

Preliminary communication

SYNTHESIS AND CRYSTAL STRUCTURE OF μ -CHLORO- μ -(DIPHENYL-ETHENYL)HEXACARBONYLDIIRON(*Fe—Fe*)

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Summary

Treatment of $\text{PPh}_4[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-C}(\text{Ph})\text{C}(\text{Ph})\text{H})]$ with $\text{Me}_3\text{OSbCl}_6$ gives the chloro-bridged derivative $[\text{Fe}_2(\text{CO})_6(\mu\text{-Cl})(\mu\text{-C}(\text{Ph})\text{C}(\text{Ph})\text{H})]$. The structure of this compound has been established by X-ray diffraction. The title complex appears to be formed by successive methylation of bridging carbon monoxide and replacement of the methoxycarbonyl by the chloride ligand.

Among the many organometallic dinuclear iron complexes containing a bridging heteroatom which are known, there are only a few cases in which this bridge is a halogen [1]. Thus μ -halide- μ -vinyl dinuclear complexes are obtained from the reaction of $\text{Fe}_2(\text{CO})_9$ with *trans*-1,2-dihalogenoethylenes [2]. On the other hand, the organometallic zwitterions $[\text{Fe}(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-CHC}(\text{Ph})\text{NRR}')]$ react with hydrogen halides to give the $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-X})]$ complexes [3]; the crystal structure of the chloro derivative was resolved, and this was the first chloro-bridged carbonyldiiron complex to be fully characterized [4]. The synthetic potential of such kind of compounds is apparent from the fact that their reactions with appropriate alkali metal or silver salts provide a direct method of introducing other bridging ligands.

The properties of the dinuclear anionic iron complex $\text{PPh}_4[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-C}(\text{Ph})\text{C}(\text{Ph})\text{H})]$ (I) have recently been described [5], especially the reactions

with carbocations [6, 7]. In one of these reactions $\text{Me}_3\text{OSbCl}_6$ was used, and unexpected chlorination of I occurred. When equimolar amounts of I and $\text{Me}_3\text{OSbCl}_6$ are dissolved in dichloromethane at room temperature a vigorous reaction takes place and the solution turns dark-violet; in a few minutes the reaction is complete, as indicated by IR monitoring. The solution is evaporated and the residue extracted with light petroleum ether. Crystallization in dichloromethane/methanol mixture at -20°C gives crystals of the neutral complex II in a 40% yield. The analyses (Found: C, 48.5; H, 2.3. $\text{Fe}_2\text{C}_{20}\text{H}_{11}\text{O}_6\text{Cl}$ calcd.: C, 48.6; H, 2.2%), and the infrared ($\nu(\text{CO})$ region in C_6H_{12} solution: 2076m, 2050vs, 2012s, 2000s, 1987m cm^{-1}), ^1H NMR (CDCl_3 solution 7.21 (C_6H_5), 4.73s (H)) and mass spectra ($m/z = 495$) are consistent with the formulation $\text{Fe}_2(\text{CO})_6(\mu\text{-Cl})(\mu\text{-C}(\text{Ph})\text{C}(\text{Ph})\text{H})$. In order to determine the structural features of complex II a single crystal X-ray diffraction study was undertaken.

Crystal data. $\text{C}_{20}\text{H}_{11}\text{O}_6\text{ClFe}_2$, $M = 494.4$, triclinic, space group $P\bar{1}$, a 12.126(3), b 10.445(2), c 9.024(2) Å, α 111.37(2), β 110.47(2), γ 89.94(2) $^\circ$, V 986.6(7) Å 3 , D_{calc} 1.664 g cm^{-3} , $Z = 2$. Reflections between $2^\circ < \theta < 25^\circ$ were measured with a Philips PW 1100 four circle diffractometer using the ω -scan technique with graphite monochromated Mo- K_α radiation. 2785 reflections were measured and 2769 with $I > 2.5\sigma(I)$ were used. The final R was 0.054 ($R_w = 0.063$) for all observed reflections. A representation of the molecular structure and some selected bond parameters are given in Fig. 1.

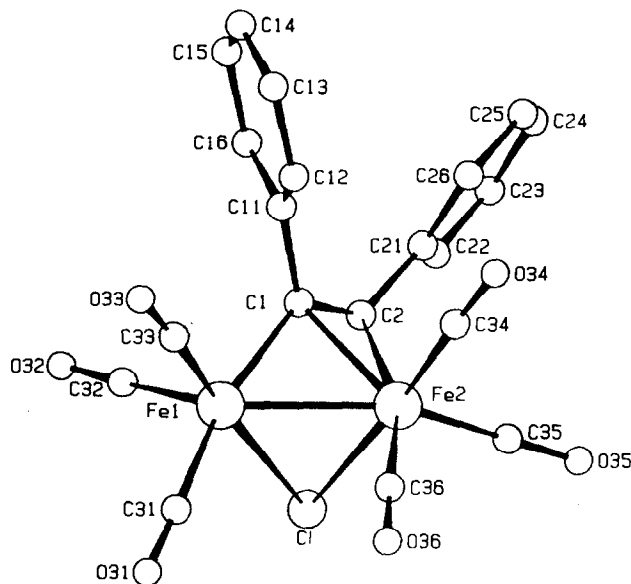
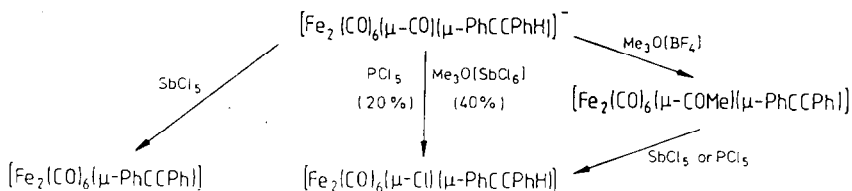


Fig. 1. View of the molecular structure of $[\text{Fe}_2(\text{CO})_6(\mu\text{-Cl})(\mu\text{-C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{H})]$ (II) with the atomic numbering scheme. Selected bond distances: $\text{Fe}(2)\text{-Fe}(1)$ 2.533(1), $\text{Cl}\text{-Fe}(1)$ 2.335(1), $\text{C}(1)\text{-Fe}(1)$ 1.990(5), $\text{Cl}\text{-Fe}(2)$ 2.315(1), $\text{C}(1)\text{-Fe}(2)$ 2.128(5), $\text{C}(2)\text{-Fe}(2)$ 2.201(5), $\text{C}(2)\text{-C}(1)$ 1.424(8) Å.

The structure consists of dimeric $\text{Fe}_2(\text{CO})_6$ units linked to a Cl atom and a $\text{C}(\text{Ph})\text{C}(\text{Ph})\text{H}$ unit which act as bridges between the two Fe atoms. The 1,2-diphenylethenyl ligand is η^1 -bonded to Fe(1) and unsymmetrically η^2 -bonded to Fe(2) as is usual in μ -disubstituted vinyl complexes [8]. The chlorine atom is slightly unsymmetrically bonded to the iron atoms (2.335(1) and 2.315(1) Å),

the bond distances being significantly longer than the Fe—Cl distances in $\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-Cl})$ (2.289(1) Å) [4]. The Fe(1)—Fe(2) bond length (2.533(1) Å) is shorter than the Fe—Fe distance in the $\mu\text{-chloro-}\mu\text{-phosphido}$ complex (2.560(5) Å). This shortening accounts for the lower value of the Fe(1)—Cl—Fe(2) angle (66.0(0)°). Another important feature of the molecule is the planarity of Fe(1), Cl, C(1), C(2), and C(21) atoms, which allows electronic delocalization; this accounts for the lengthening of Fe(1)—Cl with respect to Fe(2)—Cl and the lengthening of the Fe(1)—C(31) bond *trans* to the Fe(1)—C(1) bond. The presence of the bridging halogen also causes the shortening of both Fe(1)—C(33) (1.777(6) Å) and Fe(2)—C(34) (1.758(5) Å) bonds *trans* to this bridge.



SCHEME 1

The formation of II instead of the expected methyl derivative prompted us to investigate the mechanism of the reaction and alternative syntheses (Scheme 1). Treatment of I with Me_3OBF_4 followed by addition of SbCl_5 or PCl_5 gave the $\mu\text{-chloro}$ complex II and traces of $\text{Fe}_3(\text{CO})_{12}$. This suggests that the first step in the reaction with $\text{Me}_3\text{OSbCl}_6$ is methylation of the bridging CO ligand. When SbCl_5 was used instead of $\text{Me}_3\text{OSbCl}_6$ only “ $\text{Fe}_2(\text{CO})_6(\mu\text{-PhCCPh})$ ” [9] was formed, but when PCl_5 was used II was obtained (20% yield) along with $\text{Fe}_3(\text{CO})_{12}$ and “ $\text{Fe}_2(\text{CO})_6(\mu\text{-PhCCPh})$ ”; the products were separated by column chromatography on silica using light petroleum ether as eluant. With both halides extensive decomposition occurred.

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