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Synthesis of a novel bidentate complex of η^5-$C_5H_4CH_2CH(CH_3)\overline{N(CH_3)(C_3H_5)Mn}(CO)_2$

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Abstract

Irradiation of the half-sandwich manganese tricarbonyl complex η^5-$C_5H_4CH_2CH(CH_3)NH(CH_3)$-$Mn(CO)_3$, which itself contained a secondary amine branch on the cyclopentadienyl group, to give bidentate complex, η^5-$C_5H_4CH_2CH(CH_3)\overline{NHCH_3Mn}(CO)_2$. Deprotonation followed by allylation gave *N*-allylation compound, η^5-$C_5H_4CH_2CH(CH_3)\overline{N(CH_3)(C_3H_5)Mn}(CO)_2$, which was unequivocally identified by spectroscopic and X-ray diffraction studies.

Introduction

Although numerous half-sandwich manganese complexes have been reported [1], very few contain amine ligand [2]. We are interested in the half-sandwich complexes which contain an amine ligand, especially in an intramolecular fashion; namely, bidentate complexes which contain a cyclopentadienyl and an amine ligand linked by a carbon chain. This type of bidentate complexes have not been previously reported. We have succeeded in preparing complex and characterizing, by spectroscopic and X-ray diffraction studies, such a complex. The successful preparation of η^5-$C_5H_4CH_2CH(CH_3)\overline{N(CH_3)(C_3H_5)Mn}(CO)_2$ (4) constitutes the first example of cyclopentadienyl and amine bidentate half-sandwich manganese complex. The results are reported herein.

Experimental

All reactions were performed under argon by use of Schlenk techniques. Tetrahydrofuran (THF) and n-hexane were distilled from sodium benzophenone ketyl; methylene chloride (CH_2Cl_2) was distilled from CaH_2. $Mn(CO)_5Br$ was prepared by a published procedure [3]. Infrared solution spectra were recorded on a Perkin–Elmer 882 infrered spectrophotometer using 0.1 mm cells with NaCl windows. Melting points were determined by using a Yanaco model MP micro melting point apparatus and are uncorrected. ^1H NMR (200 MHz) and ^{13}C NMR (50 MHz) were obtained with a Bruker AC-200 FT spectrophotometer. All chemical shifts are

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reported in parts per million (ppm) relative to Me_4Si. Elemental analyses were obtained on a Perkin–Elmer 2400 CHN elemental analyzer. Mass spectra were recored on a VG 70-250S mass spectrophotometer at 70 eV mode.

Preparation of η^5-$C_5H_4CH_2CH(CH_3)NH(CH_3)Mn(CO)_3$ *(2)*

A solution of $Mn(CO)_5Br$ (2.2 g, 8 mmol) in THF (20 ml) was added to a stirred solution of $LiC_5H_4CH_2CH(CH_3)NHCH_3$ (25 ml, 0.34 *M* in THF) at 0 °C. The orange solution was then refluxed for 12 h. The resulting yellow-orange solution was concentrated under reduced pressure. The residue was then distilled (Kugelrohr) at 0.1 Torr. After heating at 90 °C for 30 min to remove small amounts of $Mn_2(CO)_{10}$, desired product **2** was collected at 150 °C as a yellow liquid, 1.50 g (68% yield). IR (CH_2Cl_2): 2018, 1926 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 4.05 (1H, br. s), 3.98 (1H, br. s), 3.91 (2H, br. s), 2.26–2.10 (1H, m), 2.06 (3H, br. s), 1.98 (2H, d, *J* 4.5 Hz), 0.69 (3H, d, *J* 5.5 Hz). Analysis. Found: C, 52.38; H, 5.18; N, 5.04. $C_{12}H_{14}NO_3Mn$ calcd.: C, 52.38; H, 5.13; N, 5.09%.

Preparation of η^5-$C_5H_4CH_2CH(CH_3)\overline{NHCH_3Mn}(CO)_2$ *(3)*

In a borosilicate test tube was placed complex **2** (195 mg, 0.71 mmol). The open end was sealed with a rubber septum. The vessel was evacuated and then flushed with argon. Hexane (15 ml) was added. The resulting yellow solution was cooled in a circulating ice-water bath and irradiated under an argon balloon, using Hanovia 500 W watts medium pressure Hg lamp for 1.5 h to allow the reaction to go to completion. The products appeared as solids adsorbed on the glass walls. The solution was decanted and the precipitates was washed with hexane. After evaporation to dryness, **3** was collected as orange crystals, 125 mg (71% yield). m.p.: 80–82 °C. IR (THF): 1913, 1841 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 4.77 (1H, br. s), 4.60 (1H, br. s), 3.51 (1H, br. s), 3.48 (1H, br. s), 2.06–1.86 (1H, m), 1,64 (3H, d, $J = 5.4$ Hz), 1.48 (1H, dd, $J = 14$, 4.7 Hz), 0.76 (1H, dd, *J* 14, 12.8 Hz), −0.02 (3H, d, *J* 5.6 Hz). ^1H NMR (CD_2Cl_2, 200 MHz): δ 5.20 (1H, br. s), 5.05 (1H, br. s), 3.66 (1H, br. s), 3.56 (1H, br. s), 2.98–2.85 (1H, m), 2.37 (1H, dd, *J* 13.7, 5.5 Hz), 2.29 (3H, d, *J* 6.1 Hz), 2.12–1.92 (1H, br, -NH), 1.73 (1H, dd, *J* 13.7, 11.6 Hz), 0.96 (3H, d, *J* 6.1 Hz). ^{13}C NMR (CD_2Cl_2, 50 MHz): 116.2, 81.6, 78.9, 77.6, 76.5, 72.6, 43.9, 35.9, 19.0 ppm. Analysis. Found: C, 53.38; H, 5.85; N, 5.56. $C_{11}H_{14}NO_2Mn$ calcd.: C, 53.45; H, 5.71; N, 5.67%.

Preparation of η^5-$C_5H_4CH_2CH(CH_3)\overline{N(CH_3)(C_3H_5)Mn}(CO)_2$ *(4)*

To a stirring orange solution of **3** (81 mg, 0.328 mmol) in THF (10 ml) at −78 °C was added sodium bis(trimethylsilyl)amide (2 ml, 0.9 *M* in THF). After stirring at −78 °C for 10 min, allyl brimide (0.2 ml, 2.3 mmol) was added. The dry ice–acetone bath was removed and the mixture was stirred at room temperature for 2 h. The precipitates were removed by Celite filter. Evaporation of the filtrates gave orange solids which were subjected to flash chromatography [4] through silica gel (230–400 mesh, 10% ethyl acetate in hexane). After evaporation of the solvents, complex **4** was obtained as orange solids, 71 mg (75% yield). m.p.: 91–93 °C (dec). IR (THF): 1915, 1843 cm^{-1}. TLC (silica gel): $R_f = 0.23$ (10% ethyl acetate in hexane). mass spectra *m/e* (rel intensity (%)): 287 (M^+, 27), 231 ($M - 2CO$, 100), 190 ($M - 2CO - C_3H_5$, 45), 174 (71), 160 (32), 153 (50), ^1H NMR ($CDCl_3$, 200 MHz): δ 6.50–6.30 (1H, m, C(9)-H), 5.30 (1H, d, *J* 9.9 Hz, C(10)-H), 5.16 (1H, d, *J* 16 Hz, C(10)-H),

Table 1

Crystal data and refinement details for complex **4**

Formula	$C_{14}H_{17}NO_2Mn$	Transmission factors (max; min)	1.000; 0.902
Formula weight	286.23	2θ max.	50 °
Crystal system	orthorhombic	Octants	*h*, *k*, *l* 0–15, 0–12, 0–12
Space group	*Pnma*	No. of data collected	1297
a (Å)	13.1887(20)	No. of unique data	1297
b (Å)	10.3618(14)	No. of unique data used with $I \geq 2.0\sigma(I)$	1119
c (Å)	10.1909(17)		
		K	0.000100
Volume (Å^3)	1392.7	*R*	0.040
Z	4	R_w	0.048
D_c (g cm^{-3})	1.365	GoF	2.47
F(000)	595.89	max. shift/σ ratio	0.057
Crystal dimension (mm)	0.40 × 0.22 × 0.27	ρ_{max} (e Å^{-3})	0.360

5.11–5.07 (2H, m, Cp-H's), 3.51 (1H, br. s, Cp-H), 3.43 (1H, br. s, Cp-H), 3.27–3.08 (1H, m, C(2)-H), 2.98 (2H, d, *J* 6.6 Hz, C(8)-H's), 2.34 (1H, dd, *J* 14, 5.0 Hz, C(3)-H), 2.16 (1H, dd, *J*14, 11.9 Hz, C(3)-H), 2.28 (3H, s, N–CH_3), 0.81 (3H, d, *J* 6.5 Hz, -CH_3). ^{1}H NMR (C_6D_6, 200 MHz): δ 6.68–6.48 (1H, m, C(9)-H), 5.08 (1H, d, *J* 10.4 Hz, C(10)-H), 4.85 (1H, d, *J* 17.0 Hz, C(10)-H), 4.69 (1H, br. s, Cp-H), 4.65 (1H, br. s, Cp-H), 3.32 (1H, br. s, Cp-H), 3.25 (1H, br. s, Cp-H), 2.58–2.42 (3H, m), 1.75 (3H, s), 1.51 (1H, dd, *J* 11.7, 5.7 Hz, C(3)-H), 1.36 (1H, t, *J* 11.7 Hz, C(3)-H), 0.01 (3H, d, *J*6.8 Hz).

Crystal structure of η^5-$C_5H_4CH_2CH(CH_3)\overline{N(CH_3)(C_3H_5)Mn}(CO)_2$ *(4)*

A single crystal of **4**, suitable for the X-ray diffraction study was obtained by slow diffusion of a CH_2Cl_2 solution of **4** into hexane (CH_2Cl_2/hexane = 1/10) at 25 °C overnight. Intensities were measured with an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.7093 Å) in the θ–2θ scan mode. Unit cell dimensions were obtained by least-squares refinement of 21 centered reflections for which $18.75° < 2\theta < 36.65°$. Other crystal data and refinement details are listed in Table 1.

Supplementary material. Lists of atomic coordinates and B_{iso} (1 page), bond lengths and angles (2 pages) and structure factors of **4** (5 pages) are available from T.-F.W.

Results and discussion

Lithium salt of *N*-methylamino cyclopentadienyl anion **1** [5*] was treated with manganese pentacarbonyl bromide in THF to provide a yellow liquid of manganese tricarbonyl complex **2** in 68% yield [6]. The infrared spectrum revealed in the carbonyl stretching region a sharp, strong absorption at 2018 cm^{-1} and a broad, strong absorption at 1926 cm^{-1}. Irradiation of **2** in THF liberated carbon monoxide

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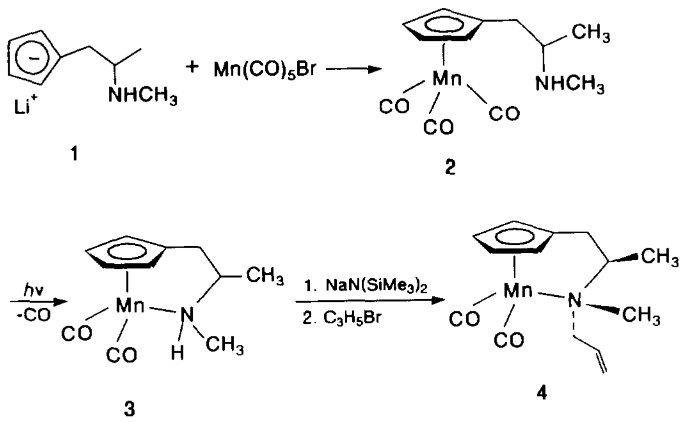
* A reference number with an asterisk indicates a note in the list of references.



Scheme 1

[7] and gave rise to intramolecular amine group ligation [8*] to provide the bidentate complex **3**. Better results were obtained when **2** was irradiated in n-hexane. Thus complex **3** was obtained directly from the reaction medium as orange crystals in 71% yield (see Scheme 1). Dicarbonyl stretching frequencies appear at 1913 and 1841 cm^{-1} with equal intensity in the infrared spectrum [9]. N–H stretching was observed as a broad absorption at 3579 cm^{-1}. In the ^1H NMR spectrum, the N–H proton resonance appeared at δ 2.02 as a very broad signal.

While liberation of carbon monoxide is indicated by the shift and shape of the carbonyl stretching frequencies in the infrared spectra, the amine ligation was evidenced by chemical shifts of the Cp protons in the ^1H NMR spectra. When amine ligation occurred, the Cp ring became much more rigid than the free amine precursor, changing the chemical and magnetic environment of the Cp protons to a greater extent than that of the more flexible Cp protons of the precursor. This phenomenon was evident from the ^1H NMR spectra of complexes **2** and **3**. The Cp protons of complex **2** appear at δ 4.05 (1H, br. s), 3.98 (1H, br. s) and 3.91 (2H, br. s), while Cp protons of complex **3** appears as wider speration at δ 4.77 (1H, br. s), 4.60 (1H, br. s), 3.51 (1H, br. s) and 3.48 (1H, br. s).

Deprotonation of complex **3** with sodium bis(trimethylsilyl)amide, followed by addition of allyl bromide, providing an alkylation product in 75% yield as orange crystals. The infrared spectrum shows two carbonyl absorptions at 1915 and 1843 cm^{-1}. ^1H NMR spectrum displays the typical allylic pattern at δ 6.50–6.30 (1H, m), 5.30 (1H, d, J 9.9 Hz), 5.16 (1H, d, J 16 Hz) and 2.98 (2H, d, J 6.6 Hz). Mass spectrum reveals strong molecular ion peak at $m/e = 287$ (27%). At this juncture however, we were not able to assign definitely the position of the allyl group—whether it is on the manganese or on the nitrogen. The X-ray analysis (*vide infra*), it is clearly showed that allylation occurred on nitrogen and *trans* to the methyl group to give *cis* vicinal dimethyl complex **4**.

Solid state structure of 4

The molecular structure of **4** (Fig. 1) shows that two methyl groups are *cis* to each other. That means allylation occurred from the less hinder side. Bond length

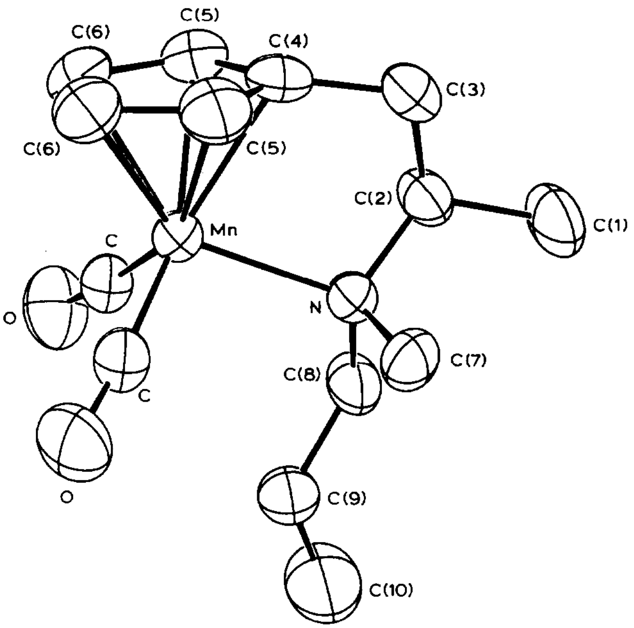


Fig. 1. The ORTEP drawing of complex **4**.

(Table 2) Mn–N of 2.148(3) Å lies between covalent radius (1.92 Å) and the sum of the van der Waals radii (2.54 Å). Bond length of N–C(7) (1.627 Å) is about 0.16 Å longer than that of N–C(2) (1.463 Å) and N–C(8) (1.460 Å).

The torsion angle (Table 3) of N–Mn–C(4)–C(3) is zero degrees, which indicates coplanarity of Mn–N and C(3)–C(4) bonds. Torsion angle of 166.5° of C(3)–C(4)–C(5)–C(6), suggesting C(4)–C(3) bond is bent 13.5° away from the cyclopentadienyl plane.

Table 2

Selected bond lengths (Å) and bond angles (°) in complex **4**

Mn–N	2.148(3)	O–C	1.170(4)
Mn–C	1.754(3)	C(1)–C(2)	1.534(8)
Mn–C(4)	2.136(4)	C(2)–C(3)	1.534(7)
Mn–C(5)	2.131(3)	C(3)–C(4)	1.495(6)
Mn–C(6)	2.112(3)	C(4)–C(5)	1.404(4)
N–C(2)	1.463(6)	C(5)–C(6)	1.408(4)
N–C(7)	1.627(6)	C(8)–C(9)	1.528(7)
N–C(8)	1.460(6)	C(9)–C(10)	1.229(8)
N–Mn–C	99.99(11)	C(2)–N–C(7)	106.4(3)
C(2)–C(3)–C(4)	108.4(3)	C(2)–N–C(8)	113.3(3)
Mn–N–C(2)	109.0(3)	C(7)–N–C(8)	106.8(4)
Mn–N–C(7)	105.49(22)	Mn–C–O	174.7(3)
Mn–N–C(8)	115.1(3)	N–C(2)–C(3)	111.8(4)

Table 3

Torsion angles (°) in complex **4**

C–Mn–N–O(2)	110.0(3)	C–Mn–N–C(7)	–136.0(3)
C–Mn–N–C(8)	–18.5(2)	C(4)–Mn–N–C(2)	–23.4(2)
C(4)–Mn–N–C(7)	90.6(2)	C(4)–Mn–N–C(8)	–151.9(3)
C(5)–Mn–N–C2)	9.3(2)	C(5)–Mn–N–C(7)	123.3(2)
C(5)–Mn–N–C(8)	–119.2(3)	C(6)–Mn–N–C(2)	6.9(2)
C(6)–Mn–N–C(7)	120.8(2)	C(6)–Mn–N–C(8)	–121.7(3)
N–Mn–C–O	–169.3(3)	C(4)–Mn–C–O	–83.9(2)
C(5)–Mn–C–O	–67.2(2)	C(6)–Mn–C–O	–29.1(2)
N–Mn–C(4)–C(3)	0.0(1)	N–Mn–C(4)–C(5)	121.2(2)
C–Mn–C(4)–C(3)	–94.0(2)	C–Mn–C(4)–C(5)	27.1(2)
C(5)–Mn–C(4)–C(3)	–121.2(2)	C(5)–Mn–C(4)–C(5)	0.0(2)
C(6)–Mn–C(4)–C(3)	–158.6(2)	C(6)–Mn–C(4)–C(5)	–37.4(2)
N–Mn–C(5)–C(4)	–58.8(2)	N–Mn–C(5)–C(6)	–177.4(3)
C–Mn–C(5)–C(4)	–160.7(3)	C–Mn–C(5)–C(6)	80.7(2)
C(4)–Mn–C(5)–C(4)	0.0(1)	C(4)–Mn–C(5)–C(6)	–118.6(2)
C(6)–Mn–C(5)–C(4)	118.6(2)	C(6)–Mn–C(5)–C(6)	0.0(2)
N–Mn–C(6)–C(5)	3.8(1)	C–Mn–C(6)–C(5)	–102.6(2)
C(4)–Mn–C(6)–C(5)	37.0(2)	C(5)–Mn–C(6)–C(5)	0.0(2)
Mn–N–C(2)–C(1)	172.3(5)	Mn–N–C(2)–C(3)	43.3(2)
C(7)–N–C(2)–C(1)	58.9(4)	C(7)–N–C(2)–C(3)	–70.1(3)
C(8)–N–C(2)–C(1)	–58.2(4)	C(8)–N–C(2)–C(3)	172.9(5)
Mn–N–C(8)–C(9)	–59.0(2)	C(2)–N–C(8)–C(9)	174.5(5)
C(7)–N–C(8)–C(9)	57.7(3)	N–C(2)–C(3)–C(4)	–43.2(2)
C(1)–C(2)–C(3)–C(4)	–175.8(5)	C(2)–C(3)–C(4)–Mn	22.1(2)
C(2)–C(3)–C(4)–C(5)	–60.5(3)	Mn–C(4)–C(5)–Mn	0.0(0)
Mn–C(4)–C(5)–C(6)	60.2(2)	C(3)–C(4)–C(5)–Mn	106.3(2)
C(3)–C(4)–C(5)–C(6)	166.5(4)	Mn–C(5)–C(6)–Mn	0.0(0)
C(4)–C(5)–C(6)–Mn	–60.9(2)	N–C(8)–C(9)–C(10)	–147.9(6)

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