Preparation of a Cyclopentadienyl Ligand from the Pauson–Khand Reaction Product and Its Use in Complex Chemistry

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From the Pauson–Khand products **1** and **5** as starting materials, the novel cyclopentadiene compounds **3** and **7** were prepared efficiently. Metalation of **3** with $Mn_2(CO)_{10}$ resulted in a new bicyclic pentadienylmanganese compound, **4**. Reaction of **7** with $M_2(CO)_{10}$ (M = Mn, Re) and $Fe_2(CO)_9$ gave the corresponding organometallic compounds **9–12**. **7** also reacts with KH to produce the cyclopentadienide anion **8**, which reacts with $M(CO)_3(CH_3CN)_3$ (M = Cr, W), $Mo(CO)_6$, and $FeCl_3$ to yield compounds **13–16**. The molecular structures of **9** and **16** have been determined.

Introduction

Cyclopentadienyl ligands are one of the most popular ligands in organometallic chemistry and have been synthesized by various methods.[2] One of the strategies for synthesizing cyclopentadienylmetal compounds is to use cyclopentenone as a starting material. Vollhardt et al.[3] reported the use of cyclopentenone to synthesize cyclopentadienylmetal complexes and heterobimetallic fulvalene complexes.

We have recently been investigating the Pauson–Khand reaction,[4] which is a very effective method for synthesizing cyclopentenones by the cocyclization of alkyne, alkene, and carbon monoxide. We found[5,6] that the use of Me_3NO or DMSO as a promoter improves this reaction. We have shown how to make high yields of cyclopentenone compounds having various substituents. Thus, the use of cyclopentenones as starting materials in the synthesis of cyclopentadienylmetal complexes would be a useful strategy. Herein we report the synthesis of a cyclopentadienyl ligand from cyclopentenone (the Pauson–Khand reaction product) and its reaction with organometallic reagents and also report the molecular structures of **9** and **16**.

Experimental Section

All reactions were conducted under nitrogen using standard Schlenk flask and cannula techniques. Workup procedures were done in air.

Elemental analyses were done at the Korea Basic Science Center. ^1H NMR and ^{13}C NMR spectra were obtained with either a Varian XL-200 or a Bruker ARX 300 instrument. Infrared spectra were recorded on a Perkin-Elmer 782 spectrometer or on a Nicolet FT-IR spectrometer (spectra measured as films on NaCl by evaporation of solvent). Mass spectra were recorded with a VG ZAB-E double-focusing mass spectrometer.

Compounds **1**, **5**, and $M(CO)_3(CH_3CN)_3$ (M = Cr, W) were synthesized according to the published procedures.[6,7] Compound **3** was synthesized by a modification of the published procedure.[2c] Compound **7** was made by a modification of the published procedure.[8,9]

Synthesis of Compounds 2 and 3. To $CeCl_3$ (2.40 g, 9.7 mmol) in THF (15 mL) at −78 °C was added PhLi (5.4 mL, 9.7 mmol) under N_2. The reaction mixture was stirred for 30 min at −78 °C, compound **1** (1.29 g, 6.5 mmol) in THF (5 mL) was added dropwise, and then the reaction mixture was stirred overnight at room temperature. The reaction mixture was quenched with water. The layers were separated, and the aqueous portion was extracted with diethyl ether (3 × 30 mL). After removal of the solvent, the residue was purified by flash column chromatography on silica gel with hexane/ethyl acetate (v/v, 20:

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1) as eluent. The physical properties of **2** were as follows: IR (NaCl) ν_{OH} 3550 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.48–7.12 (m, Ph, 10 H), 6.27 (d, 2.4 Hz, 1 H), 3.30–3.23 (m, 1 H), 2.77–2.67 (m, 1 H), 2.15 (s, 1 H, OH), 2.03–1.95 (m, 1 H), 1.78–1.74 (m, 1 H), 1.64–1.57 (m, 4 H) ppm; HRMS M$^+$ obsd *m/z* 276.1513, calcd *m/z* 276.1514.

Benzene (50 mL) and *p*-toluenesulfonic acid hydrate (0.248 g, 1.3 mmol) were added to the intermediate allylic alcohol **2**, and this mixture was then stirred overnight at room temperature. The acid was neutralized with K_2CO_3 and the solution dried with $MgSO_4$. The solvent was removed by rotary evaporator, and the crude product was purified by flash column chromatography on silica gel with hexane as eluent. The yield of **3** was 1.07 g (63.5%). ^{1}H NMR ($CDCl_3$): δ 7.42–7.09 (m, Ph, 10 H), 5.51 (t, 1.19 Hz, 0.5 H), 4.82 (m, 0.5 H), 3.35 (t, 2.3 Hz, 1 H), 3.02–2.30 (m, 6 H) ppm. HRMS: M$^+$ obsd *m/z* 258.1406, calcd *m/z* 258.1409.

Synthesis of Compound 4. Compound **3** (0.163 g, 0.63 mmol) and $Mn_2(CO)_{10}$ (0.246 g, 0.756 mmol) in *p*-xylene (20 mL) were refluxed for 2 days. After the reaction mixture was cooled, the solvent was removed by rotary evaporator. The residue was purified by flash column chromatography with hexane/ether (v/v, 40:1) as eluent. The yield was 0.162 g (64.9%). IR (NaCl): ν_{CO} 2005, 1918 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.31–6.96 (m, Ph, 10 H), 4.28 (s, Cp, 1 H), 2.33–1.75 (m, CH_2, 6 H) ppm. ^{13}C NMR (C_6D_6): δ 226.26 (CO), 133.84, 133.74, 130.64, 129.97, 128.69, 128.57, 128.36, 128.06 (Ph), 113.01, 109.24, 108.67, 94.29, 73.63 (Cp), 28.65, 25.94, 25.78 (CH_2) ppm. HRMS: M$^+$ obsd *m/z* 396.0558, calcd *m/z* 396.0558.

Synthesis of Compounds 6 and 7. To compound **5** (3.34 g, 12.6 mmol) in MeOH (30 mL) was added $CeCl_3 \cdot 7H_2O$ (4.69 g, 12.6 mmol). The reaction mixture was stirred for 20 min at room temperature, $NaBH_4$ (0.48 g, 12.6 mmol) added, and then aqueous 1 N HCl added to neutralize the solution. The layers were separated, and the aqueous portion was extracted with ether (3 × 30 mL). The ether extracts were washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), concentrated, and purified by flash column chromatography on silica gel with hexane/ethyl acetate (v/v, 4:1) as eluent. The yield was 3.20 g (95%). IR (hexane): ν_{OH} 3500 cm^{-1}, $\nu_{C=O}$ 1732 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.91–5.65 (1 H), 5.04–5.40 (1 H), 4.10–4.30 (4 H), 1.32–3.12 (8 H), 1.13–1.34 (6 H) ppm (due to the presence of two isomers, it was not feasible to assign the splitting patterns). HRMS: (M) calcd *m/z* 268.1310, obsd *m/z* 268.1302.

To the intermediate allylic alcohol **6** (1.37 g, 5.13 mmol) in hexane (120 mL) was added $MgSO_4$ (10 g). The resulting solution was refluxed for 6 h. After the solution was cooled, any solids were filtered off. The filtrate was concentrated and purified by flash column chromatography on silica gel with hexane/ethyl acetate (v/v, 40:1) as eluent. The yield of **7** was 0.765 g (59.6%). IR (hexane): $\nu_{C=O}$ 1737 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.21–6.32 (m), 5.82–5.86 (m), 5.38 (d, 3.9 Hz), 4.05–4.21 (m), 3.31–3.50 (m), 3.00–3.29 (m), 2.85–2.60 (m), 2.60–2.12 (m), 1.91 (d, 12.2 Hz), 1.86 (d, 12.2 Hz), 1.26–1.12 (m) ppm. Due to the presence of the isomers, it was not feasible to assign the splitting patterns. However, we could confirm the number of the protons as follows: δ 5.3–6.4 ppm (2 H), 4.0–4.3 (4 H), 1.8–3.5 (6 H), 1.1–1.3 (6 H) ppm). HRMS: M$^+$ calcd *m/z* 250.1205, obsd *m/z* 250.1207.

Synthesis of Compounds 9 and 10. Compound **7** (0.442 g, 1.76 mmol) and $Mn_2(CO)_{10}$ (0.686 g, 1.76 mmol) in *p*-xylene (30 mL) were refluxed for 2 days. After the reaction mixture was cooled, the solvent was removed by rotary evaporator. The residue was purified by flash column chromatography with hexane/ethyl acetate (v/v, 40:1) as eluent. The first compound to elute was **9** (41.1%), and the second was **10** (11.4%). **9**: mp 94.7 °C; IR ($CDCl_3$) ν_{CO} 2025, 1923 cm^{-1}, ν_{CO_2} 1732 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.85 (t, 2.7 Hz, 1 H), 4.32 (d, 2.7 Hz, 2 H), 4.29 (q, 7.1 Hz, 2 H), 4.20 (q, 7.1 Hz, 2 H), 3.35 (d, 16.2 Hz, 2 H), 3.13 (d, 16.2 Hz, 2 H), 1.29 (t, 7.3 Hz, 3 H), 1.25 (t, 7.3 Hz, 3 H) ppm; EI-MS *m/z* 388 (M$^+$). Anal. Calcd for $C_{17}H_{17}MnO_7$: C, 52.62; H, 4.42. Found: C, 53.07; H, 4.64. **10**: IR ($CDCl_3$) ν_{CO} 2017, 1918 cm^{-1}, ν_{CO_2} 1732 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.80 (t, 2.5 Hz, 1 H), 4.43 (d, 2.5 Hz, 2 H), 4.20 (q, 7.2 Hz, 2 H), 4.18 (q, 7.2 Hz, 2 H), 3.48 (quint, 9.0 Hz, 1 H), 1.31 (t, 6.7 Hz, 3 H) ppm; ^{13}C NMR ($CDCl_3$) δ 225.30 (CO), 173.74 (C=O), 109.41, 87.52, 72.86, 61.20, 48.19, 29.22, 14.46 ppm; HRMS M$^+$ calcd *m/z* 316.0140, obsd *m/z* 316.0103.

Synthesis of Compound 11. A typical procedure is almost the same as the synthesis of compound **9**, except for the reaction time (5 days). **7** (0.67 g, 2.66 mmol), $Re_2(CO)_{10}$ (1.74 g, 2.66 mmol), and xylene (40 mL) have been used to prepare **11**, and the yield was 31.8% (0.44 g): mp 83.7 °C; IR ($CDCl_3$) ν_{CO} 2023, 1931 cm^{-1}, ν_{CO_2} 1731 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.37 (t, 2.7 Hz, 1 H), 5.00 (d, 2.7 Hz, 2 H), 4.29 (q, 7.1 Hz, 2 H), 4.20 (q, 7.1 Hz, 2 H), 3.55 (d, 15.8 Hz, 2 H), 3.39 (d, 15.8 Hz, 2 H), 1.30 (t, 7.1 Hz, 3 H), 1.25 (t, 7.1 Hz, 3 H) ppm. Anal. Calcd for $C_{17}H_{17}ReO_7$: C, 39.30; H, 3.30. Found: C, 38.53; H, 3.45.

Synthesis of Compound 12. Excess $Fe_2(CO)_9$ was added to the benzene solution (30 mL) of compound **7** (0.163 g, 0.65 mmol) at room temperature. The reaction mixture was refluxed for 24 h. After the solution was cooled, any solids were filtered off. The filtrate was evaporated to dryness and column-chromatographed on silica gel with hexane/diethyl ether (v/v, 10:1) as eluent. The yield was 55.3%: mp 94.2 °C dec; IR (NaCl) ν_{CO} 1978, 1940, 1760 cm^{-1}, $\nu_{C=O}$ 1732 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.39 (t, 2.6 Hz, 2 H), 4.32 (q, 7.1 Hz, 4 H), 4.23 (q, 7.1 Hz, 4 H), 4.12 (d, 2.7 Hz, 4 H), 3.58 (d, 16.6 Hz, 4 H), 3.13 (d, 16.6 Hz, 4 H), 1.34 (t, 7.1 Hz, 6 H), 1.27 (t, 7.1 Hz, 6 H) ppm. Anal. Calcd for $C_{32}H_{34}Fe_2O_{12}$: C, 53.21; H, 4.74. Found: C, 53.09; H, 4.78.

Synthesis of Compound 13. KH (0.096 g, 2.41 mmol) and 10 mL of THF were placed in a Schlenk flask at 0 °C. Compound **7** (0.404 g, 1.61 mmol) in 10 mL of THF was added to the flask at 0 °C. After it was stirred for 1.5 h at 0 °C, the reaction mixture was warmed to room temperature and stirred for 0.5 h. The resulting solution was transferred via cannula to another flask containing $W(CO)_3(CH_3CN)_3$ (generated by the reaction of 0.7 g of $W(CO)_6$ with refluxing CH_3CN) in 10 mL of THF. The reaction mixture was refluxed for 14 h and then cooled to room temperature. MeI (0.37 mL) was added to the resulting solution. The solution was stirred for 5 h, and the solvent was removed on a rotary evaporator. The resulting residue was extracted with diethyl ether. The ether extracts were evaporated to dryness. The yellow residue was purified by flash column chromatography on silica gel with hexane as eluent. The yield was 31.3% (0.268 g): mp 91.5 °C; IR ($CDCl_3$) ν_{CO} 2010, 1905 cm^{-1}, ν_{CO_2} 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.21 (t, 2.87 Hz, 1 H), 5.03 (d, 2.4 Hz, 2 H), 4.29 (q, 7.1 Hz, 2 H), 4.22 (q, 7.1 Hz, 2 H), 3.39 (br s, 4 H), 1.29 (t, 6.8 Hz, 3 H), 1.26 (t, 6.8 Hz, 3 H), 0.33 (s, 3 H) ppm. Anal. Calcd for $C_{18}H_{20}O_7W$: C, 40.65; H, 3.79. Found: C, 40.72; H, 3.78.

Synthesis of Compound 14. A typical procedure is almost the same as the synthesis of compound **13**, except Diazald is used instead of MeI. **7** (0.34 g, 1.35 mmol), KH (0.08 g, 2.0 mmol), $Cr(CO)_6$ (0.43 g, 1.95 mmol), and Diazald (0.32 g, 1.65 mmol) have been used to prepare **14**, and the yield was 66.5% (0.35 g): mp 82 °C; IR ν_{CO} 2017, 1950 cm^{-1}, ν_{NO} 1730.9 cm^{-1}, $\nu_{C=O}$ 1693.2 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.15 (t, 2.9 Hz, 1 H), 4.63 (d, 2.9 Hz, 2 H), 4.28 (q, 7.1 Hz, 2 H), 4.21 (q, 7.1 Hz, 2 H), 3.34 (d, 16.1 Hz, 2 H), 3.22 (d, 16.1 Hz, 2 H), 1.31 (t, 5.6 Hz, 3 H), 1.24 (t, 5.6 Hz, 3 H) ppm. Anal. Calcd for $C_{16}H_{17}CrNO_7$: C, 49.62; H, 4.42; N, 3.62. Found: C, 49.96; H, 4.95; N, 3.21.

Synthesis of Compound 15. A typical procedure is almost the same as the synthesis of compound **13**, except $M(CO)_6$ (M = Mo) is used instead of $M(CO)_3(CH_3CN)_3$ (M = Mo). KH (0.096 g, 2.4 mmol), **7** (0.30 g, 1.2 mmol), $Mo(CO)_6$ (0.35 g, 1.32 mmol), and Diazald (0.28 g, 1.32 mmol) have been used to prepare **15**, and the yield was 21.3% (0.11 g): mp 92.5 °C; IR ν_{CO} 2005, 1927 cm^{-1}, $\nu_{C=O}$ 1727 cm^{-1}, ν_{NO} 1647 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.53 (t, 2.8 Hz, 1 H), 5.13 (d, 2.8 Hz, 2 H), 4.21 (q, 7.1 Hz, 2 H), 4.14 (q, 7.1 Hz, 2 H), 3.36 (d, 15.9 Hz, 2 H), 3.25 (d, 15.9 Hz, 2 H), 1.22 (t, 7.1 Hz, 3 H), 1.19 (t, 7.1 Hz, 3 H) ppm. Anal. Calcd for $C_{16}H_{17}MoNO_7$: C, 44.56; H, 3.97; N, 3.24. Found: C, 44.59; H, 4.26; N, 2.41.

Synthesis of Compound 16. While nitrogen gas was vigorously flushed through, anhydrous $FeCl_3$ (4.87 g, 3.0 mmol) was

Table I. Crystal and Refinement Data for 9 and 16

	9	16
mol formula	$C_{17}H_{17}MnO_7$	$C_{28}H_{33}FeO_8$
fw	388.2	553.4
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	7.2692(13)	22.565(2)
b, Å	10.8788(10)	5.9968(11)
c, Å	11.9403(9)	21.094(3)
α, deg	103.738(7)	
β, deg	102.794(10)	109.484(10)
γ, deg	92.411(10)	
V, Å^3	890.0(2)	2690.6(7)
Z	2	4
D(calcd), Mg/m^3	1.449	1.366
cryst size, mm	0.67 × 0.53 × 0.55	0.23 × 0.31 × 0.17
λ/Å	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
total no. of unique rflns	3080	4641
no. of unique rflns	2817 ($I > 2\sigma(I)$)	1999 ($I > 4\sigma(I)$)
2θ range/deg	4–50	3.5–50
no. of params	226	334
R	0.0396	0.070
R_w	0.0566	0.047
goodness of fit	1.48	1.39

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for 9

	x	*y*	*z*	*U*(eq)[a]
Mn(1)	1528(1)	1969(1)	4021(1)	45(1)
O(1)	5161(3)	2439(2)	8005(2)	55(1)
O(2)	6421(3)	2757(2)	6545(2)	76(1)
O(3)	6272(3)	5420(2)	8429(2)	65(1)
O(4)	3341(3)	5581(2)	8697(2)	84(1)
O(5)	4897(3)	1956(2)	3058(2)	76(1)
O(6)	2888(4)	207(2)	5475(2)	96(1)
O(7)	–647(4)	–90(3)	2065(3)	120(1)
C(1)	2153(3)	3907(2)	5067(2)	41(1)
C(2)	1176(3)	3873(2)	3883(2)	48(1)
C(3)	–616(3)	3185(2)	3677(2)	54(1)
C(4)	–754(3)	2784(2)	4708(2)	54(1)
C(5)	958(3)	3248(2)	5560(2)	44(1)
C(6)	1803(3)	3368(2)	6853(2)	49(1)
C(7)	3865(3)	3966(2)	7042(2)	43(1)
C(8)	3928(3)	4523(2)	5958(2)	44(1)
C(9)	5308(3)	2994(2)	7142(2)	49(1)
C(10)	4430(4)	5071(2)	8170(2)	53(1)
C(11)	6462(5)	1482(3)	8179(3)	75(1)
C(12)	6180(6)	1027(4)	9195(3)	102(2)
C(13)	6980(6)	6510(4)	9442(3)	97(2)
C(14)	8863(8)	6857(6)	9571(5)	206(4)
C(15)	3573(3)	1932(2)	3434(2)	52(1)
C(16)	2358(4)	887(2)	4884(3)	61(1)
C(17)	217(4)	708(3)	2822(3)	71(1)

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

added to 8 (generated in situ) in THF (30 mL). The reaction mixture was refluxed for 24 h, cooled to room temperature, and filtered over anhydrous $MgSO_4$ in a fritted-glass filter. The solution was evaporated to dryness, and the yellow residue was purified by column chromatography on silica gel with hexane as eluent. The yield was 32.6% (0.486 g): mp 154–155 °C; IR ($CDCl_3$) ν_{CO_2} 1728 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.33 (q, 7.1 Hz, 4 H), 4.17 (q, 7.1 Hz, 4 H), 3.78 (s, 6 H), 3.44 (d, 15.8 Hz, 4 H), 2.95 (d, 15.8 Hz, 4 H), 1.36 (t, 7.1 Hz, 6 H), 1.24 (t, 7.1 Hz, 6 H) ppm; ^{13}C NMR ($CDCl_3$) δ 172.07 (C=O), 171.95 (C=O), 91.84, 73.00, 65.48, 62.62, 61.80, 34.15, 14.14, 14.02 ppm; EIMS *m/z* (M$^+$) 554. Anal. Calcd for $C_{28}H_{34}FeO_8$: C, 60.71; H, 6.19. Found: C, 61.11; H, 6.42.

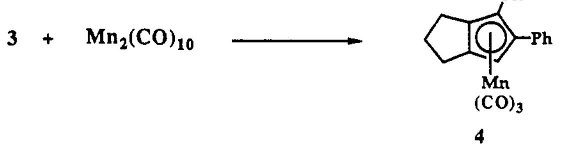
X-ray Structure of 9. Yellow crystals grown from hexane solution were cut to appropriate sizes. The data crystal (approximately 0.67 × 0.53 × 0.55 mm) was mounted on a Siemens P4 diffractometer with SCANS software, and the unit cell parameters were obtained from a least-squares fit of the reflections (4.0° < 2θ < 50.0°). Data were collected with graphite-monochromated Mo Kα radiation by using ω/2θ scan method. The data were corrected for Lorentz and polarization effects and averaged (R_{av} = 1.22%) to yield 3080 independent reflections and observed reflections greater than 2σ used in the final refinement. The absorption correction was made empirically. The Patterson map was solved for the Mn position. Subsequent full-matrix least-squares, difference Fourier cycles located all the remaining heavy atoms. Hydrogen atoms were included in calculated positions with fixed isotropic thermal parameters. Thermal parameters of non-hydrogen atoms were treated anisotropically. The model converged to the unweighted and weighted *R* factors 0.0396 and 0.0566, respectively. In the final difference Fourier, the largest residual peak was 0.42 e/Å^3. Crystal data, details of the data collection, and refinement parameters for 5 are listed in Table I. The final atomic parameters for 5 are given in Table II.

X-ray Structure of 16. Yellow large crystals grown from hexane solution were cut to appropriate size. The data crystal, approximately 0.23 × 0.31 × 0.17 mm, was mounted on a Siemens P4 diffractometer with XSCANS software, and the unit cell parameters were obtained from a least-squares fit of the reflections (3.5° < 2θ < 50.0°). Data were collected with graphite-monochromated Mo Kα radiation by using the ω/2θ scan method. The data were corrected for Lorentz and polarization effects and yielded 1999 independent reflections greater than 4σ which were used in the final refinement. No correction was made for absorption. The Patterson map was solved for the Fe position. Subsequent full-matrix least-squares, difference Fourier cycles located all the remaining heavy atoms. Hydrogen atoms were included in calculated positions with fixed isotropic thermal parameters. Thermal parameters of non-hydrogen atoms were treated anisotropically. The model converged to the unweighted and weighted *R* factors 0.07 and 0.0447, respectively. In the final difference Fourier, the largest residual peak was 0.48 e/Å^3. Crystal data, details of the data collection, and refinement parameters for 12 are listed in Table I. The final atomic parameters for 12 are given in Table III.

Results and Discussion

Synthesis of Cyclopentadienylmetal Compounds. One of the general synthetic strategies for the synthesis of cyclopentadienes is the derivatization of cyclopentenones.[3] To synthesize the appropriate cyclopentadienyl ligand, we utilized the high-yield synthesis of cyclopentenone by the intermolecular Pauson–Khand reaction. As we have been already shown,[6] the Pauson–Khand reaction between phenylacetylene and cyclopentene produced compound 1 in 70.5% yield. This cyclopentenone can be easily converted to the corresponding cyclopentadiene (Scheme I). The product is a colorless, viscous liquid, which is obtained as a mixture of all possible isomers.

The novel cyclopentadiene compound proved to be a useful precursor to the cyclopentadienylmanganese compound. Refluxing 3 with $Mn_2(CO)_{10}$ in xylene for 2 days resulted in the formation of the yellow oil 4 (eq 1).



(1)

4

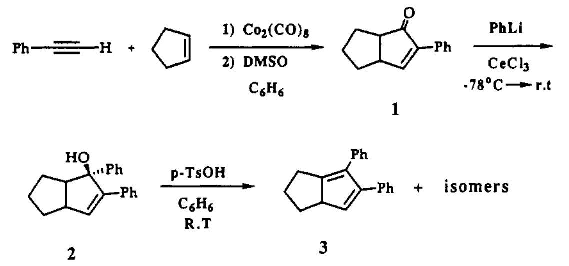
We also utilized the intramolecular Pauson–Khand reaction of α,ω-enyne to synthesize the novel cyclopentadiene 7. The bicyclic ketone compound 5 was obtained in 92% yield.[5] This cyclopentenone compound was converted to a novel cyclopentadiene compound. Treatment of 5 with $NaBH_4$ in the presence of $CeCl_3·7H_2O$ and acid produced 6, and dehydration of 6 by using $MgSO_4$

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for 16

	x	*y*	*z*	*U*(eq)[a]
Fe(1)	2377(1)	744(2)	1247(1)	33(1)
O(1)	1345(3)	1066(11)	−1084(3)	70(3)
O(2)	1939(3)	3920(10)	−593(3)	57(3)
O(3)	478(3)	5323(12)	−1011(3)	77(3)
O(4)	−44(3)	2931(11)	−594(3)	79(3)
O(21)	4636(3)	3739(11)	3408(3)	64(3)
O(22)	4949(3)	708(12)	2988(3)	78(3)
O(23)	3660(2)	677(11)	3653(3)	60(3)
O(24)	3119(3)	3635(10)	3104(3)	60(3)
C(1)	1412(3)	595(16)	829(4)	35(4)
C(2)	1622(3)	−698(16)	1417(4)	40(4)
C(3)	1948(3)	724(16)	1958(4)	44(4)
C(4)	1957(3)	2957(14)	1698(4)	39(4)
C(5)	1611(3)	2827(14)	994(4)	34(4)
C(6)	1366(3)	4374(14)	400(3)	38(3)
C(7)	1089(4)	2746(13)	−202(4)	31(4)
C(8)	1033(3)	414(13)	100(3)	38(4)
C(9)	1517(4)	2712(16)	−634(5)	44(4)
C(10)	434(4)	3612(16)	−637(5)	48(5)
C(11)	1719(5)	767(21)	−1523(5)	105(7)
C(12)	1676(6)	−1418(17)	−1768(6)	139(9)
C(13)	−147(6)	6335(26)	−1374(8)	163(9)
C(14)	−114(6)	7662(26)	−1782(7)	180(11)
C(21)	3281(4)	−470(16)	1671(4)	34(4)
C(22)	2933(4)	−1764(14)	1103(4)	45(4)
C(23)	2745(4)	−266(16)	542(4)	44(4)
C(24)	2956(4)	1912(16)	764(4)	39(4)
C(25)	3292(4)	1754(15)	1464(4)	33(4)
C(26)	3655(3)	3210(13)	2034(4)	42(4)
C(27)	3834(4)	1578(13)	2665(4)	35(4)
C(28)	3670(3)	−849(14)	2393(3)	40(4)
C(29)	4542(4)	1867(17)	3033(5)	49(5)
C(30)	3489(4)	2182(17)	3147(5)	40(4)
C(31)	5285(4)	4354(20)	3754(5)	86(5)
C(32)	5301(4)	6148(22)	4211(5)	140(8)
C(33)	3361(4)	834(18)	4159(4)	79(5)
C(34)	3579(5)	−1084(19)	4612(5)	142(9)

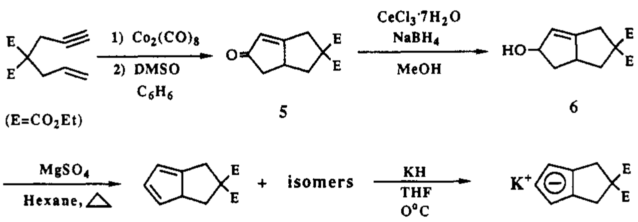
[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Scheme I



1 2 3

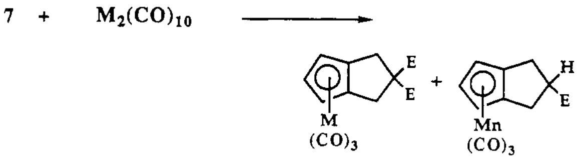
Scheme II



(E=CO₂Et) 5 6 7 8

yielded a mixture of all possible isomers of 7. KH cleanly converts the inseparable mixture into the potassium salt 8 (Scheme II).

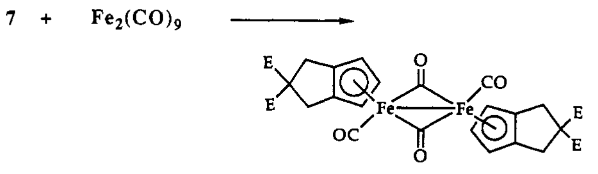
Refluxing 7 with $Mn_2(CO)_{10}$ in xylene for 3 days leads to the formation of the light yellow crystalline solids 9 (41%) and 10 (11%), and refluxing 7 with $Re_2(CO)_{10}$ in xylene for 5 days produces the light yellow solid 11 (31.8%) (eq 2). When 7 was treated with $Re_2(CO)_{10}$ in refluxing xylene, we could see the formation of two kinds of compounds. One of them was 11, and the other was not obtained in the pure form. However, we expect that the other would be the same kind of species 10, except with rhenium instead of manganese. The yellow crystalline compounds 9 and 11 are air-stable and are very soluble in polar organic solvents. Single crystals of 9 suitable for X-ray studies were grown in hexane solution. The structure of 9 will be described later.



(2)

9 (M=Mn)
11 (M=Re)
10

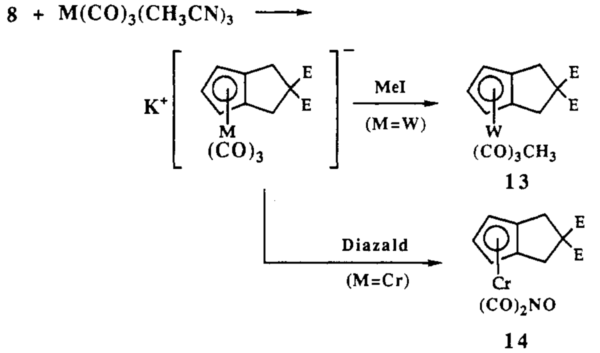
Refluxing 7 with $Fe_2(CO)_9$ in benzene for 24 h produces the dimeric compound 12 (55.3%) (eq 3). The IR spectrum of 12 displays a bridging carbonyl frequency at 1760 cm^{-1}. Compound 12 might serve as a useful precursor to a variety of bicyclic diester cyclopentadienyliron dicarbonyl compounds.



(3)

12

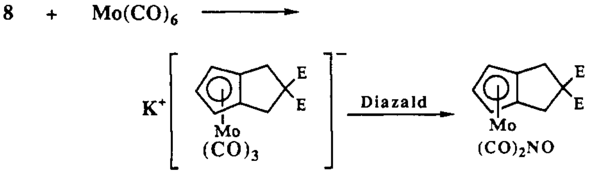
Treatment of 8 with $W(CO)_3(CH_3CN)_3$ and then with MeI led to the isolation of 13 (31.3%), and refluxing of 8 with $Cr(CO)_3(CH_3CN)_3$ and then with Diazald led to the isolation of the orange solid 14 (66.5%) (eq 4). When 8 was treated with $Mo(CO)_3(CH_3CN)_3$ and Diazald, the corresponding compound was not obtained. However, treatment of 8 with $Mo(CO)_6$ and then with Diazald led to the isolation of compound 15 with a rather low yield (eq 5).



(4)

13

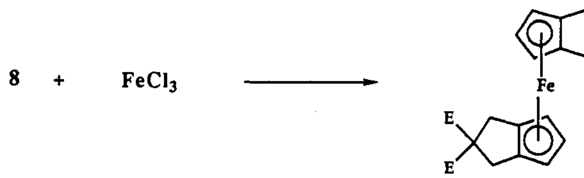
14



(5)

15

Refluxing 8 with ferric chloride in THF for 24 h led to the formation of a yellow solid of ferrocene derivative 16 (32.6%), after chromatographic purification of the crude product (eq 6). The ^1H NMR spectrum of 16 does not



(6)

show the typical pattern of disubstituted ferrocene systems.[10] One slightly deshielded singlet at δ 3.78 ppm is observed for the cyclopentadienyl ring protons. Single crystals of 16 suitable for X-ray studies were grown in hexane solution. The structure of 16 will be described later.

Molecular Structures of 9 and 16. The geometry of 9 along with the atomic numbering scheme used is depicted in Figure 1, and bond distances and angles are given in Table IV. The Mn atom in 9 has the usual piano-stool[11] coordination characteristic of monocyclopentadienyl complexes. The dienyl carbon atoms C(1), C(2), C(3), C(4), and C(5) define a nearly perfect plane with a maximum deviation of 0.005(2) Å. The atoms C(6) and C(8) of the substituents are not strictly within the ring plane but are displaced from it on opposite sides by 0.160(2) and 0.129(2) Å, respectively. A similar pattern is observed for other cyclopentadienylmanganese compounds.[12] The manganese atom is located 1.771(1) Å below the plane of the dienyl ring. The Mn–C(Cp ring) bond lengths range from 2.120(3) to 2.158(2) Å (average 2.142 Å), which is very close to the average Mn–C(Cp ring) value in the molecules of cymantrene.[11] The C(1)–C(2) and C(3)–C(4) bonds, lying across the metal carbonyls, are rather longer than other C–C bonds. The Mn–carbonyl bonds are linear normal lengths of Mn–C (average 1.781 Å) and C–O (average 1.149 Å).

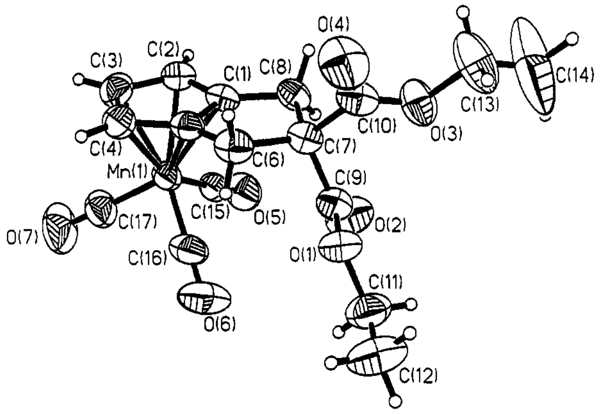


Figure 1. Molecular structure of compound 9, with the atom-labeling scheme.

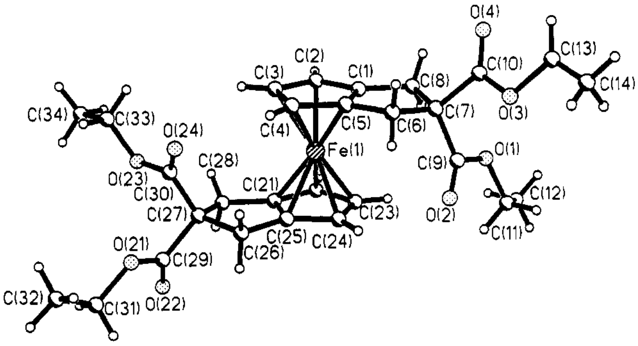


Figure 2. Molecular structure of compound 16, with the atom-labeling scheme.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for 9

Mn(1)–C(1)	2.151(2)	Mn(1)–C(2)	2.138(3)
Mn(1)–C(3)	2.120(3)	Mn(1)–C(4)	2.143(3)
Mn(1)–C(5)	2.158(2)	Mn(1)–C(15)	1.776(3)
Mn(1)–C(16)	1.782(3)	Mn(1)–C(17)	1.787(3)
O(1)–C(9)	1.333(3)	O(1)–C(11)	1.456(4)
O(2)–C(9)	1.190(4)	O(3)–C(10)	1.323(3)
O(3)–C(13)	1.457(4)	O(4)–C(10)	1.193(4)
O(5)–C(15)	1.151(4)	O(6)–C(16)	1.159(4)
O(7)–C(17)	1.138(4)	C(1)–C(2)	1.427(3)
C(1)–C(5)	1.410(4)	C(1)–C(8)	1.493(3)
C(2)–C(3)	1.416(4)	C(3)–C(4)	1.422(4)
C(4)–C(5)	1.407(3)	C(5)–C(6)	1.502(3)
C(6)–C(7)	1.555(3)	C(7)–C(8)	1.563(4)
C(7)–C(9)	1.526(4)	C(7)–C(10)	1.540(3)
C(11)–C(12)	1.465(6)	C(13)–C(14)	1.370(7)
C(1)–Mn(1)–C(2)	38.9(1)	C(1)–Mn(1)–C(3)	64.5(1)
C(1)–Mn(1)–C(15)	95.9(1)	C(2)–Mn(1)–C(15)	91.8(1)
C(15)–Mn(1)–C(16)	92.4(1)	C(4)–Mn(1)–C(15)	157.1(1)
C(16)–Mn(1)–C(17)	91.8(1)	C(4)–C(5)–C(6)	139.2(3)
C(2)–C(1)–C(5)	108.1(2)	C(5)–C(6)–C(7)	103.4(2)
C(5)–C(1)–C(8)	112.0(2)	C(6)–C(7)–C(9)	112.2(2)
C(1)–C(2)–C(3)	106.5(2)	C(6)–C(7)–C(10)	111.4(2)
C(1)–C(5)–C(6)	111.2(2)	C(1)–C(8)–C(7)	103.2(2)
C(6)–C(7)–C(8)	107.4(2)	O(4)–C(10)–C(7)	124.6(2)
Mn(1)–C(16)–O(6)	178.0(3)	O(3)–C(13)–C(14)	111.3(4)

The geometry of 16 along with the atomic numbering scheme used is depicted in Figure 2, and selected bond distances and angles are given in Table V. The average C–C distance is 1.424 Å in ring 1 (atoms C(1)–C(5)) and 1.420 Å in ring 2 (atoms C(21)–C(25)). The Cp rings are planar (with a maximum deviation of 0.010(7) for ring 1 and 0.010(9) Å for ring 2, respectively) and nearly parallel, the angle between the planes being 1.22°. The atoms C(6) and C(8) of the substituents on ring 1 are not strictly within the ring plane but are displaced from it on opposite sides by 0.054(6) and 0.113(7) Å, respectively. In the same way, atoms C(26) and C(28) of the substituents on ring 2 are not strictly within the ring plane but are displaced from it on opposite sides by 0.027(7) and 0.130(6) Å, respectively. The iron is located 1.651(2) Å from the plane of ring 1 and 1.648(2) Å from the plane of ring 2. The Fe–C(Cp ring) bond lengths range from 2.023(10) to 2.067(8) Å (average 2.045 Å). The longest Fe–C distances are to C(1) and C(21), which are opposite each other. The average Fe–C(Cp ring) distances agree with those found in 1,3′-diacetylferrocene of 2.046 Å[13] and in bis(π-azulene)iron of 2.044 Å.[14] The bond lengths in the two ester groups are similar to the values expected for organic ester compounds.[15] 16 adopts an eclipsed conformation with the bicyclic ester located in a manner almost identical with that previously reported for 1,1′-bis(*N*-methylcarbamyl)ferrocene.[16] This mini-

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Table V. Selected Bond Distances (Å) and Bond Angles (deg) for 16

Fe–C(1)	2.060(7)	Fe–C(2)	2.045(9)
Fe–C(3)	2.039(9)	Fe–C(4)	2.041(9)
Fe–C(5)	2.054(8)	O(1)–C(9)	1.334(11)
O(1)–C(11)	1.458(15)	O(2)–C(9)	1.177(12)
O(3)–C(10)	1.318(12)	O(3)–C(13)	1.491(13)
O(4)–C(10)	1.185(12)	C(1)–C(2)	1.404(12)
C(1)–C(5)	1.417(12)	C(1)–C(8)	1.494(10)
C(2)–C(3)	1.419(11)	C(3)–C(4)	1.450(13)
C(4)–C(5)	1.432(11)	C(5)–C(6)	1.508(11)
C(6)–C(7)	1.557(11)	C(7)–C(8)	1.559(11)
C(7)–C(9)	1.532(15)	C(7)–C(10)	1.546(11)
C(11)–C(12)	1.399(16)	C(13)–C(14)	1.193(23)
C(1)–Fe–C(2)	40.0(3)	C(1)–Fe–C(3)	67.8(3)
C(2)–Fe–C(4)	69.5(4)	C(1)–Fe–C(21)	156.8(4)
C(2)–Fe–C(21)	122.3(4)	C(3)–Fe–C(21)	108.7(3)
C(4)–Fe–C(21)	124.9(3)	C(5)–Fe–C(21)	161.8(3)
C(5)–Fe–C(22)	156.0(3)	C(21)–Fe–C(22)	40.5(3)
C(9)–O(1)–C(11)	116.8(8)	C(10)–O(3)–C(13)	122.2(9)
Fe–C(1)–C(2)	69.4(4)	Fe–C(1)–C(8)	127.2(6)
C(2)–C(1)–C(5)	108.6(7)	C(2)–C(1)–C(8)	141.1(8)
C(5)–C(1)–C(8)	110.3(7)	Fe–C(2)–C(1)	70.6(5)
C(1)–C(2)–C(3)	108.1(8)	C(2)–C(3)–C(4)	108.6(7)
C(1)–C(5)–C(6)	112.3(7)	C(4)–C(5)–C(6)	138.6(7)
C(6)–C(7)–C(8)	107.2(6)	C(6)–C(7)–C(9)	109.4(6)
O(1)–C(9)–O(2)	122.8(10)	O(1)–C(9)–C(7)	110.0(8)

mizes steric repulsion between substituents and would allow very efficient packing in the unit cell.

It has been demonstrated that inter- and intramolecular Pauson–Khand reaction products, cyclopentenones, can be used to make novel cyclopentadienyltransition-metal compounds. This method will probably find wider application than the commonly used synthetic methodology[17] based on functionalization at the ring periphery of Cp or Cp* metal complexes. Now we are continuing to explore the use of the Pauson–Khand reaction products to make highly substituted cyclopentadienylmetal compounds.[18] The preliminary studies[19] show that the retro Diels–Alder reaction of the Pauson–Khand reaction products generates high yields of cyclopentadienyl precursors, which would then be used to prepare 1,2-disubstituted and/or 1,2,3-trisubstituted cyclopentadienyl complexes. Studies related to properties of these novel cyclopentadienylmetal compounds are in progress.

Acknowledgment. This work was supported by a grant from the Korea Science and Engineering Foundation.

Supplementary Material Available: Crystallographic data, including complete tables of bond angles, positional parameters for hydrogens, thermal parameters, and torsion angles for **9** and **16** and a complete table of bond distances for **16** (11 pages). Ordering information is given on any current masthead page.

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