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Preliminary communication

CARBON—CARBON FORMATION AT A DIIRON CENTRE BY INTRAMOLECULAR COUPLING OF ETHOXYCARBYNE AND 1,2-DIPHENYLETHENYL LIGANDS IN $Fe_2(CO)_6(\mu\text{-}COC_2H_5)(\mu\text{-}C(C_6H_5)C(C_6H_5)H)$. X-RAY CRYSTAL STRUCTURE OF HEXACARBONYL-μ-($1\eta^2$,2-DIPHENYL- 3-ETHOXY-η^3-η^1-ALLYL)-DIIRON

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Summary

$[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}C(C_6H_5)C(C_6H_5)H)]^-$ reacts with triethyloxonium tetrafluoroborate to yield $Fe_2(CO)_6(\mu\text{-}COC_2H_5)(\mu\text{-}C(C_6H_5)C(C_6H_5)H)$. This compound is smoothly transformed at room temperature or more quickly in refluxing hexane into the title compound resulting from the coupling of the ethoxycarbyne and 1,2-diphenylethenyl bridges.

In a recent publication [1] we reported that the $[HFe_3(CO)_{11}]^-$ anion reacts with diphenylacetylene at 60°C to give two products, one in which the trinuclear unit is maintained, $[HFe_3(CO)_9(\mu_3\text{-}C(C_6H_5)C(C_6H_5))]^-$ (I), and the other which is dinuclear, $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}C(C_6H_5)C(C_6H_5)H)]^-$ (II). The anionic nature of II suggests that the bridging carbon monoxide should be sufficiently nucleophilic to react with carbocations, as is the case for bridging carbon monoxide in cluster anions [2—4].

Complex II does, indeed, react quickly with triethyloxonium tetrafluoroborate to give the neutral complex $Fe_2(CO)_6(\mu\text{-}COC_2H_5)(\mu\text{-}C(C_6H_5)C(C_6H_5)H)$

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(III)*, the presence of the μ-COC_2H_5 bridge being revealed by the high value of its ^{13}C chemical shift resonance (383.8 ppm) [3]. During a study of the reactions of III with alkynes and alkenes [5] we observed that this compound undergoes a smooth transformation at room temperature to form a new compound. This process is accelerated by heating III in refluxing hexane. The product, IV, was isolated, and found to give an analysis still consistent with the formula $Fe_2(CO)_6(COC_2H_5)(C(C_6H_5)H)$. However, its spectroscopic properties are very different** and, specifically, the characteristic ^{13}C resonance of the COC_2H_5 bridge has disappeared. Moreover, the hydrogen-coupled ^{13}C spectrum shows the presence of two types of CH resonances, in addition to the phenyl resonances. These results indicated that there had been a considerable rearrangement of III, and the precise nature of IV was determined by an X-ray crystal structure study.

Crystal data: $C_{23}H_{16}O_7Fe_2$, M = 515.61, monoclinic, space group $P2_1/n$, a 17.801(3), b 10.006(2), c 12.971(2) Å, β 106.03(2)°, V 2220(1) Å^3, D_c 1.54 g cm^{-3}, $Z = 4$. Full matrix least-squares based on 2288 observed ($I > 2.5\ \sigma(I)$) of 2325 measured reflections, $\theta < 25°$, on a Philips PW-1100 diffractometer using the Mo-K_α radiation monochromatized by reflection from a graphite crystal. Final R_w value = 0.054.

The molecular structure of IV is shown in Fig. 1, the legend to which lists the important bond parameters***. There are two iron atoms at a single-bond distance bridged by a $C(OC_2H_5)C(C_6H_5)C(C_6H_5)H$ group. Thus, IV results from coupling of the ethoxy carbyne bridge with the 1,2-diphenylethenyl group. In the light of C(4)—C(6) carbon—carbon distances and the iron—carbon distances, this 3-carbon group is best described as an allylic group σ-bonded to Fe(2) and π-bonded to Fe(1). Indeed, C(4) is closer to Fe(2), and the C(4), C(5), C(6) carbon atoms are nearly equidistant from Fe(1). This situation contrasts with that found for the products resulting from coupling of a methylcarbyne ligand with propene [6] or from coupling of a methyl carbene with an alkyne [7] in which the distinction between a vinyl carbene and an allyl group is less clear.

Examination of the structure reveals another feature: the interaction of the C(61) and C(62) carbons of one of the phenyl groups with the Fe(2) centre. The carbon—iron distances are quite long, but indicate an interaction which

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*The reaction of $Fe_2(CO)_6(\mu$-$CO)(\mu$-$C(C_6H_5)C(C_6H_5)H)P(C_6H_5)_4$ with a stoichiometric amount of $(C_2H_5)_3OBF_4$ at room temperature in dichloromethane gave an almost quantitative yield of $Fe_2(CO)_6(\mu$-$COC_2H_5)(\mu$-$C(C_6H_5)H)$, which was extracted with pentane. Crystallization from this solvent gave orange crystals of III; ν(CO) in hexadecane: 2066m, 2034vs, 2000s, 1996sh, 1985s, 1966 cm^{-1}. ^1H NMR: 7.20 (C_6H_5), 5.09 qt (J 7.3) (OCH_2), 3.48 (CH_3), 1.65 t (J 7.3) (CH_3) ppm. ^{13}C NMR; 383.8 (COC_2H_5), 211.2 (CO); 182.8 (Fe—CC_6H_5); 152.8, 141, 129.8, 128.2, 127.2, 126.5 (C_6H_5); 87.9 ($CH(C_6H_5)$); 87.2 (OCH_2CH_3); 15.3 (OCH_2CH_3) ppm. Anal. Found: C, 53.60; H, 3.11. $C_{16}H_{11}Fe_2O_7$ calcd.: C, 53.73; H, 3.09%.

**IV red crystals in hexane; ν(CO) in hexadecane: 2068s, 2018s, 1988vs, 1978s, 1962m, 1955m cm^{-1}. ^{13}C NMR: 212.5 (CO); 204.5 ($FeCOC_2H_5$); 137.3, 136, 133.2, 131.5, 130.7, 128.3, 128.1, 128, 127.9, 124.3, (C_6H_5); 90.4 (CH); 87.2 ($C(C_6H_5)$); 71.7 (OCH_2CH_3); 51.4 (CH); 15.2 (OCH_2CH_3) ppm.

***The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

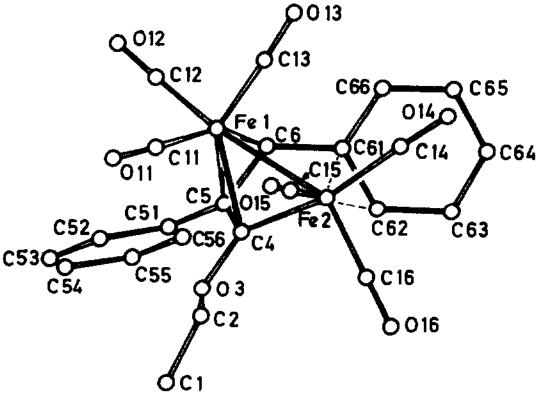

Fig. 1. View of the molecular structure of $Fe_2(CO)_6(\mu\text{-}C(OC_2H_5)C(C_6H_5)C(C_6H_5)H)$ with the atomic numbering scheme. Selected bond distances: Fe(1)—Fe(2) 2.635(1), Fe(1)—C(4) 2.129(7), Fe(1)—C(5) 2.085(6), Fe(1)—C(6) 2.069(7), Fe(2)—C(4) 1.970(7), Fe(2)—C(61) 2.431(7), Fe(2)—C(62) 2.433(7), C(4)—C(5) 1.415(9), C(5)—C(6) 1.440(9), C(61)—C(62) 1.393 (9), C(62)—C(63) 1.443(9), C(63)—C(64) 1.370(9), C(64)—C(65) 1.405(9), C(65)—C(66) 1.381(9), C(61)—C(6) 1.421(9).

can be attributed to the fact that otherwise the Fe(2) centre would be surrounded by only 16 valence electrons. A similar situation was found in the closely related product of the reaction of 1,2,3-triphenylcyclopropene with diiron nonacarbonyl [8]; the distances between the iron and the carbons of the phenyl ring are of the same order (2.404(4) Å). This bonding induces a localization of the bonds in the C(6) bonded phenyl ring, which are alternatively long and short. This phenomenom also explains the appearance of the new CH resonance in the ^{13}C NMR spectrum of IV.

The ease of the intramolecular coupling of the ethoxycarbyne and 1,2-diphenylethenyl ligands in complex III is certainly attributable to the close proximity of the two ligands in III, a phenomenom recently observed in $Os_3(CO)_9(\mu\text{-}CH_2)(\mu_3\text{-}C_2(C_6H_5)_2)$ [9].

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