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Electrophilic Behavior of Tetracyanoethylene toward Transition Metal–Carbon σ Bonds. Reactions with the Alkyl Complexes

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Reactions of transition metal–alkyl complexes with tetracyanoethylene (TCNE) vary markedly depending on the type of metal complex, its alkyl group R, and the attendant ligands. The complexes η^5-$C_5H_5Fe(CO)_2R$ (R = CH_3, C_2H_5, *n*-C_3H_7, $CH_2C_6H_5$, and $CH(CH_3)C_6H_5$) react slowly with TCNE in CH_2Cl_2 at 25° to afford the cyanoalkyls η^5-$C_5H_5Fe(CO)_2C(CN)_2C(CN)_2R$ and the isomeric keteniminates, η^5-$C_5H_5Fe(CO)_2N{=}C{=}C(CN)C(CN)_2R$, in 5–45% yield. These complexes were characterized by ^1H nmr and infrared spectroscopy; they do not interconvert in solution. A qualitative order of the reactivity, R = $CH_2C_6H_5 > CH(CH_3)C_6H_5 > CH_3$, C_2H_5, *n*-$C_3H_7 \gg C_6H_5$, may be indicative of a free-radical pathway for these reactions. The molybdenum tricarbonyls η^5-$C_5H_5Mo(CO)_3R$ (R = CH_3 and $CH_2C_6H_5$) do not form any detectable insertion products with TCNE, but the dicarbonyls η^5-$C_5H_5Mo(CO)_2(L)CH_3$ (L = $P(C_6H_5)_3$ and $P(OC_6H_5)_3$) furnish η^5-$C_5H_5Mo(CO)_2(L)C(CN)_2C(CN)_2CH_3$ and η^5-$C_5H_5Mo(CO)_2(L)N{=}C{=}C(CN)C(CN)_2CH_3$ in 10–40% yield. The two molybdenum–cyanoalkyl complexes isomerize to the corresponding keteniminato complexes in solution. The phosphine- and phosphite-substituted iron alkyls of the formula η^5-$C_5H_5Fe(CO)(L)R$ insert TCNE to give η^5-$C_5H_5Fe(CO)(L)N{=}C{=}C(CN)C(CN)_2R$ when R = $CH_2C_6H_5$; however, when R = CH_3, C_2H_5, or *n*-C_3H_7, they afford η^5-$C_5H_5Fe(L)(TCNE)COR$ instead in 50–78% yield. These acyl–η^2-TCNE complexes undergo rearrangement reactions upon storage at room temperature or upon heating to yield η^5-$C_5H_5Fe(CO)(L)R$ and/or η^5-$C_5H_5Fe(CO)(L)$-$N{=}C{=}C(CN)C(CN)_2R$. Evidence is presented that TCNE behaves as an electrophile toward metal–carbon σ bonds, and possible mechanisms of the observed insertion reactions are discussed.

Introduction

One of the most important reactions of transition metal–alkyl complexes is the so-called insertion of unsaturated, generally electrophilic molecules into metal–carbon σ bonds.[1-4] In the context of our investigation of such processes[4,5] we have examined the propensity toward the insertion of a powerful electrophile, tetracyanoethylene (TCNE).[6] Investigated reactions have yielded a number of new cyanocarbon complexes which are reported herein.

Cyanocarbon derivatives of transition metals have received considerable recent attention. Complexes have been prepared and studied with such diverse CN-containing ligands as TCNE and dicyanoacetylene η^2-bonded to the metal,[6-8] keteniminates ($-N{=}C{=}C(CN)X$; X = CN or $C(CN)_2R$),[9-11] polycyanovinyls ($-C(X){=}C(CN)_2$; X = Cl, CN, or H),[12] terminal or bridging dicyanovinylidene ($C{=}C(CN)_2$),[12,13] bridging dicyanomethylene ($C(CN)_2$),[12] polycyanomethyls ($-C(CN)_2X$; X = CN or H),[12,14] polycyanocyclopentadienyls,[15] and a host of others.[6,16-19]

In this paper we report the results of our study on reactions of TCNE with iron–, molybdenum–, and manganese–alkyl complexes. Some aspects of this work were communicated earlier.[5,20] Insertion of TCNE into a transition metal–hydrogen bond has also been the subject of recent reports.[10,21]

Experimental Section

General Procedures. A nitrogen atmosphere was employed routinely for all of the reactions reported herein. Chromatographic separations and purifications were carried out using either Ventron neutral alumina deactivated with H_2O (6 or 10% by weight) or Florisil (60–100 mesh) from Fisher. Ultraviolet irradiations were performed with a Hanovia 450-W high-pressure quartz mercury-vapor lamp, Model 679A-36. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Molecular weights were determined in chloroform solution (*ca.* 1×10^{-2} *M*) using a Mechrolab Model 301-A osmometer. Elemental analyses were performed by Dr. F. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany, and by Galbraith Laboratories, Inc., Knoxville, Tenn.

Materials. TCNE, procured from Columbia Organic Chemicals, was sublimed (60–80° at *ca.* 1×10^{-6} Torr) prior to use. Diphenylmethylenemalononitrile, $(C_6H_5)_2C{=}C(CN)_2$, and fumaronitrile, $NCCH{=}CHCN$, were purchased from Aldrich and K & K Laboratories, respectively, and used as received. Triphenylphosphine, from Matheson Coleman and Bell, was recrystallized from ethanol. Triphenyl phosphite and tri-*n*-butylphosphine were used as received from Aldrich. $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ was purchased from Strem Chemicals and used without further purification. Tetrahydrofuran (THF) was distilled from CaH_2 under a nitrogen atmosphere immediately before use. Dichloromethane was dried over anhydrous $CaCl_2$ and distilled. Benzene was distilled from CaH_2. All other chemicals and solvents were reagent grade or equivalent.

The following organoiron, -molybdenum, and -manganese compounds were prepared according to published procedures: η^5-$C_5H_5Fe(CO)_2R$ where R = CH_3,[22] C_2H_5,[22] $CH_2C_6H_5$,[23] C_6H_5,[24] $CH(CH_3)C_6H_5$,[25] and $(+)_{546}$-$CH(CH_3)C_6H_5$;[25] η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]R$ where R = CH_3,[26] C_2H_5,[27] and $CH_2C_6H_5$;[28] η^5-$C_5H_5Fe(CO)[P(OC_6H_5)_3]CH_3$;[27] η^5-$C_5H_5Mo(CO)_3R$ where R = CH_3[22] and $CH_2C_6H_5$;[29] η^5-$C_5H_5Mo(CO)_2(L)CH_3$ where L = *trans*-$P(C_6H_5)_3$[30] and *cis,trans*-$P(OC_6H_5)_3$;[31] $Mn(CO)_5CH_3$;[32] and *cis*-$Mn(CO)_4[P(C_6H_5)_3]CH_3$.[33] The alkyl η^5-$C_5H_5Fe(CO)_2$(*n*-C_3H_7) was obtained in 60% yield as a yellow oil by the general method of Piper and Wilkinson:[22] $\nu_{C\equiv O}$ 2012, 1957 cm^{-1} (pentane); ^1H nmr τ 8.7–8.3 m ($CH_2CH_2CH_3$), 5.41 s (C_5H_5) ($CDCl_3$). The remaining complexes of general formula η^5-$C_5H_5Fe(CO)(L)R$ used in this work were synthesized from η^5-$C_5H_5Fe(CO)_2R$ and L by a suitable adaptation of the method of Treichel, *et al.*[26] η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]$(*n*-$C_3H_7$) was isolated in 40% yield as a red solid after 3 hr of irradiation at 27°: mp 120–121°; $\nu_{C\equiv O}$ 1901 cm^{-1} (CH_2Cl_2); ^1H nmr τ 9.06 t (CH_3, J = 6 Hz), 8.43 m, c (CH_2CH_2), 5.71 d (C_5H_5, J_{P-H} = 1 Hz), 2.54 m, c (C_6H_5) (CS_2). *Anal.* Calcd for $C_{27}H_{27}OPFe$: C, 71.38; H, 5.99. Found: C, 71.39; H, 6.05. η^5-$C_5H_5Fe(CO)[P(n\text{-}C_4H_9)_3]CH_2C_6H_5$ was obtained in 60% yield as a red oil after 20 min of irradiation at 0–5°: $\nu_{C\equiv O}$ 1902 cm^{-1} (CH_2Cl_2).

Reactions of TCNE with Metal–Carbon σ-Bonded Complexes. A representative reaction of TCNE with complexes of general formula η^5-$C_5H_5Fe(CO)_2R$ is described in detail.

A CH_2Cl_2 solution (50 ml) of η^5-$C_5H_5Fe(CO)_2CH_3$ (1.9 g, 9.9 mmol) was treated with TCNE (1.45 g, 11.3 mmol) dissolved in a minimum volume of CH_2Cl_2, and the resulting mixture was stirred at 25°. The color of the solution gradually darkened as the course of the reaction was monitored by infrared spectroscopy in the region of 2500–1500 cm^{-1}. After *ca.* 72 hr the solvent was removed under reduced pressure (25° at 20 Torr). The dark residue was dissolved in 15 ml of $CHCl_3$ and introduced onto a 2.5 × 30 cm column of alumina (6% H_2O). The chromatogram was developed with $CHCl_3$ to give four bands which were eluted as described below, with some black insoluble material remaining at the top of the column.

The leading, yellow band was removed from the column with $CHCl_3$ and concentrated to 10 ml in a stream of nitrogen. Addition of pentane (50–60 ml) with stirring resulted in the precipitation of a yellow solid which was filtered off, washed with pentane, and dried;

yield 0.65 g (20%) of η^5-$C_5H_5Fe(CO)_2C(CN)_2C(CN)_2CH_3$. The compound was recrystallized from 1:1 pentane–$CHCl_3$ at −15° to furnish yellow needles. Removal of the solvent from the initial filtrate afforded 0.40 g (21% recovery) of η^5-$C_5H_5Fe(CO)_2CH_3$.

A narrow orange-red band was eluted next with CH_2Cl_2. Evaporation of the solvent afforded a red oil. Dissolution of this oil in 5 ml of $CHCl_3$ containing a few drops of pentane and cooling in a Dry Ice–isopropyl alcohol bath for 12 hr afforded 0.15 g (5% yield) of shiny red needles of η^5-$C_5H_5Fe(CO)_2N{=}C{=}C(CN)C(CN)_2CH_3$.

Elution of a narrow yellow band with CH_2Cl_2, concentration to 5 ml, and addition of 20 ml of pentane with stirring afforded 0.01 g (<1% yield) of η^5-$C_5H_5Fe(CO)_2CN$, which was characterized by infrared spectroscopy.[34] Finally, a narrow red-purple band was eluted off the column with acetone. Evaporation of the solvent left a purple oil (*ca.* 0.01 g) which was insoluble in $CHCl_3$, CH_2Cl_2, and hydrocarbons. Its infrared spectrum showed a single medium-intensity ν_{CN} band at 2212 cm^{-1} (neat oil) and no $\nu_{C\equiv O}$ absorptions. The quantity of this material was insufficient for a further characterization.

Reactions of TCNE with various η^5-$C_5H_5Fe(CO)_5R$ alkyls and aryls are summarized in Table I, whereas analytical data and physical properties of all new complexes prepared herein are provided in Table II.

The complexes of type I, **1**–**5** (see Table II), are yellow crystalline solids which appear to be very stable to air, especially when refrigerated. They are soluble in polar organic solvents such as $CHCl_3$, CH_2Cl_2, THF, or acetone but insoluble in ether, CCl_4, and saturated hydrocarbons. Their solutions are stable under nitrogen for 1–2 days; after this period 5–10% η^5-$C_5H_5Fe(CO)_2CN$ may be isolated upon workup. The Fe–C bond in **1** and **2** is cleaved by gaseous HBr to give η^5-$C_5H_5Fe(CO)_2Br$ and unidentified organic products.

The red or orange-red complexes of type II, **8**–**12**, are also soluble in polar but insoluble in nonpolar organic solvents. They are stable in CH_2Cl_2 solution under nitrogen for about 12 hr, but after 24–36 hr 5–10% η^5-$C_5H_5Fe(CO)_2CN$ may be isolated upon work-up; in air, decomposition to an insoluble brown material is evident after 8–12 hr. Storage of solutions of **8**, **9**, or **11** in CH_2Cl_2 at 25° for 72–144 hr does not yield any detectable **1**, **2**, or **4**, respectively; likewise, there is no observable isomerization of **1** to **8**, **2** to **9**, or **4** to **11** under comparable conditions in 48–72 hr (*vide infra*).

Reactions of TCNE with each of $Mn(CO)_5CH_3$, $Mn(CO)_4[P(C_6H_5)_3]CH_3$, and molybdenum alkyls of the type η^5-$C_5H_5Mo(CO)_3R$ proceeded sluggishly and did not give any isolable adducts; these experiments are summarized in Table I. By way of contrast, TCNE reacted readily with the alkyls η^5-$C_5H_5Mo(CO)_2(L)CH_3$ (L = $P(C_6H_5)_3$ and $P(OC_6H_5)_3$); details of these reactions are furnished also in Table I. In all of these experiments the formation of a brown or black insoluble solid showing no $\nu_{C\equiv O}$ bands was noted; in some cases, this decomposition was very extensive.

The isolated 1:1 adducts of η^5-$C_5H_5Mo(CO)_2(L)CH_3$ and TCNE are yellow solids except for **14**, which remained a yellow oil after several attempts at crystallization. All of these complexes are soluble in polar organic solvents but only sparingly soluble in saturated hydrocarbons. They appear to be very stable under refrigeration. In CH_2Cl_2 solution at 25°, **6** and **7** undergo isomerization to **13** and **14**, respectively, and after 60–72 hr, the two keteniminato complexes can be isolated in 16–24% yield. The complexes **13** and **14** show no sign of isomerization to **6** and **7**, respectively, under comparable conditions (*vide infra*).

The behavior of TCNE toward several η^5-$C_5H_5Fe(CO)(L)R$ (L = $P(C_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, and $P(OC_6H_5)_3$) complexes differed markedly from that toward the corresponding dicarbonyls, η^5-$C_5H_5Fe(CO)_2R$. A representative reaction is described in detail.

To a benzene solution (50 ml) of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ (1.3 g, 3.0 mmol) at 5–10° was added finely powdered TCNE (0.40 g, 3.1 mmol). Immediately the color of the solution changed from orange to dark green. The reaction mixture was stirred for 15 min, solvent was evaporated in a stream of nitrogen, and the residue was dissolved in 15 ml of $CHCl_3$. Chromatography on alumina (10% H_2O) eluting with $CHCl_3$ gave a broad dark green band which gradually developed an orange-red front. The orange-red effluent was collected and yielded 0.05 g of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ upon removal of the solvent. The next fraction of the collected effluent was comprised of the tail end of the orange-red band and the overlapping front part of the green band; it was discarded. The dark green band was then collected and solvent was removed in a stream of nitrogen to leave an oil. Addition of pentane (50 ml) to this oil with scratching afforded 1.15 g (70% yield) of η^5-$C_5H_5Fe[P(C_6H_5)_3](C_6N_4)COCH_3$ as a green powder.

Finally, a narrow purple band that remained on the column was eluted with CH_2Cl_2. Removal of the solvent gave 0.01 g of a dark purple solid which showed a medium-intensity ν_{CN} band at 2212 cm^{-1} (CH_2Cl_2). No signals were discernible in the ^1H nmr spectrum of this solid in CD_3COCD_3. Further characterization of this material was precluded by the small quantity isolated.

The reactions of TCNE with various η^5-$C_5H_5Fe(CO)(L)R$ alkyls are summarized in Table I. When R = CH_3, C_2H_5, or $n\text{-}C_3H_7$, they are rapid and yield η^5-$C_5H_5Fe(L)(TCNE)COR$ as the main product. However, when R = $CH_2C_6H_5$, these reactions are similar to those of the dicarbonyls η^5-$C_5H_5Fe(CO)_2R$, described above.

The complex **18** (see Table II) is stable to air in the solid and moderately stable in benzene solution but **19**, a reddish brown oil, decomposes in air within 1 hr. The L = $P(C_6H_5)_3$ complexes of type III, **21**–**23**, are dark green solids which are reasonably stable under nitrogen at −15° but decompose above room temperature (*vide infra*). They are readily soluble in $CHCl_3$, CH_2Cl_2, acetone, and benzene but insoluble in CS_2 and saturated hydrocarbons. Their solutions decompose in air within 5–10 min depositing an insoluble brown material. The L = $P(n\text{-}C_4H_9)_3$ and $P(OC_6H_5)_3$ complexes, **24** and **25**, respectively, are green oils which turn brown within 20–30 min upon exposure to air (*vide infra*).

Isomerization of Cyanoalkyl and Keteniminato Complexes. Typically, a solution of the cyanoalkyl, $[M]C(CN)_2C(CN)_2R$, or keteniminato, $[M]N{=}C{=}C(CN)C(CN)_2R$, complex (0.05–0.5 g) in 25–50 ml of CH_2Cl_2, CH_3CN, or C_6H_6 was stirred at 25°, with frequent monitoring of its infrared spectrum in the 2300–1500-cm^{-1} region. After an appropriate period of time, the solution was concentrated in a stream of nitrogen and chromatographed on alumina as described earlier in the Experimental Section. Specific details follow.

For η^5-$C_5H_5Fe(CO)_2C(CN)_2C(CN)_2R$ (R = CH_3, C_2H_5, and $CH_2C_6H_5$) in CH_2Cl_2 or CH_3CN (R = C_2H_5 only), infrared spectra showed no evidence of isomerization; after 72–144 hr small amounts of unreacted cyanoalkyl complex and η^5-$C_5H_5Fe(CO)_2CN$ were isolated.

For η^5-$C_5H_5Fe(CO)_2N{=}C{=}C(CN)C(CN)_2R$ (R = CH_3, C_2H_5, and $CH_2C_6H_5$) in CH_2Cl_2, infrared spectra showed no evidence of isomerization; after 48–72 hr unreacted keteniminato complex (*ca.* 50%) and a trace of η^5-$C_5H_5Fe(CO)_2CN$ were isolated.

For η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]C(CN)_2C(CN)_2CH_3$ in CH_2Cl_2, after 16 hr the infrared $\nu_{C\equiv O}$ and ν_{CN} bands characteristic of the corresponding keteniminato complex became discernible; after 60 hr the keteniminato complex (16%) and a trace of unreacted cyanoalkyl complex were isolated.

For η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]N{=}C{=}C(CN)C(CN)_2CH_3$ in CH_2Cl_2, no isomerization was detected in 68 hr.

For η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]C(CN)_2C(CN)_2CH_3$ in CH_2Cl_2, after 12 hr the infrared $\nu_{C\equiv O}$ and ν_{CN} bands characteristic of the corresponding keteniminato complex became discernible; after 72 hr 24% keteniminato complex and 15% η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CN$ were isolated.

For η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]N{=}C{=}C(CN)C(CN)_2CH_3$ in CH_2Cl_2, infrared spectra showed no evidence of isomerization; extensive decomposition was noted; after 96 hr η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CN$ (15%) was isolated.

For η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]N{=}C{=}C(CN)C(CN)_2CH_2C_6H_5$ in C_6H_6, after 93 hr unreacted keteniminato complex (68%) and trace amounts of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CN$[35] and purple and blue solids (see Table I) were isolated.

Rearrangement of η^5-$C_5H_5Fe(L)(TCNE)COR$ Complexes. (a) L = $P(C_6H_5)_3$, R = CH_3. A benzene solution (25 ml) of 0.2 g of η^5-$C_5H_5Fe[P(C_6H_5)_3](C_6N_4)COCH_3$ was stirred at 25°, with frequent monitoring of its infrared spectrum in the 2300–1500-cm^{-1} region. The dark green solution gradually turned brown. After 36 hr the solution was concentrated to 15 ml and chromatographed on alumina eluting with $CHCl_3$. Usual work-up gave, in the indicated order, 0.03 g of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ and 0.01 g of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CN$. Extensive decomposition was observed.

The same products were isolated when the above reaction was conducted at 65° for 2 hr.

Solid η^5-$C_5H_5Fe[P(C_6H_5)_3](C_6N_4)COCH_3$ (1.0 g, 1.8 mmol) was heated at 65° for 2 hr either under nitrogen or in air. After cooling

Table I. Summary of Reactions of TCNE with Metal–Carbon σ-Bonded Complexes ([M]R or [M](CO)R)

Compd						Isolated materials,[d] % yield or recovery				
[M]	R	TCNE:compd mole ratio	Solvent	Temp, °C	Reacn time	[M]C(CN)$_2$C(CN)$_2$R	[M]N=C=C(CN)C(CN)$_2$R	[M]CN	Other	[M]R
η^5-$C_5H_5Fe(CO)_2$	CH_3	1.1:1	CH_2Cl_2	25	72 hr	20	5	t	Purple oil,[e] t	21
		2:1	THF	25	72 hr			t		60
		2:1	CH_3CN	25	48 hr				Purple oil,[e] t	50
	C_2H_5	1.4:1	CH_2Cl_2	25	48–72 hr	20	25	t		10
	n-C_3H_7	1.5:1	CH_2Cl_2	25	72–96 hr	15	15	~1	*f*	8
	$CH_2C_6H_5$	1:1	CH_2Cl_2	25	9–12 hr	15	45	5		
		1:1	CH_3CN	25	9–12 hr	10	30			
	$CH(CH_3)C_6H_5$[a]	1.1:1	CH_2Cl_2	25	24–30 hr	5	25	1		12
	C_6H_5	5:1	CH_2Cl_2	25	120 hr			t		15
		2:1	THF	25	144 hr			15	Brown oil[g]	t
η^5-$C_5H_5Mo(CO)_3$	CH_3	10:1	THF	25	36 hr			t	Red oil,[h] t; purple oil,[e] t	
		10:1	THF	66	36 hr				*f*	
		10:1	CH_2Cl_2	25	168 hr				*i*	
		1:1	C_6H_6 (*hν*)	30	1 hr				*f*	10
	$CH_2C_6H_5$	10:1	THF	25	48 hr			2	Purple oil,[e] t	t
$Mn(CO)_5$	CH_3	10:1	THF	25	24 hr				Red oil,[j] t	t
		10:1	THF	66	8 hr				*f*	
$Mn(CO)_4[P(C_6H_5)_3]$	CH_3	8:1	THF	25	24 hr				Orange solid,[k] t; yellow oil,[l] t	
		8:1	C_6H_6	25	24 hr				*i*	
η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]$	CH_3	2:1	CH_2Cl_2	5–10	6 hr	40	10		Purple oil[e]	
η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$	CH_3	4:1	CH_2Cl_2	25	7–8 hr	15	20	6	Purple oil,[e] t	
η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]$	$CH_2C_6H_5$	1:1	C_6H_6	5–10	2–3 hr		45	28	Purple solid,[m] t; blue solid,[n] t	
η^5-$C_5H_5Fe(CO)[P(n\text{-}C_4H_9)_3]$	$CH_2C_6H_5$	1.4:1	C_6H_6	25	15 min		50			

Compd						Isolated materials,[d] % yield or recovery		
[M](CO)	R	TCNE:compd mole ratio	Solvent	Temp, °C	Reacn time	[M](TCNE)(COR)	Other	[M](CO)R
η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]$	CH_3	1:1	C_6H_6[c]	5–10	15 min	70	Purple solid,[e] t	4
	C_2H_5	1:1	C_6H_6	5–10	15 min	70	Purple oil,[e] t	4
	n-C_3H_7	1.4:1	C_6H_6	5–10	1–3 min	78	Purple oil,[e] t	3
η^5-$C_5H_5Fe(CO)[P(n\text{-}C_4H_9)_3]$	CH_3	1.4:1	C_6H_6	5–10	15 min	75	Purple oil,[e] t	
η^5-$C_5H_5Fe(CO)[P(OC_6H_5)_3]$	CH_3[b]	1:1	CH_2Cl_2	25	15–20 min	50		

[a] Also conducted using the optically active $(+)_{546}$-alkyl complex, with similar results. [b] Corresponding reactions in THF (3 hr) and benzene (4–5 hr) were accompanied by formation of side products. [c] Similar results were obtained in THF and ether. [d] Products are listed in the order of chromatographic elution; t, trace. [e] ν_{CN} at 2212 cm^{-1}. [f] Extensive decomposition noted. [g] Infrared absorptions at 2201 (w), 2123 (w), 2084 (sh), 2062 (s), 2045 (sh), 2018 (s) cm^{-1} (CH_2Cl_2). [h] Infrared absorptions at 2206 (m), 2062 (s), 1984 (s) cm^{-1}. [i] No discernible reaction. [j] No infrared $\nu_{C\equiv O}$ or ν_{CN} bands. [k] Infrared absorptions at 2212 (m), 2162 (m), 2106 (s), 2023 (s), 1946 (m) cm^{-1} (CH_2Cl_2). [l] Infrared absorptions at 2200 (vw), 2129 (vw), 2095 (s), 2034 (sh), 2012 (s), 1990 (sh), 1968 (sh) cm^{-1} (CH_2Cl_2). [m] ν_{CN} at 2212 cm^{-1} and $\nu_{C\equiv O}$ at 1984 cm^{-1} (CH_2Cl_2). [n] ν_{CN} at 2201 cm^{-1} and $\nu_{C\equiv O}$ at 1984 cm^{-1} (CH_2Cl_2).

Table II. Analytical Data and Physical Properties of New Complexes: $[M]C(CN)_2C(CN)_2R$ (I), $[M]N{=}C{=}C(CN)C(CN)_2R$ (II), $[M](TCNE)(COR)$ (III), and $[M]CN$ (IV)

Compd			Mp or (dec pt), °C	Color	Analysis, %						Mol wt	
					C		H		N			
No.	[M]	R			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
				Type I								
1	η^5-$C_5H_5Fe(CO)_2$	CH_3	103–104	Yellow	52.53	52.81	2.52	2.71	17.50	16.95	320	311
2	η^5-$C_5H_5Fe(CO)_2$	C_2H_5	107	Yellow	53.92	53.67	3.02	3.06	16.77	17.04		
3	η^5-$C_5H_5Fe(CO)_2$	n-C_3H_7	107	Yellow	55.20	55.22	3.47	3.54	16.09	15.82		
4	η^5-$C_5H_5Fe(CO)_2$	$CH_2C_6H_5$	133–134	Yellow	60.63	60.39	3.05	3.11			396	396
5	η^5-$C_5H_5Fe(CO)_2$	$CH(CH_3)C_6H_5$	125[a]	Yellow	61.49	61.26	3.44	3.38				
6	η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]$	CH_3	111–112[a]	Yellow	61.75	61.40	3.72	3.74				
7	η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$	CH_3	117[a]	Yellow	57.32	57.13	3.46	3.42				
				Type II								
8	η^5-$C_5H_5Fe(CO)_2$	CH_3	*b*	Red	52.53	52.29	2.52	2.63				
9	η^5-$C_5H_5Fe(CO)_2$	C_2H_5	Oil[c]	Red	53.92	53.70	3.02	2.86			334	374
10	η^5-$C_5H_5Fe(CO)_2$	n-C_3H_7	Oil[c]	Red	55.20	55.80	3.47	3.45				
11	η^5-$C_5H_5Fe(CO)_2$	$CH_2C_6H_5$	131–132	Orange-red	60.63	59.44	3.05	3.02			396	405
12	η^5-$C_5H_5Fe(CO)_2$	$CH(CH_3)C_6H_5$	Oil[c]	Red	61.49	61.23	3.44	3.39				
13	η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]$	CH_3	120[a]	Yellow	61.75	61.80	3.72	3.78				
14	η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$	CH_3	Oil[c]	Yellow	57.32	57.09	3.46	3.49				
15	η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]$	CH_3	Oil[c]	Reddish brown				*d*				
16	η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]$	C_2H_5	Oil[c]	Reddish brown	67.62	67.68	4.43	4.29				
17	η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]$	n-C_3H_7	Oil[c]	Reddish brown				*d*				
18	η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]$	$CH_2C_6H_5$	138–139	Reddish brown	70.49	70.19	4.32	4.35				
19	η^5-$C_5H_5Fe(CO)[P(n$-$C_4H_9)_3]$	$CH_2C_6H_5$	Oil[c]	Reddish brown	65.27	56.55[e]	6.89	6.28[e]				
20	η^5-$C_5H_5Fe(CO)[P(OC_6H_5)_3]$	CH_3	Oil[c]	Red				*d*				
				Type III								
21	η^5-$C_5H_5Fe[P(C_6H_5)_3]$	CH_3	(70)	Dark green	67.16	65.43	4.18	3.96	10.11	9.14		
22	η^5-$C_5H_5Fe[P(C_6H_5)_3]$	C_2H_5	(87)	Dark green	67.62	67.91	4.43	4.69	9.86	8.99		
23	η^5-$C_5H_5Fe[P(C_6H_5)_3]$	n-C_3H_7	(112)	Dark green	68.05	68.51	4.67	4.43	9.62	9.12		
24	η^5-$C_5H_5Fe[P(n$-$C_4H_9)_3]$	CH_3	Oil[c]	Greenish blue	60.73	58.60[e]	7.14	6.63[e]	11.33	9.25[e]		
25	η^5-$C_5H_5Fe[P(OC_6H_5)_3]$	CH_3	Oil[c]	Green								
				Type IV								
26	η_5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$		143	Yellow	56.43	56.60	3.64	3.61				

[a] With decomposition. [b] Not measured. [c] At 25°. [d] Insufficient amounts available for commercial analyses; characterized spectroscopically (see Table III). [e] Poor analyses because of instability.

to 25° the brown material was treated with CH_2Cl_2 (25 ml), the mixture was filtered, and the filtrate was chromatographed on alumina. Elution with $CHCl_3$ and usual work-up afforded 0.25 g (33% yield) of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$, a trace of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]N{=}C{=}C(CN)C(CN)_2CH_3$, and a minute quantity of a purple compound showing a weak infrared absorption at 2201 cm^{-1} and a medium-intensity one at 1973 cm^{-1} (CH_2Cl_2).

(b) L = $P(C_6H_5)_3$, R = C_2H_5. A benzene solution (25 ml) of η^5-$C_5H_5Fe[P(C_6H_5)_3](C_6N_4)COC_2H_5$ (0.28 g) was stirred at 35–40° for 12 hr. Usual work-up, including chromatography on alumina with $CHCl_3$ eluent, afforded 0.03 g of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]C_2H_5$, 0.01 g of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]N{=}C{=}C(CN)C(CN)_2C_2H_5$, and 0.01 g of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CN$.

Solid η^5-$C_5H_5Fe[P(C_6H_5)_3](C_6N_4)COC_2H_5$ (1.0 g, 1.8 mmol) was heated at 65° for 1 hr and then cooled to 25°. The rust-colored material was dissolved in 15 ml of $CHCl_3$ and the resulting solution was chromatographed on alumina eluting with $CHCl_3$. Addition of pentane to the effluent of the first, reddish brown band furnished 0.30 g (33% yield) of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]N{=}C{=}C(CN)C(CN)_2C_2H_5$; removal of the solvent from the effluent of the second, yellow band afforded 0.01 g of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CN$.

The rearrangement of η^5-$C_5H_5Fe[P(C_6H_5)_3](C_6N_4)COC_2H_5$ to η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]N{=}C{=}C(CN)C(CN)_2C_2H_5$ was also effected, in 1–2 hr at 25°, by the addition of a few drops of CH_2Cl_2 or $CHCl_3$ to the solid acyl complex.

(c) L = $P(C_6H_5)_3$, R = n-C_3H_7. The dark green η^5-$C_5H_5Fe[P(C_6H_5)_3](C_6N_4)(CO$-$n$-$C_3H_7)$ turned reddish brown on storage for 12 hr at 27°. Dissolution of this material (0.5 g) in 10 ml of CH_2Cl_2 and chromatography on alumina resulted in the appearance of two bands. Elution with CH_2Cl_2 and usual work-up first yielded 0.10 g of a reddish brown oil, characterized as η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]N{=}C{=}C(CN)C(CN)_2(n$-$C_3H_7)$, and then 0.01 g of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CN$.

(d) L = $P(OC_6H_5)_3$, R = CH_3. The green acyl η^5-$C_5H_5Fe[P(OC_6H_5)_3](C_6N_4)COCH_3$ turned reddish brown on storage in air for 10 min. After 2.5 hr, the infrared absorptions at 2218 and 1662 cm^{-1} (Nujol), characteristic of the acyl complex, were no longer discernible. The reddish brown oil (0.2 g) was then dissolved in 5 ml of CH_2Cl_2 and chromatographed on alumina. Elution with CH_2Cl_2 and work-up afforded 0.05 g of η^5-$C_5H_5Fe(CO)[P(OC_6H_5)_3]CH_3$ and 0.06 g of η^5-$C_5H_5Fe(CO)[P(OC_6H_5)_3]N{=}C{=}C(CN)C(CN)_2CH_3$ in this same order.

The keteniminato complexes **15–17** and **20** (see Table II), obtained as red or reddish brown oils which could not be induced to crystallize, are unstable to air either in neat form or in solution.

Attempted Reactions of Other Cyanoolefins with Metal–Carbon σ-Bonded Complexes. (a) Fumaronitrile and η^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$. A THF solution (35 ml) of η^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ (0.14 g, 0.52 mmol) and fumaronitrile (0.30 g, 3.8 mmol) was stirred at 25°. No reaction was detected by infrared spectroscopy in 24 hr.

The same reaction was also carried out in CH_2Cl_2 solution at 25 and 40° for 48–72 hr. Only an insoluble decomposition material and the starting benzyl complex were isolated.

When a benzene solution (30 ml) of η^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ (0.30 g, 1.1 mmol) and fumaronitrile (0.30 g, 3.8 mmol) was irradiated for 6 hr at 30°, considerable amounts of an insoluble brown material were formed. No products containing infrared ν_{CN} or $\nu_{C{\equiv}O}$ bands were detected.

(b) $(C_6H_5)_2C{=}C(CN)_2$ and η^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$. No reaction was observed, by infrared spectroscopy, between η^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ (0.30 g, 1.1 mmol) and $(C_6H_5)_2C{=}C(CN)_2$ (1.2 g, 5.2 mmol) in CH_2Cl_2 solution (50 ml) at 25° within 52 hr. Heating at 40° for an additional 12 hr resulted in the formation of an insoluble brown decomposition material.

(c) Fumaronitrile and η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$. A benzene solution (50 ml) of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ (0.20 g, 0.47 mmol) and fumaronitrile (0.60 g, 7.7 mmol) was stirred at 25° for 48 hr. No reaction was detected by infrared spectroscopy. A similar result was obtained in THF solution at 25°; at 66° in THF, considerable decomposition was noted.

(d) $(C_6H_5)_2C{=}C(CN)_2$ and η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$. A benzene solution (30 ml) of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ (0.20 g, 0.47 mmol) and $(C_6H_5)_2C{=}C(CN)_2$ (0.70 g, 3.0 mmol) was stirred at 25° for 72 hr. No reaction was observed by infrared spectroscopy. When the temperature was raised to 50°, some decomposition resulted.

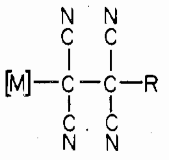
Reaction of TCNE with $[\eta^5$-$C_5H_5Fe(CO)_2]_2$. A CH_2Cl_2 solution (50 ml) of $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ (0.50 g, 1.4 mmol) and TCNE (0.30 g, 2.3 mmol) was stirred at 25°. The reaction was monitored by infrared spectroscopy and appeared to reach virtual completion in 3 hr. Chromatography on a Florisil column (2.5 × 20 cm) eluting with $CHCl_3$ gave two bands. Concentration of the effluent of the first band to 10 ml and addition of 50 ml of pentane afforded 0.40 g (70% yield) of η^5-$C_5H_5Fe(CO)_2CN$. The second band gave a trace of unreacted $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ upon removal of the solvent.

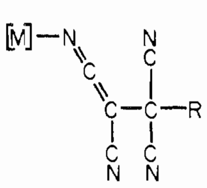
When the same reaction was carried out in benzene solution at 25° for 48 hr, considerable decomposition was noted; a trace of η^5-$C_5H_5Fe(CO)_2CN$ was isolated and 50% starting iron carbonyl was recovered after chromatography on Florisil.

Physical Measurements. Infrared spectra were recorded with a Perkin-Elmer Model 337 spectrophotometer. A 0.1-mm NaCl sample cell was employed in conjunction with a variable-thickness reference cell for solution measurements. Hydrogen-1 nmr spectra were obtained using a Varian Associates A-60 or A-60A spectrometer, with tetramethylsilane as an internal standard. Specific rotations, $[\alpha]_{546}$, were measured with a Perkin-Elmer Model 141 polarimeter using a 1-dm cell. All values of $[\alpha]_{546}$ reported herein are averages of four measurements.

Results and Discussion

Synthesis and Characterization of New Complexes. Reactions of TCNE with transition metal compounds containing M–C σ bonds yielded new tetracyanoethylene-containing complexes of three types: (1) metal cyanoalkyls (I; complexes **1–7** in Tables II and III), (2) metal keteniminates (II; complexes **8–14**, **18**, and **19** in Tables II and III), and (3) metal–tetracyanoethylene acyls (III; complexes **21–25** in Tables II and III).


I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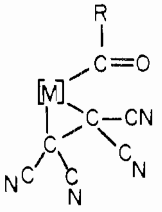

III

Alkyl compounds of formulas η^5-$C_5H_5Fe(CO)_2R$ and η^5-$C_5H_5Mo(CO)_2(L)CH_3$ (L = $P(C_6H_5)_3$ and $P(OC_6H_5)_3$) afford both I and II upon reaction with TCNE, whereas η^5-$C_5H_5Fe(CO)(L)R$ (L = phosphine and phosphite) yield either II or III, depending on the group R. Molybdenum alkyls of the type η^5-$C_5H_5Mo(CO)_3R$ (R = CH_3 and $CH_2C_6H_5$) were found to undergo insertion reaction with TCNE extremely slowly and with considerable decomposition. Only trace quantities of η^5-$C_5H_5Mo(CO)_3CN$[36] and red or purple oils of unknown composition could be isolated from these reactions. Similarly, the manganese complexes $Mn(CO)_5CH_3$ and $Mn(CO)_4[P(C_6H_5)_3]CH_3$ did not yield any characterizable products upon reaction with TCNE.

Products derived from reactions of metal compounds with TCNE will be now considered according to the type of precursor complex.

(a) From η^5-$C_5H_5Fe(CO)_2R$ and TCNE. Two new products were isolated in 5–45% yield from reaction of each η^5-$C_5H_5Fe(CO)_2R$ alkyl with TCNE. Elemental analyses and molecular weights indicate that the products are isomeric 1:1 adducts of η^5-$C_5H_5Fe(CO)_2R$ and TCNE. In addition, these reactions yield up to 15% η^5-$C_5H_5Fe(CO)_2CN$ and trace amounts of a purple oil which shows an infrared ν_{CN} band at 2212 cm^{-1} and no $\nu_{C{\equiv}O}$ absorptions. The small quantities of this latter material precluded its complete characterization. The cyano complex, η^5-$C_5H_5Fe(CO)_2CN$, may have resulted from partial decomposition of the 1:1 adducts or from hydrolysis of TCNE to give HCN and its subsequent cleavage reaction with η^5-$C_5H_5Fe(CO)_2R$, or from both. Some insoluble brown decomposition material was also observed in

Table III. Infrared and Proton Magnetic Resonance Spectra of [M]C(CN)$_2$C(CN)$_2$R (I), [M]N=C=C(CN)C(CN)$_2$R (II), [M](TCNE)(COR) (III), and [M]CN (IV)

Compd			Ir,[a] cm^{-1}				^{1}H nmr,[f] τ	
No.	[M]	R	$\nu_{C\equiv O}$	$\nu_{C=O}$	ν_{CN}	$\nu_{N=C=C}$	C_5H_5	Other protons
					Type I			
1	η^5-$C_5H_5Fe(CO)_2$	CH_3	2062 vs, 2017 vs		2223 w		4.39 s	7.55 s (CH_3)
2	η^5-$C_5H_5Fe(CO)_2$	C_2H_5	2056 vs, 2012 vs		2223 w		4.43 s	8.30 t (CH_3, $J = 7$ Hz), 7.20 q (CH_2, $J = 7$ Hz)
3	η^5-$C_5H_5Fe(CO)_2$	n-C_3H_7	2057 vs, 2012 vs		2212 w		4.67 s	9.0–7.5 m ($CH_2CH_2CH_3$)
4	η^5-$C_5H_5Fe(CO)_2$	$CH_2C_6H_5$	2062 vs, 2017 vs		2217 w		4.44 s	6.15 s (CH_2), 2.30 m, c (C_6H_5)
5	η^5-$C_5H_5Fe(CO)_2$	$CH(CH_3)C_6H_5$	2057 vs, 2018 vs		2212 w		4.77 s	8.17 d (CH_3, $J = 7$ Hz), 6.22 q (CH, $J = 7$ Hz), 2.74–2.57 m (C_6H_5)
6	η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]$	CH_3	1984 s, 1901 vs		2212 w		4.47 d ($J = 1.5$ Hz)	7.63 s (CH_3), 2.70–2.56 m (C_6H_5)
7	η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$	CH_3	2006 s, 1918 vs		2212 w		4.55 d ($J = 2.0$ Hz)	8.23 s (CH_3), 2.70 m, c (C_6H_5)
					Type II			
8	η^5-$C_5H_5Fe(CO)_2$	CH_3	2079 vs, 2034 vs		2212 m	2162 s, 2140 sh (as), 1295 s (s)[b]	4.68 s	8.11 s (CH_3)
9	η^5-$C_5H_5Fe(CO)_2$	C_2H_5	2079 vs, 2034 vs		2206 m	2145 s (as), 1302 m (s)[c]	4.79 s	8.83 t (CH_3, $J = 7$ Hz), 8.00 q (CH_2, $J = 7$ Hz)
10	η^5-$C_5H_5Fe(CO)_2$	n-C_3H_7	2073 vs, 2034 vs		2201 m–w	2145 s (as), 1306 s (s)[b]	4.72 s	9.0–8.0 m ($CH_2CH_2CH_3$)
11	η^5-$C_5H_5Fe(CO)_2$	$CH_2C_6H_5$	2073 vs, 2034 vs		2206 m–w	2151 s (as), 1296 s (s)[d]	4.68 s	6.56 s (CH_2), 2.41 s (C_6H_5)
12	η^5-$C_5H_5Fe(CO)_2$	$CH(CH_3)C_6H_5$	2074 vs, 2029 vs		2212 m–w	2151 s (as), 1305 m (s)[b]	4.92 s	8.35 d (CH_3, $J = 7$ Hz), 6.72 q (CH, $J = 7$ Hz), 2.69–2.56 m (C_6H_5)
13	η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]$	CH_3	2007 s, 1918 vs		2201 m	2168 sh, 2134 s (as), 1257 m (s)[d]	4.78 d ($J = 2.0$ Hz)	8.11 s (CH_3), 2.40 m, c (C_6H_5)
14	η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$	CH_3	2012 vs, 1934 s		2201 m	2156 sh, 2134 s (as), 1306 m (s)[d]	4.79 s	8.18 s (CH_3), 2.72 m, c(C_6H_5)
15	η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]$	CH_3	1984 vs		2212 m	2134 s (as), *e*		*g*
16	η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]$	C_2H_5	1990 vs		2212 m	2145 s (as), 1302 m (s)[d]	4.7 s	*h*
17	η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]$	n-C_3H_7	1979 vs[b]		2201 m[b]	2134 s (as), 1306 m (s)[b]		*g*
18	η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]$	$CH_2C_6H_5$	1979 vs		2201 m	2145 s (as), 1298 s–m (s)[d]	5.13 d ($J_{P-H} \approx 1$ Hz)	6.63 d (CH_2, sepn <1 Hz), 2.34 m, c (PC_6H_5), 2.22 s (CC_6H_5)
19	η^5-$C_5H_5Fe(CO)[P(n\text{-}C_4H_9)_3]$	$CH_2C_6H_5$	1973 vs[b]		2195 m[b]	2145 s (as), 1273 m (s)[b]	5.35 d ($J_{P-H} = 1.5$ Hz)	9.15–8.05 m (C_4H_9), 6.76 d (CH_2, sepn <1 Hz), 2.6 s (C_6H_5)
20	η^5-$C_5H_5Fe(CO)[P(OC_6H_5)_3]$	CH_3	2006 vs[b]		2201 m[b]	2156 s, 2134 sh (as), 1306 m (s)[b]		*g*
					Type III			
21	η^5-$C_5H_5Fe[P(C_6H_5)_3]$	CH_3		1651 s, 1618 sh	2217 sh, 2195 s, sp		4.83 d ($J_{P-H} = 1.0$ Hz)	7.18 s (CH_3), 2.54–2.34 m (C_6H_5)
22	η^5-$C_5H_5Fe[P(C_6H_5)_3]$	C_2H_5		1646 s, br	2229 sh, 2206 s, sp		5.15 s, br	9.4–7.0 m (CH_2CH_3), 2.8–2.6 m (C_6H_5)
23	η^5-$C_5H_5Fe[P(C_6H_5)_3]$	n-C_3H_7		1651 s, br	2223 sh, 2201 s, sp		5.16 s, br	9.4–7.0 m ($CH_2CH_2CH_3$), 2.7–2.6 m (C_6H_5)
24	η^5-$C_5H_5Fe[P(n\text{-}C_4H_9)_3]$	CH_3		1646 s, br, 1612 sh[b]	2223 sh, 2212 s, sp[b]		5.05 s, br	9.35–8.35 m (C_4H_9), 7.15 s (CH_3)
25	η^5-$C_5H_5Fe[P(OC_6H_5)_3]$	CH_3		1662 s, br[b]	2218 sh, 2201 s, sp[b]			*g*
					Type IV			
26	η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$		1996 vs, 1923 s		2123 m–w		4.90 s	2.63 m, c (C_6H_5)

[a] Measured in CH_2Cl_2 solution unless otherwise noted. Abbreviations: w, weak; m–w, medium to weak; m, medium; s–m, strong to medium; s, strong; vs, very strong; br, broad; sh, shoulder; sp, sharp; (as), asymmetric; (s), symmetric. [b] Neat oil. [c] In hexachlorobutadiene. [d] Nujol mull. [e] 1350–1250-cm^{-1} region not measured. [f] Measured in $CDCl_3$ solution. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, complex multiplet or other pattern; m, c, center of a multiplet; br, broad. [g] Not measured. [h] Measurement precluded by instability in solution.

these reactions, and a considerable amount of unreacted η^5-$C_5H_5Fe(CO)_2R$ was recovered. Both factors account for the relatively low yields of the products of types I and II ([M] = η^5-$C_5H_5Fe(CO)_2$). In contrast to the η^5-$C_5H_5Fe(CO)_2R$ alkyls, η^5-$C_5H_5Fe(CO)_2C_6H_5$ does not yield any detectable 1:1 adducts with TCNE.

The infrared and ^{1}H nmr spectra of the complexes of types I and II are presented in Table III. Since the assignment of structure to these products largely rests on spectroscopic evidence, particular attention here focuses on the data which best differentiate among various rational formulations.

Considering first the complexes of type I, it is to be noted that the ^{1}H nmr spectra support insertion of TCNE into the Fe–R bonds. Accordingly, the CH_3 protons in **1** and the CH_2 protons in **4** absorb at much lower fields than in their alkyl precursors.[23,37] The C_5H_5 protons of **1–5** are also significantly deshielded when compared with those of the appropriate iron alkyls.[23,37] Similar shifts to lower fields have been observed upon insertion of SO_2 into η^5-$C_5H_5Fe(CO)_2R$.[23,38] In the infrared spectra of **1–5**, $\nu_{C\equiv O}$ absorptions are appreciably higher (*ca.* 45–65 cm^{-1})[23,37] than those of the precursor iron alkyls but are reasonably close to the values reported for η^5-$C_5H_5Fe(CO)_2C(CN)_2H$.[12] They thus indicate that the negative charge on the metal has been substantially reduced, as one would expect in a structure which resulted from insertion of TCNE into the Fe–R bond.

The position of the weak-intensity ν_{CN} absorption of **1–5** points to a cyanoalkyl, $-C(CN)_2C(CN)_2R$, structure of the newly formed ligand TCNE·R. In organic compounds containing a $C(CN)_2$ or $C(CN)_2C(CN)_2$ moiety, ν_{CN} absorbs, also weakly, around 2260–2250 cm^{-1};[39,40] in organometallic cycloaddition complexes of the type η^5-$C_5H_5M(CO)_x\overline{C}(R'')C(R)(R')C(CN)_2C(CN)_2\overline{C}H_2$ (M = Fe, x = 2; M = Mo, x = 3), a ν_{CN} band occurs at 2250–2245 cm^{-1};[17] and in η^5-$C_5H_5Fe(CO)_2C(CN)_2H$, ν_{CN} absorbs at 2230 cm^{-1}.[12] The above assignment of structure for TCNE·R receives further support from the position of the CH_2 proton resonance of **4** which occurs in the same range as the CH_2 resonances in $(C_6H_5)_2\overline{C}CH_2\mathit{CH_2}C(CN)_2\overline{C}(CN)_2$ (τ 6.88),[41] $C_6H_5\mathit{CH_2}C(CN)_2H$ (τ 6.78),[42] and η^5-$C_5H_5Fe(CO)_2\overline{C}(CH_3)\mathit{CH_2}C(CN)_2C(CN)_2\overline{\mathit{CH_2}}$ (τ 6.98 and 6.62).[17]

The ^{1}H nmr and infrared spectra of the complexes of type II show features which are qualitatively similar to those of the cyanoalkyl complexes, I. Thus, both the C_5H_5 protons and the α-carbon protons of R have undergone a substantial deshielding compared to their positions in the parent iron alkyls. In the infrared spectra, the carbonyl stretching frequencies of **8–12** are substantially higher than those of their alkyl precursors. These combined data again point to insertion of TCNE into the Fe–R bonds.

The infrared spectra of **8–12** in the 2300–2100 cm^{-1} region contain, in addition to a ν_{CN} absorption at 2212–2201 cm^{-1}, a strong band at 2162–2145 cm^{-1}. In the 1350–1250-cm^{-1} region, an absorption is observed at 1306–1295 cm^{-1}. The last two bands are assigned to the asymmetric and symmetric $\nu_{N=C=C}$, respectively, and point to the presence of a keteniminato linkage, $-N{=}C{=}C(CN)C(CN)_2R$, in these complexes. For comparison, $Ir(CO)[P(C_6H_5)_3](C_6N_4)$-$N{=}C{=}C(CN)C(CN)_2H$, whose structure was elucidated crystallographically,[21] absorbs at 2198 and 1253 cm^{-1}.[43] The complex η^5-$C_5H_5Fe(CO)_2N{=}C{=}C(CN)_2$, which is structurally related to **8–12**, exhibits infrared bands at 2036, 1990 ($\nu_{C\equiv O}$), 2185, 1264, and 1248 ($\nu_{N=C=C}$) cm^{-1}.[44]

It is noteworthy that the carbonyl stretching frequencies of the keteniminato complexes **8–12** are 11–23 cm^{-1} higher than those of the isomeric cyanoalkyls, **1–5**. This shift may be a manifestation of a substantial polarity of the Fe—N linkage in $Fe{-}N{=}C{=}C(CN)C(CN)_2R$[11] which is to be contrasted with the less polar Fe—C bond in $Fe{-}C(CN)_2C(CN)_2R$. A softer nature of the cyano group bearing carbon as compared to the keteniminato nitrogen is very likely responsible for the above difference in bond polarity. It is interesting that the $\nu_{C\equiv O}$ absorptions of η^5-$C_5H_5M(CO)_xNCS$ (M = Fe, x = 2; M = Mo, x = 3) also occur at frequencies which are higher than those of the isomeric η^5-$C_5H_5M(CO)_xSCN$,[45] no doubt for similar reasons.

(b) From η^5-$C_5H_5Mo(CO)_2(L)CH_3$ and TCNE. Reactions of η^5-$C_5H_5Mo(CO)_2(L)CH_3$ (L = $P(C_6H_5)_3$ and $P(OC_6H_5)_3$) with TCNE in CH_2Cl_2 at 5–25° afford two isomeric 1:1 adducts of the reactants (**6**, **7**, **13**, and **14**) in 10–40% yield. In addition, minute amounts of an uncharacterized purple oil showing a ν_{CN} absorption at 2216 cm^{-1} were isolated upon chromatography of the reaction mixtures. The reaction of η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_3$ with TCNE also affords the corresponding cyano complex, **26**, in 6% yield. As with the η^5-$C_5H_5Fe(CO)_2R$ alkyls, extensive decomposition to a black, insoluble material accompanies each reaction.

The infrared and ^{1}H nmr spectra of **6**, **7**, **13**, and **14** are provided in Table III. On the basis of the spectroscopic criteria presented in the preceding section for analogous iron complexes, **6** and **7** are assigned a cyanoalkyl structure (I, [M] = η^5-$C_5H_5Mo(CO)_2L$)[45a] whereas **13** and **14** are given a keteniminato structure (II, [M] = η^5-$C_5H_5Mo(CO)_2L$). All four complexes show infrared $\nu_{C\equiv O}$ absorptions at much higher frequencies and their C_5H_5 and CH_3 proton nmr signals at substantially lower fields than do the precursor molybdenum alkyls.[30,31] The complexes **13** and **14** exhibit absorptions at 2168–2134 and 1306–1257 cm^{-1} which are missing in the infrared spectra of **6** and **7**; these bands are assigned to the $\nu_{N=C=C}$(as) and $\nu_{N=C=C}$(s) modes, respectively.[43,44]

The relative intensities of the two $\nu_{C\equiv O}$ absorptions for each of **6**, **7**, and **13** suggest a trans arrangement of the four ligands other than η^5-C_5H_5. This is supported[46] by the appearance of a doublet for the nmr signals of the C_5H_5 protons. In contrast, **14** appears to have a cis disposition of the two CO's and of $P(OC_6H_5)_3$ and $N{=}C{=}C(CN)C(CN)_2CH_3$, as evidenced[46] by the higher intensity of its $\nu_{C\equiv O}$(s) than of its $\nu_{C\equiv O}$(as) infrared band and by a singlet appearance of its C_5H_5 nmr peak. It is of interest that the precursor alkyl complexes were *trans*-η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]CH_3$[30] and *ca.* 1:1 *cis,trans*-η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_3$.[31] The reason for the observed stereoselectivity in the insertion is not entirely clear, but it may be related to a crowding of the cyanoalkyl or keteniminato ligand by $P(C_6H_5)_3$ or $P(OC_6H_5)_3$ in cis positions. Only when the sterically less demanding $N{=}C{=}C(CN)C(CN)_2CH_3$ and $P(OC_6H_5)_3$ are present together does a cis structure result.

(c) From η^5-$C_5H_5Fe(CO)(L)R$ and TCNE. Two different types of behavior were observed when TCNE was allowed to react with η^5-$C_5H_5Fe(CO)(L)R$, generally in benzene at 5–10°. When R = $CH_2C_6H_5$, the reaction requires a longer time for completion than when R = CH_3, C_2H_5, or n-C_3H_7 (see Table I) and affords complexes of type II ([M] = η^5-$C_5H_5Fe(CO)L$), **18** and **19**, in 45–50% yield. In addition, 28% η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CN$ and minute amounts of uncharacterized purple and blue solids were isolated when L = $P(C_6H_5)_3$. No cyanoalkyl complexes I, isomeric with **18** and **19**, were detected in these reactions, and no isomerization was observed upon storage of a benzene solution of **18** for 93 hr at 25°. As before, formation of an insoluble decomposition material accompanied the insertion.

Compounds **18** and **19** show a single $\nu_{C\equiv O}$ band at 1979–1973 cm^{-1} which is raised by 68–71 cm^{-1} from the corresponding frequency of the parent iron alkyl.[28] In addition, the infrared spectra show absorptions at 2145 and 1298–1273 cm^{-1}, characteristic of the keteniminato moiety.[43,44] The ^{1}H nmr spectra exhibit features previously noted for complexes of type II and are in agreement with the assigned structures. It is noteworthy, however, that the benzylic CH_2 proton signals in both **18** and **19** appear as a closely spaced (separation <1 Hz) doublet. This doublet is almost certainly part of an AB quartet and indicates a very small difference in the chemical shift of the two protons which are considerably removed from the chiral iron center.

When R = CH_3, C_2H_5, or *n*-C_3H_7, η^5-$C_5H_5Fe(CO)(L)R$ and TCNE afford complexes of type III ([M] = η^5-C_5H_5FeL), **21**–**25**, in 50–78% yields, along with trace amounts of uncharacterized purple oils or solids.

The infrared and ^1H nmr spectra of III, presented in Table III, support the assigned structures. Thus, no terminal $\nu_{C\equiv O}$ infrared absorptions are present, but a strong band at 1662–1642 cm^{-1} dominates the acyl $\nu_{C=O}$ region. In agreement with the above data, the nmr spectra of **21** and **24** show the acyl CH_3 resonance at τ 7.18 and 7.15, respectively. These are to be compared with the corresponding resonances at τ 7.48 for η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]COCH_3$ and at τ 7.25 for η^5-$C_5H_5Fe(CO)[P(n\text{-}C_4H_9)_3]COCH_3$.[47] The CN stretching frequencies in the infrared spectra of **21**–**25** occur as a strong, sharp absorption at 2212–2195 cm^{-1} and a shoulder at 2229–2217 cm^{-1}. For comparison, ν_{CN} in η^2-TCNE complexes of Pt, Ir, and Rh is observed at 2235–2220 cm^{-1},[1,48-50] and in TCNE itself at 2260 and 2228 cm^{-1}.[50] It is noteworthy that the $\nu_{C=O}$ absorption in **21**–**25** is 46–56 cm^{-1} higher than in the corresponding η^5-$C_5H_5Fe(CO)(L)COR$.[47] This would indicate that a η^2-bonded TCNE is a much more effective π acid than CO, thus reducing the extent of $Fe{=}C(O)R$ π bonding in its complexes.

Chromatography of III on an alumina column causes some (5–10%) decomposition involving ligand rearrangement and loss of TCNE as shown in eq 1. The alkyls η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]R$ (R = CH_3 and C_2H_5) are also formed, in small quantities, along with η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CN$, upon storage of benzene solutions of **21** and **22** at 25–40°. With **22**, the corresponding keteniminato complex, **16**, can be isolated as well, in *ca.* 3% yield. Extensive decomposition to an insoluble brown solid accompanies these reactions.

$$\text{III} \rightarrow \eta^5\text{-}C_5H_5Fe(CO)(L)R + \text{TCNE} \qquad (1)$$

The extent of such decomposition during rearrangement can be reduced by heating **21** or **22** in the solid. Thus, upon treatment at 65° for 2 hr, **21** affords 33% η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ and a trace of the keteniminate **15**. Under comparable conditions in 1 hr, **22** furnishes the keteniminate **16** (33% yield) and some η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CN$. The complex **23** affords the keteniminate **17** in 20% yield, as well as some η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CN$, upon storage for 12 hr at 27°, whereas **25** decomposes to **20** (*ca.* 30% yield) and η^5-$C_5H_5Fe(CO)[P(OC_6H_5)_3]CH_3$ (*ca.* 30% yield) upon storage in air for 10 min.

The infrared spectra of **15**–**17** and **20**, listed in Table III, compare well with those of the keteniminato complexes **18** and **19**, thus implicating a structure of type II ([M] = η^5-$C_5H_5Fe(CO)L$).

(d) From [η^5-$C_5H_5Fe(CO)_2$]$_2$ and TCNE. In an attempt to ascertain whether TCNE will insert into a metal–metal bond, a reaction was conducted between [η^5-$C_5H_5Fe(CO)_2$]$_2$ and TCNE in CH_2Cl_2 at 25°. After 3 hr, only η^5-$C_5H_5Fe(CO)_2CN$ (70% yield) and a trace of the unreacted dimer were isolated. This same reaction was found to proceed extremely slowly in benzene.

Relative Reactivities of Metal–Alkyl Complexes and Mechanistic Considerations. The relative reactivities of metal–alkyl compounds toward TCNE and the nature of products of these reactions both depend markedly on the type of metal complex employed, on its group R, and on the attendant ligands. In the discussion to follow the alkyl complexes of molybdenum and iron will be considered in turn with respect to their reactivity and possible mechanism.

(a) Molybdenum Complexes. The molybdenum alkyls η^5-$C_5H_5Mo(CO)_3R$ (R = CH_3 and $CH_2C_6H_5$) do not yield any isolable products, other than those of decomposition, upon prolonged reaction with TCNE in THF or CH_2Cl_2. In contrast, the alkyls η^5-$C_5H_5Mo(CO)_2(L)CH_3$ (L = $P(C_6H_5)_3$ and $P(OC_6H_5)_3$) insert TCNE within hours at 5–25°, with the L = $P(C_6H_5)_3$ complex reacting faster than its $P(OC_6H_5)_3$ analog. The above order of reactivity is similar to that observed for some of these same complexes toward SO_2[51] and reflects electrophilic properties of TCNE in these reactions.

Since each of η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]CH_3$ and η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_3$ yields two insertion products with TCNE (I and II), it is relevant to inquire whether both products are formed independently. Isomerization studies indicate that II does not rearrange to I over periods of at least 68 hr; in contrast, I does afford spectroscopically discernible amounts of II within 12–16 hr. However, the time required for completion of the insertion of TCNE into η^5-$C_5H_5Mo(CO)_2(L)CH_3$ is substantially shorter than that for the isomerization of I to II. Hence it appears that some II, as well as all of I, is formed directly in the insertion. Considerable decomposition encountered in these reactions prevents drawing more quantitative conclusions.

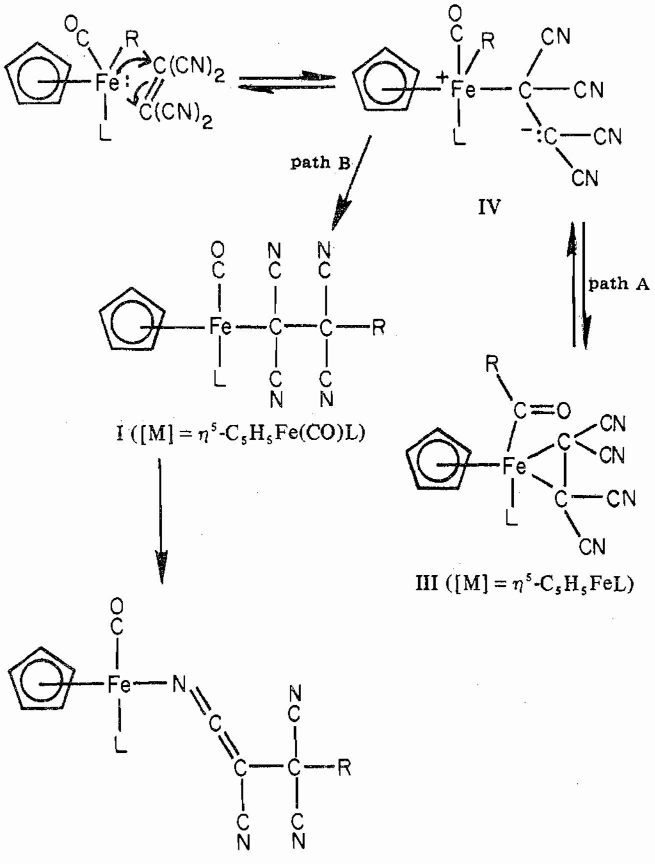
(b) Iron Complexes. Reactions between complexes of formula η^5-$C_5H_5Fe(CO)_2R$ and TCNE were generally carried out in CH_2Cl_2 solution at 25°. An attempt was made to explore solvent effects on the insertion in η^5-$C_5H_5Fe(CO)_2CH_3$ by using CH_2Cl_2, THF, and CH_3CN as the reaction medium. However, these reactions proved to be very slow and insufficiently clean to allow making meaningful comparisons from the observations summarized in Table I.

The rate of the TCNE insertion in η^5-$C_5H_5Fe(CO)_2R$ varies with R in the order R = $CH_2C_6H_5$ > $CH(CH_3)C_6H_5$ > CH_3, C_2H_5, *n*-C_3H_7 >> C_6H_5. This order is somewhat different from that found for the SO_2 insertion; there, the reactivity decreases with R as CH_3, C_2H_5 > $CH_2C_6H_5$ > $CH(CH_3)C_6H_5$ > C_6H_5.[38] However, the faster reaction of the benzylic complexes than of the alkyl complexes toward TCNE accords with the earlier observation[52] that η^5-$C_5H_5Cr(NO)_2CH_2C_6H_5$ reacts more rapidly with TCNE than does η^5-$C_5H_5Cr(NO)_2CH_3$. Furthermore, this dependence of the reactivity on the nature of R is similar to that reported for the insertion of O_2 into the Co–R bond of $RCo(dmgH)_2C_5H_5N$ (dmgH = dimethylglyoximato), where benzylic complexes react more readily than the alkyl complexes.[53] For the insertion of O_2, this dependence on the nature of R and results of stereochemical experiments[54] suggest that a free-radical pathway involving the alkyl fragment is a likely mechanism. Similarly, the insertion of TCNE would appear to proceed through formation of an alkyl radical.

In order possibly to shed more light on this problem we investigated the reaction of TCNE with optically active η^5-$C_5H_5Fe(CO)_2CH(CH_3)C_6H_5$, which showed $[\alpha]_{546}$ +78.5° in $CHCl_3$ solution. This complex, like its inactive form, yielded **5** and **12**. Chloroform solutions of the cyanoalkyl **5** from the optically active iron alkyl showed a rotation, $[\alpha]_{546}$, of +9°; unfortunately, solutions of the corresponding keteniminate, **12**, were too turbid for a measurement of specific rotation. Although the observed rotation of **5** cannot be correlated with a per cent stereospecificity for the insertion, its low value certainly does not preclude the possibility of a free-radical mechanism in these reactions. In fact, as stated above, such a mechanism appears to merit serious consideration.[54a]

It is of further interest that isomers of types I and II derived from η^5-$C_5H_5Fe(CO)_2R$ (R = CH_3, C_2H_5, and $CH_2C_6H_5$)

Scheme I



I ([M] = η^5-$C_5H_5Fe(CO)L$)

III ([M] = η^5-C_5H_5FeL)

II ([M] = η^5-$C_5H_5Fe(CO)L$)

do not interconvert upon prolonged storage in solution at room temperature. This is in contrast to the behavior of the analogous molybdenum complexes, discussed above, and indicates that the iron complexes I and II are formed independently in the insertion.

In contrast to the relatively slow insertion reactions between η^5-$C_5H_5Fe(CO)_2R$ and TCNE, reactions between η^5-$C_5H_5Fe(CO)(L)R$ (L = phosphine or phosphite) and TCNE generally proceed rapidly, even at 5–10° in benzene solution. When R = $CH_2C_6H_5$, they afford complexes of type II, and when R = CH_3, C_2H_5, or *n*-C_3H_7, they yield complexes of type III. The reaction of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2C_6H_5$ with TCNE in each of *n*-butyl ether (–65°), C_6H_6 (5–10°), and CH_3CN (25°) was monitored by infrared spectroscopy with a view to detecting a possible intermediate of type III. However, no $\nu_{C=O}$ bands attributable to η^5-$C_5H_5Fe[P(C_6H_5)_3](C_6N_4)COCH_2C_6H_5$ could be found in the 1700–1550-cm^{-1} region. Thus it would appear that these reactions of the benzylic complexes proceed directly to II, without the intermediacy of III.

Qualitatively, the rates of these insertions show the following dependence on the nature of L and R. When R remains constant, L = $P(n\text{-}C_4H_9)_3 > P(C_6H_5)_3 > P(OC_6H_5)_3$ for R = CH_3 and L = $P(n\text{-}C_4H_9)_3 > P(C_6H_5)_3$ for R = $CH_2C_6H_5$. When L is fixed, R = CH_3, C_2H_5, and *n*-C_3H_7 > $CH_2C_6H_5$ for L = $P(C_6H_5)_3$. These variations reflect an enhancement of rate with an increasing basicity of L and R and are similar to those observed for the SO_2 insertion in various complexes η^5-$C_5H_5Fe(CO)(L)R$.[28] They support electrophilic cleavage of the Fe–R bond by TCNE.

A plausible pathway for the formation of II and III from η^5-$C_5H_5Fe(CO)(L)R$ and TCNE is depicted in Scheme I. Electrophilic attack of TCNE at iron first generates a dipolar intermediate, IV. Formation of IV is supported by the observed solvent dependence of the rate of reaction of η^5-$C_5H_5Fe(CO)[P(OC_6H_5)_3]CH_3$ with TCNE at 25°. Accordingly, the $\nu_{C=O}$ band of the starting alkyl complex disappears within 20 sec in CH_3CN, 480 sec in CH_2Cl_2, 10,800 sec in THF, and 14,400 sec in C_6H_6. It is noteworthy that cycloaddition reactions between iron–propargyl or –σ-allyl complexes and TCNE also appear to proceed *via* zwitterionic intermediates.[17]

Intermediate IV can collapse either by attack of its negative terminus at iron with a simultaneous migration of R onto the coordinated CO (path A) or by nucleophilic attack of this terminus at R (path B). The latter rearrangement affords a complex of type I which would then require isomerization to II in order to account for the structure of the isolated product. A rapid isomerization from a soft cyanoalkyl–iron linkage to the corresponding hard keteniminato–iron bond is entirely possible for η^5-$C_5H_5Fe(CO)(L)(C_6N_4R)$. This is because of the observed occurrence of such a rearrangement for η^5-$C_5H_5Mo(CO)_2(L)(C_6N_4CH_3)$ and the known tendency of phosphine-substituted metal carbonyls to bond to the hard end of an ambidentate ligand.[35,45,55] Path A occurs with R = CH_3, C_2H_5, or *n*-C_3H_7, all of which readily migrate in CO insertion reactions.[3] Path B was observed for the Fe–$CH_2C_6H_5$ linkages, from which the benzyl group is known not to migrate readily onto coordinated CO in competitive insertion reactions.[3,4] Thus, for example, η^5-$C_5H_5Fe(CO)_2CH_2C_6H_4X$ and $C_6H_{11}NC$ afford η^5-$C_5H_5Fe(CO)_2C(CH_2C_6H_4X){=}NC_6H_{11}$ rather than the products of CO insertion.[56]

Complexes III undergo ligand rearrangement reactions to yield either η^5-$C_5H_5Fe(CO)(L)R$ and TCNE or II ([M] = η^5-$C_5H_5Fe(CO)L$), or both. These reactions are generally accompanied by considerable decomposition, and therefore little can be said about possible mechanisms. However, it is not unlikely that they proceed by the reverse of path A in Scheme I, followed by either path B or fragmentation into the parent iron alkyl and TCNE.

Finally, we wish to call attention to our observation that cyanoolefins with fewer cyano groups, and therefore less electrophilic, than TCNE are essentially inert toward iron–alkyl compounds. Thus, neither $(C_6H_5)_2C{=}C(CN)_2$ nor *trans*-$NCCH{=}CHCN$ was found to react with η^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ or η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ at 25° over extended periods of time. Under more forcing conditions, only decomposition was noted.

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Registry No. **1**, 32965-30-3; **2**, 52928-77-5; **3**, 52928-78-6; **4**, 52928-79-7; **5**, 52928-80-0; **6**, 52992-52-6; **7**, 52928-75-3; **8**, 32965-31-4; **9**, 52928-81-1; **10**, 52928-82-2; **11**, 52928-83-3; **12**, 52928-84-4; **13**, 52992-53-7; **14**, 52928-76-4; **15**, 52928-74-2; **16**, 52928-66-2; **17**, 52928-67-3; **18**, 32984-30-8; **19**, 52993-90-5; **20**, 52928-68-4; **21**, 34676-38-5; **22**, 52993-91-6; **23**, 52993-92-7; **24**, 52928-71-9; **25**, 52928-72-0; **26**, 52928-73-1; η^5-$C_5H_5Fe(CO)_2CH_3$, 12080-06-7; η^5-$C_5H_5Fe(CO)_2C_2H_5$, 32611-65-7; η^5-$C_5H_5Fe(CO)_2(n\text{-}C_3H_7)$, 51177-83-4; η^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$, 12093-91-3; η^5-$C_5H_5Fe(CO)_2CH(CH_3)C_6H_5$, 36182-37-3; η^5-$C_5H_5Fe(CO)_2C_6H_5$, 12126-73-7; η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]CH_3$, 32007-82-2; η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_3$, 33056-74-5; η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2C_6H_5$, 33135-99-8; η^5-$C_5H_5Fe(CO)[P(n\text{-}C_4H_9)_3]CH_2C_6H_5$, 52928-69-5; η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$, 12100-51-5; η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]C_2H_5$, 32824-72-9; η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3](n\text{-}C_3H_7)$, 32611-01-1; η^5-$C_5H_5Fe(CO)[P(n\text{-}C_4H_9)_3]CH_3$, 52928-70-8; η^5-$C_5H_5Fe(CO)[P(OC_6H_5)_3]CH_3$, 12290-98-1; TCNE, 670-54-2.

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(a) **Note Added in Proof.** The structure of **6** has been now confirmed by X-ray crystallography; see M. R. Churchill and S. W.-Y. Chang, following paper.
(46) Infrared and nmr spectroscopic criteria which may be used to distinguish cis and trans complexes of general type η^5-$C_5H_5Mo(CO)_2(L)X$ are given, *inter alia*, in J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, **92**, 5852 (1970), and in K. W. Barnett and D. W. Slocum, *J. Organometal. Chem.*, **44**, 1 (1972).
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(a) **Note Added in Proof.** In the study reported herein no attempt was made at examining the reaction mixtures by esr spectroscopy. However, after this paper was accepted for publication we have learned that reactions of TCNE with each of η^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$, $Mn(CO)_5CH_2C_6H_5$ ([M]$CH_2C_6H_5$), and $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ ($[M]_2$) yield initially the corresponding metal–iminotricyanoallyl radicals, [M]-$N{=}C{=}C(CN)\dot{C}(CN)_2$; see P. J. Krusic, H. Stoklosa, L. E. Manzer, and P. Meakin, *J. Amer. Chem. Soc.*, submitted for publication. We thank Dr. P. J. Krusic for communicating these results to us prior to publication.
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Crystal and Molecular Structure of Dicarbonyl(η^5-cyclopentadienyl)triphenylphosphine(1-η-1,1,2,2-tetracyanopropyl)molybdenum, the Product of Insertion of Tetracyanoethylene into a Molybdenum–Methyl Linkage

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Dicarbonyl-η^5-cyclopentadienyltriphenylphosphine(1-η-1,1,2,2-tetracyanopropyl)molybdenum, $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)[C(CN)_2C(CN)_2CH_3]$, formed by the reaction of $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)(CH_3)$ with tetracyanoethylene, has been subjected to a full three-dimensional X-ray structural analysis. The complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ [C_i^1; No. 2] with $a = 8.606$ (1) Å, $b = 12.158$ (2) Å, $c = 13.987$ (2) Å, $\alpha = 85.60$ (2)°, $\beta = 75.95$ (1)°, $\gamma = 88.37$ (1)°, and $V = 1415.4$ Å^3. The observed density of 1.468 (5) g cm^{-3} is consistent with that of 1.460 g cm^{-3} calculated for mol wt 622.48 and $Z = 2$. X-Ray diffraction data complete to $2\theta = 47.5°$ (Mo Kα radiation) were collected with a Picker FACS-1 diffractometer and the structure was solved by means of Patterson, Fourier, and least-squares refinement techniques. All atoms, including hydrogens, have been located and their thermal and positional parameters refined. The resulting discrepancy indices are $R_F = 3.98\%$ and $R_{wF} = 4.76\%$ for the 4346 independent reflections (none rejected). The molybdenum atom has a coordination environment resembling a "four-legged piano stool." The Mo–C(π-C_5H_5) distances range from 2.300 (3) to 2.359 (3) Å, the Mo–P bond length is 2.518 (1) Å, and the Mo–CO bonds are 1.973 (3) and 1.996 (3) Å in length. The Mo–$[C(CN)_2C(CN)_2CH_3]$ σ-bond distance of 2.414 (4) Å is compared with Mo–C distances in molybdenum alkyls, perfluoroalkyls, acyls, and aryls. Within the tetracyanopropyl group, one 2-cyano group and the methyl group are disordered.

Introduction

We have, for some time, been interested in so-called "insertion reactions."[1] Following some studies on the products of the insertion of sulfur dioxide into metal–carbon[2-4] and metal–metal[5,6] bonds, we have turned our attention to the products derived from the interaction of tetracyanoethylene with various organo-(transition metal) complexes. We have shown previously that tetracyanoethylene reacts with a σ-allyl *via* a net [3 + 2] cycloaddition reaction[7] (as shown in Scheme I).

We now report the results of a single-crystal X-ray diffraction study on $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)[C(CN)_2C$-