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**Preliminary communication**

# CARBON—CARBON BOND FORMATION VIA COUPLING OF ISONITRILES WITH $\mu_2$-$\eta^2$-ACETYLIDES

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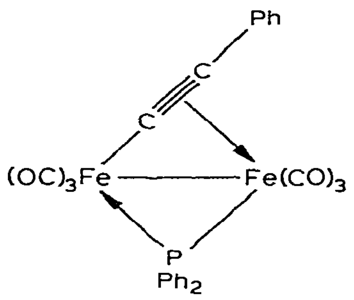
## Summary

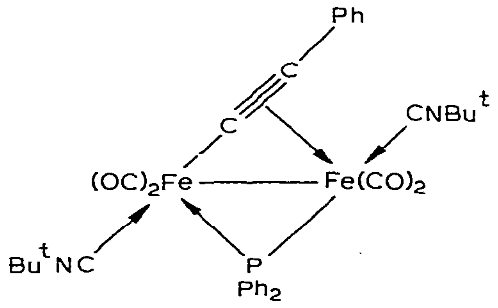
The synthesis of carbon—carbon bonds via coupling of isonitriles RNC with the $\mu_2$-$\eta^2$-acetylide in $Fe_2(CO)_6(C{\equiv}CPh)(PPh_2)$ via nucleophilic attack at carbocationic carbon is described.

Activation of an unsaturated ligand via multi-site coordination to several metal atoms in a polynuclear complex plays a pivotal role in organometallic synthesis and metal cluster catalysis [1]. In the continuing search for homogeneous Fischer—Tropsch type catalysts for the synthesis of hydrocarbon fuels from CO and $H_2$ attention has recently focussed on the unusual reactivity of cluster bound carbide carbon atoms [2,3]. Thus Bradley and coworkers [3] have synthesised methylacetate from CO, $H_2$, solvent methanol and a transition metal carbide cluster in which the carbide carbon atom is derived from CO. A key feature of the proposed reaction sequence is carbon—carbon bond formation between a cluster bound "carbocationic" carbide carbon atom and carbon monoxide. We have observed that multi-site bound acetylides, like their close relatives the carbides, exhibit pronounced "carbocationic" reactivity and in this communication we describe the synthesis of carbon—carbon bonds between acetylenic carbon atoms in $\mu_2$-$\eta^2$-acetylides and one class of weak, uncharged carbon nucleophiles, the isonitriles RNC. The synthesis of adducts $Fe_2(CO)_6\{C(CNR)CR'\}(PPh_2)$ from isonitriles RNC and sideways bound acetylide in $Fe_2(CO)_6(C{\equiv}CR')(PPh_2)$ via attack at acetylidic carbon and their subsequent conversion to carbene derivatives has significance not only for cluster mediated coupling but also for the elaboration of multisite bound unsaturated species.

The $\mu_2$-$\eta^2$-acetylide $Fe_2(CO)_6(C{\equiv}CPh)(PPh_2)$ (I) reacts readily with an excess of $Bu^tNC$ at room temperature in benzene. After 4 h, IR and thin layer



(I)



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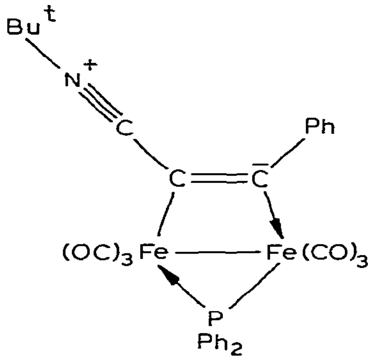

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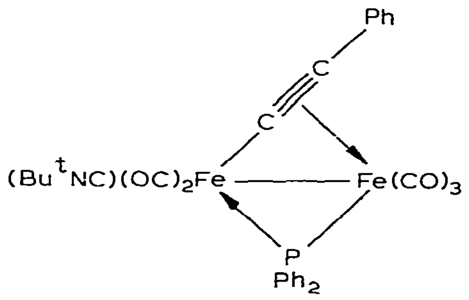

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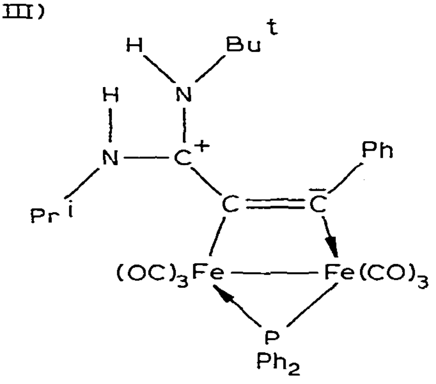

(V)

monitoring of the reaction mixture indicated the presence of two products. Chromatography on Florisil eluted a small amount of starting material (petr. ether), followed by a dark red band of $Fe_2(CO)_4(CNBu^t)_2(C_2Ph)(PPh_2)$ (II) (benzene/petr. ether 60/40) which readily crystallised from heptane at −10°C (II, 46% m.p. 157°C, dec., IR $C_6H_{12}$, $\nu$(CO): 1998m, 1973vs, 1947s, 1931m; Nujol, $\nu$(N≡C), 2140s cm$^{-1}$; $^1$H NMR, $C_6D_6$; $\delta$ 0.8 s (≡N—$CMe_3$), 6.9—7.9m ($C_6H_5$); $^{31}$P NMR, $C_6D_6$; $\delta$ 144.5). Benzene then eluted a bright orange band containing the adduct $Fe_2(CO)_6\{C(CNBu^t)CPh\}(PPh_2)$ (III), which crystallised from heptane (III, 30%, m.p. 149—150°C, IR, $C_6H_{12}$; $\nu$(CO). 2046s, 2005vs, 1987s, 1964w, 1955m, 1937m; Nujol, $\nu$(N≡C) 2190m cm$^{-1}$; $^1$H NMR, $C_6D_6$;

0.7s (≡NCMe$_3$), 6.9—7.9m (C$_6$H$_5$); $^{31}$P NMR, C$_6$D$_6$; δ 194.2). When the reaction was carried out at 0°C in heptane, carbonyl substitution was retarded and excellent yields (~75%) of III were obtained. Over shorter (~1 h) reaction periods in addition to III the monosubstituted derivative $Fe_2(CO)_5(C{\equiv}CPh)(PPh_2)(CNBu^t)$ (IV) could be isolated. Infrared (ν(CO), C$_6$H$_{12}$; 2044vs, 2008s, 1994vs, 1982m, 1980m, 1972s, 1962m, 1950m cm$^{-1}$) and $^{31}$P NMR (C$_6$D$_6$; δ 150.0s, 144.8s) data suggested that IV consisted of a mixture of isomers which could not be separated by repeated chromatography. On further reaction IV converted smoothly in the presence of excess Bu$^t$NC to II, while III remained unchanged. The higher $^{31}$P shift of III compared to II or IV indicated a larger angle at the phosphido bridge, [4] a longer Fe—Fe bond and the presence of a 2-carbon bridging ligand in III. Single crystal X-ray analysis* revealed the nature of III (Fig. 1). The principal structural feature is the dipolar ligand resulting from attack by the isonitrile carbon atom at the

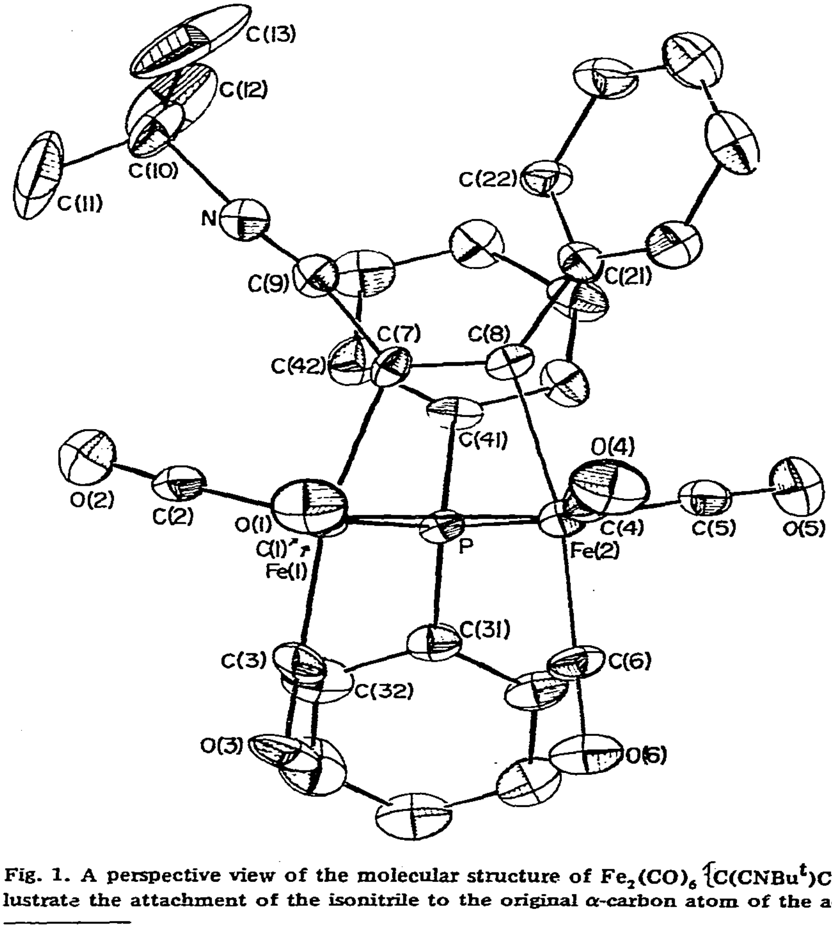

Fig. 1. A perspective view of the molecular structure of $Fe_2(CO)_6\{C(CNBu^t)CPh\}(PPh_2)$ drawn to illustrate the attachment of the isonitrile to the original α-carbon atom of the acetylide.

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*Crystal data: $Fe_2PNO_6C_{31}H_{24}$, mol. wt. 649.21; orthorhombic crystals, space group *Pbca*, *a* 21.359(4), *b* 16.080(3), *c* 17.641(4) Å; $Z = 8$, $\rho_n$ 1.41, $\rho_c$ 1.423 g cm$^{-3}$. The structure was solved and refined using 1456 observed ($I \geqslant 3\sigma(I)$) reflections measured on a Syntex P2$_1$ diffractometer with Mo-$K_\alpha$ radiation. With anisotropic thermal parameters for all non hydrogen atoms the $R$ and $R_w$ values were 0.055 and 0,064, respectively.

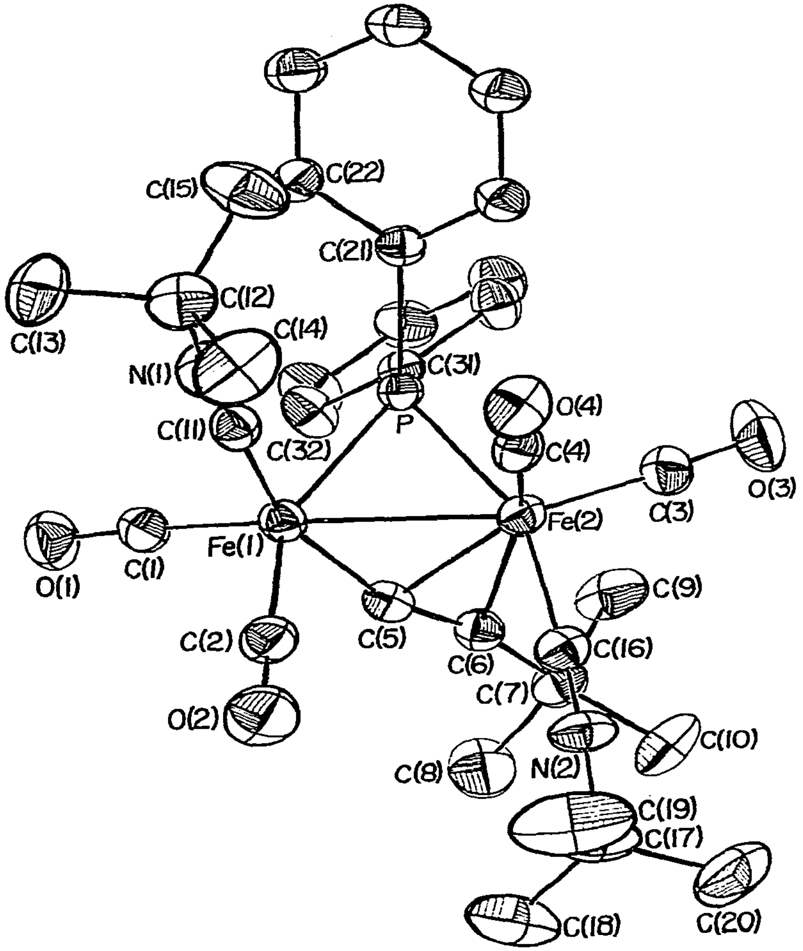

Fig. 2. The structure of $Fe_2(CO)_4(Bu^tCN)_2(C{\equiv}CPh)(PPh_2)$ showing the atomic numbering.

α-carbon atom of the acetylide in I. The carbon—carbon bond formed by coupling of the isonitrile and the acetylide is short (C(7)—C(9) 1.37(2) Å) indicative of a strong, partially multiple bond. The "carbon coordinated" isonitrile remains essentially linear in III with angles C(7)—C(9)—N of 171.8(6)° and C(9)—N(1)—C(10) of 169.8(8)°. The zwitterionic ligand with C(7) bonded to Fe(1) (Fe(1)—C(7) 2.01(1) Å) and C(8) to Fe(2) (Fe(2)—C(8) 2.04(1) Å) is best represented as a 1,4-dipole with the positive charge localised on nitrogen and the negative charge formally on C(8) delocalised into the $Fe_2(CO)_6P$ skeleton. As expected from the $^{31}P$ shift, the Fe(1)—Fe(2) 2.671(2) Å bond length is significantly longer than in I and the Fe(1)—P—Fe(2) angle (74.1(0)°) is larger. X-ray data for the $Bu^t$ analogue of II* (Fig. 2)

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* Crystal data: $Fe_2PN_2O_4C_{37}H_{37}$, mol. wt. 656.33, monoclinic crystals, space group $P2_1/c$ with $a$ 9.702(1), $b$ 28.268(3), $c$ 12.739(2) Å; $\beta$ 102.98(1)°; $Z = 4$, $\rho_c$ 1.280, $\rho_n$ 1.28 g $cm^{-3}$. Intensity data were collected on a Syntex $P2_1$ automatic diffractometer using Mo-$K_\alpha$ radiation and a $\theta$—$2\theta$ scan method. A total of 3453 observed reflections ($I \geqslant 3\sigma(I)$) were used in structure solution and refinement. The refinement converged at $R$ and $R_w$ values of 0.031 and 0.036, respectively, all non-hydrogen atoms having anisotropic thermal parameters.

confirmed the substitution of two carbonyl groups of I by isonitrile ligands. One $Bu^tNC$ ligand is *trans* to the phosphido bridge, the other approximately *trans* to the $\alpha$-carbon of the acetylide. Remarkably, disubstitution has a negligible effect on the structural parameters for the central $Fe_2C_2P_2$ core of the $Bu^t$ analogue of I*.

There are several notable features of the reaction of $Bu^tNC$ with I. Firstly, it is clear that at ambient temperature nucleophilic attack by $Bu^tNC$ competes with CO substitution despite the known affinity of isonitriles for low oxidation state metal sites. Furthermore, at lower temperatures where CO substitution is disfavoured, nucleophilic attack occurs predominantly at carbon. These results not only confirm that the $\mu_2$-$\eta^2$-acetylide in I is highly activated, they suggest extreme carbocationic character for the alkynyl carbon atoms, analogous to that implied by Bradley et al. for a cluster bound carbide [3]. Remarkably, the "carbon coordinated" isonitrile in III is susceptible to addition of primary amines, generating "carbon coordinated" carbenes quite analogous to the reactions of metal bound isonitriles. Thus III reacts with neat $Pr^iNH_2$ over 0.5 h affording after chromatography on Florisil a 65% yield of $Fe_2(CO)_6\{CC(NHPr^i)(NHBu^t)CPh\}(PPh_2)$ V (IR $\nu$(CO): 2039s, 1993s, 1971s, 1950m, 1940m, 1919m $cm^{-1}$; $^1H$ NMR ($C_6D_6$) −0.17d ($CH_3(Pr^i)$) $J$ 6.0 Hz; 0.7s ($CH_3(Bu^t)$); 0.81d ($CH_3(Pr^i)$) $J$ 6.0 Hz, 3.7 septet (C—H($Pr^i$)) $J$ 6.0 Hz, 4.1—4.4s (NH), 6.8—8.0m ($C_6H_5$); $^{31}P$ NMR, $C_6D_6$; $\delta$ 191.7). These spectroscopic data confirm that addition of the amine has occurred across the C—N multiple bond of the "carbon coordinated" isonitrile.

Although several examples are now known of nucleophilic attack by a phosphine or phosphite on an activated unsaturated moiety in a neutral cluster [6] to our knowledge the results reported here for isonitriles are unprecedented. The susceptibility of acetylidic carbon atoms to attack by uncharged carbon nucleophiles generating C—C bonds and the subsequent chemical transformations which can be accomplished on the adducts may have important general ramifications for the elaboration of unsaturated molecules in clusters.

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*In $Fe_2(CO)_6(C{\equiv}CBu^t)(PPh_2)$ [5] the Fe(1)—Fe(2) distance is 2.5959(6) Å, the Fe(1)—P—Fe(2) angle 71.7(0)°, the C≡C bond length 1.223(4) Å. These compare with values of 2.5946(7) Å, 71.5(0)° and 1.225(5) Å in $Fe_2(CO)_4\ (C{\equiv}CBu^t)(PPh_2)(CNBu^t)_2$.