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^{55}Mn,^{13}CO and ^{55}Mn,^{31}P Coupling Constants of Organomanganese Complexes: Comparison of NMR Results from Experiments in Solution and in the Solid State†

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Scalar spin–spin coupling constants of some organomanganese complexes, $Mn(CO)_{5-n}(R)L_n$, were evaluated by lineshape analysis from ^{13}C and ^{31}P solution NMR spectra and from solid-state magic angle spinning spectra showing first-order splitting. Consistent results were obtained for favourable complexes, but each method has only limited applicability in the general case. The merits of both methods are discussed. © **1997 John Wiley & Sons, Ltd.**

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INTRODUCTION

The determination of indirect spin–spin coupling constants J(I,S) in solution between spin-$\frac{1}{2}$ nuclei I and quadrupolar nuclei S with spin $\geqslant 1$ depends critically on the quadrupolar relaxation rate of the nucleus S.[2] For low relaxation rates, J(I,S) can be obtained directly from the spin-$\frac{1}{2}$ NMR J-multiplet spectra. For very high relaxation rates, the resonance line of S broadens beyond detectability, whereas the I-spin multiplet collapses to a single, narrow line. For such cases approaches to obtain scalar coupling constants from relaxation measurements of the slowly relaxing nucleus I were reviewed by Mlynárik.[3] For intermediate S-spin relaxation rates with relaxation rate factors T_1(S)J(I,S) < 2,[4] the J-multiplet structure of the NMR signal of I is partially or completely collapsed and the NMR spectrum of the quadrupolar nucleus significantly broadened. The coupling constant can then be indirectly evaluated via a lineshape analysis, e.g. with the PC program QUADR.[4–6] The theoretical lineshape of the spin-$\frac{1}{2}$ NMR signal is determined by three parameters: J(I,S), the spin–lattice relaxation time T_1(S) of the quadrupolar nucleus, and T_2*, that accounts for non-quadrupolar contributions to the linewidth of the spin-$\frac{1}{2}$ NMR signal. For completely collapsed multiplet structures, these three parameters are strongly correlated and their simultaneous determination is impossible. However, T_1(S) can be extracted from the resonance linewidth of S via $\Delta\nu_{1/2}(S) = 1/[\pi T_1(S)]$, and T_2* is obtained from a spin-$\frac{1}{2}$ reference line, which is not affected by quadrupolar interactions.

Alternatively, the indirect coupling constants J(I,S) can be obtained from high-resolution solid-state NMR spectra. The effects produced by quadrupolar nuclei on the solid-state NMR signals of I-spins $\frac{1}{2}$ are well established.[7,8] In addition to the J-coupling, residual dipolar effects (and anisotropy of indirect coupling) contribute to the line splitting. This phenomenon is brought about by the incomplete averaging of the dipole coupling between I and S spins by magic angle spinning (MAS) originating from the different quantization directions of the two spins. If the quadrupole coupling constant of the S nucleus is smaller than its Zeeman frequency ν_s, first-order theory predicts the NMR signal for the I nucleus to appear as a $(2S + 1)$-multiplet at positions relative to the isotropic chemical shift δ_{iso} given by[7]

$$\Delta\nu_m = -mJ_{(I,S)} - \left[\frac{S(S+1) - 3m^2}{S(2S-1)}\right]\Delta \qquad (1)$$

where m is the magnetic spin quantum number of S, with $m = S, S-1, \ldots, -S$, and Δ, the anisotropic contribution to the multiplet structure of the NMR signal, is defined by Eqn (2). According to Eqn (1), a six-line multiplet with non-symmetric splitting is expected for the NMR spectrum of a spin I, coupled to ^{55}Mn ($S = 5/2$). From this spectrum, $|J_{(I,S)}|$, δ_{iso} and Δ are readily obtained. Equation (1) is valid only for long relaxation times T_1(S). Therefore, as in analogous situations in solution, unfavourable quadrupolar relaxation rates of the order of J and Δ can (partially) remove the coupling effects from the I-spin NMR spectra; the multiplet structure broadens out or S and I effectively decouple.

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$$\Delta = -\left(\frac{3\chi}{20\nu_s}\right)\left[D(3\cos^2\beta^D - 1 + \eta\sin^2\beta^D\cos 2\alpha^D) - \left(\frac{\Delta J}{3}\right)(3\cos^2\beta^J - 1 + \eta\sin^2\beta^J\cos 2\alpha^J)\right] \quad (2)$$

In Eqn (2), D is the dipolar I,S coupling constant, η is the asymmetry parameter of the quadrupolar tensor and χ the quadrupole coupling constant. The anisotropy $\Delta J = J_{\parallel} - J_{\perp}$ of the **J** tensor is assumed to be axially symmetric, α^D and β^D are angles defining the orientation of the **r**(I,S) vector in the principal-axes system (PAS) of the quadrupolar interaction, and α^J and β^J fix the orientation of the unique z-axes of the **J** tensor in the PAS of the quadrupolar tensor. Inspection of Eqn (2) implies that Δ is determined by a complex interplay between angles and magnitudes for χ, D and ΔJ (including their signs). However, if reasonable assumptions can be made or further information from x-ray or NQR measurements is available, Δ can be calculated and compared with experimental values. In this way valuable information can be extracted, e.g. concerning the sign of χ and the anisotropy ΔJ of the **J** tensor, a magnitude not easily accessible by other methods.[9]

In this paper $^1J(^{55}Mn,^{31}P)$ and $^1J(^{55}Mn,^{13}C)$ data that were extracted via lineshape analysis from spin-$\frac{1}{2}$ NMR spectra in solution or from solid-state MAS measurements are compared. Preliminary results have already been presented recently.[10,11]

RESULTS AND DISCUSSION

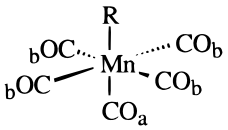
^{55}Mn,^{13}C coupling constants

Values for $^1J(^{55}Mn,^{13}CO)$ of the three (pentacarbonyl)manganese halide complexes **1**–**3** in solution were readily obtained via lineshape analysis of the corresponding quadrupole-broadened spin-$\frac{1}{2}$ NMR signals with the aid of the PC program QUADR and are shown together with the corresponding ^{13}C chemical shifts in Table 1. Our ^{55}Mn data are in satisfactory agreement with those reported earlier.[12,13] ^{13}C data from NMR in solution were also derived for the σ-organo(tetracarbonyl)manganese complexes **4**–**15**. Since significant ^{13}C results could not be extracted from solid-state NMR experiments of these compounds (see below), their data[14] will be published separately. The principle of the analysis in solution has been described in detail.[5,6] Additional line broadening effects on the S resonance line, such as from chemical exchange of S, may complicate the analysis, but were not observed here. The values of the J-couplings are independent of solvent and temperature within the reproducibility of the data ($\pm 5\%$).[6]

The choice of a suitable solvent, however, in which the complexes are reasonably soluble but do not decompose, is not always trivial and may limit the general applicability of the NMR experiments in solution. Owing to this low solubility, long measurement times of up to 24 h were necessary, e.g. for **1**. The ^{13}C NMR spectrum of the carbonyl region of **1** is presented in Fig. 1. The value of T_1(S) (536 μs) was obtained from the linewidth of the ^{55}Mn NMR signal (see Table 1) and T_2* (33 ms) was determined from a ^{13}C resonance line, not affected by quadrupolar interaction. The ^{55}Mn,^{13}CO coupling constants were obtained by lineshape analysis of the corresponding ^{13}CO signals. The calculated lineshape is superimposed on the experimental spectrum, and the difference spectrum is shown above. The values of the ^{55}Mn,^{13}CO coupling constants for **1**–**3** (131–163 Hz) are in the range for alkyl(pentacarbonyl)manganese complexes (128–174 Hz).[6] The increasing values of $^1J(Mn,CO_a)$ for **1** (148 Hz), **2** (156 Hz) and **3** (162 Hz) may be interpreted with increasing σ-donor ability in the order Cl < Br < I, resulting in increasing Mn → CO back-bonding.

The ^{13}C high-resolution MAS solid-state NMR spectra could be interpreted only for selected molecules (see Table 1 and Fig. 2). For complexes **1** and **3**, the coupling constants and isotropic chemical shifts are in good agreement with the data obtained from measurements in solution. Their ^{13}C NMR solid-state spectra are a superposition of two six-line multiplets for CO_a (at high frequency) and CO_b (at low frequency). The ^{13}C chemical shift difference of the two different car-

Table 1. δ(^{55}Mn) (ppm), linewidths $\Delta\nu_{1/2}$(Mn) (Hz), δ(^{13}CO) (ppm) and $^1J(^{55}Mn,^{13}CO)$ (Hz) of pentacarbonylmanganese halide complexes $Mn(CO)_5R$ from NMR measurements in solution and in the solid state



1 : R= Cl
2 : Br
3 : I

Compound	δ(^{55}Mn)	$\Delta\nu_{1/2}$(Mn)	δ($^{13}CO_a$)	δ($^{13}CO_b$)	J(Mn, CO_a)	J(Mn, CO_b)
1[a]	−995	590	211.0	205.3	148	134
1[b]			212.1	207.0	148	134
2[a]	−1128	1030	212.5	206.5	156	134
3[a]	−1512	660	212.5	206.2	162	134
3[b]			214.1	206.3	163	131

[a] **1** and **2** in CD_3NO_2, **3** in toluene.
[b] Solid-state measurement.

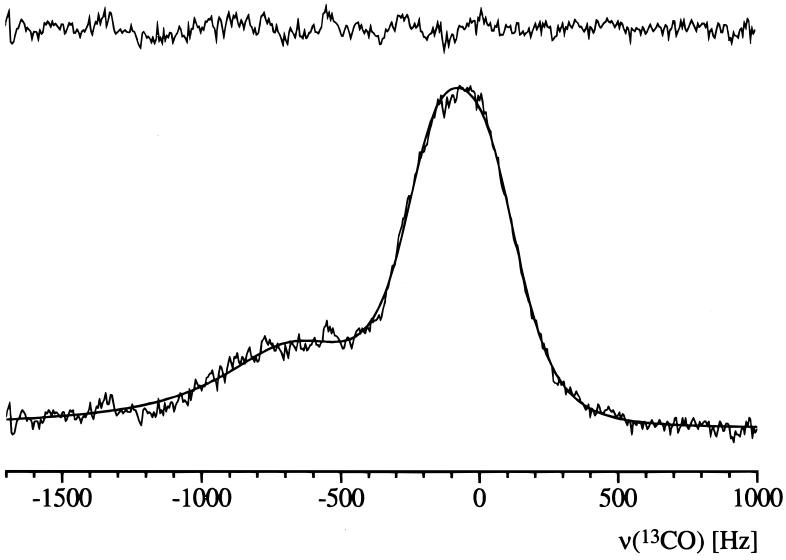


Figure 1. Carbonyl region of the experimental and calculated ^{13}C NMR spectra of **1** in CD_3NO_2 solution. The difference spectrum is shown above. (Conditions: 150.9 MHz, 300 K).

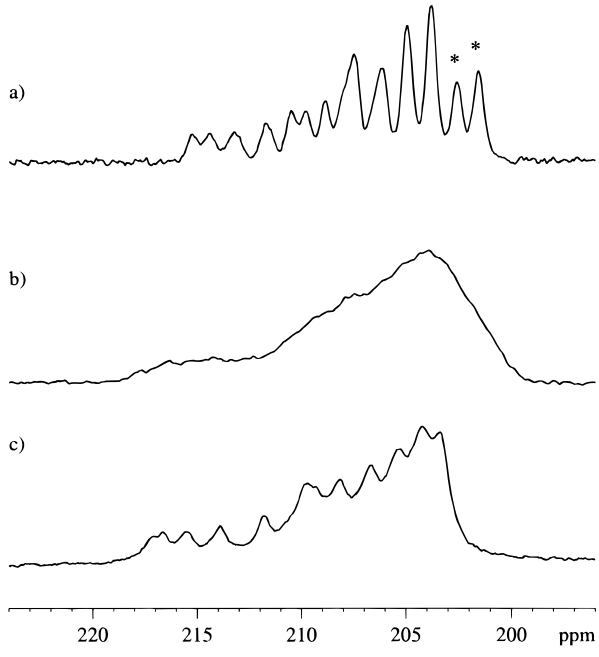


Figure 2. ^{13}C solid-state NMR spectra of the $Mn(CO)_5R$ halide complexes (a) R = Cl (**1**), (b) R = Br (**2**) and (c) R = I (**3**). The resonances marked with asterisks are discussed in the text. 100.61 MHz, 298 K, MAS rate 10 kHz.

bonyl groups is $\Delta\delta = 5.1$ ppm for **1** and 7.8 ppm for **3**. Therefore, the multiplets overlap only slightly (Fig. 2). For other σ-organo(pentacarbonyl)manganese(I) complexes, e.g. pentacarbonyl(phenyl)manganese or acetyl(pentacarbonyl)manganese, $\Delta\delta$ is <1.5 ppm,[5] which results in significant overlapping of the different ^{13}C NMR resonance signals in the solid state; hence the evaluation of the J and Δ data was not possible. The same is true for complexes **4**–**15**, with the additional complication that three different carbonyl groups are present and the signals are further split by two-bond $^{31}P,^{13}C$ coupling, which is in the range of 0–35 Hz.[14]

For **1** and **3**, crystallographic data and quadrupole coupling constants are available,[15–17] and the theoretical values for $\Delta(CO_a)$ and $\Delta(CO_b)$ could be calculated according to Eqn (2), whereby $\Delta J = 0$ was assumed. The values of the calculated residual dipolar couplings Δ_{calc} are presented in Table 2, together with the experimental data. The dipolar coupling constants $D = (\mu_0/4\pi)(\gamma_C \gamma_{Mn}/r^3_{C,Mn})(h/4\pi^2)$ and the polar and azimuthal angles α^D and β^D of the $\mathbf{r}_{Mn,CO}$ vectors in the principal-axes system of the quadrupole coupling tensor, calculated from the published data,[15–17] are also shown in Table 2. For **1**, the Zeeman frequency $\nu(^{55}Mn) = 99.08$ MHz has been determined from NMR measurements in

Table 2. Dipolar coupling constant D, polar and azimuth angles α^D and β^D [15–17] and calculated and experimental values for Δ of $Mn(CO)_5Cl$ (1) and $Mn(CO)_5I$ (3)

Parameter	CO_a (1)	CO_b (1)[a]	CO_b (1)[a]	CO_a (3)	CO_b (3)
D (Hz)	1271.9	1108.0	1106.3	1196.8	1116.9
α^D (°)	-90	44.1	−44.9	—	45
β^D (°)	0.8	90.6	92.9	0	93.1
Δ_{calc} (Hz)	−53.4	23.2	23.0	−72.0	33.3
Δ_{exp} (Hz)	−52 ± 8	21 ± 5	21 ± 5	−75 ± 8	31 ± 4

[a] With two non-equivalent crystallographic sites for CO_b.

solution. The quadrupole coupling constant for **1** is 13.858 MHz and $\eta(^{55}Mn) = 0.0433$.[15] For **3**, $\nu(^{55}Mn) = 99.05$ MHz, $\chi(^{55}Mn) = 19.849$ MHz and $\eta(^{55}Mn) = 0.024$[15] were used for the calculation of the Δ_{calc} values.

For complex **1**, it must be taken into consideration that the crystal symmetry is C_s with two non-equivalent pairs of CO groups.[16] The corresponding Δ_{calc} values are, however, almost identical (Table 2). The calculated residual dipolar effects, $\Delta(CO_a)$ and $\Delta(CO_b)$, are in good agreement with the experimental values, which is consistent with the assumption of $\Delta J = 0$. Additionally, this calculation did not take into account the presence of the additional pair of quadrupolar nuclei ($^{35/37}Cl$) in the molecule. If a spin-$\frac{1}{2}$ nucleus I is coupled to more than one quadrupolar nucleus, the overall splitting pattern may be analysed as the convolution of the individual splitting.[8] With the reasonable assumption that $J(^{35,37}Cl,^{13}CO) = 0$, Eqn (1) predicts that each of the ^{13}C NMR resonance lines should be split additionally into two doublets due to the two chlorine isotopes. The ^{35}Cl quadrupole coupling constant is 36.07 MHz,[15] from which we estimated $\chi(^{37}Cl) \approx 28.6$ MHz [$Q(^{35}Cl)/Q(^{37}Cl) = 1.26$[18]]. With $\nu(^{35}Cl) \approx 40.5$ MHz and $\nu(^{37}Cl) \approx 33.72$ MHz (at 9.4 T), the splitting for each resonance line of the carbonyl multiplets should be 21.8 Hz (17.3) for $^{13}CO_a$ and 23.7 Hz (18.8) for both pairs of $^{13}CO_b$ groups owing to the presence of ^{35}Cl (^{37}Cl). Thereby, we assumed equal directions of the principal-axes systems of the quadrupolar interactions at chlorine and manganese. In fact, there is no evidence for this additional splitting in the ^{13}C MAS spectrum of **1**. Probably these small effects of the chlorine nuclei are not detectable in consideration of the experimental linewidth of more than 60 Hz of the individual ^{13}C NMR resonances (see Fig. 2).

The good agreement between isotropic chemical shifts and *J*-coupling constants for **1** from measurements in solution and the solid state may indicate that the two additional resonance lines marked with asterisks in Fig. 2 do not have to be taken into account for the data evaluation, and we have no conclusive explanation for their occurrence. On a trial basis, they could be explained as being due to the lowered crystal symmetry of **1**. Although the deviation from C_{4v} symmetry is small and the theoretical residual dipolar couplings for the two pairs of CO_b are almost identical, their isotropic chemical shift need not necessarily be the same. The two extra lines may originate from the six-line multiplet of one of the two non-equivalent carbonyl groups in an equatorial position resonating at lower frequency ($\Delta\delta = -2.2$ ppm). This explanation is not unlikely, since it is well known that solid-state NMR spectra are very sensitive to the local molecular environment in the crystal and that a lower molecular symmetry or non-equivalent molecules in the unit cell may result in additional solid-state NMR resonance lines.[19,20] In any case we exclude a $^{35,37}Cl$ isotope effect on the ^{13}C chemical shifts causing the two extra resonance lines. Similar effects in solution amount to some ppb at most.[21] Finally, impurities in the sample could also be excluded. A sample of $Mn(CO)_5Cl$, used for MAS measurements, was investigated by powder diffraction x-ray analysis. From the single-crystal data[16] we calculated all possible powder reflections; the experimentally determined data corresponded well with these theoretical reflections.

The single-crystal structure of **3** exhibits higher molecular symmetry than that for **1**.[17] The ^{13}CO region of the MAS NMR spectrum (see Fig. 2) shows two partially overlapping six-line multiplets for the CO_a and CO_b groups in *trans*- and *cis*-positions with respect to the iodine ligand. The data calculated for the residual dipolar effects again fit well with the experimentally determined Δ values (Table 2). As for **1**, a possible anisotropy of the *J*-coupling was thereby neglected. However, it must be noted that this supposition remains questionable for both complexes and anisotropies $\Delta J \neq 0$ cannot be excluded, owing to the experimental error limits of more than 4 Hz. Assuming, e.g. for **3**, axial symmetry of **J** and the PAS of **J** aligned with the **r**(Mn, CO) vector, $^{8}\Delta J$ was evaluated according to Eqn (2), using angles, dipolar couplings and Δ_{exp} values from Table 2. The values $\Delta J(CO_a) = -150$ Hz, $\Delta J(CO_b) = 230$ Hz for $\chi > 0$ and $\Delta J(CO_a) = 7330$ Hz, $\Delta J(CO_b) = 6470$ Hz for $\chi < 0$ were obtained from these calculations (with ± 400 Hz error limits for all ΔJ values). In the literature, ΔJ values with a ratio $\Delta J/J \gg 1$ are usually disregarded.[20] Thus, although the interpretation of our data does not allow us to give a precise answer about the anisotropy of **J**, it indicates for **3** a positive sign of χ. The same is true for complex **1**. A positive value of χ has already been predicted by Bancroft *et al.*[22] for complexes **1**–**3** by the calculation of $\chi(^{55}Mn)$ from partial quadrupole splitting values of the isoelectronic Fe(II) species.

Since the ^{127}I quadrupole coupling constant $\chi = 973$ MHz is large[15] and Eqn (1) would no longer be valid to predict the iodine–carbon interaction ($\chi \gg \nu_S$), a complex splitting of the ^{13}C resonance of **3** could be expected. The absence of additional ^{13}C resonance line splitting may indicate that the ^{127}I quadrupolar relaxation rate in complex **3** is very high also in the solid state. This results in effective decoupling between ^{127}I and ^{13}C. The same effect of self-decoupling has been observed in the solid-state proton NMR spectrum of *trans*-diiodoethylene.[23]

In contrast to **1** and **3**, the multiplet fine structure of the ^{13}C NMR resonance lines is completely washed out for the bromine complex **2** [see Fig. 2(b)] and no analysis could be carried out. In analogy to NMR in solution, this may point to unfavourable relaxation rates of $^{79,81}Br$ and/or ^{55}Mn, which are in the order of the relevant couplings in **2**. Significant quadrupolar relaxation in the solid state occurs for nuclei with large quadrupolar coupling constants (e.g. ^{127}I in **3**), or can be induced by dynamic effects.[8,24,25] Molecular motion, inducing fast ^{55}Mn spin relaxation, might indeed be present for tricarbonyl(cyclopentadienyl)manganese and pentacarbonyl(methyl)manganese.[26] For both ^{13}C MAS spectra, very broad and unstructured signals were observed.

$^{55}Mn,^{31}P$ coupling constants

The tetracarbonyl manganese complexes $Mn(CO)_4(R)L$ may exist in two isomeric forms, with the ligands R and

L in either the *cis* or *trans* configuration. Except for **7**–**9**, where the *trans* form amounts to *ca.* 5%,[14] only the isomers with a *cis* configuration of R and L were detected with ^{55}Mn and ^{31}P NMR experiments in solution. The lineshape analysis of the ^{31}P NMR resonance signals in solution works well as long as the quadrupole relaxation rate and the ^{55}Mn linewidth are not too large (e.g. for **7**). The $\delta(^{55}\text{Mn})$, $\Delta\nu_{1/2}(^{55}\text{Mn})$,$^1J(^{55}\text{Mn}, ^{31}\text{P})$ and $\delta(^{31}\text{P})$ data for the $Mn(CO)_4(R)L$ complexes **4**–**15** are listed in Table 3, together with the pertinent data from the solid-state NMR study.

Cross-polarization (CP) MAS NMR spectra for several complexes were readily interpreted and the coupling constants $J(^{55}\text{Mn},^{31}\text{P})$ extracted (see Table 3). Within the accuracy limit of ± 5 Hz, solid-state J values are generally in good agreement with the NMR data from solution. The isotropic chemical shifts $\delta(^{31}\text{P})_{iso}$ show no systematic deviation between the two methods, which indicates that there are no substantial changes between the solid-state and the solution structures. The value of $^1J(^{55}\text{Mn},^{31}\text{P}) = 206$ Hz for **10** corresponds well with the value obtained by Lindner *et al.*[27]

For the *cis*-tetracarbonyl(phosphine)organomanganese complexes **4**–**11** and **13**–**15**, J(Mn,P) values of 210 ± 20 Hz were obtained. Compared with $J = 252$ Hz for *trans*-**7**[14] and $J = 245$ Hz for *trans*-**8**,[28] these coupling constants are generally smaller. The same trend has already been observed for J(Mn,CO) in complexes **1**–**3** and for a series of σ-organo(pentacarbonyl) manganese complexes, where CO_a shows a larger coupling constant than CO_b.[5,6] The ^{55}Mn,^{31}P coupling constant of the trimethylphosphite complex **12** (373 Hz) is substantially larger, but within the range of the data of 330–405 Hz for complexes of the type $[MnLL'(CO)_2[P(OMe)_3]_2]$.[29]

Overlapping multiplets from non-equivalent crystallographic ^{31}P sites or from partial disorder due to the simultaneous occurrence of isomers with *cis* and *trans* configurations in the unit cell complicate the analysis from solid-state NMR spectra. The structural disorder for **9** is known from the literature,[30] and its ^{31}P NMR spectrum shows an additional broad, apparent doublet signal at low frequency (see Fig. 3) with a spacing of 540 Hz [$\delta(^{31}\text{P}) = 55.9$ ppm]. A lower crystal symmetry with ^{31}P nuclei having different isotropic chemical shifts is also expected for **5** (Fig. 3) and **6**, since for both complexes an additional doublet was detected. The same effect has been observed for the $^{13}CO_b$ region of the solid-state NMR spectrum of $Mn(CO)_5Cl$ (**1**) (see Fig. 2). With $\delta(^{31}\text{P}) = 38.6/39.8$ ppm for **5** and $\delta(^{31}\text{P}) = 33.4/$

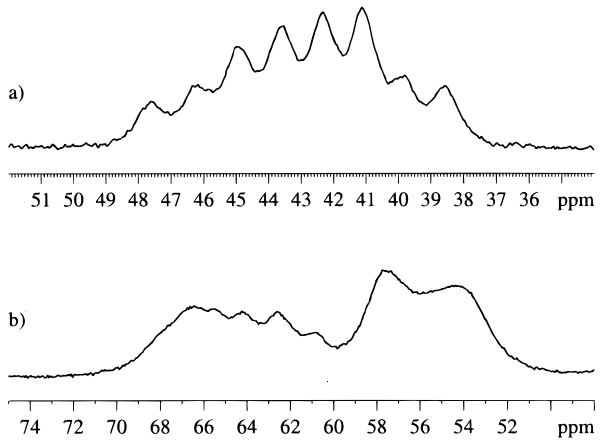
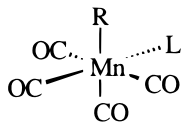


Figure 3. Central signals of the ^{31}P CP/MAS spectra of σ-organotetracarbonyl(triphenylphosphine)manganese complexes with (a) R = Br (**5**) and (b) R = CH_3 (**9**).

Table 3. $\delta(^{55}\text{Mn})$ (ppm), $\Delta\nu_{1/2}(^{55}\text{Mn})$ (kHz), $\delta(^{31}\text{P})$ (ppm), $^1J(^{55}\text{Mn},^{31}\text{P})$ (Hz) coupling constants and Δ (Hz) of *cis*-tetracarbonyl(phosphine)organomanganese complexes $Mn(CO_4)(R)L$ from solution at 300 K and from solid-state NMR



Compound	R	L	$\delta(^{55}\text{Mn})$	$\Delta\nu_{1/2}$(Mn)	$\delta(^{31}\text{P})$ soln[a]	J(Mn,P) soln	$\delta(^{31}\text{P})$ solid	J(Mn,P) solid	Δ solid
4	Cl	PPh_3	−944	2.4	42.2	206	40.9	205	3.4 ± 1.5
5	Br	PPh_3	−1108	5.5	40.8	215	44.3	211	9.4 ± 2.7
6	I	PPh_3	−1372	5.1	39.4	226	39.5	216	9.6 ± 4.1
7	Ph	PPh_3			52.9		49.3	213	−82 ± 13
8	Benz	PPh_3	−1939	22.0	61.8	211	67.4	204	−67 ± 21
9	Me	PPh_3	−2125	20.1	63.6	206	64.5	216	−77 ± 18
10	Br	$PPh_2{}^nPr$	−1192	5.0	37.1	205	36.5	206, 207[c]	20.7 ± 4.5
11[b]	Br	PMe_3	−1335	3.9	4.9	191			
12	Me	$P(OMe)_3$	−2278	3.7	176.2	373			
13	Me	PEt_3	−2259	4.4	41.8	199			
14	Ac	PEt_3	−1953	7.0	38.7	221			
15	Ac	PBu_3	−1958	13.7	33.6	207			

[a] **4**–**7**, **9**–**12** and **15** in benzene-d_6; **8**, **13** and **14** in $CDCl_3$.
[b] **11**–**15** are oils at room temperature.
[c] From Ref. 27.

34.6 ppm for **6**, respectively, the two doublets appear at low frequency from the evaluated six-line multiplets. ^{31}P NMR measurements in solution gave no resonance signals at these positions.

The absence of NQR data for the tetracarbonyl complexes complicates the interpretation of the residual anisotropic effects Δ. Generally, Δ shows small and positive values for the tetracarbonyl(phosphine)manganese halide complexes **4**–**6** and **10**. The complexes **7**–**9** (R = Ph, Benz, Me) exhibit larger values for Δ with a negative sign. On the assumptions of $|\Delta J| \ll D$ and of positive signs of χ for **7**–**9**, this would indicate that the *z*-axes of the quadrupolar interactions at manganese are parallel to the bond direction Mn—R for R = halogen, and along Mn—PPh_3 for the alkyl complexes. A further analysis of Δ for the complexes **4**–**10**, as was possible for **1** and **3**, however, would require additional information from NQR and x-ray measurements. Small alterations of the ligands L and R resulted in large variations of Δ (see **4** → **5** → **10**). This points to a more complex interplay between the relevant parameters. Additionally, the error limits for small values of Δ are large. Since $\Delta \propto 1/\nu_s$, more precise data should be obtained from measurements at lower magnetic fields.

EXPERIMENTAL

$Mn_2(CO)_{10}$ was purchased from Strem Chemicals and all other reagents were purchased from Fluka and distilled before use, if necessary. The following complexes were prepared according to literature procedures: pentacarbonylmanganese chloride (**1**) and pentacarbonylmanganese bromide (**2**),[31] pentacarbonylmanganese iodide (**3**),[32] tetracarbonyl(triphenylphosphine)manganese chloride (**4**), tetracarbonyl(triphenylphosphine) manganese bromide (**5**) and tetracarbonyl(triphenylphosphine)manganese iodide (**6**),[33] tetracarbonyl(phenyl)(triphenylphosphine)manganese (**7**), benzyl(tetracarbonyl)(triphenylphosphine)manganese (**8**) and tetracarbonyl (methyl) (triphenylphosphine) manganese (**9**),[34,35] tetracarbonyl(diphenyl-*n*-propylphosphine)-manganese bromide (**10**),[27] tetracarbonyl(trimethylphosphine)manganese bromide (**11**), tetracarbonyl(methyl)(trimethoxyphosphine)manganese (**12**), tetracarbonyl(methyl)(triethylphosphine)manganese (**13**) and acetyl(tetracarbonyl)(triethylphosphine)manganese (**14**)[36] and acetyl(tetracarbonyl)(tributylphosphine)manganese (**15**).[37]

The NMR spectra in solution were measured on a Bruker AMX-600 NMR spectrometer at 300 K. The ^{13}C NMR spectra were recorded at 150.904 MHz with a 90° pulse length of 7.2 μs on a broad band probe with ^{1}H decoupling (WALTZ 16)[38] and a digital resolution of 1–2.5 Hz per point. The chemical shift of the corresponding solvent relative to tetramethylsilane was used as a primary reference. The ^{31}P NMR spectra were measured with the same ^{1}H decoupling conditions on an H,C,P triple resonance probe with pulse lengths of 9.7 μs. A capillary containing 85% H_3PO_4 was used as an external reference. The ^{55}Mn NMR spectra were recorded at 148.77 MHz (90° pulse of 8.7 μs) relative to 0.1 M $KMnO_4$ in H_2O. For the evaluation of the *J* coupling constants, the FIDs were processed with the Macintosh version of the Bruker software package WIN-NMR 3.0, transferred to a PC(80486) and evaluated with the program QUADR.[4,6]

The solid-state NMR spectra were acquired at 297 ± 2 K on a Bruker ASX-400 NMR spectrometer using a 4 mm magic angle (MAS) probe head. The ^{13}C polarization for **1**–**3** was generated by 45° single-pulse excitation (PW = 2.5 μs) at 100.6 MHz, and MAS rates of 10–14 kHz and recycle delays of 2–5 s were applied. ^{13}C chemical shifts were externally referenced to TMS at 0 ppm and the magic angle was optimized on glycine. ^{31}P CP spectra at 161.98 MHz were obtained for MAS rates of 4–6 kHz, contact times of typically 1.5 ms and recycle delays of 2–5 s. The ^{1}H,^{31}P Hartmann–Hahn condition for CP was adjusted with KH_2PO_4. The chemical shifts were externally referenced to H_3PO_4, and the proton decoupling field was 62.5 kHz. Because of the danger of excessive ^{1}H decoupling power we restricted the ^{31}P CP/MAS acquisition time to 100 ms and thereby the digital resolution to 5 Hz. In all spectra, only peak maxima of the resonance lines at the isotropic chemical shifts were evaluated and spinning sidebands were not considered.

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