Carbon-13 Nuclear Magnetic Resonance Spectra of Some Carbonyl Complexes of Chromium, Molybdenum, and Tungsten

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^{13}C N.m.r. spectra and some i.r. (carbonyl) stretching frequencies of the complexes $[M(CO)_6]$, $[W(CO)_nL_{6-n}]$, $[M'(CO)_4(\text{norbornadiene})]$, and $[M(CO)_3L']$ [M = Cr, Mo, or W; M' = Cr or Mo; and n = 1, 2, or 3; L = PEt_3 and $P(OMe)_3$ and n = 1; L' = mesitylene, 1,2,4,5-tetramethylbenzene, hexamethylbenzene, or cyclohepta-1,3,5-triene] are reported. The work includes the first reported measurement of $^1J(^{95}Mo-^{13}C)$.

WHEN this work was commenced, there were very few data in the literature on ^{13}C n.m.r. spectra of organometallic compounds. It was therefore decided to investigate two types of derivatives of chromium, molybdenum, and tungsten hexacarbonyl complexes, namely those where the carbonyl ligand was replaced by either a phosphorus ligand or by an unsaturated carbon ligand. Very few ^{13}C n.m.r. data have been reported previously on such complexes,[1,2] with only limited data being available for $[(cp)Mo(CO)_3R]$ (R = Cl, C_3F_7, CO, $MeSCH_2$, or CF_3Et), $[(cp)Mo(CO)_2NO]$ (cp = cyclopentadienyl), $[(nbd)Mo(CO)_4]$ (nbd = norbornadiene), and $[Mo(CO)_5PPh_3]$. A preliminary report of the present investigations has already appeared giving ^{13}C n.m.r. data for the complexes $[L'M(CO)_3]$ [M = Cr, Mo, or W; L' = mesitylene (mst), 1,2,4,5-tetramethylbenzene (tmb), or cyclohepta-1,3,5-triene (cht)].[3] Concurrent with this work another preliminary report appeared containing data on the complexes $[(OC)_5Cr(COMe)Me]$, $[(\text{benzene})Cr(CO)_3]$, $[(OC)_5Mo\{P(OPr^i)_3\}]$, $[(m\text{-xylene})Mo(CO)_3]$, and $[(cp)W(CO)_3Me]$.[4] Recently, ^{13}C n.m.r. data have been reported for a number of complexes $[LW(CO)_5]$ (L = phosphorus ligand, $AsPh_3$, $SbPh_3$, $BiPh_3$, or $C_6H_{11}NH_2$),[5] $(Me_4N)_2Fe[7,9\text{-}B_9H_9CHPCr(CO)_5]_2$ and $(Me_4N)[7,9\text{-}B_9H_{10}CHPMo(CO)_5]$.[6]

RESULTS AND DISCUSSION

^{13}C Chemical shifts for the complexes $[(nbd)M'(CO)_4]$ (M' = Cr or Mo; nbd = norbornadiene) and $[L'M(CO)_3]$ [M = Cr, Mo, or W; L' = mesitylene (mst), 1,2,4,5-tetramethylbenzene (tmb), hexamethylbenzene (hmb), and cyclohepta-1,3,5-triene (cht)] are given in Table 1; ^{13}C chemical shifts and coupling constants for the complexes $[L_nW(CO)_{6-n}]$ (L = phosphorus ligand) are given in Table 2.

Carbonyl Group Chemical Shifts.—Examination of the data given in Tables 1 and 2 shows that replacement of the carbonyl ligand in the complexes $[M(CO)_6]$ (M = Cr, Mo, or W) by another ligand in every case causes the ^{13}C (carbonyl) shift to move to high frequency (low field). Only one exception to this behaviour for carbonyl complexes of chromium, molybdenum, or tungsten has so far been reported in the literature, $(Me_4N)[7,9\text{-}B_9H_{10}CHPMo(CO)_5]$.[6]

It has been already noted that for the complexes $[LW(CO)_5]$ [L = $P(OPh)_{3-n}Bu$ (n = 0—3), PPh_3, $AsPh_3$, $SbPh_3$, $BiPh_3$, and $C_6H_{11}NH_2$] and $[Fe(CO)_2(cp)X]$ (X = anionic ligand, cp = cyclopentadienyl) a linear relation exists between the ^{13}C (carbonyl) chemical shift and the Cotton–Kraihanzel carbonyl stretching force constant.[5,7] The applicability of this relation to a wider range of complexes of tungsten was therefore examined. The ^{13}C chemical shifts and the force constant calculated by the method of Cotton and Kraihanzel[8] are given in Table 3. Caution had to be exercised in the use of literature values as both ^{13}C chemical shifts and C–O stretching frequencies appear to be solvent dependent. For example the ^{13}C chemical shift of the complex

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TABLE 1

^{13}C N.m.r. chemical shifts/p.p.m. measured at 22·62 MHz in CH_2Cl_2 of the ligands mst, tmb, hmb, and cht and their complexes with $[M(CO)_3]$ (M = Cr, Mo, or W) and $[(nbd)M'(CO)_4]$ (M′ = Cr or Mo) *

	Free ligand		$[LM(CO)_3]$	
mst	L	Cr	Mo	W
$^{13}CH_3$	21·4	21·0	21·2	20·9
^{13}CH	127·6	92·4	94·7	90·9
^{13}CMe	138·6	111·5	111·7	111·1
^{13}CO	181·5 [a]	235·1	223·7	212·6
tmb				
$^{13}CH_3$	19·2	18·6	19·1	18·9
^{13}CH	131·6	99·0	101·4	97·3
^{13}CMe	134·4	107·6	118·8	107·9
^{13}CO	181·5 [a]	235·5	224·4	213·7
hmb				
$^{13}CH_3$	16·9	17·4	18·0	17·9
^{13}CMe	132·5	107·5	111·7	107·9
^{13}CO	181·5 [a]	236·3	225·9	215·7
cht				
$^{13}CH_2$ C(7)	28·7 [b]	24·8	28·0	28·7
^{13}CH C(1,6)	121·3 [b]	57·6	61·3	52·3
^{13}CH C(2,5)	127·3 [b]	99·0	98·1	94·2
^{13}CH C(3,4)	131·3 [b]	101·9	103·7	101·7
^{13}CO	181·5 [a]	232·7	220·6	211·6
nbd				
$^{13}CH_2$	76·0	62·5	65·5	
^{13}CH	51·5	48·3	49·8	
^{13}CH (olefinic)	144·1	76·0	79·6	
^{13}CO	181·5 [a]	226·8	215·0	
^{13}CO	181·5 [a]	234·5	218·8	

* The shifts (±0·1 p.p.m.) are relative to Me_4Si and increasing frequency is regarded as being positive. mst = Mesitylene, tmb = 1,2,4,5-tetramethylbenzene, hmb = hexamethylbenzene, cht = cyclohepta-1,3,5-triene, and nbd = norbornadiene.

[a] Calculated from data of R. Ettinger, P. Blume, A. Patterson, jun., and P. C. Lauterbur, *J. Chem. Phys.*, 1960, 33, 1547, measured as a gas at 8·5 MHz. [b] Assignment as in H. Gunther and T. Keller, *Chem. Ber.*, 1970, **103**, 3231.

$[W(CO)_6]$ in $CHCl_3$ is 192·4 p.p.m. but that in CH_2Cl_2 is 193·7 p.p.m.,[9] and C–O stretching frequencies of $[(mst)Cr(CO)_3]$ in MeCN are 1 874·2 and 1 955·9 cm^{-1} but in n-hexane are 1 903·0 and 1 970·7 cm^{-1}.[10] Thus as far as possible, i.r. data measured in the same solvent as the n.m.r. data are quoted. In cases such as $[Cr(CO)_3(cht)]$, where the i.r. (C–O stretch) spectrum can be interpreted as being due to two types of carbonyl group but the ^{13}C n.m.r. spectrum shows only one type of carbonyl group, a weighted average of the force constants was calculated and it is this which is quoted in Table 3.

TABLE 2

^{13}C N.m.r. chemical shifts/p.p.m. and coupling constants/Hz measured at 22·62 MHz for the complexes $[M(CO)_6]$ (M = Cr, Mo, or W), $[W(CO)_{6-n}(PEt_3)_n]$ (n = 1, 2, or 3), and $[W(CO)_5\{(POMe)_3\}]$ *

	Carbonyl resonances			Phosphorus ligand resonances		
Complex	δ(^{13}C)	$^1J(M–^{13}CO)$	$^2J(^{31}P–M–^{13}C)$	δ($^{13}CH_2$)	$^1J(^{31}P–^{13}C)$	δ($^{13}CH_3$)
$[Cr(CO)_6]$ [a]	212·3					
$[Mo(CO)_6]$ [a]	204·1	68				
$[W(CO)_6]$ [a]	191·9	126				
$[W(CO)_5PEt_3]$ [b]	200·2 [c]	142	19	22·8	25·3	8·7
	198·5 [d]	129	6			
cis-$[W(CO)_4(PEt_3)_2]$ [e]	204·4		15·2 [c, i]	24·4	25·2 [f]	8·6
	204·7		6·3 [d]			
trans-$[W(CO)_4(PEt_3)_2]$ [e]	204·7		5	22·9	24·8 [f]	8·6
fac-$[W(CO)_3(PEt_3)_3]$ [c]	212·4	135	14 [g]; 5·5 [h]	23·7	21	9·2
$[W(CO)_5P(OMe)_3]$ [b]	198·8 [c]	135	36			
	196·2 [d]	123	10			

* See footnote * in Table 1.

[a] In $CHCl_3$. [b] Neat liquid. [c] *trans* to phosphorus. [d] *trans* to carbon. [e] In CH_2Cl_2. [f] $|^1J(^{31}P–^{13}C) + {}^3J(^{31}P–M–P–^{13}C)|$. [g] $^2J(^{31}P–M–^{13}C)$ (*trans*). [h] $^2J(^{31}P–M–^{13}C)$ (*cis*). [i] $|^2J(^{31}P–M–^{13}C)$ (*cis*) $+ {}^2J(^{31}P–M–^{13}C)$ (*trans*)$|$.

TABLE 3

Cotton–Kraihanzel force constants/mdyn Å and ^{13}C chemical shifts/p.p.m. for the carbonyl groups in a number of tungsten complexes

	Complex	Force constant	δ(^{13}CO)
(1)	$[W(CO)_6]$	16·41 [a]	191·9
(2)	$[W(CO)_5PEt_3]$	15·67; 15·85 [b]	200·2; 198·5
(3)	$[W(CO)_5\{P(OMe)_3\}]$	15·81; 15·92 [c]	198·8; 196·2
(4)	*trans*-$[W(CO)_4(PEt_3)_2]$	14·97 [d]	204·7
(5)	*fac*-$[W(CO)_3(PEt_3)_3]$	13·79 [e]	212·4
(6)	$[MeW(CO)_3(cp)]$	15·33; 15·68 [f]	239·2; 217·8 [g]
(7)	$[W(CO)_3(mst)]$	14·60 [e]	212·6
(8)	$[W(CO)_3(tmb)]$	14·51 [e]	213·7
(9)	$[W(CO)(cht)]$	14·86 [e]	211·6
(10)	$[W(CO)_5(CSMe)Me]$	15·52; 15·91 [h]	207·4; 198·1 [i]

cp = Cyclopentadienyl, mst = mesitylene, tmb = 1,2,4,5-tetramethylbenzene, and cht = cyclohepta-1,3,5-triene.

[a] Ref. 8. [b] J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1968, 1195. [c] Assumed to be the same as that of $[W(CO)_5\{P(OBu^n{}_3)\}]$ (R. A. Brown and G. R. Dobson, *Inorg. Chim. Acta*, 1972, **6**, 65). [d] Calculated from data of R. Poilblanc and M. Bigorgne, *Compt. rend.*, 1960, **250**, 1064, assuming f_i = 0·34 mdyn $Å^{-1}$. [e] This work. [f] R. B. King and L. W. Houk, *Canad. J. Chem.*, 1969, **47**, 2959. [g] Ref. 4. [h] E. O. Fischer, M. Leapold, C. G. Kreiter, and J. Muller, *Chem. Ber.*, 1972, **105**, 150. [i] C. G. Kreiter and V. Formacek, *Angew. Chem. Internat Edn.*, 1972, **11**, 141.

The Figure shows a plot of the ^{13}C (carbonyl) chemical shifts against Cotton–Kraihanzel force constants. Points due to complexes of the type $[W(CO)_{6-n}L_n]$ (L = Group Vb donor ligand) fall on a reasonably good straight line but those due to many of the other complexes fall off the line, especially in the case of $[(cp)W(CO)_3Me]$. These deviations from the linear relationship could arise, in part, from approximations made in the Cotton–Kraihanzel treatment of the C–O stretching frequencies. The treatment ignores vibrations in the rest of the

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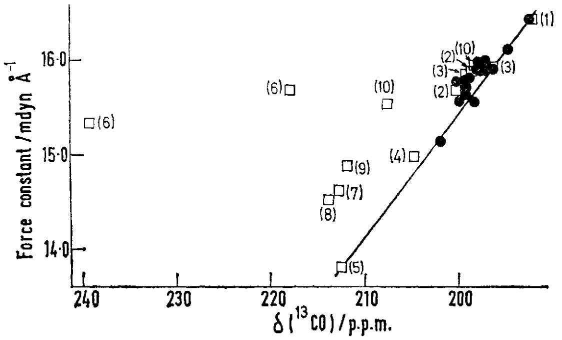
molecule. Thus there will be a considerable error resulting from mixing of other vibrations with the C–O vibration when there is only a small difference in frequency. This could account for the deviations observed for [(arene)W(CO)$_3$] complexes where the arene vibrations might be expected to mix with the CO vibrations. However, it is difficult to believe that this can account for the marked deviations observed for the complex [(cp)W(CO)$_3$Me]. It therefore appears erroneous to extend the linear correlation between the ^{13}C(carbonyl) chemical shifts and Cotton–Kraihanzel force constants beyond the series [W(CO)$_{6-n}$L$_n$] (L = Group Vb donor ligand) until the factors causing these deviations are fully understood.*



Plot of force constant against ^{13}C chemical shift for the carbonyl group in some tungsten carbonyl complexes: (□), points taken from Table 3; (●) points taken from ref. 5 for complexes of the type [W(CO)$_5$L]

Chemical Shifts of π-Ligands.—Chemical shifts of the free π-ligands mst, tmb, hmb, cht, and nbd and their complexes with chromium, molybdenum, and tungsten carbonyls are given in Table 2. In the case of the complex [(cht)Mo(CO)$_3$], the ^{1}H n.m.r. spectrum has been assigned [11] and, by use of the proton-decoupling technique described by Feeney *et al.*,[12] it has been shown that C(3,4) are at 98·1, C(2,5) at 103·7, and C(1,6) at 61·3 p.p.m.

On co-ordination the ^{13}C n.m.r. signal of an olefin or arene ligand moves to low frequency (high field).[1,4,13-18] It has been shown that for sp^2 carbon atoms the ^{13}C chemical shift is proportional to the charge on the carbon atom, moving to low frequency (high field) with increasing charge. The gradient is *ca.* −150 p.p.m. per electron.[19] Thus it is possible to account for the observed chemical shifts of π-ligands by postulating the presence of a negative charge on the π-ligand. For the complexes reported in this paper, this approach requires the transfer of approximately one electron from the metal to the arene ligand. Experiments have shown that for the complex [(benzene)$_2$Cr] the charge on each benzene ring is 0·55 e, while a calculation places 0·75 e on each ring.[20]

Alternatively, it is known that a methyl group attached to a transition metal has a ^{13}C chemical shift of *ca.* 0 p.p.m.,[4,21] while an unco-ordinated olefinic carbon atom has a ^{13}C chemical shift of *ca.* 130 p.p.m.[22] It is thus possible to consider that the bonding of a π-ligand, *e.g.* benzene, to a metal causes the carbon atoms of the π-ligand to rehybridise making them more saturated in character. Thus to account for the ^{13}C chemical shift of the [(arene)M(CO)$_3$] complexes, it is necessary to postulate that the arene carbon atoms have moved 25% from being olefinic towards being saturated in character. Consistent with this postulate, it is known that when benzene is co-ordinated to chromium, the carbon–carbon bond lengthens to 1·40 ± 0·02 Å for [(benzene)-Cr(CO)$_3$], 1·42 ± 0·02 Å for [(hmb)Cr(CO)$_3$], and 1·423 ± 0·002 Å for [(benzene)$_2$Cr].[23-26] It is thus probable that both these mechanisms are operative in producing the shift on co-ordination of a π-ligand.

Metal–Carbonyl Group Coupling Constants.—In addition to the coupling constants listed in Table 2, $^1J(^{183}W–^{13}C)$ for the complex [(tmb)W(CO)$_3$] is 186 Hz. Thus $^1J(^{183}W–^{13}CO)$ covers the range 123—186 Hz. In order to interpret $^1J(M–^{31}P)$, previous workers have used the Fermi contact equation (1), where γ_A and γ_B are the

$$^1J(A–B) = \frac{\hbar}{2\pi}\cdot\frac{256\pi^2}{9}\beta^2\gamma_A\gamma_B\langle s_A(0)\rangle^2\langle s_B(0)\rangle^2 c_A{}^2 c_B{}^2/\Delta E \quad (1)$$

gyromagnetic ratios for the nuclei A and B, $\langle s_A(0)\rangle^2$ and $\langle s_B(0)\rangle^2$ the valence *s*-electron densities at the nuclei A and B, $c_A{}^2$ and $c_B{}^2$ the coefficients of the valence *s* orbital in the molecular orbital of atoms A and B, and ΔE is a 'mean excitation energy.' For metal carbonyl complexes of the type [M(CO)$_n$] it is assumed that $c_A{}^2 = 1/n$, *i.e.* the metal valence *s* orbital is equally and totally shared among the carbonyl ligands and $\langle s_A(0)^2\rangle$ is approximately known.[27] Then equation (2) is applicable, where ^1K(A–B) is the reduced coupling constant and

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* The author wishes to thank a referee for the suggestion that the deviations may, in part, be due to changes in the valency of the metal atom.

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values are given in Table 4. The spread of values is due to the uncertainty in $\langle s_{\mathrm{A}}(0)\rangle^2$. It is clear that for these

$$\frac{{}^1K(\text{A–B})n}{\langle s_{\mathrm{M}}(0)\rangle^2} = \frac{{}^1J(\text{A–B})n2\pi}{\hbar\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}\langle s_{\mathrm{A}}(0)\rangle^2} = \frac{256\pi^2}{9}\langle s_{\mathrm{B}}(0)\rangle^2 c_{\mathrm{B}}{}^2/\Delta E \quad (2)$$

complexes ${}^1J(\text{A–B})n2\pi/\hbar\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}\langle s_{\mathrm{M}}(0)\rangle^2$ is approximately constant. This constancy is consistent with the qualitative use of the Fermi-contact equation to analyse the direct metal–carbon coupling constants, but does not justify the quantitative use of the equation.

TABLE 4

Values of ${}^1J(\text{M–}^{13}\text{C})$, ${}^1K(\text{M–}^{13}\text{C})$, and ${}^1K(\text{M–}^{13}\text{C})n/\langle s_{\mathrm{A}}(0)\rangle^2$ for some metal carbonyl complexes of the type $[\text{M(CO)}_n]$

Complex	${}^1J(\text{M–}^{13}\text{C})$/Hz	$\dfrac{10^{-20}\,{}^1K(\text{M–}^{13}\text{C})}{\text{cm}^{-3}}$	${}^1K(\text{M–}^{13}\text{C})n/\langle s_{\mathrm{A}}(0)\rangle^2$
$[\text{Mo(CO)}_6$	68	346	50·3—61·2
$[\text{W(CO)}_6]$	126	1 003	42·7—56·6
$[\text{V(CO)}_6]^-$ [a]	116	146	41·7—43·9
$[\text{Fe(CO)}_5]$ [b]	23·4	238	40·5—51·3
$[\text{Co(CO)}_4]^-$ [c]	287	402	49·6—55·6

[a] Ref. 1. [b] B. E. Mann, *Chem. Comm.*, 1971, 1173. [c] E. A. C. Lucken, K. Noack, and D. F. Williams, *J. Chem. Soc.* (*A*), 1967, 148.

Qualitatively, the changes in ${}^1J(^{183}\text{W–}^{13}\text{C})$ are interesting. These coupling constants cover the range of 186 Hz for the complex $[(\text{tmb})\text{W(CO)}_3]$ to 123 Hz for the *cis*-carbonyl ligands in $[\text{W(CO)}_5\text{P(OMe)}_3]$. These appear to give a measure of the *trans*-effect of the ligands giving an order tmb $<$ PEt_3 $<$ P(OMe)_3 $<$ CO.

Other Coupling Constants.—In addition to the phosphorus–carbon coupling constants given in Table 2 it has proved possible to measure ${}^2J(^{31}\text{P–W–}^{31}\text{P})$ for the complexes *trans*-$[\text{W(CO)}_4(\text{PEt}_3)_2]$ and *fac*-$[\text{W(CO)}_3(\text{PEt}_3)_3]$ as 39 and 28 Hz respectively, by observing the AA′X or AA′A″X spectrum of the $^{13}\text{CH}_2$ carbon atom. These values are consistent with known values of 65 Hz for the complex *trans*-$[\text{W(CO)}_4(\text{PBu}_3{}^{\text{n}})(\text{PPh}_3)]$ [28] and −25·0 Hz for *cis*-$[\text{W(CO)}_4(\text{PMe}_3)_2]$.[29]

EXPERIMENTAL

All the complexes were prepared as described previously [30–37] and characterised by m.p., and i.r. and n.m.r. spectroscopy. I.r. spectra were measured in CH_2Cl_2 solution using a Grubb–Parsons GS4 spectrometer. ^{13}C N.m.r. spectra were measured on a continuous-wave Bruker HFX-90 spectrometer at 22·62 MHz in CH_2Cl_2 solution containing *ca.* 10% C_6F_6 to provide an internal field–frequency lock and *ca.* 5% tetramethylsilane to provide an internal ^{13}C reference signal. ' Pseudo-random noise ' ^{1}H decoupling was used. All ^{13}C chemical shifts are quoted with respect to $^{13}\text{CH}_3\text{Si(Me)}_3$ with the sign convention that shifts to high frequency are positive.

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