Preliminary communication

ACETYLENEIRON TETRACARBONYLS: CLASSICAL ORGANOMETALLIC INTERMEDIATES. SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF $Fe_2(CO)_8(Ph_2PC \equiv CBu\text{-}t)$

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Summary

The synthesis of $Fe_2(CO)_8(Ph_2PC \equiv CBu\text{-}t)$, a molecule containing $Fe(CO)_4$-(phosphine) and $Fe(CO)_4$(acetylene) moieties is described. A single crystal X-ray structure analysis has provided for the first time, accurate molecular parameters for a classical intermediate of the type $Fe(CO)_4$(acetylene).

Although acetyleneiron tetracarbonyls $Fe(CO)_4(RC \equiv CR)$ are the presumed intermediates in reactions of acetylenes with $Fe(CO)_5$ and $Fe_2(CO)_9$ [1], only two compounds of this type, namely $Fe(CO)_4(Me_3SiC \equiv CSiMe_3)$ [2,3] and $Fe(CO)_4(t\text{-}BuC \equiv CBu\text{-}t)$ [2,4] have been isolated and no report of an X-ray structure analysis has yet appeared. In the absence of stabilising bulky groups on the acetylene, these simple π-complexes $Fe(CO)_4(RC \equiv CR)$ are presumed to be exceedingly reactive to further acetylene additions resulting in the generation of a multitude of coordinated organic ligands via acetylene coupling [1]. In our efforts to understand the mechanics of acetylene coupling by iron carbonyls we have utilised phosphinoalkynes to lend stability to the initial, classical π-complex intermediates. We describe herein the synthesis and spectroscopic characterisation of $Fe_2(CO)_8(Ph_2PC \equiv CBu\text{-}t)$, a molecule containing $Fe(CO)_4$(phosphine) and $Fe(CO)_4$(acetylene) moieties. An X-ray structure analysis has provided for the first time accurate molecular parameters for the iron—acetylene interaction in an $Fe(CO)_4(\pi\text{-}alkyne)$ complex.

Diiron nonacarbonyl and t-butylethynyldiphenylphosphine react at room temperature in degassed benzene under a carbon monoxide atmosphere to yield (30% after chromatography and recrystallisation from heptane) pale yellow crystals of a complex analysing as $Fe_2(CO)_8(Ph_2PC \equiv CBu\text{-}t)$.

The IR spectrum in the 2300—1700 cm^{-1} region [(C_6H_{12}) 2093s, 2049vs, 2032s, 2011vs, 1987vs, 1975s, 1944vs, 1936vs and 1848w] suggested two

non-equivalent $Fe(CO)_4$ groups and a coordinated triple bond, since $\nu(C{\equiv}C)$ of the free ligand (2169 cm^{-1}) was absent.

Crystal data: $C_{26}H_{19}O_8PFe_2$, mol.wt. 602.11. Crystals are monoclinic space group $P2_1/n$ (C_{2h}^5, No. 14) with a 10.271(2), b 14.628(3), c 18.415(3) Å, β 90.83(2)^c. With $Z = 4$ and $V = 2766.4$ Å^3 the calculated density of 1.446 g cm^{-3} agrees with the measured value of 1.44 g cm^{-3}. The structure was solved using 2682 [$I > 3\sigma(I)$] diffractometer data with $0° < 2\theta\,(Mo\text{-}K_\alpha) < 45°$. Full matrix least-squares refinement with anisotropic temperature coefficients for non-hydrogen atoms and isotropic factors for hydrogen atoms has reduced R to 0.036. The molecular structure and atomic numbering scheme are illustrated in Fig. 1.
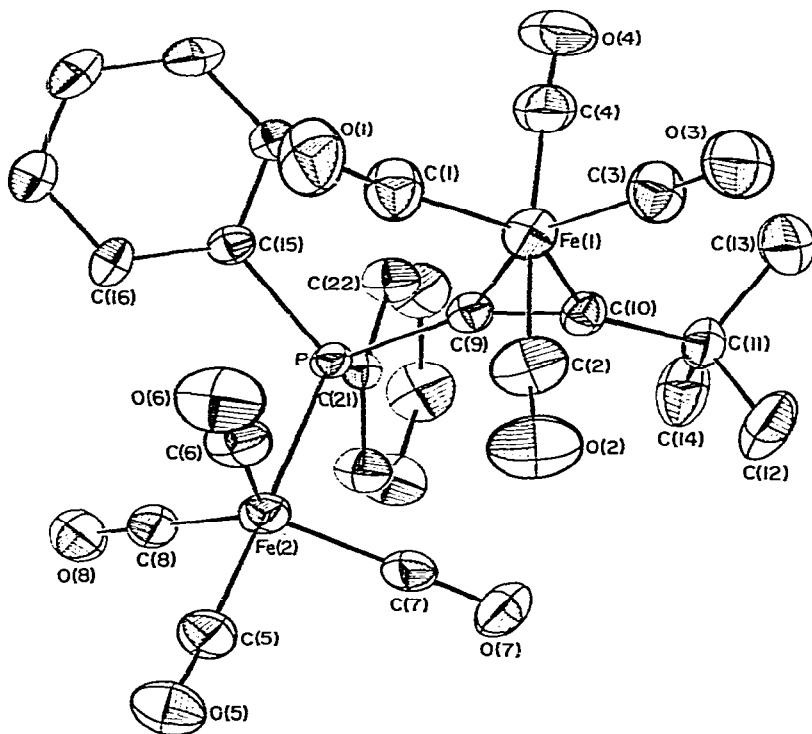

Fig. 1. A perspective view of the molecular structure of $Fe_2(CO)_8(Ph_2PC{\equiv}CBu\text{-}t)$ showing the atomic numbering. Thermal ellipsoids are drawn at the 30% level. Important bond distances (Å), angles and esd's not mentioned specifically in the text are: Fe(1)—C(1), 1.816(5); Fe(1)—C(2), 1.829(6); Fe(1)—C(3), 1.798(5); Fe(1)—C(4), 1.834(5); Fe(1)—C(9), 2.107(4); Fe(1)—C(10), 2.057(4); Fe(2)—P, 2.259(1); Fe(2)—C(5), 1.784(5); Fe(2)—C(6), 1.792(5); Fe(2)—C(7), 1.792(4); Fe(2)—C(8), 1.803(4); Fe(2)—P—C(9), 113.9(1)°; P—C(9)—C(10), 150.0(1)° and C(9)—C(10)—C(11), 153.0(2)°. Average C—O distances around Fe(1): 1.143 ± 0.003 (equatorial), 1.128 ± 0.005 Å (axial); around Fe(2); 1.152 ± 0.005 (equatorial), 1.152(6) Å (axial).

In the bimetallic complex, the iron atoms are well separated (4.780(1) Å) with the phosphorus atom of the phosphinoalkyne coordinated to Fe(2) and the triple bond to Fe(1). The stereochemistry of Fe(2) is trigonal bipyramidal with the stronger σ-donor atom, phosphorus occupying the axial position as predicted by Hoffman [5] but with very little distortion of the equatorial

carbonyl groups towards the phosphine. The major structural feature of interest is the interaction of the acetylenic triple bond with Fe(1). In stereo-chemical terms the centroid of the C(9)—C(10) bond corresponds to one equatorial position of a trigonal bipyramid of ligands around Fe(1) with carbonyl carbon atoms C(1) and C(3) occupying the other equatorial sites. None of the atoms C(9), C(10), Fe(1), C(3) and C(1) deviate from a best least squares plane by more than 0.02 Å. However, the bipyramid is otherwise quite distorted, with axial carbonyl groups C(2)—O(2) and C(4)—O(4) bent distinctly towards the alkyne (C(2)—Fe(1)—C(4) 173.5(2)°) and a small C(1)—Fe(1)—C(3) angle (108.2(2)°). These structural features are reminiscent of those in $Fe(CO)_4$(π-alkene) derivatives [6] where the hydrocarbon invariably coordinates equatorially in a trigonal bipyramid. There also appears to be a noticeable difference between the Fe(1)—CO(axial) (1.832 ± 0.003 Å) and Fe(1)—CO(equatorial) (1.807 ± 0.009 Å) bond lengths suggesting perhaps that the alkyne is a poorer π-acceptor than an equatorial CO group. Corresponding differences in C—O(axial) and C—O(equatorial) bond lengths are apparent.

The strength of metal—acetylene bonds has frequently been gauged by the increase Δr in C≡C bond length from the standard value for acetylene (1.202(5) Å) [7] on coordination, the magnitude of bend-back angles and the shortness of metal—carbon(acetylene) distances [8]. For $Fe_2(CO)_8$-(Ph_2PC≡CBu-t) the C(9)—C(10) distance is 1.275(7) Å while the bend-back angles at C(10) and C(9) respectively are 27.0(2) and 30.0(2)°; ν(C≡C) appears at 1848 cm^{-1} in the IR spectrum. The C≡C bond length and bend back back angles are rather similar to values (1.284(16) Å, 31.4(1.4)°; 1.280(14) Å(av), 27.3(6)°(av), respectively) in the zerovalent, trigonal nickel complexes Ni(Bu-t-NC)$_2$(PhC≡CPh) [9] and Ni$_2$(CO)$_2$(Ph$_2$PC≡CBu-t)$_2$ [10] as well as to corresponding parameters in the phosphine stabilised iron(0) derivative $Fe_2(CO)_6$(Ph$_2$PC$_2$Ph)$_2$ [11], which is the only other structurally characterised acetyleneiron(0) complex in which the alkyne is non-bridging. There is also an interesting comparison with the two alkyne bridged derivatives $Fe_2(CO)_4$(t-BuC≡CBu-t) [12] and $Fe_2(CO)_6$(t-BuC≡CBu-t) [4], where the "acetylenic" bond lengths are 1.283 and 1.311(10) Å and bend-back angles 37.2 and 35°, respectively. The iron—acetylene interactions in these bridged species are clearly stronger than in the present case, a fact also confirmed by the Fe—C(alkyne) bond lengths (2.082 Å in $Fe_2(CO)_4$(t-BuC≡CBu-t)$_2$ and $Fe_2(CO)_6$(t-BuC≡CBu-t) compared to 2.102 Å (av) in $Fe_2(CO)_8$(Ph$_2$PC≡CBu-t).

It is significant that for $Fe(CO)_4$(acenaphthylene [6] the Fe—C(olefin) distances average 2.151 Å while in (cis-2,3-dicarbomethoxymethylene cyclopropane)iron tetracarbonyl the length of the Fe—C(2)(olefin) bond is 2.092(7) Å. We believe that the results for $Fe_2(CO)_8$(Ph$_2$PC≡CBu-t) and the above comparisons establish that the characteristics of the iron(0)—alkyne interaction are not substantially different from those between acetylenes and nickel(0) or olefins and iron(0). Mössbauer parameters (4 line spectrum; δ 0.13 ppm, Δ 2.52 mm s^{-1} (Fe(2)); δ 0.23 ppm, Δ 1.63 mm s^{-1} Fe(1) with respect to sodium nitroprusside) for the Fe(1) site confirm that a similar bonding description is relevant for $Fe(CO)_4$(π-alkene) and $Fe(CO)_4$(π-acetylene).

Quadrupole splittings in both cases are intermediate between trigonal bipyramidal iron(0) (~ 2.50 mm s^{-1}) and distorted octahedral (<1.0 mm s^{-1}) stereochemistry while δ values are displaced towards the positive side of the iron(0) range.

The apparent instability of $Fe(CO)_4$(acetylene) complexes thus reflects the hyper-reactivity of these species towards further acetylene addition rather than the instability of the iron(0)—acetylene bond. It is an interesting question as to whether these additions proceed via direct attack on the coordinated acetylene or via displacement of CO from $Fe(CO)_4$(acetylene) creating an $Fe(CO)_3$(acetylene)$_2$ species prior to coupling. We are currently exploring these reactions in detail.

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