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SUBSTITUENT EFFECTS IN ALLYLMETAL CARBONYLS

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Summary

The Mössbauer and IR spectra of $(\pi\text{-}C_3H_4X)Fe(CO)_2NO$ ($X = H$, 1-CH_3, 2-CH_3, 1-Cl) indicate that the carbonyl and nitrosyl groups absorb the inductive effects of allyl substituents, leaving the metal *s* electron density relatively unaffected. The NMR spectra and carbonyl vibrational frequencies of $(\pi\text{-}C_3H_4X)Co(CO)_2PPh_3$ ($X = H$, 1-CH_3, 2-CH_3, 2-Cl) show that the electronic effects are similar to those found in the parent $(\pi\text{-}C_3H_4X)Co(CO)_3$ compounds, and that there is no evidence of asymmetric π,σ-bonding in $(\pi\text{-}C_3H_4X)$-$Co(CO)_2PPh_3$.

Introduction

The substituent in $(\pi\text{-}C_3H_4X)Co(CO)_3$ ($X = H$, 1-CH_3, 1-Cl, 2-CH_3, 2-Cl) [1] has been shown to have an inductive electronic effect on the IR carbonyl frequencies similar to that found in $(\pi\text{-}C_6H_5R\text{-}\pi\text{-}C_4H_5)Fe(CO)_3$ [2] and $(\pi\text{-}C_6H_5R)M(CO)_3$ [3 - 5], in which $\nu(CO)$ correlates with the Hammett σ-function. The substituent also has a small effect on the OC—M—CO angle [6] and influences significantly the isomer proportion of the phosphine and phosphite compounds $(\pi\text{-}C_3H_4X)Co(CO)_2PY_3$ ($Y = Ph$, OPh, OCH_3) [7]. The carbonyl vibrational frequencies, however, do not correlate with the anomalous relative rates of monosubstitution by PPh_3 of $(\pi\text{-}C_3H_4X)Co(CO)_3$ [8]. Although substituent effects on the rates of nucleophilic substitution reactions of metal carbonyls are not well documented [9,10], it seems likely that the relative rates of substitution of $(\pi\text{-}C_3H_4X)Co(CO)_3$ are not due to electronic inductive effects of the substituents. The PMR spectra of $(\pi\text{-}C_3H_4X)Co(CO)_3$ show that they are normal π-allyl compounds [11]. The effects of substituents in $(\pi\text{-}C_3H_4X)Fe(CO)_2NO$ and $(\pi\text{-}C_3H_4X)Co(CO)_2PPh_3$ using Mössbauer, IR and PMR spectroscopy are now reported.

Results and discussion

Allyldicarbonylnitrosyliron compounds

Compounds containing the iron—allyl group include π-$C_3H_5Fe(CO)_3X$ (X = Cl, Br, I) [12 - 18], [π-$C_3H_5Fe(CO)_3]_2$ [19], (π-$C_3H_5)_2Fe(CO)_2$ [20] and π-$C_3H_5Fe(CO)_2NO$ [21 - 25]. Only the first group of compounds has been studied using Mössbauer spectroscopy [17,18].

The Mössbauer results (Table 1) indicate that the chemical shift values (which measure the metal *s* electron density), occur within a narrow velocity range and are equal within experimental error (with the exception of the 2-methyl compound). The carbonyl stretching frequencies ν(CO), however, clearly show the effects of the substituents (Table 2). The electron-donating methyl group weakens the CO bond (qualitatively $CH_3 \rightarrow C_3H_4 \rightarrow M{=}C{=}O$) by electron donation into antibonding π^* CO orbitals and lowers ν(CO), whereas the chlorine atom withdraws electrons and increases (ν(CO) $Cl \leftarrow C_3H_4 \leftarrow Fe \leftarrow C{\equiv}O$).

The substituents have similar effects on the nitrosyl stretching frequencies ν(NO) (Table 2).

The constancy of δ and the changes in ν(CO) and ν(NO) with substituents suggest that the electronic effect of the substituent is absorbed by the carbonyl and nitrosyl groups with the metal acting as an electron conductor.

δ increases with decreasing π-acceptor power of the ligand by increasing the metal *d* orbital population and consequently shielding the metal *s* electrons. The effect of σ-donation from the ligand varies depending on whether the donation is mainly to *s* or to *d* and *p* orbitals. Rate constant data for the S_N2 reactions of π-$C_3H_5Fe(CO)_2NO$ and $Fe(CO)_2(NO)_2$ with phosphines, and car-

TABLE 1

MÖSSBAUER PARAMETERS[a] OF (π-C_3H_4X) Fe $(CO)_2NO$

X	Chemical shift (δ) (mm · sec^{-1})	Quadrupole splitting (Δ) (mm · sec^{-1})
H	0.372 ± 0.001	1.178 ± 0.002
1-CH_3	0.373 ± 0.001	1.148 ± 0.003
2-CH_3	0.363 ± 0.001	1.188 ± 0.002
1-Cl	0.374 ± 0.002	1.250 ± 0.004

[a] Measured at 77 K with reference to a sodium nitroprusside absorber as standard.

TABLE 2

INFRARED CARBONYL AND NITROSYL FREQUENCIES OF (π-$C_3H_4X)Fe(CO)_2NO$

(Cyclohexane solution, ± 1 cm^{-1})

X	ν (CO) (cm^{-1})		ν (NO) (cm^{-1})
	A_1	B_1	
H	2037(vs)	1984(vs)	1756(vs)
1-CH_3	2030	1978	1754
2-CH_3	2030	1978	1754
1-Cl	2046	2000	1762
2-Cl	2044	1998	1761

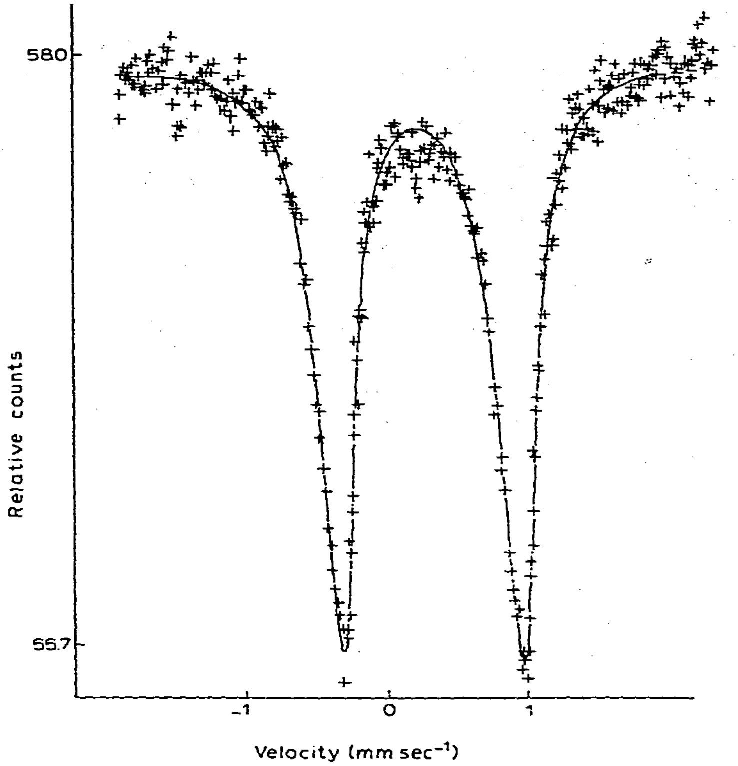
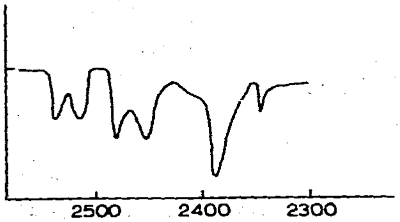


Fig. 1. Mössbauer spectrum at 77 K of (1-CH_3-π-C_3H_4)Fe$(CO)_2$(NO). The velocity scale is relative to sodium nitroprusside, and the solid lines represent a least squares fit to Lorentzian line shapes.

bonyl frequencies of both compounds [k_2 and ν(CO) of π-C_3H_5Fe$(CO)_2$NO are lower [24]] indicate that there is a higher electronic charge to the metal in π-C_3H_5Fe$(CO)_2$NO due to the weaker π-acceptor or stronger σ-donor property of the π-allyl ligand relative to the nitrosyl. The chemical shifts of π-C_3H_5Fe-$(CO)_2$NO (δ 0.372 mm·sec^{-1}) and Fe$(CO)_2$$(NO)_2$ [26] (δ 0.32 mm·sec^{-1}) therefore indicate that the π-allyl ligand is a weaker π-acceptor than the nitrosyl or (since increasing σ-donor power of the ligand to metal *p* and *d* orbitals increases δ) that σ-donation by the π-allyl ligand to *p* and *d* orbitals is more important than σ-donation by the nitrosyl to the *p* and *d* orbitals of the metal.

Further information on the metal—carbonyl and metal—nitrosyl groups may be had from the 600 - 250 cm^{-1} region of the IR, where the metal—carbonyl and metal—nitrosyl stretching and bending modes normally occur.



2035 + 500,475 = 2535,2510
1980 + 500,475 = 2480,2455
1745 + 635,600 = 2380,2345

Fig. 2. 2500 cm^{-1} region of the infrared spectrum of π-C_3H_5Fe$(CO)_2$NO.

TABLE 3

INFRARED SPECTRA OF (π-C_3H_4X)Fe(CO)$_2$NO
(600—400 cm^{-1} region, polythene cells, CH_2Cl_2 solution, ± 2 cm^{-1})

X	δ (M—C—O) (cm^{-1})			ν (M—C) (cm^{-1})	
H	601(s)	565(sh)	541(s)	500(m)	472(m)
1-CH_3	603(s)	568(sh)	549(s)	499(m)	460—470(m)
2-CH_3	602(s)	580(sh)	541(s)	499(m)	473(m)
1-Cl	593(s)	567(sh)	541(s)	490(m)	462(m)
2-Cl	595(s)	579(sh)	541(s)	491(s)	464(m)

Assignment of M—CO and M—NO bands in this spectral region is facilitated by some general considerations. Usually in (π-moiety)M(CO)$_3$ compounds δ(M—C—O) bands are found [28,29] at 500 - 700 cm^{-1} while ν(M—C) bands are expected at ≈ 500 cm^{-1}. Metal—nitrosyl bands are found to be more intense than metal—carbonyl bands, with ν(M—NO) at higher frequencies than δ(M—N—O) [30 - 33], the reverse of that found for the M—C—O modes. The δ(M—C—O) ($A_1 + B_1 + A_2 + B_2$ in C_{2v} symmetry) and ν(M—C)-($A_1 + B_1$) modes are therefore assigned as in Table 3. It is noted that ν(M—C) is lowered appreciably by the chloro-substituent.

Unusually intense combination bands are found in the 2500 cm^{-1} region. From their positions, relative intensities and shapes, these bands are likely to be combinations of ν(CO), ν(M—CO) and ν(NO), ν(M—NO) modes, and support the assignments in Table 3.

The relative intensity ratio of the A_1 and B_1 ν(CO) bands, $I(B_1)/I(A_1) = 1.6$, shows that the OC—M—CO angle [34] is 103°, which is nearly equal to that of π-C_3H_5Co(CO)$_3$ [6,35]. π-C_3H_5Fe(CO)$_2$NO therefore has a normal π-allyl structure, i.e. the compound has a distorted tetrahedral structure and the π-allyl group occupies between one and two coordination sites. π-C_3H_5Fe(CO)$_2$NO has, formally, a $3d^{10}$ electron configuration, is diamagnetic and is in the low-spin state. The only contribution to the quadrupole splitting is the asymmetry parameter.

The quadrupole splitting, Δ, of π-C_3H_5Fe(CO)$_2$NO (Δ 1.178 mm·sec^{-1}) is much higher than that of Fe(CO)$_2$(NO)$_2$ [26] (Δ 0.34 mm·sec^{-1}), indicating that the allyl group causes greater asymmetry of the electric field than the nitrosyl. This is not surprising in view of the lower π-acceptor ability of the allyl ligand and its mode of bonding through three carbon atoms, which would be expected to reduce considerably the cubic symmetry of the tetrahedral field.

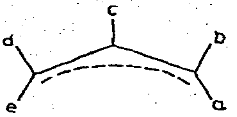
The electronic effects of the substituents are not reflected in the quadrupole splitting (Table 1), which shows that the substituents distort the electric field not simply by electronic effects. Delocalisation of the allyl π-electrons may determine the relative quadrupole splitting; the 1-Cl-substituted compound has the most delocalised bond and the largest quadrupole splitting.

Allyldicarbonyl(triphenylphosphine)cobalt compounds

The proton chemical shifts and proton—proton coupling constants of the (π-C_3H_4X)Co(CO)$_2$PPh$_3$ compounds are given in Table 4. The spectra are

TABLE 4

PMR SPECTRA OF π-$C_3H_4XCo(CO)_2PY_3$
($CHCl_3$ solution)



X	Y	Chemical shifts (τ ppm)			Coupling constants (Hz)	
H	Ph	5.58 (c)	7.50 (b, d)	7.96 (a, e)	5.0 (b, d)	11.8 (a, e)
2-Cl	Ph		7.07 (b, d)	7.87 (a, e)		
2-CH_3	Ph		7.46 (b, d)	8.12 (a, e) 8.4 (CH_3)		
1-CH_3	Ph	5.69 (c)	7.82 (b) 7.17 (d)	8.12 (a) 8.4 (CH_3)		
H	OPh	6.11 (c)	7.50 (b)	8.4 (a)		
2-Cl	OPh		6.90 (b)	7.93 (a)		

those of normal π-allyl compounds [36]. The spectra of the 2-CH_3- and 2-Cl-$C_3H_4Co(CO)_2PPh_3$ compounds were of particular interest in view of the asymmetrically-bonded π-allyl with a partial σ-bond in (2-Cl-π, σ-C_3H_4)Fe-(CO)(PPh_3)NO [37]. However, only two allyl peaks due to the *syn-* and *anti*-protons of a π-allyl group were found in each, indicating a completely delocalised π-bond. The spectrum of (2-ClC_3H_4)$Co(CO)_2P(OPh)_3$ also showed only two peaks.

The peaks due to the *syn-* and *anti*-protons of π-$C_3H_5Co(CO)_2PPh_3$ were split by ^{31}P—H coupling. A coupling constant of ≈ 2Hz was observed for the *syn*-protons and ≈ 0Hz for the *anti*-protons, which indicates that the *anti*-protons are *cis* to the PPh_3 group [38]. The allyl group must then be tilted with respect to the PPh_3 group.

The allyl protons are more screened by the metal in (π-C_3H_4X)$Co(CO)_2$-PPh_3 relative to (π-C_3H_4X)$Co(CO)_3$, due largely to the poorer π-acceptor ability of PPh_3 relative to CO.

The AK_2X_2 spin system of the π-allyl group does not simplify to AX_4 in the presence of excess PPh_3, unlike compounds of the type π-$C_3H_5PdL_1L_2$ ($L_1 \neq L_2$) [36].

The carbonyl stretching frequencies (Table 5) show that the electron-accepting Cl atom in both the 1- and 2-positions lowers the carbonyl π^* orbital

TABLE 5

IR SPECTRA OF (π-C_3H_4X) Co $(CO)_2$ PPh_3: CARBONYL STRETCHING FREQUENCIES
(Cyclohexane solution, ± 1 cm^{-1})

X	B_1	A_1	k (CO) ^{a} (md · $Å^{-1}$)
H	1948	2000	15.75
2-Cl	1958	2008	15.89
2-CH_3	1938	1991	15.60
1-Cl	1961	2011	15.94
1-CH_3	1940	1992	15.62

^{a}Ref. [39].

population and increases ν(CO), whereas the electron-donor, CH_3, lowers ν(CO). The trend parallels that found for (π-C_3H_4X)Co$(CO)_3$ [1], indicating that the nature of the allyl—metal bond does not change significantly. The relative intensity ratio of the ν(CO) bands, $I(B_1)/I(A_1) = 1.43$, indicates that the OC—M—CO bond angle [34] is ≈ 100° and is almost equal to that of π-$C_3H_5Co(CO)_3$ [6,35]. This shows that the PPh_3 group has little effect on the ligand distribution.

Experimental

(π-C_3H_4X)Fe$(CO)_2$NO compounds were prepared from NaFe$(CO)_3$NO [40] in ether and the corresponding allyl halide. Infrared spectra were obtained using a Perkin - Elmer 457 spectrometer, and were calibrated using H_2O and polystyrene. Mössbauer measurements were obtained using a Harwell Mössbauer Drive unit and electronics in conjunction with a Nuclear Data 4410 Analyser. The samples were run as frozen liquids at 77 K, which was facilitated by the use of a Harwell top-loading Mössbauer Cryostat enabling quick freezing. The source was ^{57}Co in a Pd matrix and was of nominal strength 4 mCi. All measurements were made with reference to a sodium nitroprusside absorber as standard. The spectra were fitted on an IBM 1130 computer using a least squares curve fitting programme. NMR spectra were obtained of $CHCl_3$ solutions at 30° using a Varian HR60 spectrometer, with reference to TMS as standard.

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