Inorganica Chimica Acta, *175* (1990) 187–191

^{55}Mn chemical shifts in carbonylmanganese alkyl and acyl complexes

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(Received February 5, 1990)

Abstract

The ^{55}Mn NMR chemical shifts in three series of compounds, $[(CO)_5MnCH_2C_6H_4X]$, $[(CO)_4(L)MnCOCH_2C_6H_4X]$ and $[(CO)_4(L)MnCH_2C_6H_4X]$, where X is a *meta* or *para* substituent and L a tertiary phosphine, trend linearly with the Hammett sigma constant of the substituent, with shielding increasing with electron donating ability of X. $^1J(^{31}P-^{55}Mn)$ coupling is observed in the ^{55}Mn NMR spectra of $[(CO)_4(L)MnCOCH_2C_6H_4X]$ complexes and in the solid-state ^{31}P CPMAS spectra of $[(CO)_4(PPh_3)MnCH_2C_6H_5]$ and $[(CO)_4(PPh_3)MnCOCH_2C_6H_{5-n}X_n]$, where X = H and Me$_3$ – 2, 4, 6.

Introduction

As part of our investigation of the steric and electronic effects of alkyl groups and tertiary phosphines on the ligand-induced insertion of carbon monoxide into manganese–carbon sigma bonds [1–3], we have examined the ^{55}Mn NMR chemical shift trends, with variation in *meta* and *para* aromatic substituent, in a series of benzyl–manganese complexes, $[(CO)_5MnCH_2C_6H_4X]$ and the acyl compounds, $[(CO)_4(L)MnCOCH_2C_6H_4X]$, where L = tertiary phosphine. NMR spectra for the phosphine-substituted alkyl species, $[(CO)_4(L)MnCH_2C_6H_4X]$, which are formed by slow decarbonylation of the acyl complexes in solution, were also recorded. A preliminary study has been made of solid-state ^{31}P CPMAS NMR spectra of phosphine-substituted alkyl- and acyl–manganese complexes.

Experimental

The compounds, $[(CO)_5MnCH_2C_6H_5]$, were prepared as described previously [2]. Solid samples of a mixture of *cis*- and *trans*-$[(CO)_4(L)MnCOCH_2C_6H_4X]$ and *cis*-$[(CO)_4(L)MnCH_2C_6H_4X]$ were obtained by evaporation of solvent after the reaction of $[(CO)_5MnCH_2C_6H_5]$ and tertiary phosphine in acetonitrile.

NMR solution spectra were recorded in $CDCl_3$ solution, generally at a concentration of 0.3 M; in the case of $[(CO)_4(L)MnCOCH_2C_6H_4X]$ and $[(CO)_4(L)MnCH_2C_6H_4X]$, spectra were recorded for the reaction mixtures. No concentration dependence of ^{55}Mn chemical shift was observed over a concentration range of 0.08 to 0.8 M. A temperature dependence of around 1–2 ppm/degree was noted from 20 to 45 °C; in order to minimise localised sample heating at the probe temperature of 21 °C, spectra were recorded without a decoupling pulse. ^{55}Mn spectra were obtained either on a Jeol JNM-FX-100 spectrometer operating at 24.64 MHz (90° pulse angle, 8 kHz spectral width, 16384 data points) or on a Bruker CXP-300 spectrometer operating at 74.224 MHz (45° pulse angle, 70 kHz spectral width, 16384 data points). ^{31}P spectra were recorded at 161.70 MHz (16.026 kHz spectral width, 65536 data points) on a Jeol JNM-GX-400 spectrometer. ^{55}Mn chemical shifts are expressed in ppm relative to saturated aqueous $KMnO_4$, via $Mn_2(CO)_{10}$ ($\delta = -2287$ ppm) as an internal reference, and ^{31}P chemical shifts relative to 85% phosphoric acid (coaxial capillary).

Solid-state ^{31}P NMR spectra were recorded at 121.5 MHz on a Bruker CXP-300 spectrometer at a spinning rate of 4 kHz using ^{1}H–^{31}P cross polarisation with radio-frequency fields of 0.8 and 2 mT, respectively, and referenced to 85% phosphoric acid via Ph_3P ($\delta = -9.9$ ppm).

Results and discussion

The ^{55}Mn NMR chemical shifts for the series of unsubstituted alkyl compounds, $[(CO)_5MnCH_2C_6H_4X]$, the triphenylphosphine-substituted alkyls,

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0020-1693/90/$3.50

cis-$[(CO)_4(Ph_3P)MnCH_2C_6H_4X]$ and the triphenylphosphine-substituted acyls, *cis*-$[(CO)_4(Ph_3P)MnCOCH_2C_6H_4X]$, are listed in Table 1. For a given aromatic substituent, X, the resonances are well separated, with the unsubstituted alkyl compounds being most shielded, and the phosphine-substituted acyls the least. In solution, the acyl complexes are known to exist as a *cis*/*trans* mixture, but, for non-sterically demanding substituents, the *cis* isomer predominates [4] and the resonance for the *trans* isomer is not observed. The alkyl compounds ($W_{1/2}$ = 4000–5000 Hz) and the phosphine-substituted acyls ($W_{1/2}$ = 1900–2500 Hz) give very broad resonances. The peaks for the substituted alkyls are, in most cases, relatively narrow ($W_{1/2}$ = 400–600 Hz) which has allowed the observation of phosphorus–manganese coupling, $^1J(^{31}P-^{55}Mn)$. The chemical shift values for $[(CO)_5MnCH_2C_6H_5]$ and $[(CO)_4(PPh_3)MnCH_2C_2C_6H_5]$ agree exactly with those reported previously [5].

The range of chemical shift values (51 ppm) with variation in the aromatic substituent, X, for the manganese alkyls, $[(CO)_5MnCH_2C_6H_4X]$, is approximately 10 times greater than that in the ^{13}C chemical shift in the benzylic carbon atom. There is close correlation (Fig. 1) of the chemical shift values with the Hammett sigma constant (values taken from ref. 6) for the *meta* or *para* aromatic substituent, with a systematic upfield shift (increased shielding) with increase in the electron donor ability of the substituent. The trend is the same as, and the chemical shift range very similar to, that observed previously for $\delta(^{95}Mo)$ in the $[(\eta^5-C_5H_5)(CO)_3MoCH_2C_6H_4X]$ series [7]. The electronic effect is in the same direction as that noted for the series $[(CO)_5MnCH_{3-n}F_n]$, where n = 0–3 [8]. The linear Hammett relationships of the ^{55}Mn and ^{95}Mo chemical shifts parallel those of the rate constants for the k_1 step in the phosphine-induced CO insertion reactions [2, 9].

A recent theoretical study concluded that ^{55}Mn chemical shifts are predominantly determined by the 3d contributions of the paramagnetic term, with increases in paramagnetic shift arising from increases in π-donating ability of the ligand and its hardness (decreasing σ-donating ability) [10]. Our results for the substituted benzylic systems are in accord with the σ-donation criterion.

The variation in ^{55}Mn chemical shift for the *cis*-$[(CO)_4(PPh_3)MnCH_2C_6H_4X]$ complexes is very similar. The linear Hammett relationship is maintained in the $[(CO)_4(PPh_3)MnCOCH_2C_6H_4X]$ system but the insertion of the carbonyl group results in significantly reduced sensitivity to the substituent, X.

We have observed [4] that the proportion of the *trans* isomer in the reaction mixture increases as the size of the benzylic group, achieved by substitution in the *ortho* aromatic positions, increases. In two cases, for the 2,4,6-tri-isopropylbenzyl and the 2,6-dichlorobenzyl complexes, ^{55}Mn resonances at $\delta = -1623$ and -1628 ppm, respectively, are observed downfield of the resonances assigned to the *cis* isomer ($\delta = -1793$ and -1754 ppm) and are tentatively assigned to the *trans* isomer.

A range of more than 200 ppm is observed in the ^{55}Mn chemical shifts of both the phosphine-substituted acyl and phosphine-substituted benzyl compounds with variation in the tertiary phosphine (Table 2). DeShong *et al.* [5] previously observed a similar phosphine effect for the complexes, $[(CO)_4(L)MnCH_2C_6H_5]$, for L = $P(n-Bu)_3$ and PPh_3, and concluded that the chemical shift difference was the result of a "subtle interplay of σ-effects in the phosphine complexes". Although we are unable to make a more definitive statement we have observed

TABLE 1. ^{55}Mn and ^{31}P NMR chemical shifts (and coupling constants, $^1J(^{31}P-^{55}Mn)$)

X	$[(CO)_5MnCH_2C_6H_4X]$ $\delta(^{55}Mn)$ (ppm)	$[(CO)_4(PPh_3)MnCH_2C_6H_4X]$ $\delta(^{55}Mn)$ (ppm) ($^1J(^{31}P-^{55}Mn)$ (Hz))	$[(CO)_4(PPh_3)MnCH_2C_6H_4X]$ $\delta(^{31}P)$ (ppm)	$[(CO)_4(PPh_3)MnCOCH_2C_6H_4X]$ $\delta(^{55}Mn)$ (ppm)	$[(CO)_4(PPh_3)MnCOCH_2C_6H_4X]$ $\delta(^{31}P)$ (ppm)	Hammett sigma constant
4-OMe	−2040	−1839(271)	61.84	−1682	51.23	−0.28
4-Me	−2032	−1833(257)	61.42	−1680	51.08	−0.14
3-Me	−2025	−1825(244)	61.28	−1681	51.08	−0.06
H	−2020	−1820(252)	61.25	−1677	51.16	0
4-F	−2018	−1821(208)	60.93	−1676	50.97	0.06
3-OMe	−2015	−1813(217)	62.27	−1673	51.14	0.10
4-Cl	−2008	−1804(253)	–	−1670	–	0.22
3-F	−1999	−1794(229)	–	−1672	–	0.34
3-Cl	−2002	−1789(285)	–	−1666	–	0.37
$3-CF_3$	−1994	−1790(212)	60.03	−1668	50.84	0.46
$4-CF_3$	−1989	−1777(298)	–	−1660	–	0.53

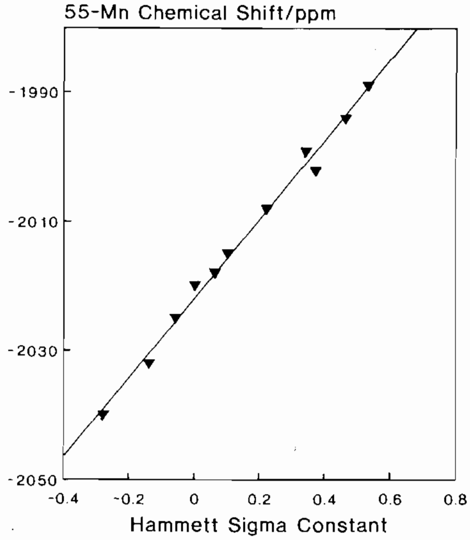

Fig. 1. Plot of variation in ^{55}Mn chemical shift with Hammett sigma constant for [(CO)$_5$MnCH$_2$C$_6$H$_4$X] complexes.

that, although it is generally the case that the more basic phosphines cause a smaller chemical shift, the values, for our wider series of phosphines, do not correlate closely with the Tolman electronic parameter [11]. Likewise there is no overall correlation with the cone angle [11] of the phosphine, although larger phosphines, with the notable exception of the strongly basic tricyclohexylphosphine, appear to be associated with the greater chemical shifts.

The $^1J(^{31}P-^{55}Mn)$ coupling constants for the [(CO)$_4$(PPh$_3$)MnCH$_2$C$_6$H$_5$] complexes are listed in Table 1. The value for the benzyl complex is comparable with that reported previously [5]. There is no apparent trend with substituent.

The ^{31}P chemical shifts in phosphine–alkyl and –acyl compounds (Table 1) vary only slightly with aromatic substituent, with the greater change being, as expected, in the alkyl series. With the exception of the 3-MeO group, donor substituents on the aromatic ring deshield the phosphorus nucleus in the alkyl compounds. $^1J(^{55}Mn-^{31}P)$ coupling was not observed in the ^{31}P spectra of the phosphine–alkyl complexes.

A further example of coupling to ^{55}Mn was observed in the ^{55}Mn solution spectrum of [(CO)$_5$MnSnCl$_3$]; the resonance ($\delta = -1996$ ppm) is sharp ($W_{1/2} \approx 90$ Hz) and $^1J(^{117/119}Sn-^{55}Mn) = 790$ Hz. The coupling was not reported in previous investigations [12, 13] of the ^{55}Mn NMR spectrum of this compound. We obtained the compound as a product of the reaction between [(CO)$_5$MnCH$_2$C$_6$H$_5$] and SnCl$_2$ in dimethyl sulfoxide; the expected insertion product, [(CO)$_5$MnSnCl$_2$(CH$_2$C$_6$H$_5$)], was also identified in the reaction mixture from the ^{55}Mn ($\delta = -2196$ ppm, $W_{1/2} = 480$ Hz) and ^{13}C ($^{117/119}$Sn coupling to benzylic carbon) NMR spectra. A third compound, tentatively identified as [(CO)$_5$Mn]$_2$SnCl$_2$, ($\delta(^{55}Mn) = -2126$ ppm, $W_{1/2} \approx 750$ Hz) is also present.

A ^{31}P solid-state CPMAS study of [(CO)$_4$(PPh$_3$)MnCH$_2$C$_6$H$_5$] and [(CO)$_4$(PPh$_3$)MnCOCH$_2$C$_6$H$_{5-n}$X$_n$], where X = H and Me$_3$-2,4,6, has been made. The results are shown in Table 3. In each case the ^{31}P resonance shows five peaks, with a probable shoulder on that to lowest field. The spectrum of [(CO)$_4$(PPh$_3$)MnCOCH$_2$C$_6$H$_2$Me$_3$-2,4,6] is shown in Fig. 2. The multiplicity arises from coupling from ^{55}Mn ($I = 5/2$). The splitting between the bands ranges from 100 to 300 Hz with a regular decrease in the splitting in going from high to low field. Asymmetric couplings in solid-state ^{31}P NMR spectra have been observed in a number of systems, e.g. in the copper–phosphine complexes, [(PPh$_3$)$_3$CuCl] [14], and interpreted theoretically [15]. On the basis of this analysis, we conclude that, as is the case with the copper nucleus, the quadrupolar interaction of the high spin manganese nucleus is not small compared with the Zeeman interaction and that, accordingly, Mn–P dipolar interactions and J-tensor interactions are also seen in the splitting, along with the J-coupling. These added interactions are field

TABLE 2. Variation in ^{55}Mn NMR chemical shifts with tertiary phosphine in [(CO)$_4$(L)MnCH$_2$C$_6$H$_5$] and [(CO)$_4$(L)MnCOCH$_2$C$_6$H$_5$]

L	Cone angle, θ (°)	Electronic parameter, ν (cm^{-1})	[(CO)$_4$(L)MnCH$_2$C$_6$H$_4$X] $\delta(^{55}Mn)$ (ppm)	[(CO)$_4$LMnCOCH$_2$C$_6$H$_4$X] $\delta(^{55}Mn)$ (ppm)
PMe$_2$Ph	122	2065.3	−2011	−1873
P(n-Bu)$_3$	132	2060.3	−2060^a	−1933^a
PMePh$_2$	136	2067.0	−1876	−1759
PPh$_3$	145	2068.9	−1819	−1677
P-t-BuPh$_2$	157	2064.7	−1774	−1633
PCy$_3$	170	2056.4	−1924	−1778

[a] Data from ref. 5.

TABLE 3. ^{31}P CPMAS resonances (and line spacings)

	$\delta(^{31}P)$ (ppm)^a (line spacings (Hz)^b)
$[(CO)_4(PPh_3)MnCH_2C_6H_5$	68.9, 68.1, 66.4, 64.2, 61.6 (102, 208, 264, 318)
$[(CO)_4(PPh_3)MnCOCH_2C_6H_5]$	56.0, 54.8, 52.9, 50.6, 47.7 (144, 235, 273, 356)
$[(CO)_4(PPh_3)MnCOCH_2C_6H_2Me_3$–2,4,6]	50.6, 48.7, 46.6, 44.2, 41.5 (229, 262, 293, 324)

^{a}Chemical shifts in ppm relative to PPh_3 ($\delta = -9.9$ ppm relative to 85% H_3PO_4). ^{b}Line spacings from low field end of multiplet.

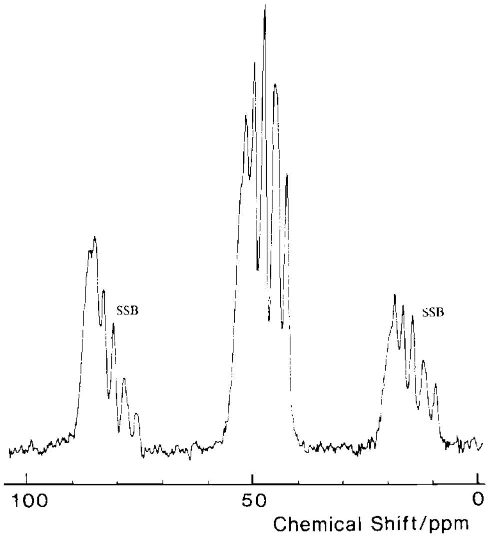

Fig. 2. ^{31}P CPMAS NMR spectrum of $[(CO)_4(PPh_3)MnCOCH_2C_6H_2Me_3$–2,4,6], referenced to 85% H_3PO_4.

dependent, causing the increase in coupling to higher field. We note a much smaller range of splitting in the trimethylbenzyl–acyl compared with the benzyl compound.

Although the *cis* and *trans* isomers of the acyl complexes, $[(CO)_4(PPh_3)MnCOCH_2C_6H_5]$, have been characterised in solution [4, 16], the isomeric form of the solid is uncertain. Our CPMAS study was initiated by our inability to grow crystals of the compound suitable for X-ray analysis and with the hope that characteristic chemical shifts in the solid could be used to identify the species present. The ^{31}P solid-state study suggests, based on the observation of a single set of resonances for each of the acyl complexes, that one of the geometrical isomers predominates or is solely present. Unfortunately the ^{31}P solid-state chemical shift for each compound is intermediate between those for the isomers in solution (*cis*, $\delta \simeq 46$ ppm; *trans*, $\delta \simeq 53$ ppm) and assignment is not possible. The solid-state ^{31}P resonance for $[(CO)_4(PPh_3)MnCH_2C_6H_5]$ is significantly to lower field of that for the *cis* isomer which predominates in solution. Again the ^{31}P chemical shift is unable to provide a definitive identification of the isomeric form of the solid. An X-ray structural study of $[(CO)_4(PPh_3)MnCH_3]$ showed the presence of both *cis* and *trans* isomers in the disordered crystal [17].

Acknowledgements

We thank the Australian Research Grants Scheme for financial support and Ms Lynette Lambert, Ms Tracey Bent and Dr Peter Barron for assistance in recording spectra.

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