Preliminary communication

UNEXPECTED DIRECT FORMATION OF
A BRIDGING 4-CYANOBUTA-1,3-DIENYLIDENE GROUP FROM REACTION
OF [(C$_5$H$_5$)Fe(CO)]$_2$(μ-CO)(μ-C=CH$_2$) WITH HC≡CCN

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Summary

The ethenylidenediiron complex [(C$_5$H$_5$)Fe(CO)]$_2$(μ-CO)(μ-C=CH$_2$) reacts with the nitrile substituted alkyne HC≡CCN to give high yield of [(C$_5$H$_5$)Fe(CO)]$_2$(μ-CO)(μ-C=CHCH=C(CN)H). It is suggested that this bridging 4-cyanobuta-1,3-dien-ylidenediiron complex is formed by attack of the electron rich double bond of the ethenylidenediiron complex on the electrophilic protonated carbon of the alkyne. An IR study has indicated that hydride reduction of the complex occurs selectively at the bridging vinylidene carbon atom to give an anionic bridging cyanovinylalkylidenediiron complex.

It was shown recently that cyanoalkynes (NCC≡CH and NCC≡CCN) can show very unusual reactions with metal–hydrogen bonds and highly regio- and stereo-selective insertions of alkynes in both metal–hydrogen bonds of (C$_5$H$_5$)$_2$MH$_2$ (M = Mo or W) were observed for the first time [1], while photochemical reaction of triphenylphosphine with, for example (C$_5$H$_5$)Mo(CO)$_3$[σ-C(CN)=C(CN)H], was found to give the phosphorus ylide complex (C$_5$H$_5$)Mo(CO)$_2$[η^2-C(CN)PPh$_3$-C(CN)H] [2]. We were also interested in the reactions with dinuclear complexes [3], since such species can lead to enhanced activation. Subsequently Casey and his co-workers [4] described the synthesis of metallacyclopentenone [(C$_5$H$_5$)-Fe(CO)]$_2$(μ-η^2,η^{2}COC(Ph)C(Ph)C=CH$_2$) (1) as well as the bridging σ,π-allyl complex (C$_5$H$_5$)(CO)FeFe(C$_5$H$_5$)(μ-CO)(μ-η^1,η^3-C(Ph)C(Ph)C=CH$_2$) (2) by photolysis of the known μ-ethenylidene complex [5] [(C$_5$H$_5$)Fe(CO)]$_2$(μ-CO)(μ-C=CH$_2$) (3) and PhC≡CPh.

We describe here the thermal reactions of 3 with activated terminal alkynes, and the unexpected formation of a μ-4-cyanobuta-1,3-dienylidene complex from NCC≡CH.

Reaction of the μ-ethenylidene complex [(C$_5$H$_5$)Fe(CO)]$_2$(μ-CO)(μ-C=CH$_2$) (3) with NCC≡CH in toluene (70°C, slight vacuum overnight) led to isolation of a

purple dinuclear complex (**4**) (up to 60% yield after work up, along with small amounts of starting material **3**) which was shown by elemental analysis (C, H, N, Fe) to be a 1/1 adduct. The IR spectrum shows bands in the terminal and bridging carbonyl stretching region, indicating that the $[(C_5H_5)Fe(CO)]_2(\mu\text{-CO})$ core is preserved. A characteristic sharp absorption at 2200 cm^{-1} is ascribed to the nitrile group and bands arising from double carbon–carbon bonds are also present. These preliminary results indicate that no complex of the type as described by Casey and his co-workers (i.e. **1** and **2**) is formed, and, that no loss of CO occurs.

The identity of this new compound was established by ^{1}H and ^{13}C NMR spectroscopies. The distinguishing features in the ^{1}H NMR spectrum of the crude product (**4**) are two sets (in a 1.7/1 ratio) of AMX type signals in the region of olefinic protons (1/1/1 intensity) (see Fig. 1): these sets are due to two isomers (Z and E), which can be separated by recrystallization from THF/petroleum ether. The typical Z-complex thus obtained was shown by ^{13}C NMR spectroscopy to be $[(C_5H_5)Fe(CO)]_2(\mu\text{-CO})(\mu\text{-}Z\text{-C=CHCH=C(CN)H})$ (**4-Z**), a totally unexpected μ-buta-1,3-dienylidene complex [6], which results from insertion of an alkyne in a C_{sp^2}–H bond. Although an analogous complex has been reported previously, the route to **4** described here is novel [7].
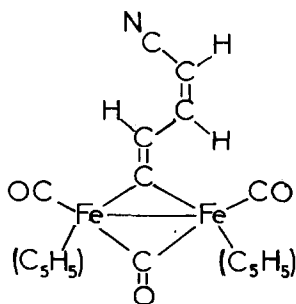
(4-Z)

We attempted to extend this reaction to other terminal alkynes, but found to our surprise that no reaction took place with PhC≡CH, $CH_3O_2CC≡CH$ or $CF_3C≡CH$, under similar conditions. This illustrates the high reactivity of NCC≡CH and provides insight into a possible mechanism. The main relevant observations are (i) complex **4** is the only nitrile-containing compound formed in the reaction of **3** with NCC≡CH; (ii) the nitrile group is always in the δ position relative to the bridging vinylidene carbon atom, and a mixture of Z and E isomers is always obtained so that the reaction is thus highly regio- but not stereo-selective; and (iii) a highly activated (polarized) alkyne must be used.

These observations, together with the findings of Casey's group who observed that **3** could act as a nucleophile towards protonated aldehydes [8], enable us to suggest a mechanism based on the nucleophilic attack of the electron rich carbon of **3** on the electron deficient carbon of the alkyne (see Scheme 1). Electron donating $(C_5H_5)Fe(CO)$ moieties are able to stabilize a positive charge on the α carbon and the nitrile in the δ position allows the negative charge to be delocalized, leading to a stabilized intermediate that can rearrange by proton transfer to the more electron rich carbon atom.
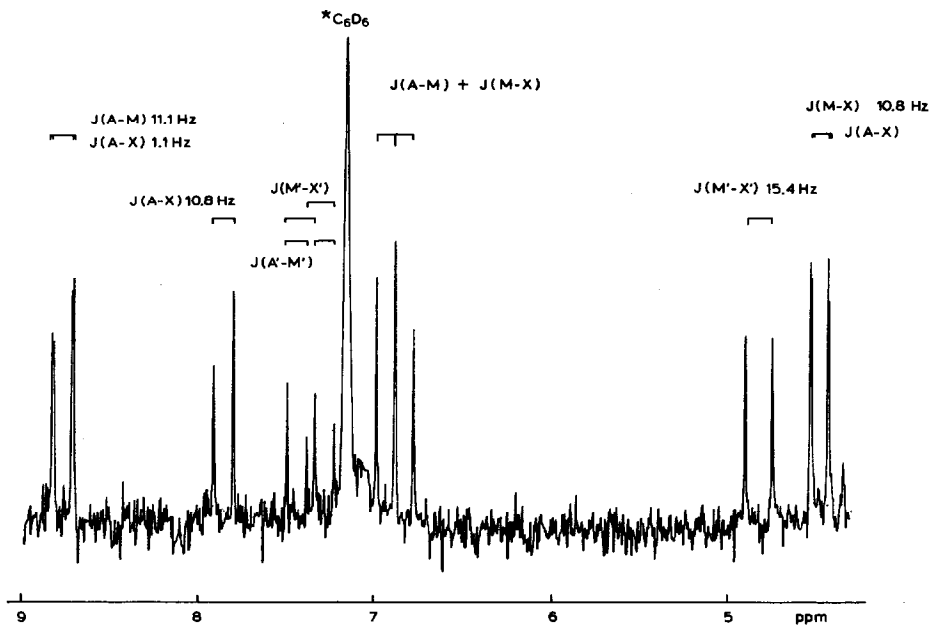
Fig. 1. ^{1}H NMR spectrum (99.6 MHz, C_6D_6) of the μ-C=CH$_A$CH$_M$=C(CN)H$_x$ part of (4-Z) and (4-E). The prime refers to the (4-E) isomer (see ref. 6).

We begun a study of reactions of the new complex. It does not react with CO, with or without UV irradiation. The chemistry of μ-vinylidene complexes is essentially limited to the ready reaction with strong acids to yield the corresponding cationic μ-alkylidyne [9]. Reaction of **4** with, for example, HBF$_4$ · O(CH$_3$)$_2$ does lead to a cationic species, which can be viewed as a bridging alkylidyne complex (IR spectrum), but this undergoes rapid fragmentation by a mechanism not yet understood. We are investigating the possibility that replacement of CO ligands by Ph$_2$PCH$_2$PPh$_2$ will stabilize the cationic species.
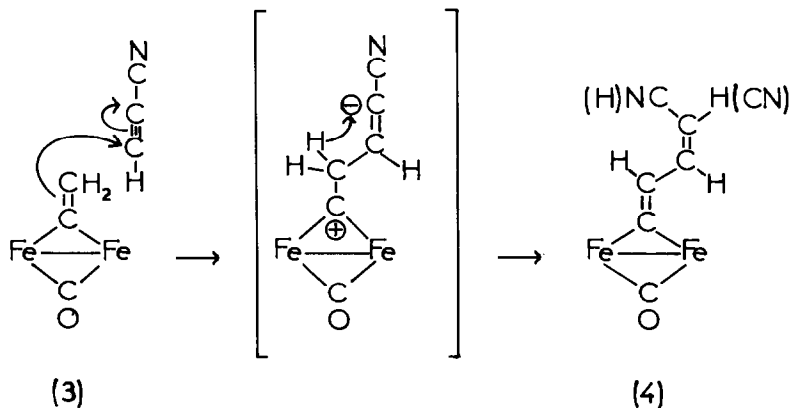
SCHEME 1.

The most interesting feature is nucleophilic attack by hydride reagents, a type of reaction which has been little studied [9]. Complex **4** does not react with $NaBH_4$, but addition of one equivalent of $LiB(C_2H_5)_3H$ leads to a stable anionic species whose IR spectrum [10] shows that there has been no reduction of CO to a formyl group. This strongly suggests that the hydride selectively attacks the bridging vinylidene carbon to yield an anionic bridging cyanovinyl substituted alkylidene in which the negative charge is stabilized by the nitrile group. We have not succeeded in isolating this compound.

The reactions of this anion towards electrophiles, and those of readily available μ-vinylidene complexes such as **3** with NCC≡CCN, are being studied.

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6 (4) Anal. Found: C, 53.89, H, 3.36; N, 3.53; Fe, 27.68. $C_{18}H_{13}O_3NFe_2$ calcd.: C, 53.64; H, 3.23; N, 3.48; Fe, 27.74%. (4-*Z*) IR (CH_2Cl_2, cm^{-1}) ν(CN) 2200m; ν(CO) 1998s, 1960m, 1806s, ν(C=C) 1565m, 1535w; ^{1}H NMR (99.6 MHz, C_6D_6, δ in ppm relative to TMS, *J* in Hz); 8.70 (dd, *J* 11.0, 1.1; C=C*H*CH=C(CN)H); 6.89 (pseudo t., *J* 11.0, C=CHC*H*=C(CN)H); 4.48 (dd, *J* 10.8, 1.1; C=CHCH=C(CN)*H*); 4.13 (s, C_5H_5); 4.02 (s, C_5H_5); ^{13}C NMR (25.05 MHz, $CDCl_3$, δ in ppm relative to TMS); 304.8 (μ-*C*=CHCH=C(CN)H); 266.7 (μ-*C*=O); 209.6, 209.1 (Fe*C*O); 150.8 (C=*C*HCH=C(CN)H); 141.6 (C=CH*C*H=C(CN)H); 88.4, 87.6 (C_5H_5); 88.2 (C=CHCH=*C*(CN)H). (4-*E*) IR same as (4-*Z*) excepted 1960s ^{1}H NMR (same conditions as above); 7.86 (d,J 10.8; C=C*H*CH=(CN)H); 7.36 (dd, *J* 10.8; 15.4; C=CHC*H*=C(CN)H); 4.83 (d, *J* 15.4; C=CHCH=(CN)*H*).

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