A Cyclopropenylidene Approach to Tricarbide Complexes: Synthesis and Structure of $[M(CO)_5\{\mu_2\text{-}C_3(OCH_2CH_3)\}Fe(CO)_2(Cp)]$ (M = Cr, Mo, W)

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Summary: The diethoxycyclopropenylidene complexes $[M(CO)_5\{C_3(OCH_2CH_3)_2\}]$ (M = Cr, Mo, W) react with $K[Fe(CO)_2(Cp)]$ to give the bimetallic cyclopropenylidene complexes $[M(CO)_5\{\mu_2\text{-}C_3(OCH_2CH_3)\}Fe(CO)_2(Cp)]$, but the second ethoxide is not displaced by excess $K[Fe(CO)_2(Cp)]$. Spectroscopic evidence (^1H NMR, ^{13}C NMR, and IR) as well as a X-ray crystal structure determination of $[Cr(CO)_5\{\mu_2\text{-}C_3(OCH_2CH_3)\}Fe(CO)_2(Cp)]$ suggests that the central C_3 ring has a great deal of cyclopropenium character.

Transition metal complexes with pure carbon ligands are of growing interest. This research is driven by the hope that these new complexes may exhibit strong structural characteristics, electrical conductivity (i.e., behave as "molecular wires"), nonlinear optical properties, or liquid crystalline characteristics. There are several examples of complexes with C_1, C_2, C_3, and C_4 chains connecting two or more metals.[1−4] The current focus of much of this research is on linear C_x ligands, complementing work on fullerenes, three-dimensional carbon allotropes,[5−8] but the organometallic chemistry of two-dimensional carbon networks is barely investigated.[9−16] We are interested in preparing metal complexes of small planar C_x ligands, in particular. Recently we reported the first trimetallic complex of cyclo-C_3, $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$.[17] We report here our extension of this work toward neutral cyclo-C_3 (cyclopropenylidene) complexes.

We utilized the known group 6 diethoxycyclopropenylidene complexes as precursors.[18] The reaction of 1 equiv of potassium cyclopentadienyldicarbonylferrate with $[M(CO)_5\{C_3(OCH_2CH_3)_2\}]$ (M = Cr (**1**), Mo (**2**), W (**3**)) produced bimetallic $[Cr(CO)_5\{\mu_2\text{-}C_3(OCH_2CH_3)\}Fe(CO)_2(Cp)]$ (**4**),[19] $[Mo(CO)_5\{\mu_2\text{-}C_3(OCH_2CH_3)\}Fe(CO)_2(Cp)]$ (**5**),[20] and $[W(CO)_5\{\mu_2\text{-}C_3(OCH_2CH_3)\}Fe(CO)_2(Cp)]$ (**6**)[21] (Scheme 1) in 65%, 60%, and 61% yields, respectively.

An X-ray crystal structure determination[22] shows that **4** has a scalene C_3 ring with a chromium center, iron center, and ethoxide bound to the vertices (Figure 1). The $Cr-C_{ring}$ distance, 2.066(3) Å, falls within the range of known chromium cyclopropenylidene complexes.[18,23,24]

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(19) A solution of $K[Fe(CO)_2(Cp)]$, from $[Fe_2(CO)_4(Cp)_2]$ (225 mg, 0.600 mmol) and $NaK_{2.8}$ (0.38 mL, 0.60 mmol), was slowly added at −78 °C to a solution of $[Cr\{C_3(OCH_2CH_3)_2\}(CO)_5]$ (402 mg, 1.30 mmol) in THF (10 mL). Slow warming to ambient temperature and conventional workup (see Supporting Information) led to yellow crystals of $[Cr(CO)_5\{\mu_2\text{-}C_3(OCH_2CH_3)\}Fe(CO)_2(Cp)]$ (423 mg, 65%): Mp 101−104 °C (dec); ^1H NMR (200 MHz, C_3D_6O) δ 5.45 (s, 5, Cp), 4.72 (q, $J = 7$ Hz, 2, OCH_2CH_3), 1.51 (t, $J = 7$ Hz, 3, OCH_2CH_3); ^{13}C NMR (400 MHz, C_3D_6O) δ 226.13 (Cr−C), 225.27 (*trans* Cr−CO), 219.81 (*cis* Cr−CO), 216.21 (O−C), 213.25 (Fe−CO), 201.98 (Fe−C), 87.48 (Cp), 71.62 (OCH_2CH_3), 15.64 (OCH_2CH_3); MS (EI) *m/e* 450 (M^+), 422 (M − CO), 394 (M − 2CO), 366 (M − 3CO), 338 (M − 4CO), 310 (M − 5CO), 282 (M − 6CO), 254 (M − 7CO); IR (CH_2Cl_2) ν 2058, 2043, 2002, 1922 (CO) cm^{-1}. Anal. Calcd for $C_{17}H_{10}CrFeO_8$: C, 45.36; H, 2.24. Found: C, 45.74; H, 2.55.

(20) A solution of $K[Fe(CO)_2(Cp)]$, from $[Fe_2(CO)_4(Cp)_2]$ (393 mg, 1.10 mmol) and $NaK_{2.8}$ (0.66 mL, 1.1 mmol), was slowly added at −78 °C to a solution of $[Mo\{C_3(OCH_2CH_3)_2\}(CO)_5]$ (802 mg, 2.20 mmol) in THF (10 mL). Slow warming to ambient temperature and conventional workup (see Supporting Information) led to yellow crystals of $[Mo(CO)_5\{\mu_2\text{-}C_3(OCH_2CH_3)\}Fe(CO)_2(Cp)]$ (651 mg, 60%): Mp 112−114 °C; ^1H NMR (200 MHz, C_3D_6O) δ 5.46 (s, 5, Cp), 4.71 (q, $J = 7$ Hz, 2, OCH_2CH_3), 1.51 (t, $J = 7$ Hz, 3, OCH_2CH_3); ^{13}C NMR (400 MHz, C_3D_6O) δ 219.33 (Mo−C), 214.78 (O−C), 214.34 (*trans* Mo−CO), 213.24 (Fe−CO), 208.14 (*cis* Mo−CO), 201.76 (Fe−C), 87.52 (Cp), 71.07 (OCH_2CH_3), 15.66 (OCH_2CH_3); MS (EI) *m/e* 494 (M^+); IR (CH_2Cl_2) ν 2063, 2045, 2002, 1927 (CO) cm^{-1}. Anal. Calcd for $C_{17}H_{10}FeMoO_8$: C, 41.33; H, 2.04. Found: C, 40.88; H, 2.02.

(21) A solution of $K[Fe(CO)_2(Cp)]$, from $[Fe_2(CO)_4(Cp)_2]$ (40 mg, 0.113 mmol) and $NaK_{2.8}$ (0.07 mL, 0.11 mmol), was slowly added at −78 °C to a solution of $[W\{C_3(OCH_2CH_3)_2\}(CO)_5]$ (109 mg, 0.24 mmol) in THF (10 mL). Slow warming to ambient temperature and conventional workup (see Supporting Information) led to yellow crystals of $[W(CO)_5\{\mu_2\text{-}C_3(OCH_2CH_3)\}Fe(CO)_2(Cp)]$ (86 mg, 61%): Mp 124−126 °C; ^1H NMR (200 MHz, C_3D_6O) δ 5.47 (s, 5, Cp), 4.71 (q, $J = 7$ Hz, 2, OCH_2CH_3), 1.51 (t, $J = 7$ Hz, 3, OCH_2CH_3); ^{13}C NMR (400 MHz, C_3D_6O) δ 213.12 (Fe−CO), 212.02 (O−C), 207.22 (W−C, $J = 48$ Hz), 204.99 (*trans* W−CO, $J = 67$ Hz), 200.29 (Fe−C), 199.09 (*cis* W−CO, $J = 62$ Hz), 87.52 (Cp), 71.16 (OCH_2CH_3), 15.67 (OCH_2CH_3); MS (EI) *m/e* 582 (M^+); IR (CH_2Cl_2) ν 2062, 2045, 2003, 1919 (CO) cm^{-1}. Anal. Calcd for $C_{17}H_{10}FeO_8W$: C, 35.08; H, 1.73. Found: C, 34.91; H, 1.67.

(22) X-ray crystallography of **3**: pale yellow fragment, 0.3 × 0.4 × 0.6 mm^3, Mo Kα radiation, $\mu = 2.645\ mm^{-1}$, $P\bar{1}$, $a = 9.905(2)$ Å, $b = 10.054(2)$ Å, $c = 11.099(2)$ Å, $\alpha = 89.50(3)°$, $\beta = 77.91(3)°$, $\gamma = 61.09(3)°$, $Z = 2$, 3297 unique data, 285 refined parameters, $R_1 = 0.0301$, $wR_2 = 0.0870$ for data with $I > 2\sigma(I)$.

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S0276-7333(96)00681-4 CCC: $12.00

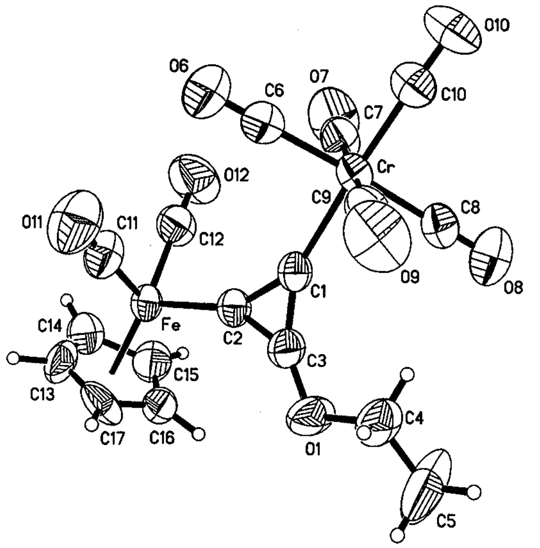
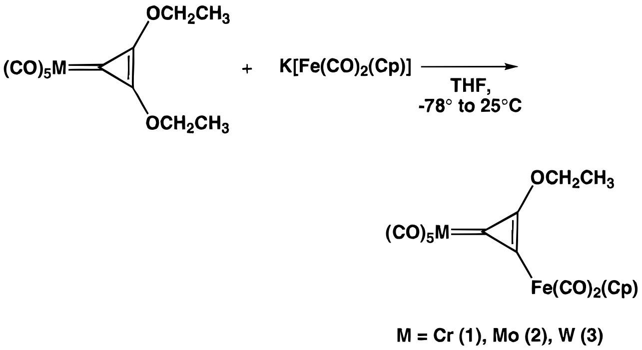


Figure 1. ORTEP plot of [$Cr(CO)_5\{\mu_2\text{-}C_3(OCH_2CH_3)\}Fe(CO)_2(Cp)$] (**4**) showing 50% thermal ellipsoids. Selected distances (Å): Cr−C1, 2.066(3); Fe−C2, 1.911(2); O1−C3, 1.310(3); C1−C2, 1.419(3); C1−C3, 1.367(4); C2−C3, 1.339(3). Selected angles (deg): Cr−C1−C2, 151.5(2); Cr−C1−C3, 151.1(2); Fe−C2−C1, 150.4(2); Fe−C2−C3, 150.2(2); O1−C3−C1, 150.7(2); O1−C3−C2, 146.1(3); C3−C1−C2, 57.4(2), C1−C2−C3, 59.3(2); C2−C3−C1, 63.2(2).

Scheme 1



This bond length is appreciably shorter than a bond between Cr and a sp^2-hybridized carbon (2.21 Å)[25] and longer than those in most Fischer carbenes. Specifically, the Cr−C bond is longer than that in [$Cr\{C_3(OCH_2CH_3)_2\}(CO)_5$] (**1**, 2.010(7) Å)[18] but about the same as those in the less electron-rich complexes **7** and **8** (2.05(1) and 2.071(8) Å).[23,24] The *trans* Cr−CO bond is shorter than the *cis* Cr−CO bonds, thus indicating that the cyclopropenylidene group is a poor π-acceptor but a good σ-donor as seen in similar Fischer carbene complexes with strongly electron-donating substituents on the carbene ligand.

The Fe−C_{ring} bond length, 1.911(2) Å, falls in the range of Fe−C bonds with some multiple character. Compared to neutral [$Fe(R)(CO)_2(Cp)$] compounds, the Fe−C bond in **4** is shorter than typical Fe−C_{sp^3} or Fe−C_{sp^2} single bonds (2.0−2.1 Å)[26] but about the same length as Fe−C_{sp} bonds (1.9 Å).[27,28] This bond is shorter than in the cycloheptatrienylidene complex (**9**, 1.979(3) Å)[29] (Chart 1), similar to the trimetallic cyclopropenium salt **10** (1.913(6), 1.917(6), 1.919(7) Å)[17] and the cyclobutenylidene complex **11** (1.91(2) Å)[30] but longer than the Fe−C bond to the strong π-acceptor CCl_2 (1.808(12) Å).[31] In an 18-electron [$M(CR_2)(CO)_2(Cp)$] complex with strong M−C π-donation, the carbene ligand lies in the [$M(CO)_2(Cp)$] symmetry plane, with Cp(centroid)−M−C−R torsion angles of 0 and 180°. In compound **4**, the two torsion angles are 171.9 and −13.5° suggesting that Fe to cyclopropenyl π-donation may be of some importance in the structure.

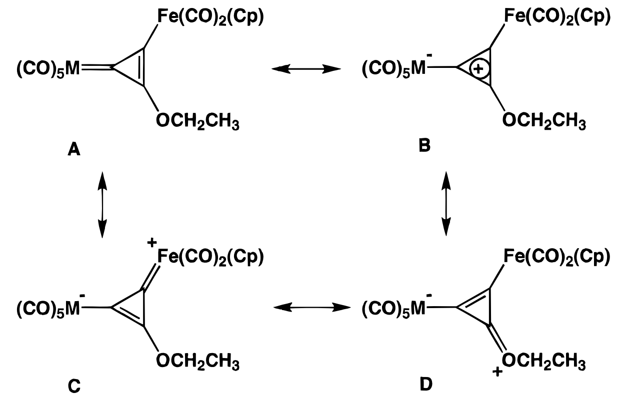
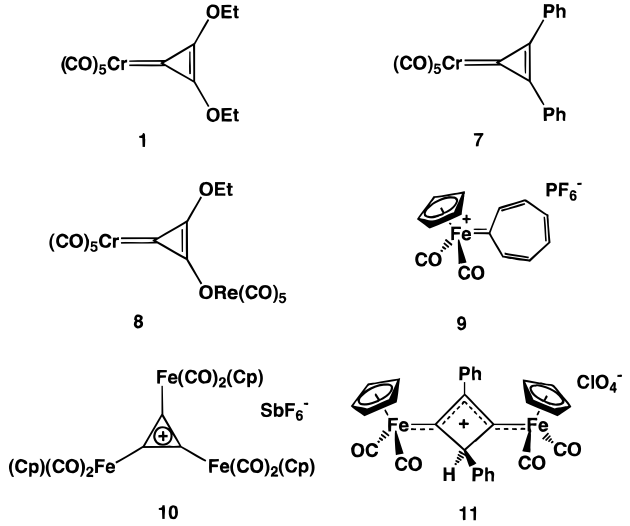


Figure 2.

Chart 1



The structural data of **4** would suggest that, of the four major resonance structures of these compounds (Figure 2), resonance form **B** is the most important, followed by **A** and **C**, with **D** playing little to no role in the structure.

Spectroscopic properties of **4**−**6** are in accord with the solid-state structure of **4**. ^1H NMR and $^{13}C\{^1H\}$ NMR spectra show single [$M(CO)_5$], [$Fe(CO)_2(Cp)$], and ethoxide environments at room temperature, indicating free rotation about all bonds between the ligands and the C_3 ring. Both the ethoxide−C_{ring} and group 6 metal−

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Table 1. Selected ^{13}C-NMR Resonances of Compounds 1−6

compd	M−C$_{ring}$	O−C$_{ring}$	Fe−C$_{ring}$
1 (M = Cr)	191.74	170.73	na
2 (M = Mo)	183.12	169.10	na
3 (M = W)	170.21	167.01	na
4 (M = Cr)	226.13	216.21	201.98
5 (M = Mo)	219.33	214.78	201.76
6 (M = W)	207.22	212.02	200.29

C$_{ring}$ ^{13}C NMR resonances of **4**−**6** are shifted downfield from the resonances of the [M{C$_3$(OCH$_2$CH$_3$)$_2$}(CO)$_5$] compounds (Table 1).[18] This observation is consistent with the LUMO of compounds **4**−**6** being localized on the C$_3$-ring to a greater extent than in **1**−**3**.[32,33] The ^{13}C NMR shifts of the ring carbons attached to the group 6 metal moved upfield with increasing atomic weight of the metal (M = Cr, 226.1 ppm; M = Mo, 219.3 ppm; M = W, 207.2 ppm), which is typical of Fischer carbene complexes.[34] The solution infrared spectra (CH$_2$Cl$_2$) display four characteristic carbonyl stretching absorptions, tentatively assigned as two Fe−CO absorptions at 2060, 2000 cm^{-1} and two group 6 M−CO absorptions at 2050, 1920 cm^{-1}.

While dimetal-substituted cyclopropenylidenes are unprecedented, several monometal-substituted cyclopropenylidenes[23,35−43] and cyclopropenium salts[37−39,44,45] are known. Despite the fact that we are able to displace the ethoxide group from **4** with NH(CH$_3$)$_2$ to form [Cr(CO)$_5${μ_2-C$_3$(NMe$_2$)}Fe(CO)$_2$(Cp)],[46] we have not been able to generate [M(CO)$_5$(μ-C$_3$){Fe(CO)$_2$(Cp)}$_2$] either by reacting the diethoxycyclopropenylidenes **1**−**3** with 2 equiv of K[Fe(CO)$_2$(Cp)] or by displacing the ethoxide substituents from **4**−**6** by using K[Fe(CO)$_2$(Cp)] in THF at room temperature. Attempts to promote the ethoxide loss by electrophilic activation are currently underway.

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Supporting Information Available: Text giving experimental details of the preparation of **4**−**6** and tables of crystallographic data, positional and thermal parameters, bond distances and angles, and planes and conformation angles for **4** (12 pages). Ordering information is given on any current masthead page.

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