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Preliminary communication

Reaction of a bridged ethenylidene diiron complex with tetracyanoethylene. Synthesis and crystal structure of the μ-3,4,4-tricyanobuta-1,3-dienylidene complex $[(C_5H_5)Fe(CO)]_2(\mu\text{-}CO)[\mu\text{-}C{=}CH(NC)C{=}C(CN)_2]$

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Abstract

The reaction of μ-ethenylidene $[(C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ (**1**) with tetracyanoethylene gives the μ-3,4,4-tricyanobuta-1,3-dienylidene complex $[(C_5H_5)Fe(CO)]_2(\mu\text{-}CO)[\mu\text{-}C{=}CH(NC)C{=}C(CN)_2]$ (**2**), whose crystal structure has been determined ESR studies suggest that a radical process may be involved.

The studies of reactions of bridging alkenylidene complexes have been largely confined to the effects of the ready protonation at the β-carbon that leads to bridging cationic carbyne compounds [1]. In the case of cyclopentadienyldiiron complexes, extensive work of Casey's group on hydrocarbation of alkenes [2] with the μ-methylidyne complex $[(C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH)^+$ has provided a general route for synthesis of various μ-alkenylidene complexes [3], which means that their chemistry can now be extended. Recent studies have dealt with the reactions of the parent μ-ethenylidene $[(C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ (**1**); diazo derivatives react with this to give μ-cyclopropylidenes, which rearrange to μ-allene complexes [4,5], and alkynes insert photochemically into an iron–carbon bond of the ligand, to give σ-π-allyl complexes via metallacyclopentenone intermediates [6]. We recently initiated a study of the behavior of electrophilic cyanocarbons towards **1**, and found that cyanoethyne HC≡CCN is inserted into a $C(sp^2)$–H bond of **1** to give a μ-4-cyanobuta-1,3-dienylidene diiron complex [7]. We now report that the reaction of **1** with tetracyanoethylene, which can act as both an electrophile and an electron acceptor [8], gives a μ-3,4,4-tricyano-1,3-dienylidenediiron complex.

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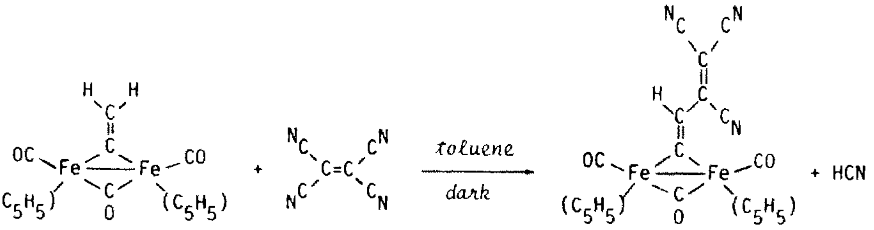
The μ-ethenylidenediiron complex (**1**) [9] reacts cleanly with TCNE in the dark in toluene under nitrogen at ambient temperature. When **1** (191 mg, 0.54 mmol) and sublimed TCNE (63 mg, 0.49 mmol) were mixed in 35 ml of toluene, the colour changed from red to bright orange-red within a few minutes. The solution was stirred for 18 h then filtered and concentrated to ca. 15 ml and set aside to deposit red-orange crystals of **2** slowly. More product was obtained by addition of light petroleum to the mother liquor (total yield ca. 70% from **1**). Analytical and spectroscopic data [10*] indicate the product was the μ-3,4,4-tricyanobuta-1,3-dienylidenediiron complex $[(C_5H_5)Fe(CO)]_2(\mu\text{-}CO)[\mu\text{-}C{=}CH(NC)C{=}C(CN)_2]$ (**2**) [11*], the structure of which was confirmed by X-ray diffraction (vide infra). The main features of the spectroscopic data are; (i) in the IR spectrum the high frequencies of the infrared carbonyl absorption bands; (ii) in the ^{13}C NMR spectrum, the low and high field resonances, respectively, of the bridging and the terminal (Cδ) carbons of the tricyanobutadienylidene ligand (the signal from the μ-alkenylidene carbon at δ 343 ppm is shifted more than 60 ppm downfield from the corresponding signal from **1** [9,12*]). These features illustrate the strong π-acceptor properties of the ligand.

The data are consistent with the structure of **2** determined by X-ray diffraction which is shown in Fig. 1 [13*]. There is a bridging planar 3,4,4-tricyanobuta-1,3-dienylidene group, together with a carbonyl group and two $Fe(CO)(C_5H_5)$ units in a *cis*-disposition. The iron atoms are linked by a single bond. There is substantial electron delocalization in the ligand: the alkenylidene C4–C5 bond length is 1.358(5) Å, the C5–C6 bond length (1.406(5) Å) lies between that of a single and a double bond, and the C6–C8 bond (1.382(5) Å) is rather long (compare 1.344(3) Å in TCNE [14]).

We demonstrated that the missing hydrogen, carbon and nitrogen atoms, can be recovered as hydrogen cyanide. In separate experiments, the gas above the reaction mixture was analyzed by IR spectroscopy, and hydrogen cyanide identified from its rotation-vibration spectrum [15].



(1) (2)

In connection with the mechanism of this reaction, it should be noted that the reaction proceeds cleanly in the dark (in the light, there is considerable formation of untractable materials), and involves highly coloured intermediates. This prompted us to study the course of the reaction by means of ESR spectroscopy. Similar results were obtained from reaction mixtures up on mixing **1** and TCNE in toluene directly in the ESR tubes. Two strong overlapping ESR signals appeared at the same time with an intense orange color. The two ESR signals persisted for several hours. The *g*

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[*] This and other references marked with asterisks indicate notes occurring in the list of references.

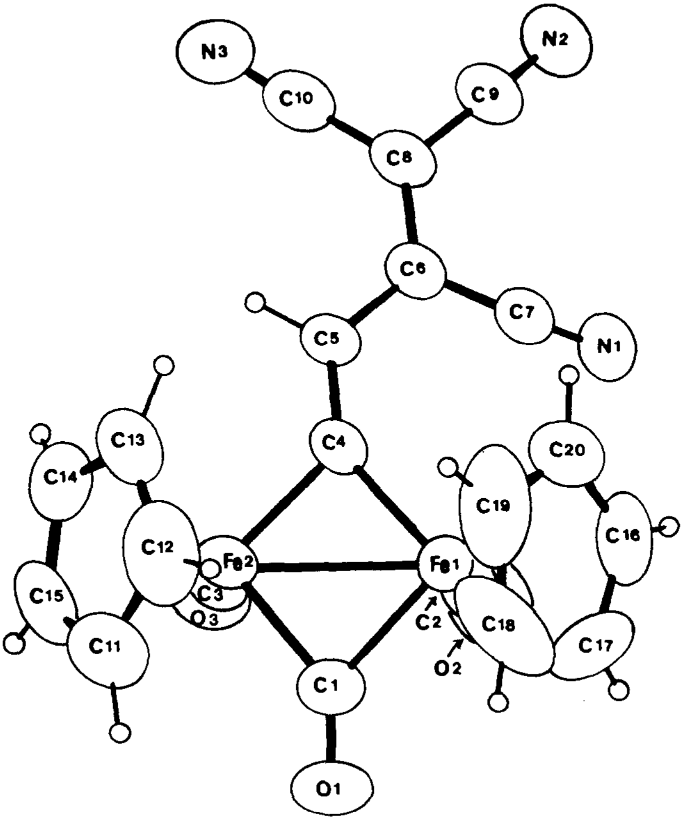
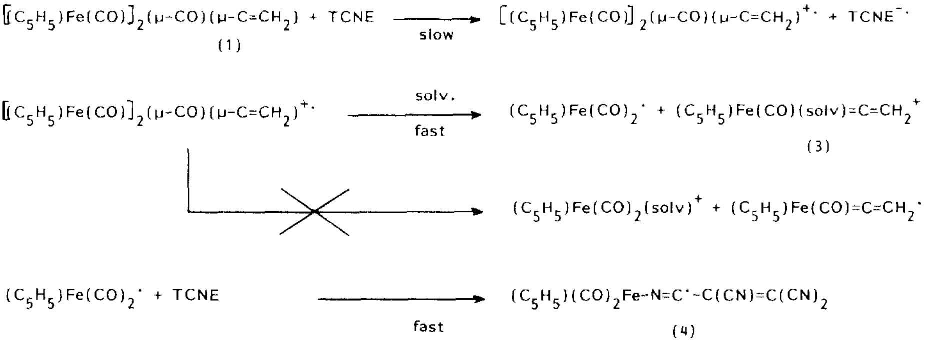


Fig. 1. The molecular structure of 2. Selected bond lengths (Å): Fe1–Fe2 2.503(1), Fe1–C4 1.874(3), Fe2–C4 1.888(3), Fe1–C1 1.954(4), Fe2–C1 1.897(4), C4–C5 1.358(5), C5–C6 1.406(5), C6–C8 1.382(5). Selected bond angles (°): Fe1–C4–Fe2 83.4(1), Fe1–C1–Fe2 81.1(2), Fe1–C4–C5 144.2(3), Fe2–C4–C5 132.4(3), C4–C5–C6 127.9(4), C5–C6–C8 124.5(4).

values and the hyperfine structures of those signals [16*] are characteristic of the radical anion TCNE$^{-\cdot}$ and the iminotricyanoallyl radical (C$_5$H$_5$)(CO)$_2$FeN=C$^\cdot$(NC)C=C(CN)$_2$ (4) as observed by Krusic and his co-workers [17]. This implies that electron transfer and cleavage of the iron–iron bond had occurred (see Scheme 1). It is noteworthy that no coupling to hydrogen was observed in the ESR spectrum, which means that a sequence in which breaking of the iron–iron bond in [(C$_5$H$_5$)Fe(CO)]$_2$(μ-CO)(μ-C=CH$_2$)$^{+\cdot}$ to generate a mononuclear ethenylideneiron radical (similar to an "allenyl" type radical) and a carbonyl iron cation can be ruled out. It also suggests that the generation of an intermediate biradical arising from the addition of TCNE and **1** acting as an olefin is unlikely [18*].

Even if a mechanism involving nucleophilic attack of the electron-rich ethenylidene on the electrophilic TCNE (followed by hydrogen cyanide loss) cannot be ruled out, we believe that a radical process involving metal–metal bond cleavage may compete with it [20*]. The sequence that leads to re-formation of a binuclear complex such as **2** may be: (i) reaction of iminotricyanoallyliron radical **4** with the cationic ethenylideneiron (3), and (ii) energy minimization by loss of hydrogen cyanide and electron transfer from TCNE$^{-\cdot}$. These proposals are supported by



Scheme 1

recent finding of Selegue et al. [21], who observed that oxidative activation could lead to carbon–carbon coupling between two alkenylidene iron complexes.

We are investigating in greater detail the mechanism of this and related carbon–carbon bond-forming reactions.

References

1 M.I. Bruce, A.G. Swincer, Adv. Organomet. Chem., 22 (1983) 59.

2 C.P. Casey, P.J. Fagan, J. Am. Chem. Soc., 104 (1982) 4950.

3 C.P. Casey, M.W. Meszaros, P.J. Fagan, R.K. Bly, S.R. Marder, E.A. Austin, J. Am. Chem. Soc., 108 (1986) 4043.

4 C.P. Casey, E.A. Austin, Organometallics, 5 (1986) 584.

5 (a) E.L. Hoel, G.B. Ansell, S. Leta, Organometallics, 5 (1986) 585; (b) 3 (1984) 1633.

6 C.P. Casey, W.H. Miles, P.J. Fagan, K.J. Haller, Organometallics, 4 (1985) 559.

7 M. Etienne, J.E. Guerchais, J. Organomet. Chem., 314 (1986) C81.

8 J.K. Kochi, Organometallic mechanisms and catalysis, Academic press, New-York, NY, 1978.

9 G.M. Dawkins, M. Green, J.C. Jeffery, C. Sambale, F.G.A. Stone, J. Chem. Soc. Dalton Trans., (1983) 499.

10 For **2**: ^{1}H NMR ($(CD_3)_2CO$, 99.6 MHz, 251 K) δ (ppm) 8.97 (s, 1H, μ-C=CH(NC)C=C$(CN)_2$), 5.39 (C_5H_5), 5.36 (C_5H_5) (total 10H); ^{13}C NMR ($CDCl_3$, 25.05 MHz, 0.075 M Cr$(acac)_3$) δ (ppm) 342.6 (μ-C=), 259.6 (μ-CO), 207.5, 207.1 (Fe-CO), 139.3 (d, $J(^1H-^{13}C)$ 159 Hz, μ-C=CH(NC)C=C$(CN)_2$), 132.5 (μ-C=CH-(NC)C=C$(CN)_2$), 114.7, 113.6, 112.8 (CN), 89.6, 89.2 (C_5H_5), 73.6 (μ-C=CH-(NC)C=$C$$(CN)_2$); IR ($CH_2Cl_2$, cm^{-1}): ν(CN) 2205(m), ν(CO) 2015(s), 1980(m), 1815(s-br), ν(C=C) 1470(s), 1460(s); Anal. Found: C, 53.15; H, 2.33; N, 9.27. $Fe_2O_3N_3C_{20}H_{11}$ calcd.: C, 53.01; H, 2.43; N, 9.28%.

11 There is very little precedent for this type of compound; (a) deprotonation of μ-vinylcarbyne complex $[(C_5H_5)Fe(CO)]_2(\mu$-CO$)[\mu$-C-HC=C(H)$CH_2CH_3)]^+$ PF_6^- led to the μ-penta-1,3-dienylidene complex $[(C_5H_5)Fe(CO)]_2(\mu$-CO$)[\mu$-C=CH-HC=C(H)$CH_3]$. See: C.P. Casey, S.R. Marder, Organometallics, 4 (1985) 411. (b) we have previously synthesized a μ-4-cyanobuta-1,3-dienylidene complex $[(C_5H_5)Fe(CO)]_2(\mu$-CO$)[\mu$-C=CH-HC=C(H)CN]. See ref. 7.

12 To our knowledge it is the most deshielded among the μ-alkenylidene diiron complexes [3], and its resonance lies close to those of cationic mononuclear ones [1].

13 Crystal data for **2**: $Fe_2O_3N_3C_{20}H_{11}$, $M_r = 469$, monoclinic space group $P2_1/c$, a 11.621(4), b 7.904(4), c 20.546(5) Å, β 94.00(2)°, V 1182.6(7) Å^3, $Z = 4$, D_{calc} 1.65 Mg m^{-3}, λ(Mo-K_α) 0.71073 Å, μ 14.8 cm^{-1}, $F(000) = 912$, T 296 K. Crystal dimensions 0.15×0.15×0.20 mm. Enraf–Nonius CAD4 diffractometer. The structure was solved by Patterson and difference Fourier methods. A total of 3521 reflections were collected, of which 2025 independent were used ($I > 3\sigma(I)$) to give final $R = 0.032$, $R_w = 0.031$. Tables of atomic coordinates and a complete list of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

14 R.G. Little, D. Pautler, P. Coppens, Acta Cryst., B, 27 (1971) 1493.

15 A.R.H. Cole, Tables of wavenumbers for the calibration of infrared spectrometers, IUPAC, Pergamon Press, Oxford, 1977, p. 28.

16 For TCNE$^{\cdot-}$: $g = 2.003$, a(N) 1.525 G; for $(C_5H_5)(CO)_2Fe\text{-}N^3{=}C^{\cdot}\text{-}C(CN^2){=}C(CN^1)_2$: $g = 2.001$, $a(N^3)$ 2.710 G, $a(N^2)$ 1.195 G, $a(N^1,N^1)$ 1.685 G (values obtained from computer simulation). Since these values differ slightly from those reported previously in ref. 17, in which experiments were carried out in tetrahydrofuran, we have confirmed that the same spectrum is obtained by mixing TCNE and $[(C_5H_5)Fe(CO)_2]_2$ in toluene.

17 P.J. Krusic, H. Stoklosa, L.E. Manzer, P.J. Meakin, J. Am. Chem. Soc., 97 (1975) 667.

18 Reactions of TCNE with transition-metal acetylides gave a variety of butadienyl type complexes, and ESR species with four equivalent nitrogen atoms were observed. See ref. 19. For example with $W(C{\equiv}CPh)(CO)_3(C_5H_5)$ and TCNE in benzene, the spectrum has $g = 1.997$, a(N) 1.59 G.

19 M.I. Bruce, T.W. Hambley, M.R. Snow, A.G. Swincer, Organometallics, 4 (1985) 494 and 501.

20 Similar trends were found in the reaction of Grignard reagents with TCNE: H.C. Gardner, J.K. Kochi, J. Am. Chem. Soc., 98 (1976) 558, but insertion of TCNE into the metal–carbon bond of tetraalkyltin compounds has been shown to proceed entirely through an electron-transfer process: Fukuzumi, S.; Mochida, K.; Kochi, J.K. J. Am. Chem. Soc., 101 (1979) 5961. See also ref. 17 for Sn–Sn, Mn–Mn and other metal–metal bond breaking.

21 R.S. Iyer, J.P. Selegue, J. Am. Chem. Soc., 109 (1987) 910.