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The Manganese-55 NMR Spectra of Phosphine Substituted Phosphinothioformamide Carbonylmanganese Complexes, $\overline{\text{MnSC(NR)P}}\text{Ph}_2(\text{CO})_{4-n}(\text{PZ}_3)_n$†

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We have recently reported the classification of carbonyl manganese complexes containing *P*,*S*-chelating ligands, based on specific shift ranges in the ^{55}Mn NMR spectra [2,3]: $\delta(^{55}\text{Mn})$ values for $\overline{\text{MnSC(NR)P}}\text{R}'_2(\text{CO})_4$ are around −1570 ppm, while shielding of the ^{55}Mn nucleus in the halide complexes $\text{X}\overline{\text{MnSC(NR}_2\text{)P}}\text{R}'_2(\text{CO})_3$ (−730 to −190) and $\text{X}\overline{\text{MnSMeC(NR)P}}\text{R}'_2(\text{CO})_3$ (−270 to +70 ppm) is substantially less and shows a normal halogen dependence, *i.e.* an increase in the order X = Cl < Br < I.

Deshielding effects in metal NMR have also been observed with carbonyl transition metal complexes as the strongly π-accepting CO is substituted by phosphine ligands PZ_3, and interpreted in terms of decreasing overall π interaction. Among the systems which have been thoroughly investigated are the pseudo-octahedral complexes $[\text{V(CO)}_{6-n}(\text{PZ}_3)_n]^-$ [4–7] and $\text{Mo(CO)}_{6-n}(\text{PZ}_3)_n$ [8–11], where the $|\delta(^{51}\text{V})|$ and $|\delta(^{95}\text{Mo})|$ values decrease with increasing n, increasing bulk of the phosphine, and with decreasing electronegativity of Z. On the other hand, it has been shown that $|\delta(^{55}\text{Mn})|$ in the complexes $[\text{Mn(CO)}_5\text{PZ}_3]^+$ may also increase with respect to the parent carbonyl, possibly affected by an expansion of the Mn(3d) cloud due to enhanced Mn(3d) $\longrightarrow$ CO(π*) donation, an effect which, in this case, is dominant over the decrease in the overall π interaction [5, 12]. In the present work, which deals with the phosphine derivatives of $\text{Mn}\widehat{\text{PS}}(\text{CO})_4$ ($\widehat{\text{PS}} = \text{Ph}_2\text{PC(NR)S}^-$), a trend is noted which again conforms with the findings in carbonyl vanadium and molybdenum complexes.

Table I contains the chemical shift values $\delta(^{55}\text{Mn})$. Substitution of one CO by PZ_3 at room temperature leads to *fac*-$[\text{Mn}\widehat{\text{PS}}(\text{CO})_3\text{PZ}_3]$ ($\text{PZ}_3 = \text{P(OR)}_3$, PHPh_2, PMePh_2, PClPh_2, PEt_3) which, upon warming, slowly rearrange ($\text{PZ}_3 = \text{P(OR)}_3$, PMePh_2, PEt_3) to the thermodynamically more stable *mer*-$[\text{MnPS(CO)}_3\text{-PZ}_3]$. In some cases ($\text{PZ}_3 = \text{PCy}_3$, PPh_3), only the meridional isomer is observed [13]. The meridional isomers give rise to broad (half widths $W_{1/2}$ several KHz) signals shifted to low field of the resonance position of $\text{Mn}\widehat{\text{PS}}(\text{CO})_4$ by up to *ca.* 200 ppm (Z = Ph). In the facial isomers, the ^{55}Mn nucleus is further deshielded (a comparable observation has been reported for the pairs *mer*/*fac*-$[\text{Mo(CO)}_3\{\text{P(OMe)}_3\}_3]$ [8, 14]), and this trend prevails as two CO groups are replaced by trimethylphosphite. The general ordering (identical phosphine ligands provided) hence is $[\text{Mn}\widehat{\text{PS}}(\text{CO})_4]$ > *mer*-$[\text{MnPS(CO)}_3\text{PZ}_3]$ > *fac*-$[\text{Mn}\widehat{\text{PS}}(\text{CO})_3\text{PZ}_3]$ > *cis*-$[\text{Mn}\widehat{\text{PS}}(\text{CO})_2(\text{PZ}_3)_2]$. Superimposed to this trend are effects arising from the nature of Z. The phosphine induced manganese shielding decreases in the sequence $\text{P(OMe)}_3 > \text{P(OPh)}_3 > \text{PHPh}_2 > \text{PEt}_3 \approx \text{PCy}_3 > \text{PMePh}_2 > \text{PPh}_3 > \text{PClPh}_2$ which should be interpreted in terms of decreasing ligand strength of the phosphine on a magneto–chemical π acceptor scale. Except for the position of PHPh_2, this is again in accord with findings in comparable Mo and V systems. An extreme low-field position of the PPh_2Cl derivative on the δ(M) scale has also been observed for the complexes *cis*-$[\text{Mo(CO)}_4(\text{PPh}_2\text{Z})_2]$ [15].

The complexes *fac*-$[\text{Mn}\widehat{\text{PS}}(\text{CO})_3\text{PZ}_3]$ exhibit relatively sharp signals ($W_{1/2}$ around 600 Hz; an exception is the PClPh_2 complex). This is indicative of comparatively low relaxation rates. The ^{55}Mn nucleus (spin 5/2) has a nuclear quadrupole moment of *ca.* 0.5×10^{-28} m^2, and relaxation is governed by the quadrupole mechanism. Only where the ^{55}Mn nucleus is in a cubic environment, quadrupole relaxation becomes ineffective, and very sharp signals are observed ($[\text{MnO}_4]^-$, $[\text{Mn(CO)}_6]^+$). The point charge model predicts that the nuclear field gradient also vanishes for pseudo-octahedral C_{3v} complexes (*fac*-$[\text{MA}_3\text{B}_3]$). Although our complexes $[\text{Mn}\widehat{\text{PS}}(\text{CO})_3\text{PZ}_3]$ with a facial arrangement of the three CO ligands are far from falling into this category, we might nonetheless expect a considerable sharpening of the resonance lines with respect to the isomers, where the CO groups occupy meridional positions, and in fact the differences in $W_{1/2}$ are about one order of magnitude.

In agreement with theory, further line narrowing occurs as the molecular reorientation is facilitated by decreasing the viscosity of the solution. In two cases (*fac*-$[\text{Mn}\widehat{\text{PS}}(\text{CO})_3\text{P(OPh)}_3]$ and $[\text{Mn}\widehat{\text{PS}}(\text{CO})_2]\text{-}\{\text{P(OMe)}_3\}_2]$) we have thus been able to observe $^1J(^{55}\text{Mn}-^{31}\text{P})$ coupling by running the spectra at elevated temperatures. For the triphenylphosphite complex, a structured signal (J(Mn–P(OPh)) = 400 Hz, J(Mn–PPh) (only partially resolved) *ca.* 140 Hz)

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† Part XV of 'Phosphine-Substituted Chelate Ligands'; for Part XIV see ref. [1].

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0020-1693/85/$3.30

TABLE I. $\delta(^{55}Mn)$ Data[a].

Complex	$\delta(^{55}Mn)$ (ppm)	
	298 to 300 K	333 to 335 K
$[\overline{MnSC(NPh)P}Ph_2(CO_4)]^b$	−1530	
mer-$[\overline{MnSC(NPh)P}Ph_2(CO)_3PPh_3]$	−1400^c	
fac-$[\overline{MnSC(NPh)P}Ph_2(CO)_3P(OMe)_3]$	*−1481*	*−1433*
$[\overline{MnSC(NMe)P}Ph_2(CO)_4]^b$	−1545, −1570	
mer-$[\overline{MnSC(NMe)P}Ph_2(CO)_3PZ_3]$		
$PZ_3 = P(OMe)_3$	−1534	
$P(OPh)_3$	−1516	
PEt_3	−1496	*−1432*
PCy_3	−1457	
$PMePh_2$	−1370	
PPh_3	−1345	
fac-$[\overline{MnSC(NMe)P}Ph_2(CO)_3PZ_3]$		
$PZ_3 = P(OMe)_3$	−1477	*−1450*^{d}
$P(OPh)_3$	*−1431*^{e}	*−1414*^{f,g}
$PHPh_2$	*−1437*	*−1395*^{d}
PEt_3	*−1381*^{d}	*−1340*^{d}
$PMePh_2$	*−1302*	*−1264*^{d}
$PClPh_2$	−1090	
cis-$[\overline{MnSC(NMe)P}Ph_2(CO)_2\{P(OMe)_3\}_2]$	−1319	*−1261*^{g}

[a] Values in italics are from a Bruker WH 90 PFT spectrometer at 22.31 MHz (error ±2 ppm), others from a Bruker SWL 3–100 wide–line spectrometer (central field $B_0 = 1.518$ T; 16.0 MHz; error ±20 ppm). All data are in THF solution (*ca.* 0.05 M) and relative to $[MnO_4]^-$ ($B_{MnO_4^-} = 1.51688$ T). [b] From refs. [1] and [2]. [c] ±50 ppm. [d] Coupling incompletely resolved. [e] At 305 K. [f] At 320 K. [g] Coupling resolved; *cf.* text.

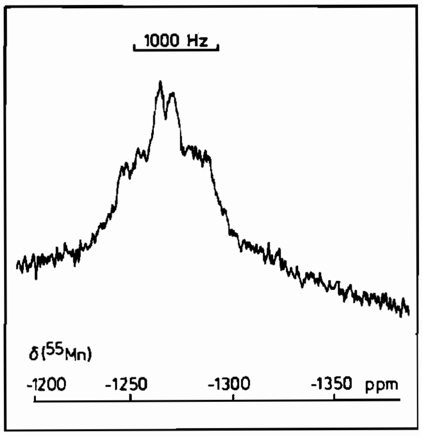

Fig. 1. 22.31 MHz $^{55}Mn\{^1H\}$ NMR spectrum of *cis*-$[\overline{MnSC(NMe)P}Ph_2(CO)_2\{P(OMe)_3\}_2]$ at 333 K in THF.

arises. For $[Mn\widehat{PS}(CO)_2\{P(OMe)_3\}_2]$, the coupling pattern is more complex (Fig. 1): a pseudo-triplet (J(Mn–P(OMe)) = 405 Hz) with a doublet splitting (J(Mn–PPh) = 165 Hz) of each of the triplet lines is observed for this ABXM system (A, B = $P(OMe)_3$, X = $Ph_2PC(NMe)S^-$) at 333 K. Manganese coupling has formerly only been observed in a few $[Mn(CO)_{6-n}(PZ_3)_n]^+$ complexes (*e.g.* n = 1, $PZ_3 = PMePh_2$: J = 170 Hz; n = 2, Z = OMe; J = 330 Hz [5, 7, 12]).

Another interesting feature is the strong temperature dependence of $\delta(^{55}Mn)$ which amounts to 1.2 ppm/deg. The ^{55}Mn nucleus is deshielded as the temperature increases, which is the expected trend [16]: the increase of the occupation of vibronic levels with increasing temperature is, in its effect, comparable to a decrease of the ligand field strength as a weakly interacting ligand (PR_3) is introduced into the complex.

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