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Electrophilic Behavior of Tetracyanoethylene toward Transition Metal–Carbon σ Bonds. Reactions with 2-Alkenyl and 2-Alkynyl Complexes

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Transition metal–2-alkenyl complexes h^5-$C_5H_5Fe(CO)_2CH_2C(R'')=CRR'$ *and* h^5-$C_5H_5Mo(CO)_3CH_2C(R'')=CRR'$ $(R=R'=H, R''=CH_3, R=R'=CH_3; R''=H)$ *react rapidly with tetracyanoethylene (TCNE) to yield the products derived by (3+2) cycloaddition with 1,2 metal migration,* $[M]\overline{C(R'')C(R)(R')C(CN)_2C(CN)_2CH_2}$. *Similarly,* h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ $(R=CH_3, CH_2Fe(CO)_2(h^5\text{-}C_5H_5))$, h^5-$C_5H_5Mo(CO)_3CH_2C{\equiv}CR$ $(R=C_6H_5)$, *and* h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2C{\equiv}CR$ $(R=CH_3)$ *afford complexes of the type* $[M]\overline{C{=}C(R)C(CN)_2C(CN)_2CH_2}$ *on treatment with TCNE. In contrast, reaction between* h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2CH=C(CH_3)_2$ *and TCNE proceeds very slowly to produce the keteniminato derivative* h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]N=C=C(CN)C(CN)_2CH_2CH=C(CH_3)_2$ *as well as* h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CN$. *The infrared and proton nmr spectra of the new compounds are discussed in the context of assignment of structures. Evidence is presented in support of the intermediacy of dipolar metal–olefin and metal–allene complexes in these reactions.*

Introduction

As part of a broad program concerned with the chemistry of transition metal–carbon σ bonds, we have been investigating reactions of such compounds with various electrophilic reagents. The behavior of SO_2 toward metal–carbon bonds has been thoroughly explored in this context[1]; both insertion[2] and cycloaddition[3] reactions were noted depending on the nature of the hydrocarbon moiety attached to the metal.

In an effort to ascertain the scope of such electrophilic reactions we have extended our investigation to a powerful π-acid, tetracyanoethylene (TCNE). TCNE is known readily to form complexes with transition metals, and these have been the subject of numerous studies.[4] Insertions of TCNE into metal–hydrogen[5] and metal–carbon[6] bonds have been also reported. Described herein in detail are the results of our investigation on reactions of transition metal–2-alkenyl (σ-allyl) and -2-alkynyl (propargyl) complexes with TCNE. Some aspects of this work were communicated earlier.[7]

Experimental Section

General Procedures

A nitrogen atmosphere was employed routinely for all of the reactions reported herein. The alumina used in chromatographic separations and purifications was deactivated with H_2O (6–10%). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Physical Measurements

Infrared spectra were recorded on a Perkin–Elmer Model 337 spectrophotometer. Except as noted, hydrogen-1 nmr spectra were obtained on a Varian Associates A–60A spectrometer using tetramethylsilane as an internal reference. Melting (decomposition) points were taken on a Thomas–Hoover capillary melting point apparatus and are uncorrected.

Materials

TCNE, procured from Columbia Organic Chemical Co., was sublimed prior to use. 3-Chloro-2-methyl-1-propene, from Aldrich Chemical Co., was purified by distillation. $[h^5\text{-}C_5H_5Fe(CO)_2]_2$ and $[h^5\text{-}C_5H_5Mo(CO)_3]_2$ were used as received from Strem Chemicals. Anhydrous grade SO_2 was passed through concentrated H_2SO_4 and a P_4O_{10}–$CaCl_2$ column before condensation. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under a nitrogen atmosphere immediately before use. All other chemicals and solvents were reagent grade or equivalent.

The organoiron and -molybdenum compounds h^5-$C_5H_5Fe(CO)_2CH_2CH=C(CH_3)_2$[8], h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$[3], h^5-$C_5H_5Fe(CO)_2CH_2CH_2C{\equiv}CCH_3$[3], h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO_2(h^5\text{-}C_5H_5)$[9], h^5-$C_5H_5Mo(CO)_3CH_2CH=C(CH_3)_2$[8], h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2CH=C(CH_3)_2$[10], h^5-$C_5H_5Mo(CO)_3CH_2C{\equiv}CC_6H_5$[11], and h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2C{\equiv}CCH_3$[3] were prepared according to published methods. The methylallyl complexes h^5-$C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$ and h^5-$C_5H_5Mo(CO)_3CH_2C(CH_3){=}CH_2$ were synthesized by treating $[h^5$-$C_5H_5Fe(CO)_2]^-$[12] and $[h^5$-$C_5H_5Mo(CO)_3]^-$[13], respectively, in THF with a slight excess of $ClCH_2C(CH_3){=}CH_2$, also in THF, and stirring the resulting mixture for 1–3 h at 0–25°. Removal of the solvent, extraction of the residue with pentane, filtration of the extract, chromatography of the resultant solution on alumina (10% H_2O), and evaporation of the solvent afforded the h^1-allyl complexes which were characterized by infrared and ^1H nmr spectroscopy. h^5-$C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$ was obtained in 40% yield as an amber oil: ir(cm^{-1}, CH_2Cl_2 soln) 2018vs, 1962vs (ν_{CO}), nmr (τ, $CDCl_3$ soln) 7.86 ~s(CH_3), 7.50s,br (CH_2), 5.34s (=CH), 4.92s (C_5H_5, =CH). h^5-$C_5H_5Mo(CO)_3CH_2C(CH_3){=}CH_2$ was isolated in 35% yield as an orange-yellow oil: ir (cm^{-1}, pentane soln) 2023vs, 1940vs,br (ν_{CO}), nmr (τ, $CDCl_3$ soln) 8.21 ~s(CH_3), 7.57s (CH_2), 5.42br (=CH_2), 4.77s (C_5H_5).

Reactions of 2-Alkenyl and 2-Alkynyl Complexes with TCNE

The following general procedure proved to be most satisfactory with respect to simplicity and high yields of the products.

A solution of the alkenyl or alkynyl complex in CH_3CN, THF, or benzene (*ca.* 2×10^{-2} *M*) was treated with an equimolar amount of TCNE at 25°. The mixture was stirred magnetically as progress of the reaction was monitored by thin layer chromatography on alumina. Generally, the reaction reached completion in 1–2 min, although h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2(h^5$-$C_5H_5)$ and h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2C{\equiv}CCH_3$ appeared to react more slowly. The solvent was next evaporated and the residue washed thoroughly with pentane. In this manner, almost quantitative yields of the product were usually obtained. Alternatively, pentane was employed as a solvent for the reaction, in which case the product precipitated out within 5–10 min. Purification by chromatography on alumina (10% H_2O) eluting with CH_2Cl_2 or $CHCl_3$ was found to reduce the yields by 25–30% owing to considerable decomposition. However, crystallization from CH_2Cl_2–pentane gave very pure products in good yields.

Analytical data and physical properties of TCNE-containing compounds are presented in Table I. In some preparations, the above-described optimum conditions were not employed; this accounts for the lower yields of the product.

The reaction between h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2CH{=}C(CH_3)_2$ and TCNE differed from those described above. h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2CH{=}C(CH_3)_2$ (2.0 g, 3.4 mmol) in 80 ml of CH_2Cl_2 was treated with TCNE (1.5 g, 12 mmol) and the resulting solution stirred magnetically at 25°. The reaction was monitored by infrared spectroscopy and appeared to reach completion in *ca.* 50 hr. The mixture was then filtered to remove a black decomposition material and excess TCNE. The filtrate was concentrated to 10 ml in a stream of N_2 and chromatographed on alumina (6% H_2O). The two yellow bands that developed were elut-

TABLE I. Analytical data and physical properties of TCNE-containing complexes: $[M]C(R'')C(R)(R')C(CN)_2C(CN)_2CH_2$ (I), $[M]C{=}C(R)C(CN)_2C(CN)_2CH_2$ (II), and $[M]N{=}C{=}C(CN)C(CN)_2CH_2C(R''){=}CRR'$ (III).

Compound [M]	R	R′	R″	Yield %	Color	Dec., °C	Analysis, % C Calcd	C Found	H Calcd	H Found	N Calcd	N Found
(I)												
h^5-$C_5H_5Fe(CO)_2$	H	H	CH_3	90–95	amber	140	56.67	56.33	3.33	3.62	15.56	16.17
h^5-$C_5H_5Fe(CO)_2$	CH_3	CH_3	H	90–95	bright yellow	150	57.75	56.75	3.74	4.05	14.97	14.43
h^5-$C_5H_5Mo(CO)_3$	H	H	CH_3	45–50	lemon yellow	142	50.46	49.75	2.80	3.00	13.08	13.67
h^5-$C_5H_5Mo(CO)_3$	CH_3	CH_3	H	85–90	bright yellow	140	51.58	51.40	3.16	3.66	12.67	12.74
(II)												
h^5-$C_5H_5Fe(CO)_2$	CH_3	–	–	70–75	amber	175	56.98	57.08	2.76	2.89	15.64	15.39
h^5-$C_5H_5Fe(CO)_2$	$CH_2Fe(CO)_2(h^5$-$C_5H_5)$	–	–	45–50[a]	yellow	194–196	53.93	53.38	2.62	2.66	10.84	9.89
h^5-$C_5H_5Mo(CO)_3$	C_6H_5	–	–	70	yellow	140	56.56	56.12	2.46	2.40		
h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$	CH_3	–	–	65–70[a]	orange–yellow	[b]			[c]			
(III)												
h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$	CH_3	CH_3	H	15	yellow	oil at 25°	59.67	59.09	4.00	4.30	7.74	7.30

[a] Some loss sustained during chromatography. [b] Not determined. [c] Characterized by infrared and nmr spectroscopy.

ed off with CH_2Cl_2 and $CHCl_3$, respectively. Removal of the solvent from the first band afforded 0.4 g of a yellow oil which was characterized as h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]N=C=C(CN)C(CN)_2CH_2CH=C(CH_3)_2$ (see Table I for analysis). Concentration of the solution from the second band to 5 ml and addition of 20 ml of pentane with stirring yielded 0.3 g of a light yellow powder, mp 143°, which was shown to be *cis*-h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CN$. *Anal.* Calcd for $C_{26}H_{20}MoO_5NP$: C, 56.42; H, 3.62. Found: C, 56.60; H, 3.61. Ir (cm^{-1}, CH_2Cl_2 soln) 2123w–m (ν_{CN}), 1996vs, 1923s (ν_{CO}), nmr (τ, $CDCl_3$ soln) 4.90s (C_5H_5), ~2.6c (C_6H_5).

Attempted Reaction of h^5-$C_5H_5Fe(CO)_2CH_2CH_2C{\equiv}CCH_3$ with TCNE

A solution of h^5-$C_5H_5Fe(CO)_2CH_2CH_2C{\equiv}CCH_3$ (0.5 g, 2.0 mmol) and TCNE (0.75 g, 6.0 mmol) in 30 ml of CH_2Cl_2 or THF was stirred at 25° for 3 days. Usual work-up, including chromatography on alumina (6% H_2O), gave 50% unreacted alkynyl. Some brown insoluble decomposition material remained at the top of the alumina column.

Reaction of h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(CN)_2C(CN)_2CH_2$ with HCl

HCl was passed slowly through a solution of h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(CN)_2C(CN)_2CH_2$ (0.2 g) in THF (30 ml). Within about 30 min, the solution turned deep red. After 2 hr, solvent was removed and the resultant red residue dissolved in CH_2Cl_2 and chromatographed on alumina. The yield of h^5-$C_5H_5Fe(CO)_2Cl$[14], characterized by infrared spectroscopy, was 0.05 g. No other products could be identified.

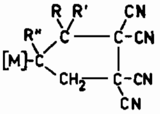
Attempted Reaction of h^5-$C_5H_5Fe(CO)_2C(CH_3)CH_2C(CN)_2C(CN)_2CH_2$, h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(CN)_2C(CN)_2CH_2$ and h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(CN)_2C(CN)_2CH_2$ with SO_2

Sulfur dioxide was condensed onto each of the title compounds and the resulting solution maintained at reflux for 12–16 h. Evaporation of the solvent yielded only the starting iron-carbon complex.

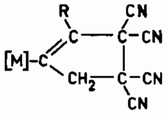
Results and Discussion

Characterization and Properties of New Complexes

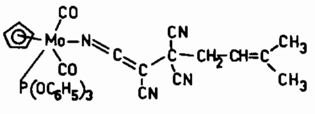
Metal–2-alkenyl complexes of h^5-$C_5H_5Fe(CO)_2$ and h^5-$C_5H_5Mo(CO)_3$ react rapidly with TCNE to afford cycloaddition products of type I. In contrast, the reaction between h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2CH=C(CH_3)_2$ and TCNE proceeds very slowly and results in the formation of III and *cis*-h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CN$. All of the metal–2-alkynyl complexes examined readily yield II when treated with TCNE.



I



II



III

The new complexes derived by (3 + 2) cycloaddition with 1,2 metal migration are yellow to amber crystalline solids. They are stable to air at room temperature and decompose without melting at 140–200° (see Table I). Their stability in solution is lower than in the solid; however, characterization studies in solution at ambient conditions could be accomplished if performed within about 30 min of dissolution. All of the iron complexes are soluble in acetone, moderately soluble in $CHCl_3$ or CH_2Cl_2, slightly soluble in benzene, and insoluble in saturated hydrocarbons. The molybdenum complexes of type I and II show moderate solubility in acetone and slight solubility in $CHCl_3$ or CH_2Cl_2.

The insertion product III, a yellow oil, decomposes to an insoluble green solid when exposed to air for a few hours at room temperature. It is soluble in polar organic solvents but insoluble in hydrocarbons.

The infrared and ^1H nmr spectra of the TCNE-containing complexes prepared in this investigation are listed in Table II. For compounds of type I, the values of ν_{CO} are similar to those reported for various alkyls h^5-$C_5H_5Fe(CO)_2R$ and h^5-$C_5H_5Mo(CO)_3R$[2,15,16], thus suggesting the presence of an M–C (alkyl) linkage therein. They unambiguously rule out the possibility of insertion of TCNE into the M–C (allyl) bond with the formation of metal keteniminato (1,4 insertion) or metal–cyanoalkenyl (1,2 insertion) derivatives.[6] Such insertion products show ν_{CO} at considerably higher frequencies (45–84 cm^{-1} for h^5-$C_5H_5Fe(CO)_2$[17]) than the parent metal–carbon complexes.

The ^1H nmr spectra of the compounds derived by the reaction of TCNE with h^5-$C_5H_5M(CO)_xCH_2C(CH_3)=CH_2$ (M = Fe, x = 2; M = Mo, x = 3) are particularly informative. That of the iron complex is given in Figure 1. Both show the CH_2 signal as an AB pattern of relative intensity = 4 compared with the absorption of C_5H_5 being 5. The values of J_{AB} (14.5 and 15 Hz) are those expected for magnetically nonequivalent geminal protons.[3,18] These data, coupled with the average position of the CH_2 proton chemical shift of τ 6.80 and 6.56[19], militate against a structure derived by 1,2 addition of TCNE to the allylic double bond (IV). However, they are entirely consistent with the formulation Ia (I: R = R' = H, R" = CH_3). Recently, the structure of

TABLE II. Infrared and proton magnetic resonance spectra of $[M]C(R'')C(R)(R')C(CN)_2C(CN)_2CH_2$ (I), $[M]C{=}C(R)C(CN)_2C(CN)_2CH_2$ (II), and $[M]N{=}C{=}C(CN)C(CN)_2CH_2C(R''){=}CRR'$ (III).

Compound [M]	R	R'	R''	Ir, cm^{-1} CO stretch[a]	Ir, cm^{-1} CN stretch[b]	CH wag of C_5H_5[b]	Nmr, τ[c] C_5H_5	Nmr, τ[c] Other protons
(I)								
h^5-$C_5H_5Fe(CO)_2$	H	H	CH_3	2018vs 1968vs	2250w	852s	4.86s	8.32s (CH_3), 6.98, 6.62q_{AB}(CH_2, J=14.5Hz)
h^5-$C_5H_5Fe(CO)_2$	CH_3	CH_3	H	2023vs 1968vs	2245w	854s	5.18s	9.17s, 8.82s (CH_3), 7.66c (CH_2CH)
h^5-$C_5H_5Mo(CO)_3$	H	H	CH_3	2023s, 1962s 1918s[b]	2245w	835s	4.14s	8.16s (CH_3), 6.80, 6.32q_{AB}(CH_2, J=15Hz)
h^5-$C_5H_5Mo(CO)_3$	CH_3	CH_3	H	2034vs 1946vs,br	2245w	835s	4.55s	8.64s, 8.50s (CH_3), 7.05c (CH_2CH)
(II)								
h^5-$C_5H_5Fe(CO)_2$	CH_3	–	–	2034vs 1990vs	2234w	852s	5.26s	8.30t (CH_3, J=2.0Hz), 6.77q (CH_2, J=2.0Hz)
h^5-$C_5H_5Fe(CO)_2$	$CH_2Fe(CO)_2$ (h^5-C_5H_5)	–	–	2034vs 2008s 1979vs 1950s	2245w	852s	4.88s 4.72s	7.40t (CH_2Fe, J=1.2Hz), 6.50t (CH_2, J=1.2Hz)
h^5-$C_5H_5Mo(CO)_3$	C_6H_5	–	–	2040s 1970s 1930s[b]	2256w	835s	4.69s[d,e]	6.35s (CH_2), 2.55c (C_6H_5)[d,e]
h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$	CH_3	–	–	1980s 1900vs	2256w	830m	5.18d (J=1.0Hz)[d]	8.02t (CH_3, J=1.5Hz), 6.72q (CH_2, J=1.5Hz), 2.72c (C_6H_5)[d]
(III)								
h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$	CH_3	CH_3	H	2012s 1940vs	2201m 2140s (antisym. N=C=C stretch) 1298m (symm. N=C=C stretch)	825s	4.82s[d]	8.27s, 8.18s (CH_3), 7.47d (CH_2, J=9Hz), 4.74t (CH, J=9Hz), 2.68c (C_6H_5)[d]

[a] In CH_2Cl_2 solution except as noted. [b] In Nujol mull; w, weak; m, medium; s, strong; vs, very strong; br, broad. [c] In $CD_3C(O)CD_3$ solution except as noted. s, singlet; d, doublet; t, triplet; q, quartet; q_{AB}, AB quartet; c, complex multiplet or other pattern. [d] In $CDCl_3$ solution. [e] Recorded on a JEOL HA–100 spectrometer.

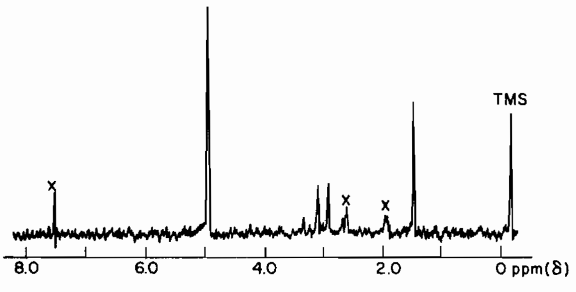
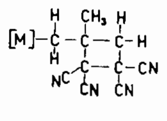
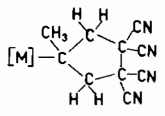


Figure 1. The ^1H nmr spectrum of h^5-$C_5H_5Fe(CO)_2C(CH_3)CH_2C(CN)_2C(CN)_2CH_2$ in $CD_3C(O)CD_3$ (peaks marked x are due to extraneous materials).



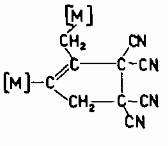
IV

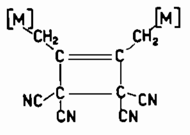


Ia

h^5-$C_5H_5Fe(CO)_2C(CH_3)CH_2C(CN)_2C(CN)_2CH_2$ was confirmed by X-ray crystallography.[20] The spectra of the remaining complexes ot type I indicate the same kind of a ring structure.

Considering next the complexes of type II, it is to be noted that the values of ν_{CO} are very similar to those for the compounds derived by the reaction of transition metal–2-alkynyls with SO_2,[3] SO_3,[21] and $ClSO_2NCO$.[22] Accordingly, they support the presence of an M–C (vinyl) bond in these TCNE-containing derivatives. The ^1H nmr spectrum of the product from the bimetallic h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2(h^5$-$C_5H_5)$ is particularly illuminating. It exhibits two cyclopentadienyl and two CH_2 proton signals, the latter appearing as triplets with J = 1.2 Hz. These data support structure IIa (II: R = CH_2[M]) and exclude the product of 1,2 addition of TCNE to the propargylic triple bond (V). The other complexes II


IIa


V

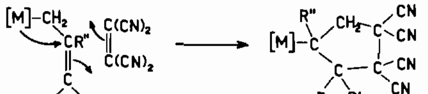
are assigned analogous structures from their infrared and nmr spectra. Interestingly, h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2C{\equiv}CCH_3$ which is a 2:1 *trans–cis* mixture[3] yields *trans*-h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]C{=}C(CH_3)C(CN)_2C(CN)_2CH_2$. This geometry of the product has been inferred from appearance of a C_5H_5 doublet (J = 1.0 Hz) in the ^1H nmr spectrum and from the relative intensities of the two infrared ν_{CO} bands.[23]

The CO stretching frequencies of complex III are appreciably higher than those of the last-discussed molybdenum dicarbonyl product (see Table II). This, coupled with the appearance of a strong absorption at 2140 cm^{-1} and a medium-intensity one at 1298 cm^{-1}, indicates presence of a metal-keteniminato linkage, $M{-}N{=}C{=}C\langle$, therein. For comparison, keteniminato complexes of formula h^5-$C_5H_5Fe(CO)_2N{=}C{=}C(CN)C(CN)_2R$ show the two N=C=C stretching modes at 2145–2162 and 1295–1306 cm^{-1} [6,17], whereas $Ir(CO)(TCNE)[P(C_6H_5)_3]_2N{=}C{=}C(CN)C(CN)_2H$, whose structure was elucidated crystallographically, absorbs at 2168 and 1355 cm^{-1}.[5a] It is noteworthy that the above iron keteniminato derivatives display the ν_{CO} bands at frequencies (2073–2079 and 2029–2034 cm^{-1} [6,17]) which are considerably higher than those of analogous compounds with Fe–C (vinyl) bonds (usually 2020–2030 and 1970–1990 cm^{-1} [3,21,22,24]), as noted for complex III. The relative intensities of the two ν_{CO} absorptions of III suggest a trans arrangement of the four ligands other than h^5-C_5H_5, even though the C_5H_5 proton nmr signal is observed as a singlet. The allyl precursor of III was a mixture of the *trans* (major) and *cis* (minor) isomers.[10] Finally, the appearance of two CH_3 resonances at τ 8.27 and 8.18 and of the CH_2 resonance as a doublet at τ 7.47 indicates that the allyl group remained unrearranged in the course of the insertion.

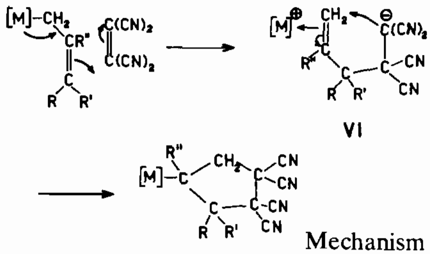
Some preliminary experiments were conducted with a view to elucidating chemical reactivity of the M–C bonds in I and II. Thus, treatment of h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(CN)_2C(CN)_2CH_2$ with HCl in THF results in cleavage of the Fe–C linkage to give h^5-$C_5H_5Fe(CO)_2Cl$, but the fate of the TCNE-containing ring could not be determined. In contrast, this same cycloaddition complex, as well as h^5-$C_5H_5Fe(CO)_2C(CH_3)CH_2C(CN)_2C(CN)_2CH_2$ and h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(CN)_2C(CN)_2CH_2$, can be recovered unchanged after a prolonged treatment with SO_2 at reflux.

Mechanism of Formation of New Complexes

The two types of mechanism which merit serious consideration are depicted below for the reactions of TCNE with the 2-alkenyl derivatives. Strictly analogous mechanisms may be drawn for the reactions with the 2-alkynyl compounds; both of them are consistent with the observed lack of reactivity of TCNE toward h^5-$C_5H_5Fe(CO)_2CH_2CH_2C{\equiv}CCH_3$. Pathway A occurs in a concerted fashion whereas B involves the intermediacy of a dipolar metal-olefin complex (VI) (or a metal-allene complex, for the 2-alkynyls).



Mechanism A
I



VI
Mechanism B
I

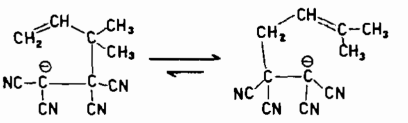
The ionic course of these reactions (mechanism B) receives strong support from the following observations and comparisons.

(1) When the reaction between h^5-$C_5H_5Mo(CO)_3CH_2CH{=}C(CH_3)_2$ (1.6 × 10^{-2} *M*) and equimolar TCNE is carried out at 25° in CH_2Cl_2, complete disappearance of the allyl complex may be noted spectroscopically after *ca.* 30 sec. However, in pentane this reaction requires almost 30 min for completion. Similarly, h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ and TCNE (each *ca.* 2 × 10^{-2} *M*) react in less than 60 sec in CH_3CN, about 60 sec in THF or benzene, and approximately 30 min in pentane. The above rate dependence of these reactions on the polarity of the solvent is consistent with mechanism B but not with mechanism A.

(2) Recently, a dipolar metal–olefin complex analogous to VI was detected and characterized in the reaction of h^5-$C_5H_5Fe(CO)_2CH_2CH{=}CH_2$ with neat SO_2[25], which, like TCNE, is a good electrophile.

(3) The reactions of olefins with TCNE proceed by an ionic mechanism.[26]

It is noteworthy that reaction of TCNE with h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2CH{=}C(CH_3)_2$ is exceedingly slow and results in the formation of the insertion product III rather than a corresponding cycloaddition derivative. The slow course of this reaction may be a consequence of the bulky nature of $P(OC_6H_5)_3$ which would hinder electrophilic attack of TCNE on the allylic double bond. The incipient dipolar metal-olefin intermediate of type VI is expected to be unstable and, if formed, may dissociate rapidly generating h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]^+$ and the anion VII. Rearrangement of the latter to VIII through a facile "internal return"[27], depicted below, and combination of VIII with h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]^+$ would then account for the formation of III.



VII VIII

Although the foregoing mechanism seems attractive, an alternative pathway, similar to that for the insertion of TCNE into M–R (alkyl) bonds[17], is likewise reasonable and cannot be dismissed. The cyano complex *cis*-h^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CN$, also isolated in this reaction, probably arises from decomposition of III. Such decomposition has been noted for some organometallic keteniminato compounds.[17]

Finally, it is relevant to draw attention to a few related reactions of TCNE with organometallic compounds. Thus, TCNE undergoes 1,3 additions to coordinated cycloheptatriene in h^4-$C_7H_8Fe(CO)_3$ and the azepine in h^4-*N*-methoxycarbonylazepineruthenium tricarbonyl, but mainly a 1,6 addition to the azepine ring in h^4-*N*-methoxycarbonylazepineiron tricarbonyl.[28] h^4-Cyclooctatetraeneiron tricarbonyl also adds TCNE in a 1,3 manner; this reaction is thought to proceed through a dipolar intermediate.[29] With h^5-$C_5H_5Fe(CO)_2CH_2CHCH_2CH_2$, TCNE affords, presumably *via* a zwitterionic metal–olefin complex similar to VI, the cyclic derivative h^5-$C_5H_5Fe(CO)_2CHCH_2C(CN)_2C(CN)_2CH_2CH_2$.[30] On the other hand, the reaction between h^5-$C_5H_5Fe(CO)_2CHCH_2CH_2$ and TCNE to give h^5-$C_5H_5Fe(CO)_2CHC(CN)_2C(CN)_2CH_2CH_2$ probably involves a dipolar metal–carbene intermediate.[31]

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