case.

TABLE 1

Spectroscopic data for Group VIA metal carbonyls and derivatives

Compound	No.	δCO [a] *cis* (p.p.m.)	δCO [a] *trans* (p.p.m.)	$^2J(^{31}P-^{13}C)$ [b] *cis* (Hz)	$^2J(^{31}P-^{13}C)$ [b] *trans* (Hz)	$^1J(^{183}W-^{13}C)$ [c] *cis* (Hz)	$^1J(^{183}W-^{13}C)$ [c] *trans* (Hz)	$^1J(^{183}W-^{31}P)$ (Ref.) (Hz)	$\delta^{31}P$ [h] (Ref.) (p.p.m.)	$^2J(^{31}P-^{31}P)$ (Ref.) (Hz)	$k_1(t)$	$k_2(c)$	Lowest metal-ligand charge-transfer band (cm^{-1})
$Cr(CO)_6$	(1)	212·1 [d] (214·6) [e]									16·49		
$Mo(CO)_6$	(11)	202·0 [d,f] (204·1) [e]									16·52		34,900
$Mo(CO)_5P(OMe)_3$ [g]	(III)	206·4	209·2	7·3	18·3				−162 (2)		15·86	16·03	31,750
$Mo(CO)_5P(OEt)_3$ [g]	(IV)	206·8	208·7	6·7	18·9						15·81	15·99	31,800
$Mo(CO)_5P(OPr^i)_3$ [g]	(V)	206·3	209·7	14·6 [i]	12·2 [i]						15·76	15·95	31,500
$Mo(CO)_5PPh_3$ [j]	(VI)	206·5	211·0						−37·5 (2)		15·57	15·99	
trans-$Mo(CO)_4[P(OMe)_3]_2$	(VII)	210·3		13·4					−174 (2)	+162 (15)			28,900
cis-$Mo(CO)_4\{Ph_2PCH_2\}_2$ [d]	(VIII)	210·6	218·5	8·4	24·0						14·64	15·41	
$W(CO)_6$	(IX)	192·1 [d] (193·7) [e]				125·0					16·41		34,700
$W(CO)_5P(OMe)_3$ [g]	(X)	196·5	199·5	11·6	37·2	125·1	139·1	398 (2)	−137·3 (2)		15·78	15·95	31,250
$W(CO)_5P(OEt)_3$ [g]	(XI)	197·2	199·6	10·9	36·6	125·1	138·5	391 (2)			15·73	15·91	31,450
$W(CO)_5P(OBu)_3$ [j]	(XII)	196·1	198·8	9	36			390 (2)			15·79	15·90	
$W(CO)_5P(OPh)_3$ [j]	(XIII)	194·5	197·0	10·5	45·4			417 (2)			15·88	16·08	
$W(CO)_5PBu_3$ [g]	(XIV)	198·6	200·4	7·3	18·9	124·4	142·1	227 (2)	+6·4 (2)		15·45	15·75	28,450
$W(CO)_5PEt_3$ [k]	(XV)	198·5	200·2	6	19	127	140						
$W(CO)_4\{Ph_2PCH_2\}_2$	(XVI)	204·6	[l]	9	[l]						14·58	15·32	
$W(CO)_3(PEt_3)_3$(*fac*-) [k]	(XVII)	212·4		5	14	135							
$W(CO)_5PPh_3$ [j]	(XVIII)	198·0	199·8	7	22	129		280 (2)	−20·6 (2)		15·52	15·88	
$W(CO)_5AsPh_3$ [j]	(XIX)	197·5	199·7			124					15·53	15·90	
$W(CO)_5NH_2C_6H_{11}$ [j]	(XX)	199·1	201·9			132					15·12	15·76	
$W(CO)_5C(OMe)Ph$	(XXI)	198·6	204·6			125·0							

[a] ±0·3 p.p.m. positive downfield relative to internal TMS. [b] ±0·6 Hz unless otherwise noted. [c] ±0·6 Hz. [d] Run in 85% $CDCl_3$ + 10% C_6F_6 + 5% Me_4Si. [e] Run in 95% C_6F_6 + 5% Me_4Si. [f] $^1J^{95}Mo-^{13}CO$ = 68 Hz, data from ref. 8. [g] Run as a neat liquid with 5% Me_4Si + 10% C_6F_6. [h] $\delta^{31}P$ = chemical shift with respect to external 85% H_3PO_4 (high field positive). [i] ±2·4 Hz. [j] Data from refs. 9 and 17. [k] Data from ref. 8. [l] Not observed.

δCO For organic carbonyls[12] and co-ordinated carbon monoxide in octahedral monosubstituted tungsten carbonyls[9] has been correlated with C–O stretching parameters. A similar correlation holds for the Mo and W complexes here. Equation (1) has been applied to the case of substituted organic carbonyls[12] and the results interpreted in terms of changes in the C–O π-bond polarity [affecting $\langle r^{-3}\rangle_{2p}$ and Q_{AB} in equation (1) with the r term dominant] as a function of the electronegativity of the substituent such that electronegative groups decrease the π-bond polarity, increase r, and give upfield shifts. This essentially inductive argument could be adapted to the case of metal carbonyls by postulating that the ligands L are better charge donors than the CO groups being replaced. Such inductive effects are however thought to be small for carbon monoxide complexes compared with the effects produced by dative ($p - d$) π-bonding as inferred from i.r. evidence.[3]

π-Donation to organic carbonyls causes an upfield shift[12b] and a similar result would be expected for co-ordinated CO. We disagree with Gansow *et al.*[9b] who have argued that increased π-donation from metal to CO causes downfield shift by increasing the C–O π-bond polarity. These authors have apparently neglected a negative sign in the expression for σ_p.[10] They also assume that ΔE is constant in the series $(CO)_2(\pi-C_5H_5)FeI$.

Alternatively, the observed downfield shifts on re-

---

[10] J. A. Pople, *Mol. Phys.*, 1964, **7**, 301.

[11] A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 1964, 2747.

[12] (*a*) G. E. Maciel, *J. Chem. Phys.*, 1965, **42**, 2746; (*b*) D. H. Marr and J. B. Stothers, *Canad. J. Chem.*, 1964, **86**, 2984.

placement of CO by L can be related to changes in ΔE resulting from interaction of metal *d*-orbitals with CO* π-orbitals. The frequency of the lowest-energy u.v. band of any appreciable intensity, assigned by one of us [4a] to the charge transfer from the metal to the π^*-orbitals of a CO *cis* to a substituent, correlates well with δCO (*cis*). Contributions from the Q_{AB} terms associated with the metal would be expected to be small for the cylindrically symmetrical MCO group, just as Q_{AB} averages to zero in acetylenes.[10]

The ΔE argument is also supported by the fact that $\delta^{31}P$ is to lower field for *trans* disubstituted derivatives than for the analogous *cis*-compounds.[13] A lower ΔE on phosphorus is expected for the *trans*-isomer in which phosphorus competes more effectively with another phosphorus for metal *d*-electrons than with CO.[13] The lower field chemical shifts for a *trans*-CO with respect to a *cis*-CO can be rationalized in the same way.

This difference between the *cis*- and *trans*-shifts appears to be sensitive to the nature of the unique ligand in the monosubstituted compounds as shown by the results for the carbene (XXI), and the phosphine and phosphite cases.

The charge donor ability of a particular ligand is clearly reflected in δCO. Thus the order carbene > amine > phosphine $\simeq$ arsine > phosphite is consistent with the expected charge donor abilities of these ligands as ascertained by other spectroscopic techniques.[1-3] Successive replacement of CO by better charge donors increases δCO again indicating the full importance of the charge donated to the metal.

The order of δCO for different metals (*viz.* Cr > Mo > W) cannot readily be attributed to differences in π-bonding since their carbonyl i.r. stretching frequencies,[3] metal–ligand charge-transfer bands,[4,5] and orbital electronegativities [5] are all essentially the same. Furthermore the change in δCO with metal is independent of the nature of the other ligands and the overall symmetry of the complex. The same order Cr > Mo > W is seen in $\delta^{31}P$ for these compounds. We suggest that paramagnetic currents which are dependent on the *d–d* transition energies on the metal have a direct field effect on δCO and $\delta^{31}P$. This idea is similar to those presented in the theoretical treatment of transition-metal hydride chemical-shifts which suggest that *d*-orbital energies affect the magnitude of σ_p.[11] For the hexacarbonyls themselves δCO falls [9] as one of the *d–d* splittings increases [9,5] from Cr through Mo to W.

$\delta^{13}C$ For the directly bound carbon atom of the carbene ligand is also independent of the metal in the same sense as δCO but with a larger magnitude: it is 32 p.p.m. to high field in (XXI) compared with the chromium case.[14]

Finally it is important to take note of the relatively large solvent-induced chemical shift (*ca.* 2 p.p.m.) for the metal hexacarbonyls. The shift is to high field with $CDCl_3$ in relation to C_6F_6, contrary to what one would expect if the CO π-bond polarity were enhanced by hydrogen bonding to the solvent.

Phosphorus–Carbonyl Coupling Constants $^2J(^{31}P\text{–}M\text{–}^{13}CO)$.—The general trends in $^2J(^{31}P\text{–}M\text{–}^{13}CO)$ are the same as in $^2J(^{31}P\text{–}M\text{–}^{31}P)$ for complexes of Cr, Mo, and W.[1] Thus $J(trans) \gg J(cis)$ and the couplings in the phosphite complexes are larger than in the phosphine complexes. Also the *trans*- and *cis*-couplings are in the same order W > Mo with the *cis*-case showing a smaller effect. The magnitude of $^2J(^{31}P\text{–}M\text{–}^{13}CO)$ also increases with successive substitution by L. The larger magnitudes of $^2J(^{31}P\text{–}M^{31})$ in *trans*-complexes have been attributed to the larger mutual polarizability of two ligands when *trans* rather than *cis*.[1] An analogous explanation may be offered for $^2J(^{31}P\text{–}M\text{–}^{13}CO)$ as well, especially since the *trans*-coupling is larger in the disubstituted and trisubstituted complexes.

The dependence of $^2J(^{31}P\text{–}M^{31}P)$ on the electronegativity of the group attached to the phosphorus has been ascribed to the dependence of these couplings on the *s*-electron density in the bonds and the effective nuclear charge of phosphorus.[15] A similar dependence is seen for $^2J(^{31}P\text{–}M\text{–}^{13}CO)$ so that it increases linearly with $^1J(^{183}W\text{–}^{31}P)$ (see Table 1).

The fact that the ratio of $^1J(M\text{–}^{13}CO)$ in the hexacarbonyls is approximately equal to the ratio of $^2J(^{31}P\text{–}M\text{–}^{13}CO)$ in analogous molybdenum and tungsten complexes further suggests that *s*-electron density at the metal nucleus is an important factor.[8]

The values of $^2J(^{31}P\text{–}M\text{–}CO)$ in (V) suggest an angular dependence for this coupling. Distortion from octahedral symmetry by the bulky isopropyl group would cause the P–M–CO (*cis*) angle to increase. A similar phenomenon was observed for *cis* $^2J(^{31}P\text{–}M\text{–}^{31}P)$ with NR_2 groups on the phosphorus.

The spectrum obtained for (VIII) is worthy of comment. The negligible value of *cis* $^2J(^{31}P\text{–}M\text{–}^{31}P)$ reported for complexes of this ligand [16] leads us to conclude that the observed spectrum is first order (*i.e.* has no virtual coupling) with a triplet resonance arising from *cis*-coupling of the two axial carbonyls to two equivalent phosphorus atoms and a doublet of doublets arising from one *cis*- and one *trans*-coupling to the equatorial carbonyls. The *trans*-coupling is assigned the larger value on the basis of results for other complexes.

Tungsten–Carbonyl Coupling Constants $^1J(^{183}W\text{–}^{13}CO)$.—The insensitivity of *cis* $^1J(^{183}W\text{–}^{13}CO)$ to changes in L for the series $(CO)_5WL$ has been attributed to a balancing of changes in $[\psi_m(0)]^2$ with changes in W–C bond strength.[9] Although data on *trans* $^1J(^{183}W\text{–}^{13}CO)$ is limited at the moment, the larger value of the coupling relative to the *cis* and the larger value of $^1J(^{183}W\text{–}^{13}CO)$

---

[13] S. O. Grim and D. A. Wheatland, *Inorg. Chem.*, 1969, **8**, 1716 and references therein.

[14] J. A. Connor, E. M. Jones, E. W. Randall, and E. Rosenberg, *J.C.S. Dalton*, 1972, 2419.

[15] F. B. Ogilvie, J. M. Jenkins, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1970, **92**, 1916.

[16] S. O. Grim, D. A. Wheatland, and P. R. McAllister, *Inorg. Chem.*, 1968, **7**, 161.

for the trisubstituted complex (durene)W$(CO)_3$ (189 Hz)[17] suggest the importance of $[\psi_m(0)]^2$.

TABLE 2

^{13}C N.m.r. chemical shifts of some free and complexed tertiary phosphines and phosphites [a]

Compound	δC_1	δC_2, δC_6	δC_3, δC_5	δC_4	δC_7
PMe_3 [b]	49·7				
$Mo(CO)_5P(OMe)_3$ [b]	52·1				
$W(CO)_5P(OMe)_3$ [b]	52·8				
$Mo(CO)_4[P(OMe)_3]_2$ [c]	51·7				
$P(OEt)_3$ [b]	57·0	17·2			
$Mo(CO)_5P(OEt)_3$ [b]	62·1	16·7			
$W(CO)_5P(OEt)_3$ [b]	61·8	16·3			
$P(OPr^i)_3$ [b]	67·7	25·6			
$Mo(CO)_5P(OPr^i)_3$ [b]	57·0	24·3			
$PBu^n{}_3$ [b]	28·6	27·9	24·8	14·0	
$W(CO)_5PBu_3$ [b]	29·8	26·8	24·7	13·6	
$Ph_2PCH_2PPh_2$ [d]	139·3	133·2	128·6	128·9	28·4 [e]
$Mo(CO)_4Ph_2PCH_2PPh_2$ [d]	*f*	133·0	129·5	131·2	30·1 [e]
$W(CO)_4Ph_2PCH_2PPh_2$ [d]	*f*	132·4	129·5	131·2	32·5 [e]
$Ph_2PCH_2CH_2PPh_2$ [d]	139·3	133·1	128·4	128·5	24·1 [e]
$Mo(CO)_4Ph_2PCH_2CH_2PPh_2$ [d]	135·7	130·5	127·1	128·8	27·1 [e]
$W(CO)_4Ph_2PCH_2CH_2PPh_2$ [d]	136·6	132·1	128·9	130·4	33·4 [e]
PPh_3 [g]	138·3	134·4	129·2	129·3	
$Mo(CO)_5PPh_3$ [g]	136·4	133·7	129·3	130·7	

[a] Resonances reported ±0·3 p.p.m. positive downfield with respect to Me_4Si. [b] Run as a neat liquid with 10% C_6F_6 + 5% Me_4Si. [c] Run in CH_2Cl_2 (40% w/v) + 10% C_6F_6 + 5% Me_4Si. [d] Run in $CDCl_3$ (saturated solution) + 10% C_6F_6 + 5% Me_4Si. [e] CH_2 resonance. [f] Resonance not observed. [g] Data from ref. 17.

TABLE 3a

$^{31}P-^{13}C$ Coupling constants in free and complexed tertiary phosphines and phosphates [a]

Compound	$^1J(^{31}P-^{13}C)$	$^2J(^{31}P-^{13}C)$	$^3J(^{31}P-^{13}C)$	$^4J(^{31}P-^{13}C)$ (Hz)
$P(OMe)_3$		10·5		
$Mo(CO)_5P(OMe)_3$		4·3		
$W(CO)_5P(OMe)_3$		3·6		
$Mo(CO)_1[P(OMe)_3]_2$		<0·6		
$P(OEt)_3$		12·2	4·9	
$Mo(CO)_5P(OEt)_3$		3·6	6·0	
$W(CO)_5P(OEt)_3$		4·3	6·1	
$P(OPr^i)_3$ [b]		12·0	2·4	
$Mo(CO)_5P(OPr^i)_3$		<2·4	17·0	
$PBu^n{}_3$	13·4	14·6	10·9	<0·6
$W(CO)_5PBu^n{}_3$	25·0	<0·6	12·2	<0·6

[a] ±0·6 Hz unless otherwise noted. [b] ±2·4 Hz.

TABLE 3b

$^{31}P-^{13}C$ Coupling constants in free and complexed bisdiphenylphosphino-methane and -ethane [a]

Compound	$^1J[^{13}C(1)^{31}P]$ + $^nJ[^{13}C(1)^{31}P']$ [a]	$^2J[^{13}C(2,6)^{31}P]$ + $^nJ(^{13}C-^{31}P')$ [b]	$^3J[^{13}C(3,5)^{31}P]$ + $^nJ(^{13}C-^{31}P')$	$^4J[^{31}P-^{13}C(4)]$	$^1J[^{13}C(7)-^{31}P]$ + $^nJ[^{13}C(7)-^{31}P']$
$Ph_2PCH_2PPh_2$	4·8 (t)	9·6 (t)	7·2 (t)	<1·2 (s)	24·4 (t)
$Ph_2PCH_2PPh_2W(CO)_4$	*b*	7·2 (t)	4·8 (t)	<1·2 (s)	*b*
$Ph_2PCH_2PPh_2Mo(CO)_4$	*b*	6·0 (t)	4·8 (t)	<1·2 (s)	*b*
$Ph_2PCH_2CH_2PPh_2$	7·2 (t)	9·6 (t)	3·6 (t)	<1·2 (s)	<1·2 (s)
$Mo(CO)_4(Ph_2PCH_2CH_2PPh_2)$	39·0 (d)	9·6 (d)	12·2 (d)	<1·2 (s)	31·8 (d)
$W(CO)_4(Ph_2PCH_2CH_2PPh_2)$	34·2 (d)	12·2 (d)	7·3 (d)	<1·2 (s)	41·5 (d)

[a] ±1·2 Hz, Multiplicity of peak given in parentheses; s = singlet, d = doublet, t = triplet. [b] Not obtained.

Ligand Chemical Shifts.—Except in $P(OPr^i)_3$, the carbon atoms directly bound to phosphorus in the complexed alkyl phosphines and those bound to oxygen in the complexed phosphites all show small downfield shifts with respect to the free ligand. This trend could reflect an inductive effect accompanying the donation of charge to the metal by the phosphorus atom. Mann has suggested, however, that ^{13}C-chemical shifts in tertiary phosphines increase with the C–P–C bond angle when changes in electronegativity are small.[18] It is known that for both tertiary phosphines and phosphites C–P–C and O–P–O bond angles increase on complexation. The dependence of $\delta^{13}C$ on bond angle is also supported by the fact that $\delta^{13}C$ for the CH group in the bulky ligand shows an upfield shift. Steric crowding could preclude an increase in the O–P–O bond angle on complexation since this angle is already large in the free ligand.

The chelating ligands $Ph_2PCH_2PPh_2$ and $(Ph_2PCH_2)_2$ show variable shifts on complexation for carbons 2—6 in the phenyl ring. The C(1) phenyl carbons (XVIII) and (XVI), however, show an upfield shift which is also observed for the same carbon in (VI).[19] This has been rationalized as reflecting an increase in P–C π-bond order[19] but this seems inconsistent with the downfield shifts observed for C(1) carbons in aliphatic tertiary phosphines on complexation. An increase in the C(1)–C(2—6) π-bond order as a result of σ-electron withdrawal could account for the upfield shifts.

Ligand Phosphorus–Carbon Coupling Constants.—The most obvious trend here is the increase in $^2J(^{31}P-O^{13}C)$ and $^2J(^{31}P-C-^{13}C)$ on complexation (Table 3). These changes could be rationalized, as Mann has done for $^1J(^{31}P-^{13}C)$ cases, on the basis of a dominant Fermi-contact mechanism and the bond-angle changes mentioned above,[18] provided that ^2J is negative as for $^2J(^{31}P-C-^1H)$.[2] $^2J(^{31}P-O-^{13}C)$ In $PPr^i{}_3$, unlike the shifts, is apparently not anomalous unless it has undergone a sign change.

---

[17] B. E. Mann, *Chem. Comm.*, 1971, 976.
[18] B. E. Mann, *J.C.S. Perkin II*, 1972, 30.
[19] O. A. Gansow and B. Y. Kimura, *Chem. Comm.*, 1970, 1621.

$J(^{31}P-^{31}P)$ Is evidently smaller for the phenyl groups in complexed $(Ph_2PCH_2)_2$ than in the free ligand since deceptively simple 1 : 2 : 1 triplets of phenyl carbons 1,2,6 and 3,5 reduce to 1 : 1 doublets on complexation. The same is not true for $Ph_2PCH_2Ph_2$ since triplets are obtained in both cases.

CONCLUSIONS

It can be seen that the ambiguity in assessing which factors dominate the shifts naturally leads to a lack of discrimination between different bonding arguments. As ever, piecemeal rationalization is easy, comprehensive and consistent rationalization more difficult. The situation is further confused by ambiguities in the bonding approaches, for example the general problem of factorization of bonding types into σ and π.

One definitive statement is possible however for the shift data: The charge-donor ability of a given ligand L is directly related to δCO.

EXPERIMENTAL

Materials.—All compounds were prepared by published methods.[1-4] $CDCl_3$, CH_2Cl_2, and C_6F_6 were dried over molecular sieves and sample tubes were flushed with nitrogen before use. Spectra were obtained on neat ligands or saturated solution as noted in Table 1.

Spectra.—Spectra were obtained on a Bruker HFX-13 n.m.r. spectrometer operating in the Fourier Transform mode at 22·63 MHz. Proton noise decoupling was performed with the use of a 90 MHz broad band decoupler. Spectra were recorded first with a spectral width of 12·5 KHz to obtain chemical shifts using accumulation times of 10 min to 2 h and then with a spectral width of 1·25 or 2·5 Kz using accumulation times of 3—18 h to obtain coupling constants and tungsten satellites. It was necessary to use short pulse lengths (6 μs in the single-coil time-sharing mode) for the carbonyl peaks owing to their long T_1 values. Unfortunately, we were unable to obtain spectra for the carbonyl groups in the bisdiphenylphosphinomethane complexes probably due to their low solubility (20% w/v) in $CDCl_3$, the additional complexity of the spectra expected for these compounds and the long T_1 values for carbonyl groups in general. Dielectric heating of the sample in the probe was offset by blowing air at ambient temperature over the sample to give an average temperature of 35—40 °C.

Spectral Assignment.—Spectral assignments in the hydrocarbon region were made on the basis of off-resonance broad-band decoupling experiments and known substituent parameters. Carbonyl resonances were assigned on the basis of relative intensities (*cis–trans* in the range 4—7 for the monosubstituted complexes).

We thank B. E. Mann for access to data before publication and the S.R.C. for research support.

[2/1807 *Received*, 31*st July*, 1972]