Inorganica Chimica Acta, 198–200 (1992) 533–541

Manganese(II)cyclopentadienide and cyclopentadienylmanganese-(biphenyl) as starting materials for the synthesis of carbonyl free organomanganese complexes

Klaus Jonas*, Claus-Christian Häselhoff, Richard Goddard and Carl Krüger
Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-4330 Mülheim an der Ruhr (FRG)

Abstract

The manganate(−II) $[Li(dme)]_2[Mn(cod)_2]$ (**1**) (DME = dimethoxyethane, COD = 1,5-cyclooctadiene) prepared by total reductive degradation of manganese(II)cyclopentadienide (Cp_2Mn) and structurally characterized by X-ray structure analysis is the first example of a homoleptic manganese olefin complex. Moreover, it expands the series of the bis(cyclooctadiene)transition metallates for which only examples with the 3d elements of Group VIIIB have existed until now. The manganese(I) compound CpMn(biphenyl) (**2**), which can be prepared in high yield from Cp_2Mn and lithium biphenylide, is an ideal starting material for the synthesis of new carbonyl free organomanganese compounds. Reactions of **2** with alkali metal naphthalenide or with alkali metals in the presence of 1,5-cyclooctadiene or phosphane lead to (η^6-biphenyl)manganates with manganese in the oxidation state −I. In contrast, reactions of **2** with alkali metals and ethene proceed with loss of both ring ligands. Depending on the reaction temperature either the manganaspirononane $[K(thf)_x][(C_4H_8)_2Mn]$ (**7a**) with manganese in the oxidation state +III is formed or the bis(ethene)manganacyclopentanes $[M_A(thf)_x]_2[(C_4H_8)Mn(C_2H_4)_2]$ (M_A = K (**8a**), Na (**8b**)) with manganese in the oxidation state 0 can be isolated. The crystal structure of $[Na(pmdeta)]_2[(C_4H_8)Mn(C_2H_4)_2]$ (**8c**), which is obtained from **8b** and PMDETA (pentamethyldiethenetriamine), has been determined. One-electron oxidation of the bis(ethene)manganacyclopentane **8a** affords the manganaspironane **7a**. Thus the ring closure of the two coordinated ethene molecules with the manganese atom is oxidatively induced.

Introduction

In the past we have been able to show with a large number of examples that the metallocenes Cp_2M_T (M_T = V, Cr, Fe, Co, Ni) are ideal starting materials for the synthesis of reactive and in many cases novel compounds that have even now not been prepared in any other way. The synthetic principle leading to these compounds comprises the removal of one or both five-membered ring ligands. This can be achieved in most cases even at low temperatures by reaction of Cp_2M_T with alkali metal in the presence of a complexing agent (e.g. olefin, phosphane, dinitrogen) or by reaction with alkali metal naphthalenide [1].

All our attempts to prepare organomanganese compounds by applying these procedures to Cp_2Mn, which in contrast to the 'real' metallocenes can be considered as being mainly ionic, have been unsuccessful. However, using a further variation of the reductive five-membered ring abstraction we succeeded in the synthesis of new organomanganese complexes. This modification involves reacting Cp_2M_T not solely with alkali metal naphthalenide, but in the presence of an additional complexing agent. The reaction of Cp_2Mn in THF with PMe_3 and lithium naphthalenide affords the manganate(−I) $[Li(thf)_x][(\eta^4\text{-naphthalene})Mn(PMe_3)_3]$ which on treatment with TMEDA (tetramethylethenediamine) gives $[Li(tmeda)_2][(\eta^4\text{-naphthalene})Mn(PMe_3)_3]$. If PMe_3 is replaced by ethene and utilizing potassium naphthalenide, subsequent addition of pyridine results in the formation of $[K(pyridine)_2][(C_4H_8)_2Mn(pyridine)]$. This manganate(III) is the first example of a metallaspironane having a $(C_4H_8)_2M_T$ framework that originates from the coupling of a metal atom with four ethene molecules [2].

In this paper we wish to report further examples of how Cp_2Mn can be used as a synthetic starting material. Of major importance is the high yield synthesis of CpMn(biphenyl) from Cp_2Mn and lithium biphenylide since this sandwich compound can be partially or totally degraded under mild conditions leading to a large number of carbonyl free organomanganese compounds.

---

*Author to whom correspondence should be addressed.

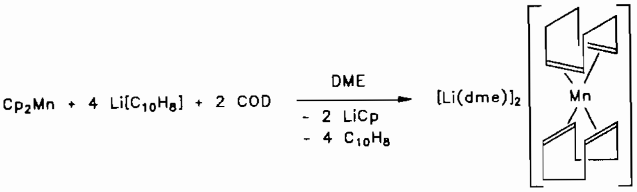
0020-1693/92/$5.00

Results and discussion

[Li(dme)]$_2$[Mn(cod)$_2$] – the first example of a homoleptic olefin manganate

Following the syntheses of the alkali metal–transition metal complexes $[Li(dme)]_2[Fe(cod)_2]$, $[Li(thf)_2][Co(cod)_2]$ and $[Li(thf)_2]_2[Ni(\eta^4\text{-cod})(\eta^2\text{-cod})]$ [3], we were interested to know whether the series of bis(cyclooctadiene)transition metallates could be extended to a bis(cyclooctadiene)manganate. Recently we succeeded in preparing $[Li(dme)_2][Mn(cod)_2]$ (**1**), the structure of which has been determined by X-ray analysis.

The novel manganate **1** is synthesized by reacting Cp_2Mn with 4 equiv. of lithium naphthalenide in the presence of 1,5-cyclooctadiene (Scheme 1). Dimethoxyethane proved to be the most suitable solvent since **1** is only slightly soluble even at room temperature and precipitates in pure form immediately as soon as it is formed. It is worthy of note that the yield of **1** increases from 30 to 60% when lithium 2-methylnaphthalenide is used as the reducing agent instead of lithium naphthalenide.



1

Scheme 1. Synthesis of $[Li(dme)]_2[Mn(cod)_2]$ (1) by total degradation of manganese(II)cyclopentadienide.

Whereas $[Li(dme)]_2[Fe(cod)_2]$, $[Li(thf)_2][Co(cod)_2]$ and $[Li(thf)_2]_2[Ni(\eta^4\text{-cod})(\eta^2\text{-cod})]$ are diamagnetic 18e complexes the new manganate **1** is a paramagnetic 17e complex. **1** is also the first example of a manganate with manganese in the oxidation state –II. Before this compound was prepared the only homoleptic manganates with manganese in a negative oxidation state were the carbonyl complexes $Na[Mn(CO)_5]$ [4] and $Na_3[Mn(CO)_4]$ [5].

The results of the crystal structure analysis of **1** are summarized in Fig. 1. The central manganese atom is bonded to two cyclooctadiene ligands which are twisted relative to one another by 41.6°. The manganese atom forms two short (Mn–C2 = Mn–C2* = 2.063(3) Å and Mn–C6 = Mn–C6* = 2.065(3) Å) and two long (Mn–C1 = Mn–C1* = 2.120(2) Å and Mn–C5 = Mn–C5* = 2.123(2) Å) manganese carbon atom bonds. The transition metal sits directly on the midpoint of the line joining the two lithium atoms. Each lithium atom bears a DME molecule and is bonded to those carbon atoms of the COD ligands that have the longer bonds to the manganese atom. It is noticeable that the bond lengths differ very little from those found for the lithium cobaltate $[Li(thf)_2][Co(cod)_2]$ [6].

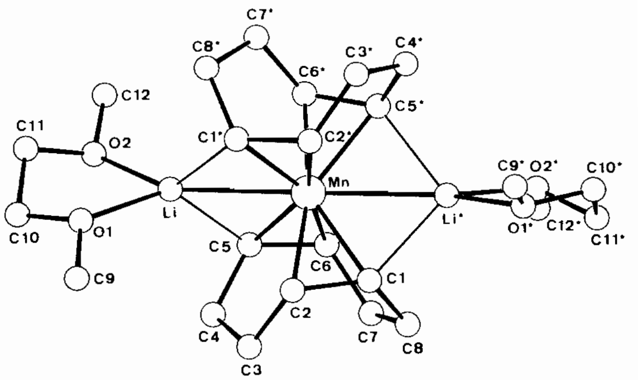
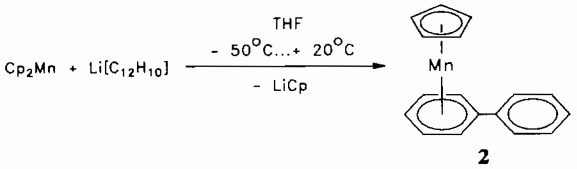


Fig. 1. Crystal structure of $[Li(dme)]_2[Mn(cod)_2]$ (1). Selected distances (Å) and angles (°): Mn–Li 2.574(5), Mn–C(1) 2.120(3), Mn–C(2) 2.063(3), Mn–C(5) 2.123(2), Mn–C(6) 2.065(3), Li–O(1) 2.036(5), Li–O(2) 2.045(5), C(1)–C(2) 1.453(4), C(5)–C(6) 1.451(4), Mn–D(1) 1.962, Mn–D(2) 1.964; D(1)–Mn–D(2) 87.1, C(2)–Mn–C(6)* 169.8(1), C(6)–Mn–C(1)* 149.5(1), C(5)–Li–C(1)* 104.0(2) (D(1): midpoint C(1)–C(2), D(2): midpoint C(5)–C(6)).

Synthesis of cyclopentadienylmanganese(biphenyl) by partial degradation of manganese(II)cyclopentadienide with lithium biphenylide

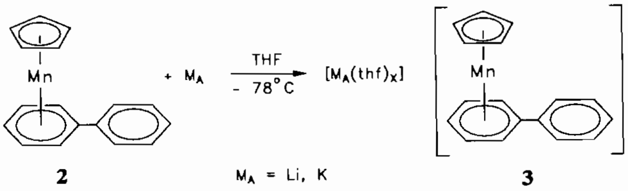
Reactions of Cp_2V, Cp_2Cr and Cp_2Fe with 2 equiv. of alkali metal naphthalenide proceed with exchange of one five-membered ring ligand by a naphthalene ligand to form the ate complexes $M_A[CpM_T(\text{naphthalene})]$ (M_A = Li or K; M_T = V, Cr, Fe). On treatment with dichloroethane or methanol the ate complexes K[CpV(naphthalene)] and Li[CpCr(naphthalene)] form the neutral sandwich complexes CpV(naphthalene) and CpCr(naphthalene), both of which have easily displaceable naphthalene ligands [1, 7]. These findings stimulated us to attempt the synthesis of CpMn(naphthalene) from Cp_2Mn and alkali metal naphthalenide. Unfortunately, all efforts to prepare this unknown sandwich complex or related complexes from Cp_2Mn and alkali metal arene compounds of other benzoannelated arenes (phenanthrene or anthracene) failed [8, 9]. Cp_2Mn reacts, however, with alkali metal compounds of non-benzoannelated arenes with loss of one cyclopentadienyl ligand to give the complexes CpMn(biphenyl) (**2**), CpMn(*p*-terphenyl) (two isomers) and CpMn(9,10-dihydrophenanthrene). The synthesis of these three sandwich complexes demonstrates that the reductive partial degradation of Cp_2Mn can also be utilized preparatively [9].

The sandwich compound **2**, which has been known for over 25 years [10], can now be prepared according to Scheme 2 in high yields (80%).



Scheme 2. The synthesis of CpMn(biphenyl) (**2**) from manganese(II)cyclopentadienide and lithium biphenylide.

The properties of CpMn(biphenyl) and its parent compound CpMn(benzene) [10] resemble those of the structurally related ferrocene. All three compounds are exceptionally thermally stable 18e sandwich complexes (destillable or sublimable), which are not hydrolyzed and are only slightly or not at all air sensitive. Even in its redox behaviour CpMn(biphenyl) shows certain similarities with ferrocene. The reversible one-electron reduction of ferrocene has been shown electrochemically ($E_0 = -2.93$ V) by Mugnier *et al.* [11a] and Sajo and co-workers [11b]. Recently, we have been able to demonstrate that CpMn(biphenyl) can be converted to the thermally labile monoanion $[CpMn(biphenyl)]^-$ by reduction with alkali metal (Scheme 3).



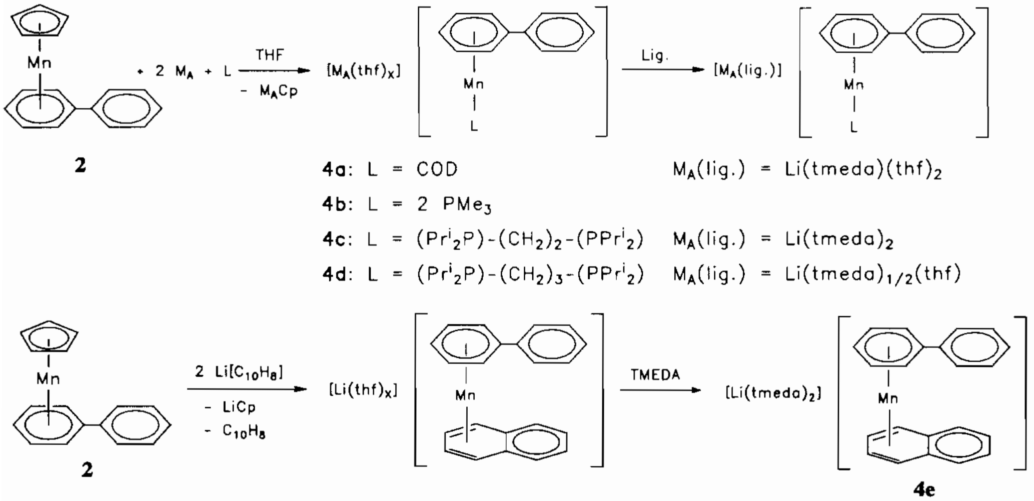
Scheme 3. Reduction of CpMn(biphenyl) with alkali metal.

Evidence that orange CpMn(biphenyl) reacts with alkali metal in the ratio of 1:1 was obtained gravimetrically using potassium as the reducing agent. The potential of the redox pair CpMn(biphenyl)/$[CpMn(biphenyl)]^-$ probably lies at a more negative value than that of biphenyl/$[biphenyl]^-$ ($E_0 = -2.7$ V [12], $[biphenyl]^-$ is dark blue). This is supported by the observation that a violet solution of **3** immediately becomes dark blue on addition of biphenyl. In accordance with this we have found that sodium, which is known to be the weakest reducing agent amongst the alkali metals, does not react with CpMn(biphenyl) whereas it does reduce biphenyl (see later, however, the reaction of **2** with sodium and ethene). Due to the high thermal lability of $[CpMn(biphenyl)]^-$ the exact determination of the redox potential by electrochemical methods failed. An irreversible reduction step was observed at −10 °C ($E_0 = -2.8$ V).

Organomanganese complexes from CpMn(biphenyl) by reductive five-membered ring abstraction

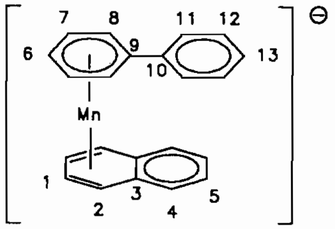
The behaviour of CpMn(biphenyl) towards alkali metals as well as the fact that the fragments (η^5-Cp)Fe and (η^6-arene)Mn and consequently $[(\eta^5\text{-Cp})Fe]^-$ and $[(\eta^6\text{-arene})Mn]^-$ are isolobal caused us to examine whether CpMn(biphenyl) could be used for the synthesis of manganates corresponding to the well-known ferrates [Li(tmeda)][CpFe(cod)], $[Li(tmeda)][CpFe(C_2H_4)_2]$[3] and $[Li(thf)_2]$[CpFe(naphthalene)] [1], which are themselves obtained by partial degradation of ferrocene. Furthermore, it seemed to be promising to use phosphanes as complexing agents. It was expected that this would result in the first preparation of manganates of the type $M_A[(arene)Mn(PR_3)_2]$. Scheme 4 summarizes the (η^6-biphenyl)manganates(−I) prepared by partial degradation of CpMn(biphenyl).

The coordination mode of the biphenyl and the naphthalene ligand in $[Li(tmeda)_2][(\eta^6\text{-biphenyl})Mn(\eta^4\text{-naphthalene})]$ (**4e**) can be clearly inferred from the ^{13}C NMR spectrum (d^8-THF). The spectrum shows a total of thirteen signals for both the arene ligands, eight for the η^6-bonded biphenyl ligand and five for the η^4-bonded naphthalene (Table 1).

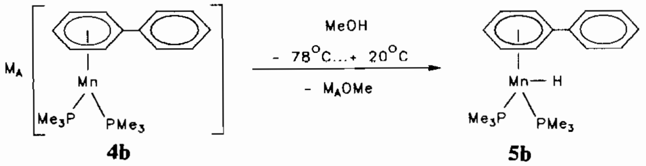


Scheme 4. (η^6-Biphenyl)manganates(−I) starting from CpMn(biphenyl).

TABLE 1. Chemical shifts of the free arenes (δ_F) [13] and complexed arenes (δ_C) in **4e** together with the corresponding complexation shifts ($\delta_F - \delta_C$)



Atom	δ_F	δ_C	$\delta_F - \delta_C$
Naphthalene			
1	125.6	72.5	53.1
2	127.7	49.4	77.8
3	133.3	155.6	−22.3
4	127.7	118.6	9.1
5	125.6	114.9	10.7
Biphenyl			
6	127.5	72.7	54.8
7	129.0	75.4	53.6
8	127.4	74.2	53.2
9	141.5	79.3	62.2
10	141.5	148.6	−7.1
11	127.4	126.7	0.7
12	129.0	127.8	1.2
13	127.5	122.6	4.9

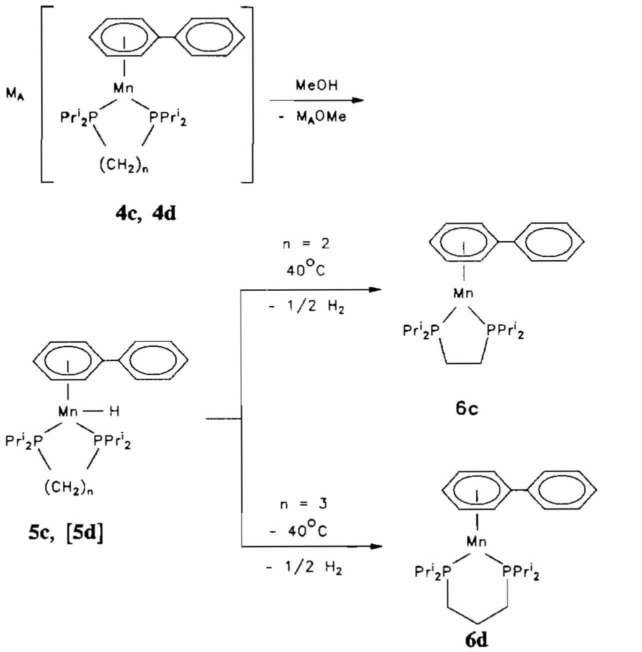


Scheme 5. Methanolysis of **4b**.

A shift of the NMR signal to lower field is characteristic for the bridging carbon atoms of a η^4-bonded naphthalene ligand [14]. This is also observed for the new manganese compound **4e** ($\delta_F - \delta_C = -22.3$ ppm). In contrast, the signals of the naphthalene carbon atoms bonded to the manganese atom exhibit a strong high field shift. The complexation shifts are 53.1 and 77.8 ppm. For the lithium iron compound $[Li(thf)_2][CpFe(\eta^4$-naphthalene)] we observed 53.7 and 88.1 ppm [15].

The manganates(−I) with phosphane ligands, **4b**, **c** and **d**, are suitable starting materials for the synthesis of new hydridomanganese(I) compounds and new manganese(0) compounds. Reaction of **4b** with methanol (Scheme 5) gives the hydridomanganese(I) compound (biphenyl)Mn(H)$(PMe_3)_2$ (**5b**) (ν(Mn–H) = 1930 cm^{-1}, KBr). The parent compound (benzene)Mn(H)$(PMe_3)_2$ is already known. Green *et al.* have prepared it in 2% yield by metal vapourization [16].

In attempting to convert the manganates **4c** and **4d** into the corresponding hydridomanganese compounds by methanolysis the following results were obtained (Scheme 6). Whereas **4d** reacts even at low temperatures with the formation of a manganese(0) compound (**6d**) and evolution of hydrogen, the hydridomanganese compound **5c** (ν(Mn–H) = 1830 cm^{-1}, KBr), in which manganese, the phosphorus atoms and the methylene groups form a five-membered ring, is considerably more thermally stable than **5d**. **5c** is converted to the manganese(0) complex **6c** only above 40 °C. Treatment of **4c** with MeOD gives the expected deuteridomanganese compound (η^6-biphenyl)Mn(D)$(Pr^i_2PCH_2CH_2PPr^i_2)$ (ν(Mn–D) = 1320 cm^{-1}, KBr).

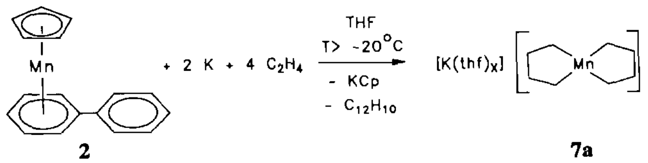


Scheme 6. Hydridomanganese(I) and manganese(0) compounds starting from **4c**, **d**.

The CpMn(biphenyl)/alkali metal/ethene system

Reactions of CpMn(biphenyl) with alkali metals and ethene are distinctly different from the degradation reactions described in the previous section. In the presence of ethene not only the five-membered but also the six-membered ring ligand is lost. An ethene saturated solution of CpMn(biphenyl) in THF takes up four mole equivalents of ethene at −20 °C when stirred with potassium if at least 2K/Mn are used (Scheme 7). If one employs more potassium, the excess is consumed for the reduction of the liberated biphenyl. Work-up results in the isolation of a manganese compound (**7a**), which is a yellow oil stable at room temperature. Methanolysis of **7a** yields exclusively C_4-hydrocarbons (n-butane together with very little 1-butene).

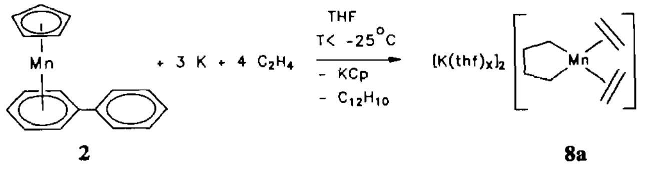
The conversion of $[K(thf)_x][(C_4H_8)_2Mn]$ (**7a**) into crystalline manganates results from its reaction with



Scheme 7. Synthesis of the manganaspironane $[K(thf)_x][(C_4H_8)_2Mn]$ (**7a**) starting from CpMn(biphenyl).

pyridine or triglyme (TG). In the former case the spiro compound $[K(pyridine)_2][(C_4H_8)_2Mn(pyridine)]$ (**7b**) is formed in high yield. Its crystal structure is already known [2]. **7a** and triglyme give crystalline $[K(tg)_2][(C_4H_8)_2Mn]$ (**7c**). Both manganates(III) react with methanol to give exactly two mole equivalents of the C_4-hydrocarbons.

It is also possible to synthesize a manganate with manganese in the oxidation state 0 from the same starting materials that were used for the synthesis of the spiro compound **7a**. All that is required is to lower the reaction temperature. Below −25 °C it is necessary to use one additional mole equivalent of potassium to ensure that all of the CpMn(biphenyl) is consumed. Products of this reaction are KCp, biphenyl and $[K(thf)_x]_2[(C_4H_8)Mn(C_2H_4)_2]$ (**8a**) (Scheme 8). If less than three mole equivalents of potassium are used, **8a** is also obtained but in correspondingly lower yields. The analogous disodium manganate $[Na(thf)_x]_2[(C_4H_8)Mn(C_2H_4)_2]$ (**8b**) is formed if sodium is used instead of potassium under identical conditions. Both compounds are stable at room temperature and form red crystals which on drying in vacuum effloresce owing to loss of THF even at low temperatures. However, **8b** can be converted into $[Na(pmdeta)]_2[(C_4H_8)Mn(C_2H_4)_2]$ (**8c**) by reacting it with PMDETA. The manganate **8c** is not changed during drying. The evidence that **8a**, **b** and **c** are manganates with a single butanediyl ligand and two coordinated ethene molecules came from protolysis and the crystal structure of **8c**. The three manganates(0) **8** give, in contrast to the spiro compounds **7**, ethene and ethane in addition to n-butane on treatment with methanol. The molar ratio of these hydrocarbons is in all cases almost exactly 1:1:1. For the disodium compound **8c** it could also be shown that the three hydrocarbons are obtained in the calculated amounts.



Scheme 8. Synthesis of the bis(ethene)manganacyclopentane $[K(thf)_x]_2[(C_4H_8)Mn(C_2H_4)_2]$ (**8a**) starting from CpMn(biphenyl).

The results of the crystal structure analysis of **8c** are summarized in Fig. 2. The compound is a trinuclear complex with two Na(pmdeta) groups attached to a central $Mn(C_4H_8)(C_2H_4)_2$ fragment. The distances between the manganese atom and the carbon atoms of the metallacycle attached to the metal (C5 and C8) are at 2.120(4) and 2.142(4) Å, respectively, slightly longer than those between the manganese atom and the carbon atoms of the two ethene ligands (Mn–C1 = 2.098(4), Mn–C2 = 2.099(4), Mn–C3 = 2.102(3) and Mn–C(4) = 2.089(3) Å). The carbon atoms C1, C2, C3, C4, C5 and C8 are bonded simultaneously to the manganese atom and one of the sodium atoms (Na1–C1 = 2.791(4), Na1–C3 = 2.654(3), Na1–C5 = 2.797(4), Na2–C2 = 2.832(4), Na2–C4 = 2.707(4), Na2–C8 = 2.724(4) Å). The sodium atoms are approximately octahedrally coordinated. One of the triamine ligands is disordered.

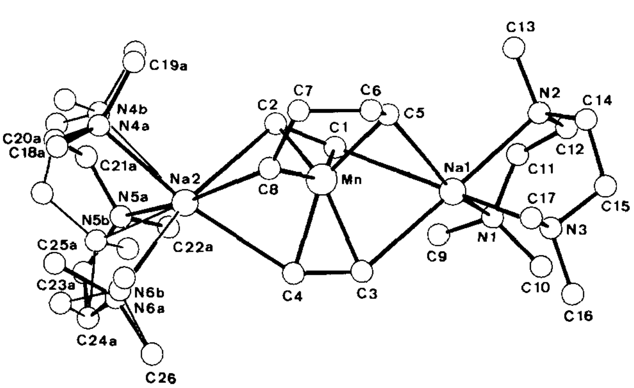
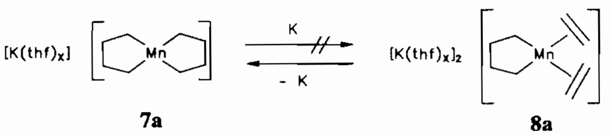


Fig. 2. Crystal structure of $[Na(pmdeta)]_2[(C_4H_8)Mn(C_2H_4)_2]$ (**8c**). Selected distances (Å) and angles (°): Mn–C(1) 2.098(4), Mn–C(2) 2.099(4), Mn–C(3) 2.102(3), Mn–C(4) 2.089(3), Mn–C(5) 2.120(4), Mn–C(8) 2.141(4), Mn–D(1) 1.975, Mn–D(2) 1.968, Mn...Na(1) 2.896(1), Mn...Na(2) 2.888(1), D(1)–Mn–D(2) 110.6 (D(1): midpoint C(1)–C(2), D(2): midpoint C(3)–C(4)).

The oxidatively induced ring closure of two π-bonded ethene molecules and a manganese atom

The observation that CpMn(biphenyl) at temperatures above −20 °C in the presence of ethene gives the spiromanganate(III) **7a** and not the dipotassium manganate(0) **8a** even with an excess of potassium (K:Mn > 2:1) suggested to us that the spiro compound does not react with potassium. An independent experiment in which a solution of $[K(tg)_2][(C_4H_8)_2Mn]$ (**7c**) in THF was stirred with potassium confirmed this.

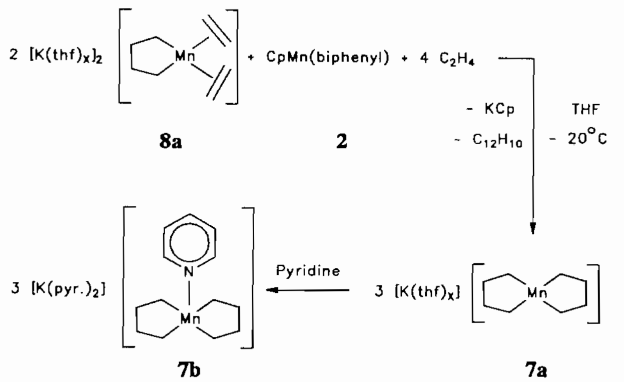
As **7a** does not react with potassium, $[K(thf)_x][(C_4H_8)_2Mn]$ (**7a**) cannot be the precursor of the dipotassium manganate(0) $[K(thf)_x]_2[(C_4H_8)Mn(C_2H_4)_2]$ (**8a**). If, however, **8a** is the precursor of **7a** then it must be possible to transform **8a** into the spiro compound **7a** by one-electron oxidation.



Scheme 9. The inertness of **7a** towards potassium and the conversion of **8a** to **7a** by removal of potassium.

At this point it is worth mentioning an observation that indicates the strong reductive ability of **8a**. The dark red solution of **8a** in THF becomes dark blue at −10 °C if biphenyl is added. The colour change is most probably caused by the formation of K[biphenyl]. Whether this oxidation induces ring closure is not known.

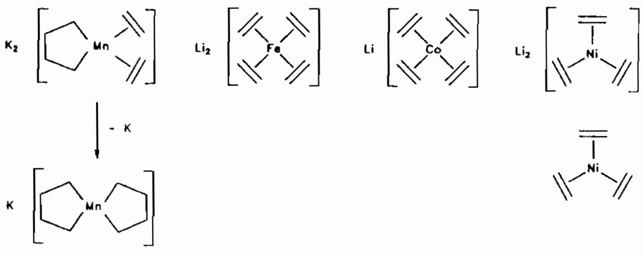
We then substituted biphenyl by the sandwich complex CpMn(biphenyl) as the potassium consuming compound because we knew that it reacts with potassium and ethene to give the spiro compound **7a** according to Scheme 7. Thus the strategy was to combine the one-electron oxidation of **8a** with the degradation of CpMn(biphenyl), which in the presence of ethene requires two mole equivalents of potassium.



Scheme 10. Synthesis of **7a** from **8a**, **2** and ethene, and the conversion of **7a** to **7b** with pyridine.

The high yield (93%) with which the spiro compound [K(pyridine)$_2$][(C$_4$H$_8$)$_2$Mn(pyridine)] (**7b**) can be prepared according to Scheme 10 leaves no doubt that the ring closure of the two π-bonded ethene molecules with the manganese atom leading to the spiro compound **7a** is oxidatively induced. The manganese atom changes its oxidation state by three during the entire process (see also Scheme 9). The actual ring closure proceeds with an increase of the oxidation state of the manganese atom by two. This step is induced by a one-electron oxidation. As was shown in a separate experiment, the oxidation using CpMn(biphenyl) in the presence of ethene does not take place below −25 °C.

In order to put the results described in the last two sections into a wider context the 3d transition metal complexes whose hydrocarbon ligands are exclusively derived from ethene [1–3, 17] are summarized in Scheme 11 (for clarity, the n-donor ligands bonded to the alkali metal atoms are omitted). The difference between the behaviour of low-valent manganese towards ethene and that of iron, cobalt and nickel is conspicuous. Whereas the 3d transition metals of Group VIIIB form homoleptic ethene π-complexes, manganese tends to form (C$_4$H$_8$)Mn rings.



Scheme 11. Are homoleptic 3d transition metal ethene complexes restricted to Group VIIIB?

Experimental

All reactions were carried out under oxygen-free argon using Schlenk-tube techniques. Solvents were dried rigorously before use. The ^{13}C NMR spectrum of **4e** was measured with a Bruker AC 200. IR spectra were recorded with a Nicolet-FT-IR 7199 in a KBr mull (4000–460 cm^{-1}). The mass spectra were measured with a Finnigan MAT 311A spectrometer at 70 eV. The composition of the mixtures of gases were determined by regression analysis of the mass spectrometric data (Finnigan MAT CH7A). Elemental analyses were performed by the microanalytical laboratory Dornis and Kolbe, Mülheim/Ruhr. Cp$_2$Mn was prepared according to Wilkinson *et al.* [18]. It was further purified by recrystallizing the sublimed product from hot toluene.

Synthesis of [Li(dme)]$_2$[Mn(cod)$_2$] (1)

A DME solution of lithium 2-methylnaphthalenide, prepared from 11.64 g (81.86 mmol) of 2-methylnaphthalene, 0.716 g (102.19 mmol) of lithium and 200 ml of DME at −20 °C, was treated at −50 °C with 40 ml of 1,5-cyclooctadiene and 4.74 g (25.60 mmol) of Cp$_2$Mn. The solution was allowed to reach −20 °C and stirred for a further 2 h at this temperature. The green precipitate was filtered off and washed at room temperature with DME and Et$_2$O. The precipitate was subsequently dissolved in THF at room temperature. The solution was filtered to remove the small amount of remaining insoluble solids, and 20–30 ml of DME was added. On cooling to −30 °C **1** crystallized out. The mother liquor was removed by filtration and **1** was washed with Et$_2$O and dried at room temperature at reduced pressure. Yield 6.55 g (55%).

Anal. Calc. for C$_{24}$H$_{44}$Li$_2$MnO$_4$ (**1**): Li, 2.98; Mn, 11.80. Found: Li, 2.88; Mn, 11.88%.

TABLE 2. Crystal data and details of data collection for **1** and **8c**

	1	**8c**
Formula	$C_{24}H_{44}Li_2MnO_4$	$C_{26}H_{62}MnN_6Na_2$
M_r	465.4	559.7
Space group	*Pccn* (No. 56)	$P2_1/a$ (No. 14)
a (Å)	9.934(2)	16.129(5)
b (Å)	19.517(3)	13.967(3)
c (Å)	12.646(2)	16.763(3)
α (°)	90.0	90.0
β (°)	90.0	116.78(1)
γ (°)	90.0	90.0
V (Å^3)	2451.7	3371.5
T (°C)	−173	−173
D_{calc} (g cm^{-3})	1.26	1.10
μ(cm^{-1})	5.41	4.22
Z	4	4
λ (Å)	0.71069	0.71069
Measured reflections	6010 ($\pm h$, $+k$, $+l$)	8288 ($\pm h$, $+k$, $+l$)
$[(\sin\theta)/\lambda]_{max}$ (Å^{-1})	0.65	0.65
Independent reflections	2789	7681
Observed reflections ($I > 2\sigma(I)$)	2306	6326
Refined parameters	229	406
R	0.049	0.066
R_w ($w = 1/\sigma^2(F_o)$)	0.056	0.088
Residual electron density (e Å^{-3})	0.36	0.98
		50:50 disordered PMDETA

TABLE 3. Atomic coordinates and isotropic thermal parameters (Å^2) of **1**

Atom	x	y	z	U_{eq}^{a}
Mn	0.2500	0.7500	0.0830(1)	0.011(1)
Li	0.0648(5)	0.6578(2)	0.0812(4)	0.021(2)
O(1)	−0.0296(2)	0.5934(1)	0.1838(1)	0.021(1)
O(2)	−0.0633(2)	0.6111(1)	−0.0229(1)	0.019(1)
C(1)	0.4341(3)	0.7441(1)	0.1672(2)	0.014(1)
C(2)	0.3409(3)	0.6900(1)	0.1967(2)	0.014(1)
C(3)	0.3661(3)	0.6148(1)	0.1698(2)	0.018(1)
C(4)	0.2959(3)	0.5933(1)	0.0663(2)	0.017(1)
C(5)	0.2608(3)	0.6560(1)	−0.0009(2)	0.015(1)
C(6)	0.3676(3)	0.7029(1)	−0.0304(2)	0.014(1)
C(7)	0.5145(3)	0.6892(1)	−0.0024(2)	0.016(1)
C(8)	0.5573(3)	0.7259(1)	0.1007(2)	0.016(1)
C(9)	0.0261(4)	0.5669(2)	0.2794(3)	0.028(2)
C(10)	−0.1095(3)	0.5441(1)	0.1289(2)	0.022(1)
C(11)	−0.1708(3)	0.5799(1)	0.0356(2)	0.021(1)
C(12)	−0.1106(3)	0.6428(2)	−0.1183(3)	0.026(2)

$^aU_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

Synthesis of CpMn($C_{12}H_{10}$) (2)

A THF solution of lithium biphenylide, prepared from 180 g (1167.21 mmol) of biphenyl, 7.92 g (1141.38 mmol) of lithium and 2 l of THF at 0 °C (stirring *c.* 12 h), was treated at −50 °C with 196.8 g (1063.04 mmol) of Cp_2Mn. The mixture was stirred for 2 h at −50 °C and the red solution was allowed to reach room temperature. After removal of the solvent at reduced pressure the residue was taken up with toluene and the LiCp was filtered off. The toluene was distilled off at reduced pressure and biphenyl was removed in high vacuum at 90 °C. **2** was then distilled in high vacuum at 150 °C. The distillate was dissolved in *c.* 1 l of boiling hexane. **2** appeared as red crystals at −30 °C. After removal of the mother liquor by filtration the crystals were dried at reduced pressure at room temperature. Yield 214.85 g (74%).

Mass spectrum: Calc. for $C_{17}H_{15}Mn$ (**2**): 274. Found: 274.

Synthesis of [Li(tmeda)$_2$][(η^6-$C_{12}H_{10}$)Mn(η^4-$C_{10}H_8$)] (4e)

A THF solution of lithium naphthalenide, prepared from 11 g (85.82 mmol) of naphthalene, 0.5 g (72.06 mmol) of lithium and 200 ml of THF at -20 °C, was treated with 9.2 g (33.55 mmol) of **2** at the same temperature. The reaction mixture was warmed to room temperature after 12 h and allowed to stand for a further 2 h. The solvent was distilled off. Liberated naphthalene was removed in high vacuum at room temperature. The residue was taken up in a 1:3 mixture of THF/Et_2O. After removal of the LiCp by filtration, the filtrate was evaporated to dryness and the residue dissolved in a mixture of 200 ml of Et_2O and 20 ml of TMEDA. A dark red oil formed, which changed to finely crystalline black **4e** on standing at 0 °C for a long period. Yield 17.13 g (89%).

TABLE 4. Atomic coordinates and isotropic thermal parameters (Å^2) of **8c**

Atom	x	y	z	U_{eq}^{a}
Mn	0.2532(1)	0.0345(1)	0.7521(1)	0.024(1)
Na(1)	0.2665(1)	−0.0972(1)	0.6250(1)	0.030(1)
Na(2)	0.3087(1)	0.2023(1)	0.8647(1)	0.031(1)
N(1)	0.4046(2)	−0.1271(2)	0.5900(2)	0.034(2)
N(2)	0.2816(2)	−0.2732(2)	0.6231(2)	0.033(2)
N(3)	0.1348(2)	−0.1530(2)	0.4789(2)	0.034(2)
C(1)	0.3855(3)	−0.0252(3)	0.7935(3)	0.052(3)
C(2)	0.3791(3)	0.0159(3)	0.8678(3)	0.054(3)
C(3)	0.2288(2)	0.0876(2)	0.6261(2)	0.031(2)
C(4)	0.2697(3)	0.1606(2)	0.6937(2)	0.042(3)
C(5)	0.1837(3)	−0.0975(2)	0.7400(2)	0.041(3)
C(6)	0.0923(2)	−0.0746(2)	0.7435(2)	0.040(2)
C(7)	0.1067(2)	0.0038(3)	0.8108(2)	0.041(2)
C(8)	0.1541(2)	0.0902(2)	0.7923(2)	0.040(2)
C(9)	0.4802(3)	−0.0579(3)	0.6361(3)	0.061(3)
C(10)	0.3863(3)	−0.1272(3)	0.4964(3)	0.052(3)
C(11)	0.4328(3)	−0.2213(3)	0.6304(2)	0.046(2)
C(12)	0.3557(2)	−0.2949(2)	0.5973(2)	0.039(2)
C(13)	0.3062(3)	−0.3150(3)	0.7107(3)	0.056(3)
C(14)	0.1910(2)	−0.3092(2)	0.5583(3)	0.044(3)
C(15)	0.1497(2)	−0.2572(2)	0.4708(2)	0.043(2)
C(16)	0.1238(3)	−0.1079(3)	0.3960(3)	0.051(3)
C(17)	0.0544(3)	−0.1346(3)	0.4916(3)	0.063(4)
N(4a)	0.3431(9)	0.217(2)	1.019(1)	0.10(1)
N(4b)	0.3655(6)	0.1992(7)	1.0361(7)	0.023(5)
N(5a)	0.4701(6)	0.2722(6)	0.9394(4)	0.054(5)
N(5b)	0.4338(6)	0.334(1)	0.9308(5)	0.10(1)
N(6a)	0.270(1)	0.3797(7)	0.8328(6)	0.08(1)
N(6b)	0.2211(7)	0.371(1)	0.8289(9)	0.10(1)
C(18a)	0.282(1)	0.286(2)	1.030(2)	0.27(4)
C(18b)	0.2957(8)	0.2304(9)	1.0661(6)	0.053(7)
C(19a)	0.353(2)	0.115(2)	1.050(1)	0.19(3)
C(19b)	0.3816(8)	0.0964(7)	1.0620(8)	0.042(6)
C(20a)	0.446(2)	0.268(2)	1.064(1)	0.09(1)
C(20b)	0.448(1)	0.249(1)	1.079(1)	0.048(9)
C(21a)	0.5092(4)	0.2451(6)	1.0321(4)	0.040(4)
C(21b)	0.4587(7)	0.3337(8)	1.0298(7)	0.077(8)
C(22a)	0.521(1)	0.238(2)	0.8942(8)	0.15(2)
C(22b)	0.5055(8)	0.304(1)	0.9132(9)	0.08(1)
C(23a)	0.466(3)	0.379(2)	0.923(1)	0.29(4)
C(24a)	0.3779(6)	0.4208(5)	0.8602(8)	0.061(8)
C(24b)	0.2918(9)	0.4438(7)	0.8813(9)	0.09(1)
C(25a)	0.255(1)	0.414(1)	0.917(1)	0.15(2)
C(25b)	0.1394(7)	0.362(1)	0.8203(9)	0.11(1)
C(26)	0.2048(5)	0.4044(4)	0.7355(5)	0.104(6)

$^a U_{eq} = \frac{1}{3}\Sigma_i \Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

Anal. Calc. for $C_{34}H_{50}LiMnN_4$ (**4e**): Li, 1.20; Mn, 9.53; N, 9.72. Found : Li, 1.25; Mn, 9.61; N, 9.52%.

Synthesis of [Na(pmdeta)]$_2$[(C$_4$H$_8$)Mn(C$_2$H$_4$)$_2$] (8c)

A solution of 10.93 g (39.86 mmol) of CpMn(biphenyl) in 200 ml of THF saturated with ethene at −30 °C was stirred with 2.86 g (119.62 mmol) of sodium pellets in an ethene atmosphere. Within 16 h 3.6 mol equiv. of ethene/Mn were taken up (90% of the theoretical amount). On cooling the reaction mixture to −78 °C a red finely crystalline precipitate was formed. **8c** was filtered off and washed at −78 °C with THF and then with Et_2O at room temperature. The deposit on the scintillation filter was taken up in *c.* 100 ml of THF and the solution filtered. 50 ml of Et_2O and 50 ml of PMDETA were added to the filtrate and the solution was cooled to −30 °C. The large red crystals so formed were removed from the mother liquor by filtration, washed with Et_2O and dried at reduced pressure at room temperature. Yield 14.22 g (64%).

Anal. Calc. for $C_{26}H_{62}MnN_6Na_2$ (**8c**): Mn, 9.82; Na, 8.21; N, 15.01. Found: Mn, 9.52; Na, 7.88; N, 14.71%.

Crystal structure determination of [Li(dme)]$_2$-[Mn(cod)$_2$] (1) and [Na(pmdeta)]$_2$[(C$_4$H$_8$)-Mn(C$_2$H$_4$)$_2$] (8c)

Diffraction intensities were measured on an Enraf-Nonius-CAD4 diffractometer. Crystal data and details of data collection are given in Table 2. The structures were solved by heavy atom methods and refined with the program GFMLX. Atomic positional and thermal parameters for **1** and **8c** are given in Tables 3 and 4, respectively.

Supplementary material

Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 56188, the names of the authors, and the journal citation.

Acknowledgement

The authors express their gratitude to Professor G. Wilke, the director of the Max-Planck-Institut für Kohlenforschung, for his continuous support and interest in this work.

References

1 (a) K. Jonas, *Pure Appl. Chem., 56* (1984) 63; (b) *Angew. Chem., 97* (1985) 292; *Angew. Chem., Int. Ed. Engl., 24* (1985) 295; (c) *Pure Appl. Chem., 62* (1990) 1169; (d) *J. Organomet. Chem., 400* (1990) 165, and refs. therein.

2 K. Jonas, G. Burkart, Ch. Häselhoff, P. Betz and C. Krüger, *Angew. Chem., 102* (1990) 291; *Angew. Chem., Int. Ed. Engl., 29* (1990) 322.

3 K. Jonas and C. Krüger, *Angew. Chem., 92* (1980) 513; *Angew. Chem., Int. Ed. Engl., 19* (1980) 520, and refs. therein.

4 W. Hieber and G. Wagner, *Z. Naturforsch., Teil B, 13* (1958) 339.

5 J. E. Ellis and R. A. Faltynek, *J. Am. Chem. Soc., 99* (1977) 1801.

6 K. Jonas, R. Mynott, C. Krüger, J. C. Sekutowski and Y.-H. Tsay, *Angew. Chem., 88* (1976) 808; *Angew. Chem., Int. Ed. Engl., 15* (1976) 767.

7 K. Jonas, W. Rüsseler, C. Krüger and E. Raabe, *Angew. Chem., 98* (1986) 904; *Angew. Chem., Int. Ed. Engl., 25* (1986) 925.

8 G. Burkart, *Dissertation,* University of Bochum, FRG, 1985.

9 Ch. Häselhoff, *Dissertation,* University of Bochum, FRG, 1991.

10 E. O. Fischer and S. Breitschaft, *Chem. Ber., 99* (1966) 2213.

11 (a) Y. Mugnier, C. Moise, J. Tirouflet and E. Lavinon, *J. Organomet. Chem., 186* (1980) C49; (b) N. Ito, T. Sajo and S. Aoyagui, *J. Organomet. Chem., 247* (1983) 301.

12 E. Heilbronner and H. Bock, *Das HMO-Modell und seine Anwendung,* Verlag Chemie, Weinheim, 1978, p. 338.

13 H.-O. Kalinowski, S. Berger and S. Brown, *^{13}C-NMR-Spektroskopie, Thieme, Stuttgart, 1984.*

14 U. Zenneck, *Organometallics, 8* (1989) 396.

15 A. Frings, *Dissertation,* University of Bochum, FRG, 1988.

16 M. L. H. Green, D. S. Joyner and J. M. Wallis, *J. Chem. Soc., Dalton Trans.,* (1987) 2823.

17 K. Fischer, K. Jonas and G. Wilke, *Angew. Chem., 85* (1973) 620; *Angew. Chem., Int. Ed. Engl., 12* (1973) 565.

18 G. Wilkinson, F. A. Cotton and J. M. Birmingham, *J. Inorg. Nucl. Chem., 2* (1956) 95.