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^{13}C, ^{17}O and ^{55}Mn NMR studies on substituted manganese carbonyl complexes. A contribution to the mechanism of demetalation reactions†‡

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ABSTRACT: ^{13}C and ^{17}O chemical shifts and $^{55}Mn,^{13}C$ coupling constants of nine pentacarbonylmanganese complexes $RMn(CO)_5$ (**6**–**14**), 13 tetracarbonylmanganese complexes $RMn(CO)_4PR'_3$ (**15**–**27**) and five tetracarbonylmanganacycle complexes (**1a**–**e**) were determined and are discussed in terms of σ-inductive substituent effects on axial and equatorial CO ligands. Linear correlations are observed between $\sigma_I(R)$ and $\delta(^{13}C)$ of equatorial CO ligands and $\delta(^{17}O)$ of axial CO ligands, respectively. In the tetracarbonylmanganacycle complexes **1a**–**e** the ^{17}O chemical shifts of the axial $(CO)_a$ ligands exhibit the largest substituent effect (*trans* influence), they correlate with the rates log k_{obs} of the demetalation reaction and the mechanistic implications are discussed. The $^{55}Mn,^{13}C$ coupling constants of the axial $(CO)_a$ ligands (144–159 Hz) likewise show a large and steady substituent dependence. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{13}C NMR; ^{17}O NMR; ^{55}Mn NMR; chemical shifts; $^{55}Mn,^{13}C$ coupling constants; manganese carbonyl complexes; substituent effects; quantitative correlations

INTRODUCTION

From the production of commodity chemicals to the synthesis of fine chemicals and pharmaceuticals, transition metal-mediated transformations occupy an ever increasing role in organic synthesis.[2] The importance of these processes has also spawned mechanistic studies designed to elucidate the precise role of the metal in these processes, and to determine the scope and limitations of the transformations.[3] One critical phase of the transition metal-mediated process involves the release of the ligand from the metal complex, and a variety of mechanisms for the metal–ligand scission have been elucidated.

Recently, a method for the preparation of ketone and carboxylic acid derivatives by the sequential insertion of carbon monoxide and alkenes/alkynes into alkylmanganese pentacarbonyl complexes has been described.[4–14] This methodology has been employed for the synthesis of *C*-glycosyl derivatives and natural products.[3–10] In addition, the mechanism of these transformations has been studied in detail because in this process the metal undergoes a novel acid-catalyzed migration during metal–carbon bond scission. Previous papers from our laboratories have reported on the mechanism of the acid-catalyzed demetalation reaction of manganacycles **1a**–**e** to produce enone **5** (Scheme 1).[12–14] In these previous studies, it was demonstrated that (1) the manganacycle underwent reversible protonation at C-4 under acidic conditions, (2) the rate of demetalation was unimolecular in manganacycle **1**, (3) the rate of demetalation had a Hammett σ^+-correlation with the *para*-substituent of the aromatic ring of $\rho = -0.76$ and (4) the rate of demetalation could be correlated with the Mn-55 chemical shift of manganacycles **1a**–**e**. These observations were consistent with the mechanism shown in Scheme 1, in which the rate-determining step in the demetalation of manganacycle **1** under acidic conditions was the simultaneous 1,2-shift of hydrogen and metal from cationic complex **2** to olefin complex **4** via transition state **3**. In this process, the correlation of the rate of rearrangement with the σ^+-value of R on the aryl ring was attributed to development of cationic character at C-5 in the rate-determining step (Scheme 1).[13]

The linear correlation of log k_{obs} with the chemical shift of Mn-55 for demetalation of manganacycle **1** was remarkable and was the first example of a quantitative relationship between a kinetic parameter and a transition metal NMR chemical shift.[13] In subsequent studies on the correlation of ^{103}Rh and ^{57}Fe chemical shifts with the rates of CO–PPh_3 ligand exchange in

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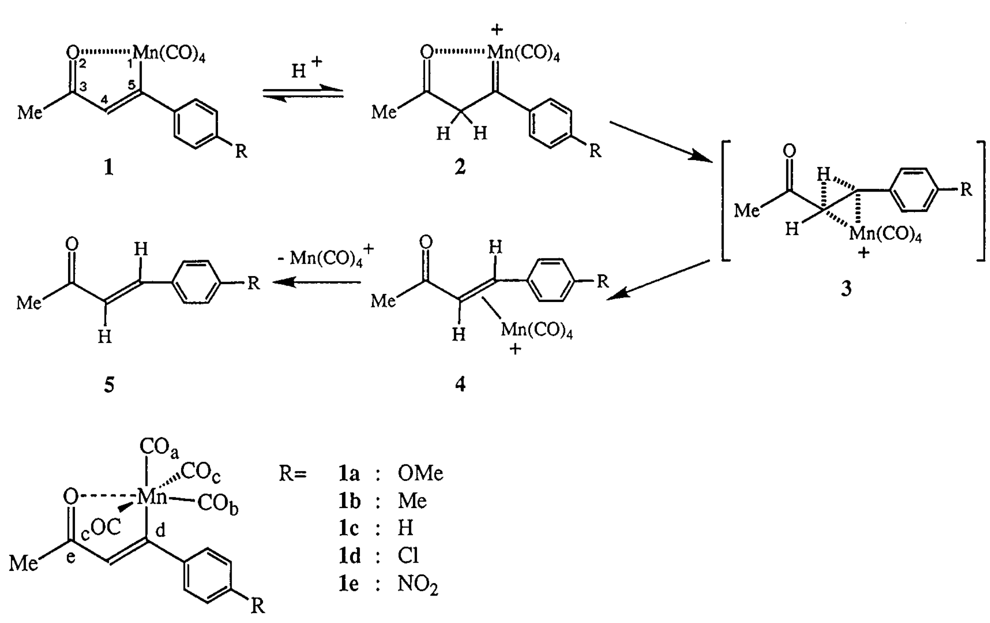


Scheme 1

(X)CpRh(CO)$_2$ complexes,[15] PPh$_3$ induced alkyl insertion in CpFe(CO)$_2$R complexes[16] and PPh$_3$ induced aryl migration in Cp(Me$_5$)Rh(I)(CO)(aryl) complexes,[17] the Zürich group was able to demonstrate that such correlations can indicate the occurrence of either *early*[15,16] or *late*[17] transition states for such organometallic reactions. On this basis, the above-mentioned log $k_{obs}/\delta(^{55}Mn)$ correlation supports an *early* transition state **3** resembling the starting complex **1** or its protonated form **2**, respectively. Further work on ^{49}Ti, ^{53}Cr, ^{91}Zr and ^{103}Rh NMR showed that both chemical shifts and linewidths of spin-1/2 and quadrupolar transition metal nuclei can be correlated with coordination geometry,[18] stability[19] and reactivity[20,21] of organometallic complexes.

The purpose of this study was to extend the application of NMR spectroscopy to the study of the demetalation process for manganese complexes. In particular, we sought to determine whether the one-bond coupling constants between ^{55}Mn and ^{13}C of C-5 in the manganacycles would correlate with the rate of demetalation as this bond is broken in the rate-determining step. In addition, the chemical shifts of the ^{13}C and ^{17}O nuclei of the terminal carbonyl ligands were measured in this context as part of an extended study of ^{17}O chemical shifts of organomanganese carbonyl complexes. In particular, it was anticipated that ^{17}O chemical shifts would be a sensitive probe of the electronic environment of the transition metal center.

RESULTS AND DISCUSSION

One-bond ^{55}Mn,^{13}C coupling constants of manganacycles 1a–e

The ^{55}Mn,^{13}C coupling constants were determined by lineshape analysis of the quadrupole-broadened ^{13}C NMR signals of C_d and the terminal carbonyl groups a, b, c of the manganacycles **1a**–**e** (Scheme 1) with the aid of the computer program QUADR as described recently for a series of R–Mn(CO)$_5$ and R-Mn(CO)$_4$L [L = PR'$_3$, P(OR')$_3$] complexes.[22,23]

The data are summarized in Table 1. The values for the Mn—C$_d$(sp^2) bond (65–81 Hz) are in the typical range for alkylmanganese pentacarbonyl and tetracarbonyl(phosphine) complexes.[22] However, there is no regular trend discernible when the electronic nature of the aryl substituents R (e.g. σ_R or $\sigma_R{}^+$) is considered, and also there is no correlation of J(Mn, C$_d$) with the rate constants k_{obs} of the demetalation reaction, as was observed for the ^{55}Mn chemical shifts.[13] The ^{55}Mn,^{13}CO one-bond coupling constants are larger (144–163 Hz). The smallest R-substituent dependence

Table 1. $^1J(^{55}Mn,^{13}C)$ coupling constants (Hz, ±5%), ^{13}C chemical shifts (ppm) and demetallation rates of manganacycles 1a–e

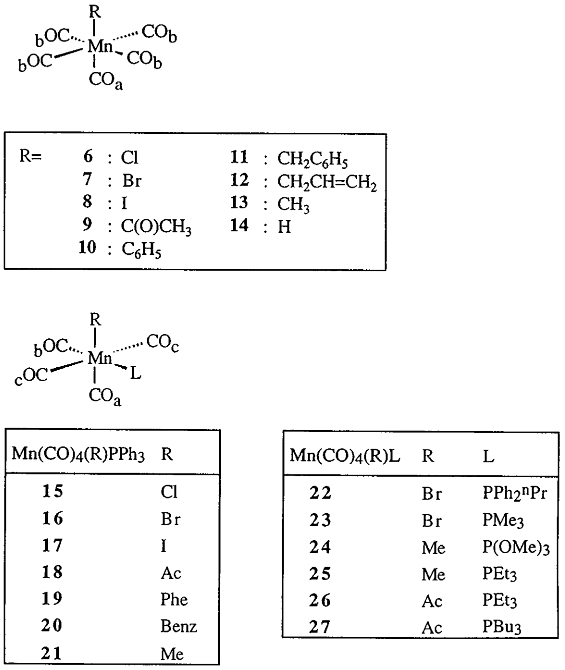
Compound	^1J(Mn, C$_a$)	^1J(Mn, C$_b$)	^1J(Mn, C$_c$)	^1J(Mn, C$_d$)[a]	$\delta(^{13}C_a)$	$\delta(^{13}C_b)$	$\delta(^{13}C_c)$	$\delta(^{13}C_d)$	$\delta(^{13}C_e)$	k_{obs} (h^{-1})[b]
1a	144	155	150	71	214.8	220.1	211.8	250.3	213.9	0.502 ± 0.019
1b	148	156	151	81	214.6	219.8	211.6	251.4	214.3	0.261 ± 0.018
1c	149	150	151	67	214.5	219.6	211.5	251.4	214.7	0.155 ± 0.006
1d	159	153	151	65	214.2	219.5	211.2	248.7	214.9	0.120 ± 0.003
1e	158	163	151	81	213.8	219.0	210.6	246.5	215.5	0.033 ± 0.003

[a] These values are subject to experimental errors ≥ 15%, see Experimental.
[b] Values taken from Ref. 13.

($\Delta J = 1$ Hz) is observed for the two equatorial [The $(CO)_a$—Mn—$C_d(sp^2)$ arrangement arbitrarily defines the principle axis of the ψ-octahedral structure] $(CO)_c$ carbonyls, which can be unambiguously assigned from the ^{13}C NMR spectrum. The other equatorial $(CO)_b$ and the axial $(CO)_a$ carbonyls exhibit a larger and comparable substituent dependence ($\Delta J = 13$–15 Hz). The value of $J(Mn,CO_a)$ increases steadily with increase in the electron-acceptor property of R, thus reflecting a typical *trans* effect[24] in the diaxial ligand–metal–ligand system, as we have recently reported for $J(^{103}Rh,^{31}P)$ in alkylrhodoximes.[25] The rate of the demetalation reactions *decreases* with increasing electron acceptor property of R. The results also support and confirm the chemical shift assignment for the axial $(CO)_a$ ligand in the manganacycles discussed in the following section.

Assignment of ^{13}CO chemical shifts in manganese carbonyl complexes

A prerequisite for the determination and structural evaluation of one-bond ^{55}Mn,^{13}C coupling constants in R–Mn$(CO)_5$ and R–Mn$(CO)_4PR_3'$ complexes, as well as the series of manganacycles **1a–e**, is an unambiguous assignment of the ^{13}C carbonyl resonance lines. In our previous study,[22] the assignment of axial and single equatorial CO groups could not be made. For this reason, we have now investigated two series of pentacarbonyl and tetracarbonyl manganese complexes with a variety of axial ligands R (Fig. 1). The principle axis is arbitrarily chosen and includes the CO ligand *trans* to the R group $(CO)_a$ ('axial' CO). The other CO ligands (b, c) are designated as 'equatorial.' The ^{13}C chemical shifts are given in Tables 2 and 3.



R=			
6	: Cl	**11**	: $CH_2C_6H_5$
7	: Br	**12**	: $CH_2CH{=}CH_2$
8	: I	**13**	: CH_3
9	: C(O)CH_3	**14**	: H
10	: C_6H_5		

Mn(CO)4(R)PPh3	R
15	Cl
16	Br
17	I
18	Ac
19	Phe
20	Benz
21	Me

Mn(CO)4(R)L	R	L
22	Br	$PPh_2{}^nPr$
23	Br	PMe_3
24	Me	$P(OMe)_3$
25	Me	PEt_3
26	Ac	PEt_3
27	Ac	PBu_3

Figure 1. Pentacarbonylmanganese complexes **6–14** and tetracarbonylmanganese complexes **15–27**.

Table 2. ^{13}C and ^{17}O chemical shifts (ppm) of (pentacarbonyl)manganese complexes R–Mn$(CO)_5$ at 300 K

Compound	$\delta(^{13}CO)_a$[a]	$\delta(^{13}CO)_b$[a]	$\delta(C^{17}O)_a$[b]	$\delta(C^{17}O)_b$[b]
6[c]	211.0	205.3	384.3	376.1
7[d]	212.5	206.5	383.9	377.4
8[e]	212.5	206.2	382.0	382.6
9	208.0	209.2	373.6	372.3
10	209.3	210.8	369.0	371.0
11	210.0	212.4	367.2	373.3
12	210.0	212.7	366.3	372.9
13	210.2	213.4	364.5	372.9
14	210.3	211.0	368.5	374.1

[a] **6**, **7** in CD_3NO_2, **8**, **14** in toluene-d_8 and **9–13** in $CDCl_3$; for J(Mn, C) values, see Ref. 23.
[b] In benzene, ±0.2 ppm.

In the case of the pentacarbonyl complexes **6–13** the chemical shifts of the equatorial carbonyl groups $(CO)_b$ correlate linearly ($r = 0.992$) with the inductive substituent constant σ_I,[26] whereby shielding increases with more positive σ_I values. The axial $(CO)_a$ chemical shifts show only a moderate correlation for carbon ligands and no correlation when the halides are included (Fig. 2).

Also in the series of substituted tetracarbonyl(triphenylphosphine)manganese complexes **15–21** the two

Table 3. ^{13}C chemical shifts (ppm) and $^2J(^{31}P,^{13}C)$ coupling constants (Hz) of tetracarbonyl(phosphine)manganese complexes R–Mn$(CO)_4$L

Compound[a]	$\delta(^{13}CO)_a$ [^2J(P,C)]	$\delta(^{13}CO)_b$ [^2J(P,C)]	$\delta(^{13}CO)_c$ [^2J(P,C)]	$\delta[^{13}C(R)]$ [^2J(P,C)]
15	214.8 —[b]	212.3 —[b]	211.2 —[b]	—
16	216.3 (~6)	211.9 (17.1)	210.6 (18.8)	—
17	218.0 (14.3)	212.5 (16.4)	210.9 (19.8)	—
18	217.7 —[b]	214.2 (12.3)	215.3 (21.3)	265.5 (15.5)
19	218.0 (11.1)	215.1 (13.5)	217.3 (21.6)	154.1 (17.0)
20	217.0 —[b]	216.0 (19.8)	219.7 (20.0)	17.1 (8.3)
21	220.0 (8.1)	216.8 (16.3)	220.4 (21.9)	− 10.6 (10.5)
22	216.9 —[b]	211.8 (12.1)	211.0 (16.7)	—
23	216.9 (19.4)	211.1 (~20)	211.1 (21.5)	—
24	217.7 (24.2)	214.1 (19.9)	217.4 (35.9)	−18.5 (17.9)
25	218.9 —[b]	215.8 (11.8)	219.8 (22.3)	−17.6 (12.5)
26	217.4 —[b]	214.9 (12.3)	215.9 (21.9)	272.9 (15.6)
27	217.7 —[b]	215.1 (11.0)	216.4 (21.5)	265.7 (14.6)

[a] **15–17**, **22–25** and **26** in CH_2Cl_2–CD_2Cl_2 (5:1) at 230 K; **18**, **19**, **21**, **27** in benzene-d_6 at 300 K; **20** in $CDCl_3$ at 300 K.
[b] $^2J(^{31}P,^{13}C)$ not resolved.

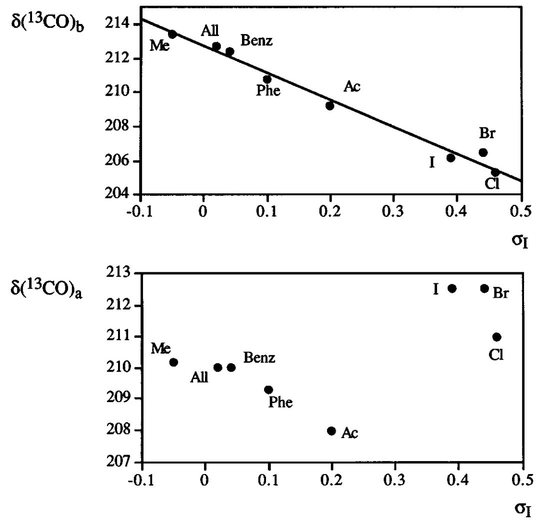


Figure 2. Correlation of $\delta(^{13}CO)_b$ with $\sigma_I(R)$, $r = 0.992$, and corresponding plot for $\delta(^{13}CO)_a$ of pentacarbonylmanganese complexes $R\text{–}Mn(CO)_5$.

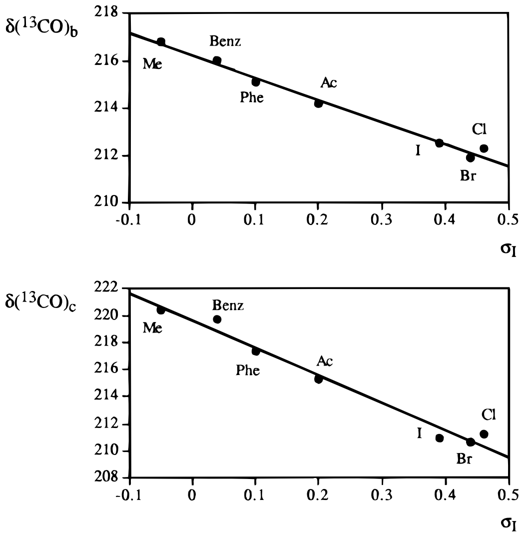


Figure 3. Correlations of $\delta(^{13}CO)_b$, $r = 0.994$, and $\delta(^{13}CO)_c$, $r = 0.988$, with $\sigma_I(R)$ of tetracarbonyl(triphenylphosphine)manganese complexes $R\text{–}Mn(CO)_4PPh_3$.

equatorial $(CO)_c$ ligands show a good correlation with $\sigma_I (r = 0.988)$. For the assignment of the two remaining single CO resonances, the magnitude of $^2J(^{31}P,^{13}C)$ coupling constants (Table 3) allows to group these resonances into two sets whereby the carbonyls with the larger coupling constants exhibit the same σ_I dependence ($r = 0.994$) as $(CO)_c$ and can, therefore, be assigned to the equatorial $(CO)_b$ *trans* to the phosphine ligand (Fig. 3). The axial $(CO)_a$ ligand again shows no correlation with σ_I. The different behavior of the axial and equatorial CO ligands with respect to substituent effects on their ^{13}C chemical shifts is significant. The ^{17}O chemical shifts are affected in an opposite sense as shielding *decreases* with increasing σ_I of the substituent R, and a linear correlation is observed only for the *axial* CO ligands. A possible explanation is discussed further below.

These results permit an unambiguous assignment of the carbonyl ^{13}C resonance lines in both series and, hence, also an assignment of the $^{55}Mn,^{13}CO$ coupling constants. These are summarized in Table 4, together with the ^{55}Mn chemical shifts and linewidths that were used to evaluate the $^{55}Mn,^{13}C$ coupling constants as described above. The $\delta(^{31}P)$ data for complexes **15**–**21** support the assignment of the ^{13}C resonances of $(CO)_b$ as they show the same overall shielding effect with increasing σ_I.[23]

The ^{13}CO chemical shifts of manganacycles **1a**–**e** (Table 1) show a high-frequency set (219.0–220.1 ppm) that can be assigned to the $(CO)_b$ carbonyls *trans* to the electron-accepting oxygen ligand. From the remaining two sets of signals the resonances of twofold intensity (210.6–211.8 ppm) must be attributed to $(CO)_c$ and hence the set at 213.8–214.8 ppm originates from $(CO)_a$ *trans* to the olefinic carbon C_d (Table 1). It is this carbonyl carbon that yields $^{55}Mn,^{13}C$ coupling constants with a steady dependence on the electron-acceptor pro-

Table 4. $^1J(^{55}Mn,^{13}C)$ (Hz), $\delta(^{55}Mn)$(ppm), and $\Delta\nu_{1/2}(^{55}Mn)$ (kHz), of tetracarbonyl(phosphine)manganese complexes $R\text{–}Mn(CO)_4L$

Compound	$^1J(Mn,CO)_a$	$^1J(Mn,CO)_b$	$^1J(Mn,CO)_c$	$^1J[Mn,C(R)]$	$\delta(^{55}Mn)$	$\Delta\nu_{1/2}(^{55}Mn)$
15	150	140	132	—	−944[a]	2.4
16	149	133	134	—	−1108[a]	5.5
17	165	140	143	—	−1372[a]	5.1
18	139	128	142	—[b]	−1825	24.6
19	132	138	138	—[b]	−1930	34.5
20	140	148	142	—[b]	−1939[a]	22.0
21	143	149	140	—[b]	−2125[a]	20.1
22	156	144	139	—	−1192[a]	5.0
23	175	138	138	—	−1335[a]	3.9
24	144	149	144	38	−2278[a]	3.7
25	140	142	131	52	−2259[a]	4.4
26	139	136	142	38	−1953[a]	7.0
27	145	138	143	44	−1958[a]	13.7

[a] From Ref. 23.
[b] Not determined.

perty of the aryl substituent R in the sense of a *trans* effect (see above). The chemical shifts of the carbonyl carbons show only a very small shielding variation (1 ppm) in the same direction, as a function of R.

^{17}O NMR chemical shifts

As the Mn—CO bond in the *trans* position to the organic ligand in the manganacycles **1a–e** appears to reflect the electronic nature of the aryl substituent R, we extended our NMR study to include the ^{17}O chemical shifts in the structure–reactivity investigation. Although ^{17}O NMR data have already been reported for several simple organomanganese carbonyl complexes including $CpMn(CO)_3$,[27] $CH_3Mn(CO)_5$,[28] $(Hal)Mn(CO)_5$[28] and $BrMn(CO)_4PPh_3$,[28a] there is no reported systematic study under standardized conditions that analyzes ligand effects on the $C^{17}O$ resonances including stereochemical assignments of axial and equatorial CO groups.

The ^{17}O NMR signals of metal carbonyl oxygen atoms are only moderately broadened by the electric quadrupole of the spin-5/2 nucleus with typical linewidths of 10–50 Hz and can, therefore, be recorded with natural isotope abundance in samples of dilute solutions (0.2–0.5 M). However, it is imperative to maintain constant medium conditions, i.e. solvent, concentration and temperature in order to achieve the best possible accuracy in the chemical shift data (±0.2 ppm) that permits a reliable interpretation.

The ^{17}O chemical shifts of nine substituted manganese pentacarbonyl complexes R—$Mn(CO)_5$ are collected in Table 2 and the corresponding data for 13 substituted manganese tetracarbonyl complexes R–$Mn(CO)_4L$ in Table 5.

In the first series, axial $(CO)_a$ and equatorial $(CO)_b$ resonances lie in the same range of 364–384 ppm and can only be differentiated and assigned based on relative intensities. Now, however, the $\delta(^{17}O)$ values of the *axial* CO groups give an excellent linear correlation ($r = 0.998$) with the σ_I substituent parameter of the *trans* substituent R, whereas there is no such correlation for the equatorial CO resonances (Fig. 4). This behavior of the ^{17}O carbonyl resonances contrasts with the corresponding ^{13}C resonances and explains why the axial ^{17}O chemical shifts correlate linearly with the equatorial ^{13}C shifts ($r = 0.989$). An analogous correlation has been reported for substituted molybdenum pentacarbonyl complexes.[29,30] Therefore, it appears that the substituent effect of R is transmitted inductively in a *trans* effect[28b] to the axial carbonyl oxygen, whereas the corresponding effect on the ^{13}C chemical shift of the axial CO ligands is evidently of a more complex nature. In addition to the σ-inductive substituent effect it may involve a change of the Mn—C bond order as a consequence of increasing π back-donation in the case of the halide substituents. This would result in creating a carbenoid carbonyl carbon with concomitant deshielding of the $(CO)_a$ resonances (Fig. 2).

Table 5. ^{17}O chemical shifts (ppm) and linewidths (Hz) of tetracarbonyl(phosphine)manganese complexes R–$Mn(CO)_4L$ in benzene

Compound	$\delta(C^{17}O)_a$ ($\Delta\nu_{1/2}$)	$\delta(C^{17}O)_b$ ($\Delta\nu_{1/2}$)	$\delta(C^{17}O)_c$ ($\Delta\nu_{1/2}$)
15	378.8	373.2	375.3
	(18)	(55)	(57)
16	379.3	374.2	376.5
	(19)	(57)	(52)
17	377.6	376.4	378.9
	(25)	(56)	(53)
18	368.4	367.5	369.4
	(23)	(47)	(53)
19	363.2	364.9	367.5
	(40)	(55)	(59)
20	362.4	365.9	369.5
	(27)	(53)	(50)
21	360.3	366.5	368.3
	(12)	(25)	(29)
22	379.3	372.5	376.1
	(18)	(54)	(56)
23	376.6	369.2	371.7
	(8)	(27)	(27)
24	357.5	366.9	366.5
	(8)	(9)	(12)
25	356.7	362.3	366.0
	(8)	(11)	(11)
26[a]	367.5	365.3	366.9
	(10)	(11)	(13)
27	367.4	365.5	366.8
	(20)	(27)	(34)

[a] In $CDCl_3$.

In the tetracarbonyl complexes (Table 5), the assignment of the ^{17}O resonances is not straightforward. The two equivalent equatorial $(CO)_c$ ligands can be attributed to the signal of twofold intensity. In each of the PPh_3 complexes **15–21** this resonance has a linewidth $\Delta\nu_{1/2}$ similar to that of one of the remaining two ^{17}O

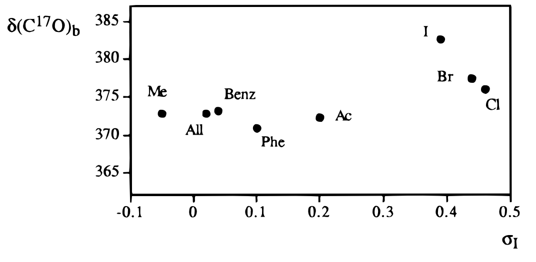


Figure 4. Correlation of $\delta(C^{17}O)_a$ with $\sigma_I(R)$, $r = 0.998$, and corresponding plot for $\delta(C^{17}O)_b$ of pentacarbonylmanganese complexes R–$Mn(CO)_5$.

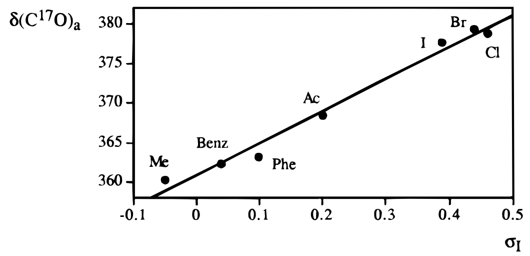


Figure 5. Correlation of $\delta(C^{17}O)_a$, with σ_I(R) of tetracarbonyl(triphenylphosphine)manganese complexes R–Mn(CO)$_4$PPh$_3$, $r = 0.992$.

signals, whereas the third resonance is considerably sharper. The latter resonances show a very similar $\delta(^{17}O)$–σ_I correlation (Fig. 5, $r = 0.992$) as observed for $(CO)_a$ in the pentacarbonyl complexes (Fig. 4) and can hence be attributed to $(CO)_a$. Thus, the inductive nature of the *trans* substituent effect on the ^{17}O carbonyl resonance is well established.

Finally, the $C^{17}O$ resonances of the manganacycle tetracarbonyl complexes were determined (Table 6). The signal with twofold intensity exhibits the smallest substituent dependence ($\Delta\delta = 1.2$ ppm) since these $(CO)_c$ ligands are *cis* to the olefinic ligand carbon C_d and the ketonic oxygen ligand. Of the two remaining resonances, one is clearly deshielded [$(CO)_b$] irrespective of the aromatic substituent R, which is attributed to the effect of the *trans* oxygen ligand ($\Delta\delta = 1.5$ ppm). The axial $(CO)_a$ resonances can thus be assigned by exclusion, but it is gratifying that this set of ^{17}O chemical shifts exhibits the largest and a steady deshielding effect ($\Delta\delta = 2.2$ ppm) with increasing electron-attracting power of the aryl substituent R, in the same sense as observed for the model complexes (Figs 4 and 5).

Table 6. ^{17}O chemical shifts (±0.2 ppm) and linewidths (Hz) of manganacycles 1a–e

Compound	$\delta(^{17}O_a)$	$\delta(^{17}O_b)$	$\delta(^{17}O_c)$
1a	376.9	383.4	372.2
	(30)	(15)	(35)
1b	377.0	383.5	372.4
	(37)	(14)	(30)
1c	377.4	383.8	3727
	(24)	(16)	(27)
1d	377.8	384.3	372.8
	(26)	(16)	(33)
1e	379.1	384.9	373.4
	(68)	(28)	(56)

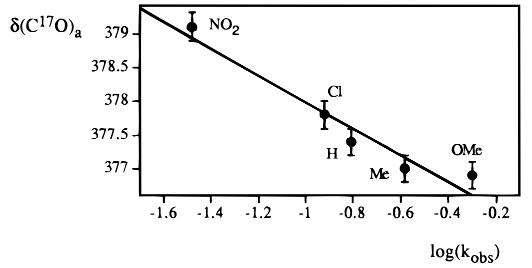


Figure 6. Correlation of $\delta(C^{17}O)_a$ with log (k_{obs}) of the demetalation reaction for manganacycle complexes 1a–e, $r = 0.971$. Error limits correspond to ±0.2 ppm.

As reported previously, the rate of demetalation of manganacycles **1a–e** correlates with both Hammett σ and σ^+ constants of the aryl substituents (correlation coefficients: $r_\sigma = 0.893$ and $r_{\sigma^+} = 0.993$).[13] In addition, there is a correlation between the demetalation rate and the ^{55}Mn chemical shift of the precursor complexes ($r_\delta = 0.956$). It was proposed on the basis of these correlations that the chemical shift of the metal was able to serve as a probe of the nature of the carbon–manganese bond in manganacycles **1** although the factors that controlled the correlation were not fully understood. Since this bond is broken in the rate-determining step of the demetalation, a correlation of the rate of demetalation with chemical shift was not unexpected.[13]

Having demonstrated a correlation between the manganese chemical shifts and rate of demetalation, it was logical to test whether such a relationship exists also for the ^{17}O chemical shifts. In the case of manganacycles **1a–e**, it was expected that as the Mn—C_d bond was varied systematically as reflected in the chemical shift of ^{55}Mn, the ^{13}C and ^{17}O chemical shifts of $(CO)_a$, the carbonyl group *trans* to C_d, would also systematically be altered. Unfortunately, the changes in ^{13}C chemical shifts of $(CO)_a$ are negligible. On the other hand, Fig. 6 illustrates the correlation of k_{obs} for demetalation and $\delta(^{17}O)$ of $(CO)_a$ ($r = 0.971$).

Note that the ^{17}O chemical shifts of $(CO)_a$ exhibit the largest substituent dependence in the series of manganacycle derivatives (Table 6). Assuming that the protonation step in the demetalation does not impose large structural changes on complex **1** [Scheme 1, fast pre-equilibrium (a fast pre-equilibrium is supported by the facile deuteration of the olefinic hydrogen of manganacycle **1** upon exposure to D_2SO_4; the deuteration half-life is *ca.* 5 min whereas the rate of acid-catalyzed demetalation is 1–6 h under these conditions)], these results are consistent with the mechanistic hypothesis that demetalation occurs via an early transition state involving hydride migration.[13,17] More importantly, the correlations of kinetic parameters with ^{17}O shielding of the metal carbonyl groups demonstrate that this technique appears to be a sensitive tool for the determination of relative reactivities in organometallic systems.

EXPERIMENTAL

Compounds

The preparation of manganacycles **1a–e** was described previously.[13] Complexes **6–8**, **15–17** and **19–27** were prepared according to literature procedures that are cited in Ref. 23. References for the synthesis of complexes **9–14** were given in two earlier papers.[22] Acetyl(tetracarbonyl)(triphenylphosphine)manganese (**18**) was also prepared following literature procedures.[31,32]

Spectra

The NMR spectra were measured on Bruker AC-300, AM-400 and AMX-600 spectrometers at 300 K. Instrumental details for the determination of the ^{13}C and ^{55}Mn spectra and the typical range of ^{13}C linewidths have been reported earlier.[22,23] The ^{17}O NMR data of the σ-organo(pentacarbonyl)manganese complexes **6–14** were recorded at 40.69 MHz with a broadband probe [BB (13.9–121.5 MHz), ^{1}H] using 90° pulse lengths of 10.0 μs. All other ^{17}O NMR spectra were measured at 81.36 MHz (AMX-600) with pulse lengths of 10.8 μs with a broadband probe [BB (18.9–156.4 MHz), ^{1}H]. Normally, relaxation delays (d_1) of 50 ms were applied, but for very broad signals d_1 was set to 10 ms, e.g. for complexes **15–20**. All ^{17}O chemical shifts are referenced externally to H_2O. The reproducibility of the ^{17}O chemical shift determination was tested by the variation of sample concentration and temperature. A temperature coefficient of 0.01 ppm K^{-1} was found and for concentrations from 0.2 to 0.6 M variation of the $\delta(^{17}O)$ values was within ± 0.2 ppm.

The $^{1}J(^{55}Mn,^{13}C)$ coupling constants were evaluated with the method reported earlier.[22,23] The error limits of the coupling constants were checked by systematic variation of all parameters, e.g. T_{1Q}, $\Delta\nu_{NQ}$, temperature and solvent. For the dimensionless lineshape factor $T_{1Q}J > 0.005$ the resulting coupling constants are subject to error limits of $\pm 5\%$. For $T_{1Q}J < 0.002$ these errors may exceed 20%.

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