(1778 cm^{-1}) and two terminal carbonyls (1874, 1830 cm^{-1}).[15] In solution, however, the spectrum of 4 becomes more complicated, and it seems likely that the carbonyl ligands undergo some type of fluctional behavior. There is only a single carbonyl resonance in the ^{13}C NMR spectrum, suggesting that interconversion of all the CO ligands in solution is rapid on the NMR time scale.[16]

Preliminary mechanistic studies of the cluster forming reaction show that no significant rate inhibition occurs upon addition of free CO to the reaction of 1 with CpMo(CO)$_3$H or of free PPh$_3$ in the CpMo(CO)$_2$(PPh$_3$)H reaction. It therefore appears unlikely that the reaction is initiated by reversible loss of a ligand from either the hydride or the vinylidene complex. Other mechanistic alternatives for the first steps of the reaction include direct, irreversible displacement of L from the molybdenum center by the vinylidene group, followed by insertion of this group into the M–H bond, or transfer of a hydrogen atom from Mo to the β-carbon of the vinylidene, leading to a radical pair, in a process analogous to that which occurs in the hydrogenation of α-methylstyrene by Cp(CO)$_3$MoH[17] or by HMn(CO)$_5$.[18,19] Kinetic and isotope effect studies aimed at distinguishing these possibilities are in progress.

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Registry No. 1, 88336-67-8; 2, 88336-69-0; 3, 88336-70-3; 4, 88343-62-8; Na[CpCo(CO)]$_2$, 62602-00-0; Cp(CO)$_3$MoH, 12176-06-6; CpMo(CO)$_2$(PPh$_3$)H, 33519-69-6; H$_2$C=CBr$_2$, 593-92-0.

Supplementary Material Available: Data collection and refinement parameters, least-squares positional parameters, positional parameters and their esd's, general temperature factor expressions and their esd's, and raw interatomic distances and angles for 1 (31 pages). Supplied with the archival edition of the journal, available in many libraries; alternatively, ordering information is given on any current masthead page.

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[14] 4: mp, no detectable melting or decomposition below 220 °C; ^{1}H NMR (C$_6$D$_6$) δ 4.74 (s, 5 H), 4.69 (s, 3 H), 4.44 (s, 10 H); ^{13}C NMR (CD$_2$Cl$_2$, gated spectrum) δ 341.2 (s, μ-CCH$_3$), 238.8 (s, CO), 92.4 (d, C$_5$H$_5$, J = 12.8 Hz), 89.7 (d, C$_5$H$_5$, J = 11.6 Hz), 55.3 (q, μ-CCH$_3$, J = 13.1 Hz, one line obscured by solvent resonances), 129.0 (very small resonance, not assignable); MS (15 eV), m/e 518, 519, 520, 521, 522, 524 (M$^+$ for each of the naturally occurring isotopes of Mo); IR (Nujol mull) 1874 (s), 1830 (s), 1778 (s) cm^{-1}; IR (C$_6$H$_6$) 1909 (s), 1840 (m), 1815 (sh), 1792 (m), 1747 (m) cm^{-1}. Anal. Calcd for C$_{20}$H$_{18}$Co$_2$MoO$_3$: C, 46.18; H, 3.49. Found: C, 46.13; H, 3.60.

[15] This assignment has been confirmed by a single-crystal X-ray diffraction study. The details of this study will appear elsewhere.

[16] Quadrupolar broadening of the bridging CO may also explain this result. We thank a reviewer for suggesting this possibility.

[17] Sweany, R. L.; Comberrel, D. S.; Dombourian, M. F.; Peters, N. A. *J. Organomet. Chem.* **1981**, *216*, 57.

[18] (a) Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335. (b) Sweany, R. L.; Butler, S. C.; Halpern, J. *J. Organomet. Chem.* **1981**, *213*, 487. (c) Feder, H. M.; Halpern, J. *J. Am. Chem. Soc.* **1975**, *97*, 7186.

[19] An analogous proton-transfer mechanism seems unlikely. The reaction of 1 with CpMo(CO)$_3$H is not accelerated in THF. Furthermore, the rate of formation of 4 is qualitatively similar in the reaction of 1 with both CpMo(CO)$_3$H and CpMo(CO)$_2$(PPh$_3$)H, despite the very different acidities of the two Mo hydrides. Cf. Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255.

(Tropone)- and (Tropothione)iron Complexes from Ring Expansion Reactions

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Summary: The benzene ring in the η^6-phenoxide ion–, *o*-chlorophenoxide ion–, or thiophenoxide ion–(η^5-cyclopentadienyl)iron complex, which may be formulated as a neutral complexed cyclic ketone or thioketone, undergoes a ring expansion upon reaction with diazomethane to give, respectively, the (η-tropone)-, (2-chlorotropone)-, or (tropothione)(η^5-cyclopentadienyl)iron cation, isolated as the hexafluorophosphate. The bonding in these complexes appears to be different from that established for the (η^4-tropone)iron tricarbonyl complex.

We wish to report a novel ring expansion reaction of certain complexed phenoxide or thiophenoxide ions to give tropone or tropothione complexes of iron. Most of the known (tropone)metal carbonyl complexes have been prepared directly from tropone,[2] although a (tetraphenyltropone)iron tricarbonyl has been obtained from a rearrangement process.[3] There are very few known ring expansion reactions involving aromatic rings in organometallic chemistry, an example has been reported by Fischer and Breitschaft[4] in the Friedel–Crafts acylation of (η^6-benzene)(η^5-cyclopentadienyl)metal complexes (metal = Cr or Mn) to give low yields of products containing a substituted seven-membered ring as a ligand. reactions of cyclic ketones with CH$_2$N$_2$ are known to give ring expansion resulting in the formation of cyclic ketones with one more C atom in the ring.[5] Helling and Hendrickson[6] have reported that the (η^6-phenol)- or (thiophenol)(η^5-cyclopentadienyl)iron cation upon deprotonation in base gave the phenoxide or thiophenoxide complex (**1a,b**) which may be formulated as the neutral complexed cyclic ketone or thioketone (**2a,b**). In the present work, we have investigated the possibility of ring expansion upon reaction of complexes such as **2a,b** with CH$_2$N$_2$.

The complex **2a** or **2b** was prepared from reaction of (η^6-chlorobenzene)(η^5-cyclopentadienyl)iron hexafluorophosphate (4) with NaOH or NaSH,[6] and upon treatment with CH$_2$N$_2$, the tropone or tropothione complex, **3a** or **3b**,

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[1] Post-doctoral fellow from the Institute of Chemistry, Silesian University, Katowice, Poland.

[2] (a) Pauson, P. L.; Todd, K. H. *J. Chem. Soc. C* **1970**, 2315–2318. (b) Hunt, D. F.; Farrant, G. C.; Rodeheaver, G. T. *J. Organomet. Chem.* **1972**, *38*, 349–363. (c) Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1975**, 829–830. (d) Domingos, A. J. P.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2288–2291.

[3] Klime, J.; Weiss, E. *Chem. Ber.* **1982**, *115*, 2175–2180.

[4] Fischer, E. O.; Breitschaft, S. *Angew Chem., Int. Ed. Engl.* **1963**, *2*, 100–101; *Chem. Ber.* **1966**, *99*, 2213–2226.

[5] Gutsche, C. D.; Redmore, D. "Carbocyclic Ring Expansion Reactions"; Academic Press: New York, 1968; Chapter 4.

[6] Helling, J. F.; Hendrickson, W. A. *J. Organomet. Chem.* **1979**, *168*, 87–95.

[7] Ikegami, Y. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 972–977.

[8] Asao, T.; Kikuchi, Y. *Chem. Lett.* **1972**, 413–416.

0276-7333/84/2303-0331$01.50/0

Table I. Yields, Analytical Data, and Some IR Absorptions for the Ring Expansion Products

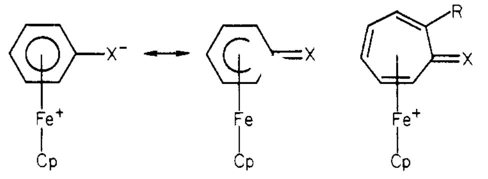
		anal., %				
		C		H		
product	yield, %	calcd	found	calcd	found	IR absorptns, cm^{-1}
(tropone)$FeCp^+PF_6^-$ (**3a**PF_6)	40	38.74	38.90	2.98	3.11	1470, 1530 (C=O, C=C)[a]
(tropothione)$FeCp^+PF_6^-$ (**3b**PF_6)	28	37.14	36.64	2.86	2.77	1020, 1080, 1505 (C=S, C=C)[b]
(2-chlorotropone)$FeCp^+PF_6^-$ (**3c**PF_6)	83	35.46	35.63	2.48	2.62	1465, 1480, 1535 (C=O, C=C)[c]

[a] The C=O and C=C absorptions for tropone[7] appear at 1580 and 1634 cm^{-1}. [b] According to a thesis quoted by Asao and Kikuchi,[8] the C=S absorption for tropothione appears at 1080 cm^{-1}. [c] The C=O and C=C absorptions for 2-chlorotropone[7] appear at 1538, 1570, and 1618 cm^{-1}.

Table II. ^{13}C NMR Data

	chemical shifts, ppm from Me_4Si				
compd	C-1	C-2,7	C-3,6	C-4,5	others
tropone[a]	187.7	141.7	135.8	134.4	
(tropone)$Fe(CO)_3$[b]	197.4	62.1 (C-2) 122.4 (C-7)	91.3 (C-3) 146.6 (C-6)	95.4 (C-4) 51.8 (C-5)	207.8 (CO)
3aPF_6[c]	149.6	87.1	77.8	75.8	74.8 (Cp)
tropothione[d]	154.8	138.1	130.4	129.2	
3bPF_6[c]	104.6	87.9	87.3	86.1	78.1 (Cp)
2-chlorotropone[a]	179.9	148.7 (C-2) 135.6 (C-7)	135.3 (C-3) 138.3 (C-6)	131.2 (C-4) 133.9 (C-5)	
3cPF_6[c]	147.9	95.4 (C-2) 87.2 (C-7)	86.9[e]	74.7 (C-4) 76.6 (C-5)	76.5 (Cp)

[a] Data from ref 9. [b] Data from ref 11. [c] Assignments of chemical shifts for C-1 to C-7 were made by analogy with the corresponding absorptions in the free ligands; in general peaks at lower fields were assigned to carbons closer to C-1. [d] Calculated from data in ref 10. [e] Tentatively assigned to both C-3 and C-6 since five peaks were observed from C-2 to C-7.



1a, X = O
b, X = S

2a, X = O
b, X = S

3a, X = O, R = H
b, X = S, R = H
c, X = O, R = Cl

respectively, was formed. In a similar way reaction of the (η^6-*o*-dichlorobenzene)(η^5-cyclopentadienyl)iron cation with NaOH followed by treatment with CH_2N_2 gave the 2-chlorotropone complex **3c**. Apparently, reaction of the *o*-dichlorobenzene complex with NaOH resulted in the displacement of only one chlorine atom, leading to the formation of **3c**.

As an illustration of a typical reaction, a solution of 1.13 g (3.0 mmol) of **4** and 0.60 g (15 mmol) of NaOH in 18 mL of tetrahydrofuran and 12 mL of H_2O was stirred overnight at room temperature and under N_2. An ether solution (15 mL) of CH_2N_2 (about 7 mmol) was then added, and stirring was continued for a further 6 h. The resulting material was treated with 0.48 g (3.0 mmol) of NH_4PF_6 and 10 mL of 5% HCl, and then the mixture was evaporated to dryness under reduced pressure at about 30 °C. The crude product was extracted from the residue with acetone. After removal of the acetone the product was purified by passage through an alumina column, any unreacted complex being removed first by elution with a 49:1 mixture of CH_2Cl_2–CH_3OH, with the desired product, the hexafluorophosphate salt of **3a**, being eluted with a 2:3 mixture of CH_2Cl_2–CH_3OH. The eluate containing the product was evaporated to dryness and placed in a vacuum desiccator over P_2O_5 for 3 days before it was recrystallized from acetone–ether to give 0.45 g (40%) of the orange-yellow hexafluorophosphate salt of **3a**.

Given in Table I are the yields, analytical data, and some IR absorptions for the hexafluorophosphates of **3a**, **3b**, and **3c**. The ^{13}C NMR chemical shifts for these products are summarized in Table II together with the corresponding data for the free ligands, tropone,[9] tropothione,[10] and 2-chlorotropone.[9] For comparison, the ^{13}C data for the (tropone)iron tricarbonyl complex (**5**)[11] are also included in Table II.

It is of interest to note that chemical and X-ray evidence[2b,12] have shown that the bonding in the tricarbonyl complex **5** is η^4 and the ^{13}C NMR data for **5** (Table II) are in agreement with η^4 bonding, since only the C-2, C-3, C-4, and C-5 absorptions of **5** show upfield shifts when compared with the corresponding absorptions for the free ligand. On the other hand, the ^{13}C peaks for all the carbons in the seven-membered ring of **3a**, **3b**, or **3c** are shifted upfield (Table II), indicating that the bonding of the seven-membered ring to iron in these complexes is different from that of **5**. However, whether the bonding in **3a**, **3b**, and **3c** is η^6 or whether it also involves the C-1 carbonyl or thiocarbonyl will require clarification by further studies. The results from the present work do show the utility of a ring expansion as a relatively easy method of synthesis of complexes with seven-membered cyclic ligands.

Registry No. **2a**, 70124-47-9; **2b**, 70124-21-9; **2c**, 87831-02-5; **3a**·PF_6, 87830-97-5; **3b**·PF_6, 87830-99-7; **3c**·PF_6, 87831-01-4; **4**, 33086-63-4; (η^6-*o*-dichlorobenzene)(η^5-cyclopentadienyl)iron cation, 77487-01-5.

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(9) Bagli, J. F.; St.-Jacques, M. *Can. J. Chem.* **1978**, *56*, 578–584.

(10) Machiguchi, T.; Inagaki, Y.; Hoshino, M.; Kitahara, Y. *Chem. Lett.* **1974**, 497–498.

(11) Johnson, B. F. G.; Lewis, J.; McArdle, P.; Norton, J. R. *J. Chem. Soc., Dalton Trans.* **1974**, 1253–1258.

(12) Dodge, R. P. *J. Am. Chem. Soc.* **1964**, *86*, 5429–5431. Smith, D. L.; Dahl, L. F. *Ibid.* **1962**, *84*, 1743–1744.