Journal of Organometallic Chemistry, 267 (1984) 107–119
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

TRANSITION METAL COMPLEXES CORRESPONDING TO THE INSERTION INTO A GROUP IVB ELEMENT–CARBON BOND

II *. PREPARATION OF MANGANESE COMPLEXES. MECHANISM OF THE DEINSERTION REACTION

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(Received January 3rd, 1984)

Summary

The anions $[(\eta^5\text{-}CH_3C_5H_4)(CO)_2(R_3M)Mn]^-$ (M = Si, Ge; $R_3 = Ph_3$, $(1\text{-}C_{10}H_7)PhMe$) react with alkyl, alkenyl or benzyl halides affording the neutral complexes $(\eta^5\text{-}CH_3C_5H_4)(CO)_2(R')(R_3M)Mn$. These new compounds possess a piano stool geometry with the CO ligands in a diagonal (*trans*) arrangement. Their thermal reaction with PPh_3 leads to the formation of R_3MR' (corresponding formally to the deinsertion reaction) and R_3MH (corresponding to the migration of the R′ group to the cyclopentadienyl ring). A mechanism for these competitive reactions is proposed.

Introduction

Recently we reported [2] the preparation of molybdenum and tungsten anions in which the transition metal was bonded to a Group IVB element. Their nucleophilicity allowed their alkylation with alkyl iodides. The square pyramidal complexes thus obtained corresponded formally to the insertion of a transition metal into a Group IVB element–carbon bond (Scheme 1). However, the lack of reactivity of these compounds prevented any study of the deinsertion reactions.

The importance of the addition–elimination process involving Si–C and Ge–C bonds in homogeneous catalysis led us to extend our investigations to the related manganese complexes. Here we report the synthesis and reactivity of these new compounds.

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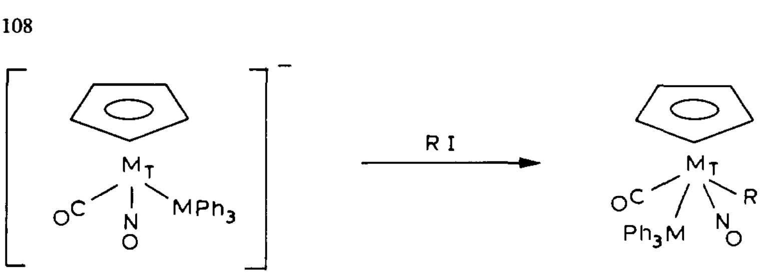
* Part I see ref. 2, and for a preliminary communication see ref. 1.

0022-328X/84/$03.00



(M_T = Mo, W ; M = Ge, Sn ; R = CH_3 , C_2H_5)

SCHEME 1

Experimental

All experiments were carried out under nitrogen, using standard vacuum line techniques. Solvents were dried, distilled and deoxygenated. Starting materials were commercial products or prepared according to the literature.

Melting points were taken under vacuum with a Tottoli apparatus. IR spectra were recorded on a Perkin-Elmer 298 spectrophotometer and NMR spectra with a Varian EM 360 or EM 390 spectrometer (chemical shifts are relative to TMS).

The physical properties of the new compounds are given in Tables 1-3.

Reaction of Ph_3SiLi with methylcymantrene

A solution of 10 mmol of Ph_3SiLi in 50 ml of THF was prepared by treating 2.94 g of Ph_3SiCl with 0.5 g of lithium [3]. This solution was added to 2.2 g (10 mmol) of $(\eta^5\text{-}CH_3C_5H_4)(CO)_3Mn$ in 50 ml of THF. The mixture was stirred at room temperature for 4 h. The IR spectra showed CO absorptions at 1910 and 1810 cm^{-1}. The solvent was pumped off. The residue was chromatographed on a silica gel column; elution with hexane/toluene (80/20) afforded the unreacted $(\eta^5\text{-}CH_3C_5H_4)(CO)_3Mn$ whereas elution with toluene provided an orange band containing 1.05 g (22%) of yellow $[\eta^5\text{-}CH_3(Ph_3Si)C_5H_3](CO)_3Mn$ (m.p. 113-114°C). ν(CO)

TABLE 1

YIELDS, MELTING POINTS AND CO STRETCHING ABSORPTIONS

Compound	Formula	Yield (%)	M.p. [a] (°C)	ν(CO) (cm^{-1}) [b]
1	$(\eta^5\text{-}CH_3C_5H_4)(CO)_2(CH_3)(Ph_3Si)Mn$	75	133-134	1970m, 1910s
2	$(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)(Ph_3Si)Mn$	73	120-121	1970m, 1910s
3	$(\eta^5\text{-}CH_3C_5H_4)(CO)_2(CH_3)(1\text{-}NpPhMeSi)Mn$ [c]	30	124-125	1965m, 1905s
4	$(\eta^5\text{-}CH_3C_5H_4)(CO)_2(CH_3)(Ph_3Ge)Mn$	65	121-122	1970m, 1910s
5	$(\eta^5\text{-}CH_3C_5H_4)(CO)_2(CH_3)(1\text{-}NpPhMeGe)Mn$	41	109-110	1960m, 1905s
6	idem [d]	26	112-113	
7	$(\eta^5\text{-}CH_3C_5H_4)(CO)_2(C_2H_5)(Ph_3Si)Mn$	73	104-105	1965m, 1905s
8	$(\eta^5\text{-}CH_3C_5H_4)(CO)_2(C_2H_5)(Ph_3Ge)Mn$	59	93-94	1965m, 1905s
9	$(\eta^5\text{-}CH_3C_5H_4)(CO)_2(\eta^1\text{-benzyl})(Ph_3Si)Mn$	56	96-98	1965m, 1905s
10	$(\eta^5\text{-}CH_3C_5H_4)(CO)_2(\eta^1\text{-benzyl})(Ph_3Ge)Mn$	65	77-79	1970m, 1910s
11	$(\eta^5\text{-}CH_3C_5H_4)(CO)_2(\eta^1\text{-butenyl})(Ph_3Si)Mn$	78	95-96.5	1970m, 1910s

[a] All the compounds are yellow. [b] In CH_2Cl_2. [c] 1-Np = 1-$C_{10}H_7$. [d] *S*-Isomer $[\alpha]_D^{25}$ +18.7° in CH_2Cl_2.

TABLE 2

^{1}H NMR DATA (in C_6D_6) [a]

Complex	δ(R–Mn) (ppm)	δ(Cp) (ppm)	δ(CH_3Cp) (ppm)
1	0.98(s)	4.09(m)–3.73(m)	1.34(s)
2	0.98(s)	4.07(s)	–
3	0.97(s)	3.90(m)–3.63(m)	1.30(s) [b]
4	0.97(s)	4.14(m)–3.77(m)	1.30(s)
5	0.99(s)	3.87(m)–3.63(m)	1.33(s) [c]
7	2.08(q)–1.58(t)	4.06(m)–3.71(m)	1.38(s)
8	2.20(q)–1.62(t)	4.10(m)–3.77(m)	1.40(s)
9	3.36(s)	4.05(m)–3.80(m)	1.37(s)
10	3.40(s)	4.07(m)–3.87(m)	1.37(s)
11	5.99(m)–5.01(m) –2.48(m)–2.08(m)	4.07(m)–3.77(m)	1.38(s)

[a] s = singlet, m = multiplet, t = triplet, q = quadruplet. [b] δ(CH_3Si) 1.31 ppm and the two signals are superimposed (6H). [c] δ(CH_3Ge) 1.31 ppm and the two signals are superimposed (6H). In CD_2Cl_2: δ(CH_3Cp) 1.77 and δ(CH_3Ge) 1.20 ppm.

(in CH_2Cl_2): 2000s and 1928s cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.63–7.17 (m, C_6H_5), 4.37 (m, 2H, Cp), 4.03 (br s, 1H, Cp), 1.43 (s, CH_3). Anal. Found: C, 68.26: H, 4.46; Mn, 11.30. $C_{27}H_{21}MnO_3Si$ calcd.: C, 67.92; H, 4.40; Mn, 11.53%. Mass: *m/e* = 477 (*M*), 393 (*M* − 3CO).

Preparation of complexes 1, 2, 7 and 9

A solution of 580 mg (1 mmol) of [(η^5-$CH_3C_5H_4$)$(CO)_2$($SiPh_3$)Mn]Et_4N, pre-

TABLE 3

ELEMENTAL ANALYSES

Compound	Formula	Found (calcd.) (%)		
		C	H	Si
1	$C_{27}H_{25}MnO_2Si$	69.64 (69.81)	5.43 (5.42)	6.05 (6.05)
2	$C_{26}H_{23}MnO_2Si$	69.50 (69.48)	5.10 (4.93)	
3	$C_{26}H_{25}MnO_2Si$	69.07 (69.03)	5.57 (5.53)	
4	$C_{27}H_{25}GeMnO_2$	63.72 (63.70)	4.91 (4.92)	
5	$C_{26}H_{25}GeMnO_2$	62.80 (62.83)	4.99 (5.03)	
7	$C_{28}H_{27}MnO_2Si$	69.86 (70.28)	5.65 (5.69)	
8	$C_{28}H_{27}GeMnO_2$	64.54 (64.30)	5.21 (5.20)	
9	$C_{33}H_{29}MnO_2Si$	73.28 (73.32)	5.43 (5.41)	
10	$C_{33}H_{29}GeMnO_2$	67.50 (67.74)	5.00 (5.00)	
11	$C_{30}H_{29}MnO_2Si$	71.54 (71.35)	5.73 (5.75)	

pared from (η^5-$CH_3C_5H_4$)$(CO)_2(SiPh_3)$(H)Mn [4] in 20 ml of THF, was treated with an excess (200 μl) of CH_3I at room temperature. A yellow solution and a white precipitate were obtained after stirring for ca. 30 min. The reaction mixture was filtered and the solvent was pumped off. The residue was taken up in the minimum amount of toluene and five volumes of pentane were added. Standing at −20°C afforded yellow crystals of **1** (350 mg, 75%).

Compounds **7** and **9** were prepared similarly using C_2H_5I and $PhCH_2Br$ (or $PhCH_2Cl$). The complex (η^5-$CH_3C_5H_4$)$(CO)_2(CD_3)(SiPh_3)$Mn, **1D**, was prepared using CD_3I. The reaction of CH_3I with [(η^5-C_5H_5)$(CO)_2(SiPh_3)$Mn]Et_4N (prepared from the related hydride, as above) led to complex **2**.

Preparation of complex 11

A suspension of 960 mg (1.7 mmol) of [(η^5-$CH_3C_5H_4$)$(CO)_2(SiPh_3)$Mn]Et_4N in 30 ml of THF was treated with an excess of 1-iodo-3-butene (500 μl) at 4°C. The reaction occurred slowly (requiring one week in a refrigerator). A similar procedure to that given above was used. Crystallization from hexane yielded 650 mg (78%) of (η^5-$CH_3C_5H_4$)$(CO)_2$(η^2-butenyl)$(SiPh_3)$Mn, **11**. At room temperature **11** decomposed slowly (see below).

Decomposition of 11

A solution of 500 mg (1 mmol) of **11** in 30 ml of THF was stirred for 10 days. The IR spectrum showed that the CO absorptions at 1960 and 1910 cm^{-1} due to **11** had disappeared while new ones at 1955 and 1895 cm^{-1} had appeared. The solvent was pumped off. Chromatography of the residue on a silica gel column afforded two bands (elution with hexane/CH_2Cl_2 mixtures). The first band (colorless) contained 195 mg of Ph_3SiH (75% yield), the second one (yellow) contained 135 mg of an oily compound. The latter could not be purified by crystallization but its IR, NMR and mass spectra were in agreement with the formula [η^5-,η^2-$(CH_3)(CH_2{=}CH(CH_2)_2)C_5H_3$]$(CO)_2$Mn. ^1H NMR (C_6D_6): δ 4.32 (m) and 4.20 (m, 3H, Cp), 3.5 (br m, 1H), 2.3 (m, 2H), 1.9–0.8 (m, 4H), 1.45 (s, CH_3). IR (CH_2Cl_2): ν(CO) 1955 and 1890 cm^{-1}. Mass: $m/e = 244$ (M), 216 (M − CO).

Preparation of complex 3

A solution of 440 mg (1 mmol) of (−)-(η^5-$CH_3C_5H_4$)$(CO)_2$((1-$C_{10}H_7$)-PhMeSi)(H)Mn ($[\alpha]_D^{25}$ − 58.6° in benzene) [5] in 20 ml of THF was treated with an excess of NaH at −15°. The suspension was allowed to warm to room temperature and stirred overnight. Then it was filtered. CH_3I (200 μl) was added. After 15 min the mixture was filtered again. The solvent was pumped off and the residue taken up in the minimum amount of toluene. Addition of hexane and cooling at −20°C afforded 136 mg (30% yield) of yellow crystals of racemic (η^5-$CH_3C_5H_4$)$(CO)_2$-(CH_3)((1-$C_{10}H_7$)PhMeSi)Mn, **3**. The mother liquor was evaporated. The optical rotation of the residue was $[\alpha]_D^{25}$ + 17.9° in CH_2Cl_2 (14 g l^{-1}). All attempts to crystallize the optically active complex failed.

Preparation of complexes 4, 8, and 10

Treatment of [(η^5-$CH_3C_5H_4$)$(CO)_2(Ph_3Ge)$Mn]Et_4N [5] (prepared by treating (η^5-$CH_3C_5H_4$)$(CO)_3$Mn with Ph_3GeLi [6] and then Et_4NCl) with CH_3I, C_2H_5I or $PhCH_2Br$, as above, led to complexes **4**, **8** and **10** (see preparation of **1**, **7** and **9**).

TABLE 4

REACTION OF COMPOUND 1 WITH Ph_3P

c^a (mol l^{-1})	Reaction time (h)	Ph_3SiH (%)	Ph_3SiCH_3 (%)
0.028	12	47	53
0.28	6	33	67

[a] Concentration of both reagents.

Preparation of complexes 5 and 6

A solution of $[(\eta^5\text{-}CH_3C_5H_4)(CO)_2((1\text{-}C_{10}H_7)PhMeGe)Mn]Et_4N$, ($[\alpha]_D^{25}$ − 3.9° in CH_2Cl_2) [7] 4.9 g, 10 mmol, in 50 ml of THF was treated with 3 ml (excess) of CH_3I at room temperature for 1 h. A white precipitate formed, the solution was filtered and the solvent was pumped off. The residue was taken up in toluene, filtered and hexane was added. Standing at −20°C yielded yellow crystals, which were recrystallized to give 1.3 g (26% yield) of optically active **6**, $[\alpha]_D^{25}$ + 7.2° in benzene (5.55 g l^{-1}) and +18.7° in CH_2Cl_2 (5.45 g l^{-1}).

Racemic **5** was obtained similarly.

Attempts of reaction with HCl, Cl_2, H_2O, CH_3OH and $LiAlH_4$

A solution of **1** in ether was treated with an excess of the reagent (HCl, H_2O, CH_3OH, $LiAlH_4$) at room temperature. Cl_2 was used in CCl_4 solution. No reaction was observed in any case.

Reactions of PPh_3 on 1, 1D, 2, 4 and 7

A solution of 650 mg (1.4 mmol) of **1** and 367 mg (1.4 mmol) of PPh_3 in benzene was refluxed (Table 4) until the CO absorptions of the starting material (1970 and 1910 cm^{-1}) disappeared. The mixture was chromatographed on an acid-washed alumina column. Two bands were obtained. The first one (colorless, elution with petrol/benzene 80/20) contained Ph_3SiH and Ph_3SiCH_3. The ratio of these products was determined by GLC (SE 30 column, 250°C) and ^1H NMR spectroscopy. The second one (yellow, elution with benzene) was a mixture (520 mg, ~ 80% yield) of $(\eta^5\text{-}CH_3C_5H_4)(CO)_2(PPh_3)Mn$ and$[\eta^5\text{-}(CH_3)_2C_5H_3](CO)_2(PPh_3)Mn$ as shown by mass spectroscopy, m/e assignment = 452 and 466 (molecular peaks). The IR spectrum showed CO absorptions at 1935 and 1860 cm^{-1} in $CHCl_3$, in agreement with the literature [8].

The same results were obtained when the reaction was carried out in C_6D_6.

The same procedure was used, starting with $(\eta^5\text{-}CH_3C_5H_4)(CO)_2\text{-}(CD_3)(Ph_3Si)Mn$, **1D**, or the related compounds **2**, **4** and **7**. Tables 5 and 6 show the products obtained from **4** and **7**.

TABLE 5

REACTION OF COMPOUND 4 WITH Ph_3P

c^a (mol l^{-1})	Ph_3GeH (%)	Ph_3GeCH_3 (%)
0.028	15	85
0.067	6	94

[a] Concentration of both reagents.

TABLE 6

REACTION OF COMPOUND 7 WITH Ph_3P

c^a (mol l^{-1})	Ph_3SiH (%)	Ph_3SiEt (%)
0.023	55	45
0.068	43	57

[a] Concentration of both reagents.

Thermal decomposition of 1 and 9

A solution of 317 mg (0.7 mmol) of **1** in 30 ml of benzene was refluxed for 12 h. Work up as above afforded 130 mg of a mixture of Ph_3SiH (31%) and Ph_3SiCH_3 (69%).

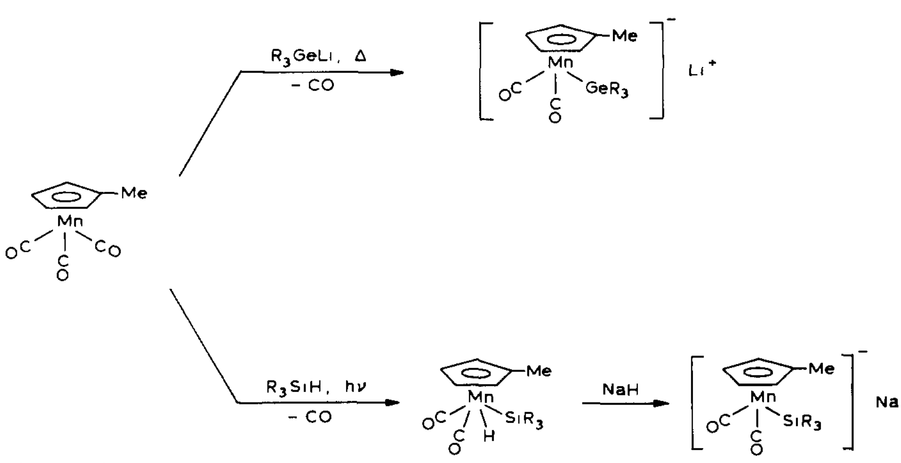
Under the same conditions **9** gave a mixture of Ph_3SiH, Ph_3SiCH_2Ph and Ph_4Si (characterized by GLC, NMR and mass spectrometry).

Results and discussion

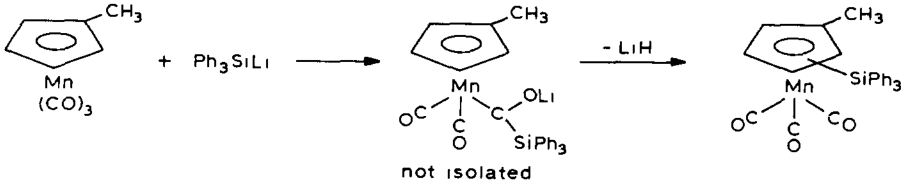
Synthesis

We previously described the synthesis of manganate anions containing either Mn–Si [4] or Mn–Ge bonds [5] according to Scheme 2.

Organogermyllithium, prepared by action of n-BuLi on R_3GeH ($R_3 = Ph_3$, $MePh(1\text{-}C_{10}H_7)$) ($1\text{-}C_{10}H_7$ = 1-naphthyl) [6,7] is able to displace one carbonyl from methylcymantrene yielding the corresponding germylmanganate. However, two steps are required to synthesize the silyl analogs: first photochemical insertion into the Si–H bond, and then deprotonation by NaH. Indeed, the reaction of Ph_3SiLi, prepared by treatment of Ph_3SiCl with lithium [3], leads to the neutral complex $[\eta^5\text{-}CH_3(Ph_3Si)C_5H_3](CO)_3Mn$, corresponding to the substitution on the cyclopentadienyl ring (with formal elimination of LiH). This reaction probably occurs via the (not isolated) carbenic anion $[(\eta^5\text{-}CH_3C_5H_4)(CO)_2(COSiPh_3)Mn]^-$ [9] (Scheme 3).



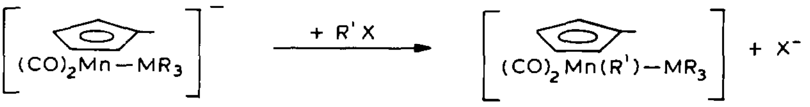
SCHEME 2



not isolated
ν(CO) 1910 and 1810 cm^{-1}

SCHEME 3

Alkyl iodides and benzyl bromide react with the anions $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)(\text{CO})_2(\text{MR}_3)\text{Mn}]^-$ (M = Si or Ge) affording the new compounds described in Tables 1–3 (Scheme 4).



(M = Si, Ge, R_3 = Ph_3, $(1\text{-}C_{10}H_7)PhMe$; R' = CH_3, C_2H_5, CH_2Ph, $(CH_2)_2CH{=}CH_2$)

SCHEME 4

Reaction of methyl iodide with the optically active salt (S)-$[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)(\text{CO})_2((1\text{-C}_{10}\text{H}_7)\text{PhMeGe})\text{Mn}]\text{Et}_4\text{N}$, ($[\alpha]_D^{25}$ − 3.9° in CH_2Cl_2) [5], leads to the optically active neutral complex (S)-$[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)(\text{CO})_2(\text{CH}_3)((1\text{-C}_{10}\text{H}_7)\text{PhMeGe})\text{Mn}]$, **6** ($[\alpha]_D^{25}$ + 18.7° in CH_2Cl_2).

The optically active (S)-$[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)(\text{CO})_2(\text{CH}_3)((1\text{-C}_{10}\text{H}_7)\text{PhMeSi})\text{Mn}]$, prepared from the optically active anions (S)-$[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)(\text{CO})_2((1\text{-C}_{10}\text{H}_7)\text{PhMeSi})\text{Mn}]^-$, could not be isolated by crystallisation.

Structure

Complexes of the general formula η^5-Cp(CO)$_2$(R')(R$_3$M)Mn (Cp = cyclopentadienyl or substituted cyclopentadienyl) can be regarded as square pyramids with the cyclopentadienyl ring in the apical position [10]. This well-known piano stool structure can exist as two isomers, according to Scheme 5. Here only the diagonal

lateral
(a)

diagonal
(b)

SCHEME 5

one (b) was always obtained. This assignment is based on IR and NMR spectroscopies. The IR spectra exhibit two carbonyl stretching modes (~ 1970 and 1910 cm^{-1}, Table 1) together with a more intense lower frequency (asymmetric) stretching one.

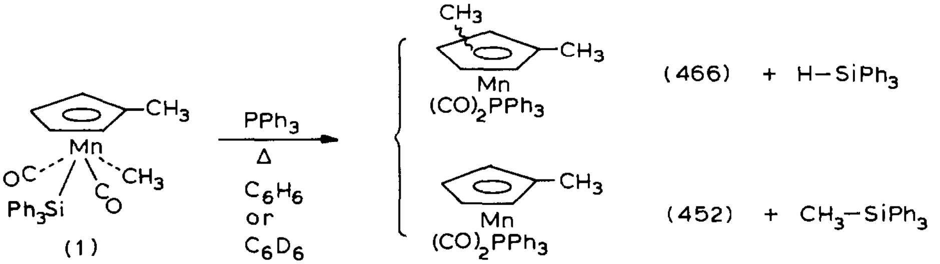
These relative intensities of absorption are typical of the diagonal arrangement [11]. The proton NMR spectra of the crude compounds shows signals corresponding to a single isomer, even when alkylation is performed on anions prepared at low temperature. This is rather surprising since all the possible isomers of the molybdenum or tungsten analogs (Scheme 1) have been observed [2]. Moreover the equivalence of the benzylic protons in the benzyl derivatives **9** and **10** (singlets at $\delta = 3.4$ ppm for both complexes, see Table 2) is attributed to the presence of a plane of symmetry in the diagonal arrangement. On the other hand the lateral isomer would involve an asymmetric centre at the Mn atom and so a split AB system would be observed for the two non-equivalent methylene protons. In the same way, the absence of diastereoisomers for the compounds **3** and **5** indicates the diagonal form.

This geometry is assumed to result from steric hindrance, as reported for rhenium analogs [11].

Deinsertion reaction

The compounds $(\eta^5\text{-}CH_3C_5H_4)(CO)_2(CH_3)(Ph_3M)Mn$ are unreactive with many reagents such as water, methanol, $LiAlH_4$, chlorine and PPh_3 at room temperature. Organolithium reagents (n-BuLi, Ph_3GeLi) cleave the Mn–C bond, as we reported previously [12]. This rather weak reactivity is surprising when compared with the behavior of the related $(\eta^5\text{-}CH_3C_5H_4)(CO)_2(Ph_3M)(H)Mn$ compounds [4,5].

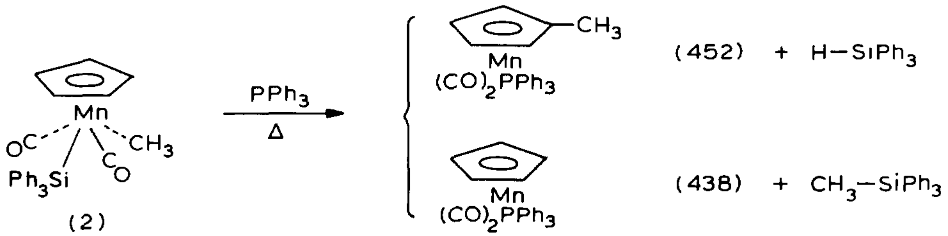
Nevertheless the overall manganese deinsertion is readily performed by heating **1** (M = Si) with one equivalent of PPh_3 in C_6H_6 (Scheme 6). Chromatography of the reaction mixture affords two bands: the first one corresponds to a mixture of Ph_3SiH and Ph_3SiCH_3 and the second one corresponds to the manganese species. It is shown (mass spectrometry) to be a mixture of $(\eta^5\text{-}CH_3C_5H_4)(CO)_2(PPh_3)Mn$ ($M = 452$) and of $[\eta^5\text{-}(CH_3)_2C_5H_3](CO)_2(PPh_3)Mn$ ($M = 466$), corresponding to a methyl-to-ring migration.



SCHEME 6. The mass of molecular peaks (m/e) are shown in parentheses (also in Schemes 7, 8, 11 and 12).

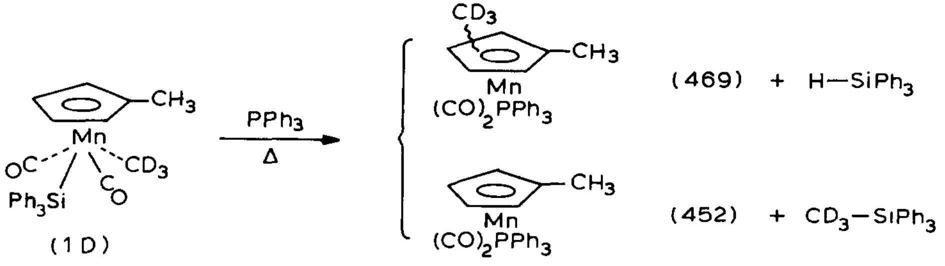
When the starting material is $(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)(Ph_3Si)Mn$, **2** (Scheme 7), the same Ph_3SiH/Ph_3SiCH_3 mixture and the manganese complexes $(\eta^5\text{-}C_5H_5)$-$(CO)_2(PPh_3)Mn$ and $(\eta^5\text{-}CH_3C_5H_4)(CO)_2(PPh_3)Mn$ ($M = 438$ and 452) are obtained.

The hydrogen atom of the silane arises from the cyclopentadienyl ring and the methyl group migrates from the metal to the ring (without exchange between the methyl groups) as shown by the following experiments.



SCHEME 7

When the reaction is carried out in C_6D_6 only Ph_3SiH (without Ph_3SiD) is obtained.



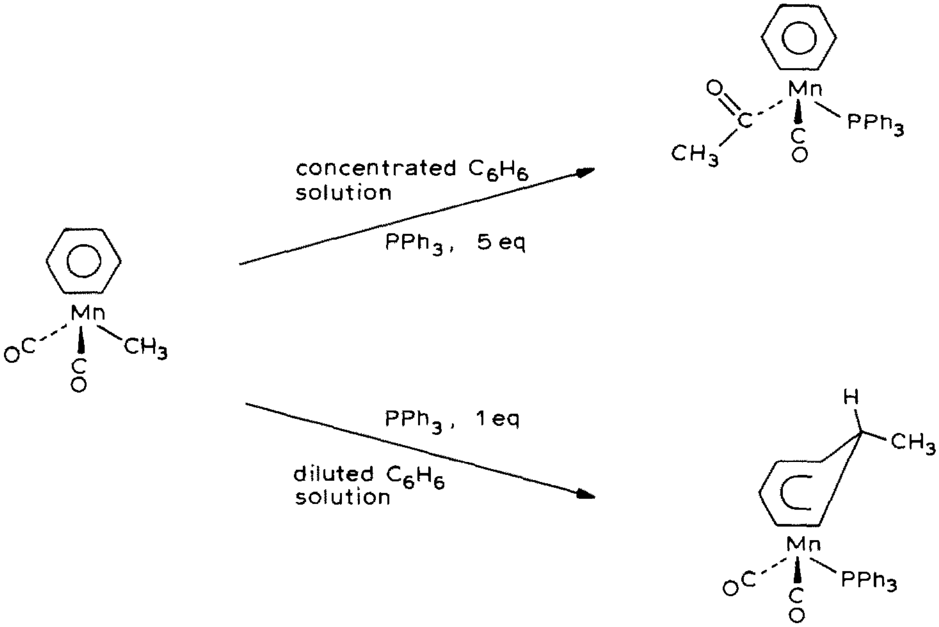
SCHEME 8

Deuterated **1D**, $(\eta^5\text{-}CH_3C_5H_4)(CO)_2(CD)_3(Ph_3Si)Mn$, gives (Scheme 8) Ph_3SiH and Ph_3SiCD_3 (without Ph_3SiD and Ph_3SiCH_3) and $(\eta^5\text{-}CH_3C_5H_4)(CO)_2(Ph_3P)Mn$ and $[\eta^5\text{-}(CH_3)(CD_3)C_5H_3](CO)_2(Ph_3P)Mn$ ($M = 452$ and 469).

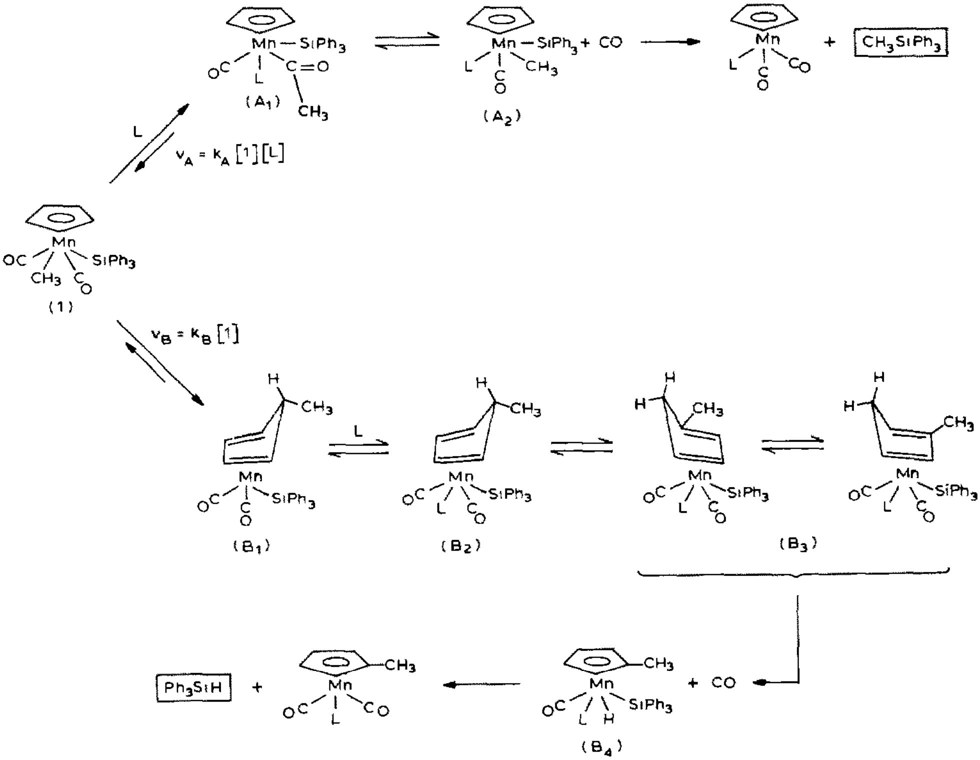
It is noticeable that **1** decomposes thermally (without Ph_3P), affording a Ph_3SiH/Ph_3SiCH_3 mixture. However, the manganese-containing moiety is not isolated in this case.

In these reactions the amounts of the manganese complex and the phosphine are equimolar. However, the final Ph_3SiH/Ph_3SiCH_3 ratio depends on the concentration (Table 4). These results can be related to those reported by Brookhart et al. [13] and summarized in Scheme 9. This work suggests the mechanism shown in Scheme 10. Two competitive routes with two different rate laws are involved. Route A leads to the reductive elimination of Ph_3SiCH_3. This elimination certainly occurs in the lateral isomer $\mathbf{A}_2$ according to the microscopic reversibility principle. Isomerization probably proceeds via the acyl complex $\mathbf{A}_1$, corresponding to the metal-to-carbonyl methyl migration. This transfer is induced by PPh_3 according to a second order rate-determining step. A simultaneous route, B, leads to the Ph_3SiH displacement. The rate determining step is assumed to be the first order intramolecular formation of the 16-electron *endo* methyl complex $\mathbf{B}_1$. The further reductive elimination of Ph_3SiH takes place in the lateral silylmanganese hydride $\mathbf{B}_4$. Hence, we propose a scrambling process of the *exo* hydrogens in $\mathbf{B}_2$ providing the *endo* hydrogens in $\mathbf{B}_3$, which are able to migrate to the metal.

An intermolecular second order process could be suggested instead of the latter. Nevertheless such a mechanism could not explain why the Ph_3SiH/Ph_3SiCH_3 ratio

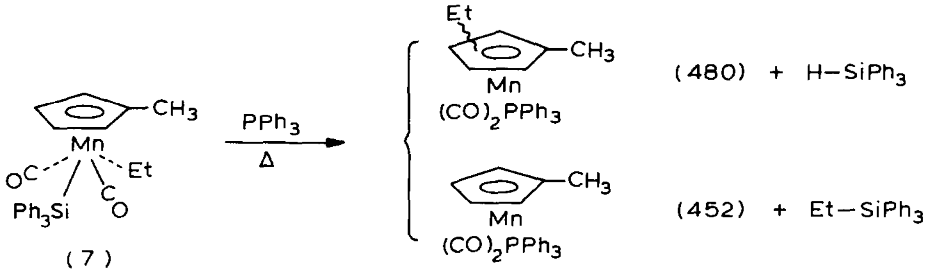


SCHEME 9

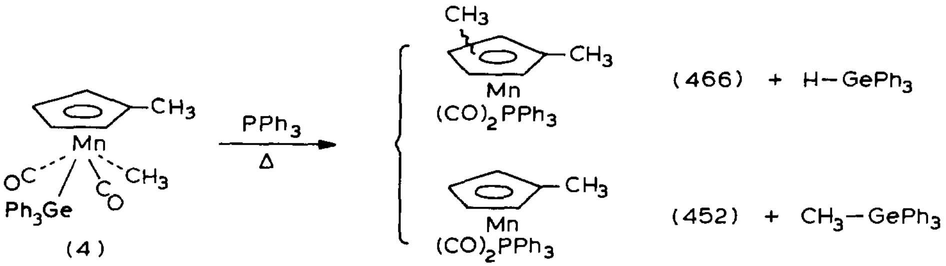


SCHEME 10

depends on the dilution. Indeed, higher concentrations direct the reaction toward the second order route A, affording Ph_3SiCH_3.



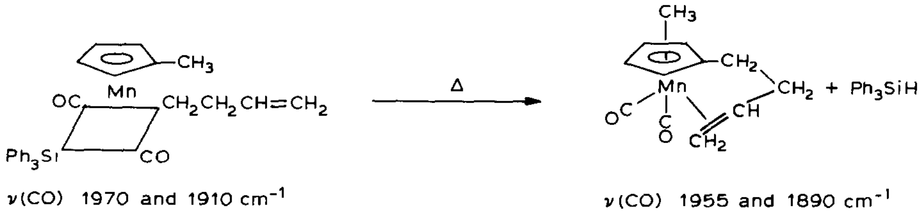
SCHEME 11



SCHEME 12

The Schemes 11 and 12 show that the reactions of PPh_3 with the ethyl analog **7**, or the related methylgermyl complex **4**, probably involve the same mechanism. In both cases the products correspond to the competition between the deinsertion process and the migration one.

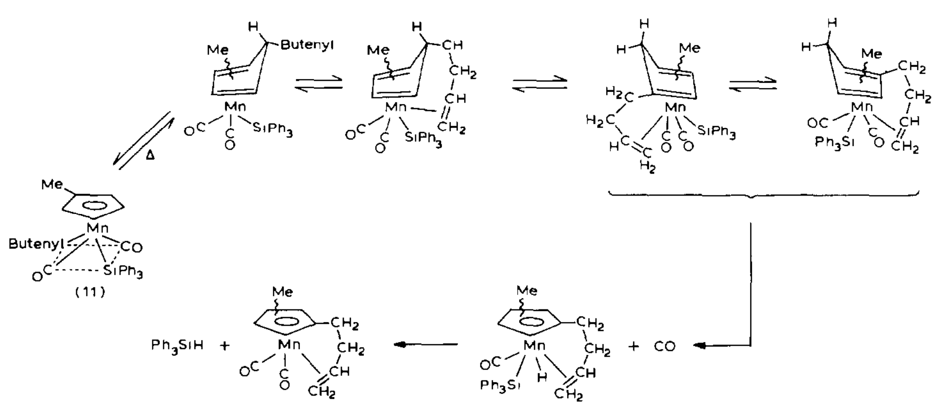
The results obtained can be related to the thermal decomposition of the butenyl compound **11** shown in Scheme 13. Here the butenyl group migrates to the ring and



SCHEME 13

then behaves as a two-electron ligand involving intramolecular coordination. This reaction is in agreement with the mechanism we propose for the metal-to-ring migration (Scheme 14).

The thermal decomposition of the benzyl derivative **9** was also observed. The silicon was isolated as a mixture containing Ph_3SiCH_2Ph and Ph_3SiH, as expected,



SCHEME 14

but also Ph_4Si. No Ph_3Si(*o*-tolyl) was found. The manganese-containing moiety was not isolated. We are unable to explain the formation of Ph_4Si.

These two reactions are quite different from those observed with the η^1-butenyl- or η^1-benzyl-molybdenum complexes, since the thermal rearrangements of these complexes lead to the η^3-butenyl or η^3-benzyl derivatives [14].

Conclusions

The alkylation of silyl and germylmanganese anions takes place with formation of stable neutral complexes with diagonal geometry, which formally corresponds to the insertion of the transition metal into a carbon–Group IVB element bond. These complexes show a great chemical inertness, however they undergo thermal decomposition in the presence of a phosphine. This decomposition corresponds to the competition between two reactions: (i) deinsertion of alkylsilane (or germane), and (ii) metal-to-ring migration of the alkyl group, followed by deinsertion of hydridosilane. In both cases the manganese moeity is isolated as a phosphine derivative and corresponds to a mixture of two complexes: one having a cyclopentadienyl ligand and the other an alkylcyclopentadienyl one.

The alkenyl migration observed in the thermal decomposition of the butenyl derivative can be explained by the stabilization resulting from intramolecular coordination.

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