Remarkable Nucleophilic Addition to and Ring Breaking of the Cycloheptatrienyl Ligand in Reactions of [μ-(1−3-η):(4−7-η)-Cycloheptatrienyl]tricarbonylirontricarbonylmanganese and -rhenium with Aryllithium Reagents

Nu Xiao,[†] Shu Zhang,[†] Zhilei Qiu,[†] Ronghua Li,[†] Beihan Wang, Qiang Xu,*,[‡] Jie Sun,[†] and Jiabi Chen*,[†]

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China, and National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

The reactions of [μ-(1−3-η):(4−7-η)-cycloheptatrienyl]tricarbonylirontricarbonylmanganese, [MnFe{μ-(1−3-η):(4−7-η)-C$_7$H$_7$}(CO)$_6$] (**1**) with 2 molar equiv of aryllithium reagent, ArLi (Ar = C$_6$H$_5$, *o*-, *m*-, *p*-CH$_3$C$_6$H$_4$), in ether at low temperature gave acylmetalate intermediates, followed by alkylation with Et$_3$OBF$_4$ in aqueous solution at 0 °C to afford the four novel ring-opened olefin-coordinated tricarbonylirontricarbonylmanganese complexes [MnFe{C$_8$H$_7$-(OC$_2$H$_5$)Ar}(CO)$_6$] (**3**, Ar = C$_6$H$_5$; **4**, Ar = *o*-CH$_3$C$_6$H$_4$; **5**, Ar = *m*-CH$_3$C$_6$H$_4$; **6**, Ar = *p*-CH$_3$C$_6$H$_4$). Analogous reactions of [μ-(1−3-η):(4−7-η)-cycloheptatrienyl]tricarbonylirontricarbonylrhenium, [ReFe{μ-(1−3-η):(4−7-η)-C$_7$H$_7$)}(CO)$_6$] (**2**), with ArLi (Ar = C$_6$H$_5$, *o*-, *m*-CH$_3$C$_6$H$_4$, *p*-CF$_3$C$_6$H$_4$) gave the corresponding products [ReFe{C$_8$H$_7$(OC$_2$H$_5$)Ar}(CO)$_6$] (**7**, Ar = C$_6$H$_5$; **8**, Ar = *o*-CH$_3$C$_6$H$_4$; **9**, Ar = *m*-CH$_3$C$_6$H$_4$; **10**, Ar = *p*-CF$_3$C$_6$H$_4$). The structures of **4** and **10** have been established by single-crystal X-ray diffraction studies.

Introduction

The synthesis, structure, and chemistry of alkene–metal carbene complexes is an area of current interest. In recent years, olefin-coordinated transition-metal carbene and carbyne complexes and/or their isomerized products, as part of a broader investigation of transition-metal carbene and carbyne complexes, have been examined extensively in our laboratory. In previous studies, we have shown[1,2] that a considerable number of the novel olefin-coordinated transition-metal carbene complexes and/or their isomerized products were isolated and several novel isomerizations of olefin ligands have been observed by the reactions of olefin-ligated metal carbonyls with aryllithium nucleophiles, followed by alkylation with Et$_3$OBF$_4$. We found that the isomerizations of the olefin ligands and the resulting products depend not only on the structures and sorts of the olefin ligands but also on the central metals.[1b,2a,3−5] In continuation of our interest in developing the methodologies of the synthesis of olefin-coordinated metal carbene and carbyne complexes, we have carried out the study of the reactions of cycloolefin-ligated di- and trimetal carbonyl compounds with aryllithium reagents followed by alkylation with alkylating reagents, resulting in the formation of novel dimetal bridging carbene and bridging carbyne complexes or their isomerized products. For instance, the reactions of (cyclooctatetraene)diiron hexacarbonyl, C$_8$H$_8$[Fe(CO)$_3$]$_2$, where the two iron atoms are not directly bonded to each other and the two Fe(CO)$_3$ units are bonded to the two butadiene-like residues of the cyclooctatetraene ligand, with aryllithium reagents give the acyliron and (alkoxycarbene)iron complexes (eq 1),[6] while the reaction of pentacarbonyl(cyclooctatetraene)diiron, [C$_8$H$_8$Fe$_2$(CO)$_5$], where the two iron atoms are directly bonded to each other, with aryllithium reagents under analogous conditions produced the cyclooctatetraene-coordinated dimetal bridging carbene complexes (eq 2).[7]

In addition, bis(cycloheptatriene)tris(tricarbonyliron), [(C$_7$H$_8$)$_2${Fe(CO)$_3$}$_3$], where the two cycloheptatriene

† Shanghai Institute of Organic Chemistry.
‡ National Institute of Advanced Industrial Science and Technology.
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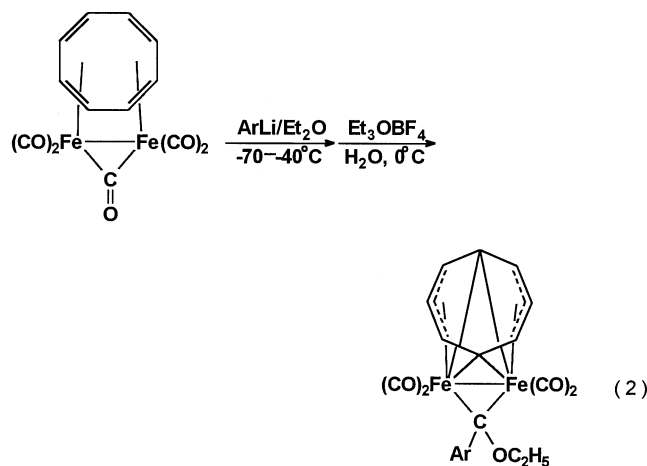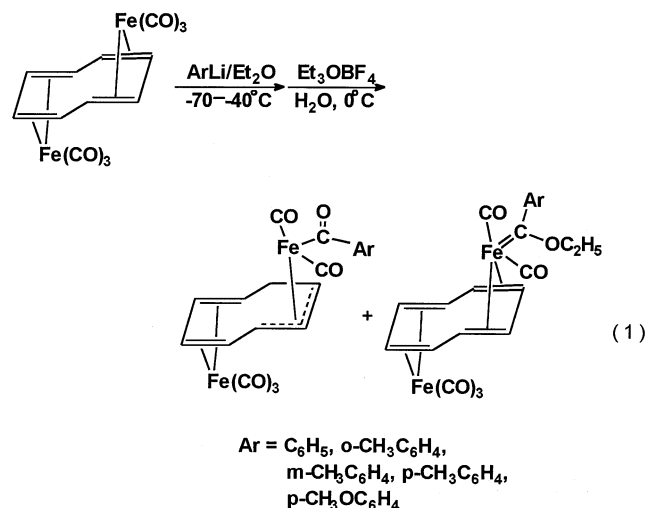
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$$Ar = C_6H_5, o\text{-}CH_3C_6H_4,$$
$$m\text{-}CH_3C_6H_4, p\text{-}CH_3C_6H_4,$$
$$p\text{-}CH_3OC_6H_4$$

(1)

(2)

$$R = H, o\text{-}CH_3, m\text{-}CH_3,$$
$$p\text{-}CH_3, p\text{-}CH_3O$$

(3)

(4)

ligands are independently η^4-bonded to the two $Fe(CO)_3$ units and each η^2-bonded to the third $Fe(CO)_3$ unit, reacted with aryllithium reagents at low temperature, which led to the coupling of the two cycloheptatriene ligands to afford the isomerized (bicycloheptatriene)bis-(tricarbonyliron)dicarbonyl[ethoxy(aryl)carbene]iron complexes (eq 3),[8] whereas the analogous reaction of the cycloheptatrienediiron hexacarbonyl, $[C_7H_8Fe_2(CO)_6]$, where the two iron atoms are directly bonded to each other, with aryllithium reagents gave the novel isomerized cycloolefin-coordinated dimetal bridging carbyne complexes (eq 4).[9]

To further investigate the effects of different dinuclear central metals on the isomerization of the cycloolefin ligand and the resulting products, we chose cycloheptatrienyl-ligated mixed-dimetal carbonyl compounds, $[\mu\text{-}(1{-}3\text{-}\eta)\text{:}(4{-}7\text{-}\eta)\text{-cycloheptatrienyl}]$tricarbonylirontricarbonylmanganese, $[MnFe\{\mu\text{-}(1{-}3\text{-}\eta)\text{:}(4{-}7\text{-}\eta)\text{-}C_7H_7\}(CO)_6]$ (**1**), and $[\mu\text{-}(1{-}3\text{-}\eta)\text{:}(4{-}7\text{-}\eta)\text{-cycloheptatrienyl}]$tricarbonylirontricarbonylrhenium, $[ReFe\{\mu\text{-}(1{-}3\text{-}\eta)\text{:}(4{-}7\text{-}\eta)\text{-}C_7H_7\}(CO)_6]$ (**2**), where the cycloheptatrienyl ligand is respectively η^3- and η^4-bonded to the $Fe(CO)_3$ and $Mn(CO)_3$ or $Re(CO)_3$ units and the Fe and Mn or Re atoms are directly bonded to each other, as the starting material for the reactions with aryllithium reagents in
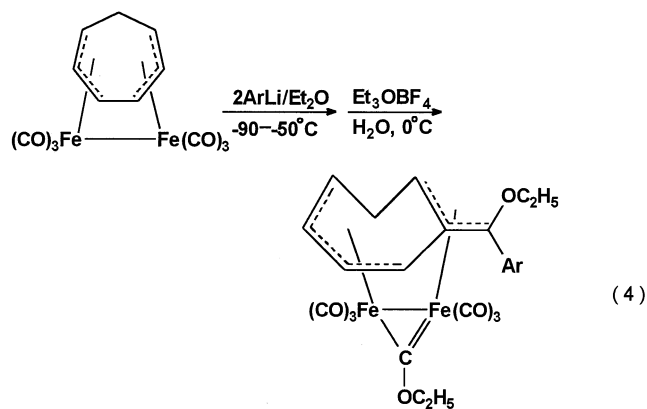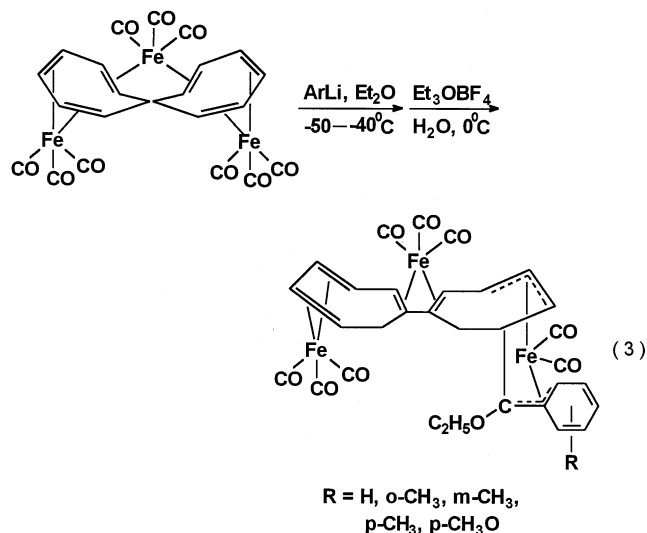
a manner similar to that previously described.[1a,6,7] These reactions led to nucleophilic addition to and ring breaking of the cycloheptatrienyl ligands to afford a series of the novel ring-opened cycloolefin-coordinated tricarbonylirontricarbonylmanganese and -rhenium complexes. In this paper we report these remarkable reactions and structural characterizations of the resulting products.

Experimental Section

All procedures were performed under a dry, oxygen-free N_2 atmosphere by using standard Schlenk techniques. All solvents employed were reagent grade and were dried by refluxing over appropriate drying agents and stored over 4 Å molecular sieves under an N_2 atmosphere. Diethyl ether was distilled from sodium benzophenone ketyl, while petroleum ether (30–60 °C) and CH_2Cl_2 were distilled from CaH_2. The neutral alumina (Al_2O_3, 100–200 mesh) used for chromatography was deoxygenated at room temperature under high vacuum for 16 h, deactivated with 5% w/w N_2-saturated water, and stored under an N_2 atmosphere. The compounds **1**,[10] **2**,[10] Et_3OBF_4,[11] and aryllithium reagents[12–15] were prepared by literature methods.

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The IR spectra were measured on a Shimadzu-IR-440 spectrophotometer. All ^{1}H NMR spectra were recorded at ambient temperature in acetone-d_6 solution with TMS as the internal reference using a Bruker AM-300 spectrometer. Electron ionization mass spectra (EIMS) were run on a Hewlett-Packard 5989A spectrometer. Melting points obtained on samples in sealed nitrogen-filled capillaries are uncorrected.

Reaction of [MnFe{μ-(1−3-η):(4−7-η)-C$_7$H$_7$}(CO)$_6$] (1) with C$_6$H$_5$Li To Give [MnFe{C$_8$H$_7$(OC$_2$H$_5$)C$_6$H$_5$}(CO)$_6$] (3). To a solution of 0.150 g (0.41 mmol) of **1** dissolved in 40 mL of ether at −70 °C was added 0.91 mmol of C$_6$H$_5$Li[12] with stirring. The reaction mixture was stirred at −70 to −60 °C for 0.5 h and then at −55 to − 40 °C for 3−4 h, during which time the orange-red solution gradually turned deep red until brown-red. The resulting solution was evaporated under high vacuum at −45 to −35 °C to dryness. To the dark red residue obtained was added Et$_3$OBF$_4$[11] (ca. 5 g). This solid mixture was dissolved in 25 mL of N$_2$-saturated water at 0 °C with vigorous stirring and the mixture covered with petroleum ether (30−60 °C). Immediately afterward, Et$_3$OBF$_4$ was added to the aqueous solution portionwise, with strong stirring, until it became acidic. The aqueous solution was extracted with petroleum ether. The combined extract was evaporated to remove the most of the solvent under vacuum and then chromatographed on an alumina column (1.6 × 15 cm) at −20 to −25 °C with petroleum ether followed by petroleum ether/CH$_2$Cl$_2$ (15:1) as the eluant. The orange-yellow band was eluted and collected. The solvent was removed under vacuum, and the residue was recrystallized from petroleum ether/CH$_2$Cl$_2$ (15:1) at −80 °C to give 0.093 g (53%, based on **1**) of orange-yellow crystals of **3**: mp 94−96 °C dec; IR (cyclohexane) ν(CO) 2040 (s), 1998 (vs), 1989 (vs), 1950 (w), 1943 (s, br) cm^{-1}; ^{1}H NMR (CD$_3$-COCD$_3$) δ 7.82 (d, 1H, C$_8$H$_7$), 6.27 (t, 1H, C$_8$H$_7$), 7.43−7.36 (m, 5H, C$_6$H$_5$), 5.57 (dd, 1H, C$_8$H$_7$), 4.95 (t, 1H, C$_8$H$_7$), 4.62 (d, 1H, C$_8$H$_7$), 4.18 (t, 1H, C$_8$H$_7$), 3.80 (m, 1H, C$_8$H$_7$), 3.76 (m, 2H, OCH_2CH$_3$), 1.29 (t, 3H, OCH$_2$CH_3); MS m/e 476 (M$^+$ − CO), 448 (M$^+$ − 2CO), 420 (M$^+$ − 3CO), 392 (M$^+$ − 4CO), 364 (M$^+$ − 5CO), 336 (M$^+$ − 6CO), 291 (M$^+$ − 6CO − Fe − OC$_2$H$_5$), 281 [M$^+$ − 3CO − Mn(CO)$_3$], 225 [M$^+$ − Fe(CO)$_3$ − Mn(CO)$_3$]. Anal. Calcd for C$_{22}$H$_{17}$O$_7$MnFe: C, 52.41; H, 3.40. Found: C, 52.74; H, 3.75.

Reaction of 1 with o-CH$_3$C$_6$H$_4$Li To Give [MnFe{C$_8$H$_7$-(OC$_2$H$_5$)C$_6$H$_4$CH$_3$-o}(CO)$_6$] (4). Similar to the reaction of **1** with C$_6$H$_5$Li, the reaction of 0.200 g (0.54 mmol) of **1** with 1.19 mmol of o-CH$_3$C$_6$H$_4$Li[13] at −55 to −40 °C for 3 h, followed by alkylation and further treatment, afforded 0.110 g (48%, based on **1**) of orange-red crystalline **4**: mp 89−91 °C dec; IR (cyclohexane) ν(CO) 2048 (s), 2000 (vs), 1991 (vs), 1955 (w), 1945 (s, br) cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$) δ 7.83 (d, 1H, C$_8$H$_7$), 7.27−7.09 (m, 4H, C$_6$$H_4CH_3$), 6.29 (t, 1H, C$_8H_7$), 5.57 (dd, 1H, C$_8H_7$), 4.95 (t, 1H, C$_8H_7$), 4.60 (d, 1H, C$_8H_7$), 4.20 (t, 1H, C$_8H_7$), 3.83 (m, 1H, C$_8H_7$), 3.80 (m, 2H, OC$H_2CH_3$), 2.32 (s, 3H, C$_6H_4CH_3$), 1.29 (t, 3H, OCH$_2CH_3$); MS m/e 490 (M$^+$ − CO), 462 (M$^+$ − 2CO), 434 (M$^+$ − 3CO), 406 (M$^+$ − 4CO), 378 (M$^+$ − 5CO), 350 (M$^+$ − 6CO), 305 (M$^+$ − 6CO − Fe − OC$_2$H$_5$), 295 [M$^+$ − 3CO −Mn(CO)$_3$], 294 [M$^+$ - 3CO − Fe(CO)$_3$], 239 [M$^+$ − Mn(CO)$_3$ − Fe(CO)$_3$]. Anal. Calcd for C$_{23}$H$_{19}$O$_7$MnFe: C, 53.31; H, 3.70. Found: C, 53.32; H, 3.55.

Reaction of 1 with m-CH$_3$C$_6$H$_4$Li To Give [MnFe{C$_8$H$_7$-(OC$_2$H$_5$)C$_6$H$_4$CH$_3$-m}(CO)$_6$] (5). The reaction of 0.200 g (0.54 mmol) of **1** with 1.19 mmol of m-CH$_3$C$_6$H$_4$Li[13] was as described in the reaction of **1** with C$_6$H$_5$Li at −55 to − 40 °C for 4 h. The subsequent alkylation and further treatment as described for the preparation of **3** gave 0.123 g (50%, based on **1**) of **5** as orange crystals: mp 30−32 °C dec; IR (cyclohexane) ν(CO) 2060 (s), 2010 (vs), 1995 (vs), 1960 (w), 1950 (s, br) cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$) δ 7.84 (d, 1H, C$_8$H$_7$), 7.25−7.16 (m, 4H, C$_6$$H_4CH_3$), 6.30 (t, 1H, C$_8H_7$), 5.59 (dd, 1H, C$_8H_7$), 4.96 (t, 1H, C$_8H_7$), 4.62 (d, 1H, C$_8H_7$), 4.22 (t, 1H, C$_8H_7$), 3.80 (m, 1H, C$_8H_7$), 3.78 (m, 2H, OC$H_2CH_3$), 2.33 (s, 3H, C$_6H_4CH_3$), 1.31 (t, 3H, OCH$_2CH_3$); MS m/e 490 (M$^+$ − CO), 462 (M$^+$ − 2CO), 434 (M$^+$

Table 1. Crystal Data and Experimental Details for Complexes 4 and 10

	4	**10·CH$_2$Cl$_2$**
formula	C$_{23}$H$_{19}$O$_7$MnFe	C$_{24}$H$_{18}$O$_7$Cl$_2$-F$_3$ReFe
fw	518.18	788.36
space group	*Pbca* (No. 61)	*P2$_1$/a* (No. 14)
a (Å)	15.255(4)	11.017(3)
b (Å)	21.605(4)	22.543(2)
c (Å)	13.954(5)	12.361(3)
α (deg)	90	
β (deg)	90	116.02(1)
γ (deg)	90	
V (Å^3)	4598(2)	2758(1)
Z	8	4
D_{calcd} (g/cm^3)	1.497	1.898
F(000)	2112.00	1520.00
μ(Mo Kα) (cm^{-1})	12.19	51.65
radiation (monochromated in incident beam)	Mo Kα (λ = 0.710 69 Å)	
diffractometer	Rigaku AFC7R	
temp (°C)	20	
orientation rflns: no.; range (2θ) (deg)	22; 13.9−17.9	18; 14.3−21.1
scan method	ω−2θ	
data collecn range, 2θ (deg)	5−45	5−51
no. of unique data, total	3401	5273
with $I > 3.00\sigma(I)$	829	3217
no. of params refined	255	330
correcn factors, max−min	0.8214−1.0791	0.8313−1.0000
R^a	0.060	0.037
R_w^b	0.060	0.043
quality of fit indicator^c	1.67	1.38
max shift/esd, final cycle	0.01	0.57
max peak, e/Å^3	0.47	1.09
min peak, e/Å^3	−0.42	−0.56

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c} Quality of fit = $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

− 3CO), 406 (M$^+$ − 4CO), 378 (M$^+$ − 5CO), 350 (M$^+$ − 6CO), 305 (M$^+$ − 6CO − Fe − OC$_2$H$_5$), 295 [M$^+$ − 3CO − Mn(CO)$_3$], 294 [M$^+$ − 3CO − Fe(CO)$_3$], 239 [M$^+$ − Mn(CO)$_3$ − Fe(CO)$_3$]. Anal. Calcd for C$_{23}$H$_{19}$O$_7$MnFe: C, 53.31; H, 3.70. Found: C, 53.56; H, 3.70.

Reaction of 1 with p-CH$_3$C$_6$H$_4$Li To Give [MnFe{C$_8$H$_7$-(OC$_2$H$_5$)C$_6$H$_4$CH$_3$-p}(CO)$_6$] (6). Compound **1** (0.200 g, 0.54 mmol) was treated, in a manner similar to that described for the reaction of **1** with C$_6$H$_5$Li, with 1.19 mmol of p-CH$_3$C$_6$H$_4$-Li[13] at −55 to −40 °C for 4 h, followed by alkylation and further treatment as described for the preparation of **3** to yield 0.108 g (52%, based on **1**) of orange crystals of **6**: mp 42−44 °C dec; IR (cyclohexane) ν(CO) 2050 (s), 2001 (vs), 1993 (vs), 1958 (w), 1948 (s, br) cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$) δ 7.85 (d, 1H, C$_8$H$_7$), 7.37−7.21 (m, 4H, C$_6$$H_4CH_3$), 6.30 (t, 1H, C$_8H_7$), 5.59 (dd, 1H, C$_8H_7$), 4.97 (t, 1H, C$_8H_7$), 4.60 (d, 1H, C$_8H_7$), 4.22 (t, 1H, C$_8H_7$), 3.81 (m, 1H, C$_8H_7$), 3.78 (m, 2H, OC$H_2CH_3$), 2.33 (s, 3H, C$_6H_4CH_3$), 1.31 (t, 3H, OCH$_2CH_3$); MS m/e 434 (M$^+$ − 3CO), 406 (M$^+$ − 4CO), 378 (M$^+$ − 5CO), 350 (M$^+$ − 6CO), 305 (M$^+$ − 6CO − Fe − OC$_2$H$_5$), 295 [M$^+$ − 3CO − Mn(CO)$_3$], 294 [M$^+$ − 3CO − Fe(CO)$_3$], 239 [M$^+$ − Mn(CO)$_3$ − Fe(CO)$_3$]. Anal. Calcd for C$_{23}$H$_{19}$O$_7$MnFe: C, 53.31; H, 3.70. Found: C, 53.08; H, 3.64.

Reaction of [ReFe{μ-(1−3-η):(4−7-η)-C$_7$H$_7$}(CO)$_6$] (2) with C$_6$H$_5$Li To Give [ReFe{C$_8$H$_7$(OC$_2$H$_5$)C$_6$H$_5$}(CO)$_6$] (7). Using the same procedures for the reaction of **1** with C$_6$H$_5$Li, 0.20 g (0.40 mmol) of **2** was treated with 0.80 mmol of C$_6$H$_5$Li at −70 to −50 °C for 3 h, during which time the orange solution gradually turned dark red. After removal of the solvent under vacuum at −40 °C, the dark brown residue was dissolved in 30 mL of CH$_2$Cl$_2$ at −70 °C. To this solution was added dropwise 0.20 g (1.10 mmol) of Et$_3$OBF$_4$ dissolved in 10 mL of CH$_2$Cl$_2$ with stirring; within 15 min, the reaction mixture turned from brown-red to orange-yellow. After being stirred at −70 to −50 °C for 2 h, the solvent was removed in vacuo at

Table 2. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for Complexes 4 and 10

	4 (M = Mn)	10 (M = Re)		4 (M = Mn)	10 (M = Re)
M−Fe	2.715(5)	2.819(1)	C(8)−C(9)	1.45(3)	1.42(1)
Fe−C(7)	1.93(2)	1.984(8)	C(9)−C(10)	1.37(3)	1.42(1)
Fe−C(11)	2.23(2)	2.211(8)	C(10)−C(11)	1.42(3)	1.46(1)
Fe−C(12)	2.30(2)	2.271(8)	C(11)−C(12)	1.43(3)	1.39(1)
M−C(7)	2.16(2)	2.257(9)	C(12)−C(13)	1.48(3)	1.48(1)
M−C(8)	2.15(2)	2.297(9)	C(13)−C(14)	1.36(3)	1.34(1)
M−C(9)	2.12(2)	2.264(8)	C(14)−C(15)		1.50(1)
M−C(10)	2.19(2)	2.375(8)	C(14)−C(17)	1.53(3)	
M−C(CO) (av)	1.77	1.913	C(14)−O(7)	1.39(2)	1.363(10)
Fe−C(CO) (av)	1.79	1.782	O(7)−C(15)	1.45(2)	
C(7)−C(8)	1.41(3)	1.40(1)	O(7)−C(22)		1.44(1)
M−Fe−C(7)	52.1(6)	52.6(2)	C(9)-M−C(10)	37.2(7)	35.7(3)
Fe−M−C(7)	45.0(6)	44.3(2)	C(7)−Fe−C(11)	91.9(9)	91.4(3)
M−C(7)−Fe	82.9(7)	83.0(3)	C(7)−Fe−C(12)	94.2(8)	92.8(3)
M−Fe−C(11)	70.4(7)	73.5(2)	Fe−C(7)−C(8)	132(1)	128.8(6)
M−Fe−C(12)	100.3(6)	102.8(2)	C(7)−C(8)−C(9)	117(1)	122.8(8)
Fe−C(11)−C(12)	74(1)	74.4(5)	C(8)−C(9)−C(10)	124(2)	122.8(8)
Fe−C(12)−C(11)	68(1)	69.6(5)	C(9)−C(10)−C(11)	129(1)	126.7(8)
C(11)−Fe−C(12)	36.7(6)	36.0(3)	C(10)−C(11)−C(12)	127(2)	128.7(8)
Fe−M−C(8)	77.3(6)	72.7(2)	C(11)−C(12)−C(13)	124(2)	126.1(8)
Fe−M−C(9)	88.5(5)	84.8(2)	C(12)−C(13)−C(14)	119(2)	124.7(8)
Fe−M−C(10)	73.8(6)	70.5(2)	C(13)−C(14)−O(7)	122(2)	125.0(8)
M−C(7)−C(8)	70(1)	73.7(5)	C(13)−C(14)−C(15)		125.2(8)
M−C(8)−C(7)	71(1)	70.6(5)	C(13)−C(14)−C(17)	128(2)	
M−C(8)−C(9)	69(1)	70.6(5)	O(7)−C(14)−C(15)		109.7(7)
M−C(9)−C(8)	71(1)	73.2(5)	O(7)−C(14)−C(17)	108(2)	
C(8)−M−C(9)	39.8(7)	36.2(3)	M−C−O (CO) (av)	177	177.2
M−C(9)−C(10)	74(1)	76.4(5)	Fe−C−O (CO) (av)	175	176.7
M−C(10)−C(9)	68(1)	67.9(5)			

[a] Estimated standard deviations in the least significant figure are given in parentheses.

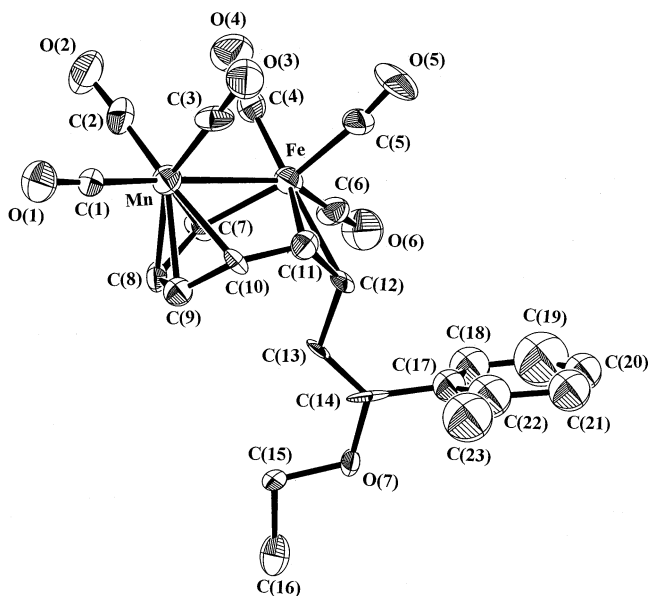**Figure 1.** Molecular structure of **4**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 45% probability.
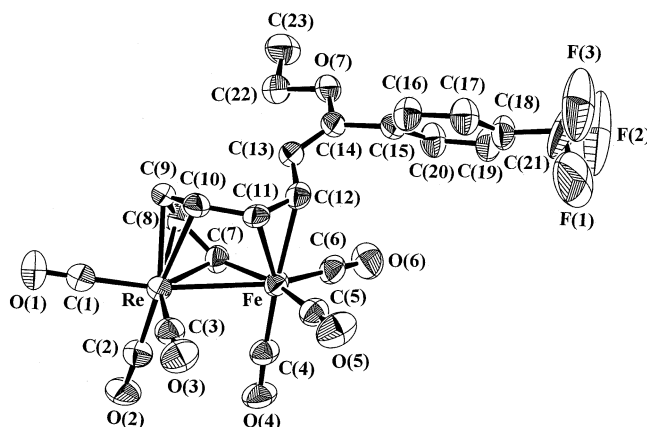

Figure 2. Molecular structure of **10**, showing the atom-numbering scheme with 45% thermal ellipsoids. CH₂Cl₂ has been omitted for clarity.

−40 °C to dryness, and the residue was chromatographed on Al₂O₃ at −25 °C with petroleum ether as the eluant. The orange-yellow band was eluted and collected. The solvent was removed under vacuum, and the residue was recrystallized from petroleum ether or petroleum ether/CH₂Cl₂ at −80 °C to give 0.180 g (74%, based on **2**) of orange-yellow crystals of **7**: mp 38−40 °C dec; IR (hexane) ν(CO) 2050 (w), 2005 (m), 1990 (s), 1960 (m), 1942 (s, br) cm⁻¹; ¹H NMR (CD₃COCD₃) δ 7.51 (d, 1H, C₈H₇), 7.45 (m, 5H, C₆H₅), 6.56 (t, 1H, C₈H₇), 5.60 (dd, 1H, C₈H₇), 5.01 (t, 1H, C₈H₇), 4.47 (d, 1H, C₈H₇), 3.98 (t, 1H, C₈H₇), 3.83 (m, 1H, C₈H₇), 3.76 (q, 2H, OC*H*₂CH₃), 1.28 (t, 3H, OCH₂C*H*₃); MS *m/e* 636 (M⁺), 608 (M⁺ − CO), 580 (M⁺ − 2CO), 552 (M⁺ − 3CO), 524 (M⁺ − 4CO), 496 (M⁺ − 5CO), 468 (M⁺

− 6CO), 367 (M⁺ − 6CO − Fe − OC₂H₅), 365 [M⁺ − 3CO − Re(CO)₃]. Anal. Calcd for C₂₂H₁₇O₇ReFe: C, 41.54; H, 2.69. Found: C, 41.96; H, 2.95.

Reaction of 2 with *o*-CH₃C₆H₄Li To Give [ReFe{C₈H₇-(OC₂H₅)C₆H₄CH₃-*o*}(CO)₆] (8). The procedure used in the reaction of **2** (0.140 g, 0.28 mmol) with *o*-CH₃C₆H₄Li (0.56 mmol) was the same as that for the reaction of **2** with C₆H₅Li at −70 to −50 °C for 2 h. Further treatment of the resulting mixture similar to that described for the preparation of **7** afforded 0.100 g (57%, based on **2**) of orange-yellow crystalline **8**: mp 42 °C dec; IR (hexane) ν(CO) 2050 (m), 2005 (s), 1998 (s), 1970 (w), 1962 (m), 1948 (s) cm⁻¹; ¹H NMR (CD₃COCD₃) δ 7.73 (d, 1H, C₈H₇), 7.50−7.28 (m, 4H, C₆H₄CH₃), 6.56 (t, 1H, C₈H₇), 5.58 (dd, 1H, C₈H₇), 4.99 (t, 1H, C₈H₇), 4.49 (d, 1H, C₈H₇), 4.19 (t, 1H, C₈H₇), 3.78 (m, 1H, C₈H₇), 3.73 (m, 2H, OC*H*₂CH₃), 2.26 (s, 3H, C₆H₄C*H*₃), 1.24 (t, 3H, OCH₂C*H*₃); MS *m/e* 650 (M⁺), 622 (M⁺ − CO), 594 (M⁺ − 2CO), 566 (M⁺ − 3CO), 538 (M⁺ − 4CO), 510 (M⁺ − 5CO), 482 (M⁺ − 6CO), 381 (M⁺ − 6CO − Fe − OC₂H₅), 427 [M⁺ − 3CO − Re(CO)₃].

Anal. Calcd for $C_{23}H_{19}O_7ReFe$: C, 42.50; H, 2.95. Found: C, 42.41; H, 3.01.

Reaction of 2 with *m*-CH₃C₆H₄Li To Give [ReFe{C₈H₇- (OC₂H₅)C₆H₄CH₃-*m*}(CO)₆] (9). As used for the reaction of **2** with C₆H₅Li, compound **2** (0.200 g, 0.40 mmol) was treated with 0.80 mmol of *m*-CH₃C₆H₄Li to yield 0.110 g (54%, based on **2**) of **9** as orange-yellow crystal: mp 34−36 °C dec; IR (hexane) ν(CO) 2050 (m), 2002 (m), 1990 (s), 1960 (m), 1942 (s, br) cm⁻¹; ¹H NMR (CD₃COCD₃) δ 7.51 (d, 1H, C₈H₇), 7.49− 7.30 (m, 4H, C₆H₄CH₃), 6.57 (t, 1H, C₈H₇), 6.12 (dd, 1H, C₈H₇), 5.00 (t, 1H, C₈H₇), 4.46 (d, 1H, C₈H₇), 4.03 (t, 1H, C₈H₇), 3.85 (m, 1H, C₈H₇), 3.77 (m, 2H, OC*H*₂CH₃), 2.35 (s, 3H, C₆H₄C*H*₃), 1.29 (t, 3H, OCH₂C*H*₃); MS *m/e* 650 (M⁺), 622 (M⁺ − CO), 566 (M⁺ − 3CO), 538 (M⁺ − 4CO), 510 (M⁺ − 5CO), 482 (M⁺ − 6CO), 381 (M⁺ − 6CO − Fe − OC₂H₅), 427 [M⁺ − 3CO − Re- (CO)₃]. Anal. Calcd for $C_{23}H_{19}O_7ReFe$: C, 42.50; H, 2.95. Found: C, 42.29; H, 3.10.

Reaction of 2 with *p*-CF₃C₆H₄Li To Give [ReFe{C₈H₇- (OC₂H₅)C₆H₄CF₃-*p*}(CO)₆] (10). A solution of 0.22 g (0.97 mmol) of *p*-CF₃C₆H₄Br in 20 mL of ether was mixed with 0.97 mmol of *n*-C₄H₉Li.[14] After 40 min of stirring at room temperature, the resulting ether solution of *p*-CF₃C₆H₄Li[15] reacted, as in the reaction of **2** with C₆H₅Li, with 0.200 g (0.40 mmol) of **2** at −75 to −50 °C for 4 h, followed by alkylation; further treatment as described for the preparation of **7** gave 0.20 g (74%, based on **2**) of brown-yellow crystals of **10**: mp 46−48 °C dec; IR (hexane) ν(CO) 2050 (m), 2000 (s), 1990 (s), 1960 (m), 1942 (s), 1900 (w) cm⁻¹; ¹H NMR (CD₃COCD₃) δ 7.78 (d, 1H, C₈H₇), 7.57−7.47 (m, 4H, C₆H₄CH₃), 6.58 (t, 1H, C₈H₇), 6.38 (dd, 1H, C₈H₇), 5.01 (t, 1H, C₈H₇), 4.47 (d, 1H, C₈H₇), 4.03 (t, 1H, C₈H₇), 3.95 (m, 1H, C₈H₇), 3.78 (m, 2H, OC*H*₂CH₃), 1.28 (t, 3H, OCH₂C*H*₃); MS *m/e* 676 (M⁺ − CO), 648 (M⁺ − 2CO), 620 (M⁺ − 3CO), 592 (M⁺ − 4CO), 564 (M⁺ − 5CO), 536 (M⁺ − 6CO). Anal. Calcd for $C_{23}H_{16}O_7F_3ReFe$: C, 39.24; H, 2.33. Found: C, 39.46; H, 2.29.

X-ray Crystal Structure Determinations of Complexes 4 and 10. The single crystals of **4** and **10** suitable for X-ray diffraction analysis were obtained by recrystallization from petroleum ether/CH₂Cl₂ solution at −80 °C. Single crystals were mounted on a glass fiber and sealed with epoxy glue. The X-ray diffraction intensity data for 3401 and 5273 independent reflections, of which 829 and 3217 with $I > 3.00\sigma(I)$ for **4** and **10** were observable, were collected with a Rigaku AFC7R diffractometer at 20 °C using Mo Kα radiation with a $\omega-2\theta$ scan mode.

The structure of **4** was solved by direct methods and expanded using Fourier techniques, while the structure of **10** was solved by heavy-atom Patterson methods and expanded using Fourier techniques. For complexes **4** and **10**, some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. For both complexes, the hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was respectively based on 829 and 3217 observed reflections and 255 and 330 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.060$ and $R_w = 0.060$ for **4** and $R = 0.037$ and $R_w = 0.043$ for **10**, respectively.

The details of the crystallographic data and the procedures used for data collection and reduction information for complexes **4** and **10** are given in Table 1. The selected bond lengths and angles are listed in Table 2. The atomic coordinates, B_{iso}/B_{eq} values, anisotropic displacement parameters, all bond lengths and angles, and least-squares planes for **4** and **10** are presented in the Supporting Information. The molecular structures of **4** and **10** are given in Figures 1 and 2, respectively.

Results and Discussion

[μ-(1−3-η):(4−7-η)-Cycloheptatrienyl]tricarbonyl-irontricarbonylmanganese, [MnFe{μ-(1−3-η):(4−7-η)-

C_7H_7}(CO)₆] (**1**), was treated with 2 molar equiv of aryllithium reagents, ArLi (Ar = C₆H₅, *o*-, *m*-, *p*-CH₃C₆H₄), in ether at low temperature (−55 to −40 °C) for 3−4 h to give acylmetalate intermediates, which were subsequently alkylated with Et₃OBF₄ in aqueous solution at 0 °C. After removal of the solvent under high vacuum at low temperature, the solid residue was chromatographed on an alumina column at −25 °C, and the crude product was recrystallized from petroleum ether solution at −80 °C to afford the four orange-red crystalline complexes [MnFe{C₈H₇(OC₂H₅)Ar}(CO)₆] (**3**, Ar = C₆H₅; **4**, Ar = *o*-CH₃C₆H₄; **5**, Ar = *m*-CH₃C₆H₄; **6**, Ar = *p*-CH₃C₆H₄) (eq 5) in 48−53% isolated yields. [μ-(1−3-η):(4−7-η)-Cycloheptatrienyl]tricarbonylirontricarbonylrhenium, [ReFe{μ-(1−3-η):(4−7-η)-C₇H₇}(CO)₆] (**2**), reacted similarly with aryllithium reagents, ArLi (Ar = C₆H₅, *o*-, *m*-CH₃C₆H₄, *p*-CF₃C₆H₄), to give the analogous complexes [ReFe{C₈H₇(OC₂H₅)Ar}(CO)₆] (**7**, Ar = C₆H₅; **8**, Ar = *o*-CH₃C₆H₄; **9**, Ar = *m*-CH₃C₆H₄; **10**, Ar = *p*-CF₃C₆H₄) in higher yields (57−74%) (eq 5).
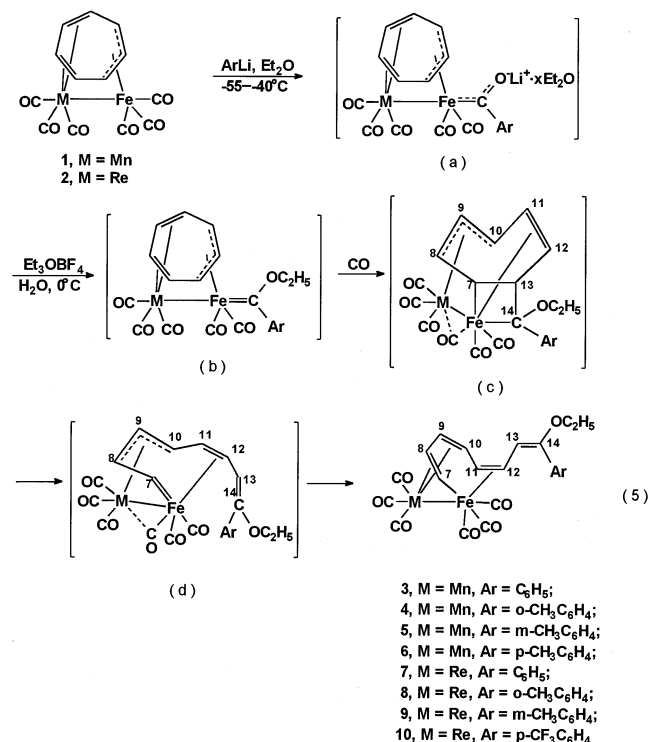
On the basis of elemental analyses, spectral analyses, and single-crystal X-ray diffraction studies of complexes **4** and **10**, complexes **3**−**6** and **7**−**10** are formulated as the ring-opening cycloolefin-coordinated tricarbonyliron-tricarbonylmanganese and -rhenium complexes, respectively, in which the alkene ligand is now a conjugated octatetraene chain with an C(OC₂H₅)Ar group added on a carbon of the ring-opened cycloheptatrienyl ligand.

There are two cycloolefin-coordinated M(CO)₃ units in starting materials **1** and **2**; one is Mn(CO)₃ or Re-(CO)₃, and the other is Fe(CO)₃. However, no dialkoxy-(aryl)-substituted complexes or their derivatives were obtained in the reactions, even though more than 3−4 molar equiv of the aryllithium reagents was used. This might be ascribed to the different carbonyls of the two kinds of M(CO)₃ units in **1** and **2**, owing to the different coordinating modes of the Fe(CO)₃ and Mn(CO)₃ or Re-

$(CO)_3$ units with the cycloheptatrienyl ligand. It is well-known that the reactivity of the CO ligands depends on the strength of the C−O bond. In general, the weaker the strength of the C−O bond, the more reactive the CO ligand.[16] In compounds **1** and **2**, the C−O bond strength of the $Fe(CO)_3$ unit is possibly weaker than that of the $Mn(CO)_3$ or $Re(CO)_3$ unit and tends to be like that of the C=O double bond; hence, the $Fe(CO)_3$ moiety is more easily attacked by nucleophiles to produce the acylmetalate intermediates (a) (eq 5). In fact, the reactions of metal carbonyl compounds with nucleophiles are very complicated and depend not only on the structures of metal carbonyl compounds and the nucleophilicity of nucleophiles but also on the stability of the intermediate formed and the experimental conditions.

Although a mechanism for the cycloheptatrienyl ring opening in reaction 5 has not yet been established, it seems possible that aryllithium nucleophile first attacks the $Fe(CO)_3$ unit, giving an acylmetalate intermediate (a), which was subsequently alkylated with Et_3OBF_4 to yield an unstable ethoxycarbene intermediate (b). Then a 2 + 2 cycloaddition and abstracting one molecule of CO generated by decomposition of the unstable intermediate (a) or (b) could occur at the same time to form a metal cyclobutane intermediate (c). The latter gives a transition state (d) upon opening of the cycloheptatrienyl ring. Subsequent rearrangement leads to the stable ring-opened products **3**−**10**, similar to those in the reaction of [tetrafluorobenzobicyclo[2.2.2]octatriene]-tricarbonyliron with aryllithium nucleophiles.[2b] In contrast to **2**, compound **1** does not react with aryllithium reagents having a strong electron-withdrawing group, p-$CF_3C_6H_4Li$, under the same conditions to give analogous products, which could be arising from the extreme lability of the intermediate (b) formed owing to the strong electron-withdrawing effect of the p-$CF_3C_6H_4$ group.

Products **3**−**10** are soluble in polar and nonpolar organic solvents. They are very sensitive to air and temperature in solution but stable for short periods on exposure to air at room temperature in the crystalline states. The IR, the solution ^1H NMR spectra, and the mass spectra are consistent with the structures shown in eq 5. The IR spectra of complexes **3**−**6** and **7**−**10** in the $\nu(CO)$ region, given in the Experimental Section, show five absorption bands at ca. 2060−1940 and 2050−1942 cm^{-1}, respectively, indicating the presence of an $M(CO)_3Fe(CO)_3$ moiety in these complexes. The ^1H NMR spectra of complexes **3**−**10** with seven proton signals for the olefin ligand are very different from those with single-line signals of the original seven-membered ring in starting materials **1** and **2**, which is fluxional,[10,17] which suggests that ring cleavage of the cycloheptatrienyl ligand has occurred; the X-ray diffraction studies of **4** and **10** were therefore undertaken, which unequivocally established the opening of the cycloheptatrienyl ring. From the ^1H NMR spectral data of **3**−**10**, it can be seen that there appears a proton signal at downfield at ca. 7.85−7.82 ppm in **3**−**6** and 7.78−7.51 ppm in **7**−**10**, which are comparable with that of the analogous

complex **I**,[18] in which the chemical shift of a vinyl proton

I
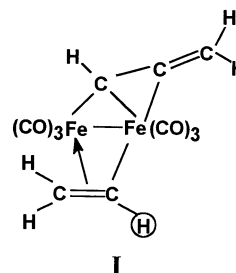
bonding to the two metals in a σ and π bond was 8.15 ppm. Thus, the proton signals at ca. 7.85−7.82 ppm for **3**−**6** and 7.78−7.51 ppm for **7**−**10** can be assigned to the H(7) proton on the C(7) atom of the ring-opened alkene ligand. In addition, in the ^1H NMR spectra of complexes **3**−**10**, a triplet (ca. 1.31−1.24 ppm), a multiplet (ca. 3.80−3.73 ppm), and a set of multiplet bands (ca. 7.50−7.09 ppm) were observed from each of the complexes, which show characteristically the presence of the ethoxy and aryl groups in the formed alkene ligand.

The crystallographic investigations of **4** (Figure 1) and **10** (Figure 2) reveal a highly unusual structure. The core grouping $M(CO)_3$−$Fe(CO)_3$ (M = Mn, Re) is retained, but the cycloheptatrienyl ring has opened to form the chain C(7)−C(14), carrying an ethoxy and an aryl group on C(14). In **4** and **10**, the C(13) atom is now linked to the C(14) atom forming a C(13)−C(14) double bond; thus, the alkene ligand has become a conjugated octatetraene chain. The C(7) atom is bonded to the Fe atom, constructing a MnFeC(7) or ReFeC(7) core. Atoms C(7)−C(10) form a butadiene-like unit η^4-bonded to the Mn or Re atom, while C(11) and C(12) are η^2-bonded to the Fe atom.

The molecular structures of complexes **4** and **10** have approximate configuration and many common features. The $Mn(CO)_3$ unit and $C(OC_2H_5)C_6H_4CH_3$-o moiety in **4** and the $Re(CO)_3$ unit and $C(OC_2H_5)C_6H_4CF_3$-p moiety in **10** are on the opposite side of the plane defined by C(7) through C(10), as can be visualized in the ORTEP diagrams of **4** and **10** represented in Figures 1 and 2, respectively. Of six terminal CO ligands, three are attached to the Mn or Re atom and other three to the Fe atom, as anticipated from the IR spectra. The Fe atom is bonded to the Mn or Re atom in a σ bond and to the C(11) and C(12) atoms in an η^2 bond, while the Mn or Re atom is linked to the C(7), C(8), C(9), and C(10) atoms in an η^4 bond, in addition to linking to the Fe atom in a σ bond, thus giving each metal an 18-electron configuration.

The structures of **4** and **10** rather resemble that of the previously determined olefin-coordinated dimetal bridging carbene complex $[C_8H_8Fe_2\{\mu$-$C(OC_2H_5)C_6H_4$-CF_3-$p\}(CO)_4]$.[7] In **4** and **10**, the structure of the MFeC-(7) (M = Mn, Re) core is similar to that of the dimetallacyclopropane moiety in the analogous dimetal bridging carbene complexes. The Mn−Fe distance of 2.715(5) Å in **4** is very close to those in the bridging carbene complexes $[MnFe\{\mu$-$C(COC_2H_5)C_6H_5\}(CO)_5(\eta$-$C_5H_5)]$

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(2.6929(8) Å)[19] and [MnFe{μ-C(n-C$_4$H$_9$S)C$_6$H$_5$}(CO)$_5$(η-C$_5$H$_5$)] (2.705(4) Å)[20] but is obviously longer than that in the bridging carbyne complex [(CO)(η-C$_5$H$_5$)Fe(μ-COC$_2$H$_5$)(μ-CO)Mn(η-C$_5$H$_4$Me)(CO)] (2.572(1) Å).[21] The C(7)−Mn bond length (2.16(2) Å) in **4** is somewhat longer than the corresponding μ-C−Mn distance in [MnFe{μ-C(COC$_2$H$_5$)C$_6$H$_5$}(η-C$_5$H$_5$)(CO)$_5$] (2.021(4) Å)[19] and [MnFe{μ-C(n-C$_4$H$_9$S)C$_6$H$_5$}(CO)$_5$(η-C$_5$H$_5$)] (2.02(1) Å).[20] Similarly, the Re−Fe bond distance of 2.819(1) Å in **10** is approximately close to that in the bridging carbene complexes [ReFe{μ-C(n-C$_4$H$_9$S)C$_6$H$_5$}(CO)$_5$(η-C$_5$H$_5$)] (2.784(2) Å)[20] and [ReFe{μ-C(H)C$_6$H$_5$}(CO)$_6$(η-C$_5$H$_5$)] (2.7581(8) Å).[22] The C(7)−Re bond length (2.257-(9) Å) in **10** is also longer than that of [ReFe{μ-C(H)C$_6$H$_5$}(CO)$_6$(η-C$_5$H$_5$)] (2.120(5) Å)[22] and [ReFe{μ-C(n-C$_4$H$_9$S)C$_6$H$_5$}(CO)$_5$(η-C$_5$H$_5$)] (2.128(10) Å).[20] The C(7)−Fe bond lengths in **4** and **10** at 1.93(2) and 1.984-(8) Å, respectively, are shorter than those in the bridging carbene complex [ReFe{μ-C(H)C$_6$H$_5$}(CO)$_6$(η-C$_5$H$_5$)] (2.097(5) Å)[22] and in the bridging carbyne complex [(CO)$_2$(η-C$_5$H$_5$)Mo{μ-C(C$_6$H$_4$CH$_3$-p)}Fe(CO)$_4$] (2.008(5) Å).[23] This might be due to the back-donation of partial d electrons from the Mn or Re atom to the π^* back-bonding orbital of the C(7)−C(8) double bond to increase the electron density on the C(7) atom, leading to the increase of the bond order of the C(7)−Fe bond and the shortening of the C(7)−Fe bond distance. The C(7)−C(8), C(9)−C(10), and C(11)−C(12) bonds have the bond lengths 1.41(3), 1.37(3), and 1.43(3) Å in **4** and 1.40(1), 1.42(1), and 1.39(1) Å in **10**, respectively, which are in normal range of the C−C double-bond distance. It is worth noting that the bond lengths of C(14)−O(7) in **4** and **10** are 1.39(2) and 1.363(10) Å, respectively, lying between the normal C=O double-bond and C−O single-bond length. This could be ascribed to the conjugation of a lone pair electron on the O(7) atom with the C(13)−C(14) double bond, leading to the partial double-bond character of the C(14)−O(7) bond.

The C(7), C(8), C(9), and C(10) atoms of the C$_8$ chain lie in the same plane in both complexes. The perpendicular distances from the Mn and Re atoms to the C(7)C(8)C(9)C(10) plane are 1.618 and 1.7830 Å, respectively. The angle between the plane defined by C(7) through C(10) and the plane comprised of the Fe, C(11), and C(12) atoms is 89.37° in **4** and 93.19° in **10**. The benzene ring plane in both structures is, respectively, oriented at an 147.79 and 59.86° in **4** or 33.96 and 65.87° in **10** with respect to the C(7)C(8)C(9)C(10) plane and the FeC(11)C(12) plane.

In summary, we have discovered novel reactions involving ring breaking of the coordinated cycloheptatrienyl rings in mixed-dimetal carbonyl compounds. The title reaction shows a quite different reaction pattern of the cycloolefin-ligated mixed-dimetal carbonyl compounds **1** and **2** as compared with that of the homonuclear dimetal carbonyl compounds shown in eqs 1−4. In the title reaction, the cycloheptatrienyl ring has broken and a new carbon−carbon (C(13)−C(14)) bond is formed at low temperature, giving the ring-opening products **3**−**10**. To date, no such ring opening of the cycloheptatrienyl ligand in a dimetal compound at low temperature has been reported. Moreover, the title reaction results further indicate that the different dinuclear central metals exert great effects on the isomerization of the cycloolefin ligands and the resulting products in the reaction of the cycloolefin-ligated metal carbonyl compounds with aryllithium nucleophiles. However, the different center metals of the same VIIB group, Mn and Re, have no obvious effect on the isomerization pattern of the cycloheptatrienyl ligand, which led to similar ring-opening products.

Supporting Information Available: Tables of the positional parameters and temperature factors, H atom coordinates, anisotropic displacement parameters, all bond angles and least-squares planes for **4** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020328W

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