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Synthesis and Characterization of a Polycarbon Organometallic Cluster, $[PPN]_2[Fe_6(CO)_{18}C_4]$

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The polycarbon metal cluster $[Fe_6(CO)_{18}C_4]^{2-}$ is formed by the reaction of $CF_3SO_3SO_2CF_3$ with $[Fe_3(CO)_9(CCO)]^{2-}$. Apparently, the SO_2CF_3 moiety abstracts an oxygen from the ketenylidene (CCO) ligand and C−C coupling occurs to form the C_4 ligand. A single-crystal X-ray structure determination reveals that the pattern of C−C bond lengths of the C_4 ligand in $[Fe_6(CO)_{18}C_4]^{2-}$ mimic those in free butadiene.

Introduction

Previous work in our laboratory demonstrated that the reaction of an equimolar ratio of $CF_3O_2SOSO_2CF_3$ and $[PPN]_2[Fe_3(CO)_9(CCO)]$ results in the formation of $[PPN][Fe_3(CO)_8(CCOSO_2CF_3)]$.[1] The infrared spectrum of this product in THF contains bands at 2056 (w), 2040 (vw), 2001 (vs), 1993 (vs), 1974 (s), and 1951 (m). The pattern and relative intensities of these stretching frequencies match those of fully characterized metal carbonyl clusters containing $C\equiv C$ ligands, so the product was formulated as $[Fe_3(CCOSO_2CF_3)(CO)_9]^-$, where the $C\equiv C$ moiety bridges a triangle of three Fe atoms. In the present research, we find that a 2-fold molar excess of triflic anhydride over $[PPN]_2[Fe_3(CO)_9CCO]$ results in the formation of a new cluster containing a chain of four carbon atoms, $[Fe_6(CO)_{18}(C_4)]^{2-}$.

Experimental Section

All manipulations were performed under an atmosphere of purified N_2 with Schlenk techniques or with high-vacuum techniques.[2] Solids were handled in an oxygen-free/N_2-filled drybox. Solvents were distilled from drying agents (CH_2Cl_2 from P_2O_5; THF and Et_2O from sodium/benzophenone; *i*-PrOH from Mg/I_2) and were stored and dispensed under N_2. Triflic anhydride was freeze−pump−thaw degassed and vacuum distilled from P_2O_5. Published synthetic procedures were used to prepare $[PPN]_2[Fe_3(CO)_9(CCO)]$,[1] $[PPN][Fe_3(CO)_9CCFeCp(CO)_2]$,[3] and $[Mn(CO)_3(CH_3CN_3)][PF_6]$.[4]

Solution IR spectra were recorded on a Bomem MB series FTIR at 2 cm^{-1} resolution with cells having a 0.1 mm path length and CaF_2 windows. NMR spectra were recorded on a Varian XLA-400 (^1H, 399.942 MHz; ^{13}C, 100.577 MHZ) spectrometer. ^1H and ^{13}C chemical shifts are reported as positive if downfield from TMS and were internally referenced to solvent; ^{19}F NMR spectra were referenced to $CFCl_3$. FAB mass spectra were recorded on a VG70/250SE spectrometer. Cs^+ ion bombardment was used on samples in a *m*-nitrobenzyl alcohol matrix. Negative ion detection was used to collect all of the mass spectral data.

Synthesis of $[PPN]_2[Fe_6(CO)_{18}(C_4)]$. A sample of $[PPN]_2[Fe_3(CO)_9(CCO)]$ in CH_2Cl_2 (200 mg in 25 mL) was cooled to −78 °C and stirred as a 10-fold molar excess of triflic anhydride, $CF_3O_2SOSO_2CF_3$, was added, whereupon the red-brown solution turned bright red. The reaction mixture was allowed to stir for 5 min and warmed to room temperature, and solvent was removed under vacuum. The resulting solid was washed with diethyl ether and extracted with THF to yield a solution of the new compound $[PPN]_2[Fe_6(CO)_{18}C_4]$, along with insoluble $[PPN][OSO_2CF_3]$. The yield of $[PPN][Fe_6(CO)_{18}C_4]$ was 63 mg, 49.3% based on the ketenylidene starting material. The infrared spectrum of $[PPN]_2[Fe_6(CO)_{18}C_4]$ in CH_2Cl_2 contains bands at 2027 (m), 1991 (vs), and 1950 (m) cm^{-1}, and the negative ion FAB mass spectrum displays a parent peak at 889 amu, corresponding to $[(Fe_6(CO)_{18}C_4]$, along with fragments resulting from the successive loss of nine carbonyl ligands.

An alternate synthesis of $[PPN]_2[Fe_6(CO)_{18}C_4]$ was achieved by the reaction of $[PPN][Fe_3(CO)_9CCFeCp(CO)_2]$ in CH_2Cl_2 with an equimolar quantity of $[Mn(CO)_3(CH_3CN)_3][PF_6]$ in the same solvent. After 2 days, the solution contained IR bands of the product at 2049 (m), 2021 (m), 1988 (vs), 1978 (vs), 1959 (vs), and 1940 (s) cm^{-1}. This mixture was filtered, the filtrate was evaporated to dryness, and diethyl ether was added to yield an ether-insoluble mixture of brown and white solids, which were isolated by filtration and then treated with CH_2Cl_2. $[PPN]_2[Fe_6(CO)_{18}C_4]$ was identified in the solution by the presence of IR bands at 2021 (m), 1991 (s), and 1959 (m) and the negative ion FAB MS of the solid, which contained a parent peak at 889 amu, corresponding to $Fe_6(CO)_{18}C_4 + H^+$. The fragmentation pattern indicates the successive loss of nine carbonyl ligands. An ether-soluble component in the reaction mixture was identified as $[FeCp(CO)_2]_2$ by infrared and mass spectra.

X-ray Structure Determination. Red, equidimensional crystals of $[PPN]_2[Fe_6(CO)_{18}(C_4)]$ were grown by slow diffusion of pentane into a CH_2Cl_2 solution of $[PPN][Fe_6(CO)_{18}(C_4)]$; crystallographic data were collected at 120 °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Unit cell parameters were obtained by least-squares refinement of the setting angles of 25 uniquely centered reflections. Parameters for the triclinic crystal are listed in Table 1. Intensities of three representative reflections remained constant during the data collection. Lorentz and polarization corrections were applied, and transmission factors ranged from 0.79 to 0.83. The structure was solved by direct methods (SHELXS-86),[5] and a full-matrix least squares refinement was employed using the TEXSAN 4.0 crystallographic software package.[6] Hydrogen atoms were introduced in idealized positions and were not refined. The largest peak remaining in the final difference map was 0.58 e/Å^3. All non-hydrogen atoms were refined with anisotropic thermal parameters. A CH_2Cl_2 solvent

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Table 1. Unit Cell and Collection and Refinement Parameters for $[PPN]_2[Fe_6(CO)_{18}C_4]\cdot CH_2Cl_2$

formula	$Fe_6P_4O_{18}N_2C_{96}H_{64}Cl_4$
M	1067.18
cryst size, mm	0.210 × 0.220 × 0.230
cryst system	triclinic
space group	$P\bar{1}$ (No. 2)
a, *b*, *c*, Å	12.384(2), 12.909(3), 14.999(4)
β, deg	96.55(2)
V, deg Å^3	2311
Z	2
d(calc), g cm^{-3}	1.533
μ(Mo Kα), cm^{-1}	11.7
radiation	Mo **Kα** (λ = 0.710 69)
scan type	$\omega-\theta$
2$\boldsymbol{\theta}$ max, deg	48.0
unique data	7235
obsd data, I > 3σ(I)	4240
no. of variables	586
reflcn/param ratio	7.24
R(F)	0.042
R_w(F)	0.043
GOF	1.75

Table 2. Selected Bond Distances (Å) with Standard Deviations for $[PPN]_2[Fe_6(CO)_{18}C_4]\cdot CH_2Cl_2$

Fe1−Fe2	2.495(1)	O10−C10	1.149(6)
Fe1−Fe3	2.639(1)	O10−C11	1.149(6)
Fe1−Cl	2.046(5)	O11−C11	1.147(6)
Fe1−C2	2.079(5)	O10−C10	1.149(6)
Fe1−C10	1.775(6)	O11−C11	1.147(6)
Fe1−C11	1.781(6)	O12−C12	1.157(7)
Fe1−C12	1.779(7)	O20−C20	1.143(6)
Fe2−Fe3	2.663(1)	O21−C21	1.153(7)
Fe2−C1	2.026(5)	O22−C22	1.148(6)
Fe2−C2	2.079(5)	O30−C30	1.180(7)
Fe2−C20	1.781(6)	O31−C31	1.146(7)
Fe2−C21	1.784(6)	O32−C32	1.148(7)
Fe2−C22	1.776(6)	C1−C2	1.306(7)
Fe3−C1	1.803(5)	C2−C3	1.42(1)
Fe3−C30	1.773(7)		
Fe3−C31	1.776(7)		

molecule was found in the structure. The final R factor was 0.042 (R_w = 0.43); bond lengths and bond angles are listed in Tables 2 and 3, respectively.

Results and Discussion

Characterization of $[PPN]_2[Fe_6(CO)_{18}C_4]$. The FAB mass spectrum of $[PPN]_2[Fe_6(CO)_{18}(C_4)]$ contains a prominent high-mass peak at 889 amu corresponding to ($Fe_6(CO)_{18}C_4 + H^+$), and fragments displayed the successive loss of 11 carbonyl ligands. The isotope distribution of the parent peak agrees closely with the calculated distribution as shown by $R_p < 0.10$, where $R_p = [\Sigma(I_o - I_c)^2]^{1/2}/\Sigma I_o$. I_o *and* I_c are the observed and calculated intensities for various masses in the fragmentation envelope of the parent ion. The infrared spectrum contains CO stretching bands at 2028 (m), 1991 (vs), and 1950 (m) cm^{-1}.

Details of the X-ray structure data collection for $[PPN]_2[Fe_6(CO)_{18}(C_4)]$ are summarized in Table 1. An ORTEP diagram, Figure 1, illustrates the presence of a bent C_4 ligand, connecting the two three-iron arrays. The bond distances suggest a C═C−C═C bonding pattern. The interior C1−C2−C3 bond angle is 148.0(6)°. The two halves of the cluster are related by a center of inversion between C2 and C3. The C_4 linkage in this compound is similar to that of a series of two-metal compounds linked by linear carbon atom arrays.[7] In contrast to these earlier structures, all four carbon atoms in $[PPN]_2[Fe_6C(CO)_{18}(C_4)]$ are bound to metal atoms. Significant bond distances and angles for $[PPN]_2[Fe_6(CO)_{18}(C_4)]$ are summarized in Tables 2 and 3. Atomic coordinates are provided in Table 4.

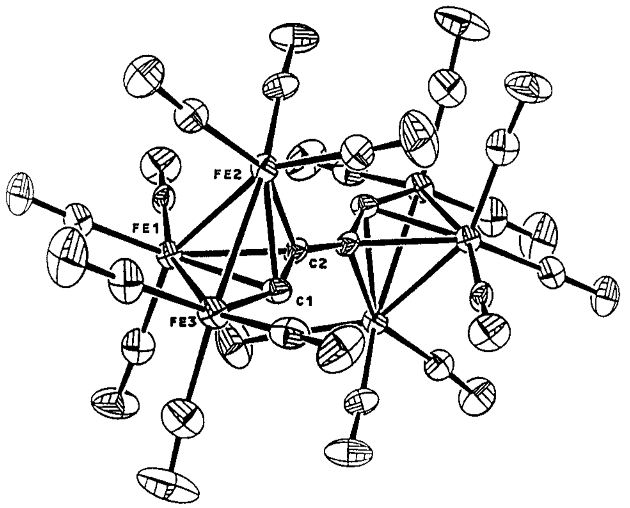

Figure 1. ORTEP drawing of $[Fe_6(CO)_{18}C_4]^{2-}$ with thermal ellipsoids at 50%.

Table 3. Bond Angles (deg) Involving the Non-Hydrogen Atoms for $[PPN]_2[Fe_6(CO)_{18}C_4]$

Fe1−Fe2−Fe3	62.41(4)	C1−Fe1−C21	99.8(2)
Fe1−Fe2−C1	51.8(1)	Fe3−Fe2−C1	42.6(1)
Fe1−Fe2−C2	53.1(1)	Fe3−Fe2−C2	78.6(1)
Fe1−Fe3−C1	43.0(1)	C1−Fe2−C2	37.1(2)
Fe1−Fe3−C2	79.1(1)	C1−Fe2−C20	125.4(2)
Fe1−C1−C22	128.3(2)	C2−Fe2−C20	88.4(2)
Fe1−C1−C2	36.9(2)	C2−Fe2−C2	105.8(2)
Fe1−C1−C10	125.9(2)	C2−Fe2−C22	153.2(2)
Fe1−C1−C11	125.8(2)	Fe1−C2−C1	70.2(3)
Fe1−C1−C12	102.0(2)	Fe3−C1−C2	155.0(4)
Fe1−C2−C10	89.0(2)	Fe2− C1− Fe3	87.9(2)
Fe1−C2−C11	148.6(2)	Fe1−Fe3−Fe2	56.14(3)
Fe1−C2−C12	108.0(2)	Fe1−Fe3−C1	50.7(2)
Fe1−C10−C11	99.6(2)	Fe1−Fe3−C30	102.7(2)
Fe2−Fe1−Fe3	61.45(3)	Fe2−Fe3−C1	49.5(2)
Fe2−Fe1−C1	52.6(2)	Fe2−C2−C3	131.8(5)
Fe2−Fe1−C2	53.1(1)	Fe2−C2−C1	69.3(3)
Fe3−C1−C30	147.6(3)	Fe1−C2−C3	133.2(5)
Fe3−C1−C31	103.6(3)	C1−C2−C3	148.0(6)
Fe3−C1−C32	101.2(3)	Fe1−C1−Fe2	75.6(2)
C1−Fe1−Fe3	86.3(2)	Fe1−C1−C2	72.9(3)
C1−Fe2−C2	73.7(3)	Fe1−C2−Fe2	73.8(2)

The metric parameters of the C_4 ligand resemble those of the *trans*-butadiene molecule; however the C1−C2−C3 angle, 148.0(6)°, for $[PPN]_2[Fe_6(CO)_{18}(C_4)]$ is significantly larger than that in butadiene, 122.4°.[8] This large angle may result from steric repulsion between the bulky $Fe_3(CO)_9$ groups. A similar increase in the C1−C2−C3 bond angle has been observed for *s-trans*-butadiene coordinated to two $Os_3(CO)_{10}$ groups.[8] By contrast simple bimetallic compounds linked by *trans*-butadiene generally have angles similar to that of free *trans*-butadiene.[9]

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Table 4. Atomic Coordinates for the Anion in $[PPN]_2[Fe_6(CO)_{18}C_4$

atom	x	y	z
Fe1	0.59925(6)	−0.3378(6)	0.85521(5)
Fe2	0.53228(6)	0.13931(6)	0.89495(5)
Fe3	0.42322(7)	−0.00467(6)	0.75193(5)
O10	0.7816(3)	−0.0143(3)	1.0025(3)
O11	0.7266(3)	0.0295(3)	0.7149(3)
O12	0.5751(4)	0.0295(3)	0.7149(3)
O20	0.6855(4)	0.2371(3)	1.0614(3)
O21	0.3615(4)	0.2683(4)	0.9375(3)
O22	0.6300(4)	0.2576(3)	0.7662(3)
O30	0.5175(4)	0.0702(4)	0.5977(3)
O31	0.2105(4)	0.0663(3)	0.7252(3)
O32	0.3475(4)	−0.2317(4)	0.6747(3)
C1	0.4426(4)	0.0057(4)	0.9536(3)
C2	0.4990(4)	0.0057(4)	0.9536(3)
C10	0.7109(4)	−0.0200(4)	0.9442(4)
C11	0.6733(5)	0.0037(4)	0.7676(4)
C12	0.5818(5)	−0.1754(5)	0.8260(4)
C20	0.6279(5)	0.2001(4)	0.9948(4)
C21	0.4270(5)	0.2087(4)	0.8145(4)
C22	0.5900(5)	0.2087(4)	0.8145(4)
C30	0.4794(5)	0.0392(5)	0.6587(4)
C31	0.2949(5)	0.0402(4)	0.7353(4)
C32	0.3785(5)	−0.1423(6)	0.7021(4)

Related Compounds. Organometallic clusters containing the C_4 ligand bound only to metal atoms are rare, but polycarbon cobalt carbonyls have been synthesized, such as $Co_6(CO)_{18}C_4$, **4**, which was isolated in low yield.[10] This compound consists of two Co_3 triangles linked by a linear chain of four carbon atoms. By contrast with $[PPN]_2[Fe_6(CO)_{18}(C_4)]$ only the terminal carbons in the C_4 chain of **4** interact with the metal atoms. Figure 2 compares the structures of several six-metal clusters containing the C_4 ligand.

A related compound, $[Co_2(CO)_6(SiMe_3CC)]_2$, which contains a nearly linear C_4 ligand capped at each end by $SiMe_3$, was synthesized by Magnus and Becker[11] by the reaction of dicobalt hexacarbonyl (trimethylsilyl)ethyne with $LiN(SiMe_3)_2$ to yield a lithium acetylide intermediate $[Co_2CO)_6(SiMe_3)CCLi]$, which reacts with water to form $[Co_2CO)_6(SiMe_3CC)]_2$.

Adams and co-workers[12] have shown that the reaction of $Ph_3PCCCCPPh_3$ with $Ru_3(CO)_{12}$ produces a six-metal system linked by a four-carbon chain, $[Ru_3(\mu\text{-}PPh_2)(CO)_9]_2(\mu_3{:}\mu_3\text{-}C_4)$, where the C_4 chain is bent.

Our route to $[PPN]_2[Fe_6(CO)_{18}(C_4)]$ is reminiscent of the reaction of organic ketenes with triflic anhydride discovered by Stang and co-workers,[13] where C−C bond formation was proposed to occur by the attack of triflic anhydride on the oxygen atom. Subsequent reaction with *t*-BuOK in glyme at −20 °C may then produce a carbine, which evolves into extended polycarbon system. In a related reaction, triflic anhydride appears to attack a face capping carbonyl in $[Ru_6(CO)_{18}]^{2-}$, to form $Ru_6C(CO)_{17}$, where the C atom resides in the center of the Ru_6 octahedron.[14]

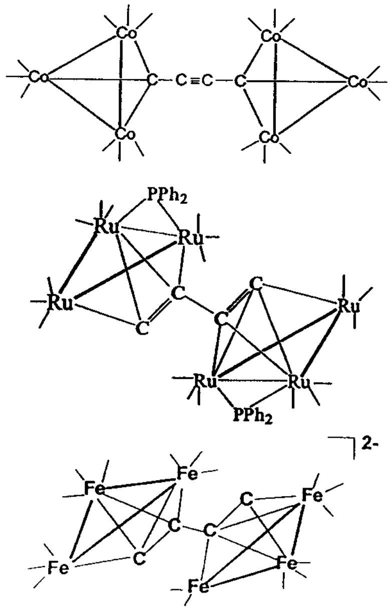

Figure 2. Structures of representative organometallic clusters containing C_4 units.

The pathway to $[PPN]_2[Fe_6(CO)_{18}C_4]$ must be complex. The starting cluster $[PPN][Fe_3(CO)_9(CCO)]^{2-}$ is a dianion as is the product, $[PPN]_2[Fe_6(CO)_{18}C_4]$, so $[Fe_3(CO)_9CCO]^{2-}$ must undergo redox disproportionation. In line with this interpretation oxidized metal carbonyl compounds are indicated among the byproducts, as judged by the appearance of CO stretching vibrations in the region of 2003−2109 cm^{-1}.

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