^{13}C-Fourier Magnetic Resonance of Organometallic Compounds—A Functional Group Survey

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Summary ^{13}C Shifts of diamagnetic transition-metal complexes for the ligands CO, CN^-, CNR COMe, Me, σ-Ph C-(carbene), π-C_2H_4, π-arene, and π-allyl show very wide variations, and, specifically for the series $(\pi$-$C_5H_5)$ Fe-$(CO)_{3-n}X_n$ vary significantly with X

THE applications in organometallic chemistry of ^{13}C magnetic resonance have been rare and difficult [1] [8] The increased signal-to noise ratio made available by pulsed Fourier and, in the case of compounds containing C–H bonds noise decoupling, techniques allows the systematic study of a much wider range of organometallic compounds We report here a general survey of a wide range of transition metal–carbon bonds and structural types, and a study of the particular series $(\pi$-$C_5H_5)Fe(CO)_{3-n}X_n$

The shift range (see Table) for the ligands studied is large (400 p p m or 9 kHz at 21 kG) and the line width commonly attainable is low (*ca* 1 Hz) so that the 'resolution' of the ^{13}C environment is good Compounds (**8**)—(**10**), for example each give internal shift differences of *ca* 250 p p m or more, the highest and lowest field resonances being from σ-methyl and carbene respectively Spectra were obtained for saturated solutions (10—25% w/w) using accumulation times of 10 min to 2 h In general, all the resonances within a given compound could be obtained only after several runs at various pulse lengths This is attributable to widely different relaxation times for various carbon atoms Detailed studies of these differences could thus prove both interesting and important

The observed shifts correlate reasonably well with, though show significant differences from, values expected from functional group surveys in purely organic samples [10] The cyanide resonances for compounds (**4**) and (**5**) are intermediate between the free ligand value (+169 p p m)[9] and the range observed in alkyl cyanides (+120 to +130 p p m) [9] The isocyanide resonance in (**6**) is similarly shifted upfield from the range for uncomplexed isocyanides (+157 to +169 p p m) [9] The acyl carbonyl in compound (**7**) on the other hand is found to low field of the range for organic aldehydes and ketones (+165 to +225 p p m) [10]

The methyl groups in (**8**) and (**10**) have shifts to high field of Me_4Si whereas the σ-aryl carbon bound to titanium in (**18**) shows an anomalously large downfield effect with respect to the same carbon in toluene (+138 p p m) [11] This large downfield shift could be due to a decrease in average excitation energies brought about by π-overlap with metal *d* orbitals † The carbene carbon [in (**9**)] absorbs in the very low field region usually associated with carbonium ions,[10] which is consistent with its formulation as an electron-deficient carbon [12]

TABLE [a]

No	Compound	$\delta(^{13}C{\equiv}O)$ p p m	$\delta(\pi\ ^{13}C_5H_5)$ p p m	$\delta(^{13}C$–Ligand carbons) p p m
(**1**)	$(CO)_2(\pi\ C_5H_5)FeCl^b$	+212 9	+85 6	—
(**2**)	$(CO)_2(\pi\ C_5H_5)FeBr^b$	+213 2	+85 4	—
(**3**)	$(CO)_2(\pi\ C_5H_5)FeI^b$	+213 8	+84 8	—
(**4**)	$(CO)_2(\pi\ C_5H_5)FeCN^{b\ f}$	+211 1	+85 9	+154 7 (CN)
(**5**)	$[(CO)(\pi\ C_5H_5)Fe(CN)_2]^-K^{+d\ f}$	+219 2	+82 6	+159 0 (CN)
(**6**)	$[(CO)(\pi\ C_5H_5)Fe(CNCH_2Ph)_2]^+Br^{-\ b}$	+212 1	+85 3	+147 4 (CNR) +51 4 (CH_2) +132 5 (C_1) +128 0 ($C_{2\ 6}$) +129 5 ($C_{3\ 5}$ +129 0 (C_4)
(**7**)	$(CO)_2(\pi\ C_5H_5)FeCOMe^b$	+215 7	+86 9	+254 4 (COR) +52 0 (Me)
(**8**)	$(CO)_2(\pi\ C_5H_5)FeMe^b$	+218 4	+85 3	−23 5 (Me)
(**9**)	$(CO)_5CrC(OMe)(Me)^{b\ f}$	+217 6 (*cis*) +223 6 (*trans*)	—	+362 3 (>C–) +49 1 (Me) +67 2 (OMe)
(**10**)	$(CO)_3(\pi\ C_5H_5)WMe^{b\ f}$	+239 2 (*cis*) +217 8 (*trans*)	+92 4	−28 9 (Me)
(**11**)	$(CO)_5MoP(OPr^i)_3{}^{g\ f}$	+206 2 (*cis*) +209 7 (*trans*)	—	+24 3 (Me) +57 0 (CH) *J*(P–M–C *cis*) 14 6 ± 2 Hz *J*(P–M–C *trans*) 12 2 ± 2 Hz
(**12**)	$(CO)_9Co_3CBr^{b\ h}$ ..	+186 2	—	Not observed (> CBr)
(**13**)	$(\pi\ C_6H_6)Cr(CO)_3{}^c$	+223 8	—	+93 7 (C_6H_6)
(**14**)	(π *m* xylene)$Mo(CO)_3{}^c$	+223 1	—	+115 6 ($C_{1\ 3}$) +96 4 (C_2) +98 2 ($C_{5\ 3}$) +92 7 ($C_{6\ 4}$) +21 5 (Me)
(**15**)	$[(\pi\ C_3H_5)PdCl]_2{}^b$	—	—	+111 3 (CH) +62 8 (CH_2)
(**16**)	$[(\pi\ C_2H_4)PtCl_3]^-K^{+e}$	—	—	+75 1 (C_2H_4)
(**17**)	$(\pi\ C_5H_5)_2TiCl_2{}^c$	—	+121 3	—
(**18**)	$(\pi\ C_5H_5)_2Ti(\sigma\ Ph)_2{}^{c,f}$	—	+116 8	+192 9 (C_1) +136 0 ($C_{2\ 6}$) +127 3 ($C_{3\ 5}$) +124 3 (C_4)

[a] Resonances reported (±0 3 p p m) downfield relative to internal Me_4Si = 0 p p m and using internal C_6F_6 for the ^{19}F lock system [b] Saturated $CHCl_3$ solution [c] Saturated CH_2Cl_2 solution [d] Aqueous solution with internal MeOH referred to Me_4Si and external C_6F_6 [e] Aqueous solution with external Me_4Si and external C_6F_6 [f] Assignments made on the basis of line intensities after multiple runs at various pulse lengths [g] Neat liquid with internal Me_4Si and C_6F_6 [h] Spectrum obtained after 5 h accumulation

The π-bonded ligands in (**13**), (**14**), and (**16**) all show large upfield shifts with respect to the free ligand [$\delta(C_6H_6)$ = + 129 p p m ,[11] δ(*m*-xylene) = + 120 to + 129 p p m [11] and $\delta(C_2H_4)$ = + 124 p p m [3]] This shift has been attributed to the changes in hybridization associated with the use of π-orbitals for σ-bonding with metal *d* orbitals [2,6,7,13] It is of interest that the ^{13}C-resonances of the methyl groups on the ring in (**14**) are unaffected by complexation, [(Me) in (*m*-xylene) = + 21 5[11]], whereas their proton resonances are shifted upfield,[14] contrary to what one would expect if diminution in ring currents were the major cause of the upfield shift The differences between σ-aryl and π-arene shifts are notable The large chemical shift difference between the central and terminal carbon atoms in (**15**) is consistent with results for tricarbonyl butadieneiron [7,8]

Restriction to any one ligand naturally reduces the observed ^{13}C shift range since a major part of the ^{13}C environment is conserved Nevertheless, for the most common

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† The ^{13}C chemical shift is dominated by the paramagnetic shielding term which varies inversely with ΔE, the average excitation energy.

ligand studied here (CO) the range is still high nearly 55 p p m The technique can consequently distinguish different stereochemical environments for CO in any one case Thus *cis*- and *trans*-differences are obtained for (**9**), (**10**), and (**11**) The sense of the shift difference apparently depends on the local stereochemistry at the metal atom since it is different in the octahedral and pyramidal examples (**9**) and (**10**) respectively

An alternative explanation is that this CO shift is primarily dependent on the steric and electronic requirements of the other ligands This possibility is shown to be reasonable by the results for the series $(\pi\text{-}C_5H_5)Fe(CO)_{3-n}X_n$ in which variations of X gives a 10 p p m shift for CO and a 5 p p m shift range for $(\pi\text{-}C_5H_5)$

In (**11**) the *cis*-^{31}P–M–^{13}C coupling constant is slightly larger than the *trans*- as has been previously reported for $^2J(^1H\text{–}M\text{–}^{13}C)$ in $(CO)_5MnH$ [8]

Other investigators have been unable to observe carbonyl resonances for cobalt compounds presumably because they are broadened by spin–spin coupling of ^{13}C with ^{59}Co ($I = 7/2$) undergoing moderately rapid quadrupole-induced relaxation [1,5] We have successfully observed such a broadened carbonyl resonance ($W_{\frac{1}{2}}$ 40 Hz) but only for (**12**) We were unable to observe a resonance for the carbinyl carbon (C–Br) in this compound

We conclude that ^{13}C studies of organometallic compounds will prove a powerful structural tool, particularly for groups like CO unamenable to proton studies Additionally, the large ^{13}C shifts facilitate mechanistic studies of fluxional complexes [15]

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