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Preliminary communication

CARBIDE FORMATION AND SIMULTANEOUS INTRAMOLECULAR CARBIDE-ETHYLIDYNE COUPLING AS THE RESULT OF THE REDUCTION OF TRINUCLEAR CLUSTERS CONTAINING THE $Fe_3(CO)_9(\mu_3\text{-}CCH_3)$ UNIT

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Summary

Reduction of $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ molecule with two equivalents of $[Mn(CO)_5]^-$ or treatment of the electrochemically generated $[Fe_3(CO)_{10}(\mu_3\text{-}CCH_3)]^{2-}$ with methanol gives the cluster anion $[Fe_3(CO)_9(\mu_3 C{\equiv}CCH_3)]^-$. Experiment with the ^{13}CO-enriched $[Fe_3(CO)_{10}(\mu_3\text{-}CCH_3)]^-$ cluster shows that the $[Fe_3(CO)_9(\mu_3 C{\equiv}CCH_3)]^-$ complex results from the coupling of a carbide, produced by carbon-oxygen breaking, with the μ_3-ethylidyne ligand of the original cluster.

The recent report by Shriver et al. of a three-metal system having carbide-like reactivity [1] prompts us to publish our results in the same field, and we present the results of two independent investigations which unexpected yielded the same complex. The report provides the first example of intramolecular coupling with an ethylidyne ligand of a carbide generated by carbon oxygen scission.

The first investigation was carried out to find out whether adding electrons to or removing them from $[P(C_6H_5)_4][Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}CO)]$ (I) [2] could induce rearrangement in the mode of bonding of the ligands in the cluster unit. The second involved an attempt to synthetize new mixed clusters starting from $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ (II) [3] by the action of a carbonylate transition metal anion, as examplified by Geoffroy et al. [4].

Complex I gives a one-electron reduction wave at –1.44 V at the dropping mercury electrode (SCE) in a 10^{-1} *M* solution of acetonitrile/$P(C_6H_5)_4Br$ and electrolysis at –1.6 V at –20°C leads to a paramagnetic complex III. The infrared spectrum of III in the CO stretching region is shifted by ca. 65 cm^{-1}

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to lower frequencies compared with I which suggests a $[Fe_3(CO)_{10}CCH_3]^{2-}$ formulation.

The species III is very unstable, and regenerates I on contact with air. Attempts to crystallize III in methanol gives a new diamagnetic purple compound IV, whose infrared spectrum in the ν(CO) stretching region is shifted by ca. 65 cm^{-1} to higher frequencies (CH_2Cl_2 solution, 2044m, 1982s, 1976s, 1955s, 1930m cm^{-1}), and there is no evidence for bridging CO.

The same compound IV is generated when II is stirred at room temperature with two equivalents of $[P(C_6H_5)_4][Mn(CO)_5]$. The $Mn_2(CO)_{10}$ also formed in the reaction is removed by washing with petroleum ether, and crystallization from methanol gives pure $[P(C_6H_5)_4][Fe_3(CO)_9C_3H_3]$ (IV) (Anal. Found: C, 53.80; H, 2.79. $C_{36}H_{23}O_9PFe_3$ calcd.: C, 54.13; H, 2.88%.

The $Fe_3(CO)_9C_3H_3$ formulation of the molecule has been unambiguously confirmed by the mass spectrum of the protonated form of IV i.e. the molecular complex, $HFe_3(CO)_9C_3H_3$ (V) obtained by the action of trifluoroacetic acid (*m/e* 460 with successive loss of nine CO's; IR hexadecane solution, 2093w, 2054s, 2938s, 2017s, 2010m, 2005w, 1984w cm^{-1}).

The nature of the C_3H_3 group has been established by the use of ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectrum of IV shows two signals in the integration ratio 3/20, one a singlet at δ 2.75 ppm and the other a complex multiplet from the $P(C_6H_5)_4$ group; for V, a singlet is observed at δ 2.05 ppm with intensity 3 times that of the hydride resonance at −27.3 ppm indicating the presence of a CH_3 group.

In the ^{13}C NMR of IV, in addition to the $P(C_6H_5)_4$ resonances there are five peaks. There are two signals for CO carbons at 217.1 and 216.0 ppm in 2/1 integration ratio, a methyl-carbon signal at 17.7 ppm and two peaks at 184.7 and 99.5 ppm which cannot be assigned with certainty, they are consistent with either a μ_3 acetylide ligand [5] or a ketenylidene ligand as found by Shriver et al. [1] in $[PPN]_2[Fe(CO)_9CCO]$. In our case, both structures $[Fe_3(CO)_9\text{-}\mu_3\text{-}C{\equiv}CCH_3]^-$ (IVa) and $[Fe_3(CO)_8(\mu_3\text{-}CCH_3)(CCO)]^-$ (IVb) were reasonable possibilities.

In the case of IVb we expect a resonance for the quaternary carbon but it is often difficult to observe [6] and its non-observation is not proof of its absence. To overcome this difficulty, we prepared IV from ^{13}CO-enriched I. In the ^{13}C NMR spectrum only the 184.7 ppm and the CO resonance are increased in intensity (the ratio of the 184.7 and 99.5 ppm resonances increases from 0.66 to 5.7), and this is consistent only with structure IVa (Fig. 1). Furthermore, even though the enrichment in ^{13}C nucleus was not sufficient to permit observation of ^{13}C—^{13}C coupling for the ^{13}C resonance at 99.5 ppm, the proton NMR resonance of the CH_3 group at 2.75 ppm shows a $J(^{13}C\text{—}C\text{—}CH)$ coupling constant of 5.1 Hz which agrees well with the value found for the alkyne $CH_3C{\equiv}^{13}CH$ (4.8 Hz) [7].

The mechanism of the carbon—oxygen breaking during the formation of IV from II is probably the same as that in the formation of $[Fe_3(CO)_9(CCO)]^{2-}$ (i.e. elimination of $C_2H_5O^-$) [1], but the mechanism of the carbon—oxygen breaking starting from III is less clear. Species III can be isolated in crude form by precipitation with diethyl ether from a dichloromethane solution. In the solid state it is not very stable at −20°C under nitrogen, but it can be

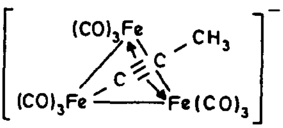

Fig. 1. Structure of complex IV.

handled for a short time when freshly prepared. For instance, we found that its infrared spectrum shows a weak and broad band centered at 1600 cm^{-1} indicating the presence of a μ_3-CO group, and that it reacts with acetic acid to give IV. Thus we assume that methanol protonates III and that the protonation occurs at the oxygen atom of the CO bridge, which would weaken the carbon—oxygen bond [8]. However, the question of the mode of breaking of the C—OH bond remains open: elimination of an hydroxide anion would necessitate adding one electron to the cluster, and it is difficult to suggest a source for this electron. An homolytic bond cleavage would be more realistic, but we have not detected a hydroxide radical during the reaction.

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