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The cyclo-C_3 ligand: trimetallic cyclopropenium complexes of Group 6–8 metals, including the X-ray crystal structure of $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$

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Abstract

Several trimetallic cyclopropenium cations have been prepared via reactions of three equivalents of a metallate anion with $[C_3Cl_3][SbF_6]$. The X-ray crystal structure of $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**1**) shows a nearly equilateral C_3 ring with an iron center bonded to each vertex. The cyclopropenium complexes $[\{Ru(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**2**), $[\{Mo(CO)_3(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**3**), $[\{W(CO)_3(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**4**), and $[\{Re(CO)_5\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**5**) were spectroscopically characterized. Because of the 3-fold symmetrical nature of these complexes, their NMR spectra display a single *cyclo*-C_3 ring carbon resonance and a single set of resonances for the metal moiety. Compound **1** reacts with $Li[BHEt_3]$ and LiMe to give complex reaction mixtures. We were not able to add a fourth metal center to the C_3 ring of **1**. The spectroscopically characterized C_9 complex $[\{Fe(CO)_2(Cp)\}_3\{\mu_3\text{-}C_3(C\equiv C)_3\}][SbF_6]$ (**6**), prepared by the reaction of three equivalents of $[Fe(C\equiv CSiMe_3)(CO)_2(Cp)]$ with $[C_3Cl_3][SbF_6]$, was not stable enough to isolate in analytically pure form. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carbide; Cyclopropenium; Iron; Molybdenum; Rhenium; Ruthenium; Tungsten

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1. Introduction

Small, unsaturated carbon fragments are important in fields ranging from organometallic chemistry [1] to materials science [2] to astrophysics [3,4]. Small, gaseous carbon fragments are the essential building blocks in the formation of macroscopic carbonaceous materials such as graphite, diamond and fullerenes. Species such as C_1, C_2, C_3, and C_4 can be generated in the laboratory by subjecting hydrocarbons or graphite to an electrical arc, high temperatures or irradiation [3,5]. The fullerenes (C_{60}, C_{70}, etc.) are formed by resistive heating [6,7] or the arc-heating of graphite under an inert atmosphere [8,9], probably via the coalescence of small carbon fragments [10]. Surface-bound carbon fragments have been proposed as intermediates in metal-catalyzed Fischer–Tropsch and hydrocarbon conversion reactions [11–16]. In fact, Fischer and Tropsch originally proposed the buildup of larger hydrocarbons via reactive surface carbides [17,18]. Small carbon fragments such as C_2 and C_3 have been spectroscopically observed in interstellar space and in the tail of a comet [3,4].

C_3 is one of the most important and abundant species in carbon vapor [3]. The ground state of C_3 has been calculated to be a linear, symmetrical singlet with an excited singlet state and several metastable triplet states [19]; cyclic C_3 is much higher in energy [3]. Metal complexes of linear C_3 have recently been prepared by Gladysz [20,21] and Templeton [22]. We report here additional details on $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**1**) [23] and several new *cyclo*-C_3 complexes.

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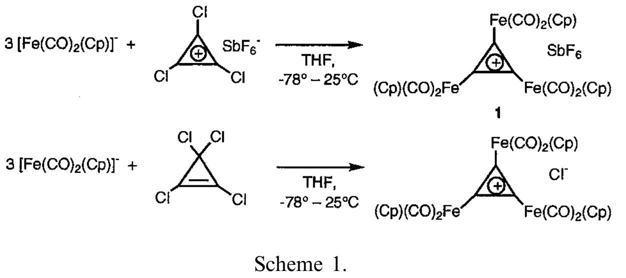
2. Results

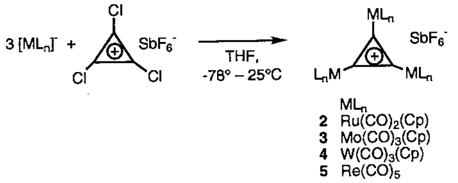
2.1. Synthesis

Reactions of nucleophilic metallates with $[C_3Cl_3][SbF_6]$ resulted in cyclopropenium cations with three organometallic substituents. For example, the reaction of three equivalents of $[Fe(CO)_2(Cp)]^-$ with $[C_3Cl_3][SbF_6]$, generated by reacting C_3Cl_4 with $AgSbF_6$, in THF resulted in the formation of $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**1**) in about 65% yield (Scheme 1). Reduction of $[Fe_2(CO)_4(Cp)_2]$ with $NaK_{2.8}$ [24] rather than Na/Hg led to a simpler workup with superior yields. Dark amber–brown crystals of **1** are stable in air indefinitely, and in solution for several days. The reaction of three equivalents of $[Fe(CO)_2(Cp)]^-$ with tetrachlorocyclopropene resulted in the formation of $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][Cl]$ which could be converted to $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][PF_6]$ by anion exchange (Scheme 1). Attempts to prepare $[Fe(\eta^1\text{-}C_3Cl_2)(CO)_2(Cp)]^+$ and $[\{Fe(CO)_2(Cp)\}_2(\mu\text{-}C_3Cl)]^+$ by reacting $[C_3Cl_3][SbF_6]$ with less than three equivalents of $[Fe(CO)_2(Cp)]^-$ simply resulted in lower yields (40–50%) of **1**. Reactions of $[C_3Cl_3][SbF_6]$ with more than three equivalents of $[Fe(CO)_2(Cp)]^-$, or of $Na[Fe(CO)_2(Cp)]$ with pre-formed **1**, again resulted in **1**, rather than neutral $[\{Fe(CO)_2(Cp)\}_4(C_3)]$. An attempt to prepare $[\{Fe(CO)_2(Cp)\}_2(\mu_2\text{-}C_3O)]$ by reacting $K[Fe(CO)_2(Cp)]$ with dichlorocyclopropenone failed similarly.

Several other metallate anions reacted with $[C_3Cl_3][SbF_6]$ to give M_3C_3 complexes. $[\{Ru(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**2**) was prepared via the reaction of $K[Ru(CO)_2(Cp)]$ with $[C_3Cl_3][SbF_6]$ (Scheme 2). Cyclopentadienyl-containing impurities were present in all samples. Three equivalents of $K[Mo(CO)_3(Cp)]$ or $K[W(CO)_3(Cp)]$ reacted with $[C_3Cl_3][SbF_6]$ to give $[\{M(CO)_3(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**3**, M = Mo, **4**, M = W, Scheme 2). The yield of Mo complex **3** (15%) was much lower than that of W complex **4** (42%). The reaction of $Na[Re(CO)_5]$ [24] with $[C_3Cl_3][SbF_6]$ resulted in $[\{Re(CO)_5\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**5**, Scheme 2), the first M_3C_3 complex with only carbonyl ancillary ligands. Re complex **5** decomposes in a few hours in solution to a mixture of rhenium-containing species. Similar reactions of $[C_3Cl_3][SbF_6]$ with $[Mn(CO)_5]^-$ or $[Co(CO)_4]^-$ did not lead to stable M_3C_3 products.



Scheme 1.



Scheme 2.

The reaction of three equivalents of $[Fe(C{\equiv}CSiMe_3)(CO)_2(Cp)]$ [25] with $[C_3Cl_3][SbF_6]$ in THF resulted in $[\{Fe(CO)_2(Cp)\}_3\{\mu_3\text{-}C_3(C{\equiv}C)_3\}][SbF_6]$ (**6**, Scheme 3). In this complex, each metal center is separated from the cyclopropenium ring by an ethynediyl group. Like the Ru complex **2**, we were unable to obtain an analytically pure sample of **6**.

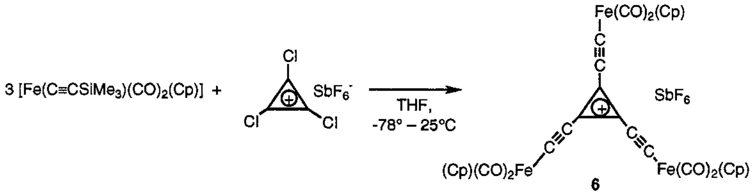
Samples of these metal-containing cyclopropenium cations uniformly gave poor elemental analyses, analyzing low by three or more carbon atoms per formula unit, even with combustion aids. Presumably this was caused by the formation of refractory metal carbide phases leading to incomplete combustion. The formation of metal carbide phases was supported by the thermogravimetric analysis of **1**. Upon heating the sample to 1000°C, mass losses consistent with the loss of SbF_5, carbon monoxide and cyclopentadienyl fragments occurred. The residue presumably consisted of mixed iron carbides and fluorides.

2.2. Characterization

The structure of (**1**) was determined by X-ray crystallographic methods. Crystal data and experimental conditions for **1** are listed in Table 1. A plot of the molecular structure is shown in Fig. 1. Selected bond distances and angles are listed in Tables 2 and 3. The structure shows a nearly equilateral C_3 ring with a $[Fe(CO)_2(Cp)]$ center bonded to each vertex, accompanied by a well-separated $[SbF_6]^-$ counterion. The spectroscopic characterization of compounds **1**–**6** by ^1H- and ^{13}C-NMR, IR, MS and TGA is discussed below.

2.3. Attempted reactions of $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (1)

Complex **1** is surprisingly unreactive. The reaction of **1** with Br_2 gave a low yield of $[FeBr(CO)_2(Cp)]$ and an intractable, black precipitate, whereas **1** did not react with I_2 or Me_3NO. Reduction of $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][Cl]$ with Na/Hg gave small amounts of $[Fe_2(CO)_4(Cp)_2]$ and $[FeCl(CO)_2(Cp)]$, and some recovered starting material. Reactions of **1** with the small nucleophiles $Li[BHEt_3]$ and LiMe gave complex reaction mixtures plus recovered starting material. Similarly, we were unable to prepare tetrametallic C_3 complexes from **1** and $[Fe(CO)_2(Cp)]^-$, $[Co(CO)_4]^-$ or $[Pd(dba)_2]$ (dba = PhCH = CHCOCH = CHPh).



Scheme 3.

3. Discussion

The cyclopropenium cation, with two π electrons delocalized over three carbon atoms, is the smallest Hückel-aromatic ring [26]. Substituted cyclopropenium compounds have been known for about 40 years, starting with the triphenylcyclopropenium cation in 1957 [27,28]. The preparation of substituted cyclopropenium cations via nucleophilic additions to $C_3Cl_3^+$ [29] is well precedented [30,31]. For example, triferrocenylcyclopropenium tetrachloroaluminate was prepared in 1975 by the Friedel–Crafts reaction of ferrocene with $[C_3Cl_3][AlCl_4]$ [32,33]. Cyclopropenium cations with one directly-bonded metal substituent have been prepared from halo- and amino-substituted cyclopropenium precursors. $[Fe(C_3Ph_2)(CO)_2(Cp)][BF_4]$ was obtained by reacting $[Fe(SiMe_3)(CO)_2(Cp)]$ with 1-chloro-2,3-diphenylcyclopropenium tetrafluoroborate and $[Fe\{C_3(NEt_2)_2\}(CO)_2(Cp)][ClO_4]$ was prepared by reacting $[Fe(CO)_2(Cp)]^-$ with tris(diethylamino)-cyclopropenium perchlorate [34]. The reaction of 1,1-dichloro-2,3-diphenylcyclopropene with palladium black gave $[Pd_2Cl_2(\mu\text{-}Cl)_2(C_3Ph_2)_2]$ [35], and the same method was used for analogous di-*tert*-butyl and bis(di-isopropylamino) compounds [36]. No cyclopropenium cation with more than one σ-metal substituent had been reported prior to our study [23].

3.1. Synthesis

The reaction of three equivalents of a metallate anion with $[C_3Cl_3][SbF_6]$ is a rather general method for the synthesis of trimetallic cyclopropenium ions such as $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**1**). Alternatively, $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][Cl]$ was prepared by reacting $[Fe(CO)_2(Cp)]^-$ with tetrachlorocyclopropene in THF without prior halide abstraction. The chloride counterion was readily exchanged for hexafluorophosphate (Scheme 1) Attempts to add fewer than three equivalents of $[Fe(CO)_2(Cp)]^-$ to $[C_3Cl_3]^+$ did not lead to $[\{Fe(CO)_2(Cp)\}_x(C_3Cl_{3-x})]^+$ ($x = 1, 2$), but rather gave reduced yields of **1** and unreacted trichlorocyclopropenium salt.

Congeneric $[\{Ru(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**2**), prepared by reacting $[Ru(CO)_2(Cp)]^-$ with $[C_3Cl_3][SbF_6]$, could not be obtained analytically pure. Even after multiple recrystallizations, the ^{1}H-NMR spectrum of **2** showed one major and several minor Cp resonances. The result was the same whether $[Ru(CO)_2(Cp)]^-$ was produced by reducing the dimer with $NaK_{2.8}$, sodium amalgam or potassium metal. The impurities may be partially substituted $[\{Ru(CO)_2(Cp)\}_x(C_3Cl_{3-x})]^+$ ($x = 1,2$) species. The relative kinetic inertness of ruthenium may account for the observation of these partial substitution products which are not seen for iron.

The Group 6 cyclopropenium complexes, $[\{Mo(CO)_3(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**3**) and $[\{W(CO)_3(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**4**), were similar to their Group 8 analogs. Yields of **3** and **4** were lower than that of **1**, possibly owing to less efficient metal-anion formation [24,37,38] or lower nucleophilicity of the Group 6 anions [39–41]. We did not try to prepare the analogous Cr complex.

A trimetallic cyclopropenium complex with only carbonyl ancillary ligands, $[\{Re(CO)_5\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**5**), was prepared in 34% yield from $Na[Re(CO)_5]$ and $[C_3Cl_3][SbF_6]$. We were not able to prepare the manganese analog. Compound **5** appears to be sensitive to either heat or light, decomposing in solution over a few hours. Insoluble **5** dissolves in ethyl ether over about 5 h to give an orange solution containing $[Re_2(CO)_{10}]$, $[Re_3H_3(CO)_{12}]$, and $[Re(CO)_6]^+$.

A series of large, raft-like polycarbon ligands can be envisioned by placing C≡C linkages between a C_3 ring and the appended metal centers. As an approach to a C_9 complex, we investigated the reaction of three equivalents of $[Fe(C{\equiv}CSiMe_3)(CO)_2(Cp)]$ with $[C_3Cl_3][SbF_6]$. Chlorotrimethylsilane elimination led to $[\{Fe(CO)_2(Cp)\}_3\{\mu_3\text{-}C_3(C{\equiv}C)_3\}][SbF_6]$ (**6**) in 34% yield. We were not able to obtain analytically pure **6** even after repeated recrystallizations from CH_2Cl_2–ethyl ether.

3.2. X-ray crystal structure of $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (1)

The structure of **1** has a nearly equilateral C_3 ring with an iron center bonded to each vertex. The average $Fe–C_{ring}$ bond length, 1.92 Å, falls near the middle of the range of Fe–C bonds with some multiple character. The Fe–C bonds in **1** are shorter than typical $Fe–C_{sp^3}$ or $Fe–C_{sp^2}$ single bond lengths of 2.0–2.1 Å in several $[Fe(R)(CO)_2(Cp)]$ compounds [42], and shorter than the 1.979(3) and 1.996(2) Å Fe–C bonds in the cycloheptatrienylidene complexes [Fe(η^1-C_7H_6)$(CO)_2$(Cp)][PF_6] (**7**) and [Fe(η^1-$C_{11}H_8$)$(CO)_2$(Cp)][PF_6] (**8**) [43,44]. The Fe–C bonds in **1** are about the same length as the Fe–C_{sp} bond in [Fe(C≡CPh)$(CO)_2$(Cp)] [45], the average 1.91(2) Å Fe–C_{ring} bond in the cyclobutenylidene complex [{Fe$(CO)_2$(Cp)}$_2$(μ_2-C_4HPh_2)][ClO_4] (**9**) [46,47], and the 1.92(3) Å Fe–C bond in the cyclobutenylidene complex [{Fe$(CO)_2$(Cp)}(μ_2-C_4PhMe_2){Cr$(CO)_5$}] (**10**) [48], but longer than the 1.81(1) Å Fe–C bond to the strong π-acceptor CCl_2 in [Fe(CCl_2)$(CO)_2$(Cp)][BCl_4] [49]. Thus, the Fe–C bond lengths in **1** exhibit some degree of multiple bond character.

Table 1
Crystallographic data and experimental details for [{Fe$(CO)_2$(Cp)}$_3$(μ_3-C_3)][SbF_6] (**1**)

Formula	$C_{24}H_{15}F_6Fe_3O_6Sb$
Formula weight	802.66
Temperature (K)	297(1)
Color and form	Dark amber–brown fragment
Space group	$P\bar{1}$ (No. 2)
a (Å)	10.265(2)
b (Å)	10.833(2)
c (Å)	13.821(3)
α (°)	101.04(3)
β (°)	111.00(3)
γ (°)	100.80(3)
V (Å^3)	1352.2(5)
Z	2
Imposed symmetry	None
$D_{calc.}$ (g cm^{-3})	1.971
Absorption coefficent μ (mm^{-1})	2.645
F(000)	780
Crystal size (mm^3)	$0.15 \times 0.40 \times 0.45$
Theta range for data (°)	1.64–24.97
Index range	$-12<h<12$, $0<k<12$, $-16<l<16$
Reflections collected	5027
Reflections observed [$I>2\sigma(I)$]	2724
Independent reflections	4753 ($R_{int}=0.0195$)
Diffractometer	Enraf–Nonius CAD-4
Radiation	Mo–K_α ($\lambda=0.7107$ Å)
Monochromator	Graphite
Scan type	ω–2θ
Scan range (°)	0.70+0.35°tanΘ
Max counting time	100 s
X-ray exposure	90 h
No. of standard reflections	3
Max. variation standard reflections	12.6% (random)
Absorption correction	Empirical (CAMEL)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4753/0/361
Final R indices [$I>2\sigma(I)$]^a	$R_1=0.0480$, $wR_2=0.1235$
R indices (all data)^a	$R_1=0.1244$, $wR_2=0.1393$
Goodness-of-fit on F^{2b}	0.950
$(\Delta/\sigma)_{max}$ and $(\Delta/\sigma)_{mean}$	0.980 and 0.072
Largest difference peak and hole (e Å^{-3})	0.825 and −1.154

[a] $R=(\Sigma||F_o|-|F_c||/\Sigma|F_o|)$; $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$, where $w=4I/(\sigma^2(I)=0.02I^2)$.

[b] $GOF=[\Sigma w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$.

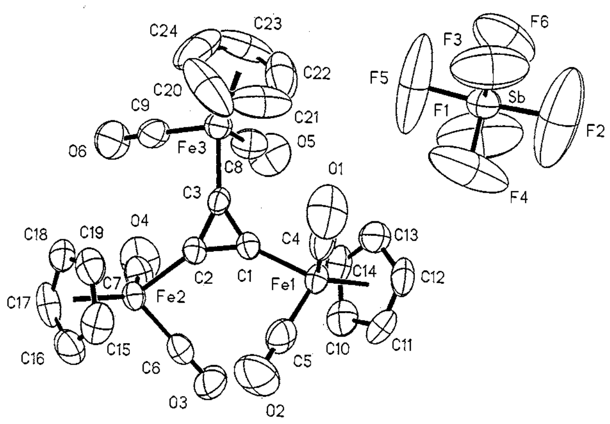
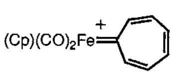


Fig. 1. Perspective drawing of the molecular structure of [{Fe$(CO)_2$(Cp)}$_3$(μ_3-C_3)][SbF_6] (**1**). The ellipsoids correspond to 50% probability contours of atomic displacement.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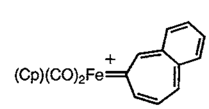
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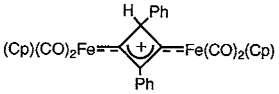
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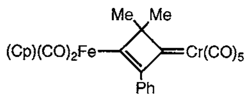
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The C–C bond lengths in the cyclopropenium ring are about equal, averaging 1.39(1) Å, nearly equal to the mean C–C distance in a localized cyclopropenylidene complex such as [Mn(*cyclo*-C_3Ph_2)$(CO)_2$(Cp)] (d(C–C) = 1.349(6) and 1.424(6) Å) [50,51]. In an 18-electron [M(CR_2)$(CO)_2$(Cp)] complex with significant M–C π-donation, the carbene ligand is expected to be 'vertical', i.e. Cp(centroid)–M–C–R torsion angles are 0 and ± 180°. In compound **1**, two of the cyclopentadienyl rings are above and the other is below the C_3 plane, with scattered Cp(centroid)–Fe–C_α–C_β torsion angles (about Fe1–C1: 99.7°, −65.5°; Fe2–C2: 105.5°, −78.0°; Fe3–C3: 132.0°, −52.2°). This evidence suggests that Fe to cyclopropenyl π-donation is of minor importance in the structure of **1** [52].

3.3. Spectroscopy

Spectroscopic properties of the trimetallic complexes **1-6** reflect their effective threefold symmetry. ^{1}H- and ^{13}C-NMR spectra show a single [Fe$(CO)_2$(Cp)] environment in **1** from −80°C to room temperature, consistent with free rotation about the Fe–C bonds in solution. The cyclopropenyl carbon atoms display a single ^{13}C-NMR resonance at 256.6 ppm, downfield of most organic cyclopropenium ions (118–175 ppm) [53].

Table 2
Selected bond distances (Å) with Esd's for the structure of [{Fe(CO)$_2$(Cp)}$_3$(μ_3-C$_3$)][SbF$_6$] (**1**)

Fe(1)–C(5)	1.755(9)
Fe(1)–C(4)	1.762(8)
Fe(1)–Cp1[a]	1.721(8)
Fe(1)–C(1)	1.913(6)
Fe(1)–C(11)	2.083(7)
Fe(1)–C(12)	2.091(8)
Fe(1)–C(10)	2.098(7)
Fe(1)–C(14)	2.101(8)
Fe(1)–C(13)	2.100(8)
Fe(2)–C(7)	1.776(8)
Fe(2)–C(6)	1.778(9)
Fe(2)–C(2)	1.917(6)
Fe(2)–C(18)	2.079(8)
Fe(2)–C(15)	2.081(8)
Fe(2)–C(17)	2.092(8)
Fe(2)–C(16)	2.094(8)
Fe(2)–C(19)	2.106(7)
Fe(2)–Cp2[b]	1.725(8)
Fe(3)–C(9)	1.742(9)
Fe(3)–C(8)	1.752(10)
Fe(3)–C(3)	1.919(7)
Fe(3)–C(23)	2.039(10)
Fe(3)–C(24)	2.064(11)
Fe(3)–C(20)	2.064(12)
Fe(3)–C(21)	2.073(10)
Fe(3)–C(22)	2.074(11)
Fe(3)–Cp3[c]	1.731(11)
O(1)–C(4)	1.125(9)
O(2)–C(5)	1.146(9)
O(3)–C(6)	1.123(9)
O(4)–C(7)	1.105(9)
O(5)–C(8)	1.145(10)
O(6)–C(9)	1.158(9)
C(1)–C(2)	1.388(9)
C(1)–C(3)	1.394(9)
C(2)–C(3)	1.375(9)
C(10)–C(11)	1.393(12)
C(10)–C(14)	1.403(12)
C(11)–C(12)	1.375(12)
C(12)–C(13)	1.426(12)
C(13)–C(14)	1.423(12)
C(15)–C(19)	1.362(12)
C(15)–C(16)	1.404(12)
C(16)–C(17)	1.389(13)
C(17)–C(18)	1.413(12)
C(18)–C(19)	1.371(11)
C(20)–C(21)	1.27(2)
C(20)–C(24)	1.39(2)
C(21)–C(22)	1.30(2)
C(22)–C(23)	1.30(2)
C(23)–C(24)	1.33(2)
Sb–F(5)	1.728(8)
Sb–F(1)	1.790(7)
Sb–F(4)	1.793(7)
Sb–F(6)	1.802(7)
Sb–F(2)	1.812(9)
Sb–F(3)	1.838(7)

[a] Cp1 is the centroid of the C10–C14 cyclopentadienyl ring.
[b] Cp2 is the centroid of the C15–C19 cyclopentadienyl ring.
[c] Cp3 is the centroid of the C20–C24 cyclopentadienyl ring.

Table 3
Selected bond angles (degrees) with Esd's for the structure of [{Fe(CO)$_2$(Cp)}$_3$(μ_3-C$_3$)][SbF$_6$] (**1**)

C(5)–Fe(1)–C(4)	94.5(4)
C(5)–Fe(1)–C(1)	91.1(3)
C(4)–Fe(1)–C(1)	92.7(3)
Cp1[a]–Fe(1)–C(1)	120.3(4)
Cp1[a]–Fe(1)–C(4)	124.0(4)
Cp1[a]–Fe(1)–C(5)	125.3(4)
C(7)–Fe(2)–C(6)	93.8(4)
C(7)–Fe(2)–C(2)	90.4(3)
C(6)–Fe(2)–C(2)	89.9(3)
Cp2[b]–Fe(2)–C(2)	120.7(4)
Cp2[b]–Fe(2)–C(6)	125.9(4)
Cp2[b]–Fe(2)–C(7)	125.9(4)
C(9)–Fe(3)–C(8)	94.5(4)
C(9)–Fe(3)–C(3)	89.9(3)
C(8)–Fe(3)–C(3)	88.8(3)
Cp3[c]–Fe(3)–C(3)	122.2(4)
Cp3[c]–Fe(3)–C(8)	126.1(4)
Cp3[c]–Fe(3)–C(9)	124.8(4)
C(2)–C(1)–C(3)	59.2(5)
C(2)–C(1)–Fe(1)	149.6(5)
C(3)–C(1)–Fe(1)	150.6(5)
C(3)–C(2)–C(1)	60.6(4)
C(3)–C(2)–Fe(2)	151.4(5)
C(1)–C(2)–Fe(2)	148.0(5)
C(2)–C(3)–C(1)	60.2(5)
C(2)–C(3)–Fe(3)	151.5(5)
C(1)–C(3)–Fe(3)	148.3(5)
O(1)–C(4)–Fe(1)	179.3(9)
O(2)–C(5)–Fe(1)	179.4(8)
O(3)–C(6)–Fe(2)	177.1(7)
O(4)–C(7)–Fe(2)	177.4(9)
O(5)–C(8)–Fe(3)	177.5(9)
O(6)–C(9)–Fe(3)	178.4(7)
C(11)–C(10)–C(14)	107.3(8)
C(12)–C(11)–C(10)	109.6(8)
C(11)–C(12)–C(13)	108.5(8)
C(14)–C(13)–C(12)	105.8(8)
C(10)–C(14)–C(13)	108.7(8)
C(19)–C(15)–C(16)	108.0(8)
C(17)–C(16)–C(15)	107.9(8)
C(16)–C(17)–C(18)	106.8(8)
C(19)–C(18)–C(17)	108.0(8)
C(15)–C(19)–C(18)	109.3(8)
C(21)–C(20)–C(24)	106.8(14)
C(20)–C(21)–C(22)	111(2)
C(21)–C(22)–C(23)	108.6(13)
C(22)–C(23)–C(24)	108.2(13)
C(23)–C(24)–C(20)	105.4(13)
F(5)–Sb–F(1)	88.2(6)
F(5)–Sb–F(4)	95.5(6)
F(1)–Sb–F(4)	92.7(5)
F(5)–Sb–F(6)	88.9(6)
F(1)–Sb–F(6)	88.0(4)
F(4)–Sb–F(6)	175.6(5)
F(5)–Sb–F(2)	175.8(7)
F(1)–Sb–F(2)	93.3(7)
F(4)–Sb–F(2)	88.4(6)
F(6)–Sb–F(2)	87.3(6)
F(5)–Sb–F(3)	93.2(6)
F(1)–Sb–F(3)	178.3(5)
F(4)–Sb–F(3)	86.3(4)
F(6)–Sb–F(3)	92.9(4)
F(2)–Sb–F(3)	85.3(6)

[a] Cp1 is the centroid of the C10–C14 cyclopentadienyl ring.
[b] Cp2 is the centroid of the C15–C19 cyclopentadienyl ring.
[c] Cp3 is the centroid of the C20–C24 cyclopentadienyl ring.

The carbonyls resonate at 212.6 ppm, in the typical range of $[FeL(CO)_2(Cp)]^+$ compounds [54]. The ^1H-NMR shift of the Cp ligand (δ 5.45) falls between $[FeL(CO)_2(Cp)]^+$ cations with very strong π-acceptor ligands such as $L = CO$ (δ 5.84) [55] and CS (δ 6.05) [56], and neutral $[FeR(CO)_2(Cp)]$ complexes with poorly π-accepting ligands such as $R = C{\equiv}CMe$ (δ 4.93) [57] and $R = Pr^i$, ^{t}Bu (δ 4.68) [58,59]. The ^1H-NMR Cp shift of **1** is similar to $[FeL(CO)_2(Cp)]^+$ cations with strongly delocalized carbene ligands such as [Fe(*cyclo*-C_3Ph_2)$(CO)_2(Cp)]^+$ (δ 5.55) [60], **7** (δ 5.50) [43,44], $[Fe\{C(SMe)Me\}(CO)_2(Cp)]^+$ (δ 5.36) [61], or **9**.(δ 5.20) [46,47,62]. Thus, the NMR data are consistent with weak π-acceptor character of the cyclopropenium ligand in **1**.

A solution infrared spectrum of **1** (CH_2Cl_2) displays three carbonyl stretching absorptions, fewer than the maximum of six absorptions for C_1 or C_s symmetry predicted by group theory [63]. The simple solution spectrum may be attributed to the generation of effective C_{3v} symmetry by free rotation about Fe–C bonds (unlikely on the infrared time scale), or to the overlap of carbonyl absorptions from several rotamers. A solid-state infrared spectrum (KBr) displays four carbonyl stretching absorptions and two weak shoulders, consistent with C_1 symmetry.

The mass spectrum (+FAB-MS) shows a molecular ion at 567 amu with an isotope distribution consistent with **1**. A fragmentation pattern consistent with the loss of six carbonyls can also be seen in the mass spectrum.

The spectroscopic data for $[\{Ru(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**2**) are incomplete because we were not able to completely purify it. The ^1H-NMR spectrum of **2** shows a single $[Ru(CO)_2(Cp)]$ environment at room temperature, consistent with free rotation about the Ru–C bonds in solution on the ^1H-NMR time scale. A solution infrared spectrum (CH_2Cl_2) displays two carbonyl stretching absorptions, as predicted for C_{3v} symmetry [63]. The mass spectrum (+FAB-MS) shows a molecular ion at 704 amu with an isotope distribution consistent with **2**. A fragmentation pattern consistent with the loss of six carbonyls can also be seen in the mass spectrum.

Spectroscopic data for $[\{Mo(CO)_3(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**3**) and $[\{W(CO)_3(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**4**) are similar to those of **1**. ^1H- and ^{13}C-NMR spectra show single $[M(CO)_3(Cp)]$ (M = Mo or W) environments at room temperature, consistent with free rotation about the M–C bonds in solution over the time scale of the NMR experiment. The ^1H-NMR spectra of both **3** and **4** show singlets corresponding to the cyclopentadienyl hydrogens. The ^{13}C-NMR spectra of both **3** and **4** show four resonances corresponding to the cyclopentadienyl carbons, the two magnetically inequivalent carbonyl carbons and the C_3-ring carbons. The observation of two distinct carbonyl carbon resonances shows that the carbonyls do not undergo *cis*/*trans* exchange on the NMR time scale. Solution infrared spectra (CH_2Cl_2) of **3** and **4** each display two carbonyl stretching absorptions, fewer than predicted for C_1 or C_s symmetry [63]. The mass spectra (+FAB-MS) of **3** and **4** show molecular ions at 771 and 1035 amu, respectively, each with the correct isotope distribution. The fragmentation patterns show the loss of all nine carbonyls.

The ^{13}C-NMR spectrum of $[\{Re(CO)_5\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**5**) displays a single ^{13}C-NMR resonance at 237.8 ppm for the C_3 ring, and a single (presumably *cis*) carbonyl resonance at 179.8 ppm. Because of the instability of **5** in solution and quadrupolar broadening by ^{185}Re and ^{187}Re (both $I = 5/2$), the *trans*-CO resonance was not resolved. The spectrum is consistent with free rotation about the Re–cyclopropenyl bonds, but we cannot rule out the (unlikely) possibility of rapid *cis*/*trans* carbonyl exchange on the NMR time scale. A solution infrared spectrum (CH_2Cl_2) displays three carbonyl stretching absorptions, fewer than predicted for C_1 or C_s symmetry [63]. The mass spectrum (+FAB-MS) shows a molecular ion at 1014 amu with an isotope distribution consistent with **5**. Fragments resulting from the loss of up to nine carbonyls are observed.

Spectroscopically, $[\{Fe(CO)_2(Cp)\}_3\{\mu_3\text{-}C_3(C{\equiv}C)_3\}][SbF_6]$ (**6**) closely resembles **1**. The ^1H-NMR spectrum of **6** shows a singlet corresponding to the cyclopentadienyl hydrogens. A solution infrared spectrum (CH_2Cl_2) of **6** displays two medium and two weak absorptions in the ν(CO) region. By comparison with **1**, we suggest that the weak absorption at 2071 cm^{-1} is due to $\nu(C{\equiv}C)$. Because we were unable to remove all cyclopentadienyl-containing impurities from **6**, neither a satisfactory ^{13}C-NMR spectrum nor an elemental analysis was obtained. The mass spectrum (+FAB-MS) shows a molecular ion at 643 amu, 4 amu higher than the calculated value. We attribute this to commonly observed hydrogen addition taking place during the FAB-MS experiment.

3.4. Attempted reactions of $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (1)

The structure of **1** seemed to indicate that the C_3 ring would be accessible to external reagents. We were disappointed with the lack of reactivity of this molecule and with our inability to isolate pure products when reactions did occur.

Cyclopropenium compounds generally react with small nucleophiles [64–68]. In an attempt to prepare $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3H)]$, $LiBHEt_3$ ('super hydride') was reacted with **1** in THF. The IR spectrum of the reaction mixture showed multiple carbonyl stretches distinct from those of **1**; thin-layer chromatography on silica gel revealed an inseparable mixture of components. Methyllithium was added to **1** in THF. Analysis of the ethyl-ether-soluble product showed it to contain [FeBr(CO)$_2$(Cp)], probably arising from the LiMe·LiBr used. Analysis of the ethyl-ether-insoluble residue showed a high recovery of unreacted **1**.

Reactions of [C$_3$Ph$_3$]$^+$ and other cyclopropenium ions with transition metals to give η^3-cyclopropenyl complexes and derived species are well-precedented [69–74]. For example, [Pt(PPh$_3$)$_2$(η^2-C$_2$H$_4$)] reacts with [C$_3$Ph$_3$][PF$_6$] to form [Pt(η^3-C$_3$Ph$_3$)(PPh$_3$)$_2$][PF$_6$] [75]. Zerovalent palladium and platinum dba complexes react with C$_3$Ph$_3$Br to give [Pd$_3$(μ$_2$-C$_3$Ph$_3$)$_2$Br$_2$], in which the cyclopropenyl rings have opened up [76]. [Co(CO)$_4$]$^-$ reacts with [C$_3$Ph$_3$][BF$_4$] to form the cyclobutenonyl complex [Co(CO)$_3$(η^3-C$_3$Ph$_3$CO)], which loses CO upon photolysis to give [Co(CO)$_3$(η^3-C$_3$Ph$_3$)] [73].

However, attempts to prepare M$_3$M′C$_3$ complexes by adding a fourth metal center to [{Fe(CO)$_2$(Cp)}$_3$(μ$_3$-C$_3$)][SbF$_6$] (**1**) failed. Reacting four or more equivalents of K[Fe(CO)$_2$(Cp)] with [C$_3$Cl$_3$][SbF$_6$] gave only **1** and the unreacted anion, which was converted to [Fe$_2$(CO)$_4$(Cp)$_2$] during the workup. Reacting K[Fe(CO)$_2$(Cp)] with pre-formed **1** also failed. [Co(CO)$_4$]$^-$ was reacted with **1** in CH$_3$CN, but the product was completely insoluble. Reactions of [Pd(dba)$_2$] with **1** in the presence of LiBr resulted in the deposition of Pd metal and recovery of **1**.

The failure of [{Fe(CO)$_2$(Cp)}$_3$(μ$_3$-C$_3$)]$^+$ to react with larger nucleophiles may be caused by steric hindrance created by the rotation of the metal centers. The C$_3$ ligand is apparently sufficiently protected by the metal centers so that external reagents cannot approach the ring.

Iron-carbon bonds can usually be cleaved with halogens [42]. Whereas **1** did not react with I$_2$ in refluxing CH$_2$Cl$_2$, reactions with Br$_2$ produced an intractable black precipitate along with traces of [FeBr(CO)$_2$(Cp)]. Neither reaction produced [{Fe(CO)$_2$(Cp)}$_2$(μ$_2$-C$_3$X)][SbF$_6$] (X = Br or I).

[{Fe(CO)$_2$(Cp)}$_3$(μ$_3$-C$_3$)][SbF$_6$] did not react with Me$_3$NO in refluxing CH$_2$Cl$_2$. IR analysis of the reaction mixture showed only unreacted starting materials. The reaction of K[Fe(CO)$_2$(Cp)] with dichlorocyclopropenone [77] is an alternative approach to a possible oxidative Fe–C cleavage product. Unfortunately, the only characterizable product of that reaction was [Fe$_2$(CO)$_4$(Cp)$_2$].

Reduction of triphenylcyclopropenium cation gives bis(triphenylcyclopropenyl), which thermally rearranges into hexaphenylbenzene. A similar reduction of triferrocenylcyclopropenium cation gives less well characterized Fe$_6$C$_6$ species [78,79]. The reduction of [{Fe(CO)$_2$(Cp)}$_3$(μ$_3$-C$_3$)][Cl] with sodium amalgam was studied as an approach to M$_6$C$_6$ complexes. Evidently a stronger reducing agent is needed, because only the unreacted starting material was recovered.

4. Conclusions

By reacting three equivalents of a metal anion with a trichlorocyclopropenium salt, a new class of fully metal-capped cyclopropenium cations can be prepared. [{Fe(CO)$_2$(Cp)}$_3$(μ$_3$-C$_3$)][SbF$_6$] (**1**), [{Ru(CO)$_2$(Cp)}$_3$(μ$_3$-C$_3$)][SbF$_6$] (**2**), [{Mo(CO)$_3$(Cp)}$_3$(μ$_3$-C$_3$)][SbF$_6$] (**3**), [{W(CO)$_3$(Cp)}$_3$(μ$_3$-C$_3$)][SbF$_6$] (**4**), and [{Re(CO)$_5$}$_3$(μ$_3$-C$_3$)][SbF$_6$] (**5**) have been prepared by this method. By reacting three equivalents of [Fe(C≡CSiMe$_3$)(CO)$_2$(Cp)] with a trichlorocyclopropenium salt, [{Fe(CO)$_2$(Cp)}$_3$-{μ$_3$-C$_3$(C≡C)$_3$}][SbF$_6$] (**6**) was also prepared. Spectroscopic evidence, and in the case of **1**, X-ray crystal structural determination, showed that these complexes consist of three equivalent metal centers with ancillary ligands bonded to a central C$_3$-ring. Unfortunately, reactivity studies on **1** as a representative of this new class of compounds failed to lead to new derivatives. The compound, **1** showed a lack of reactivity with reductants and nucleophiles. and as a result, no derivatives of the trimetallic cyclopropenium salts were prepared. Similarly, all attempts to use the trimetallic cyclopropenium salt, **1**, to form π-complexes with a fourth metal center failed.

5. Experimental

All reactions were carried out under a dry, nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres HE-493 glove box. Solvents were dried using appropriate drying agents, freshly distilled, and collected under nitrogen before use. (CD$_3$)$_2$CO, CDCl$_3$, C$_6$D$_6$, and CD$_2$Cl$_2$ were obtained in sealed ampoules from Cambridge Isotope Laboratories and were used without further purification. [Fe$_2$(CO)$_4$(Cp)$_2$] [80], [Ru$_2$(CO)$_4$(Cp)$_2$] [81], [M$_2$(CO)$_6$(Cp)$_2$] (M = W, Mo) [82], [Fe(C≡CSiMe$_3$)(CO)$_2$(Cp)] [25], dichlorocyclopropenone [77], [Pd(dba)$_2$] [83] and NaK$_{2.8}$ [24] were prepared according to the cited procedures. Tetrachlorocyclopropene, bis(trimethylsilyl)acetylene and Me$_3$NO (Aldrich), AgSbF$_6$ (Atochem), [Re$_2$(CO)$_{10}$] and [Co$_2$(CO)$_8$] (Pressure) were used as received. ^{1}H-NMR spectra (200 MHz) were recorded on a Varian Gemini 200 NMR spectrometer, and ^{13}C-NMR spectra (100 MHz) were recorded on a Varian VXR-400 NMR spectrometer. ^{1}H- and ^{13}C-NMR spectra were referenced to the solvent peak. IR data were recorded on a Mattson Galaxy Series 5000 FT-IR spectrometer and are reported in cm^{-1}. Mass spectra were recorded on a Kratos Concept 1H, double-focusing, EI/FAB Mass Spectrometer. Thermal analysis was performed on a TA 2950 high-resolution thermogravimetric analyzer. Chemical analyses were performed by the Microanalytical Services Laboratory, University of Illinois, Urbana.

5.1. Preparation of $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**1**)

To Na/Hg (50 mg, 2.2 mmol in 20 g, 100 mmol Hg) was added $[Fe_2(CO)_4(Cp)_2]$ (250 mg, 0.706 mmol) in THF (20 ml). The mixture was stirred for 0.5 h at room temperature. The resulting yellow solution was cooled to −78°C. To $AgSbF_6$ (144 mg, 0.419 mmol) was added C_3Cl_4 (72 mg, 0.41 mmol) in THF (20 ml) cooled to −78°C. The mixture was stirred for 0.5 h, resulting in a milky-white suspension. The Na[Fe(CO)$_2$(Cp)] solution was slowly added to the $[C_3Cl_3][SbF_6]$ suspension and allowed to stir for 15 h while warming to ambient temperature. The resulting dark brown solution was evaporated in vacuo and repeatedly washed with ethyl ether to remove the $[Fe_2(CO)_4(Cp)_2]$. The remaining brown powder was dissolved in dichloromethane (30 ml) and filtered. After removal of the solvent in vacuo, $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**1**, 244 mg, 65%) was collected. Recrystallization from CH_2Cl_2–ethyl ether led to dark amber crystals. M.p. (dec > 400°C). ^{1}H-NMR (200 MHz, CD_2Cl_2) δ_H 5.18 (s, Cp), (C_3D_6O) δ_H 5.45 (s, Cp). ^{13}C-NMR (100 MHz, CD_2Cl_2) δ_C 86.7 (s, Cp), 212.6 (s, CO), 256.6 (s, C_3). MS (+FAB) 567 amu (M^+), Calc. 567 amu for $^{12}C_{24}{}^1H_{15}{}^{56}Fe_3{}^{16}O_6$. IR ($CH_2Cl_2$) ν(CO) 2052 m, 2040 m, 1997 m. Anal. Calc. (Found) for $C_{24}H_{15}F_6Fe_3O_6Sb$: C, 35.91 (31.26), H, 1.88 (2.10).

5.2. Preparation of $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][Cl]$

To Na/Hg (120 mg, 5.22 mmol in 29.8 g, 0.148 mol Hg) was added $[Fe_2(CO)_4(Cp)_2]$ (509 mg, 1.44 mmol) in THF (20 ml). The mixture was stirred for 0.5 h at room temperature. The resulting yellow solution was slowly added at −78°C to tetrachlorocyclopropene (0.090 ml, 0.74 mmol) in THF (5 ml). The mixture was stirred for 16 h while warming to room temperature, resulting in a dark brown suspension. Evaporation of the solvent in vacuo followed by repetitive washing with ethyl ether to remove $[Fe_2(CO)_4(Cp)_2]$ and other neutral impurities gave a dark brown powder which was dissolved in CH_2Cl_2 (30 ml), filtered and evaporated to dryness. Recrystallization from CH_2Cl_2–ethyl ether led to a brown powder of $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][Cl]$ (214 mg, 48%). ^{1}H-NMR (200 MHz, C_3D_6O) δ_H 5.45 (s, Cp). IR (CH_2Cl_2) ν(CO) 2052 m, 2040 m, 1997 m.

5.3. Preparation of $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][PF_6]$

To $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][Cl]$ (214 mg, 0.355 mmol) in MeOH (25 ml) was added NH_4PF_6 (134 mg, 0.822 mmol) in H_2O (0.50 ml). The suspension was stirred for 0.5 h at room temperature, resulting in a dark yellow–orange suspension. Evaporation of the solvent in vacuo led to a dark brown powder. The powder was dissolved in CH_2Cl_2 (40 ml) and extracted with H_2O (10 ml) to remove NH_4Cl and unreacted NH_4PF_6. The CH_2Cl_2 layer was separated and evaporated in vacuo. Repetitive washing with ethyl ether followed by recrystallization from CH_2Cl_2–ethyl ether led to a brown powder of $[\{Fe(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][PF_6]$ (230 mg, 91%). M.p. (dec. > 400°C). ^{1}H-NMR (200 MHz, CD_2Cl_2) δ_H 5.18 (s, Cp). MS (+FAB) 567 amu (M^+), Calc. 567 amu for $^{12}C_{24}{}^1H_{15}{}^{56}Fe_3{}^{16}O_6$. IR ($CH_2Cl_2$) ν(CO) 2052 m, 2040 m, 1997 m.

5.4. Preparation of $[\{Ru(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**2**)

To $[Ru_2(CO)_4(Cp)_2]$ (779 mg, 1.75 mmol) was added $NaK_{2.8}$ (0.21 ml, 0.50 mmol) in THF (20 ml). The mixture was stirred for 1.5 h at room temperature, resulting in a dark yellow–brown solution which was slowly added at −78°C to a $[C_3Cl_3][SbF_6]$ suspension prepared from $AgSbF_6$ (403 mg, 1.20 mmol) and C_3Cl_4 (0.15 ml, 1.2 mmol) in THF (20 ml). The mixture was allowed to stir for 15 h while warming to ambient temperature. The resulting dark brown solution was evaporated in vacuo and repeatedly washed with ethyl ether to remove $[Ru_2(CO)_4(Cp)_2]$. The remaining brown powder was dissolved in dichloromethane (30 ml) and filtered. After removal of the solvent in vacuo, the brown powder was collected. Recrystallization from CH_2Cl_2–ethyl ether led to a brown powder of $[\{Ru(CO)_2(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**2**). M.p. (dec. >400°C). ^{1}H-NMR (200 MHz, CD_2Cl_2) δ_H 5.32 (s, Cp). MS (+FAB) 704 amu (M^+), Calc. 702 amu for $^{12}C_{24}{}^1H_{15}{}^{16}O_6{}^{101}Ru_3$. IR ($CH_2Cl_2$) ν(CO), 2055 m, 2004 m.

5.5. Preparation of $[\{Mo(CO)_3(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**3**)

To $[Mo_2(CO)_6(Cp)_2]$ (860 mg, 1.7 mmol) was added $NaK_{2.8}$ (0.30 ml, 0.50 mmol) in THF (20 ml). The mixture was stirred for 15 h, resulting in a dark rose solution which was slowly added at −78°C to a $[C_3Cl_3][SbF_6]$ suspension prepared from $AgSbF_6$ (406 mg, 1.18 mmol) and C_3Cl_4 (0.15 ml, 1.2 mmol) in THF (10 ml). The mixture was allowed to stir for 15 h while warming to ambient temperature. The resulting brown solution was evaporated in vacuo and repeatedly washed with ethyl ether to remove $[Mo_2(CO)_6(Cp)_2]$ and other neutral impurities. The remaining brown powder was dissolved in dichloromethane (30 ml) and filtered. Recrystallization from CH_2Cl_2–ethyl ether led to a brown powder of $[\{Mo(CO)_3(Cp)\}_3(\mu_3\text{-}C_3)][SbF_6]$ (**3**, 180 mg, 15%). M.p. (dec.) > 400°C. ^{1}H-NMR (200 MHz, C_3D_6O) δ_H 6.12 (s, Cp). ^{13}C-NMR (400 MHz, C_3D_6O) δ_C 95.1 (s, Cp), 224.8 (s, CO), 231.1 (s, CO), 251.3 (s, C_3). MS (+FAB) 771 amu (M^+), Calc. 771 amu for $^{12}C_{27}{}^1H_{15}{}^{96}Mo_3{}^{16}O_9$. IR ($CH_2Cl_2$) ν(CO) 2046 m, 1977 m. Anal. Calc. (Found) for $C_{27}H_{15}F_6Mo_3O_9Sb$: C, 32.31 (31.32), H, 1.50 (1.61).

5.6. Preparation of [{W(CO)$_3$(Cp)}$_3$(μ_3-C$_3$)][SbF$_6$] (**4**)

To [$W_2(CO)_6(Cp)_2$] (590 mg, 0.88 mmol) was added $NaK_{2.8}$ (0.20 ml, 0.33 mmol) in THF (40 ml). The mixture was stirred for 15 h, resulting in a brown solution which was slowly added at −78°C to a [C_3Cl_3][SbF_6] suspension prepared from $AgSbF_6$ (203 mg, 0.59 mmol) and C_3Cl_4 (0.070 ml, 0.6 mmol) in THF (20 ml). The mixture was allowed to stir for 15 h while warming to ambient temperature. The resulting dark brown solution was evaporated in vacuo and repeatedly washed with ethyl ether to remove [$W_2(CO)_6(Cp)_2$] and other neutral impurities. The remaining brown powder was dissolved in 30 ml dichloromethane and filtered. Recrystallization from CH_2Cl_2–ethyl ether led to brown powder of [{$W(CO)_3(Cp)$}$_3$(μ_3-C_3)][SbF_6] (**4**, 0.30 g, 40%). M.p. (dec.) > 400°C. ^{1}H-NMR (200 MHz, CD_2Cl_2) δ_H 6.01 (s, Cp). ^{13}C-NMR (400 MHz, CD_2Cl_2) δ_C 93.1 (s, Cp), 212.8 (s, CO), 217.7 (s, CO), 224.4 (s, C_3). MS (+FAB) 1035 amu (M^+), Calc. 1035 amu for $^{12}C_{27}{}^1H_{15}{}^{16}O_9{}^{184}W_3$. IR ($CH_2Cl_2$) ν(CO) 2041 m, 1996 m; Anal. Calc. (Found) for $C_{27}H_{15}F_6O_9SbW_3$: C, 25.52 (21.85), H, 1.19 (0.58).

5.7. Preparation of [{Re(CO)$_5$}$_3$(μ_3-C$_3$)][SbF$_6$] (**5**)

To Na/Hg (96 mg, 4.17 mmol in 5 ml, 0.3 mol Hg) was added [$Re_2(CO)_{10}$] (502 mg, 0.770 mmol) in THF (20 ml). The mixture was stirred for 1 h at room temperature. The resulting orange solution was slowly added at −78°C to a [C_3Cl_3][SbF_6] suspension prepared from $AgSbF_6$ (179 mg, 0.520 mmol) and C_3Cl_4 (0.065 ml, 0.54 mmol) in THF (10 ml). The mixture was allowed to stir for 15 h while warming to ambient temperature. The resulting orange solution was evaporated in vacuo and repeatedly washed with ethyl ether to remove neutral rhenium-containing species. The remaining grayish–brown power was dissolved in 30 ml dichloromethane and filtered. After removal of the solvent in vacuo, a brown powder was recovered. Recrystallization from CH_2Cl_2–ethyl ether led to a dark brown powder of [{$Re(CO)_5$}$_3$(μ_3-C_3)][SbF_6] (**5**, 0.218 g, 34%). In solution, the compound decomposes into intractable materials in about 5 h. M.p. (dec.) > 400°C. ^{13}C-NMR (400 MHz, CD_2Cl_2) δ_C 179.81 (s, Re-CO), 237.83 (s, C_3). MS (+FAB) 1014 amu (M^+), Calc. 1014 amu for $^{12}C_{18}{}^{16}O_{15}{}^{186}Re_3$. IR ($CH_2Cl_2$) ν(CO) 2040 m, 1982 m, 1914 m.

5.8. Preparation of [{Fe(CO)$_2$(Cp)}$_3$\{μ_3-C$_3$(C≡C)$_3$\}][SbF$_6$] (**6**)

A solution of [$Fe(C{\equiv}CSiMe_3)(CO)_2(Cp)$] (104 mg, 0.38 mmol) in THF (10 ml) was slowly added at −78°C to a [C_3Cl_3][SbF_6] suspension prepared from $AgSbF_6$ (56 mg, 0.16 mmol) and C_3Cl_4 (0.017 ml, 0.14 mmol) in THF (20 ml). The mixture was allowed to stir for 20 h while warming to ambient temperature. The resulting dark brown solution was evaporated in vacuo and repeatedly washed with ethyl ether to remove unreacted [$Fe(C{\equiv}CSiMe_3)(CO)_2(Cp)$]. The remaining brown powder was dissolved in dichloromethane (30 ml) and filtered. After removal of the solvent in vacuo, the brown powder was collected. Recrystallization from CH_2Cl_2–ethyl ether led to a brown powder of [{$Fe(CO)_2(Cp)$}$_3$\{μ_3-$C_3(C{\equiv}C)_3$\}][SbF_6] (**6**, 59 mg, 53%). M.p. (dec.) > 400°C. ^{1}H-NMR (200 MHz, CD_2Cl_2) δ_H 5.22 (s, Cp). MS (+FAB): 643 amu ($M^+ + 4$), Calc. 639 for $^{12}C_{30}{}^1H_{15}{}^{56}Fe_3{}^{16}O_6$. IR ($CH_2Cl_2$) ν(CO, C≡C) 2071 w, 2053 m, 2007 m, 1976 w.

5.9. Thermogravimetric analysis of [{Fe(CO)$_2$(Cp)}$_3$(μ_3-C$_3$)][SbF$_6$] (**1**)

A sample of **1** (6.9 mg, 0.0086 mmol) on a platinum pan was heated from 50 to 1000°C using a high-resolution temperature ramp. The sample lost 27.01% mass at 220°C, corresponding to loss of SbF_5 (Calc. 27.02%); 19.44% between 220 and 800°C, corresponding to the loss of nine COs (Calc. 20.92%); and 18.33% between 800 and 1000°C corresponding to the loss of cyclopentadienyl fragments (calc. 24.28%). The residual mass was 35.22% (Calc. for Fe_3C_3F 27.78%)

5.10. Crystal structure determination of [{Fe(CO)$_2$(Cp)}$_3$(μ_3-C$_3$)][SbF$_6$] (**1**)

Crystals of **1** suitable for X-ray diffraction were obtained by slow diffusion of a layer of Et_2O onto a concentrated CH_2Cl_2 solution of **1** at room temperature. The crystal was coated with epoxy and mounted on a glass fiber, nearly aligned along the long axis of the crystal. The structure was solved by using SHELXL-PC [84] and refined with SHELXL93 [85]. Crystal properties and details of X-ray data collection, solution and refinement for **1** are listed in Table 1.

6. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC-No. ZAJRAD for [{$Fe(CO)_2$-(Cp)}$_3$(μ_3-C_3)][SbF_6] (**1**).

Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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