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Communications

A New Route to a C_4 Ligand: Carbon–Carbon Coupling To Generate $[PPN]_2[Fe_6(CO)_{18}C_4]$

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The acylation and reduction of coordinated carbon monoxide in anionic clusters provide a convenient route to the formation of metal cluster carbides and ketenylidenes (CCO).[1] Previous studies in our laboratory revealed a rich variety of ligand transformations with the anionic ketenylidenes, $[PPN]_2[M_3(CO)_9CCO]$ (M = Fe, Ru, Os), leading to the formation of carbides, dicarbides, and, in the present report, a cluster containing an unusual tetracarbide ligand.[2–4] Of special importance to the present research are the strategies for C–O bond cleavage in the CCO ligand. We have shown previously that the attack of acetyl chloride on the O atom of CCO in $[Fe_3(CO)_9CCO]^{2-}$ generates the good leaving group OAc^-, which is readily displaced by nucleophiles to produce a wide variety of C_2-containing cluster compounds, including $[Fe_6(CO)_{18}C_2]^-$.[3,5]

The two systematic routes to dicarbide clusters involve reagents which contain two carbons: tetrachloroethane or acylated metal cluster ketenylidenes mentioned above.[6] The synthesis and chemistry of polycarbon clusters are in their infancy and are of special interest for their relation to the bulk metal carbides containing C–C-bonding species and to polycarbon species on metal surfaces.[7]

In an attempt to labilize the oxygen in the CCO ligand by the function of a triflate leaving group, triflic anhydride was added under positive nitrogen pressure in a 10-fold excess to a solution of $[PPN]_2[Fe_3(CO)_9CCO]$ (I), in CH_2Cl_2, cooled to −78 °C. The solution was warmed to room temperature, and solvent was removed under vacuum. Products were extracted with diethyl ether, and the remaining solids, $[PPN]_2[Fe_6(CO)_{18}C_4]$ (II) and $[PPN][OSO_2CF_3]$, were isolated by filtration. The infrared spectrum of II in CH_2Cl_2 shows CO stretches at 2028 (m), 1991 (vs), 1950 (m), and 1934 (vw) cm^{-1} and no bands characteristic of coordinated $OSO_2CF_3^-$.[8] Variable-temperature ^{19}F NMR spectra indicate that the reaction proceeds rapidly below room temperature, and so far no intermediates have been identified. The FAB mass spectrum contains a prominent high-mass peak at 889 amu ($Fe_6(CO)_{18}C_4 + H^+$) with successive loss of 11 carbonyls.[9] A red, equidimensional crystal of $[PPN]_2[Fe_6(CO)_{18}C_4]\cdot 2CH_2Cl_2$ was grown by slow diffusion of pentane into a solution of II in CH_2Cl_2. The X-ray single-crystal structure of II reveals two three-iron arrays linked by a C_4 chain (Figure 1).[10] The bond distances suggest a C═C—C═C structure, and the interior bond angle is 148.0(6) °. The halves of the cluster are related by a center of inversion located between C2 and C3.

The C^{α}–C^{β} bond distance of 1.28 Å in $[PPN]_2[Fe_3(CO)_9CCO]$ is only slightly lengthened to 1.306 Å in II. The extension of the C_4 unit results in a C2–C3 bond length of 1.42 Å. The metric parameters of the C_4 ligand resemble those of the butadiene molecule; however, the C1–C2–C3 angle is significantly larger than the comparable angle in butadiene, presumably as a result of steric interaction between the $Fe(CO)_4$ moieties.

Organometallic clusters containing C_4 units are rare. A conjugated chain free of hydrogen and organic side chains is even more unusual. We are aware of few related clusters: $[Co_2(CO)_6(Me_3SiCC)]_2$[11] (III), $Co_6(CO)_{18}C_4$[12] (IV), and $[M_3(\mu\text{-}PPh_2)(CO)_9]_2(\mu_3{:}\mu_3\text{-}C_4)$, M = Ru, Os, (V, VI).[13] Prior to the present, all other polycarbon ligands were derived from alkynes, arenes, or diacetylene compounds. Bimetallic compounds with a linear array of four carbon atoms linking two metals were recently prepared.[14–18] Structural analyses of these compounds

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(9) An analysis of the experimental data in comparison to the theoretical isotope distribution gave a R-factor of 0.1401 over a ten mass number range.

(10) Crystallographic data for II: $Fe_3P_2O_9NC_{48}H_{32}Cl_2$; triclinic; $a = 12.384(2)$ Å, $b = 12.909(3)$ Å, $c = 14.999(4)$ Å, $\alpha = 100.06$ (2)°, $\beta = 96.55$ (2)°, $\gamma = 98.42$ (2)°, $V = 2311$ (2) Å^3, space group $P\bar{1}$; $D_c = 1.533$ g/cm^3. The final R factor was 0.042 ($R_w = 0.043$). Two molecules of CH_2Cl_2 were located in the unit cell.

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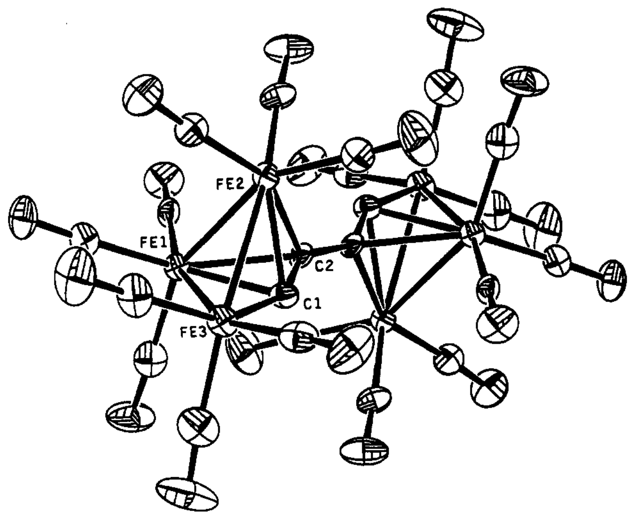


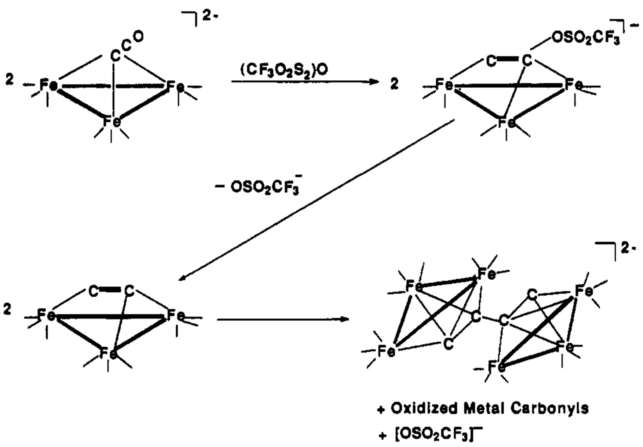
Figure 1. ORTEP drawing of $[PPN]_2[Fe_6(CO)_{18}C_4]$ (**II**). Ellipsoids are drawn at the 50% probability level.

reveal a linkage as seen in **IV**. There are noticeable similarities between the C_4 units in **II** and **III**, but the metal frameworks are quite different. While the C_4 unit in **II** bridges two iron triangles, the terminal carbons in **III** form vertices of the triangular framework. Also, the C_4 chain in **III** is bonded to a silyl group, unlike the chain in **II**, which only interacts with metals.

The structural similarities are most striking between **II** and **V**/**VI**. In each case, the C_4 units are analogous to those in butadiene. However **II** results from the condensation of two metalated acetylide fragments, while **V**/**VI** occur as diacetylenic tertiary phosphines linking two metal centers followed by C–P bond cleavage. As a result, the metal–metal interaction in **V**/**VI** is greatly weakened by the bridging phosphine. The formation of **II** involves C–O bond cleavage and loss of the triflate group to generate the acetylide species. The synthetic route to a C_4 ligand reported here is unique in that all C atoms in the C_4 unit are derived from carbonyl ligands.

The formation of **II** is reminiscent of the reaction of organic ketenes with triflic anhydrides discovered by Stang and coworkers.[19,20] These C–C-bond-forming reactions were proposed to occur by the attack of the ketone oxygen by triflic anhydride to form a triflate species. Subsequent treatment with *t*-BuOK in glyme at −20 °C, produces a carbene, and addition of an alkene leads to an extended polycarbon system. In a recent report, Bailey showed triflic anhydride can effect the reductive cleavage of CO to produce a metal cluster carbide without added reducing agent.[21] This facility was attributed to the excellent leaving ability of the triflate anion.

Scheme 1



A similar reaction may occur at the ketenylidene CO, resulting in a short-lived intermediate, $[PPN]_2[Fe_3(CO)_9CCOSO_2CF_3]$, which we postulate undergoes the displacement of the triflate ligand, concomitant with or followed by coupling of the iron moieties to achieve $[PPN]_2[Fe_6(CO)_{18}C_4]$. This reaction requires a reducing agent which may be a portion of the starting material $[Fe_3(CO)_9CCO]^{2-}$. Indeed, oxidized metal carbonyls are formed in the reaction, as judged by the appearance of CO stretching vibrations in the region of 2003–2109 cm^{-1} which are higher than those of the more reduced species, $[Fe_3(CO)_9CCO]^{2-}$, which has its highest ν_{CO} at 1932 cm^{-1}. A representation of the reaction is shown in Scheme 1.

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Supplementary Material Available: Listings of crystallographic data, positional parameters of all atoms, and complete bond distances and angles and thermal parameters for **II** (11 pages). Ordering information is given on any current masthead page.

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