Addition of Stabilized Carbanions to Cationic (η6-Arene)tricarbonylmanganese Complexes: Syntheses of Homo (Mn–Mn) and Hetero (Mn–Cr) Dinuclear Complexes

Eric Rose,*[a] Claudine Le Corre-Susanne,[a] Françoise Rose-Munch,[a] Christophe Renard,[a] Vanessa Gagliardini,[a] Fatima Teldji,[a] and Jacqueline Vaissermann[b]

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The reaction of secondary α-cyano or α-sulfonyl carbanions with cationic (η^6-arene)tricarbonylmanganese complexes affords neutral mono- and dinuclear tricarbonyl(η^5-cyclohexadienyl)manganese complexes. The X-ray analyses of three (η^5-cyclohexadienyl)Mn complexes (two mononuclear and one dinuclear) obtained by addition of α-cyano carbanion to cationic (η^6-arene)manganese complexes are reported. The addition of benzylic carbanions of (η^6-arene)tricarbonylchromium complexes to cationic (η^6-arene)manganese complexes gives rise to the formation of the corresponding heterodinuclear [(η^5-cyclohexadienyl)-manganese–(η^6-arene)chromium] complexes.

Introduction

The air-stable [(η^6-arene)$Mn(CO)_3$] cations are quite electrophilic and the addition of nucleophiles to the arene ring affording thermally stable cyclohexadienyl complexes has been the subject of numerous studies.[1] Among them, a mere handful of papers describes the use of organometallic derivatives as nucleophiles[2−4] towards (η^6-arene)tricarbonylmanganese complexes giving rise to the formation of homo- and heteropolymetallic complexes.

Our studies concerning the structure and reactivity of (η^6-arene)tricarbonylmanganese complexes and their application in organic synthesis, led us to discover the possibility of synthesizing di- or even trinuclear complexes by the simple addition of stabilized carbanions to cationic manganese complexes. In particular, during the course of our work on the synthesis of mescaline (**1**), a natural product with hallucinogenic properties, we undertook the study of the regioselectivity of the addition of primary and secondary stabilized carbanions to tricarbonyl(1,2,3-trimethoxybenzene)manganese complex **2**[5] (Equation 1). We observed the formation of mononuclear complex **3** and unexpected dinuclear complex **4**.

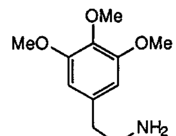
We report an extension of this work as well as a complete study of the addition of stabilized carbanions, α-cyano and α-sulfonyl carbanions to the simplest complex: the benzene manganese complex, and the structures of one dinuclear and two mononuclear complexes obtained by this method. In addition, we describe an extension of this method to the preparation of new heteropolymetallic Mn−Cr complexes.

[a] Laboratoire de Synthèse Organique et Organométallique, UMR CNRS 7611, Université P. et M. Curie, Tour 44 − 1er étage, 4, Place Jussieu, F-75252 Paris Cedex 05, France
Fax: (internat.) + 33(0)1/44277089
E-mail: rose@ccr.jussieu.fr
[b] Laboratoire de Chimie des Métaux de Transition, URA CNRS 409, Université P. et M. Curie, Bâtiment F, 4, Place Jussieu, F-75252 Paris Cedex 05, France

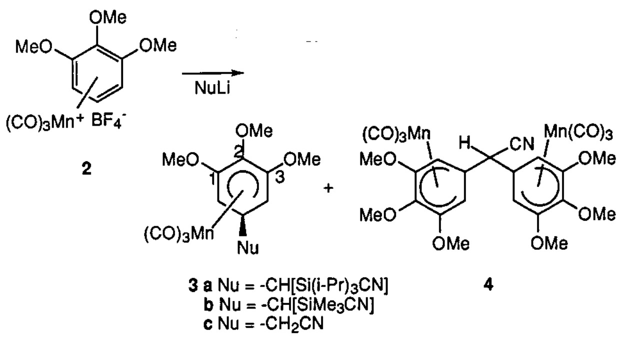
Results and Discussion

Addition of Silylated α-Cyano Carbanions to (1,2,3-Trimethoxybenzene)manganese Complex

Our first attempt at functionalizing the trisubstituted arene ring of complex **2**, in order to synthesize a precursor of mescaline (**1**), involved the reaction of lithioacetonitrile (Equation 1). Unfortunately, the reaction mixture turned black and decomposition occured very quickly. Since more substituted carbanions have previously been shown to be nucleophiles of optimum reactivity for addition to arene−Cr complexes,[6] we anticipated that the same would apply to Mn complexes. We thus decided to study the reactivity of more crowded nucleophiles such as silylated α-cyano carbanions.



1
mescaline



Equation 1. Nucleophilic addition of a nucleophile to tricarbonyl(1,2,3-trimethoxybenzene)manganese complex **2**

2-Lithio-2-(triisopropylsilyl)acetonitrile, prepared in situ by addition of lithium (diisopropyl)amide, LDA, to a solu-

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tion of one equivalent of (triisopropylsilyl)acetonitrile in THF under N_2 at −78°C, reacted with complex **2** to give the neutral complex **3a**, Equation 1, in 38% yield. An analogous reaction occured with the anion of (trimethylsilyl)acetonitrile as nucleophile, yielding complex **3b** as the major product. Unexpectedly, a silicon−carbon bond cleavage occurred after silica gel column chromatography, affording complex **3c**. We noticed also the formation of a minor dinuclear complex **4** in 12% yield, whose formation will be discussed later (vide infra, mechanism involved in the synthesis of complex **7a**).

In the case of the two mononuclear neutral complexes **3a** and **3c** we were able to obtain crystals suitable for X-ray determinations. The structures appear in Figures 1 and 2 whereas the crystallographic data, selected bond lengths and bond angles can be found in Table 1.

Table 1. Selected bond lengths [Å] and bond angles [°] for **3a** and **3c**

Bond lengths	Complex **3a**	Complex **3c**
Mn−C1	2.178(6)	2.19(1)
Mn−C2	2.143(6)	2.15(1)
Mn−C3	2.194(6)	2.19(1)
Mn−C4	2.169(6)	2.18(1)
Mn−C6	2.201(6)	2.20(1)

Bond angles	Complex **3a**	Complex **3c**
C4−C5−C6	104.3(5)	103.8(9)
C2−Mn−C6	68.1(2)	67.8(4)
C2−Mn−C4	68.3(2)	68.4(4)
C2−O2−C8	118.0(2)	113.8(10)

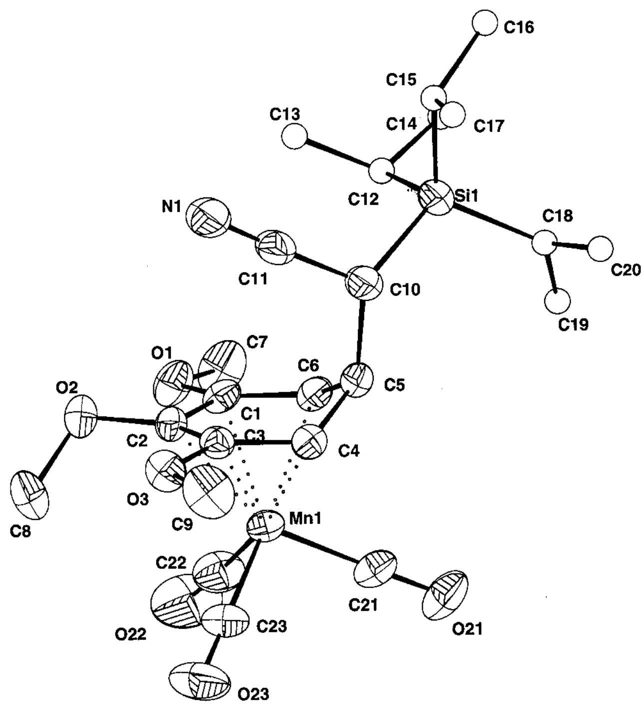


Figure1. ORTEP diagram of complex **3a**

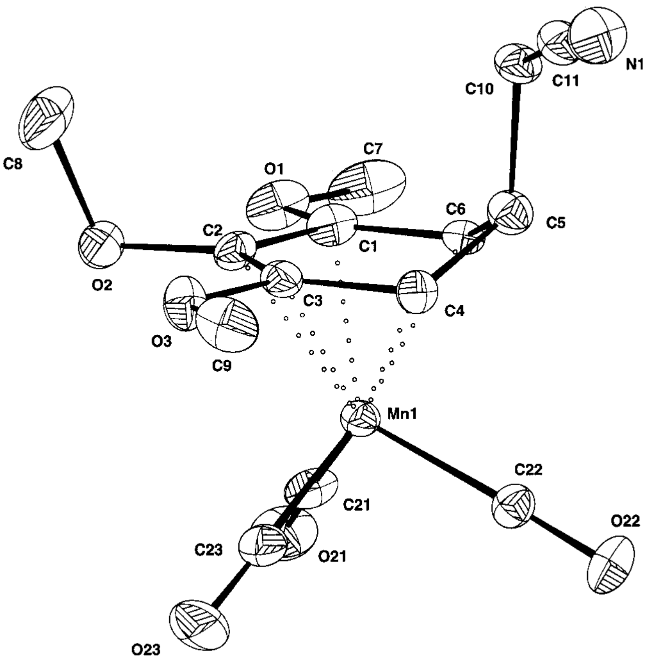


Figure 2. ORTEP diagram of complex **3c**

The ORTEP views show classical (η^5-cyclohexadienyl) structures with the five ring atoms C^1, C^2, C^3, C^4, C^5, almost coplanar while the remaining atom C^6 lies in a $C^4-C^5-C^6$ plane making an angle of 40° with the other one (in both complexes). It is worth noting the completely different position adopted by the OMe groups attached to the C^2 atoms: in the case of complex **3a**, this methoxy group is pointing away from the bulky silylated substituent attached to the sp^3 carbon atom, and thus it is located on the same side of the ring plane with respect to the $Mn(CO)_3$ moiety. The reverse is observed for the corresponding methoxy group of complex **3c**: it is opposite to the organometallic entity.

The ^1H- and ^{13}C-NMR data of complexes **3a**, **3b**, **3c**, and **4** are presented in Tables 2 and 3. We noticed that the ^{13}C-NMR data of the C^1, C^2, C^3 atoms of the four complexes (Table 3) were in good agreement with those observed in the case of unsubstituted neutral η^5-cyclohexadienyl−Mn complexes[7] or even in the case of η^5-Cr complexes.[8] This feature was attributed to a strong charge alternation in such η^5 systems as it was shown by charge density calculations at the individual carbon atoms.[9] Thus, the C^2 signals are shielded by roughly 20 ppm with respect to the C^1 and C^3 signals (Table 3).

Also interesting to note are the more shielded signals of H^4, H^5, H^6 of dinuclear complex **4** when compared to the corresponding proton signals of the mononuclear complex **3c** (Table 2).

No significant effect could be dectected comparing the chemical shifts of the OMe groups attached to the C^2 atoms of the complexes **3a** and **3c** (δ = 4.02 and 4.06, respectively, Table 2). Therefore, it was clear that the methoxy groups did not keep the same orientation in solution as in the solid state because of the free rotation of the methoxy groups.

Table 2. ^{1}H-NMR data of complexes **3a**, **3b**, **3c**, **4** (in $CDCl_3$)

	H[4[a]]	H[6[a]]	H[5]	H[7]	OMe[2]	OMe[1[b]]	OMe[3[b]]
3a	2.83	3.14	2.93	1.44	4.02	3.43	3.58
3b	2.84	3.09	2.77	1.28	4.06	3.47	3.58
3c	2.90	2.90	2.90	1.67	4.06	3.48	3.48
4	2.66	2.76	2.52	0.98	3.99	3.50	3.59

[a] H^4 or H^6. – [b] OMe^1 or OMe^3.

In order to better understand the mechanism of formation of dinuclear complexes such as **4**, we extended this study to the reactivity of α-cyano carbanions towards the simplest arene−Mn complex: that of benzene.

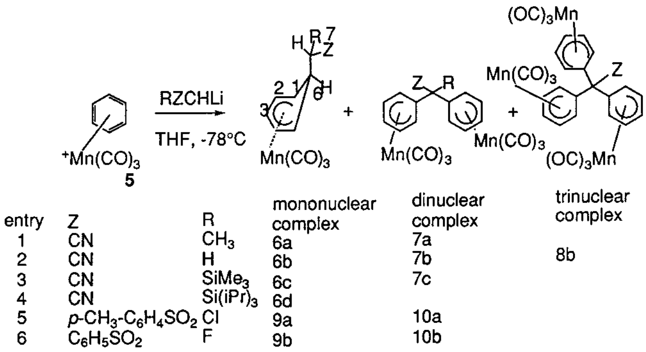
Addition of α-Cyano Carbanions to the (η^6-Benzene)manganese Complex 5

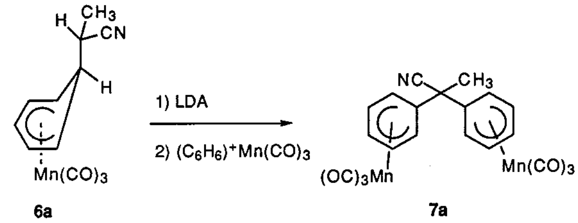
2-Lithiopropionitrile (prepared in situ by addition of LDA to a solution of one equivalent of propionitrile in THF under N_2 at −78°C) reacted with one equivalent of (η^6-benzene)tricarbonylmanganese complex **5** to give the mononuclear complex **6a** and the dinuclear complex **7a** (Table 4) in 76% and 11% yield, respectively. These complexes were purified by flash chromatography on an alumina column. An analogous reaction in the presence of an excess of **5** (two equivalents) and an excess of LDA (two equivalents) allowed us to isolate complex **7a** as the major product (61% yield) as well as complex **6a** (24% yield). It is interesting to note that, although some additions of α-cyano carbanions to (η^6-arene)manganese complexes have already been reported,[10−12] no formation of dinuclear complexes was described.

The formation of the dinuclear complex **7a** was easily explained. Indeed, in this basic medium, the acidic proton, α to the cyano group of complex **6a** could be abstracted, giving rise to a new carbanion which could, in turn, add to the arene ring of complex **5**. Two points support this mechanism: 1. The higher yield of complex **7** obtained when an excess of complex **5** and LDA were used; this is in good agreement with our mechanism proposal. 2. In a separate experiment which was carried out starting from complex **6a** itself, the addition of one equivalent of LDA to complex **6a** and further reaction with cationic complex **5**, gave complex **7a** in almost quantitative yield (Equation 2).

The ^{1}H-NMR spectrum of complex **6a** in $CDCl_3$ showed expected signals at δ = 5.80 (H^3), δ = 4.97 and 4.92 (diastereotopic protons H^2 and H^4), δ = 3.34 and 3.15 (diastereotopic protons H^1 and H^5) whose multiplicities could be unambigously interpreted (Table 5). The difference between the chemical shifts of the H^1 and H^5 signals is larger than the one between the H^2 and H^4 signals, certainly due to the proximity of the chiral center.

Table 4. Nucleophilic addition of a nucleophile to benzenetricarbonylmanganese complex





Equation 2. Preparation of dinuclear complex **7a**

The ^{1}H-NMR spectrum of complex **7a** showed the same features due to the η^5-cyclohexadienyl structure but two points warranted comment (Table 5): 1. An overall deshielding effect was observed for the protons of the dinuclear structure relative to those of the mononuclear structure. This effect can reach 1.44 ppm in the case of the H^1 signal. An opposite effect was noticed in the case of complexes **3c** and **4**, clearly showing the effect of the three methoxy groups. 2. Although the H^2 and H^4 atoms did not present distinct signals for complex **7a**, the H^1 and H^5 atoms showed two signals with a very important difference − a shift of 1.43 ppm was observed instead of 0.19 ppm for the corresponding protons of complex **6a**.

Recrystallization of complex **7a** in an acetone/ether mixture afforded yellow single crystals suitable for X-ray analysis. As can be seen from the ORTEP view in Figure 3 the structure showed a classical (η^5-cyclohexadienyl) struc-

Table 3. ^{13}C-NMR data of complexes **3a**, **3b**, **3c**, **4** (in $CDCl_3$)

	C[1a]	C[3a]	C[2b]	OMe[2]	OMe[1c]	OMe[3c]	C[5]	C[4d]	C[6d]
3a	136.2	136.9	115.8	66.3	54.7	55.3	35.8	35.7	36.4
3b	136.3	136.7	116.5	66.3	54.8	55.3	35.9	35.5	36.2
3c	137.1	137.1	115.4	66.8	55.3	55.3	34.4	33.8	33.8
4	137.2	137.5	115.1	66.2	55.4	55.6	35.3	32.3	33.2

[a] C^1 or C^3 – [b] CN or C^2 – [c] OMe^1 or OMe^3 – [d] C^4 or C^6.

Table 5. ^{1}H-NMR data of complexes **6a**, **7a** (in [D$_6$]acetone)

	H^3	H^2 or H^4	H^4 or H^2	H^1 or H^5	H^5 or H^1
Complex **6a**	5.80, t $J = 6.1$	4.97, t $J = 6.1$	4.92, t $J = 6.1$	3.34, tt $J = 6.1$ and 1.5	3.15, tt $J = 6.1$ and 1.5
Complex **7a**	5.98, tt $J = 5.7$ and 1.3	5.25, m	5.25, m	4.78, tt $J = 5.7$ and 1.3	3.35, tt $J = 5.7$ and 1.3

ture.[7] The sp^3 carbon atoms (C^6 and $C^{6'}$) of the rings are each eclipsed by a Mn−CO bond. The anion added on the *exo* face with respect to the manganese atom. The cyclohexadienyl rings are nearly planar and fold about $C^1C^6C^5$ and $C^{1'}C^{6'}C^{5'}$ with the same angle of 36°. The two metal centers are 7.556(6) Å apart. Crystallographic data, selected bond lengths and bond angles are listed in Table 6. It is worth noting that the two metal centers are not directly bonded to each other and could not be linked: our trials to form a metal−metal bond by irradiating, for example, complex **7a**, failed.

2-Lithioacetonitrile (prepared by addition of LDA to a solution of acetonitrile in THF under nitrogen at −78°C) reacted with (η^6-benzene)manganese complex **5** giving rise to the formation of three compounds (Table 4, entry 2) (overall yield 58%): the mononuclear complex **6b**, the dinuclear complex **7b** and the unexpected complex **8b** in a 80:18:2 ratio. This "caroussel-like" complex **8b** was very dif-

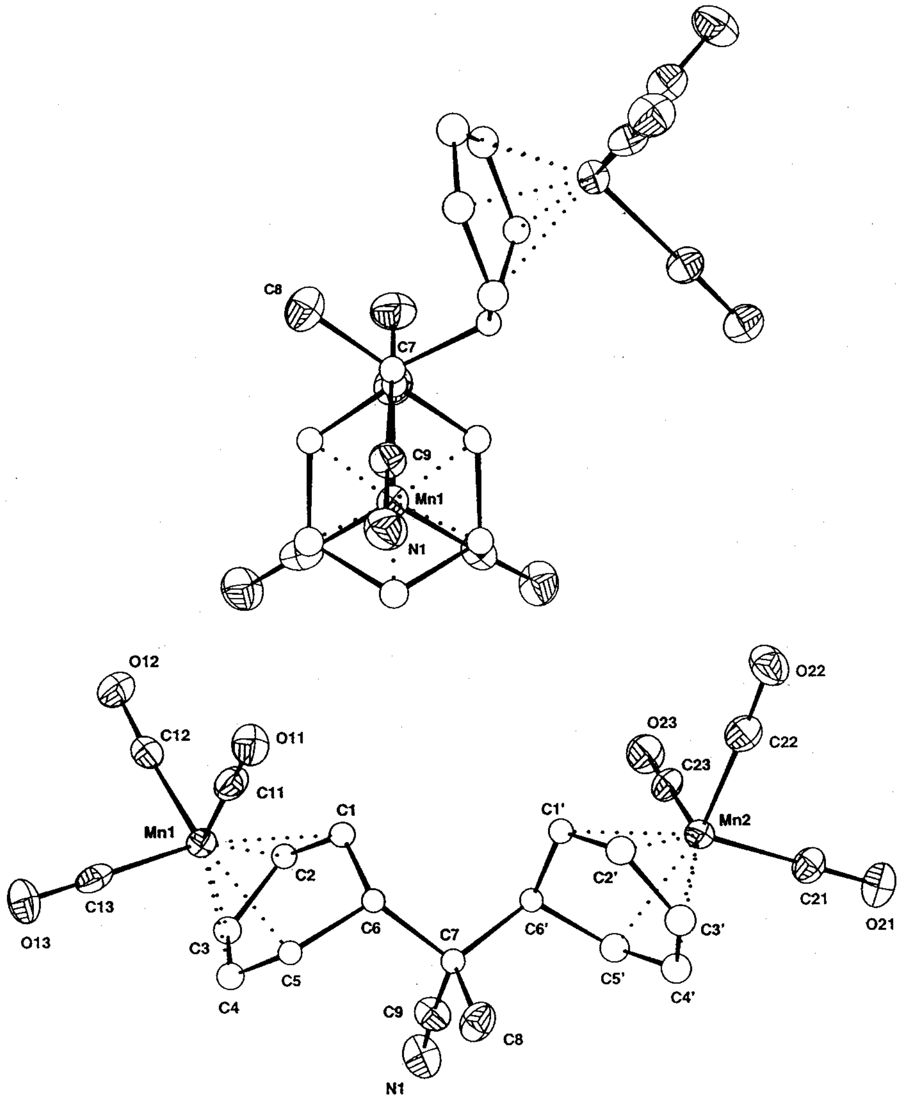


Figure 3. ORTEP diagram of complex **7a**

Table 6. Selected bond lengths [Å] and bond angles [°] for **7a**

Bond lengths	Bonds angles
Mn1−C3: 2.14 (1)	C8−C7−C9: 108.5 (11)
Mn2−C3′: 2.12 (1)	C1−C6−C5: 103.1 (10)
C7−C6: 1.58 (2)	C1′−C6′−C5′: 103.6 (10)
C7−C6′: 1.57 (2)	

ficult to isolate from the mixture of **6b** and **7b**; nevertheless we succeeded in obtaining **8b** in 11% yield by using 1.2 equivalents of LDA and 0.4 equivalents of nitrile. All attempts to obtain crystals of **8b** suitable for X-ray crystallography were unsuccessful: the sharp needles obtained so far are too small to be studied.

In solution, the ^{1}H-NMR spectrum of the "caroussel" complex **8b** showed also the atom H^3 as the less shielded one at $\delta = 5.85$, the atoms $H^{2,4}$ at $\delta = 5.04$ and the atoms $H^{1,5}$ at $\delta = 3.12$ in $CDCl_3$ (Table 7). The ^{13}C-chemical shifts of the carbon atom bearing the cyano group are in good agreement with the substitution of this bridge carbon atom. Indeed this carbon atom, which resonates at $\delta = 29$ in the case of complex **6b**, is deshielded by 26.4 ppm in the case of complex **7b** ($\delta = 55.4$) and by 37.2 ppm in the case of **8b** ($\delta = 66.2$) (Table 8).

Table 7. ^{1}H-NMR data of complexes **6b**, **7b**, **8b** (in $CDCl_3$)

	H^3	H^4	H^5	H^6
6b	5.84	4.94	3.23	2.94
7b	5.81	4.93	3.12	2.68
8b	5.85	5.04	3.12	2.79

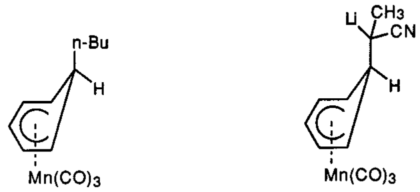
Table 8. ^{13}C-NMR data of complexes **6b**, **7b**, **8b** (in [D$_6$]acetone)

	C^1	C^2	C^3	C^6	CN	C(CN)
6b	53.2	96.9	80.7	31.7	116.7	29.0
7b	54.3	99.2	83.5	34.6	119.7	55.4
	56.4	99.0				
8b	55.4	98.0	81.7	36.7	120.0	66.2

Under the same conditions, 2-lithio-2-(trimethylsilyl)-acetonitrile (2.2 equivalents) reacted with one equivalent of complex **5** (Table 4, entry 3) to give a mixture of complexes **6c**, **7c**, **6b**, and **7b** in a 64:28:7:1 ratio in 66% overall yield after a very fast silica gel column chromatography to avoid C−Si bond cleavage. Using a bulkier anion such as 2-lithio-2-(triisopropylsilyl)acetonitrile (2.2 equivalents), the same reaction gave only complex **6d** (Table 4, entry 4). No C−Si bond scission was noticed, even after silica gel column chromatography.

Addition of α-Sulfonyl Carbanions to the (η^6-Benzene)manganese Complex 5

Lithiation of chloromethyl *p*-tolyl sulfone $CH_3-C_6H_4-SO_2-CH_2Cl$ with *n*BuLi gave the corresponding α-sulfonyl carbanion[13,14] which reacted with one equivalent of complex **5** in a THF suspension. Two complexes **9a** and **10a** were isolated in a 1:1 ratio (73% yield) (Table 4, entry 5). The ^{1}H-NMR spectra were in good agreement with an η^5-cyclohexadienyl mononuclear structure for complex **9a** and with a dinuclear structure for complex **10a**. Indeed, in the case of complex **9a**, the atom H^7 attached to the sp^3 carbon atom resonates as a doublet at $\delta = 3.65$ and is absent in the case of complex **10a**. With the phenylsulfonylfluoromethyl carbanion $C_6H_5-SO_2-CHFLi$,[15] analogous results were obtained: Two complexes **9b** and **10b** were isolated in a 9:1 ratio (48% yield) (Table 4, entry 6). When two equivalents of complex **5** and two equivalents of *n*BuLi were used, three complexes **9b**, **10b**, and **11** were isolated in 3, 52, and 16% yield, respectively. The less polar complex **11**, which was eluted first by silica gel flash column chromatography, appeared to be the neutral 6-*exo*-butyl-η^5-cyclohexadienyl derivative whose preparation by a different method was previously reported by Chung et al.[16] In a separate experiment, complex **11** could be obtained in almost quantitative



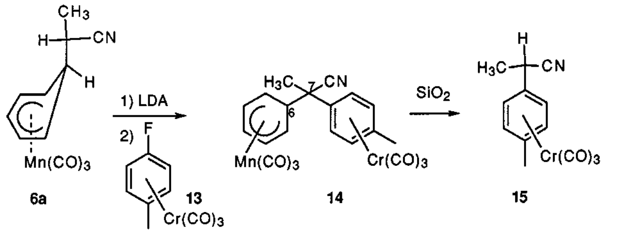
11 **12**

yield by treating one equivalent of *n*BuLi with complex **5**.[4]

We thus demonstrated the high reactivity of the α-cyano carbanion of complex **6a** towards benzene complex **5** (Equation 2), allowing us to synthesize, by this original way, homonuclear dimetallic complexes. We then tried to take advantage of these results in treating the same carbanion with other organometallic electrophilic complexes, such as chromium complexes, to obtain an access to heterodinuclear complexes.

Heterodinuclear Complex Syntheses

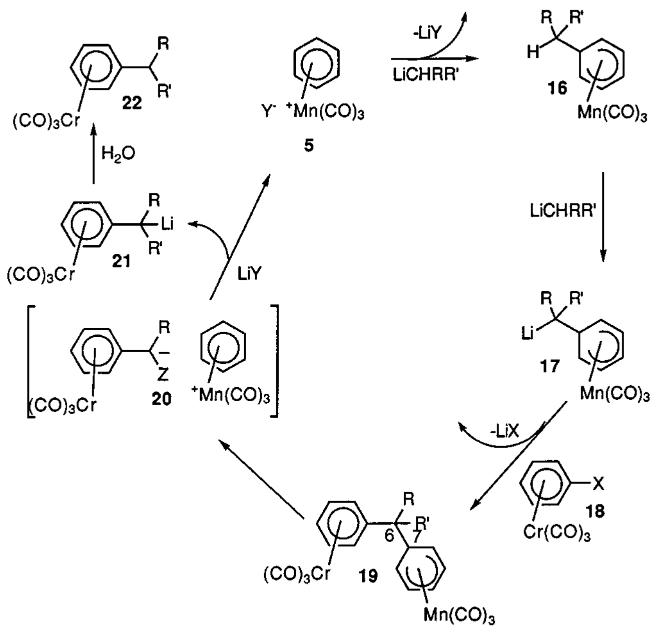
It is well known that arenes coordinated to the tricarbonylchromium entity are very electrophilic and the corresponding complexes, substituted by a good leaving group, readily undergo *ipso*,[17] *cine*,[18] or *tele*[19] nucleophilic aromatic substitutions. Addition of tricarbonyl(*p*-fluorotoluene)chromium complex **13** to the carbanion **12** of complex **6a** yielded the heterodinuclear complex **14**, detected by NMR spectroscopy in the crude mixture. However, when the reaction mixture was filtered through a silica gel chromatography column, a new unexpected *para*-disubstituted arenetricarbonylchromium complex **15** was isolated (Equation 3). This tricarbonyl[2-(*para*-tolyl)propionitrile]chromium complex **15** was obtained by cleavage of the C^6-C^7 bond and subsequent rearomatization of the (η^5-cyclohexadienyl)manganese part of complex **14**. It is worth noting that this complex **14** could be obtained in 37% yield along with complex **15** (63% yield) by adding the lithium salt of complex **15** to the arene complex **5**, followed by a simple extraction without further purification. When the mixture was subjected to chromatography, only complex **15** was obtained.



Equation 3. Synthesis of *para*-disubstituted complex **15** from **6a** and **13**

Treating the tricarbonyl(*p*-flurorotoluene)chromium complex **13** with the lithium salt **12** gave a new *para*-disubstituted arenetricarbonylchromium complex **15** and the cationic benzene complex **5**. The carbanion **12** plays an unexpected role because it is an unusual way to render the reaction of the propionitrile carbanion with (η^6-benzene)tricarbonylmanganese cation **5** reversible, by an indirect process! We can point out that *ipso* substitution of the fluoro group of **13** by a propionitrile carbanion can also give complex **15**. Thus, the carbanion **12** is a formal precursor of the carbanion of the propionitrile. It is obvious that this reaction would be of great interest if we could apply it to the addition of anions which do not react with arenechromium complexes but which react easily with arenemanganese complexes. Indeed it is well known that manganese complexes are much more reactive than chromium complexes. The reaction could maybe work in the presence of a catalytic amount of complex **5** according to the mechanism represented in Scheme 1. Indeed a primary or secondary carbanion LiCHRR′ in the presence of complexes **5** (catalytic amount) and **18** (X being a good leaving group) could react faster with the more electrophilic complex **5**, giving a catalytic amount of complex **16**. Complex **16**, in this medium, could be deprotonated yielding a catalytic amount of the complex **17** which could react with complex **18** giving complex **19** and LiX. Cleavage of the C^6-C^7 bond of the binuclear complex **19** could afford the zwitterionic complex **20**. In the presence of LiY, the complexes **22** (after hydrolysis of **21**) and **5** could be obtained; thus **5** might play a catalytic role in this process.

Having thus established the easy addition of benzylic anions such as **15-Li** to complex **5**, we turned our attention to modifications of the nature of the substituents at the bridgehead carbon atom of dinuclear complexes such as **14**, so as to increase the stability of the newly-formed C^6-C^7 bond. For this purpose, we assumed that it would be interesting to replace the electron-withdrawing cyano group by an electron-donating group such as methoxy.[20] For this reason, we treated the benzylic carbanion **23** (Z = OMe, R′ = R′′ = H) with the cationic benzene complex **5** (Table 9, entry 1). We were pleased to find that the dinuclear complex **24a** could be obtained almost quantitatively (according to the ^{1}H-NMR spectrum of the crude mixture), and that



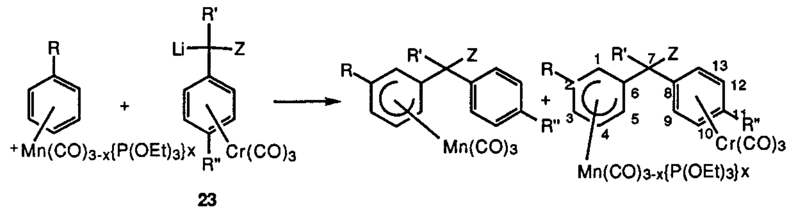
Scheme 1. Tranformation of **18** into **22**: possible mechanism for the carbon−carbon bond formation catalyzed by benzenetricarbonylmanganese complex **5**

it could be purified by silica gel chromatography without any cleavage of the C^6-C^7 bond. However, some decoordination of chromium occured giving rise to the formation of the product **25** (29%), free of Cr, besides the expected complex **24a** (41%). It is thus clear that the nature of the substituent at the benzylic position of the nucleophile plays an important role with respect to the stability of the bridge of these dinuclear complexes.

We were interested in the fate of this reaction (Table 9) when other ligands around the manganese atom were used. Indeed, it has been demonstrated that substitution of one or two CO ligands of arene manganese complexes by phosphane or phosphite could lead to cleaner reactions during the nucleophilic addition process[4,7a,24,25] and, in some cases, could even modify the regioselectivity of the addition.[23] We thus prepared complexes **5P**$_1$ and **5P**$_2$ by substituting one and two carbonyl groups by one and two triethyl phosphito groups, respectively. After addition of carbanion **23** (Z = OMe, R′ = R′′ = H) to **5P**$_1$ (or **5P**$_2$), we isolated, after column chromatography, the complex **24b** in 55% yield (or **24c** in 47% yield) and starting Cr complex **23** in 16% yield (28% in the case of **5P**$_2$) (Table 9, entries 2 and 3). In both cases, no sign of chromium decoordination was detected. The NMR study of the η^5-cyclohexadienyl rings of complexes **24** reflected the electronic influence of the phosphito ligands on the cycle coordinated to the Mn entity. A shielding effect was detected in the ^{1}H- and ^{13}C-NMR spectra (Table 10). No modification of chemical shifts of chromium ring proton signals was observed.

The role of the phosphito ligands with respect to the manganese atom could thus be two-fold: 1. The phosphito ligands, being weaker π-acceptors than CO ligands, lead to an increase of the electron density of the cycle and lower the activation of the manganese complex towards nucleophilic

Table 9. Addition of benzylic anions prepared from tricarbonylchromium complexes to cationic Mn complexes



entry	Mn complex	Cr complex Z	R'	R''	mononuclear complex	dinuclear complex
1	5 R=H, x=0	OMe	H	H	25	24a
2	$5P_1$ R=H, x=1	OMe	H	H		24b
3	$5P_2$ R=H, x=2	OMe	H	H		24c
4	26a R=OMe, x=0	OMe	CH_3	H		27a
5	26b R=OMe, x=1	OMe	CH_3	H		27b

Table 10. Shielding effect of phosphito ligands on the η^5-cyclohexadienyl ring of complexes **24**

Complexes **24**	**24a**	**24b**	**24c**
H^1 and H^5	3.30, 2.83	3.04, 2.54	2.61, 2.05
H^2 and H^4	4.91	4.73	4.53
H^3	5.79	5.53	5.18
H^6	2.60	2.62	2.51
C^1 and C^5	51.7, 54.6	48.5, 51.4	45.2, 47.8
C^2 and C^4	96.8, 97.0	95.3, 95.5	93.2, 93.7
C^3	80.4	79.5	76.8
C^6	87.0	87.0	87.2

addition. Thus, 16% and 28% of starting material was recovered when **5P**$_1$ and **5P**$_2$, respectively, were used. 2. Although the phosphito−manganese complexes were less electrophilic, better yields in **24b** and **24c** were observed (55% and 47%, respectively) due to an overall stabilization of these dinuclear complexes, which is as yet difficult to explain.

To further investigate the regioselectivity of the addition of α-benzylic carbanions to manganese complexes, we treated the carbanion **23** (Z = OMe, R′ = CH_3, R′′ = H) with the cationic (η^6-anisole) complex **26a**. We observed the formation of only one regioisomer **27a** in 47% yield as a mixture of two diastereoisomers in a 1:1 ratio (measured by integrating the methoxy protons at C2), and some Cr complex starting material (26%) (Table 9, entry 4). Addition occured, as expected, *meta* to the methoxy group.[21,22] No formation of a mononuclear Mn complex due to the decoordination of the chromium entity was observed.

An analogous reaction was carried out with the anisole dicarbonyl mono-phosphito complex **26b** in order to gain insight into the influence of the nature of manganese ligands. Thus, complex **26b** treated with the benzylic carbanion **23** (Z = OMe, R′ = CH_3, R′′ = H) yielded complex **27b** as a unique regioisomer in 64% yield (2 diastereoisomers in a 1:1 ratio) (Table 9, entry 5) and some Cr starting material was recovered. In this example again, substitution of a CO ligand by a phosphito ligand led to a significant increase of the yield of the dinuclear complex. As already observed for complexes **24**, the ^{1}H- and ^{13}C-NMR spectra of complex **27b** showed shielded signals compared to those of complex **27a**: for example, the H^3 and H^4 atoms are shielded by 0.34 and by 0.26 ppm and the C^3 and C^4 atoms are shielded by 1.3 and 0.9 ppm, respectively.

Conclusion

The reaction of stabilized carbanions with cationic (η^6-arene)tricarbonylmanganese complexes gives, as expected, neutral mononuclear tricarbonyl(η^5-cyclohexadienyl)manganese complexes. But, depending on the amount of carbanion, these reactions can also lead to dinuclear tricarbonyl(η^5-cyclohexadienyl)manganese complexes. With a primary carbanion, it was even possible to isolate a "carousel-like" trinuclear tricarbonyl(η^5-cyclohexadienyl)manganese complex, whose formation, as well as that of the dinuclear complex, was easily explained.

We have extended this reaction to the synthesis of heterodinuclear complexes with η^5 and η^6 hapticities by using other electrophiles, such as tricarbonyl(halogenoarene)chromium derivatives. In one case, we have observed a spectacular cleavage of the bond between an (η^5-cyclohexadienyl)manganese unit and a benzylic carbon atom of an arenetricarbonylchromium entity.

An alternative method to these heterodinuclear complexes involves the reaction of electrophilic Mn complexes with nucleophilic benzylic carbanions of Cr complexes.

Experimental Section

General: All reactions were carried out under dry nitrogen. All experiments were always protected from exposure to light and oxygen. Workup procedures were done in air. Tetrahydrofuran (THF) and dibutyl ether (DBE) used were distilled from sodium benzophenone ketyl under dry nitrogen. − ^{1}H- and ^{13}C-NMR spectra were obtained with Bruker AC 200 and ARX 400 spectrometers. Infrared spectra were recorded with Perkin-Elmer 1420 and Bruker FT spectrometers. Elemental analyses were performed by Le Service de Microanalyses de l'Université P. et M. Curie. Melting points were measured with a Reichert apparatus.

Preparation of (η^6-Arene)manganese and -chromium Complexes

Tricarbonyl(η^6-1,2,3-trimethoxybenzene)manganese Tetrafluoroborate (2): Prepared according to a literature method, yield: 95%, ref.[5]: 95%. − IR ($CHCl_3$): $\tilde{\nu}$ = 2058 cm^{-1}, 1997 (CO). − ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 7.00 (t, J = 7 Hz, 1 H, H^5), 6.25 (t, J = 7 Hz, 2 H, H^4 and H^6), 4.27 (s, OCH$_3$ at C^1 and C^3), 4.08 (s, OCH$_3$ at C^2). − ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 217.6 (CO), 146.6 (C^1 and C^2), 120 (C^2), 74.1 (C^4 and C^6), 65.2 (OCH$_3$ at C^2), 59.3 (OCH$_3$ at C^1 and C^3). − $C_{12}H_{12}BF_4MnO_6$ (392.07): calcd. C 36.58, H 3.07; found C 36.54, H 2.99.

(η^6-Benzene)tricarbonylmanganese Hexafluorophosphate Complex 5: Prepared according to a literature method, yield: 92%; ref.[26] 72%.

(η^6-Benzene)dicarbonylphosphitomanganese Hexafluorophosphate Complex 5P$_1$: Prepared according to a literature method, yield: 54%, ref.[28a] 88%.

(η^6-Benzene)carbonyldiphosphitomanganese Hexafluorophosphate Complex 5P$_2$: Prepared according to a modified literature method[28a] from complex **5**. Yield: 54%, yellow solid. − IR ($CHCl_3$): $\tilde{\nu}$ = 1940 cm^{-1} (CO). − ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 5.00 (t, J = 2.1 Hz, 6 H), 4.15 (m, 12 H), 1.34 (t, J = 7.1 Hz, 18 H). − ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 227.0 (d, J_{CP} = 37.5 Hz), 94.7 (CH), 63.1 (CH$_2$), 16.2 (CH$_3$). − ^{31}P NMR (162 MHz, [D$_6$]acetone): δ = 181.5. − $C_{19}H_{36}F_6MnO_7P_3$ (638.34): calcd. C 35.75, H 5.68; found C 35.85, H 5.71.

(η^6-Anisole)tricarbonylmanganese Hexafluorophosphate Complex 26a: Prepared according to a literature method, yield 70%; ref.[27] 56%.

(η^6-Anisole)dicarbonylphosphitomanganese Hexafluorophosphate Complex 26b: In a typical procedure[28b] cationic complex **26a** (500 mg, 1.27 mmol) was dissolved in freshly distilled acetone (50 mL). P(OEt)$_3$ (430 μL, 2.50 mmol), then Me$_3$NO (a pinch) were added and mixed at room temperature for 3 h. Solvents were removed under reduced pressure. The crude oil was washed with ether and the complex was recrystallised in an acetone/diethyl ether mixture to give orange-yellow needles of complex **26b** (457 mg, 0.86 mmol, 68% yield). − IR ($CHCl_3$): $\tilde{\nu}$ = 1960 cm^{-1}, 2005 (CO). − ^{1}H NMR (200 MHz, CDCl$_3$): δ = 6.32 (t, J = 5.6 Hz, 2 H, H^3 and H^5), 5.71 (d, J = 5.6 Hz, 2 H, H^2 and H^6), 5.58 (t, J = 5.6 Hz, 1 H, H^4), 4.02 [m, 6 H, P(OC*H*$_2$CH$_3$)], 3.92 (s, 3 H, CH$_3$), 1.35 [t, J = 7.0 Hz, 9 H, P(OCH$_2$C*H*$_3$)]. − ^{13}C NMR (100 MHz, CDCl$_3$): δ = 219.9 (CO−Mn), 146.1 (C^1), 101.4 (C^3 and C^5), 87.5 (C^4), 80.5 (C^2 and C^6), 63.6 [d, J = 7.0 Hz, P(O*C*H$_2$CH$_3$)], 57.3 (CH$_3$), 16.0 [d, J = 7.0 Hz, P(OCH$_2$*C*H$_3$)]. − ^{31}P NMR (162 MHz, CDCl$_3$): δ = 176.0. − $C_{15}H_{23}F_6MnO_6P_2$ (530.20): calcd. C 31.16, H 4.01; found C 31.51, H 4.42.

Tricarbonyl(η^6-*p*-fluorotoluene)chromium Complex 13: Prepared according to literature methods described for tricarbonyl(*o*- and *m*-fluorotoluene)chromium complexes.[29] Yield: 42%. − IR (CCl$_4$): $\tilde{\nu}$ = 1910 cm^{-1}, 1980 (CO). − ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 5.81 (d, J = 4.1 Hz, 4 H, H^2, H^3, H^5, and H^6), 2.11 (s, 3 H, CH$_3$). − ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 233.7 (Cr−CO), 145.8 (C^1, d, J = 260.4 Hz), 105.5 (C^4), 95.9 (C^3 and C^5, d, J = 7.1 Hz), 82.2 (C^2 and C^6, d, J = 20.4 Hz), 19.6 (CH$_3$). − $C_{10}H_7CrFO_3$ (246.16): calcd. C 48.79, H 2.87, N 21.13; found C 48.83, H 2.85, N 21.19.

(η^6-Benzyl methyl ether)tricarbonylchromium Complex 23: Prepared according to a literature method, yield 62%, ref.[30] 84%.

Syntheses of Complexes 3a, 3b, 3c, 4, 6a, 7a, 6b, 7b, 8b, 6c, 7c

Typical Procedure. − Complex 3a: To a solution of LiN(CHMe$_2$)$_2$ (1.2 mmol) [obtained by addition of *n*BuLi (755 μL, 1.2 mmol) in a solution of HN(CHMe$_2$)$_2$ (154 μL, 1.2 mmol) in THF at −78°C] in THF (10 mL) were added (*i*Pr)$_3$SiCH$_2$CN (220 μL, 1.2 mmol) and TMEDA (905 μL, 6 mmol). The mixture was stirred for 5 min at −78°C, then added, through a canula, to a solution of complex **2** (394 mg, 1 mmol) in THF (5 mL). The resulting solution was stirred for 3 min at −78°C then treated with distilled water, then with Et$_2$O. After extraction, the organic phase was washed with brine and dried with MgSO$_4$. Concentration of the organic layer gave a yellow solid. Flash chromatography on basic alumina gave compound **3a** (yield 38%). m.p. 113°C. − IR ($CHCl_3$): $\tilde{\nu}$ = 2010 cm^{-1}, 1935 (CO), 2210 (CN). − ^{1}H NMR (200 MHz, CDCl$_3$): δ = 4.02 (s, 3 H, OCH$_3$ at C^2), 3.58 (s, 3 H, OCH$_3$ at C^1 or C^3), 3.43 (s, 3 H, OCH$_3$ at C^3 or C^1), 3.14 (dd, J = 6 and 1.9 Hz, 1 H, H^4 or H^6), 2.93 (q, J = 6 Hz, 1 H, H^5), 2.83 (dd, J = 6 and 1.9 Hz, 1 H, H^6 or H^4), 1.44 (d, J = 6 Hz, 1 H, C*H*CN), 1.22 [m, 3 H, Si(CH−Me$_2$)], 1.09 {d, 18 H, [(CH$_3$)$_2$CH]$_3$Si}. − ^{13}C NMR (100 MHz, CDCl$_3$): δ = 219.3 (CO), 136.9 (C^1 or C^3), 136.2 (C^3 or C^1), 119.8 (CN or C^2), 115.8 (C^2 or CN), 66.3 (OCH$_3$ at C^2), 55.3 (OCH$_3$ at C^1 or C^3), 54.7 (OCH$_3$ at C^3 or C^1), 36.4 (C^4 or C^6), 35.8 (C^5), 35.7 (C^6 or C^4), 29.2 (CH), 18.6 (CH$_3$), 11.9 (CH). − $C_{23}H_{34}MnNO_6Si$ (503.54): calcd. C 54.86, H 6.80, N 2.78; found C 54.91, H 6.79, N 2.72.

Crystal Structure of 3a: [Mn(CO)$_3$(C$_{20}$H$_{34}$O$_3$NSi)], M = 503.5, μ = 0.548 mm^{-1}, F(000) = 1064, ρ = 1.24 g.cm^{-3}, monoclinic, $P2_1/n$, Z = 4, a = 13.264(3), b = 12.120(4), c = 17.246(6) Å, β = 104.41(2)°, V = 2685(15) Å^3, from 25 reflections (30° < 2θ < 30.5°). Cell dimensions and intensities were measured at 295 K with a Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). ω/2θ scans, two standard reflections measured every hour showed no significant variation. 1° < θ < 28° (−17 < h < 16, 0 < k < 15, 0 < l <22); 6984 measured reflections, 6461 unique reflections of which 3385 were observed [$|F_o|^2$ > 3σ($|F_o|^2$)]; R_{int} = 0.021 for equivalent reflections. Data were corrected for Lorentz and polarization effects and for absorption[31] (transmission factors min. 0.9, max. 1). The structure was solved by direct methods using SHELXS,[32] all other calculations used CRYSTALS.[33] Atomic scattering factors and anomalous dispersion terms were taken from ref.[34] Full-matrix least-squares refinement based on $|F|$ and a Chebychev weighting scheme gave final values R = 0.0576, wR = 0.0707, and s = 1.00 for 301 variables and 3385 contributing reflections. The maximum shift/esd of the last cycle was 1.32. Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were introduced in calculated positions, except for hydrogen atoms of methoxy groups which were located in a difference Fourier map; their coordinates were left in fixed positions, only an overall isotropic thermal parameter was refined. The final difference electron density map showed a maximum of 0.43 and a minimum of −0.34 eÅ^{-3}.

Complexes 3b, 3c, and 4: Same method as for complex **3a**. Preparation from LiN(CHMe$_2$)$_2$ (1.2 mmol), Me$_3$SiCH$_2$CN (164 μl, 1.2 mmol), complex **2** (393.96 mg, 1 mmol). Overall yield 60%. After a fast silica gel column chromatography, complexes **3b**, **3c**, and **4** could be isolated in a 82:12:4 ratio (50.4%, 7.2%, 2.4% yield, respectively).

Complex 3b: M.p.103°C. − IR ($CHCl_3$): $\tilde{\nu}$ = 2210 cm^{-1} (CN), 2010,1930 (CO). − ^{1}H NMR (200 MHz, CDCl$_3$): d = 4.06 (s, 3 H, OCH$_3$ at C^2), 3.58 (s, 3 H, OCH$_3$ at C^1 or C^3), 3.47 (s, 3 H, OCH$_3$ at C^3 or C^1), 3.09 (d, J = 6.2 Hz, 1 H, H^4), 2.84 (m, 2 H, H^6, H^4 and H^5), 2.77 (q, J = 6.3 Hz, 1 H, H^5), 1.28 (d, J = 6.2

Hz, 1 H, CHCNSiMe$_3$), 0.19 [s, 9 H, $(CH_3)_3Si$]. − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 219.3 (CO), 136.7 (C^1 or C^3), 136.3 (C^3 or C^1), 119.5 (CN or C^2), 116.5 (C^2 or CN), 66.4 (OCH_3 at C^2), 55.4 (OCH_3 at C^1 or C^3), 54.8 (OCH_3 at C^3 or C^1), 36.2 (C^4 or C^6), 36 (C^5), 35.5 (C^6 or C^4), 34.3 (C*H*CNSiMe$_3$), − 2.06 (CH_3 at SiMe$_3$). − $C_{17}H_{22}MnNO_6Si$ (419.4): calcd. C 48.68, H 5.28, N 3.33; found C 48.83, H 5.32, N 3.37.

Complex 3c: M.p. 91 °C. − IR ($CHCl_3$): ṽ = 2242 cm^{-1} (CN), 2010, 1935 (CO). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.06 (s, 3 H, OCH_3 at C^2), 3.48 (s, 6 H, OCH_3 at C^1 and C^3), 2.90 (m, 3 H, H^4, H^5 and H^6), 1.67 (d, J = 5.8 Hz, 2 H, CH_2CN). − ^{13}C NMR (50 MHz, $CDCl_3$,): δ = 212.1 (CO), 137.1 (C^1 and C^3), 116.4 (CN or C^2), 115.4 (C^2 or CN), 66.8 (OCH_3 at C^2), 55.3 (OCH_3 at C^1 and C^3), 34.4 (C^5), 33.8 (C^4 or C^6), 29.9 (CH_2CN). − $C_{14}H_{14}MnNO_6$ (347.2): calcd. C 48.43, H 4.06, N 4.03; found C 49.68, H 4.58, N 4.05.

Crystal Structure of 3c: [Mn(CO)$_3$($C_{11}H_{14}O_3N$)], M = 347.2, μ = 0.811 mm^{-1}, F(000) = 712, ρ = 1.43 g cm^{-3}, monoclinic, $P2_1/n$, Z = 4, a = 13.198(6), b = 12.691(6), c = 9690(2) Å, (= 97.17(3)°, V = *1*610 Å^3, from 25 reflections (30° < 2θ < 32°). Cell dimensions and intensities were measured at 295 K with a Philips PW1100 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71069Å). ω/2θ scans, two standard reflections measured every two hours showed no significant variation. 2° < θ < 25° (−15 < h < 15, 0 < k < 15, 0 < l <11); 3134 measured reflections, 2804 unique reflections of which 1124 were observed [$|F_o|^2 > 2.5\sigma(|F_o|^2)$]; R_{int} = 0.025 for equivalent reflections. Data were corrected for Lorentz and polarization effects and for absorption[31] (transmission factors min = 0.75, max = 1). The structure was solved by direct methods using SHELXS,[32] all other calculations used CRYSTALS.[33] Atomic scattering factors and anomalous dispersion terms were taken from ref.[34] Full-matrix least-squares refinement based on $|F|$ and a Chebychev weighting scheme gave final values R = 0.0666, wR = 0.0627, and s = 1.13 for 200 variables and 3385 contributing reflections. The maximum shift/esd of the last cycle was 0.26. Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were located in a difference Fourier map; their coordinates were left in fixed positions, only an overall isotropic thermal parameter was refined. The final difference electron density map showed a maximum of 0.31 and a minimum of − 0.39 eÅ^{-3}.

Complex 4: M.p. 191 °C. − IR ($CHCl_3$): ṽ = 2225 cm^{-1} (CN), 2010,1935 (CO). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.99 (s, 6 H, 2 OCH_3 at C^2), 3.59 (s, 6 H, 2 OCH_3 at C^1 or C^3), 3.50 (s, 6 H, 2 OCH_3 at C^3 or C^1), 2.76 (dd, J = 6.1 and 1.4 Hz, 2 H, 2 H^4 or 2 H^6), 2.66 (dd, J = 6.1 and 1.4 Hz, 2 H, 2 H^6 or 2 H^4), 2.52 (q, J = 6.1 Hz, 2 H, 2H^5), 0.98 (t, J = 6.1 Hz, 1 H, CHCN). − ^{13}C NMR (100 MHz, $CDCl_3$,): δ = 218.5 (CO), 137.5 (C^1 or C^3), 137.2 (C^3 or C^1), 117.8 (CN or C^2), 115.1 (C^2 or CN), 66.2 (OCH_3 at C^2), 55.6 (OCH_3 at C^1 or C^3), 55.4 (OCH_3 at C^3 or C^1), 55.1 (*C*HCN), 35.2 (C^5), 33.2 (C^4 or C^6), 32.3 (C^6 or C^4). − $C_{26}H_{25}Mn_2NO_{12}$ (653.35): calcd. C 47.75, H 3.82, N 2.14; found C 47.95, H 3.95, N 2.19.

Complexes 6b, 7b and 8b:

Typical Procedure: To a solution of LiN(CHMe$_2$)$_2$ (1.1 mmol) [obtained by addition of nBuLi (687 μL, 1.1 mmol) in a solution of HN(CHMe$_2$)$_2$ (140μL, 1.1 mmol) in THF at −78 °C] in THF (10 mL) was added acetonitrile (55 μL, 1.05 mmol). The mixture was stirred for 5 min at −78 °C , then added, through a canula, to a solution of complex **5** (362 mg, 1 mmol) in THF (5 mL). The resulting solution was stirred for 3 min at −78 °C then treated with distilled water followed by Et_2O. After extraction, the organic phase was washed with brine and dried with $MgSO_4$. Concentration of the organic layer gave a yellow oil. Flash chromatography on basic alumina gave compounds **8b** (the less polar), then **7b** and **6b** (overall yield: 58%) in a 2:18:80 ratio.

Complex 6b: M.p. 95 °C. − IR (CCl4): ṽ = 2240 cm^{-1} (CN), 1945, 2005 (CO). − ^{1}H NMR (200 MHz, CDCl3): δ = 5.84 (t, J = 6.0 Hz, 1 H, H^3), 4.94 (t, J = 6.0 Hz, 2 H, H^2 and H^4), 3.23 (t, J = 6.0 Hz, 2 H, H^1 and H^5), 2.94 (m, 1 H, H^6), 1.69 (d, J = 6.7 Hz, 2 H, CH_2). − ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 221.7 (Mn−CO), 116.7 (CN), 96.9 (C^2 and C^4), 80.7 (C^3), 53.2 (C^1 and C^5), 31.7 (C^6), 29.0 (CH_2). − $C_{11}H_8MnNO_3$ (257.13) calcd. C 51.38, H 3.14, N 5.45; found C 51.42, H 3.30, N 5.43.

Complex 7b: M.p. 201 °C. − IR ($CHCl_3$): ṽ = 2230 cm^{-1} (CN), 1940, 2100 (CO). − ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 6.04 (tt, J = 6.5 and 1.2 Hz, 2 H, 2 H^3), 5.17 (m, 4 H, 2 H^2 and 2 H^4), 3.42 (tdd, J = 6.5, 3.3 and 1.2 Hz, 2 H, 2 H^1 or 2 H^5), 3.33 (tdd, J = 6.5, 3.3 and 1.2 Hz, 2 H, 2 H^5 or 2 H^1), 2.85 (q, J = 6.5 and 6.7 Hz, 2 H, 2 H^6), 1.32 (t, J = 6.5 Hz, 1 H, H^7). − ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 224.5 (Mn−CO), 119.7 (CN), 99.0 and 99.2 (C^2 and C^4), 83.5 (C^3), 55.4 (C^7), 54.3 and 56.4 (C^1 and C^5), 34.6 (C^6). − $C_{20}H_{13}Mn_2NO_6$ (473.21) calcd. C 50.77, H 2.77, N 2.96; found C 50.90, H 2.71, N 3.02.

Complex 8b: M.p. 204 °C. − IR (CCl4): ṽ = 2330 cm^{-1} (CN), 2020, 1950 (CO). − ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 6.01 (t, J = 5.8 Hz, 3 H, H^3), 5.26 (t, J = 5.8 Hz, 6 H, H^2 and H^4), 3.46 (t, J = 5.8 Hz, 6 H, H^1 and H^5), 2.93 (t, J = 5.8 Hz, 3 H, H^6). − ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 222.9 (Mn−CO), 120 (CN), 98 (C^2 and C^4), 81.7 (C^3), 66.2 (*C*-CN), 55.4 (C^1 and C^5), 36.7 (C^6). − $C_{29}H_{18}Mn_3NO_9$ (689.27) calcd. C 50.53, H 2.63, N 2.03; found C 50.95, H 2.77, N 3.16.

Complexes 6a and 7a: Same method as for complexes **6b**, **7b**, and **8b**: Starting from 1 equiv. of complex **5**, 1 equiv. of CH_3CH_2CN and 1 equiv. of LDA, complexes **6a** and **7a** were obtained (overall yield: 87%) in a 87:13 ratio. Starting from 2 equiv. of complex **5**, 1 equiv. of CH_3CH_2CN and 2 equiv. of LDA, complexes **6a** and **7a** were obtained (overall yield 85%) in a 28:72 ratio.

Complex 6a: M.p. 139 °C. − IR (CCl_4): ṽ = 2240 cm^{-1} (CN), 1950, 2010 (CO). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.80 (t, 1 H, J = 6.1 Hz, H^3), 4.97 (t, J = 6.1 Hz, 1 H, H^2 or H^4), 4.92 (t, J = 6.1 Hz, 1 H, H^4 or H^2), 3.34 (tt, J = 6.1 and 1.5 Hz, 1 H, H^1 or H^5), 3.15 (tt, J = 6.1 and 1.5 Hz 1 H, H^5 or H^1), 2.64 (m, 1 H, H^6), 1.69 (q, J = 7.2 Hz, 1 H, H^7), 1.01 (d, J = 7.2 Hz 3 H, CH_3). − ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 225.4 (Mn−CO), 124.8 (CN), 99.9 (C^2 and C^4), 84.0 (C^3), 54.3 (C^1 and C^5), 38.9 (C^6), 38.7 (C^7), 14.9 (CH_3). − $C_{12}H_{10}MnNO_3$ (271.16): calcd. C 53.16, H 3.72, N 5.07; found C 53.06, H 3.81, N 5.17.

Complex 7a: M.p. 194 °C. − IR (CCl4): ṽ = 2240 cm^{-1} (CN), 1945, 2005 (CO). − ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 5.98 (tt, J = 5.7 and 1.3 Hz, 2 H, H^3), 5.25 (m, 4 H, 2 H^2 and 2 H^4), 4.78 (tt, J = 5.7 and 1.3 Hz, 2 H, 2 H^1 or 2 H^5), 3.35 (tt, J = 5.7 and 1.3 Hz, 2 H, 2 H^5 or 2 H^1), 2.84 (m, 2 H, 2 H^6), 0.74 (s, 3 H, CH_3). − ^{13}C NMR (50 MHz, [D$_6$]acetone): δ = 225.5 (Mn−CO), 124.7 (CN), 101.1 (C^2 and C^4), 84.0 (C^3), 56.0 and 57.4 (C^1 and C^5), 40.9 (C^6), 39.6 (C^7), 18.1 (CH_3). − $C_{21}H_{15}Mn_2NO_6$ (487.23): calcd. C 51.77, H 3.10, N 2.87; found C 52.15, H 3.09, N 2.84.

Crystal Structure of 7a: [(CO)$_3$Mn($C_{15}H_{15}N$)Mn(CO)$_3$], M = 487.21, μ = 0.126 mm^{-1}, F(000) = 492, ρ = 1.26 g.cm^{-3}, triclinic, $P\bar{1}$, Z = 2, a = 6.735(6), b = 12.779(8), c = 13.425(12) Å, α = 116.11(6), β = 92.21(1), γ = 103.94(8)°, V = 993 Å^3, from 25 reflections (20° < 2θ < 22°). Cell dimensions and intensities were measured at 295 K with a Philips PW1100 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). ω/2θ scans, two standard reflections measured every two hours showed no significant variation. 2° < θ <20° (−6 < h < 6, −12 < k < 11, 0 < l < 12); 1960 measured reflections, 1816 unique reflections of which 1232 were observed [$|F_o|^2 > 1.5\sigma(|F_o|^2)$]; $R_{int} = 0.035$ for equivalent reflections. Data were corrected for Lorentz and polarization effects and for absorption[31] (transmission factors min = 0.8, max = 1). The structure was solved by direct methods using SHELXS,[32] all other calculations used CRYSTALS.[33] Atomic scattering factors and anomalous dispersion terms were taken from ref.[34] Full-matrix least-squares refinement based on $|F|$ and a Chebychev weighting scheme gave final values $R = 0.0591$, $Rw = 0.0616$, and $s = 1.18$ for 207 variables and 1232 contributing reflections. The maximum shift/esd in the last cycle was 0.22. $Mn(CO)_3$, CN, and methyl C atoms were anisotropically refined, other C atoms were left isotropic in order to reduce the number of variables. Hydrogen atoms were introduced in calculated positions; their coordinates were left in fixed positions, only an overall isotropic thermal parameter was refined. The final difference electron density map showed a maximum of +0.52 and a minimum of −0.45 eÅ^{-3}.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101517 (**3a**), -101518 (**3c**), -101519 (**7a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Complexes 6c and 7c: Same method as for complexes **6b**, **7b**, and **8b**: prepared from $LiN(CHMe_2)_2$ (1.2 mmol), Me_3SiCH_2CN (164 µL, 1.2 mmol), and complex **5** (362.04 mg, 1 mmol). Overall yield: 66%. A fast silica gel chromatography gave complexes **6c**, **7c**, **6b**, and **7b** in a 64:28:7:1 ratio.

Complex 6c: M.p. 93°C. − IR ($CHCl_3$): ṽ = 2205 cm^{-1} (CN), 2015 and 1945 (CO). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.86 (t, J = 6.2 Hz, 1 H, H^3), 5.00 (t, J = 6.2 Hz, 1 H, H^2 or H^4), 4.93 (t, J = 6.2 Hz, 1 H, H^4 or H^2), 3.40 (t, J = 6.2 Hz, 1 H, H^1 or H^5), 3.16 (t, J = 6.2 Hz, 1 H, H^5 or H^1), 2.85 (q, J = 6.2 Hz 1 H, H^6), 1.33 (d, J = 6.2 Hz, 1 H, C*H*CNSiMe$_3$), 0.19 (s, 9 H, $(CH_3)_3Si$). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 222.3 (CO), 120.1 (CN), 96.6 (C^2 or C^4), 96.3 (C^4 or C^2), 81.3 (C^3), 55.1 (C^1 or C^5), 55.0 (C^5 or C^1), 33.5 (*C*HCNSiMe$_3$), 33.4 (C^6), −1.72 (CH$_3$ of SiMe$_3$). − $C_{14}H_{16}MnNO_3Si$ (329.31): calcd. C 51.06, H 4.89, N 4.25; found C 51.06, H 4.92, N 4.14.

Complex 7c: M.p. 163°C. − IR ($CHCl_3$): ṽ = 2200 cm^{-1} (CN), 2100 and 1945 (CO). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.86 (t, J = 6 Hz, 2 H, H^3), 5.10 (t, J = 6 Hz, 2 H, 2 H^2 or 2 H^4), 4.93 (t, J = 6 Hz, 2 H, 2 H^4 or 2 H^2), 3.32 (t, J = 6 Hz, 2 H, 2 H^1 or 2H^5), 3.16 (t, J = 6 Hz, 2 H, 2 H^5 or 2 H^1), 2.93 (t, J = 6 Hz, 2 H, 2 H^6), 0.24 (s, 9 H, SiMe$_3$). − ^{13}C NMR (200 MHz, [D$_6$]acetone): δ = 223.7 (CO), 122.5 (CN), 98.6 (C^2 and C^4), 82.4 (C^3), 58.4 (C^1 or C^5), 56.5 (C^5 or C^1), 53.3 (*C*CNSiMe$_3$), 37.7 (C^6), −0.40 (SiMe$_3$). − $C_{23}H_{21}Mn_2NO_6$ (545.38): calcd. C 50.65, H 3.88, N 2.57; found C 50.61, H 3.79, N 2.45.

Complex 6d: Same method as for complexes **6b**, **7b**, **8b**: prepared from LiN(CH*i*Pr$_2$)$_2$ (1.2 mmol), *i*Pr$_3$SiCH$_2$CN (220µL, 1.2 mmol), and complex **5** (362.04 mg, 1 mmol). Yield: 49%. − M.p. 88°C. − IR (CHCl3): ṽ = 2210 cm^{-1} (CN), 2010 and 1945 (CO). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.85 (tt, J = 6 and 1 Hz, 1 H, H^3), 5.02 (t, J = 6 Hz, 1 H, H^2 or H^4), 4.90 (t, J = 6 Hz, 1 H, H^4 or H^2), 3.46 (tt, J = 6 and 1 Hz, 1 H, H^1 or H^5), 3.19 (tt, J = 6 and 1 Hz, 1 H, H^5 or H^1), 2.96 (q, J = 6 Hz 1 H, H^6), 1.50 (d, J = 6 Hz, 1 H, C*H*CNSi*i*Pr$_3$), 1.22 [m, 3 H, (Me$_2$C*H*)$_3$Si], 1.09 {d, 18 H, [(C*H*$_3$)$_2$CH]$_3$Si}. − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 222.1 (CO), 120.3 (CN), 96.5 (C^2 or C^4), 96.1 (C^4 or C^2), 81.1 (C^3), 55.2 (C^1 or C^5), 33.0 (C^6), 28.2 {[(CH$_3$)$_2$CH]$_3$Si*C*HCN}, 18.7 and 18.6 {[(*C*H$_3$)$_2$CH]$_3$Si}, 11.9 {[(CH$_3$)$_2$*C*H]$_3$Si}. − $C_{20}H_{28}MnNO_3Si$ (413.47): calcd. C 58.09, H 6.82, N 3.38; found C 58.11, H 6.81, N 3.36.

Addition of α-Sulfonyl Carbanions to Benzenetricarbonylmanganese Complex 5: Typical procedure: *n*BuLi (692 µL of a solution 1.6 M in hexane; 1.1 mmol) was added under nitrogen to a solution of chloromethyl *p*-toluenesulfonate (204.6 mg; 1.0 mmol) in THF (10 mL). After 30 min of stirring, this solution was transferred at −78°C under nitrogen through a canula into a flask containing benzenetricarbonylmanganese complex **5** (364.5 mg; 1 mmol) and THF (10 mL). After 30 min, the reaction temperature was increased progressively to room temperature. The mixture was extracted with water and diethyl ether, the organic layer was washed with brine, and dried with $MgSO_4$. Concentration of the ether layer gave a yellow oil. After chromatography on a silica gel column, two fractions were obtained: the first one was a yellow powder consisting of a 2:1 mixture of complex **9a** (149.5 mg; 0.35 mmol; yield 35%) and starting sulfone (eluent: petroleum ether/diethyl ether, 80:20); dinuclear complex **10a** (241.9 mg; 0.38 mmol; yield 38%) was obtained from the second fraction.

Complex 9a: IR (CCl_4): ṽ = 1940 cm^{-1}, 1950, and 2010 (CO), 1150 and 1350 (SO_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 9.3 Hz, 1 H, H^9 or H^{13}), 7.54 (d, 1 H, J = 9.3 Hz, H^{13} or H^9), 7.18 (m, 2 H, H^{10} and H^{12}), 5.83 (t, J = 5.4 Hz, 1 H, H^3), 4.99 (m, 2 H, H^2 and H^4), 3.65 (d, J = 9.3 Hz, 1 H, H^7), 3.49 (m, 1 H, H^1 or H^5), 3.30 (m, 1 H, H^6), 3.12 (m, 1 H, H^5 or H^1), 2.46 (s, 3 H, CH$_3$). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 221.8 (Mn−CO), 145.9 (C^8), 133.1 (C^{11}), 130.1 (C^{10} and C^{12}), 129.5 (C^9 and C^{13}), 96.5 (C^2 and C^4), 81.2 (C^7), 78.1 (C^3), 48.9 and 53.9 (C^1 and C^5), 36.2 (C^6), 21.8 (CH$_3$). − MS (CI) (NH$_3$); m/z: 438 [MNH$_4$]$^+$.

Complex 10a: IR (CCl_4): ṽ = 1945 cm^{-1} and 2005 (CO), 1140 and 1325 (SO_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, J = 9.5 Hz, 2 H, H^9 and H^{13}), 7.38 (m, 2 H, H^{10} and H^{12}), 5.78 (t, J = 5.3 Hz, 2 H, 2 H^3), 5.09 (m, 2 H, 2 H^2 or 2 H^4), 4.89 (t, J = 5.3 Hz, 2 H, 2 H^4 or 2 H^2), 3.34 (m, 4 H, 2 H^1 and 2 H^5), 3.15 (m, 2 H, 2 H^6), 2.48 (s, 3 H, CH$_3$). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 222.0 (Mn−CO), 146.1 (C^8), 133.0 (C^{11}), 130.6 (C^{10} and C^{12}), 129.7 (C^9 and C^{13}), 97.7 and 97.9 (2 C^2, 2 C^4), 93.1 (C^7), 80.1 (C^3), 54.5 (2 C^1, 2 C^5), 39.8 (C^6), 21.8 (CH$_3$). − $C_{26}H_{19}ClMn_2O_8S$ (636.83): calcd. C 49.01, H 2.98; found C 49.00, H 2.96.

Complexes 9b and 10b: Same method as for **9a** and **10a**: starting from *n*BuLi (692 µL; 1.1 mmol), fluoromethyl benzenesulfonate (174.2 mg; 1 mmol), and complex **5** (364.5 mg; 1 mmol). A fast silica gel column chromatography gave complexes **9b** (43%) and a mixture of complex **10b** (5%) and some starting sulfone. If 2 equiv. of *n*BuLi and 2 equiv. of complex **5** were used, after chromatography, complexes **11** (16%), **9b** (3%), and a mixture of **10b** (52%) and starting sulfone were obtained.

Complex 9b: IR (CCl_4): ṽ = 1905 cm^{-1}, 1945, 1975, and 2005 (CO), 1155 and 1347 (SO_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = from 7.42 to 7.92 (several m, H^9, H^{10}, H^{11}, H^{12}, and H^{13}), 5.78 (t, J = 5.6 Hz, 1 H, H^3), 4.90 (m, 2 H, H^2 and H^4), 3.91 (dd, J_{HF} = 47.5 Hz, J_{HH} = 7.5 Hz, 1 H, H^7), 3.44 (m, 1 H, H^6), 3.06 (m, 1 H, H^1 or H^5), 2.95 (t, J = 5.6 Hz, 1 H, H^5 or H^1). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 222.4 (Mn−CO), 134.8 (C^8), 129.6 (C^{11}), 129.4 (C^{10} and C^{12}), 129.2 (C^9 and C^{13}), 97.3 and 97.6 (C^2 and C^4), 99.9 and 104.3 (C^7), 80.8 (C^3), 47.8 and 48.6 (C^1 and C^5), 33.5 and 33.9 (C^6). − MS (CI) (NH$_3$); m/z: 408 [MNH$_4^+$], 391 [MH$^+$].

Complex 10b: IR (CCl_4): $\tilde{\nu}$ = 1905 cm^{-1}, 1945, 1975, and 2005 (CO), 1155 and 1347 (SO_2). − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42−7.92 (several m, H^9, H^{10}, H^{11}, H^{12} and H^{13}), 5.71 (t, J = 6.0 Hz, 2 H, $2H^3$), 4.90 (m, 2 H, H^2 and H^4), 4.58 (t, J = 6.0 Hz, 2 H, H^2 and H^4), 3.29 (t, J = 6.0 Hz, 1 H, H^6), 3.24 (t, J = 6.0 Hz, 1 H, H^6), 3.06 (m, 2 H, H^1 and H^5), 2.76 (t, J = 6.0 Hz, 2 H, H^1 and H^5). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 222.4 (Mn−CO), 134.9 (C^8), 129.4 (C^{11}), 129.2 (C^{10} and C^{12}), 129.0 (C^9 and C^{13}), 97.5 and 97.7 (C^2 and C^4), 93.1 (C^7), 80.5 (C^3), 49.9 and 50.7 (C^1 and C^5), 36.7 and 37.2 (C^6). − MS(CI)(NH_3); *m/z*: 624 [MNH_4^+], 607 [MH^+].

Complex 15: $LiN(CHMe_2)_2$ (1.1 mmol) was added at −78 °C, under nitrogen to a solution of complex **6a** (388.8 mg; 1.43 mmol) in 5 mL of THF. After 15 min, this red solution was transferred through a canula to another flask containing a solution of tricarbonyl(*p*-fluorotoluene)chromium complex **13** (369.2 mg; 1.50 mmol) in 5 mL of THF. After 30 min of stirring at room temperature, the mixture was extracted with water and diethyl ether. The ether layer was washed with brine, dried with $MgSO_4$, concentrated, and purified by chromatography on a silica gel column. Eluting with a mixture of diethyl ether/petroleum ether (2:98) gave tricarbonyl(*p*-fluorotoluene)chromium complex **13** (160.6 mg, 0.65 mmol, 43% yield); elution with a mixture of diethyl ether/petroleum ether (60:40) gave complex **15** (157.3 mg, 0.56 mmol, 40% yield). M.p. 123 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 1900 cm^{-1} and 1945 (CO), 2220 (CN). − ^1H NMR (400 MHz, [D_6]acetone): δ = 5.89 (d, J = 6.2 Hz, 2 H, H^3 and H^5), 5.58 (d, J = 6.2 Hz, 1 H, H^2 or H^6), 5.55 (d, J = 6.2 Hz, 1 H, H^6 or H^2), 4.01 (q, J = 7.2 Hz, 1 H, H^7), 2.24 (s, 3 H, CH_3), 1.66 (d, J = 7.2 Hz, 3 H, CH_3). − ^{13}C NMR (50 MHz, [D_6]acetone): δ = 233.8 (Cr−CO), 120.5 (CN), 111.3 (C^1), 106.8 (C^4), 94.5 and 95.5 (C^3 and C^5), 93.8 and 94.0 (C^2 and C^6), 28.6 (C^7), 21.4 (CH_3), 20.2 (CH_3). − $C_{13}H_{11}CrNO_3$ (281.23): calcd. C 55.52, H 3.94, N 4.98; found C 55.74, H 3.75, N 4.31.

Complex 14: $LiN(CHMe_2)_2$ (1.1 mmol) was added at −78 °C under nitrogen to a solution of complex **15** (39.6 mg; 0.14 mmol) in 10 mL of THF. After 10 min, this solution was transferred through a canula to a suspension of benzenetricarbonylmanganese complex **5** (57.9 mg; 0.16 mmol) in 5 mL of THF. After 5 min at room temperature, the mixture was extracted with water and diethyl ether, the organic layer was washed with brine and concentrated to give 52.3 mg of a yellow powder, consisting of a mixture of compounds **14** (yield 37%) and **15** (yield 63%). Chromatography of this mixture on silica gel 15 µ column, leads only to the recovery of complex **15**. − IR ($CHCl_3$): $\tilde{\nu}$ = 1905 cm^{-1} and 1920 (Cr−CO), 1945 and 2010 (Mn−CO), 2240 (CN). − ^1H NMR (200 MHz, [D_6]acetone): δ = 5.84 (dd, J = 6.8 and 1.6 Hz, 1 H, H^{10} or H^{12}), 5.76 (dd, J = 6.8 and 1.6 Hz, 1 H, H^{12} or H^{10}), 5.50 (dd, J = 6.8 and 1.6 Hz, 1 H, H^9 or H^{13}), 5.43 (d, J = 6.8 Hz, 1 H, H^{13} or H^9), 5.30 (m, 2 H, H^2 and H^4), 3.54 (t, J = 5.9 Hz, 1 H, H^3), 3.40 (m, 1 H, H^1 or H^5), 3.32 (t, J = 5.9 Hz, 1 H, H^5 or H^1), 3.12 (t, J = 5.9 Hz, 1 H, H^6), 2.33 (s, 3 H, CH_3), 1.47 (s, 3 H, CH_3). − ^{13}C NMR (50 MHz, [D_6]acetone): δ = 233.8 (Cr−CO), 223.2 (Mn−CO), 124.5 (CN), 112.5 (C^8), 106.1 (C^{11}), 99.3 and 99.4 (C^2 and C^4), 97.0 (C^{10} and C^{12}), 92.4 and 92.5 (C^9 and C^{13}), 54.7 (C^3), 54.1 (C^1 and C^5), 47.1 (C^6), 21.4 (C^7), 20.6 (CH_3), 20.2 (CH_3). − MS(CI)(NH_3); *m/z*: 515 [MH_4^+], 498 [MH^+].

Reaction of the Anion of (Benzyl methyl ether)tricarbonylchromium Complex 23 with Complexes 5, 5P$_1$, 5P$_2$. − Typical Procedure: 750 µl of *n*BuLi (1.2 mmol) was added at −40 °C to a solution of (benzyl methyl ether)tricarbonylchromium complex **23** (258.2 mg; 1.00 mmol) in THF (20 mL). After 1 h, this solution was transferred under nitrogen through a canula to a suspension of benzenetricarbonylchromiummanganese complex **5** (434.4 mg; 1.2 mmol) in 5 mL of THF. The mixture was extracted with water and diethyl ether. The organic phase was washed with brine, dried with $MgSO_4$ and concentrated to give an oil which was purified by chromatography on a silica gel (15 µ) column. Elution with a mixture of petroleum ether/diethyl ether (92:8) gave complex **25** (96.4 mg; 0.285 mmol, 29% yield); with a mixture of petroleum ether/diethyl ether (78:22), complex **24a** (193.5 mg; 0.408 mmol, 41% yield) was isolated.

Complex 24a: Yellow oil. − IR ($CHCl_3$): $\tilde{\nu}$ = 1940 cm^{-1} and 2010 (Mn−CO), 1895 and 1970 (Cr−CO). − ^1H NMR (200 MHz, $CDCl_3$): δ = 5.79 (t, J = 6.0 Hz, 1 H, H^3), 5.39 [m, 2 H, H^{10} and H^{12} (or H^9 and H^{13})], 5.23 (t, J = 6.3 Hz, 1 H, H^{11}), 5.11 [m, 2 H, H^9 and H^{13} (or H^{10} and H^{12})], 4.91 (m, 2 H, H^2 and H^4), 3.44 (s, 3 H, OMe), 3.30 (t, J = 6.0 Hz, 1 H, H^1 or H^5), 3.03 (s, 1 H, H^7), 2.83 (t, J = 6.0 Hz, 1 H, H^5 or H^1), 2.60 (m, 1 H, H^6). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 232.7 (Cr−CO), 222.2 (Mn−CO), 107.1 (C^8), 96.8 and 97.0 (C^2 and C^4), 90.7 (C^{11}), 89.8, 90.9, 93.1 and 94.1 (C^9, C^{10}, C^{12} and C^{13}), 87.0 (C^6), 80.4 (C^3), 59.9 (OMe), 56.7 (C^7), 51.7 and 54.6 (C^1 and C^5). − $C_{20}H_{15}CrMnO_7$ (474.27) calcd. C 50.65; H 3.19; found C 51.09, H 3.45.

Complex 25: Yellow oil. − IR ($CHCl_3$): $\tilde{\nu}$ = 1940 cm^{-1} and 2010 (CO). − ^1H NMR (200 MHz, $CDCl_3$): δ = from 7.08 to 7.37 (several m, H^9, H^{10}, H^{11}, H^{12} and H^{13}), 5.78 (tt, 1 H, H^3, J = 5.9 and 1.1 Hz), 4.89 [tt, 1 H, H^2 (or H^4), J = 5.9 and 1.1 Hz], 4.80 [tt, 1 H, H^4 (or H^2), J = 5.9 and 1.1 Hz], 3.48 [m, 1 H, H^1 (or H^5)], 3.05 (s, 3 H, OMe), 3.01 (d, 1 H, H^7, J = 8.7 Hz), 2.76 (m, 1 H, H^6), 2.52 [tt, 1 H, H^5 (or H^1), J = 5.9 and 1.1 Hz]. − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 222.8 (Mn−CO), 137.8 (C^8), 127.6 and 128.4 (C^9, C^{10}, C^{12} and C^{13}), 128.0 (C^{11}), 96.4 and 96.7 (C^2 and C^4), 90.5 (C^7), 80.0 (C^3), 56.7 (OMe), 52.5 and 56.8 (C^1 and C^5), 41.6 (C^6). − $C_{17}H_{15}MnO_4$ (338.21): calcd. C 60.37, H 4.47; found C 59.80, H 4.90.

Complex 24b: Same method as for **24a** (yield 55%), yellow oil. − IR ($CHCl_3$): $\tilde{\nu}$ = 1965 cm^{-1}, 1945, 1880 (CO). − ^1H NMR (400 MHz, $CDCl_3$): δ = 5.53 (t, J = 3.6 Hz, 1 H, H^3), 5.40 (m, 2 H, H^{10}, H^{12} or H^9, H^{13}), 5.26 (t, J = 6.6 Hz, 1 H, H^{11}), 5.18 (m, 2 H, H^9, H^{13} or H^{10}, H^{12}), 4.73 (m, 2 H, H^2 and H^4), 3.92 [m, 6 H, $P(OCH_2CH_3)$], 3.47 (s, 3 H, OCH_3), 3.04 (m, 1 H, H^5 or H^1), 2.62 (m, 2 H, H^6 and H^7), 2.54 (m, 1 H, H^1 or H^5), 1.27 [t, J = 7.0 Hz, 9 H, $P(OCH_2CH_3)$]. − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 233.1 (CO−Cr), 229.0 (d, J = 31.1 Hz, CO−Mn), 108.3 (C^8), 95.3 and 95.5 (C^2 and C^4), 93.6, 94.1, 91.1, 90.0 (C^9, C^{10}, C^{11}, C^{12}, C^{13}), 87.0 (C^6), 79.5 (C^3), 60.3 [$P(OCH_2CH_3)_3$], 59.8 (OCH_3), 48.5 and 51.4 (C^1 and C^5), 42.7 (C^7), 16.2 and 16.5 [$P(OCH_2CH_3)_3$]. − $C_{25}H_{30}CrMnO_9P$ (612.43): calcd. C 49.03, H 4.94; found C 48.81, H 4.85.

Complex 24c: Same method as for **24a** (yield 47%), yellow oil. − IR ($CHCl_3$): $\tilde{\nu}$ = 1950 cm^{-1}, 1850, 1810. − ^1H NMR (200 MHz, $CDCl_3$): δ = 5.33, 5.18 (2 m, 6 H, H^9, H^{10}, H^{11}, H^{12}, H^{13}, and H^3), 4.53 (m, 2 H, H^2 and H^4), 3.92 [m, 12 H, $P(OCH_2CH_3)$], 3.41 (s, 3 H, OCH_3), 2.61 (m, 1 H, H^5 or H^1), 2.51 (m, 1 H, H^6), 2.15 (m, 1 H, H^7), 2.05 (m, 1 H, H^1 or H^5), 1.20 [t, J = 7.0 Hz, 18 H, $P(OCH_2CH_3)$]. − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 233.4 (CO−Cr), 230.4 (m, CO−Mn), 109.6 (C^8), 93.2 and 93.7 (C^2 and C^4), 89.9, 91.0, 91.2, 93.9, 94.1 (C^9, C^{10}, C^{11}, C^{12}, C^{13}), 87.2 (C^6), 76.8 (C^3), 59.7 [$P(OCH_2CH_3)$ and OCH_3], 45.2 and 47.8 (C^1 and C^5), 42.3 (C^7), 16.4 [$P(OCH_2CH_3)_3$]. − $C_{30}H_{45}CrMnO_{11}P_2$ (750.58): calcd. C 48.01, H 6.04; found C 48.06, H 6.09.

Reaction of the Anion of (Benzyl methyl ether)tricarbonylchromium Complex 23 with Anisolemanganese Complexes 26a and 26b. − Typical Procedure: To a solution of complex **23** (258 mg, 1 mmol) in THF (20 mL) at −78° C was added *n*BuLi (1.2 mmol). After stirring for 1 h at −40°C, this solution was added through a canula to cationic complex **26a** (470 mg, 1.2 mmol), dissolved in freshly distilled THF (5 mL). The reaction mixture turned orange and was stirred at room temperature for 15 min, then treated with distilled water and Et_2O. After extraction, the organic phase was washed with brine and dried with $MgSO_4$. Concentration of the organic phase under a nitrogen flow gave a yellow oil which was separated by chromatography. Dinuclear complex **27a** (2 diastereoisomers in a 1:1 ratio) was isolated first by eluting with an Et_2O/petroleum ether (15:100) mixture (239 mg, 0.47 mmol, 47% yield). Then starting complex **23** (123 mg, 0.26 mmol, 26% yield) was obtained by eluting with an Et_2O/petroleum ether (20:100) mixture.

Complex 27a: Yellow oil. − IR ($CHCl_3$): $\tilde{\nu}$ = 2005 cm^{-1}, 1930 (CO−Mn), 1970, 1890 (CO−Cr). − ^1H NMR (200 MHz, $CDCl_3$): δ = 5.67 (m, 2 H, H^3), 5.38 (m, 4 H, H^9 and H^{13}), 5.20 (m, 4 H, H^{10} and H^{12}), 5.07 (t, *J* = 6.0 Hz, 2 H, H^{11}), 4.92 (m, 2 H, H^4), 3.51 and 3.49 (s, 6 H, OCH_3 at C_2), 3.44 (s, 6 H, OCH_3 at C^7), 4.19 (m, 4 H, H^1 or H^7), 2.72 (m, 8 H, H^1, H^5, H^6 and H^{11}). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 232.9 (CO−Cr), 222.2 (CO−Mn), 143.5 (C^2), 110.8 (C^8), 94.2 (C^9 and C^{13}), 93.3 and 93.7 (C^4) 93.0 (C^{11}) 90.9 (C^9, C^{13}, C^{10}, C^{12}), 90.0 (C^{10}, C^{12}), 87.0 and 87.3 (C^6), 67.9 and 68.5 (C^3), 59.9 (OCH_3 at C^7), 55.0 (C^7), 54.4 (OCH_3 at C_2), 52.4 (C^7), 45.1 (C^5), 38.3 and 40.0 (C^1). − $C_{21}H_{17}CrMnO_8$ (504.30): calcd. C 50.02, H 3.40; found C 50.09, H 3.35.

Complex 27b: Same procedure as for **27a**. Yield: 64% of **27b** (2 diastereoisomers in a 1:1 ratio), yellow oil. − IR ($CHCl_3$): $\tilde{\nu}$ = 1965 cm^{-1}, 1870 (CO−Cr), 1940, 1880 (CO−Mn). − ^1H NMR (400 MHz, $CDCl_3$): δ = 5.33 (m, 5 H, 2 H^3, 2 H^9 and 1 H^{13}), 5.13 (m, 7 H, 2 H^{10} 2 H^{11}, 2 H^{12}, and 1 H^{13}), 4.67 (m, 2 H, H^4), 3.85 [m, 12 H, $P(OCH_2CH_3)$], 3.39 (s, 6 H, OCH_3 at C^7), 3.38 (s, 3 H, OCH_3 at C^2), 3.37 (s, 3 H, OCH_3 at C^2: the other diast.), 3.04 (m, 1 H, H^1) 2.75 (m, 1 H, H^7), 2.65 (m, 2 H, H^5), 2.54 (m, 3 H, H^2 and H^6), 2.27 (m, 1 H, H^7), 1.27 [m, 18 H, $P(OCH_2CH_3)$]. − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 232.0 (CO−Cr), 223.3 and 230.4 (m, CO−Mn), 139.5 (C^2), 107.2 (C^8), 93.0 (C^9, C^{13}), 92.5 and 92.7 (C^4) 92.4 (C^{11}), 89.9 and 90.1 (C^9 and C^{13}), 88.8, 89.0 and 89.8 (C^{10} and C^{12}), 86.0 and 86.4 (C^6), 66.7 and 67.1 (C^3), 59.2 [$P(OCH_2CH_3)$], 58.7 (OCH_3 at C^7), 53.1 and 52.8 (OCH_3 at C^2), 48.1 and 50.9 (C^7), 43.8 and 43.9 (C^5), 34.4 and 36.6 (C^1), 15.2 [$P(OCH_2CH_3)$]. − ^{31}P NMR (162 MHz, $CDCl_3$): δ = 196.7, 198.0. − $C_{26}H_{32}MnCrO_{10}P$ (642.45): calcd. C 48.61, H 5.02; found C 48.66, H 5.16.

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