Tetracyanoethylene Addition to Fe(allyl)$_2$(CO)$_2$: Occurrence of a 16-Electron Fe(II) Complex

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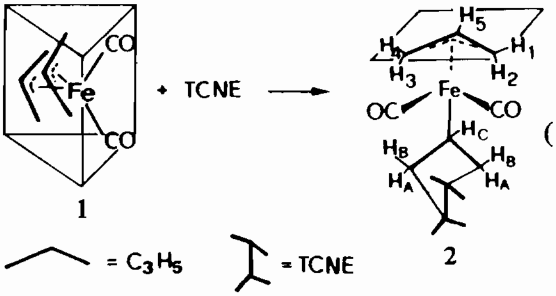
The reaction between Fe(allyl)$_2$(CO)$_2$ and tetracyanoethylene affords the 16-electron Fe(II) complex Fe(η^3-allyl)($\overline{\text{–CHCH}_2\text{–C(CN)}_2\text{C(CN)}_2\text{–CH}_2}$)(CO)$_2$, which has been fully characterized. The coordinative unsaturation of this product is demonstrated: it reacts with one equivalent of PPh$_3$ to give the 18-electron species Fe(η^3-C$_3$H$_5$)($\overline{\text{–CHCH}_2\text{–C(CN)}_2\text{C(CN)}_2\text{–CH}_2}$)(CO)$_2$(PPh$_3$), which has been also isolated and identified.

Transition metal complexes with unusual coordination deficiency may be prepared by synthesizing strategies suitable for bearing labile species where the peculiar ligand stabilization offers a chance of product isolation. Thus, electrophilic attack of H$^+$ on Fe(butadiene)(CO)$_3$ affords [Fe(η^3-1-Me·allyl)(CO)$_3$]$^+$ when the counter-anion does not display coordination properties [1]. This case remained a rare example of synthesis of a 16-electron Fe(II) species [2].

We report here the isolation of a new 16-electron Fe(II) compound obtained by reacting tetracyanoethylene, TCNE, with Fe(η^3-C$_3$H$_5$)$_2$(CO)$_2$, **1** [3], in toluene solution at –60 °C, stoichiometric TCNE addition to **1** affords an off-white solid identified as Fe(η^3-C$_3$H$_5$)(C$_3$H$_5$·TCNE)(CO)$_2$**, **2** (eqn. 1).



(1)

The structure of **2** results from ^{1}H NMR data of Table I; the spectrum in CD$_2$Cl$_2$ solution is shown in Fig. 1. η^3-allyl protons, marked by the + symbol, appear at 4.12 (multiplet), 3.43 (doublet), and 2.51 ppm (doublet) with integration ratios 1/2/2; other signals appear shared out at 1.48, 2.27, and 2.86 ppm. These resonances have been attributed to protons H$_A$, H$_B$ and H$_C$ of the 5-member ring $\overline{\text{–CHCH}_2\text{–C(CN)}_2\text{C(CN)}_2\text{–CH}_2}$ on the basis of decoupling and spectrum simulation experiments.

The analogy of the ·C$_3$H$_5$·TCNE protons resonances with those obtained in the case of Pt(PR$_3$)$_2$($\overline{\text{–CHCH}_2\text{–C(CN)}_2\text{C(CN)}_2\text{–CH}_2}$)Cl [4], is noteworthy, confirming the occurrence of |2 + 3| cyclo-

TABLE I. ^{1}H NMR Data in CD$_2$Cl$_2$ Solution.[a]

Compound	η^3-allyl protons			Cyclopenthyl protons			
2	5	4.12		C	1.48		
	1,4	3.43	$J_{5-1,4}$ = 6.7	B	2.27	J_{BC} = 14.0	J_{AB} = 14.0
	2,3	2.51	$J_{5-2,3}$ = 13.2	A	2.86	J_{AC} = 7.0	
3[b]	5	4.16		C	1.27		
	1,4	2.97	$J_{5-1,4}$ = 9.0	A	2.57	J_{AC} = 7.5	J_{AB} = 14.5
	2,3	2.05	J_{5-2} = 12.5	B	2.97	J_{BC} = 14.0	
			$J_{P-2,3}$ = 4.5				

[a] Registered with a WP 200 MHz Bruker instrument at 203 K; for attributions, see eqns. (1) and (2); δ values ±0.03 ppm; J values ±0.5 Hz. [b] PPh$_3$ H's at 7.8–7.2 ppm; ^{31}P{^{1}H} NMR: single resonance at 1.7 ppm, 85% H$_3$PO$_4$ as external standard.

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***Anal.* Calcd. for C$_{14}$H$_{10}$N$_4$O$_2$Fe: C, 52.36; H, 2.82; N, 17.45. Found: C, 51.9; H, 2.8; N, 17.8. IR: $\nu_{C\equiv N}$ multiplet centered at 2200 cm^{-1}; ν_{CO} 1980, 2060, 2100 cm^{-1} (nujol mull, room temperature, product under decomposition).

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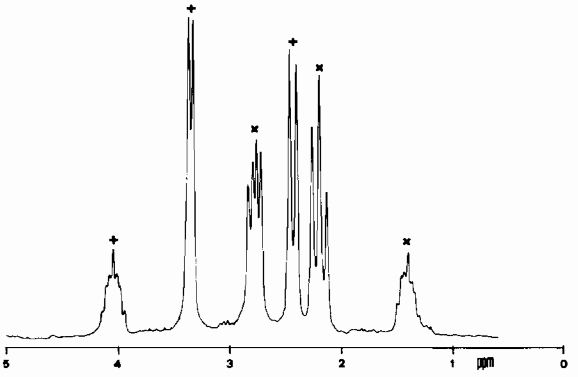
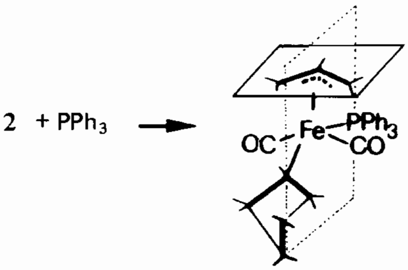


Fig. 1. ^1H NMR spectrum of 2 registered at 200 MHz in CD_2Cl_2 solution at 213 K. +: allyl protons, ×: cyclopentyl protons.

addition of TCNE on one η^3-allyl group of 1. The ^1H NMR features suggest a symmetric allyl group in agreement with proposed formulation for 2; variable temperature NMR experiments in the range 203–273 K do not indicate any change with respect to the Figure 1 spectrum. The mass spectrum of 2 does not show signals above 322 daltons; the presence of strong peaks at m/z 169 $[C_3H_5 \cdot TCNE]^+$, m/z 153 $[FeC_3H_5C_2O_2]^+$ confirms the ligand organization of compound 2[†].

The coordinative unsaturation of 2 was confirmed by reacting 2 with a stoichiometric amount of PPh_3. The reaction, carried out in toluene at –20 °C, afforded a yellow-brown product which after crystallization from toluene–pentane, was isolated and identified as $Fe(\eta^3\text{-}C_3H_5)(C_3H_5 \cdot TCNE)(PPh_3)(CO)_2$[††], 3 (eqn. 2).



3

(2)

Compound 3 is a 18-electron Fe(II) species resulting from 1/1 addition of PPh_3 to 2. NMR data of 3 are reported in the table: they suggest the proposed ligand organization with a symmetry plane defined by central allylic carbon, Fe atom, P atom and central carbon of the $-CHCH_2-C(CN)_2C(CN)_2-CH_2$ moiety.

The mechanism of reaction (1) is questionable The exhaustively studied reactions of electrophiles with 18-electron η^1-allyl Fe(II) complexes are known to bear |2 + 3| cycloaddition products via electrophylic attack on the olefinic terminus of the η^1-allyl moiety acting as a Lewis base [5–8]. In the present case a possible mechanism may involve the fomation of a η^1-allyl intermediate by TCNE coordination with subsequent collapse to 2, analogous to the mechanism proposed for the TCNE cycloaddition on allyl-Pt(II) complexes [4]. An alternative reaction path may be a Diels-Alder type of interaction between the TCNE and both terminal carbons of the coordinated η^3-allyl group, as for other condensation reactions involving organometallic species [9].

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[†] Mass spectrometric measurements were performed on a VG ZAB 2F instrument (C.N.R., Padova) operating in electron impact conditions (70 eV, 20 μA) with a source temperature at 80 °C.

[††] *Anal.* Calcd. for $C_{32}H_{20}N_4O_2PFe$: C, 65.76; H, 4.30; N, 9.59. Found: C, 64.9; H, 4.1; N, 9.9. IR: $\nu_{C\equiv N}$ multiplet centered at 2145 cm^{-1}, ν_{CO} 1920, 1985, 2055 cm^{-1} (nujol mull, room temperature).