

# Reaction of tricarbonyl(*exo*-cyclopentadienyl- $\eta^5$ -cyclohexadienyl) manganese with aryllithium reagents: crystal structures of $[C_5H_5-\{(\eta^5-C_6H_6)(CO)_2Mn=C(OC_2H_5)C_6H_5\}]$ and $[C_5H_5-\{(\eta^5-C_6H_6)(CO)_2Mn=C(OC_2H_5)C_6H_4CH_3-o\}]$

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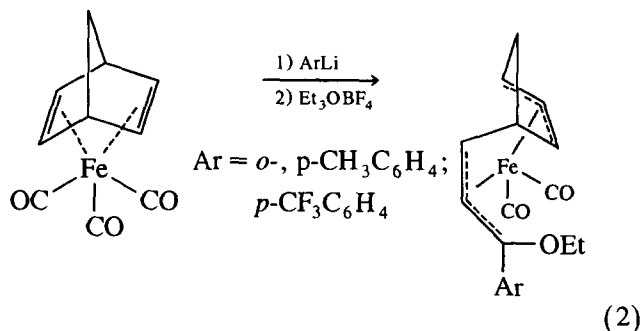
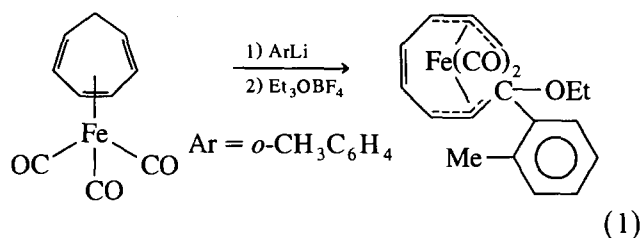
## Abstract

The reaction of tricarbonyl(*exo*-cyclopentadienyl- $\eta^5$ -cyclohexadienyl)manganese (**1**) with aryllithium reagents, ArLi (Ar=C<sub>6</sub>H<sub>5</sub>, *o*-, *m*-, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>, *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), in ether at low temperature afforded acylmetalate intermediates, followed by alkylation with Et<sub>3</sub>OBF<sub>4</sub> in an aqueous solution at 0°C to give the six alkoxy-carbene manganese complexes  $[C_5H_5-\{(\eta^5-C_6H_6)(CO)_2Mn=C(OC_2H_5)Ar\}]$  (**2**, Ar=C<sub>6</sub>H<sub>5</sub>; **3**, Ar=*o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; **4**, Ar=*m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; **5**, Ar=*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; **6**, Ar=*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>; **7**, Ar=*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>). The molecular structures of **2** and **3** have been established by X-ray diffraction studies.

**Keywords:** Manganese; Aryllithium reagents; Carbene complexes; Crystal structure; Reactions

## 1. Introduction

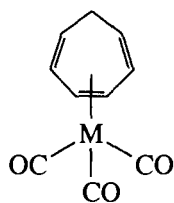
The olefin-coordinating transition-metal carbene complexes and/or their isomerized products have been explored extensively in our laboratory [1–16]. Earlier, we have shown [1–10,13,14] that several novel isomerizations of olefin ligands have been observed, and a series of isomerized carbene complexes with novel structure were isolated by the reactions of olefin-ligated metacarbonyl compounds with nucleophiles. We found that the isomerizations and reaction products depend not only on the olefin ligands but also on the central metals [2–5,11–14]. For instance, the cycloheptatriene(tricarbonyl)iron and norbornadiene(tricarbonyl)iron reacted with aryllithium reagents and subsequent alkylation with Et<sub>3</sub>OBF<sub>4</sub> to give novel ring-opened isomerized carbene complexes  $[C_7H_8(CO)_2FeC(OC_2H_5)Ar]$  [**3**] and  $[C_7H_8(CO)_2FeC(OC_2H_5)Ar]$  [**4**] respectively (Eqs. (1) and (2)).



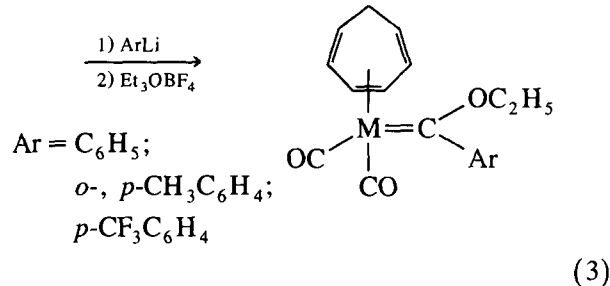
However, the reactions (Eqs. (3) and (4)) of the cycloheptatriene(tricarbonyl)-molybdenum and -chromium [11], and norbornadiene(tetracarbonyl)-chromium,

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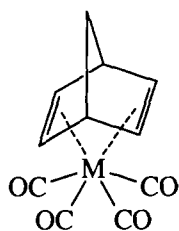
-molybdenum, and -tungsten [12,13] with aryllithium reagents under the same conditions gave normal olefin-coordinated carbene complexes in which the diene ligand and carbene ligand coexist stably.



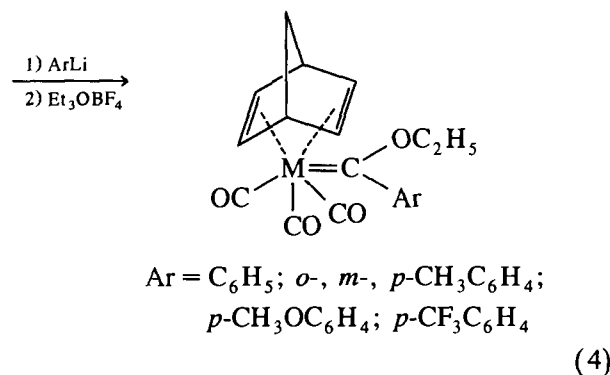
M = Cr, Mo



(3)



M = Cr, Mo, W



(4)

In our previous research the central metals were usually the Group VIIB metals ( $d^8$ ) and Group VIB metals ( $d^6$ ). In connection with studies of the transition-metal carbene and carbyne complexes, we have now extended our research to the Group VIIB metal ( $d^7$ ), such as tricarbonyl(*exo*-cyclopentadienyl- $\eta^5$ -cyclohexadienyl)manganese (1), in order to investigate the effects of a different central metal involving a different olefin ligand. Several (cyclopentadienyl- $\eta^5$ -cyclohexadienyl)(dicarbonyl)[ethoxy(aryl)carbene]manganese complexes were obtained by the reactions of compound 1 with aryllithium reagents in a similar manner as previously described [1,2,9]. Here we report on

the syntheses and structural characterizations of these new complexes.

## 2. Experimental

All procedures were performed under a dry, oxygen-free  $\text{N}_2$  atmosphere by using standard Schlenk techniques. The solvents were reagent grade and dried by refluxing over appropriate drying agents and stored over 4-Å molecular sieves under an  $\text{N}_2$  atmosphere. Tetrahydrofuran (THF) and diethyl ether ( $\text{Et}_2\text{O}$ ) were distilled from sodium benzophenone ketyl, while petroleum ether (30 to 60°C) from  $\text{CaH}_2$ , and  $\text{CH}_2\text{Cl}_2$  from  $\text{P}_2\text{O}_5$ . The neutral alumina ( $\text{Al}_2\text{O}_3$ ) used for chromatography was deoxygenated at room temperature under high vacuum for 16 h, deactivated with 5% w/w  $\text{N}_2$ -saturated water, and stored under  $\text{N}_2$ . Compound 1 [17],  $\text{Et}_3\text{OBF}_4$  [18], and aryllithium reagents [19–23] were prepared by literature methods.

The IR spectra were measured on a Zeiss Specord-75 spectrophotometer. The  $^1\text{H}$  NMR spectra were obtained on a Varian-200 spectrometer at ambient temperature in acetone- $d_6$  solution with TMS as the internal reference. Electron ionization mass spectra (EIMS) were determined on a Hewlett 5989A spectrometer. Melting points obtained on samples in sealed nitrogen-filled capillaries are uncorrected.

### 2.1. Preparation of $[\text{C}_5\text{H}_5\text{-}\{\eta^5\text{-C}_6\text{H}_6\}(\text{CO})_2\text{Mn}=\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5]$ (2)

To a solution of 1 (0.20 g, 0.71 mmol) in 40 ml of ether at  $-70^\circ\text{C}$  was added dropwise 1.5 mmol of  $\text{C}_6\text{H}_5\text{Li}$  [19] in 10 ml of ether with stirring. The solution was stirred initially at  $-60$  to  $-55^\circ\text{C}$  for 0.5 h during which time the light-yellow solution turned yellow and a light-yellow precipitate separated out from the mixture. After being stirred while warming to  $-40^\circ\text{C}$  over a 4 h period, the resulting solution was evaporated under vacuum at  $-40^\circ\text{C}$  to dryness; the yellow solid residue obtained was dissolved in 30 ml of  $\text{N}_2$ -saturated water at  $0^\circ\text{C}$  and covered with petroleum ether (30–60°C). Immediately afterward,  $\text{Et}_3\text{OBF}_4$  was added portionwise with vigorous stirring to the aqueous solution until it became acidic. The aqueous solution was extracted with petroleum ether. The combined extracts were evaporated in vacuo, and the residue was chromatographed on an alumina (neutral, 100–200 mesh) column ( $1.6 \times 10\text{--}15$  cm) at  $-20^\circ\text{C}$  with petroleum ether followed by petroleum ether- $\text{CH}_2\text{Cl}_2$  (15:1) as the eluant. The yellow band was eluted and collected. Removal of the solvent under vacuum and recrystallization of the crude product from petroleum ether- $\text{CH}_2\text{Cl}_2$  solution at  $-80^\circ\text{C}$  gave 0.21 g (76%, based on 1) of orange-red crystals of 2, m.p.  $78\text{--}80^\circ\text{C}$

(dec.). IR ( $\nu_{\text{CO}}$ ): (hexane) 1960vs, 1906vs  $\text{cm}^{-1}$ . MS:  $m/e$  388 ( $\text{M}^+$ ), 360 ( $\text{M}^+ - \text{CO}$ ), 332 ( $\text{M}^+ - 2\text{CO}$ ), 287 ( $\text{M}^+ - 2\text{CO} - \text{OC}_2\text{H}_5$ ), 198 ( $\text{M}^+ - 2\text{CO} - \text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5$ ), 143 ( $\text{C}_5\text{H}_5\text{C}_6\text{H}_6$ )<sup>+</sup>. Anal. Found: C, 68.18; H, 5.66.  $\text{C}_{22}\text{H}_{21}\text{MnO}_3$  Calc.: C, 68.04; H, 5.45%.

### 2.2. Preparation of $[\text{C}_5\text{H}_5\text{-}\{\eta^5\text{-C}_6\text{H}_6\}(\text{CO})_2\text{Mn}=\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}o\}]$ (3)

Similar to the preparation of 2, 0.20 g (0.71 mmol) of 1 reacted with 1.5 mmol of *o*- $\text{CH}_3\text{C}_6\text{H}_4\text{Li}$  [20] at  $-60$  to  $-40^\circ\text{C}$  for 4 h. The subsequent alkylation and further treatment as described above for the preparation of 2 afforded 0.23 g (81%, based on 1) of orange-red crystalline 3, m.p.  $90\text{--}92^\circ\text{C}$  (dec.). IR ( $\nu_{\text{CO}}$ ): (hexane) 1962vs, 1909vs  $\text{cm}^{-1}$ . MS:  $m/e$  402 ( $\text{M}^+$ ), 374 ( $\text{M}^+ - \text{CO}$ ), 346 ( $\text{M}^+ - 2\text{CO}$ ), 301 ( $\text{M}^+ - 2\text{CO} - \text{OC}_2\text{H}_5$ ), 198 ( $\text{M}^+ - 2\text{CO} - \text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3$ ), 143 ( $\text{C}_5\text{H}_5\text{C}_6\text{H}_6$ )<sup>+</sup>. Anal. Found: C, 68.85; H, 5.55.  $\text{C}_{23}\text{H}_{23}\text{MnO}_3$  Calc.: C, 68.66; H, 5.76%.

### 2.3. Preparation of $[\text{C}_5\text{H}_5\text{-}\{\eta^5\text{-C}_6\text{H}_6\}(\text{CO})_2\text{Mn}=\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}m\}]$ (4)

The reaction of 0.20 g (0.71 mmol) of 1 with 1.5 mmol of *m*- $\text{CH}_3\text{C}_6\text{H}_4\text{Li}$  [20] was as described for the preparation of 2 at  $-60$  to  $-40^\circ\text{C}$  for 4 h. The subsequent alkylation and further treatment as described above yielded 0.20 g (70%, based on 1) of 4 as orange-red crystals, m.p.  $60\text{--}62^\circ\text{C}$  (dec.). IR ( $\nu_{\text{CO}}$ ): (hexane) 1958vs, 1902vs  $\text{cm}^{-1}$ . MS:  $m/e$  402 ( $\text{M}^+$ ), 374 ( $\text{M}^+ - \text{CO}$ ), 346 ( $\text{M}^+ - 2\text{CO}$ ), 301 ( $\text{M}^+ - 2\text{CO} - \text{OC}_2\text{H}_5$ ), 198 ( $\text{M}^+ - 2\text{CO} - \text{C}(\text{OC}_2\text{H}_5)\text{-C}_6\text{H}_4\text{CH}_3$ ), 143 ( $\text{C}_5\text{H}_5\text{-C}_6\text{H}_5$ )<sup>+</sup>. Anal. Found: C, 68.61; H, 5.63.  $\text{C}_{23}\text{H}_{23}\text{MnO}_3$ . Calc.: C, 68.66; H, 5.76%.

### 2.4. Preparation of $[\text{C}_5\text{H}_5\text{-}\{\eta^5\text{-C}_6\text{H}_6\}(\text{CO})_2\text{Mn}=\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}p\}]$ (5)

Similarly, compound 1 (0.20 g, 0.71 mmol) dissolved in 40 ml of ether was treated with 1.5 mmol of *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{Li}$  [20] at  $-60$  to  $-45^\circ\text{C}$  for 3.5 h, followed

Table 1  
Crystal data and experimental details for complexes 2 and 3

	2	3
Formula	$\text{MnO}_3\text{C}_{22}\text{H}_{21}$	$\text{MnO}_3\text{C}_{23}\text{H}_{23}$
Formula weight	388.34	402.37
Space group	$P2_1/a$ (No. 4)	$P\bar{1}$ (No. 2)
<i>a</i> (Å)	11.902(7)	8.445(1)
<i>b</i> (Å)	9.662(6)	11.066(3)
<i>c</i> (Å)	17.02(1)	11.107(2)
$\alpha$ (deg)	90	98.58(2)
$\beta$ (deg)	105.24(5)	103.02(2)
$\gamma$ (deg)	90	99.20(2)
<i>V</i> (Å <sup>3</sup> )	1888(2)	979.6(9)
<i>Z</i>	4	2
<i>d</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.37	1.36
Crystal size (mm <sup>3</sup> )	0.40 × 0.40 × 0.05	0.52 × 0.38 × 0.042
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	6.87	6.65
Radiation (monochromated in incident beam) (Å)	Mo K $\alpha$ ( $\lambda = 0.71069$ )	Mo K $\alpha$ ( $\lambda = 0.71069$ )
Diffractometer	Rigaku AFC5R	Enraf–Nonius CAD4
Temperature (°C)	23	23
Orientation reflections number; range ( $2\theta$ )	25; 11.02–21.31°	25; 13–15.50°
Scan method	$2\theta - \omega$	$2\theta - \omega$
Data coll. range, $2\theta$ (deg)	0–50	0–51.9
No. of unique data, total	3555	3843
with $I > 3\sigma(I)$	1030	2614
No. of parameter refined	235	244
Correction factors, max. min.	1.3658, 0.7872	1.2402, 0.7886
$R^a$	0.059	0.050
$R_w^b$	0.065	0.056
Quality-of-fit indicator <sup>c</sup>	1.28	1.24
Largest shift/esd. final cycle	0.05	0.01
Largest peak, e Å <sup>-3</sup>	0.32	0.31

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$ ;  $w = 1/\sigma^2(|F_o|)$ . <sup>c</sup> Quality-of-fit =  $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$ .

Table 2  
Positional parameters and their estimated standard deviations<sup>a</sup> for **2** and **3**

Atom	<b>2</b>				<b>3</b>			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
Mn	0.3711(2)	0.1751(3)	0.2847(1)	2.37(9)	0.24144(8)	0.22166(6)	0.89730(6)	2.45(2)
O(1)	0.422(1)	0.468(1)	0.2765(6)	5.0(6)	0.1769(4)	0.4391(3)	1.0492(3)	4.5(1)
O(2)	0.541(1)	0.090(1)	0.1968(7)	6.8(7)	−0.0879(4)	0.0671(3)	0.8601(3)	5.5(1)
O(3)	0.2327(8)	0.2065(9)	0.1134(5)	3.1(5)	0.0324(4)	0.2933(3)	0.6793(3)	3.6(1)
C(1)	0.398(1)	0.352(2)	0.2776(8)	3.4(8)	0.1966(5)	0.3543(4)	0.9846(4)	3.0(1)
C(2)	0.475(1)	0.124(2)	0.235(1)	4.3(9)	0.0433(5)	0.1265(4)	0.8764(4)	3.2(2)
C(3)	0.269(1)	0.134(1)	0.1821(8)	2.3(6)	0.1595(5)	0.2442(4)	0.7318(4)	2.7(1)
C(4)	0.263(1)	0.353(1)	0.110(1)	3.9(8)	−0.0583(6)	0.3606(5)	0.7533(4)	4.6(2)
C(5)	0.194(2)	0.401(2)	0.025(1)	7(1)	−0.1987(7)	0.3908(6)	0.6628(5)	6.8(3)
C(11)	0.358(1)	0.279(1)	0.4345(8)	3.0(7)	0.5258(5)	0.2989(4)	1.0955(4)	3.2(1)
C(12)	0.262(1)	0.236(2)	0.3662(9)	3.2(7)	0.3839(5)	0.1919(4)	1.0839(4)	3.3(2)
C(13)	0.248(1)	0.098(2)	0.3452(9)	3.4(8)	0.3543(5)	0.0882(4)	0.9904(4)	3.7(2)
C(14)	0.344(2)	0.010(1)	0.363(1)	3.5(7)	0.4055(5)	0.0942(4)	0.8801(4)	3.6(2)
C(15)	0.454(1)	0.073(2)	0.396(1)	4.0(8)	0.4799(5)	0.2111(5)	0.8675(4)	3.5(2)
C(16)	0.462(1)	0.209(1)	0.4159(8)	2.5(7)	0.5042(5)	0.3143(4)	0.9603(4)	3.2(2)
C(21)	0.348(1)	0.248(2)	0.5182(8)	2.9(7)	0.6938(5)	0.2777(4)	1.1599(4)	3.1(1)
C(22)	0.424(1)	0.308(2)	0.590(1)	3.8(7)	0.7383(6)	0.2637(5)	1.2913(4)	4.3(2)
C(23)	0.393(1)	0.250(2)	0.6569(9)	4.4(8)	0.8968(6)	0.2463(5)	1.3213(5)	4.9(2)
C(24)	0.298(1)	0.154(2)	0.630(1)	4.4(8)	0.9613(6)	0.2446(5)	1.2117(5)	5.3(2)
C(25)	0.273(1)	0.158(2)	0.5395(8)	4.0(8)	0.8228(6)	0.2662(5)	1.1136(4)	4.4(2)
C(31)	0.211(1)	−0.006(2)	0.1617(8)	2.6(7)	0.2219(5)	0.1943(4)	0.6230(4)	2.8(1)
C(32)	0.095(1)	−0.013(2)	0.1199(9)	4.1(8)	0.2012(6)	0.0670(4)	0.5815(4)	3.9(2)
C(33)	0.043(2)	−0.141(2)	0.104(1)	5(1)	0.2586(7)	0.0210(5)	0.4803(5)	5.3(2)
C(34)	0.105(2)	−0.261(2)	0.121(1)	6(1)	0.3391(7)	0.1005(6)	0.4215(5)	5.5(2)
C(35)	0.219(2)	−0.258(2)	0.161(1)	5(1)	0.3599(6)	0.2263(6)	0.4615(5)	4.9(2)
C(36)	0.272(1)	−0.129(2)	0.1810(8)	3.6(8)	0.3043(5)	0.2769(4)	0.5618(4)	3.5(2)
C(37)					0.3303(7)	0.4154(5)	0.6043(5)	5.8(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $(4/3)[a^2B(1, 1) + b^2B(2, 2) + c^2B(3, 3) + ab(\cos \gamma)B(1, 2) + ac(\cos \beta)B(1, 3) + bc(\cos \alpha)B(2, 3)]$ .

by alkylation; further treatment as described for preparation of **2** gave 0.22 g (77%, based on **1**) of orange-red crystals of **5**, m.p. 46–48°C (dec.). IR ( $\nu_{\text{CO}}$ ): (hexane) 1959vs, 1903vs  $\text{cm}^{-1}$ . MS: *m/e* 402 ( $\text{M}^+$ ), 374 ( $\text{M}^+$ –

CO), 346 ( $\text{M}^+$ –2CO), 301 ( $\text{M}^+$ –2CO–OC<sub>2</sub>H<sub>5</sub>), 198 ( $\text{M}^+$ –2CO–C(OC<sub>2</sub>H<sub>5</sub>)C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 143 (C<sub>5</sub>H<sub>5</sub>C<sub>6</sub>H<sub>6</sub>)<sup>+</sup>. Anal. Found: C, 68.60; H, 5.62. C<sub>23</sub>H<sub>23</sub>MnO<sub>3</sub>. Calc.: C, 68.66; H, 5.76%.

Table 3  
Bond lengths (Å)<sup>a</sup> for complexes **2** and **3**

	<b>2</b>	<b>3</b>		<b>2</b>	<b>3</b>
Mn–C(2)	1.74(2)	1.775(4)	C(12)–C(13)	1.38(2)	1.376(6)
Mn–C(1)	1.75(1)	1.777(5)	C(13)–C(14)	1.39(2)	1.396(6)
Mn–C(3)	1.89(1)	1.881(4)	C(14)–C(15)	1.41(2)	1.386(6)
Mn–C(15)	2.13(1)	2.131(4)	C(15)–C(16)	1.36(2)	1.373(6)
Mn–C(14)	2.15(1)	2.147(4)	C(21)–C(25)	1.36(2)	1.321(6)
Mn–C(13)	2.13(1)	2.150(4)	C(21)–C(22)	1.44(2)	1.460(6)
Mn–C(16)	2.24(1)	2.196(4)	C(22)–C(23)	1.41(2)	1.357(7)
Mn–C(12)	2.21(2)	2.249(4)	C(23)–C(24)	1.43(2)	1.441(7)
O(1)–C(1)	1.16(1)	1.152(5)	C(24)–C(25)	1.50(2)	1.485(7)
O(2)–C(2)	1.19(2)	1.155(5)	C(31)–C(32)	1.38(2)	1.385(6)
O(3)–C(3)	1.34(1)	1.337(4)	C(31)–C(36)	1.38(2)	1.406(6)
O(3)–C(4)	1.46(1)	1.449(5)	C(32)–C(33)	1.38(2)	1.383(6)
C(3)–C(31)	1.51(2)	1.491(5)	C(33)–C(34)	1.35(2)	1.358(7)
C(4)–C(5)	1.54(2)	1.489(6)	C(34)–C(35)	1.34(2)	1.367(7)
C(11)–C(16)	1.51(2)	1.510(6)	C(35)–C(36)	1.40(2)	1.381(7)
C(11)–C(21)	1.49(2)	1.510(6)	C(36)–C(37)		1.499(7)
C(11)–C(12)	1.46(2)	1.512(6)			

<sup>a</sup> Estimated standard deviations in the least significant figure are given in parentheses.

### 2.5. Preparation of $[C_5H_5\{(\eta^5-C_6H_6)(CO)_2Mn=C(OC_2H_5)C_6H_4OCH_3-p\}]$ (6)

A solution of 0.30 g (1.60 mmol) of  $p\text{-CH}_3\text{OC}_6\text{H}_4\text{Br}$  in 15 ml of ether was mixed with 1.6 mmol of  $n\text{-C}_4\text{H}_9\text{Li}$  [21]. After 30 min stirring at room temperature, the resulting ether solution of  $p\text{-CH}_3\text{OC}_6\text{H}_4\text{Li}$  [22] was allowed to react, as described for the preparation of **2**, with 0.20 g (0.71 mmol) of **1** at  $-60$  to  $-40^\circ\text{C}$  for 4 h to afford 0.22 g (74%, based on **1**) of **6** as orange-red crystals, m.p.  $54\text{--}56^\circ\text{C}$ . IR ( $\nu_{\text{CO}}$ ): (hexane)  $1952\text{vs}$ ,  $1895\text{vs cm}^{-1}$ . MS:  $m/e$  418 ( $M^+$ ), 390 ( $M^+-\text{CO}$ ), 362 ( $M^+-2\text{CO}$ ), 317 ( $M^+-2\text{CO}-\text{OC}_2\text{H}_5$ ), 198 ( $M^+-2\text{CO}-\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{OCH}_3$ ), 143 ( $C_5H_5C_6H_6$ ) $^+$ . Anal. Found: C, 65.85; H, 5.36.  $C_{23}H_{23}MnO_4$ . Calc.: C, 66.03; H, 5.54%.

### 2.6. Preparation of $[C_5H_5\{(\eta^5-C_6H_6)(CO)_2Mn=C(OC_2H_5)C_6H_4CF_3-p\}]$ (7)

A solution of 1.5 mmol of  $n\text{-C}_4\text{H}_9\text{Li}$  was added to a solution of 0.32 g (1.42 mmol) of  $p\text{-CF}_3\text{C}_6\text{H}_4\text{Br}$  in 15

ml of ether at  $0^\circ\text{C}$  with stirring. After 30 min of stirring at room temperature, the resulting ether solution of  $p\text{-CF}_3\text{C}_6\text{H}_4\text{Li}$  [23] was reacted, in a manner similar to that described in preparation of **2**, with 0.20 g (0.71 mmol) of **1** in 40 ml of ether at  $-60$  to  $-40^\circ\text{C}$  for 3.5 h. Subsequent alkylation and further treatment similar to the procedures described for preparation of **2** gave 0.25 g (77%, based on **1**) of orange-red crystals of **7**, m.p.  $52\text{--}54^\circ\text{C}$  (dec.). IR ( $\nu_{\text{CO}}$ ): (hexane)  $1962\text{vs}$ ,  $1908\text{vs cm}^{-1}$ . MS:  $m/e$  456 ( $M^+$ ), 428 ( $M^+-\text{CO}$ ), 400 ( $M^+-2\text{CO}$ ), 355 ( $M^+-2\text{CO}-\text{OC}_2\text{H}_5$ ), 198 ( $M^+-2\text{CO}-\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CF}_3$ ), 143 ( $C_5H_5C_6H_6$ ) $^+$ . Anal. Found: C, 60.33; H, 4.51.  $C_{23}H_{20}F_3MnO_3$ . Calc.: C, 60.54; H, 4.42%.

### 2.7. X-ray crystal structure determinations of complexes **2** and **3**

The single crystals of complexes **2** and **3** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether- $\text{CH}_2\text{Cl}_2$  solution at  $-80^\circ\text{C}$ .

Table 4  
Bond angles (deg)<sup>a</sup> for complexes **2** and **3**

	2	3		2	3
C(1)–Mn–C(3)	103.2(6)	100.6(2)	C(14)–C(13)–Mn	71.7(8)	71.0(2)
C(1)–Mn–C(15)	117.7(7)	123.9(2)	C(15)–C(14)–Mn	70.0(8)	70.5(2)
C(1)–Mn–C(14)	145.8(6)	148.8(2)	C(13)–C(14)–Mn	70.4(8)	71.1(2)
C(1)–Mn–C(13)	122.5(7)	121.2(2)	C(16)–C(15)–Mn	76(1)	74.1(2)
C(1)–Mn–C(16)	82.9(6)	87.7(2)	C(14)–C(15)–Mn	71.4(8)	71.7(3)
C(1)–Mn–C(12)	86.0(6)	86.0(2)	C(15)–C(16)–Mn	67.7(9)	68.9(2)
C(2)–Mn–C(1)	94.6(7)	94.7(2)	C(11)–C(16)–Mn	93.7(8)	95.5(2)
C(2)–Mn–C(3)	82.1(6)	85.5(2)	C(3)–O(3)–C(4)	121(1)	122.4(3)
C(2)–Mn–C(15)	94.2(7)	141.0(2)	O(3)–C(3)–C(31)	104(1)	103.7(3)
C(2)–Mn–C(14)	108.9(7)	105.4(2)	O(3)–C(4)–C(5)	105(1)	107.0(4)
C(2)–Mn–C(13)	142.9(8)	89.5(2)	C(16)–C(11)–C(21)	113(1)	115.5(4)
C(2)–Mn–C(16)	107.7(6)	166.0(2)	C(16)–C(11)–C(12)	103(1)	101.7(3)
C(2)–Mn–C(12)	170.5(6)	102.7(2)	C(21)–C(11)–C(12)	117(1)	114.2(3)
C(3)–Mn–C(15)	139.1(7)	92.1(2)	C(13)–C(12)–C(11)	119(1)	119.8(4)
C(3)–Mn–C(14)	104.4(6)	104.4(2)	C(12)–C(13)–C(14)	120(1)	121.5(4)
C(3)–Mn–C(13)	90.8(6)	138.3(2)	C(15)–C(14)–C(13)	116(1)	116.3(4)
C(3)–Mn–C(16)	168.2(5)	107.7(2)	C(16)–C(15)–C(14)	121(1)	121.4(4)
C(3)–Mn–C(12)	107.1(5)	169.1(2)	C(15)–C(16)–C(11)	118(1)	119.5(4)
C(15)–Mn–C(14)	38.5(5)	37.8(2)	C(25)–C(21)–C(22)	110(1)	107.7(4)
C(15)–Mn–C(13)	68.0(6)	67.0(2)	C(25)–C(21)–C(11)	127(1)	129.2(4)
C(15)–Mn–C(16)	36.1(5)	37.0(2)	C(22)–C(21)–C(11)	123(1)	123.0(4)
C(15)–Mn–C(12)	77.2(6)	77.1(2)	C(23)–C(22)–C(21)	106(1)	109.0(4)
C(14)–Mn–C(13)	38.0(5)	37.9(2)	C(22)–C(23)–C(24)	111(1)	109.1(4)
C(14)–Mn–C(16)	66.7(5)	67.3(2)	C(23)–C(24)–C(25)	103(1)	103.9(4)
C(14)–Mn–C(12)	66.8(6)	66.7(2)	C(21)–C(25)–C(24)	109(1)	110.3(4)
C(13)–Mn–C(16)	77.5(5)	77.5(2)	C(32)–C(31)–C(36)	118(1)	119.1(4)
C(13)–Mn–C(12)	37.1(5)	36.4(2)	C(32)–C(31)–C(3)	120(1)	120.9(4)
C(16)–Mn–C(12)	62.9(5)	63.6(1)	C(36)–C(31)–C(3)	123(1)	120.0(4)
O(1)–C(1)–Mn	176(1)	174.6(4)	C(33)–C(32)–C(31)	119(2)	120.8(5)
O(2)–C(2)–Mn	176(1)	177.7(4)	C(34)–C(33)–C(32)	122(2)	120.2(5)
O(3)–C(3)–Mn	133(1)	132.2(3)	C(33)–C(34)–C(35)	120(2)	119.4(5)
C(31)–C(3)–Mn	123(1)	123.8(3)	C(34)–C(35)–C(36)	118(2)	122.6(5)
C(13)–C(12)–Mn	68(1)	67.9(2)	C(35)–C(36)–C(31)	122(1)	117.8(5)
C(11)–C(12)–Mn	96(1)	93.4(2)	C(35)–C(36)–C(37)		121.4(4)
C(12)–C(13)–Mn	75(1)	75.7(2)	C(31)–C(36)–C(37)		120.8(4)

<sup>a</sup> Estimated standard deviations in the least significant figure are given in parentheses.

Single crystals of approximate dimensions  $0.40 \times 0.40 \times 0.05$  mm for **2** and  $0.52 \times 0.38 \times 0.042$  mm for **3** were sealed in capillaries under an  $N_2$  atmosphere. The X-ray diffraction intensity data for 3555 and 3843 independent reflections, of which 1030 and 2614 with  $I > 3\sigma$  ( $I$ ) were observable, were collected with a Rigaku AFC5R diffractometer and an Enraf–Nonius CAD4 diffractometer at  $23^\circ C$  using Mo  $K\alpha$  radiation with a  $2\theta$ – $\omega$  scan mode within the range  $0$ – $50$  and  $0$ – $51.9^\circ$  for **2** and **3** respectively. The intensity data were corrected for Lorentz and polarization factors. An empirical absorption correction was applied to the data for **2** and **3**.

For **2**, the position of the Mn atom was solved by the direct method and those of the rest of the non-hydrogen atoms were found by a few cycles of the Fourier synthesis. The structure was refined with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms were added from the geometry and they were included in the final structure factor computation, but were not refined. Final refinement converged to  $R = 0.059$  and  $R_w = 0.065$ . All the calculations were performed on a Micro-VAX II computer using TEXSAN.

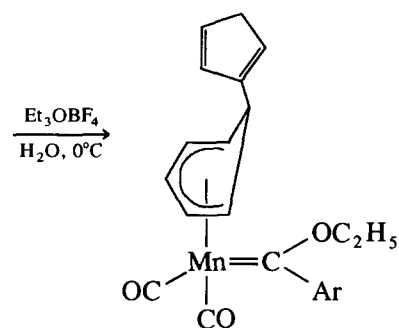
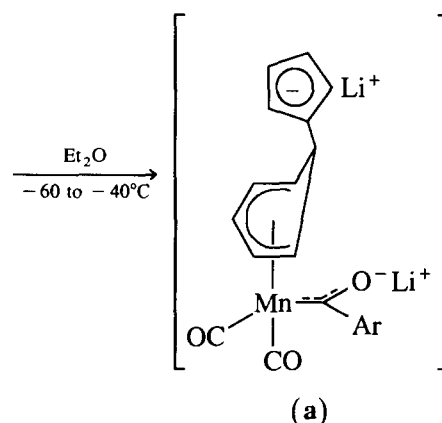
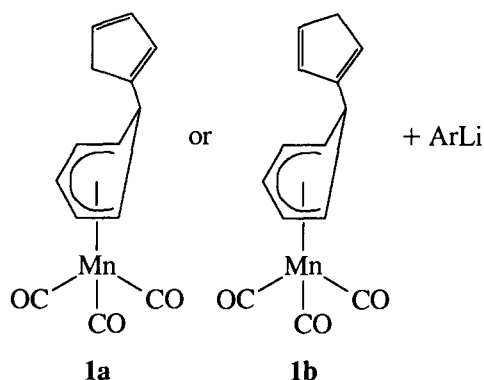
For **3**, most of the non-hydrogen atoms in the structure were solved by the direct method, giving a partial structure, which was then used to locate the rest of the non-hydrogen atoms by the difference Fourier method. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were found from the difference Fourier maps and refined. Final refinement converged to  $R = 0.050$  and  $R_w = 0.056$ . All the calculations were performed on a Micro-VAX 3100 computer using TEXSAN.

The details of the crystallographic data and the procedures used for data collection and reduction information for **2** and **3** are given in Table 1. The positional parameters and temperature factors of non-hydrogen atoms for **2** and **3** are presented in Table 2. The bond lengths and angles for **2** and **3** are listed in Tables 3 and 4, respectively.

### 3. Results and discussion

One mole of tricarbonyl(*exo*-cyclopentadienyl- $\eta^5$ -cyclohexadienyl)manganese (**1**) was reacted with two molar equivalents of aryllithium reagents, ArLi (Ar =  $C_6H_5$ , *o*-, *m*-, *p*- $CH_3C_6H_4$ , *p*- $CH_3OC_6H_4$ , *p*- $CF_3C_6H_4$ ), in ether at  $-60$  to  $-40^\circ C$  for 3.5 to 4 h, and the acylmetalate intermediates obtained were subsequently alkylated with  $Et_3OBF_4$  in an aqueous solution at  $0^\circ C$ . After removal of the solvents under vacuum at low temperature, the residue was chromatographed on an alumina column at  $-20^\circ C$ , and the crude product was recrystallized from petroleum ether– $CH_2Cl_2$  solution at  $-80^\circ C$  to give orange-red crystalline complexes

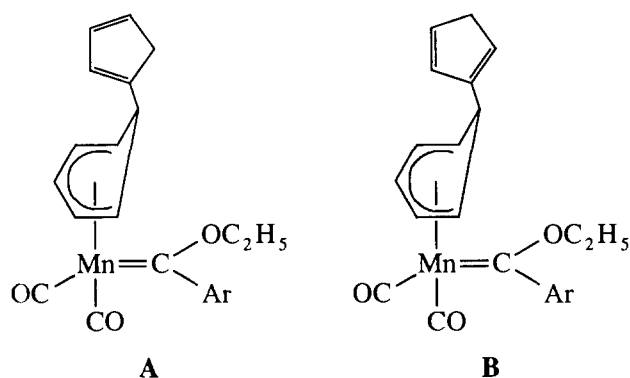
**2**–**7** with general composition  $[C_5H_5\text{--}(\eta^5\text{--}C_6H_6)(CO)_2\text{--}Mn=C(OC_2H_5)Ar]$  (Eq. (5)) in 70–81% yields.



- 2**, Ar =  $C_6H_5$ ; **3**, Ar = *o*- $CH_3C_6H_4$ ;  
**4**, Ar = *m*- $CH_3C_6H_4$ ; **5**, Ar = *p*- $CH_3C_6H_4$ ;  
**6**, Ar = *p*- $CH_3OC_6H_4$ ; **7**, Ar = *p*- $CF_3C_6H_4$                       (5)

The elemental analyses and mass spectra confirm the compositions of complexes **2**–**7**, and the X-ray diffraction studies for complexes **2** and **3** establish their structures as that shown in Eq. (5). Complexes **2**–**7** are formulated as (cyclopentadienyl- $\eta^5$ -cyclohexadienyl)-(dicarbonyl)[ethoxy(aryl)carbene]manganese complexes. Complexes **4**–**7** are assigned similar structures since their spectra data are similar to those of **2** and **3**. When one mole of aryllithium reagents, instead of two, was used for the reaction under the same conditions, the same products **2**–**7** were obtained in lower yields (35–40%). This suggested that the reaction pathway (Eq. (5)) could proceed via an intermediate (a) in which one

of the carbonyl ligands was converted into an acylmetalate by attack of one molecule of aryllithium nucleophiles on it, while the cyclopentadienyl was formed by a cyclopentadienyl anion attack of another molecule of aryllithium on it by replacing an active hydrogen atom on the saturated carbon of the ring with the lithium atom. Upon subsequent alkylation of intermediate (a) with  $\text{Et}_3\text{OBF}_4$  in aqueous solution, the acylmetalate moiety converted into a carbene ligand and the cyclopentadienyl anion moiety returned to or converted into a 1,3-cyclopentadienyl which is 2-positioned attached to the  $\eta^5$ -cyclohexadienyl moiety, resulting in the formation of complexes 2–7. However, when more than three molar equivalents of aryllithium reagents were used for the reaction with **1** under the same conditions this led to decomposition.



Starting material **1**, prepared by the reaction of  $(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3^+$  cation with NaCp, is a mixture of two types of structure, **1a** and **1b** [17]. In structure **1a**

the 1,3-cyclopentadienyl is bonded through its 1-position carbon atom to the  $\eta^5$ -cyclohexadienyl moiety, while in structure **1b** the 1,3-cyclopentadienyl is bonded through its 2-position carbon atom to that. Hence, there could exist two isomers, as shown in structures **A** and **B**, in the resulting products produced by the reaction of **1** (**1a** and **1b**) with aryllithium reagents. In contrast, only the isomer product of structure **B** was isolated, even though only one molar equivalent of aryllithium was used for the reaction. This may be explained by reaction of **1a** or **1b** with aryllithium reagent to produce the same intermediate (a); the resulting product of structure type **B** is formed, in which the 1,3-cyclopentadienyl is 2-positioned attached to the  $\eta^5$ -cyclohexadienyl moiety; this is more stable than that of structure type **A** in which the 1,3-cyclopentadienyl is 1-positioned attached to the  $\eta^5$ -cyclohexadienyl moiety.

Complexes 2–7 are readily soluble in polar organic solvents but slightly soluble in non-polar solvents. They are very sensitive to air and temperature in solution, but stable for a short period on exposure to air at room temperature in crystalline states. The complexes were satisfactorily characterized by the IR,  $^1\text{H}$  NMR, and mass spectra. The IR spectra (Experimental) of complexes 2–7 exhibit two  $\nu(\text{CO})$  bands at 1895–1962  $\text{cm}^{-1}$  which indicate the presence of two carbonyl ligands in these complexes. In the  $^1\text{H}$  NMR spectra of 2–7 (Table 5), a triplet (ca. 1.54 ppm) and a quartet (ca. 4.67 ppm), and a set of multiplet (ca. 7.00–7.70 ppm) resonances were observed from each of the complexes, which showed characteristically the presence of the ethoxy and aryl groups. From the  $^1\text{H}$  NMR spectra, it is

Table 5  
 $^1\text{H}$  NMR spectra of complexes 2–7 in acetone- $d_6$  at 20°C <sup>a</sup>

Complex	$\delta$ (cyclo-olefin-proton)	$\delta$ (aryl-proton)	$\delta$ ( $\text{OCH}_2\text{CH}_3$ )
1	6.36(d, 1H), 6.32(d, 1H), 6.30(d, 1H), 6.20(d, 1H) 6.00(s, 1H), 5.80(t, 1H), 5.12(dd, 1H), 3.55(t, 1H) 3.30(t, 1H), 2.82(s, 1H), 2.72(s, 1H)		
2	6.35(d, 1H), 6.31(d, 1H), 6.15(d, 1H), 5.90(s, 1H) 5.70(d, 1H), 5.52(d, 1H), 5.10(dd, 1H), 3.55(t, 1H) 3.20(s, 1H), 2.70(s, 1H), 2.60(s, 1H)	7.25–7.45(m, 5H)	4.65(q, 2H) 1.45(t, 3H)
3	6.35(d, 1H), 6.32(d, 1H), 6.18(d, 1H), 5.90(s, 1H) 5.70(d, 1H), 5.65(d, 1H), 5.11(dd, 1H), 3.46(t, 1H) 3.30(s, 1H), 2.77(s, 1H), 2.64(s, 1H)	7.00–7.40(m, 4H) 2.37(s, 3H)	4.60(q, 2H) 1.44(t, 3H)
4	6.34(d, 1H), 6.30(d, 1H), 6.16(d, 1H), 5.90(s, 1H) 5.71(d, 1H), 5.64(d, 1H), 5.10(dd, 1H), 3.54(t, 1H) 3.32(s, 1H), 2.76(s, 1H), 2.67(s, 1H)	7.10–7.32(m, 4H) 2.36(s, 3H)	4.65(q, 2H) 1.58(t, 3H)
5	6.35(d, 1H), 6.28(d, 1H), 6.17(d, 1H), 5.88(s, 1H) 5.72(d, 1H), 5.62(d, 1H), 5.14(dd, 1H), 3.57(t, 3H) 3.31(s, 1H), 2.78(s, 1H), 2.68(s, 1H)	7.34(m, 2H) 7.20(m, 2H) 2.35(s, 3H)	4.67(q, 2H) 1.57(t, 3H)
6	6.34(d, 1H), 6.30(d, 1H), 6.15(d, 1H), 5.89(s, 1H) 5.70(d, 1H), 5.63(d, 1H), 5.14(dd, 1H), 3.60(t, 1H) 3.32(s, 1H), 2.77(s, 1H), 2.67(s, 1H)	7.70(m, 2H) 6.94(m, 2H) 3.88(s, 3H)	4.70(q, 2H) 1.60(t, 3H)
7	6.36(d, 1H), 6.33(d, 1H), 6.18(d, 1H), 5.90(s, 1H) 5.75(d, 1H), 5.62(d, 1H), 5.15(dd, 1H), 3.60(t, 1H) 3.32(s, 1H), 2.80(s, 1H), 2.70(s, 1H)	7.75(m, 2H) 7.44(m, 2H)	4.78(q, 2H) 1.61(t, 3H)

<sup>a</sup> TMS as the internal reference.

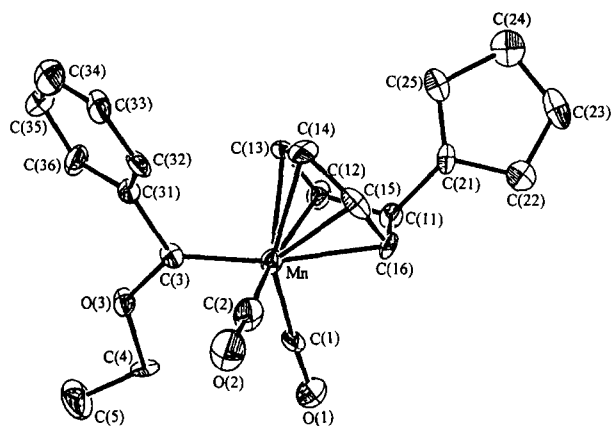


Fig. 1. Molecular structure of **2** showing the atom labeling scheme.

noted that the chemical shift, multiplicity and integral intensity of the proton signals attributed to the cyclopentadienyl- $\eta^5$ -cyclohexadienyl ligand in complexes **2–7** are principally similar to those in starting material **1** (see Table 5); this demonstrates that no isomerization of the cyclo-olefin ligand occurred, except the cyclopentadienyl ring from 1-positioned bonding to the  $\eta^5$ -cyclohexadienyl moiety in **1a** converted into 2-positioned bonding to that in complexes **2–7**, and the added ethoxy and aryl substituents exert no significant influence on the proton signals of the cyclo-olefin ligand.

The mass spectra of complexes **2–7**, given in the Experimental section, show expected molecular ion peaks and the principal fragments produced by successive loss of CO ligands and carbene ligand and the featured ion peak from the fragments generated by further cleavage of these principal fragments.

The molecular structures of **2** and **3** established by the X-ray diffraction studies are shown in Figs. 1 and 2 respectively. Both complexes have nearly the same structures, as illustrated by following parameters. The

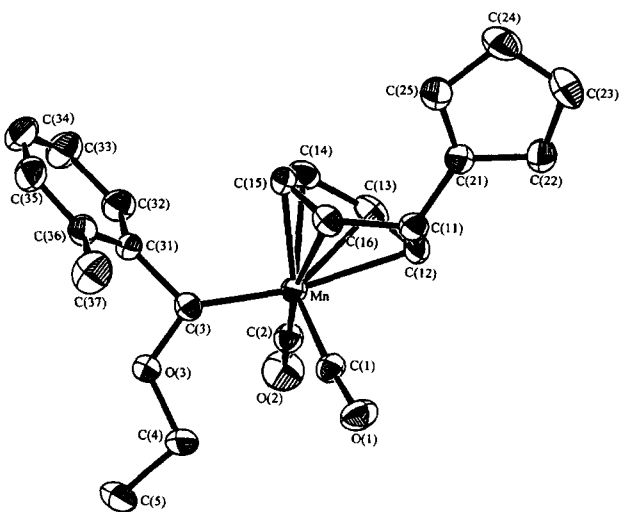


Fig. 2. Molecular structure of **3** showing the atom labeling scheme.

Mn–C(3) distances are 1.89(1) and 1.881(4) Å for **2** and **3** respectively, which signifies a high double bond character, and are slightly longer than that in the analogous carbene complex  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{MnC}(\text{OEt})\text{Ph}]$  (1.865(14) Å) [24]. The sum of the three bond angles around the C(3) atom in both structures (Mn–C(3)–O(3) of 133(1) and 132.2(3)°, Mn–C(3)–C(31) of 123(1) and 123.8(3)°, and O(3)–C(3)–C(31) of 104(1) and 103.7(3)° for **2** and **3** respectively) is almost exactly 360°, which demonstrates that these atoms are coplanar. The C(3)–O(3) bond lengths of 1.34(1) and 1.337(4) Å in **2** and **3** respectively, are essentially comparable with that found in  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{MnC}(\text{OEt})\text{Ph}]$  (1.356(17) Å) [24],  $[\text{C}_6\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}o]$  (1.34(2) Å) [15], and  $[(\eta^4\text{-C}_{10}\text{H}_{16})(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}o]$  (1.324(17) Å) [8], which shows the partial delocalization of the  $\pi$ -electron on the O(3) atom owing to the effect of the Mn–C(3)  $\pi$  bond. The average Mn–C(CO) distances are 1.745 and 1.776 Å for **2** and **3** respectively, which are slightly shorter than that found (average 1.80 Å) in  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{MnC}(\text{OEt})\text{Ph}]$  [24]. The  $\eta^5$ -dienyl carbon atoms C(12), C(13), C(14), C(15), and C(16) define a nearly perfect plane with a deviation of 0.015 Å for **2**, and of 0.010 Å for **3**. The C(11) atom is somewhat bent away from this dienyl ring plane at a distance of 0.6313 Å in **2**, and of 0.6109 Å in **3**. The manganese atom is located (1.7042 Å for **2**, 1.7019 Å for **3**) below plane of the  $\eta^5$ -dienyl ring. The average distances of the Mn atom to the  $\eta^5$ -dienyl ring carbon atoms C(12), C(13), C(14), C(15), and C(16) are 2.172 and 2.175 Å for **2** and **3** respectively, which are very closely to that of the Mn atom to the  $\eta^5$ -cyclopentadienyl ring carbon atoms in  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{MnC}(\text{OEt})\text{Ph}]$  (2.169 Å) [24]. The average C–C bond length (1.385 Å) of the  $\eta^5$ -dienyl ring moiety in **2** is essentially the same as that (1.379 Å) in **3**. The cyclopentadienyl ring moiety is positioned exo, as expected, and the average C–C bond lengths (1.403 and 1.373 Å) of the dienyl ring moiety differ by ca. 0.03 Å for both complexes.

It is of interest to note the steric configuration and conformation in the structure of the carbene complexes. In structures **2** and **3**, the  $\eta^5$ -dienyl plane defined by C(12)–through–C(16) is respectively oriented at an angle of 86.21 and 91.25° with respect to the cyclopentadienyl ring plane defined by C(21)–through–C(25); thus the cyclopentadienyl ring and  $\eta^5$ -dienyl ring planes are almost perpendicular to each other. The angles between the benzene ring C(31)C(32)C(33)C(34)C(35)C(36) and the cyclopentadienyl ring C(21)C(22)C(23)C(24)C(25) plane are 73.81 and 81.22° for **2** and **3** respectively; thus the benzene ring and cyclopentadienyl ring planes are also nearly perpendicular to each other. While the angles between the benzene ring and  $\eta^5$ -dienyl ring C(12)C(13)C(14)C(15)C(16) plane are 12.49 and 15.17° for **2** and **3** respectively, the benzene ring plane is



nearly parallel to the  $\eta^5$ -dienyl ring plane. It is worth noting that, since the  $\pi$ -bond interactions between the carbene carbon and organic substituents, there exist *Z/E* isomers in the carbene ligand which depend mainly on the steric factors [25]. In both structures, the ethoxy group adopts a *Z* conformation owing to great steric hindrance of the aryl group, as can be visualized in the ORTEP diagram of **2** and **3** represented in Figs. 1 and 2. The bond angles of Mn–C(3)–O(3), 133(1) and 132.2(3)° for **2** and **3** respectively, provide further evidence for the *Z* conformation [25].

The carbene complexes of manganese are rare. To our knowledge, only one analogous ( $\eta^5$ -cyclohexadienyl)manganese carbene complex has been reported [26]. Furthermore, its crystal structure determination is not reported.

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