

⁵⁵Mn Shielding in Carbonylmanganese Halides Containing Phosphido and Arsenido Bridges

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There has been recent concern as to the influence of group VA to VIIA ligands upon metal shielding in coordination compounds, focusing on the origin of the general trends observed with low-valent (open shell) and high-valent (closed shell) metal centers, respectively (for a summary see ref. 1). Mn(1+) (d^6) in a pseudo-octahedral environment experiences the so-called 'normal' trend [2], *i.e.*, an increase of metal shielding with decreasing ligand electronegativity χ (increasing polarizability α of the ligand). Examples are the series $(CO)_5MnX$ ($X = Cl, Br, I$) [3], $(CO)_3Mn(X)SP$ (SP is a phosphinothioformamide ligand or the isomeric thioformimidoester) [4] and $(NO)_3MnER_2$ ($E = O, S, Se, Te$) [5]. The normal trend has also been noted for dinuclear complexes of the type $\{Mn(CO)_4\}_2\mu-E'(CF_3)_2\mu-Y$ with $Y = X$ or ER_2 ($E = S, Se, Te$) and $E' = P$ or As [6]. However, in these complexes the ordering of phosphido and arsenido species is inverse, *i.e.*, the ⁵⁵Mn nucleus in the grouping $MnAs(CF_3)_2$ is deshielded with respect to that of the phosphorus analogue. We have shown that this deviating behaviour is due to counteracting effects in the terms determining the paramagnetic deshielding contribution $\sigma(p)$ of the overall shielding. $\sigma(p)$ is connected to the molecular quantities ΔE (HOMO–LUMO splitting), r^3 (expansion of the Mn-3d cloud) and C (Mn-3d LCAO coefficient) in the following manner:

$$\sigma(p) \propto \Delta E^{-1} \langle r^{-3} \rangle C^2$$

We shall make use of this relation in the following treatment of recent results for complexes of the type $(CO)_4Mn(X)E'Me_2Z$ (**A**) and $\{(CO)_4Mn\}_2(\mu-X)\mu-(E'Me_2)$ (**B**) with E', X and Z as exhibited in the data

collected in Table I**. $\delta(^{55}Mn)$ values for $\{(CO)_4Mn\}_2(\mu-I)_2$ (**1**) and a few compounds from the literature $[(CO)_4Mn(X)PEtPh_2]$ have been included.

Inspection of Table I shows that the shielding of the ⁵⁵Mn nucleus decreases on going from **1** to **A** and further to **B** if, in the two categories **A** and **B**, complexes are compared which carry the same halide ligand X directly attached to Mn. The dominant influence of X is also revealed by comparison of the very similar $\delta(^{55}Mn)$ values for $(CO)_4Mn(I)PEtPh_2$, **2**, **3** and **6**, and for $(CO)_4Mn(Cl)PEtPh_2$ and **7**, respectively. The diminished shielding in the dinuclear complexes **B** is mainly a consequence of the strains imposed by the four-membered ring structure. These strains are more than compensated in **1** by the generally high shielding induced by two iodo ligands.

The consistently high metal shielding in iodo complexes reflects the high polarizability (low electronegativity) of iodine, giving rise to an increase of r and a decrease of C . The latter is due to a decrease in the ionicity of the Mn–I relative to the Mn–Cl bond in the corresponding chloro complexes. The two factors point in the same direction, *viz.*, a relative decrease of $\sigma(p)$ and increase of the overall shielding and a more effectively shielded ⁵⁵Mn nucleus in iodo compounds (*cf.* **6** and **7**, **8** and **11**, **13** and **14**). On the other hand, iodine is a weak ligand in terms of the ligand field theory (HOMO–LUMO splitting ΔE) and therefore should give rise to an increase of $\sigma(p)$ relative to its lighter homologues. Apparently, this ΔE effect is overrun by the counteracting influence of the factor $\langle r^{-3} \rangle C^2$. In contrast, chloro ligands induce a consistently low metal shielding due to both the comparatively large ΔE and $\langle r^{-3} \rangle C^2$; this behaviour reflects the low χ (high α) of chlorine.

A similar consideration can be applied to the manganese shielding observed with the phosphido relative to the arsenido group. Phosphorous ligands are known to exhibit good to excellent π acceptor properties in low-valent metal complexes, and this will lead to a major role of ΔE . The factor $\langle r^{-3} \rangle C^2$ should be of more substantial influence in complexes containing the softer $AsMe_2$ bridge. However, arsenous ligands are also weak on the π acceptor scale. In order to achieve consistency with the observed ordering, a decrease of shielding on going from phosphorus to arsenic (**2**, **3** and **4**, **5**; **7** and **12**; **13** and **15**), one has to assume that again ΔE is the more important factor in determining the shielding parameter.

**Synthesis and spectroscopic data of these compounds will be published elsewhere [7].

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TABLE 1. ^{55}Mn Chemical Shifts

Code/Compound	E	X	Z	Solvent	δ^a (ppm)	mod ^b (mT)
(CO) ₄ Mn(Cl)PEtPh ₂ ^c				THF	-1080	
(CO) ₄ Mn(Br)PEtPh ₂ ^c				THF	-1190	
(CO) ₄ Mn(I)PEtPh ₂ ^c				THF	-1460	
1 {(CO) ₄ Mn} ₂ (μ -I) ₂				THF	-1575	0.80
				CH ₂ Cl ₂	-1560	0.50
A (CO) ₄ Mn(X)E'Me ₂ Z						
2	P	I	MoCp(CO) ₃	THF	-1580 ^d	0.32
3	P	I	WCp(CO) ₃	THF	-1505	0.13
4	As	I	MoCp(CO) ₃	THF	-1390	0.16
5	As	I	WCp(CO) ₃	THF	-1400	0.32
6	P	I	Cl	THF	-1435	0.20 ^b
				CH ₂ Cl ₂	-1455 ^e	0.16
7	P	Cl	Cl	THF	-895, -980	0.06
				CH ₂ Cl ₂	-830, -910	0.06
8	As	I	I	THF	-1220	0.13
9	As	Br	I	THF	-1220	0.13 ^b
10	As	Br	Br	THF	-1260	0.08
11	As	Cl	I	THF	-800 ^e	0.13
12	As	Cl	Cl	THF	-880	0.08
B {(CO) ₄ Mn} ₂ (μ -X) μ -E'Me ₂						
13	P	I	-	THF	-1140	0.40
14	P	Cl	-	THF	-750	1.00
15	As	I	-	THF	-1050	0.64
				CH ₂ Cl ₂	-1015 ^{e,f}	0.64
16	As	Br	-	THF	-760 ^{e,g}	0.80
17	As	Cl	-	THF	-1175 ^g	0.10

^aRelative to saturated, aqueous KMnO₄ at 16.0 MHz and a magnetic field of B(MnO₄⁻) = 1.5168 T. Estimated error: ± 20 ppm. The spectra were obtained on a Bruker SWL 3-100 wideline spectrometer in ca. 0.2 M THF solutions (except where indicated otherwise), contained in 14 mm diameter tubes at 301(2) K. ^bModulation amplitude. This is an upper limit of the peak-to-peak width W_p of the signal. The actual widths have been obtained for compounds 6 (W_p = 1.05 kHz; mod = 0.016 mT) and 9 (W_p = 1.69 kHz; mod = 0.032 mT), both in THF. ^cFrom ref. 8. ^dAt reduced modulation, two partially resolved resonances (-1490 and -1635 ppm) are observed. ^eAn additional signal around -2300 ppm is due to Mn₂(CO)₁₀ [1, 3, 8]. ^fA weak signal at -1665 ppm remains unassigned. ^gAn additional signal arises at -2020 ppm (unassigned).

References

- 1 D. Rehder, *Magn. Reson. Rev.*, **9**, 125 (1984).
- 2 R. D. Kidd, *Annu. Rep. NMR Spectrosc.*, **10A**, 1 (1980).
- 3 F. Calderazzo, E. A. C. Lucken and D. F. Williams, *J. Chem. Soc. A*, 154 (1967).
- 4 U. Kunze, A. Bruns and D. Rehder, *J. Organomet. Chem.*, **268**, 213 (1984).
- 5 D. Rehder, K. Ihmels, D. Wenke and P. Oltmanns, *Inorg. Chim. Acta*, **100**, L11 (1985).
- 6 J. Grobe, J. Vetter and D. Rehder, *Z. Naturforsch., Teil B*, **40**, 975 (1985).
- 7 J. Grobe, G. Beysel and W. Kopp, to be published.
- 8 P. Oltmanns and D. Rehder, *J. Organomet. Chem.*, **281**, 263 (1985).