X-Ray Crystal and Molecular Structure of $[Et_2NCFe(CO)_3]_2$: an Example of the Division of an Alkyne into Two Separate Units by Rupture of the C≡C Bond

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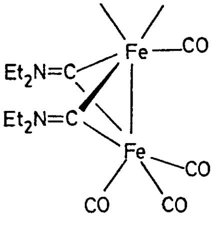
Summary *X*-Ray crystallography of the complex $[Et_2NCFe(CO)_3]_2$ obtained from $Fe(CO)_5$ and $Et_2NCC{\equiv}NEt_2$ indicates rupture of the carbon–carbon triple bond during the formation of this iron complex to give two separate bridging Et_2NC (diethylimmoniocarbene) units.

DIVISION of an alkyne RC≡CR into two separate RC units by reaction with a transition metal derivative is relatively rare. Wilke and his co-workers[1] have reported the rupture of the C≡C bond of MeC≡CMe upon reaction with $CrCl_3$ and $AlEt_3$ to give the pentamethylcyclopentadienyl derivative $[Me_5C_5CrC_6Me_6]$. The reactions of the alkyne $Et_2NC{\equiv}CNEt_2$ with $[C_5H_5M(CO)_2]$ (M = Co and Rh) give the clusters $[(Et_2NC)_2M_3(C_5H_5)_3]$ (M = Co and Rh) shown by n.m.r. spectroscopy[2] and preliminary *X*-ray crystallography studies[3] to contain a closed trigonal bipyramidal cluster with the alkyne carbon atoms in the non-adjacent apical positions. We have now found by *X*-ray diffraction that the



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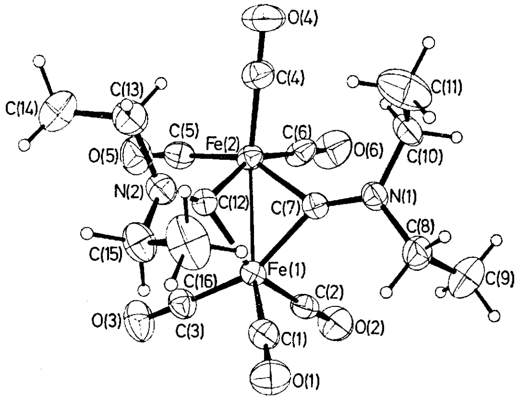

FIGURE. Structure of $[Et_2NCFe(CO)_3]_2$.

crystal structure of $[Et_2NCFe(CO)_3]_2$ obtained as previously described[2] from $Et_2NC{\equiv}CNEt_2$ and iron carbonyls indicates formulation of this complex as bis-μ-diethylimmoniocarbene-hexacarbonyldi-iron(-1) (**1**). The alkyne carbon–carbon triple bond in $Et_2NC{\equiv}CNEt_2$ has ruptured completely to form two separate Et_2NC units which function as a rare type of bridging ligand. The only other example of this type of ligand known to the authors is the structure of $[HRu_3(CO)_{10}(C{=}NMe_2)]$.[4] Here the carbene bridging ligand has its origin in the trialkyltin reagent, $[Me_2NCH_2SnMe_3]$.

Crystal data: yellow crystals of $[Et_2NCFe(CO)_3]_2$ were obtained from isopentane and characterized as follows: orthorhombic, *Pbca* with $a = 10{\cdot}723(4)$, $b = 14{\cdot}922(4)$, $c = 25{\cdot}720(8)$ Å, $Z = 8$, $D_m = 1{\cdot}43$, $D_c = 1{\cdot}45$ g cm^{-3}. Intensity data were collected using a manual General Electric XRD-700 diffractometer and employed the fixed crystal–fixed detector counting method with balanced Zr–Y filters. 2451 independent reflections were considered to be significantly above background. The space group was uniquely defined by the systematic absences. The structure was solved by the conventional heavy-atom Fourier method and refined by full-matrix least-squares calculations. The final refinement cycles included anisotropic temperature factors for all 26 atoms (235 parameters refined). Calculated positions for the 20 hydrogen atoms were used to include their scattering contribution in the structure factor calculations. The Figure presents an ORTEP perspective of the molecular structure. The final R index is 0·046.

In the original proposal for the structure of $[Et_2NCFe(CO)_3]_2$ the central carbon–carbon bond of the aminoalkyne was thought to remain intact although reduced in bond order from that in the starting alkyne.[2] However, the structure obtained from this crystallographic study indicates that these carbon atoms [C(7) and C(12)] are separated by 2·28 Å, clearly a non-bonded distance. The carbon–nitrogen distances from the carbon atoms originating from the alkyne triple bond are 1·284 and 1·280 Å, respectively to N(1) and N(2), corresponding to a carbon–nitrogen double rather than single bond.[5] This indicates that the bridging Et_2NC ligands are diethylimmoniocarbene rather than diethylaminocarbyne units. (Other somewhat analogous carbon bridging ligands are known.) The structure of $[Me_3SiCNb(CH_2SiMe_3)_2]_2$ shows two separate Me_3SiC units to bridge between two non-bonded niobium atoms.[6] In this case however, the bridge carbon is a carbyne and the bonding pattern is not the same. A similar molecular configuration is observed for $[(CF_3)_2PFe(CO)_3]_2$.[7]

The iron–carbon bond distances are as follows: to Fe(1): C(1), 1·769; C(2), 1·799; C(3), 1·804; C(7), 1·902; C(12), 1·903; to Fe(2): C(4), 1·779; C(5), 1·802; C(6), 1·797; C(7), 1·909; C(12), 1·914 Å. (All e.s.d.'s are $< 0{\cdot}01$ Å). The iron–iron distance of 2·482 Å corresponds to a single bond. Each iron atom has three terminal carbonyl groups, which, together with the bridging carbene carbon atoms, form a square pyramidal arrangement about the iron atoms. The two square pyramids share an edge through the bridging carbene carbon atoms C(7) and C(12) and the two square bases [planes containing C(2), C(3), C(7), C(12) and C(5), C(6), C(7), C(12)] make a dihedral angle of 79·0°. In similar systems Dahl and his co-workers[8] have proposed that the iron–iron bond is bent in order to complete a somewhat distorted octahedron around each iron atom. However, a recent electron density study by X-ray diffraction shows no evidence for a bent bond.[9]

We thank the Robert A. Welch Foundation of Houston, Texas for generous support of the research performed at Texas A & M University, and the National Cancer Institute and National Science Foundation for support of the work performed at the University of Georgia.

(*Received*, *2nd August* 1976; *Com.* 895.)

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