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Coordination chemistry of perhalogenated cyclopentadienes and alkynes
XIV. Synthesis of dinuclear ring-bridged cymantrenes with $-SiMe_2-$ or $-TiCp_2-$ bridges. Structures of $[(OC)_3Mn(C_5Br_4-)]_2SiMe_2$ and $[(OC)_3Mn(C_5Cl_4-)]_2TiCp_2$*

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Abstract

$[C_5Br_5]Mn(CO)_3$ reacts with butyl lithium and one equivalent of $SiMe_2Cl_2$ to yield $[C_5Br_4SiMe_2Cl]Mn(CO)_3$ (**1**). The reaction of **1** with $[C_5X_4Li]Mn(CO)_3$ (X = Br, Cl) gives the bimetallic compounds $(OC)_3Mn(C_5Br_4-SiMe_2-C_5X_4)Mn(CO)_3$ (X = Br (**2**), Cl (**3**)). **2** can also be obtained by reaction of two equivalents of $[C_5Br_4Li]$-$Mn(CO)_3$ with one equivalent of $SiMe_2Cl_2$. $[C_5Cl_4Li]Mn(CO)_3$ reacts with Cp_2TiCl_2, depending on the reaction conditions, to yield the bi- and trimetallic compounds $[C_5Cl_4TiCp_2Cl]Mn(CO)_3$ (**4**) and $(OC)_3Mn(C_5Cl_4-TiCp_2-C_5Cl_4)Mn(CO)_3$ (**5**). The molecular structures of **2** and **5** have been determined by X-ray crystallography.

Key words: Crystal structures; Manganese complexes, Carbonyl complexes; Perhalocyclopentadienyl complexes; Silyl complexes; Dinuclear complexes

Introduction

Recently there has been considerable interest in the chemistry of bimetallic metallocenes with bridged cyclopentadienyl ligands $C_5R_4-(X)-C_5R_4$, mainly because of the high catalytic activities of titanocene derivatives of these ligands for Ziegler-Natta type polymerization [2]. The bridge 'X' stands for either a simple C–C bond, i.e. a fulvalene ligand [3], a one- or two-carbon bridge [4] or heteroatomic groups like S, PR or $SiMe_2$ [5] or even an organometallic fragment like Cp_2M with M = Ti, Zr, Hf [6]. Special cases are obtained, when two cyclopentadienyl rings are bridged by a double $SiMe_2$ bridge [7] or when three [8] or even four [9] rings are combined in this manner. Usually, the remaining 'substituents' in the bridged cp ligands are just hydrogens. Since on one hand, halogen substituents on a phenyl ring labilize the bond of this ring to silicon [10], while they stabilize on the other hand σ-bonds to transition metals, e.g. of the titanium triad [11], some interesting effects can be expected by introducing halogen substituents on a cyclopentadienyl ring in such complexes. Is there a stabilizing effect of the halogens in 'ortho' positions on the metal–carbon σ-bond? Does the steric effect of Cl or Br substituents allow the formation of two σ-bonds to two different cymantrenyl residues? Will the σ-bonded metal remain in the cyclopentadienyl ring plane or will it be shifted away from it, and, if so, will there be any interaction between σ- and π-bonded metals? As part of our studies on the coordination chemistry of perhalogenated cyclopentadienyl complexes, we decided to examine the reactions of lithiated perhalocymantrenes with $SiMe_2Cl_2$ and Cp_2MCl_2 (M = Ti, Zr, Hf).

Results and discussion

When $[C_5Br_5]Mn(CO)_3$ [12] and a hexane solution of butyl lithium are mixed at −78 °C, instantaneous formation of '$[C_5Br_4Li]Mn(CO)_3$' (**Ia**) occurs[†].

Addition of one equivalent of $SiMe_2Cl_2$ leads in a clean reaction to the mononuclear $[C_5Br_4SiMe_2Cl]$-

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*For Part XIII see ref. 1.

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[†] Although the true nature of this species has not been examined, we want to use this formulation for simplicity.

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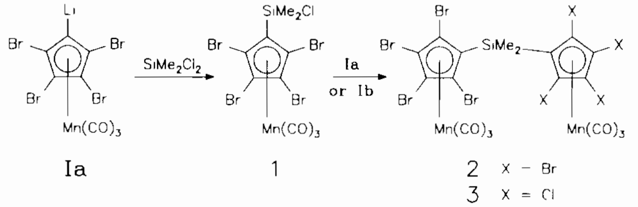
$Mn(CO)_3$ (**1**), which can easily be characterized by its IR, ^1H and ^{13}C NMR data. Mixing equivalent amounts of **1** and **Ia** in solution, produces the dinuclear compound **2** (Scheme 1).

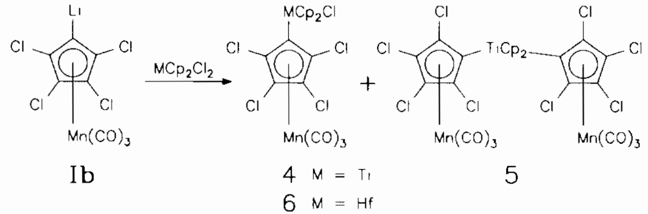
The molecular structure of **2** could be determined by X-ray diffraction (*vide infra*). In analogy to the formation of **Ia**, $[C_5Cl_4Li]Mn(CO)_3$ (**Ib**) can be obtained from the reaction of $[C_5Cl_4Br]Mn(CO)_3$ and butyl lithium [13]. If **Ib** and **1** are mixed in a 1:1 ratio, the unsymmetrical dimer **3** is formed. **2** and **3** show the expected number of signals in their ^{13}C NMR spectra, and also the other spectroscopic data show no unusual features. This means that the steric hindrance at the apparently congested central $SiMe_2$ unit cannot be of much importance.

If **Ib** and Cp_2TiCl_2 are mixed in Et_2O at −78 °C in a 2:1 stoichiometry and the temperature is raised slowly, the initial suspension gradually becomes clear and a red solution is obtained. At about −5 °C, the dinuclear **4** precipitates as an orange powder, which can be isolated by filtration. Workup of the mother liquor yields the trimetallic compound **5** as a red powder (Scheme 2). Upon recrystallization **5** gives nice red crystals that can be used for X-ray diffraction (*vide infra*).

When **Ib** and Cp_2TiCl_2 are mixed in a 1:1 ratio, **4** can be isolated as the only characterizable compound. The formation of **4** in the before-mentioned reaction, only after a temperature of −5 °C is reached, is probably a consequence of a secondary reaction between **5**, which must have formed first, and unreacted Cp_2TiCl_2 in some sort of comproportionation reaction, a known reaction with other compounds of the type Cp_2TiR_2 [14]. Both compounds are too insoluble in acetone-$[D]_6$ or CD_2Cl_2 to obtain ^{13}C NMR spectra with signals for the chlorine-substituted carbon atoms. They are soluble in DMSO-$[D]_6$ under decomposition. The formation of a fulvalene-bridged dimanganese compound $[(OC)_3Mn(C_5Cl_4-C_5Cl_4)Mn(CO)_3]$ in analogy to the decomposition reaction of the known unsubstituted parent compound [15] seems possible.



Scheme 1.



Scheme 2

We also tried to prepare the corresponding zirconium and hafnium compounds. When **Ia** was reacted with Cp_2ZrCl_2 in a 1:1 and a 2:1 ratio, similar observations could be made as with the titanium compound, but no products could be isolated or characterized besides $[C_5Cl_4H]Mn(CO)_3$ and Cp_2ZrCl_2. In the 1:1 reaction of **Ia** and Cp_2HfCl_2 a product **6** can be obtained, which has the expected composition $[C_5Cl_4HfCp_2Cl]Mn(CO)_3$ according to its analytical data. **6** dissolves in acetone-$[D_6]$ quite well, but it gradually decomposes and no ^{13}C NMR spectra could be obtained.

In conclusion it can be stated that σ-metallocenyl complexes of the titanium triad are slightly stabilized by the introduction of halogen substituents on the σ-cyclopentadienyl ring, but this effect is not at all comparable to the stability that is created by a C_6F_5 ligand [6].

Molecular structures of 2 and 5

The results of the crystal structure determinations of **2** and **5** are depicted in Figs. 1 and 2. In the silicon bridged compound, both cyclopentadienyl rings deviate only slightly from planarity (mean deviations 0.01 and 0.003 Å) and form a dihedral angle of 81° with each

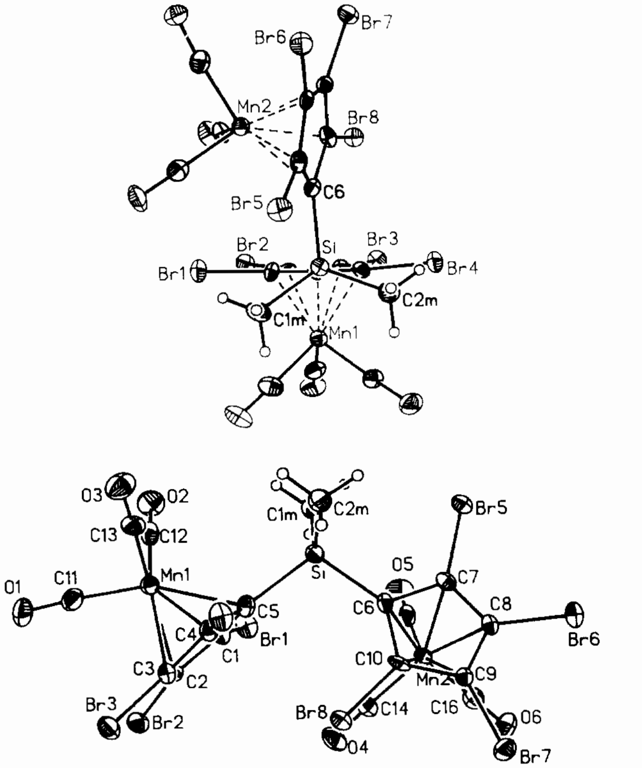


Fig 1 Two views of the molecular structure of **2**. Thermal ellipsoids drawn at the 20% probability level

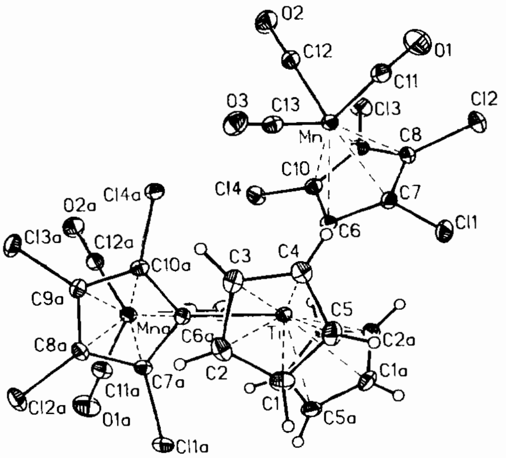


Fig. 2. Molecular structure of **5**. Thermal ellipsoids drawn at the 20% probability level

other and 94 and 22° with the central C5–Si–C6 unit. In the unbrominated parent compound **II** the latter two angles are 89.5 and 144.0° [16]. Obviously, the steric interactions of the 'ortho' bromine substituents in **2** force the two planes of the rings further apart. Thus, the closest intramolecular contact between two Br substituents of different rings is the one between Br4 and Br8 with 3.71 Å in comparison with the Br–Br distances within one ring ranging from 3.51 to 3.58 Å and the closest intermolecular Br–Br distance of 3.58 Å, which is observed between Br8 and Br2′. The other distances and angles show no unusual features and compare quite well with the parent compound. Table 1 gives the fractional atomic coordinates and equivalent isotropic temperature factors.

Compound **5** crystallizes in the same space group (*C*2/*c*) as [$(OC)_3Mn(C_5H_4$–$TiCp_2$–$C_5H_4)Mn(CO)_3$] (**III**) [15], but with a cell volume approximately 25% larger. The titanium atom is situated on a crystallographic *C*2 axis in both compounds, with the consequence that one half of the molecule is generated by space group symmetry operations from the other. The C_5H_5 and the C_5Cl_4Ti ring are both planar with mean deviations of 0.006 and 0.01 Å from the best planes and include an angle of 53° with each other. The two η^5-rings at titanium form a 129.3° angle. In **III**, the latter angle is 128.1°, only slightly different. However, the angle between the σ- and π-coordinated Cp rings is 96.3° in **III** and this shows a significant effect of the Cl substituents on the relative orientations of these rings. Another interesting feature of the structure of **5** is the close to parallel orientation of the C_5Cl_4Ti ring with the 'other' symmetry related C_5H_5 ring (dihedral angle 4.6°). The distance of the titanium atom to the σ-bonded Cp ring is 2.295(5) Å much longer than the 2.207(2) Å observed in **III**, while the Ti–C_5H_5 distances are about the same in both complexes. Also the C–Ti–C angle in **5** is 112.4(2)°, quite different from the value of 88.6° observed in the unchlorinated analogue. The Ti atom is shifted by 0.626 Å out of the C_5Cl_4 ring plane away from the $Mn(CO)_3$ group, which is nearly double the amount which is observed in **III**. The distance between Ti and the two Mn atoms is 4.29 Å, much too long for any interaction between the metals. The closest Cl–Cl distances within one ring range from 3.32 to 3.40 Å, while the closest contact between two chlorine atoms in different rings is 3.26 Å (Cl4–Cl4a). The other structural features in **5** are quite normal. Table 2 lists the fractional atomic coordinates and the equivalent isotropic temperature factors.

TABLE 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($pm^2 \times 10^{-1}$) in **2**

	x	*y*	*z*	U_{eq}
Mn(1)	−76(2)	2573(2)	8251(1)	44(1)
C(11)	−1525(20)	3555(17)	8801(11)	67(7)
O(1)	−2484(15)	4152(13)	9191(8)	89(6)
C(12)	−1037(19)	2662(18)	7244(11)	68(7)
O(2)	−1653(15)	2688(15)	6593(8)	95(7)
C(13)	1210(18)	4030(18)	8363(10)	59(7)
O(3)	2056(14)	4988(14)	8479(9)	89(6)
C(1)	−172(15)	393(14)	7821(8)	43(5)
C(2)	−779(14)	833(13)	8635(8)	38(5)
C(3)	461(15)	1617(14)	9222(8)	42(5)
C(4)	1783(15)	1694(14)	8793(8)	43(5)
C(5)	1433(15)	878(14)	7892(8)	45(5)
Br(1)	−1377(2)	−784(2)	6842(1)	62(1)
Br(2)	−2750(2)	313(2)	8891(1)	59(1)
Br(3)	360(2)	2356(2)	10422(1)	58(1)
Br(4)	3760(2)	2526(2)	9370(1)	57(1)
Si	2820(4)	450(4)	7024(2)	42(1)
C(1M)	1701(17)	335(16)	5959(8)	56(6)
C(2M)	4509(16)	1712(16)	7235(9)	58(6)
C(6)	3650(14)	−1226(13)	7020(8)	38(5)
C(7)	4512(15)	−2081(14)	6323(8)	42(5)
C(8)	5212(13)	−3106(13)	6573(7)	36(5)
C(9)	4911(14)	−3026(13)	7407(7)	37(5)
C(10)	3964(14)	−1873(15)	7677(7)	42(5)
Br(5)	4788(2)	−1697(2)	5291(1)	56(1)
Br(6)	6565(2)	−4318(2)	5955(1)	58(1)
Br(7)	5732(2)	−4010(2)	8091(1)	57(1)
Br(8)	3377(2)	−1252(2)	8807(1)	50(1)
Mn(2)	2680(2)	−3332(2)	6591(1)	41(1)
C(14)	1016(17)	−3336(16)	7186(8)	51(6)
O(4)	−49(12)	−3392(13)	7562(7)	77(5)
C(15)	1395(16)	−3408(15)	5629(10)	54(6)
O(5)	619(13)	−3462(13)	5008(7)	78(5)
C(16)	2635(19)	−5148(19)	6301(9)	61(7)
O(6)	2672(14)	−6314(12)	6151(7)	75(5)

Experimental

All reactions were carried out under nitrogen using the usual Schlenk tube technique, with absolute nitro-

TABLE 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($pm^2 \times 10^{-1}$) in **5**

	x	y	z	U_{eq}
Ti	5000	4215(1)	7500	29(1)
C(1)	5540(3)	6121(6)	8655(4)	50(3)
C(2)	5926(3)	4962(6)	9135(4)	46(2)
C(3)	5559(3)	3992(6)	9327(3)	42(2)
C(4)	4951(3)	4598(5)	8982(3)	40(2)
C(5)	4934(3)	5896(6)	8555(4)	47(3)
C(6)	4118(2)	2871(4)	7170(3)	30(2)
C(7)	3531(2)	3329(4)	7105(3)	34(2)
C(8)	3011(2)	2362(5)	6554(3)	37(2)
C(9)	3265(2)	1220(5)	6294(3)	38(2)
C(10)	3930(2)	1536(5)	6669(3)	35(2)
Cl(1)	3374(1)	4959(1)	7435(1)	50(1)
Cl(2)	2210(1)	2571(2)	6196(1)	58(1)
Cl(3)	2831(1)	−186(2)	5555(1)	58(1)
Cl(4)	4376(1)	481(1)	6333(1)	46(1)
Mn	3763(1)	1402(1)	7916(1)	33(1)
C(11)	3308(3)	1721(5)	8524(4)	48(3)
O(1)	3013(2)	1985(5)	8895(3)	80(3)
C(12)	3752(2)	−462(6)	8021(4)	45(3)
O(2)	3739(2)	−1673(4)	8038(3)	71(2)
C(13)	4488(3)	1486(5)	9153(4)	39(2)
O(3)	4929(2)	1540(4)	9965(3)	58(2)

gen-saturated solvents. The chemicals used were either commercially available or prepared according to literature procedures ($[C_5Cl_4Br]Mn(CO)_3$ [17], $[C_5Br_5]Mn(CO)_3$ [12]). The butyl lithium solutions used were 1.6 M in hexane. Chromatographic purifications were performed using silica gel 60 (Merck). The crystal structures were determined on a Syntex-Nicolet R3 diffractometer, using Mo Kα radiation with a graphite monochromator in ω-scan technique. The software used for data processing, structure solution and refinement was the SHELXTL PLUS 4.11/V program package. The experimental details are summarized in Table 3 (see also 'Supplementary material').

$[C_5Br_4SiMe_2Cl]Mn(CO)_3$ (1)

To 20 ml of an ethereal solution of $[C_5Br_5]Mn(CO)_3$ (2.0 g, 3.3 mmol) is added BuLi solution (2.1 ml, 3.3 mmol) with stirring at −75 °C. After 30 min $SiMe_2Cl_2$ (0.40 ml, 3.3 mmol) is added, and the mixture is allowed to warm up to ambient temperature overnight. Then the solution is evaporated to dryness *in vacuo*. The residue is extracted with 20 ml hexane for 10 min and the extract is chromatographed on silica gel that had been pre-treated with $SiMe_3Cl$. The eluate is evaporated to about one third *in vacuo* and cooled down to −20 °C. **1** can be isolated as yellow needles in high purity (0.20 g, 10%) (further evaporation and refrigeration of the mother liquor yields about 1 g of a less pure product, which still can be used for further reactions without any problems). *Anal.* Calc. for $C_{10}H_6Br_4ClMnO_3Si$: C, 19.62; H, 0.99. Found: C, 19.73; H, 1.29%.

TABLE 3. Crystal data for **2** and **5**

	2	5
Formula	$C_{18}H_6Br_8Mn_2O_6Si$	$C_{26}H_{10}Cl_8Mn_2O_6Ti$
Formula weight	1095.5	859.7
Space group	$P\bar{1}$	$C2/c$
a (Å)	8.494(4)	24.05(1)
b (Å)	10.295(3)	9.502(3)
c (Å)	16.357(5)	15.335(5)
α (°)	107 62(2)	90
β (°)	95.42(3)	121.38(3)
γ (°)	92.35(3)	90
V (nm³)	1.3535(9)	2.993(2)
Z	2	4
D_{calc} (g/cm³)	2.688	1.913
μ (Mo Kα) (mm⁻¹)	12.675	1.824
2θ Range (°)/index range	$4–46/-h \pm k \pm l$	$4–20/\pm h \pm k \pm l$ $20–50/\pm h + k + l$
No. reflections collected	4320	3853
No. unique data (R_{int})	3791 (1.20%)	2655 (2.12%)
No. observed reflections ($\lvert F\rvert \geq 4\sigma(\lvert F\rvert)$)	2582	2060
Absorption correction	psi scan	not applied
Transmission: min./max.	0.0067/0.0295	
Extinction correction with $F^* = F[1 + 0.002xF^2/\sin(2\theta)]^{-0\ 25}$	$x = 0.00068(7)$	not applied
Parameters refined	317	211
R/R_w (%)	4 94/5 26	4.31/4.77
Largest difference peak (e/Å³)	0.91	0.56

^{1}H NMR (C_6D_6, δ): 0.59. ^{13}C NMR (C_6D_6, δ): 94.8, 91.2, 78.2 (C_5R_5). IR (hexane, cm^{-1}): 2041, 1972 (ν(CO)).

$[(OC)_3Mn(C_5Br_4-)]_2SiMe_2$ (2)

Butyllithium solution (1.04 ml, 1.70 mmol) is added to $[C_5Br_5]Mn(CO)_3$ (1.00 g, 1.70 mmol) in 10 ml Et_2O at −75 °C. After 30 min $SiMe_2Cl_2$ (0.10 ml, 0.85 mmol) is added with stirring and the temperature is raised to ambient during 12 h. After another 6 h the solution is evaporated to dryness *in vacuo*. The residue is hydrolyzed by contact with air, washed three times with 5 ml hexane each and then with 10 ml water. After filtration the precipitate is dried *in vacuo* over P_4O_{10}. Recrystallization from CH_2Cl_2 at −20 °C yields 0.24 g of compound **2** as colorless platelets (22%). Although X-ray analysis showed this compound to be pure, no satisfying elemental analyses could be obtained. ^{1}H NMR (C_6D_6, δ): 1.02 ppm. ^{13}C NMR ($CDCl_3$, δ): 94.8, 90.6, 79.3 (C_5R_5). IR (Nujol, cm^{-1}): 2041, 2031, 1970, 1955 (ν(CO)).

$[(OC)_3Mn(C_5Br_4-SiMe_2-C_5Cl_4)Mn(CO)_3]$ (3)

A solution of $[C_5Cl_4Br]Mn(CO)_3$ (0.37 g, 0.88 mmol) in 15 ml Et_2O is reacted first with BuLi solution (0.55 ml, 0.88 mmol) and then, after 20 min, with an ethereal solution of **1** (0.54 g, 0.88 mmol). Stirring is continued for 12 h, while the temperature is gradually raised to ambient, and for another 12 h to complete the reaction. Workup is performed as described for **2**, and a yield of 0.14 g (12.9%) of **3** is obtained. *Anal.* Calc. for $[C_{18}H_6Br_4Cl_4Mn_2O_6Si]\cdot 2CH_2Cl_2$: C, 22.09; H, 0.93. Found: C, 21.71; H, 0.95%. ^{1}H NMR (CD_2Cl_2, δ): 1.01 ppm. ^{13}C NMR (CD_2Cl_2, δ): 105.5, 98.7, 74.0 (C_5Cl_4), 95.1, 91.2, 79.2 (C_5Br_4). IR (Nujol, cm^{-1}): 2040, 2032, 1974, 1961 (ν(CO)).

$[C_5Cl_4(TiCp_2Cl)]Mn(CO)_3$ (4)

Cp_2TiCl_2 (0.374 g, 1.50 mmol) is added to a solution of $[C_5Cl_4Li]Mn(CO)_3$ in Et_2O (obtained from $[C_5Cl_4Br]Mn(CO)_3$ (0.63 g, 1.50 mmol) and BuLi solution (0.94 ml, 1.50 mmol) at −78 °C. Stirring is continued at this temperature for 30 min, then for another 30 min at ambient temperature. The solvent is evaporated *in vacuo*, and the residue is extracted with 35 ml CH_2Cl_2. After careful addition of 20 ml pentane and cooling to −30 °C for 16 h, **4** is obtained as an orange powder (yield 0.507 g, 61%). *Anal.* Calc. for $C_{18}H_{10}Cl_5MnO_3Ti$: C, 38.99; H, 1.82. Found: C, 37.82; H, 2.14%. ^{1}H NMR (DMSO-[D]$_6$, δ): 6.66 ppm. IR (Nujol, cm^{-1}): 2026, 2017, 1939 (ν(CO)).

$[(OC)_3Mn(C_5Cl_4-TiCp_2-C_5Cl_4)Mn(CO)_3]$ (5)

A solution of $[C_5Cl_4Br]Mn(CO)_3$ (0.42 g, 1.00 mmol) in 20 ml Et_2O is reacted with BuLi solution (0.625 ml, 1.00 mmol) at −78 °C for 20 min. Then Cp_2TiCl_2 (0.125 g, 0.50 mmol) is added, and the temperature is raised to −5 °C for 60 min. After filtration of the orange precipitate of **4**, the red solution is evaporated to dryness *in vacuo*. The residue is washed twice with 20 ml pentane each, and then chromatographed on silica gel. Elution with CH_2Cl_2 yields first a narrow yellow band ($[C_5Cl_4H]Mn(CO)_3$) and then a broad dark red band, which gives the desired product **5** as a red powder after evaporation (yield 0.283 g, 66%). *Anal.* Calc. for $C_{26}H_{10}Cl_8Mn_2O_6Ti$: C, 36.32; H, 1.17. Found: C, 33.09; H, 1.90% (elemental analysis was performed with the same crop of crystals that was used for X-ray analysis). ^{1}H NMR (C_6D_6, δ): 5.92 ppm. IR (Nujol, cm^{-1}): 2028, 1971sh, 1959sh, 1942 (ν(CO)).

$[C_5Cl_4(HfCp_2Cl)]Mn(CO)_3$ (6)

At −70 °C, a suspension of Cp_2HfCl_2 (0.42 g, 1.11 mmol) in 10 ml Et_2O is added to an ethereal solution of $[C_5Cl_4Li]Mn(CO)_3$, obtained from $[C_5Cl_4Br]Mn(CO)_3$ (0.467 g, 1.11 mmol) and BuLi solution (0.694 ml, 1.11 mmol), and the mixture is stirred for 15 min at this temperature and for 60 min at ambient temperature. Addition of 7 ml pentane precipitates crude **6** as a yellow powder which is isolated by filtration. Extraction with 20 ml CH_2Cl_2, addition of 15 ml pentane to the filtrate and cooling down to −30 °C yields **6** as pure yellow crystals (yield 0.395 g, 52%). *Anal.* Calc. for $C_{18}H_{10}Cl_5HfMnO_3$: C, 31.56; H, 1.47. Found: C, 31.08; H, 2.14%. ^{1}H NMR (acetone-[D]$_6$, δ): 6.42 ppm. IR (Nujol, cm^{-1}): 2028, 2017, 1950sh, 1940 (ν(CO)).

Supplementary material

Further details of the crystal structure determination can be obtained from the Fachinformationszentrum, Karlsruhe, D-76344 Eggenstein-Leopoldshafen, citing the deposition no. CSD-57356, the authors and the reference.

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