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Characterization of manganese sandwich complexes by ^{55}Mn NMR spectroscopy

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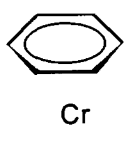
Abstract

^{55}Mn NMR data are reported for manganese sandwich complexes of the type $[(\eta^5\text{-}C_5H_5)Mn(\eta^6\text{-}C_6H_6)]$ (**1**), $[(\eta^5\text{-}C_5H_5)Mn(\eta^6\text{-}C_6H_5\text{–}R')]$ [R′ = Me (**2**) ^{i}Pr (**3**), ^{t}Bu (**4**), Ph (**5**), $SiMe_3$ (**6a**), $GeMe_3$ (**6b**), $SnMe_3$ (**6c**), $PbMe_3$ (**6d**), SMe (**6e**)], $[(\eta^5\text{-}C_5H_4\text{–}R)Mn(\eta^6\text{-}C_6H_6)]$ [R = Me (**7**), $SiMe_3$ (**8a**), $GeMe_3$ (**8b**), $SnMe_3$ (**8c**), $PbMe_3$ (**8d**)], $[(\eta^5\text{-}C_5H_4\text{–}R)Mn(\eta^6\text{-}C_6H_5\text{–}R')]$ [R = R′ = Me (**9**); R = Me, R′ = Ph (**10**); R = $SiMe_3$, R′ = Ph (**11**); R = R′ = $SiMe_3$ (**12a**), $GeMe_3$ (**12b**), $SnMe_3$ (**12c**), $PbMc_3$ (**12d**). SMe (**12e**), SeMe (**12f**), R,R′ = $SiMe_2SiMe_2$ (**13**)], $[(\eta^5\text{-}C_5R_5)Mn(\eta^6\text{-}C_7H_8)]$ [R = H (**14**), Me (**15**)] and $[(\eta^5\text{-}C_5R_5)Mn(\eta^6\text{-}C_8H_{10})]$ [R = H (**16**), Me (**17**)]. The chemical shifts δ^{55}Mn cover a range of ca. 350 ppm for complexes **1** to **12** (δ^{55}Mn ca −180 to ca. +170 relative to $[MnO_4]^-$ aq), whereas further ^{55}Mn deshielding up to ca. 1000 ppm is observed for complexes **14** to **17**. Any relationship between the formal oxidation number of Mn and ^{55}Mn magnetic shielding has to be discarded. The large range of the δ^{55}Mn data for sandwich complexes indicates that ^{55}Mn magnetic shielding depends on the electronic structure of the frontier orbitals which is significantly affected by the ring substituents. Chemical shifts δ^{53}Cr (relative to $[CrO_4]^{2-}$aq) for $[Cr(\eta^6\text{-}C_6H_6)_2]$ (−1206) and $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$ (−1580) have been determined for comparison.

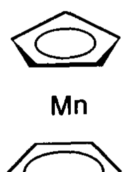
Keywords: Manganese sandwich complexes; ^{55}Mn NMR; ^{53}Cr NMR

1. Introduction

Since the discovery of ferrocene [1] and di(benzene)chromium [2], the electronic structure of sandwich compounds has been the subject of extensive discussions. However, in comparison with these two homoleptic model complexes, the mixed sandwich compound (η^5-cyclopentadienyl)manganese(η^6-benzene) (**1**) [3], whose molecular structure has recently been determined [4], has received only scant attention.

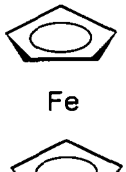


$Cr(\eta^6\text{-}C_6H_6)_2$



$(\eta^5\text{-}C_5H_5)Mn(\eta^6\text{-}C_6H_6)$

1



$Fe(\eta^5\text{-}C_5H_5)_2$

For these diamagnetic 18-electron complexes and their ring-substituted derivatives, the nuclear magnetic shielding of the respective metal nucleus provides an ideal probe for the electronic structure, since it sensitively reflects the various effects exerted by the substituents [5]. Indeed, numerous chemical shifts δ^{57}Fe of ferrocene derivatives have been measured [6,7] and used, in particular for α-ferrocenyl carbocations [8], in the discussion of bonding models. In the case of (η^5-cyclopentadienyl)iron(η^5-pentadienyl) complexes ("half-opened ferrocenes"), the influence of the HOMO-LUMO distance on δ^{57}Fe has been noted [9]. In order to make better use of the δ^{57}Fe values of ferrocenes and related compounds, chemical shift data of neighbouring metal nuclei are required for comparison. Some δ^{57}Co data for cobaltocenium cations have been reported [5]. However, δ^{53}Cr data for sandwich complexes have not been measured so far. It is even more remarkable that ^{55}Mn NMR has never been used

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for studying manganese sandwich complexes, in spite of the high ^{55}Mn NMR-sensitivity (natural abundance 100%). We now report for the first time on the ^{55}Mn NMR of sandwich complexes (**1–17**, see Table 1) derived from (η^5-cyclopentadienyl)-manganese(η^6-benzene) (**1**) [3,4].

2. Results and discussion

The chemical shifts δ^{55}Mn of the complexes **1–17** are given in Table 1. Owing to the sizeable nuclear electric quadrupole moment of the ^{55}Mn nucleus ($Q = 0.40 \cdot 10^{-28} m^2; I = 5/2$), linewidths ($h_{1/2}$) of several kHz are observed, even when the deviation from a spherical charge distribution about the ^{55}Mn nucleus is small. Nevertheless, the fairly large range of the δ^{55}Mn data and the use of a high field strength ($B_0 = 11.4$ T) allow us to obtain well-resolved ^{55}Mn NMR spectra, as shown in Fig. 1. The variations in the linewidths correspond, with few exceptions, to expectations based on changes in rotatory correlation times (τ_c) as a result of the introduction of substituents in one or both rings. The exceptions can readily be made out by comparing the linewidths ($h_{1/2}$) for the pairs **1**/**7**, **12a**/**13** and **14**/**15** (but not **16**/**17**). It appears that in these cases the substituents create a more symmetrical charge distribution at the ^{55}Mn nucleus, thus compensating for the effect of a reduced tumbling rate.

Table 1
Chemical shifts, δ^{55}Mn, and linewidths, $h_{1/2}$, of manganese sandwich complexes [a]: [(η^5-C_5H_5)Mn(η^6-C_6H_6)] (**1**), [(η^5-C_5H_5)Mn(η^6-C_6H_5-R')] (**2–6**), [(η^5-C_5H_4-R)Mn(η^6-C_6H_6)] (**7, 8**), [(η^5-C_5H_4-R)Mn(η^6-C_6H_5-R')] (**9–13**), [(η^5-C_5R_5)Mn(η^6-C_7H_8)] (**14, 15**) and [(η^5-C_5R_5)Mn(η^6-C_8H_{10})] (**16, 17**)

	R	R'	δ^{55}Mn	$h_{1/2}$ [Hz]
1	H	H	−180	1500
2	H	Me [b]	−105	2100
3	H	^{i}Pr	−91	2100
4	H	^{t}Bu	−73	2800
5	H	Ph [c]	−5	2900
6a	H	Me_3Si	−20	2000
6b	H	Me_3Ge	−52	[d]
6c	H	Me_3Sn	−51	2400
6d	H	Me_3Pb	−70	[d]
6e	H	MeS	−154	[d]
7	Me	H	−180	1320
8a	Me_3Si	H	−72	2300
8b	Me_3Ge	H	−103	[d]
8c	Me_3Sn	H	−102	2500
8d	Me_3Pb	H	−133	[d]
9	Me	Me	−105	2000
10	Me	Ph	+1	2600
11	Me_3Si	Ph	+110	2700
12a	Me_3Si	Me_3Si	+97	3400
13	$-Me_2Si-SiMe_2-$		+164	2240
12b	Me_3Ge	Me_3Ge	+32	4200
12c	Me_3Sn	Me_3Sn	+32	4200
12d	Me_3Pb	Me_3Pb	−32	5200
12e	MeS	MeS	−110	3100
12f	MeSe	MeSe	−157	[d]
14	H		+1077	2250
15	Me		+945	1900
16	H		+899	4230
17	Me		+707	7200

[a] δ^{55}Mn relative to a saturated aqueous solution of $KMnO_4$ ($\Xi(^{55}Mn) = 24.789290$ MHz).
[b] [(η^5-C_5H_5)Mn(η^6-1,2-$Me_2C_6H_4$)]: $\delta^{55}Mn = -37$, $h_{1/2} = 2400$ Hz.
[c] [(η^5-C_5H_5)Mn(η^6-4,4'-dimethoxybiphenyl)]: $\delta^{55}Mn = +85$, $h_{1/2} = 7300$ Hz.
[d] Mixture with **1**: $h_{1/2}$ is not accurately measurable because of signal overlap with **1**.

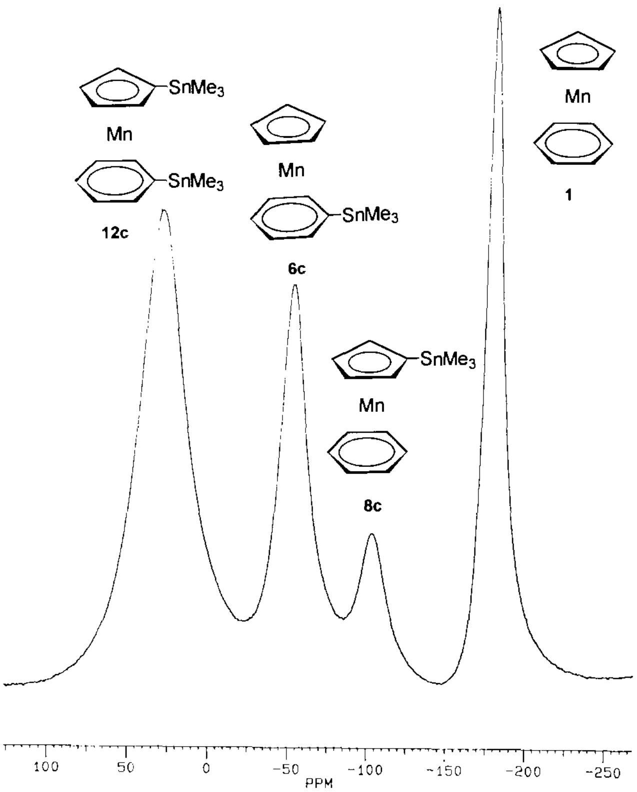

Fig. 1. 123.5 MHz ^{55}Mn NMR spectrum of a mixture of the sandwich complexes **1**, **6c**, **8c** and **12c**, which is formed in the reaction of incompletely lithiated (η^5-cyclopentadienyl)manganese(η^6-benzene) (**1**) with trimethyltin chloride.

It has repeatedly been tried to establish a loose relationship between the formal oxidation state of a transition metal and its nuclear shielding [5], assuming that an increasing oxidation number is accompanied by deshielding of the metal nucleus. Such attempts are misleading, both in the light of the data already available and, in particular, of the δ^{55}Mn data determined in the course of this work. An aqueous solution of $KMnO_4$ (manganese with a formal oxidation number +7) is generally used as an external reference for δ^{55}Mn data. In the same range as the reference appear the ^{55}Mn NMR signals of the complexes **1–13** in which the central metal possesses the formal oxidation number +1 ($\delta^{55}Mn \approx -180$ to $\approx +170$). The ^{55}Mn nuclear shielding in the complexes **14–17** is further reduced by more than 1000 ppm, although the formal oxidation number of manganese (+1) remains unchanged.

In the 18e-sandwich complexes $[Cr(C_6H_6)_2]$, $[(C_5H_5)Mn(C_6H_6)]$ (**1**) and $[Fe(C_5H_5)_2]$, the three highest occupied molecular orbitals have similar energies, being neither strongly bonding nor anti-bonding. This explains that oxidation to 17e-systems ($[Cr(C_6H_6)_2]^+$ and $[Fe(C_5H_5)_2]^+$) is easily achievable; the small energy gap (ΔE) between HOMO and LUMO even favours the formation of 19e- or 20e-systems such as $[Co(C_5H_5)_2]$ or $[Ni(C_5H_5)_2]$. The ΔE(HOMO-LUMO) values are mainly responsible for changes in nuclear magnetic shielding, as a result of the contribution of B_0-induced mixing of metal-d-levels to the magnetic shielding [10]. For small ΔE values one expects a significant increase of the paramagnetic term (σ_p) of magnetic shielding, as was indeed found in the system of the manganese sandwich complexes studied here (see also Table 2). Due to the small ΔE values, chemical shifts $\delta^{55}Mn$ are significantly dependent on the substituents R and R′. Any substitution in **1** leads to ^{55}Mn deshielding, the substitution of the benzene ring being more effective. Already the change from **1** to **2** (toluene instead of benzene as a ring ligand) causes ^{55}Mn deshielding by 75 ppm. If biphenyl is one of the ring ligands instead of benzene (**5**), the ^{55}Mn deshielding is as large as 175 ppm. In the series of the trimethylelement derivatives **6a–d**, **8a–d**, **12a–d** with Si, Ge, Sn and Pb, the lowest ^{55}Mn shielding is always observed for the Me_3Si derivatives. It is remarkable that bridging of the ring ligands by the $-Me_2Si_2SiMe_2-$ moiety (**13**) leads to stronger ^{55}Mn deshielding than the presence of two Me_3Si groups (**12a**). The influence of Me_3Ge- and Me_3Sn substituents is almost identical in the complexes of types **6**, **8** and **12**. The $\delta^{55}Mn$ data of the complexes **14–17**, in which η^6-benzene is substituted by η^6-cycloheptatriene (**14** [13], **15**), or η^6-cyclooctatriene (**16** [13], **17**) deviate drastically from the range of $\delta^{55}Mn$ values for **1–13**. Thus, in the case of **14–17** ($\delta^{55}Mn$ +1077, +945, +899, +707), an electronic structure can be assumed with an even smaller HOMO-LUMO gap than in **1–13**. The $\delta^{55}Mn$ value for **14** extends the known range of $\delta^{55}Mn$ [5] by more than 500 ppm.

Table 2 presents chemical shifts $\delta^{53}Cr$, $\delta^{55}Mn$ and $\delta^{57}Fe$ for analogous carbonyl- and arene complexes. In each case, the metal nucleus becomes significantly deshielded if carbonyl ligands are replaced by an arene ring. The greatest deshielding effect in these series is observed for the halfsandwich complex $[(C_5H_5)Mn(CO)_3]$ if the three carbonyl ligands are substituted by benzene ($\Delta\delta^{55}Mn$ + 2046].

The NMR measurements described here clearly demonstrate that ^{55}Mn NMR spectroscopy is a most important method for the chemistry of manganese sandwich complexes [4]. The magnetic shielding of metal nuclei in sandwich complexes reflects even minor changes in the energy of the frontier orbitals. Therefore such parameters as $\delta^{57}Fe$ of ferrocenes [7–9] and the new $\delta^{55}Mn$ data are expected to provide a firm basis for the adaptation of semiempirical MO calculations.

3. Experimental section

All preparative work and handling of samples was carried out under argon, and all precautions to exclude oxygen and moisture were observed. The ring-substituted derivatives (**2–13**) of $[(\eta^5-C_5H_5)Mn(\eta^6-C_6H_6)]$ (**1**) were obtained following the procedure described by Fischer and Breitschaft [3,4]. The reaction between cyclopentadienyl sodium, NaC_5H_5, and $MnCl_2$ (1 : 1) in tetrahydrofuran produces the intermediate $\{C_5H_5$-

Table 2
Chemical shifts [a] $\delta^{53}Cr$, $\delta^{55}Mn$ and $\delta^{57}Fe$ of typical carbonyl- and arene complexes of chromium, manganese and iron

	carbonyl		half sandwich		sandwich
	$[Cr(CO)_6]$		$[(C_6H_6)Cr(CO)_3]$		$[(C_6H_6)Cr(C_6H_6)]$
$\delta^{53}Cr$	−1795 [11]		−1580 [b]		−1206 [b]
$\Delta\delta^{53}Cr$		+215		+374	
	$[Mn(CO)_5]^-$		$[(C_5H_5)Mn(CO)_3]$		$[(C_5H_5)Mn(C_6H_6)]$
$\delta^{55}Mn$	−2780 [12]		−2225 [12]		−180
$\Delta\delta^{55}Mn$		+555		+2046	
	$[Fe(CO)_5]$		$[(C_5H_5)Fe(CO)_3]^+$		$[(C_5H_5)Fe(C_5H_5)]$
$\delta^{57}Fe$	0		+686.3 [11]		+1532.4 [7]
$\Delta\delta^{57}Fe$		+686.3		+846.1	

[a] $\delta^{53}Cr$ relative to a saturated aqueous solution of K_2CrO_4 ($\Xi(^{53}Cr) = 5.652502$ MHz); $\delta^{55}Mn$ (see Table 1, footnote [a]); $\delta^{57}Fe$ relative to $Fe(CO)_5$.

[b] This work.

MnCl} which, after treatment with the Grignard-reagent C_6H_5MgBr, leads to a small yield of **1** (4%) together with **5** (14%) [4]. The complexes **2** to **4** were obtained in small yields (1–2%) by using the Grignard-reagents R'-C_6H_4MgBr (R' = Me, ^iPr, ^tBu). Starting with methyl- or trimethylsilyl-cyclopentadienyl sodium, $Na(C_5H_4Me)$ or $Na(C_5H_4SiMe_3)$, respectively, the complexes **7**, **9** and **10**, as well as **8a** and **11** were prepared.

Dilithiation of **1** in the presence of tetramethylethylenediamine (tmeda), followed by treatment of the 1,1'-dilithio derivative with the trimethylelement chlorides, $Me_3E'Cl$ (E = Si, Ge, Sn, Pb), or dimethyldi-chalcogenanes, Me_2E_2 (E = S, Se), afforded almost exclusively the disubstituted complexes **12a–f** [4], and with Cl-Me_2Si-SiMe_2-Cl the [2]cyclophane **13** was formed. If the 1,1'-dilithiation was not complete, the mono-substituted complexes **6a–e** and **8–d** were observed in the NMR spectra (Fig. 1). These compounds were not isolated from the mixtures.

The complexes **14** and **16** were prepared from $[(\eta^5\text{-}C_5H_5)Mn(CO)_3]$ as described [13], and the pentamethylcyclopentadienyl derivatives **15** and **17** were obtained in the same way.

All ^{53}Cr and ^{55}Mn NMR spectra (see also Tables 1, 2 and Fig. 1) were measured by using a Bruker AM 500 spectrometer. Mixtures were also analysed by ^{1}H, ^{13}C, ^{29}Si, ^{77}Se, ^{119}Sn and ^{207}Pb NMR (Bruker AC 300, Bruker ARX 250) in order to confirm the assignments in the ^{55}Mn NMR spectra. Typical conditions for 123.5 MHz ^{55}Mn NMR spectra: solutions $\leq 5\%$ in C_6D_6; 25°C; 5 mm tube; ca. 1000 transients with 90°C pulse angle (≈ 6 μs); acquisition time 0.03 s, spectral window 60 kHz.

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