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A CARBON-13 NMR STUDY OF SOME METAL CARBONYL COMPOUNDS CONTAINING ONE-ELECTRON LIGANDS

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Summary

Carbon-13 NMR spectral data for complexes having the general formula $CpM(CO)_nX$ ($Cp = \eta^5\text{-}C_5H_5$; M = Mo or W, $n = 3$; M = Fe, $n = 2$; X = halogen, methyl or acetyl) and their phosphine and isocyanide substitution products are reported. For $CpM(CO)_3X$ complexes two carbonyl resonances (1 : 2 ratio) are observed in all cases, consistent with the retention of the "piano-stool" geometries observed in the solid state. Substituted complexes $CpM(CO)_2(L)X$ (M = Mo or W; L = PR_3 or cyclohexyl isocyanide) are unequivocally assigned *cis* or *trans* geometries on the basis of the number of observed carbonyl resonances and values of $^2J(P—C)$ for the phosphine substituted derivatives. Spectral data for $[M(CO)_5X]^-$ (M = Cr, Mo or W; X = Cl, Br or I) and $\eta^7\text{-}C_7H_7Mo(CO)_2X$ and the halide derivatives above generally show an increase in the shielding for carbonyls adjacent to the halide ligand in the order Cl < Br < I. Carbonyl resonances are more shielded in isostructural complexes in the order Cr < Mo < W (triad effect).

In recent years there has been a great increase in the use of ^{13}C NMR as a structural tool and as a probe into the electronic nature of transition metal organometallic complexes, particularly carbonyl-containing complexes. Some recent studies have been devoted to the investigation of the various factors influencing the shieldings of carbonyl carbons in substituted complexes [1—7]. In general it is found for $M(CO)_nL$ compounds (where L is a neutral 2-electron donor) that the complex containing the best donor L has the most deshielded carbonyl signals. For $M(CO)_nX$ compounds (where X is a neutral one-electron donor) much less information is available. For $Re(CO)_5X$ compounds [2] it is found that the compound with the best electron donor substituent X has the

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most deshielded carbonyl signals. Thus shielding of the carbonyl signals of (

$Re(CO)_5X$ compounds increases in the order of X groups $Me_3Pb < CH_3 < CH_3$($Cl_3Si < Br$. In the five coordinate complexes $(CO)_4CoEX_3$ (E = C, Si, Ge, Sn o Pb) resonances are deshielded for the derivatives in which X = Ph, CH_2Ph, or n-butyl, relative to those in which the Group IV bears halogen substituents [8

In this report we present our findings concerning the stereochemistry and shielding of some metal carbonyl compounds containing the one-electron liga methyl, acetyl, chlorine, bromine and iodine.

Experimental

Instrumentation and ^{13}C NMR procedures

The ^{13}C NMR spectra were obtained with a Varian XL-100-15 spectrometer operating at 25.2 MHz under conditions of proton decoupling with an externa ^{19}F lock. ^{13}C NMR chemical shifts were measured relative to internal solvent and are reported relative to tetramethylsilane (TMS) with downfield being tak as positive. The conversion factors employed in this work are:

$$\delta(TMS) = \delta(CH_2Cl_2) + 53.89 \text{ ppm}$$

$$\delta(TMS) = \delta(CHCl_3) + 77.19 \text{ ppm}$$

Tris(acetylacetonato)chromium(III), about 0.05 *M*, was added to each NMR sample as a shiftless relaxation reagent [9].

Materials

The $M(CO)_5X^-$, M = Cr, Mo, W and X = Cl, Br, I, derivatives were prepared the appropriate hexacarbonyl by the method of Abel et al. [10]. The compou $(C_7H_7)Mo(CO)_2X$ [11], $(C_5H_5)Mo(CO)_3X$ [12—14], *trans-* and *cis-*$(C_5H_5)Mo(C$ $(PPh_3)X$ [15], *trans-*$(C_5H_5)Mo(CO)(PPh_3)_2Cl$ [13], $(C_5H_5)Mo(CO)_2(L)COCH_3$ [16,17], and $(C_5H_5)Fe(CO)(L)COCH_3$ [18], were all prepared by literature methods. Purity was determined by comparison of melting points and IR spectra with published data, and where appropriate the mass spectrum was also determined.

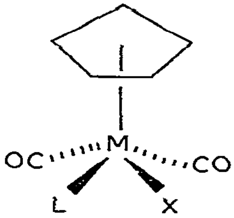
Observed ring carbon chemical shifts for cyclopentadienylmolybdenum hali were as follows: $CpMo(CO)_3Cl$, 95.9; $CpMo(CO)_3Br$, 95.4; $CpMo(CO)_3I$, 94.4; *cis-*$CpMo(CO)_2(PPh_3)Cl$, 94.3; *cis-*$CpMo(CO)_2(PPh_3)Br$, 94.1; *cis-*$CpMo(CO)_2$-$(PPh_3)I$, 93.2; *trans-*$CpMo(CO)_2(PPh_3)I$, 92.8; *trans-*$CpMo(CO)(PPh_3)_2Cl$, 93.1. All of these resonances occurred as sharp singlets.

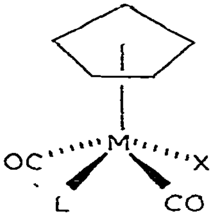
Results and discussion

Complexes of the general formula $CpM(CO)_2(L)X$ (M = Mo or W, L = CO, phosphine, or phosphite; X = halide or alkyl) exhibit structures which can be described as distorted square pyramids with the cyclopentadienyl group occup ing the apical position [19,20]. Single crystal X-ray structure determinations [21,22] and solution IR and proton NMR studies [15,19,20] have shown that these structures persist in both phases. Carbon-13 NMR studies of such complexes are limited to the early work of Lauterbur and King [23] using rapid passage techniques, and a brief mention of $CpW(CO)_3CH_3$ by Randall and coworkers [24].

A natural consequence of the geometry of the $CpM(CO)_3X$ derivatives is the expectation of two terminal carbonyl resonances. Two of the carbonyls are *cis* to the one electron ligand while the third is *trans*, and in the absence of fluxional behavior, these two types of carbonyls should be magnetically nonequivalent. As seen in Table 1 this expectation is fully realized for all of the complexes investigated in this study. In all cases, the resonance of the carbonyl carbon *trans* to the one electron ligand occurs at lowest field, the range of $\delta_{trans} - \delta_{cis}$ being 15—18 ppm.

Substituted derivatives of the formula $CpM(CO)_2(PR_3)X$ exist as *cis* or *trans* isomers, the isomer ratio depending upon R, X, and the method of preparation





[15,19,20]. The initial aim of this portion of the study was to unequivocally establish the solution structures of these complexes. Previous stereochemical assignments were based on proton NMR spectroscopy and, with less certainty, IR spectra [15]. The C-13 data obtained for these complexes are wholly consistent with conclusions based on the other methods, but are far more compelling. In all cases the complexes assigned *cis* geometries on the basis of NMR and IR give rise to two resonances, as expected; the lower field signal having $J(P—C) \simeq 28$ Hz, the other a smaller (~5.0 Hz) splitting. *trans*-$CpMo(CO)_2(PPh_3)I$ exhibits one CO resonance (doublet, $J(P—C) = 27.4$ Hz). It is tempting on the basis of size of coupling constants alone to assign the low field resonance in the *cis* isomer to the CO *cis* to the phosphorus ligand by analogy with the *trans* complex (both CO's *cis* to phosphorus). This assignment is made with greater confidence in light of the data obtained fro *trans*-$CpMo(CO)(PPh_3)_2Cl$, in which the phosphines are *trans* and thus both *cis* to the carbon monoxide ligand. In this case a triplet ($J(P—C) = 27.2$ Hz) is observed for the carbonyl carbon, firmly establishing the assignments made above. The *trans* geometry of this complex is firmly established by the observation of a triplet C_5H_5 proton resonance ($J(P—H) = 1.5$ Hz) and only one resonance in the ^{31}P spectrum.

Shielding trends of the metal carbonyl halides

There is an increase in shielding for the majority of metal carbonyl halide compounds in the order $Cl < Br < I$, when all other factors are held constant. The variation in shielding in a given series of halides (metal and other ligands remaining constant) is 4 ppm or less. It is therefore important that the solvent be held constant to eliminate solvent shifts which can be as large as 2 ppm. In certain cases the carbonyl shielding values in a halide series are nearly constant (i.e. $Cr(CO)_5X^-$ (*cis* and *trans*); $Mo(CO)_5X^-$ (*trans*); $W(CO)_5X^-$ (*trans*); $Re(CO)_5X$

TABLE 1

^{13}C NMR SHIELDING DATA OF SOME HALOCARBONYL COMPLEXES

Compound [c]	δ(CO) (ppm) (*trans* to X) (J(P—C)) [e]	δ(CO) (ppm) (*cis* to X) (J(P—C)) [e]
$[Cr(CO)_5Cl]^-$ [d]	225.3	216.7
$[Cr(CO)_5Br]^-$ [a]	224.7	216.1
$[Cr(CO)_5I]^-$ [b]	226.7	216.4
$[Mo(CO)_5Cl]^-$ [a]	213.8	205.3
$[Mo(CO)_5Br]^-$ [a]	214.0	204.8
$[Mo(CO)_5I]^-$ [b]	214.4	202.0
$[W(CO)_5Cl]^-$ [a]	201.9	199.4
$[W(CO)_5Br]^-$ [a]	201.9	198.5
$[W(CO)_5I]^-$ [b]	202.0	197.0
$CpMo(CO)_3Cl$	241.3	224.5
$CpMo(CO)_3Br$	239.0	222.8
$CpMo(CO)_3I$	236.1	220.8
$CpMo(CO)_2(PPh_3)Cl$ (*cis*)	255.6 (28.6)	242.8 (5.4)
$CpMo(CO)_2(PPh_3)Br$ (*cis*)	253.6 (28.2)	240.6 (5.8)
$CpMo(CO)_2(PPh_3)I$ (*cis*)	250.3 (28.6)	236.8 (5.0)
$CpMo(CO)_2(PPh_3)I$ (*trans*)		232.4 (27.4)
$CpMo(CO)(PPh_3)_2Cl$ (*trans*)		267.0 (27.2) [f]
$(C_7H_7)Mo(CO)_2Cl$ [g]	216.6	
$(C_7H_7)Mo(CO)_2Br$ [g]	214.9	
$(C_7H_7)Mo(CO)_2I$ [g]	212.3	
[*trans*-$W(CO)_4(CS)Cl]^-$ [b,h]	199.2	
[*trans*-$W(CO)_4(CS)Br]^-$ [b,h]	198.5	
[*trans*-$W(CO)_4(CS)I]^-$ [b,h]	196.5	
trans-$H_3CCW(CO)_4Cl$ [i]	194.0	
trans-$H_3CCW(CO)_4Br$ [i]	192.7	
trans-$H_3CCW(CO)_4I$ [i]	191.7	

[a] $(C_2H_5)_4N^+$ salt. [b] $(C_4H_9)_4N^+$ salt. [c] The solvent is CH_2Cl_2 unless otherwise indicated. [d] $(CH_3)_4N^+$ salt. [e] Coupling constants in Hz. Doublets unless otherwise specified. [f] 1 : 2 : 1 triplet. [g] $CHCl_3$ solvent. [h] Ref. 29. [i] Ref. 30.

(*trans*) [2]; $CpFe(CO)_2X$ [7]. Where a trend exists, it is found that the compound with the best electron donor halide has the most shielded carbonyl signal(s). This is opposite to previous trends in metal carbonyl compounds. However a similar shielding trend is found for α-carbon atoms of alkyl halides [25]. It has been suggested in this case that the diamagnetic contribution to the overall shielding of a carbon nucleus becomes more important as the atomic number of the neighbouring substituent atom(s) increases and causes the signal to be found at higher field [26]. There is also a decrease of this shielding contribution with increased distance of the substituent from the carbon nucleus in question. Thus the diamagnetic contribution is not observed at the β-carbon of alkyl halides [25]. It should be noted that the chemical shifts of the *trans* carbonyl carbons in $Mo(CO)_5X^-$ and $W(CO)_5X^-$ are essentially invariant.

All other things being equal, carbonyl carbon atoms in third row metal carbonyl halides are more shielded than second row compounds which are more shielded than first row compounds within a metal triad. This phenomenon has been observed before [1] and it has been suggested that the diamagnetic shielding influence of the metal itself is an important factor in this shielding trend [6].

Substitution of CO by triphenylphosphine in cyclopentadienyl metal carbonyls invariably results in a decrease in carbonyl stretching frequencies [19]. These data are taken to indicate increased electron density at the metal atom, reflected in increased retrodative M → L bonding. The data in Table 1 for the cyclopentadienylmolybdenum complexes are consistent with this idea, as the CO resonances move to lower field by 14—20 ppm on substitution, such shifts being indicative of increased metal-to-CO back-bonding [5—7]. The most dramatic example of this effect is the trend in δ(CO) for $CpMo(CO)_3Cl$ (241.3, 224.5), *cis*-$CpMo(CO)_2(PPh_3)Cl$ (255.6, 242.8), and *trans*-$CpMo(CO)(PPh_3)_2Cl$ (267.0). The resonances observed for the cyclopentadienyl ring carbons in these complexes are relatively insensitive to changes in the number and type of other attached ligands (Experimental section) and thus convey no obvious information about changes in metal—ring bonding.

Methyl and acetyl complexes

In conjunction with studies described above we have obtained the C-13 NMR spectra of a related series of molybdenum, tungsten and iron complexes containing the one-electron carbon ligands methyl and acetyl. These results and those from previous studies are given in Table 2. The complexes $CpM(CO)_3CH_3$, (M = Mo or W) show two resonances in the carbonyl region, readily attributed to the CO *trans* to methyl (lowest field) and the two carbonyls *cis* to methyl *. This is the same pattern observed for the tricarbonyl halide complexes (Table 1). The difference in chemical shifts between the Mo and W complexes is an example of the "triad effect", consistent with trends observed for unsubstituted metal carbonyls of Groups VI, VII and VIII [1] and for the $[M(CO)_5X]^-$ complexes (Table 1).

The methyl and acetyl compounds $CpM(CO)_2(PPh_3)CH_3$ (M = Mo, W) and $CpMo(CO)_2(PPh_3)COCH_3$ have been assigned *trans* stereochemistry in solution [16] and the latter has been shown to have this structure in the solid state [21]. The data in Table 2 are consistent with these assignments. The cyclohexyl isocyanide complex $CpMo(CO)_2(CNCyh)COCH_3$ was suggested to exist as a *cis-trans* isomeric mixture on the basis of proton NMR measurements [17]. In accord with this assignment we observe two Cp resonances (Table 2) and three carbonyl resonances. On the basis of relative intensities we assign the 233.9 ppm δ(CO) resonance to the *trans* isomer and the 246.0 and 238.7 ppm resonances to the magnetically nonequivalent CO's in the *cis* isomer (vide supra). The acetyl CO resonances are assigned as 267.6 ppm = *trans*, 270.4 = *cis* on the basis of intensities. All of the acetyl complexes exhibit $\underline{C}OCH_3$ resonances at very low field indicating extensive metal-to-carbon back-bonding as previously suggested on the basis of IR evidence [27] and confirmed by X-ray for the complex $CpMo(CO)_2(PPh_3)$-

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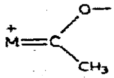
* Our data for $CpM(CO)_3CH_3$ disagree with those given in ref. 24, even taking into account ambiguous use of the *cis-trans* terminology. The values given here are consistent with the data for the halide complexes in terms of both relative chemical shifts and intensities.

TABLE 2

CARBON-13 NMR DATA FOR METHYL AND ACETYL COMPLEXES [a]

Complex	δ(CO) *trans* to R (J(P—C)) [b]		δ(CO) *cis* to R (J(P—C)) [b]	δ(CH_3) (J(P—C)) [b]	δ($\underline{C}OCH_3$) (J(P—C)) [b]	δ(Cp) [c]
$CpMo(CO)_3CH_3$	239.2 (—)		226.1 (—)	—22.37 (—)		92.13
$CpMo(CO)_2(PPh_3)CH_3$ (*trans*)			235.7 (23.0)	—19.2 (9.6)		91.8
$CpMo(CO)(PPh_3)COCH_3$ (*trans*)			238.1 (23.6)	50.51 (—)	263.2 (10.6)	96.19
$CpMo(CO)_2(PPhMe_2)COCH_3$ (*trans*)			236.9 (23.6)	51.52 (—)	266.8 (12.5)	95.40
$CpMo(CO)_2(CNCyh)COCH_3$ [d] (*trans*)			233.9 (—)	50.14 (—)	267.6	94.5
$CpMo(CO)_2(CNCyh)COCH_3$ [d] (*cis*)	246.0 (—)		238.7 (—)	48.03 (—)	270.4	94.9
$CpW(CO)_3CH_3$	228.6 (—)		215.5 (—)	—35.06 (—)		90.88
$CpW(CO)_2(PPh_3)COCH_3$ (*trans*)			230.0 (17.1)	53.12 (—)	251.2 (11.6)	94.72
$CpFe(CO)_2CH_3)$ [e]		218.4 (—)		—23.5 (—)		85.3
$CpFe(CO)(PPh_3)CH_3$		222.5 (31.9)		—22.3 (22.2)		84.15
$CpFe(CO)_2COCH_3$ [e]		215.7 (—)		52.0	254.4	86.9
$CpFe(CO)(PPh_3)COCH_3$		219.57 (30.52)		52.31 [f]	277.0	84.94
$CpFe(CO)(CNCyh)COCH_3$		217.64 (—)		50.59	268.36 (—)	84.06

[a] Chemical shifts in ppm downfield from internal TMS. [b] Coupling constants given in Hz. [c] Sharp singlets in all cases. [d] Spectrum of 30 : 70 *cis* : *trans* mixture measured. [e] Data from ref. 7 and 24. [f] Broad: phosphorus—carbon coupling not observed. See text.

$COCH_3$ [21]. These resonances approach the region of absorption associated with "carbene" ligands [1], consistent with the importance of the resonance structure  $\overset{+}{M}{=}C(O^{-})CH_3$ [27]. It has been shown that these and related acyl complexes are readily alkylated to yield cationic carbene complexes [28].

Replacement of CO by other donor ligands in $CpMo(CO)_3CH_3$ causes the resonance of the carbonyls *cis* to the one electron ligand to move to lower field by 8—12 ppm, consistent with increased M → CO back-bonding in the substituted derivatives. The same conclusions have been drawn for these complexes on the basis of proton NMR and IR data [16,17,27]. For *trans*-$CpMo(CO)_2(L)COCH_3$ (L = PPh_3, PPhMe, CNCyh), δ(CO) responds in the direction predicted by differences in σ-donor, π-acceptor abilities, while the trend in δ($\underline{C}OCH_3$) is completely opposite. Differences between the values are relatively small, however, and this in conjunction with the recognized [16,20] importance of steric effects in complexes of such low symmetry and high coordination number precludes further useful analysis of these shielding trends at present.

As shown in Table 2, substitution of CO by PPh_3 in $CpFe(CO)_2CH_3$ to produce

$CpFe(CO)(PPh_3)CH_3$ results in a downfield shift of the remaining terminal carbonyl, paralleling the trends observed for all of the complexes cited here. Comparing the data for $CpFe(CO)(L)COCH_3$, the chemical shifts $\delta(CO)$ and $\delta(\underline{C}OCH_3)$ for L = CO, CNCyh and PPh_3 decrease in the same direction. In the triphenylphosphine derivative both acetyl carbon resonances ($\underline{C}OCH_3$ and $CO\underline{C}H_3$) were very broad at room temperature, while other resonances were sharp. One possible explanation for this observation is restricted rotation of the acetyl group as a result of double bond character in the Fe—acetyl carbon linkage. We plan to examine this possibility by means of variable temperature studies of a variety of acyl complexes in the near future. (*Note added in proof:* Two studies of related Mo and W complexes have recently appeared [31,32] Structural conclusions drawn are consistent with those discussed herein.)

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