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Electrophilic Addition of Acetylenes and Olefins to σ-Bonded, Unsaturated Hydrocarbon Ligands in Transition-Metal Complexes

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The reactions of transition metal–η^1-allyl, –propargyl, and –η^1-cyclopentadienyl complexes with electrophilic acetylenes and olefins are described. Dicyanoacetylene undergoes an insertion reaction with η^5-$C_5H_5Fe(CO)_2CH_2C(R){=}CR'R''$ at 0–25 °C to give iron–η^1-alkadienyldicarbonyl products, η^5-$C_5H_5Fe(CO)_2C(CN){=}C(CN)C(R')(R'')C(R){=}CH_2$, containing a rearranged allyl fragment. By contrast, the insertion reaction of hexafluorobut-2-yne with η^5-$C_5H_5Fe(CO)_2CH_2C(R){=}CR'R''$ requires higher temperatures (60–65 °C) and affords iron–η^1,η^2-alkadienylmonocarbonyl products, η^5-$C_5H_5(CO)FeC(CF_3){=}C(CF_3)CH_2C(R){=}CR'R''$, with an unrearranged allyl moiety. Photolysis of η^5-$C_5H_5Fe(CO)_2C(CN){=}C(CN)CH_2CH{=}CH_2$ yields an analogous η^1,η^2-alkadienyl compound, η^5-$C_5H_5(CO)FeC(CN){=}C(CN)CH_2CH{=}CH_2$. Propargyl complexes of the formulas η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ and $Mn(CO)_4(L)CH_2C{\equiv}CR$ (L = CO and $P(C_6H_5)_3$) either do not react or react very nonspecifically with dicyanoacetylene and hexafluorobut-2-yne at 25 °C or on heating to give several products in insufficient yields for complete characterization. Dimethyl acetylenedicarboxylate and $Mn(CO)_5CH_2C{\equiv}CC_6H_5$ on heating afford a ring-substituted η^5-cyclopentadienylmanganese tricarbonyl compound, $[\eta^5\text{-}1\text{-}C_6H_5\text{-}2,3\text{-}(CO_2CH_3)_2C_5H_2]Mn(CO)_3$. The corresponding rhenium compound has been prepared analogously but could not be isolated pure. Fumaronitrile, unlike tetracyanoethylene, does not appear to enter into (3 + 2) cycloaddition reactions with η^5-$C_5H_5Fe(CO)_2CH_2C(R){=}CR'R''$, η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CR$, or $Mn(CO)_4(L)CH_2C{\equiv}CR$ (L = CO and $P(C_6H_5)_3$). The reactions of η^5-$C_5H_5Fe(CO)_2(\eta^1\text{-}C_5H_5)$ with electrophilic olefins (*trans*-$NCCH{=}CHCN$ and *trans*- and *cis*-$F_3C(CN)C{=}C(CN)CF_3$) and acetylenes ($NCC{\equiv}CCN$ and $F_3CC{\equiv}CCF_3$) afford 1:1 adducts of the reactants containing bicyclic norbornenyl and norbornadienyl rings, respectively. Upon storage in solution η^5-$C_5H_5Fe(CO)_2C_9H_5F_6$ rearranges to an acyl monocarbonyl derivative, η^5-$C_5H_5Fe(CO)(COC_9H_5F_6)$, and upon photolysis it yields η^5-$C_5H_5Fe(CO)C_9H_5F_6$. Possible mechanisms of these reactions are discussed.

Introduction

Reactions of olefins and acetylenes with both saturated and unsaturated hydrocarbon ligands bonded to transition metals represent important steps in oligomerization, polymerization, and related catalytic or stoichiometric processes.[2] Insertion, linear addition, and cycloaddition have all been observed in such reactions.

It has been shown in this[3,4] and other laboratories[5-8] that transition metal–η^1-allyl, –propargyl, and related complexes react with a wide range of electrophiles (EX), including SO_2, $ClSO_2NCO$, $(CF_3)_2CO$, and $(NC)_2C{=}C(CN)_2$, to mention a few. These reactions generally result either in (3 + 2) cycloaddition between the EX and unsaturated ligand accompanied by 1,2 metal migration or in insertion of the EX into the metal–carbon bond. Both types of product appear to arise through a common, dipolar intermediate. To elucidate better various factors that influence the formation of one kind of product over the other, and to extend this reaction to some unexplored electrophiles with carbon–carbon multiple bonds, we have now examined the interaction of transition metal–η^1-allyl and –propargyl complexes with several electron-poor acetylenes. A few related reactions with electrophilic olefins have been also studied for comparison, as have reactions of a η^1-cyclopentadienyl complex, η^5-$C_5H_5Fe(CO)_2(\eta^1\text{-}C_5H_5)$, with both olefins and acetylenes. Herein we report the results of our investigation on these systems.

Experimental Section

General Procedures. All thermal and photochemical reactions were conducted under an atmosphere of nitrogen. Irradiation experiments were carried out in Pyrex tubes using a Rayonet Model RPR-100 photochemical reactor with 3500-Å lamps. Neutral alumina (Ventron) used for chromatography and filtration was deactivated with distilled H_2O (6 or 10%). Melting points were measured in vacuo on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Physical Measurements. Hydrogen-1 NMR spectra were recorded on Varian Associates A-60A and HA-100 spectrometers using tetramethylsilane (Me_4Si) as an internal reference. Fluorine-19 NMR spectra were measured on a Varian Associates HA-100 spectrometer at 94.1 MHz using $C_6H_5CF_3$ as the solvent and lock or on a Bruker HX-90 spectrometer at 84.6 MHz using $CDCl_3$ as the solvent and lock and $C_6H_5CF_3$ as an internal reference. Carbon-13 NMR spectra were recorded on the Bruker HX-90 at 22.625 MHz in a Fourier transform mode. All spectra recorded on the Bruker HX-90 were obtained with the assistance of Dr. C. E. Cottrell and Mr. J. M. Geckle.

Tabulated infrared (IR) absorptions were obtained using a Beckman IR-9 spectrophotometer; routine IR spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer. Mass spectra were obtained at 70 eV on an A.E.I. Model MS-9 spectrometer by Mr. C. R. Weisenberger.

Materials. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under nitrogen. Pentane was purified by distillation from CaH_2, trichloroethylene from KOH and 1,2-dichloroethane from P_4O_{10}. Tetracyanoethylene (TCNE), from Columbia Organic Chemical Co., was sublimed before use. Other commercially procured solvents and chemicals were reagent grade quality and were used without further purification.

Dimethyl acetylenedicarboxylate was prepared from acetylenedicarboxylic acid as described in the literature.[9] Dicyanoacetylene was synthesized by dehydration of acetylenedicarboxyldiamide[10] whereas *cis*- and *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene ($C_6F_6N_2$) were obtained as described earlier.[4]

The complexes η^5-$C_5H_5Fe(CO)_2CH_2C(R){=}CR'R''$ (R = R′ = R″ = H;[11] R = CH_3, R′ = R″ = H;[12] R = R′ = H, R″ = CH_3;[11] R = H, R′ = R″ = CH_3[13]), $MCH_2C{\equiv}CR$ (M = η^5-$C_5H_5Fe(CO)_2$, R = CH_3[14] and C_6H_5;[15] M = $Mn(CO)_5$, R = CH_3[14] and C_6H_5;[16] M = $Re(CO)_5$, R = C_6H_5[4]), and η^5-$C_5H_5Fe(CO)_2(\eta^1\text{-}C_5H_5)$[17] were prepared according to published methods. The propargyl derivatives $Mn(CO)_4[P(C_6H_5)_3]CH_2C{\equiv}CR$ (R = CH_3 and C_6H_5) were obtained by the appropriately adapted procedure of Bannister et al.[5] R = CH_3, yield 68%; mp 107–108 °C; ^1H NMR ($CDCl_3$) τ 2.65 (br, C_6H_5), 8.23 (t, 2.8 Hz, CH_3), 9.08 (m, CH_2); IR ν_{CO} (CH_2Cl_2) 2065 (m), 1993 (sh), 1975 (s), 1940 (m) cm^{-1}. R = C_6H_5, yield 92%; mp 121–121.5 °C; ^1H NMR ($CDCl_3$) τ 2.61 (br, C_6H_5), 8.78 (br, CH_2); IR ν_{CO} (CH_2Cl_2) 2075 (m), 1995 (sh), 1978 (vs), 1940 (s) cm^{-1}.

Reactions of Metal Complexes with Dicyanoacetylene. Dicyanoacetylene, kept in a storage bulb at −78 °C, was transferred on a vacuum line into a round-bottom flask which was weighed before and after the transfer. The collected $NCC{\equiv}CCN$ was then vacuum transferred to another flask, containing solvent at −196 °C. The flask was warmed to −78 °C, nitrogen was admitted, and the contents were combined with a solution of the metal complex, also at −78 °C.

(a) η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CH_2$ with $NCC{\equiv}CCN$. To a CH_2Cl_2 solution (150 mL) of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CH_2$ (0.734 g, 3.41 mmol) at −78 °C was added $NCC{\equiv}CCN$ (0.262 g, 3.44 mmol) in

Table I. Analytical Data and Physical Properties of New Complexes

Complex[a, b]	Mp, °C	Color	Anal., % C Calcd	Anal., % C Found	Anal., % H Calcd	Anal., % H Found
I	97-99	Yellow-brown	57.14	57.05	3.40	3.36
II	119.5-120	Yellow-brown	58.50	58.68	3.90	4.54
IV	98-99	Red-orange	45.90	46.02	3.28	3.32
V	49-51.5	Red	45.90	45.87	3.28	3.13
VI	53-54	Yellow	38.82	39.06	1.76	1.78
VII[c]	101-102.5	Yellow	54.56	55.12	3.31	3.46
XI	124-124.5	Yellow	60.00	60.03	3.75	4.00
XII	89-91	Yellow	47.37	47.53	2.19	2.38
XIII	165 dec	Yellow	60.38	60.12	3.14	2.99
XIV	51.5-53	Yellow	47.52	47.42	2.48	2.40

[a] For structures see the text. [b] Parent ion (P^+) observed in the mass spectrum. [c] Mass spectrum: calcd for $C_{18}H_{13}MnO_7{}^+$, *m/e* 396.0042; obsd P^+, *m/e* 396.0045. Metastable peaks were noted for $P^+ - 2CO$ and $(P - 2CO)^+ - CO$.

40 mL of CH_2Cl_2, also at −78 °C. The resultant solution remained yellow while slowly warming to between −30 and −10 °C, at which temperature it turned dark brown. The flask was then maintained at 0 °C while progress of the reaction was monitored by IR spectroscopy. As only ca. 50% reaction had occurred in 2–4 h, the solution was allowed to warm to room temperature and kept there for 2 h. It was then filtered through 2 cm of alumina (6% H_2O) and solvent was removed from the filtrate. The residual oil was placed on a 1.5 × 14-cm column of alumina (6% H_2O). Elution with pentane yielded a band containing some unreacted organoiron complex whereas elution with benzene afforded a yellow-brown band. This was evaporated to an oil, dissolved in minimum benzene, and diluted with 100 mL of pentane to precipitate a yellow-brown solid (I) (0.303 g, 30%) which was collected by filtration.

Analytical data and physical properties (Table I) as well as spectroscopic data (Table II) of the new metal complexes I–XVI prepared herein are set out in the tables. Details of the mass spectra are given elsewhere.[1]

(b) η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$ with NCC≡CCN. A solution formed by the addition of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$ (0.704 g, 3.03 mmol) in 20 mL of CH_2Cl_2 to an unmeasured amount of NCC≡CCN in 10 mL of CH_2Cl_2 at −78 °C was stirred for 30 min and then allowed to warm to room temperature. It was diluted with 50 mL of pentane and filtered to remove some dark purple solid which was not characterized.

The filtrate was reduced in volume and chromatographed on alumina (10% H_2O). Elution with pentane yielded 0.472 g of unreacted iron–allyl complex whereas elution with 1:1 (v/v) pentane–CH_2Cl_2 afforded, after removal of the solvent, 0.086 g of a yellow-brown solid (II). Crystallization from 2:1 (v/v) pentane–benzene furnished a pure sample for analysis. The filtrate showed the presence of another, minor product with IR ν_{CO} (pentane) at 2012 and 1961 cm^{-1} and dominant ^1H NMR peaks ($CDCl_3$) at τ 5.32 and 8.1. This material was not characterized further.

(c) η^5-$C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$ with NCC≡CCN. A solution formed by the addition of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$ (0.77 g, 3.1 mmol) in 200 mL of CH_2Cl_2 to NCC≡CCN (0.26 g, 3.4 mmol) in 80 mL of CH_2Cl_2 at −78 °C was warmed first to 0 °C and stirred for 13 h and then to room temperature and stirred for an additional 10 h. Chromatography on alumina (6% H_2O) eluting with pentane yielded a trace amount of unreacted iron–allyl complex. Elution with $CHCl_3$ then removed a yellow band which showed IR ν_{CO} absorptions at 2045 (s), 2012 (m), 2001 (s), and 1956 (m) cm^{-1}. No further separation could be effected either by chromatography of this material on alumina eluting with 5:3 (v/v) benzene–pentane or by fractional crystallization from pentane–benzene and pentane–CH_2Cl_2. ^1H NMR peaks ($CDCl_3$) were observed at τ 3.76–4.22 (m, 1.0 H), 4.77–4.96 (m, 1.94 H), 4.97 (s, 4.5 H), 4.98–5.28 (m, 1.12 H), 8.50 (s, 5.74 H), and 8.56–8.96 (m, 0.89 H).

Photolysis of η^5-$C_5H_5Fe(CO)_2C(CN){=}C(CN)CH_2CH{=}CH_2$. The title complex in benzene was irradiated for 2 h, the solution was filtered through 2 cm of alumina (6% H_2O), and the solvent was removed from the filtrate. Addition of pentane afforded a small amount of an orange solid (III) which appeared quite unstable in solution.

Reactions of Metal Complexes with Hexafluorobut-2-yne. (a) η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$ with $F_3CC{\equiv}CCF_3$. A solution of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$ (3.14 g, 13.6 mmol) in 50 mL of $CHCl{=}CCl_2$ was syringed into a reaction flask containing ca. 5 mL of refluxing $F_3CC{\equiv}CCF_3$ under a dry ice condenser. After heating at 60–65 °C for 12 h, solvent was removed under reduced pressure and the residue was dissolved in pentane and passed through 1 cm of alumina to give a dark red solution. The volume of this solution was reduced to effect the precipitation of red-orange crystals of η^5-$C_5H_5(CO)\overline{FeC(CF_3){=}C(CF_3)CH_2CH}{=}CHCH_3$ (IV) (1.0 g, 20%), which were filtered off and washed with cold pentane. The product sublimes slowly at 50 °C (0.1 Torr).

Chromatography of the filtrate on alumina (6% H_2O) using pentane eluent developed four bands; each of the first three was found to contain several products whereas the fourth showed only IV. The first, green band yielded upon fractional crystallization ferrocene and η^5-$C_5H_5Fe(CO)_2C_9H_5F_6$ (XIV), prepared also by a more direct reaction (vide infra). In addition, minor products were present with IR ν_{CO} absorptions (pentane) at 2048, 2045, 1991, and 1951 cm^{-1}. No products could be separated from the second, yellow-green band that showed IR ν_{CO} absorptions (pentane) at 2044 (s), 2032 (m), 2017 (m), 1999 (s), 1991 (m), 1981 (m), and 1967 (m) cm^{-1}. The third, red band yielded as the main product ca. 20 mg of η^5-$C_5H_5Fe(CO)_2C(CF_3){=}CHCF_3$ (VI), which sublimes rapidly at 45 °C (0.1 Torr).

Subsequent elution with CH_2Cl_2 removed several small bands which were shown by IR spectroscopy to contain mixtures of products. Only $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ was characterized in the first band; the remaining mixtures contained polynuclear iron compounds comprised of C_5H_5, CO, and CF_3 fragments as ascertained by mass spectrometry and IR, ^1H NMR, and ^{19}F NMR spectroscopy.

There was no detectable change in the IR ν_{CO} region when the same reaction was carried out at 40 °C for 6 h.

(b) η^5-$C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$ with $F_3CC{\equiv}CCF_3$. A $CHCl{=}CCl_2$ solution (35 mL) of η^5-$C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$ (0.816 g, 3.52 mmol) and excess $F_3CC{\equiv}CCF_3$ was maintained at 60–65 °C for 1.5 h as in the previous reaction. Chromatography of the reaction mixture resulted in a similar elution of products, the major one being η^5-$C_5H_5(CO)\overline{FeC(CF_3){=}C(CF_3)CH_2C(CH_3)}{=}CH_2$ (V) (0.174 g, 14%). It decomposed on attempted sublimation at 40 °C (0.1 Torr).

(c) η^5-$C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$ with $F_3CC{\equiv}CCF_3$. The reaction between the title compounds in $CHCl{=}CCl_2$ was run under similar conditions as above to afford a mixture of products, including ferrocene and η^5-$C_5H_5Fe(CO)_2C(CF_3){=}CHCF_3$. The IR spectrum of the reaction solution showed an absorption at ca. 1990 cm^{-1}, as expected for η^5-$C_5H_5(CO)\overline{FeC(CF_3){=}C(CF_3)CH_2CH}{=}C(CH_3)_2$, but the compound decomposed upon chromatography on alumina.

(d) η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ with $F_3CC{\equiv}CCF_3$. The complex η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ (0.514 g, 1.76 mmol) and excess $F_3CC{\equiv}CCF_3$ (>2 g, >12 mmol) in 25 mL of 1,2-dichloroethane were heated in a Hoke bomb at 60 °C for 24 h. After venting and removal of the solvent, the residual oil was dissolved in 3 mL of CH_2Cl_2, diluted with 40 mL of pentane, and filtered through 2 cm of alumina. Concentration of this solution yielded a small amount of orange crystals which were collected by filtration and washed with cold pentane, mp 143–144 °C. Mass spectrum: calcd for $C_{24}H_{12}FeF_{12}O_2{}^+$ *m/e* 616, obsd P^+ *m/e* 616; calcd for $C_{17}H_7F_{12}{}^+$ *m/e*

439.0356, obsd $(P - C_5H_5Fe(CO)_2)^+$ *m/e* 439.0364. IR ν_{CO} (CH_2Cl_2) 2018.5, 1968.5 cm^{-1}; ^1H NMR ($CDCl_3$) τ 2.42 (s, C_6H_5), 5.62 (s, C_5H_5), 7.08–7.58 (m, CH_2); ^{19}F NMR ($CDCl_3$) ϕ 51.64 (s, 5.9 F), 51.94–52.55 (m, 3.5 F), 54.31 (q, 20.1 Hz, 2.6 F).

Chromatography on alumina of the pentane filtrate afforded several effluent fractions showing IR ν_{CO} absorptions. However, no additional products could be isolated pure and characterized from these solutions.

Similar results were obtained when the reaction was carried out in 1,2-dichloroethane under a dry ice condenser at 60–70 °C for 10 h.

(e) η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ with $F_3CC{\equiv}CCF_3$. A CH_2Cl_2 solution (5 mL) of the title iron complex (2.3 g, 10 mmol) and $F_3CC{\equiv}CCF_3$ (2 g, 12 mmol) was stirred for 5 h under a dry ice condenser and after removal of the solvent chromatographed on alumina (6% H_2O). Pentane eluted off unreacted propargyl complex (0.387 g) and then pentane–CH_2Cl_2 removed $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ and a mixture of iron carbonyls which could not be separated. Finally, elution with CH_2Cl_2 afforded η^5-$C_5H_5Fe(CO)_2C(CH_2OH){=}CHCH_3$ (0.075 g), mp 91.5–93.5 °C, which was first reported elsewhere.[18]

Attempted Reaction of η^5-$C_5H_5(CO)FeC(CF_3){=}C(CF_3)CH_2CH{=}CHCH_3$ with $P(C_6H_5)_3$. The title iron complex (0.060 g, 0.16 mmol) and $P(C_6H_5)_3$ (0.053 g, 0.20 mmol) in 15 mL of benzene were heated at 40 °C for 1 h. Only some decomposition was noted.

The reaction was repeated in *n*-butyl ether (20 mL) at 60 °C for 15 min and at 80–90 °C for 3.5 h with similar results.

Photolysis of the title compounds in THF for 3.5 h likewise resulted in no observable reaction.

Reactions of Metal Complexes with Dimethyl Acetylenedicarboxylate. (a) $Mn(CO)_5CH_2C{\equiv}CC_6H_5$ with $CH_3O_2CC{\equiv}CCO_2CH_3$. The title manganese complex (2.04 g, 6.56 mmol) and $CH_3O_2CC{\equiv}CCO_2CH_3$ (0.735 g, 5.17 mmol) in 125 mL of 1,2-dichloroethane were heated at 65–68 °C for 12 h to give a red-orange solution. The solvent was then removed and the residue was extracted with pentane (20 × 40 mL). The combined extracts were evaporated to a yellow solid (0.572 g). The solid was dissolved in 4:1 (v/v) pentane–CH_2Cl_2 and the solution was passed through 2 cm of ethyl acetate-washed acid alumina (10% H_2O). The solvent was then removed to yield a yellow solid (VII) (0.250 g).

The IR spectrum of the orange residue obtained in workup showed ν_{CO} bands of the above product as well as an additional band at 2015 cm^{-1}. This material was not purified further.

(b) $Re(CO)_5CH_2C{\equiv}CC_6H_5$ with $CH_3O_2CC{\equiv}CCO_2CH_3$. The title propargyl complex (0.17 g, 0.39 mmol) and $CH_3O_2CC{\equiv}CCO_2CH_3$ (0.064 g, 0.45 mmol) in 25 mL of CH_3CN were heated at 70 °C for 18 days. The solvent was removed, the residue was dissolved in minimum CH_2Cl_2, and the solution was treated with ca. 50 mL of pentane to effect the precipitation of a white solid with IR metal carbonyl stretching absorptions at 2023 (m), 1950 (sh), and 1910 (s) cm^{-1} plus an ester CO stretch at 1734 (m) cm^{-1}. The yellow filtrate showed these same bands as well as those of the starting materials. Since the ^1H NMR spectrum of the white solid was not satisfactory, attempts were made to purify this material by chromatography but without success.

Reactions of Metal Complexes with Tetracyanoethylene. The reaction of each of $Mn(CO)_5CH_2C{\equiv}CC_6H_5$, $Mn(CO)_4[P(C_6H_5)_3]CH_2C{\equiv}CC_6H_5$, and $Mn(CO)_4[P(C_6H_5)_3]CH_2C{\equiv}CCH_3$ with TCNE was carried out using the appropriate adaptation in the method of Su.[12] The yields of the respective cycloaddition products (VIII–X), all white solids, were 92, 22, and 8%.

Reactions of η^5-$C_5H_5Fe(CO)_2(\eta^1\text{-}C_5H_5)$ with Electrophiles. (a) With *trans*-$NCCH{=}CHCN$. To a stirred benzene solution (20 mL) of η^5-$C_5H_5Fe(CO)_2(\eta^1\text{-}C_5H_5)$ (0.200 g, 0.828 mmol) was added fumaronitrile (0.065 g, 0.83 mmol) in 10 mL of benzene. After 1 h the solvent was removed, the residue was dissolved in minimum CH_2Cl_2, and the solution was treated with 40 mL of pentane. The resulting yellow powder (XI) (0.150 g) was collected by filtration.

The solvent was removed from the filtrate and the residue was washed with pentane and dissolved in 2:1 (v/v) pentane–CH_2Cl_2. This solution was passed through 2 cm of alumina to give a reddish effluent which was discarded. Passing CH_2Cl_2 through the alumina then gave a yellow solution from which an additional 0.037 g of the product was obtained upon removal of the solvent.

(b) With $F_3C(CN)C{=}C(CN)CF_3$. A solution of η^5-$C_5H_5Fe(CO)_2(\eta^1\text{-}C_5H_5)$ (0.026 g, 0.11 mmol) and *trans*-$F_3C(CN)C{=}C(CN)CF_3$ (0.026 g, 0.12 mmol) in 20 mL of pentane was stirred for 10 min at 25 °C and then concentrated in a stream of nitrogen to effect the precipitation of a yellow solid (XII) which was collected by filtration (0.045 g).

The same product (^1H and ^{19}F NMR spectra identical with those of XII) was obtained when *cis*-$F_3C(CN)C{=}C(CN)CF_3$ was used in place of its trans isomer.

(c) With $NCC{\equiv}CCN$. To a stirred pentane solution (20 mL) of η^5-$C_5H_5Fe(CO)_2(\eta^1\text{-}C_5H_5)$ (0.385 g, 1.59 mmol) was added an unmeasured amount of $NCC{\equiv}CCN$ in 1:1 (v/v) pentane–CH_2Cl_2. Some precipitation of a yellow solid occurred immediately. The solvent was removed from this mixture and 0.244 g of unreacted iron carbonyl complex was recovered by extraction of the residue into pentane. The pentane-insoluble material was then dissolved in CH_2Cl_2 and the resulting solution was passed through 1 cm of alumina (10% H_2O). Addition of pentane to this filtrate and partial removal of the solvent yielded 0.082 g of yellow crystals (XIII).

(d) With $F_3CC{\equiv}CCF_3$. Addition of excess $F_3CC{\equiv}CCF_3$ to η^5-$C_5H_5Fe(CO)_2(\eta^1\text{-}C_5H_5)$ (0.620 g, 2.56 mmol) in 15 mL of CH_2Cl_2 under a dry ice condenser rapidly turned the solution from yellow to orange. IR spectroscopy revealed that the reaction was complete in 10 min. The solvent was removed, the residue was dissolved in 15 mL of pentane, the resulting solution was filtered, and the filtrate was evaporated to dryness to give 0.948 g (92%) of yellow crystals (XIV).

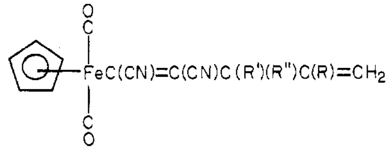
When a $CDCl_3$ solution of this product was stored for several days, the original yellow color changed to orange. The solvent was removed, the residue was dissolved in pentane, and the resulting solution was filtered through 3 cm of alumina (10% H_2O) to give a yellow filtrate of unchanged XIV. Then washing the alumina with CH_2Cl_2 yielded an orange solution, which upon treatment with pentane and concentration by partial removal of the solvent afforded orange crystals of another product (XV), mp 150 °C. Mass spectrum: calcd for $C_{16}H_{10}Fe_6O_2^+$ *m/e* 404, observed P^+ *m/e* 404.

Both compounds (XIV and XV) sublime at 40 °C (0.1 Torr).

Photolysis of η^5-$C_5H_5Fe(CO)_2C_9H_5F_6$. A solution of the title complex (0.156 g, 0.386 mmol) in 50 mL of cyclohexane was photolyzed until IR spectroscopy indicated completion of reaction (15 min). The solvent was removed, the residue was dissolved in pentane, and the resulting solution was filtered through 1 cm of alumina (10% H_2O). Removal of the solvent from the filtrate furnished 0.049 g of red-orange crystals (XVI), mp 89–91 °C. Mass spectrum: calcd for $C_{15}H_{10}FeF_6O^+$ *m/e* 376, observed P^+ *m/e* 376. The compound sublimes at 50 °C (0.1 Torr) and decomposes in $CDCl_3$ solution.

Results

Reactions of Metal–η^1-Allyl Complexes with Acetylenes. Complexes of the general formula η^5-$C_5H_5Fe(CO)_2CH_2C(R){=}CR'R''$ react with dicyanoacetylene at 0–25 °C to afford rather unstable yellow-brown solids that are sparingly soluble in saturated hydrocarbons but increasingly soluble in benzene, CH_2Cl_2, and acetone. These 1:1 adducts (from elemental analyses and mass spectra) have been assigned structures I–II on the basis of infrared ν_{CO} and ^1H NMR spectroscopic data, given in Table II. The values of ν_{CO} are appreciably higher (30–49 cm^{-1}) than those for the parent η^1-allyl complexes[13] suggesting insertion of an electron-withdrawing group into the Fe–C σ bond. The chemical shift of the methylene protons of I (τ 6.65) is lower than that for the precursor η^1-allyl complex (τ 7.93, $CDCl_3$ solution[13]) but close to that for the corresponding SO_2 insertion product, η^5-$C_5H_5Fe(CO)_2S(O)_2CH_2CH{=}CH_2$ (τ 6.24, $CDCl_3$ solution[13]), further supporting the assigned structure.



I, R = R' = R'' = H
II, R = R' = H; R'' = CH_3

The ^1H NMR spectrum of II indicates that the allyl fragment underwent 1,3 rearrangement in the course of the insertion. The apparent quintet of intensity 1 at τ 6.15 is

Table II. Infrared and NMR Spectra of New Complexes

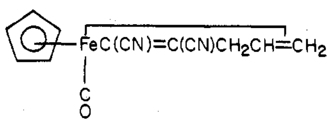
Complex[a]	Infrared, cm^{-1}				^{19}F NMR, ϕ[e]	
	ν_{CO}[b]	$\nu_{C=C}$[c]	ν_{CN}[c]	^1H NMR, τ[d]	α-CF_3	β-CF_3
I	2042 s, 1996 s	1643 w, 1532 vw	2209 m, 2184 m	3.97–4.57 (m, =CH), 4.57–4.83 (m, $=CH_2$), 4.96 (s, C_5H_5), 6.65 (d, 6.5, CH_2)		
II	2046 s, 1999 s	1637 w, 1529 vw	2212 m, 2180 m	3.9–5.1 (m, $CH=CH_2$), 4.97 (s, C_5H_5), 6.15 (q, d, 6.5, 6.5, CH), 8.73 (d, 6.5, CH_3)		
III	1973 s	*k*	*k*	4.6–5.2 (br, $=CH_2$), 5.35 (s, C_5H_5), 5.65–5.95 (br, =CH), 6.4–6.8 (m, CH_2)		
IV[f]	1990 s[i]	1601 m, 1501 w		5.05–5.57 (m, CH_2CH), 5.29 (s, C_5H_5), 6.15–6.93 (m, CH_2), 7.14 (q, d, 6, 12, $CHCH_3$), 8.49 (d, 6, CH_3)	51.88 (q, m,[n] 13.7)	60.51 (q, d[o], 13.7)
V	1995 s[i]	1601 m, 1501 w		5.43 (s, C_5H_5), 6.63 (br, CH_2), 7.12 (s), 7.93 (s, $=CH_2$), 8.14 (s, CH_3)	51.93 (q, t,[p] 14.1)	60.30 (q, 14.1)
VI	2044 s, 1999 s[i]	*k*		3.91 (q,[l] =CH), 5.03 (s, C_5H_5)	54.89 (q, 12.8)	58.73 (q, d,[q] 12.8)
VII[g,h]	2041 s, 1982 sh, 1975 s, 1723 m (ester)[i]			2.7 (br, C_5H_5), 5.30 (s), 5.33 (s, C_5H_2), 6.05 (s), 6.33 (s, CH_3)		
VIII	2037 s, 2025 sh	*k*	*k*	2.61 (br, C_6H_5), 6.30 (s, CH_2)		
IX	2080 m, 2009 m, 1992 s, 1980 sh	*k*	*k*	2.52–2.57 (br, C_6H_5), 6.92 (s, CH_2)		
X	2078 m, 2007 m, 1988 s, 1979 sh	*k*	*k*	2.54 (br, C_6H_5), 6.98 (m, CH_2), 7.81 (m, CH_3)		
XI	2013 s, 1958 s	1658 w	2234 w	3.73 (m, CH=CH), 5.24 (s, C_5H_5), 6.66–7.11 (m), 7.23–7.52 (m, CHCN, CH, FeCH)		
XII	2016 s, 1965 s	1585 vw	2247 w, 2234 w	3.28–3.78 (m, CH=CH), 5.19 (s, C_5H_5), 5.87–7.28 (m, FeCH, CH)	65.11 (s)	66.44 (s)
XIII	2014 s, 1960 s	1579 m, 1554 w	2206 w	3.18 (t, 2.2, CH=CH), 5.24 (s, C_5H_5), 5.82 (br, FeCH), 6.15, (br, CH)		
XIV	2017 s, 1967 s	1674 m, 1563 w		3.22 (t, d, 2, 0.5, CH=CH), 5.31 (s, C_5H_5), 6.00 (t, 0.5, FeCH), 6.28 (br, CH)		63.07 (s)
XV	1976 s, 1657 s (bridging)	*k*		*k*		*k*
XVI	1960 s[j]	1673 m		4.38, 5.02 (CH=CH), 5.4 (C_5H_5), 5.67, 6.32, 8.69 (CH, FeCH)[m]		*k*

[a] For structures see the text. [b] In CH_2Cl_2 solution unless otherwise noted. [c] KBr pellet. IR abbreviations: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. [d] In $CDCl_3$ solution; J_{H-H} (Hz) in parentheses. [e] Relative to $CFCl_3$, ϕ 0.00 ppm; $\phi(CFCl_3) = \phi(C_6H_5CF_3) + 63.75$ ppm; J_{F-F} (Hz) in parentheses. NMR abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. [f] ^{13}C NMR ($CDCl_3$ solution, chemical shifts, δ, relative to Me_4Si; J_{C-F}, in Hz, in parentheses) 219.64 (CO), 156.3 (q, q, 30, 3, FeC), 138.12 (q, q, 30.6, $=CCF_3$), 125.84 (q, 276, CF_3), 118.64 (q, 277, CF_3), 83.80 (C_5H_5), 72.56, 71.71 (η^2-C=C), 40.02 (br, CH_2), 22.59 (CH_3). [g] ^{13}C NMR (as in *f*, at −50 °C) 225.89, 221.92, 220.24 (CO), 167.58, 164.92 (CO_2), 131.11, 129.55, 127.8 (C_6H_5), 99.98, 98.22, 92.63, 89.38, 69.75 (C_5H_2), 53.69, 52.13 (CH_3). [h] ^{55}Mn NMR (recorded by Mr. J. M. Geckle at 14.85 MHz in Fourier transform mode on a home-built spectrometer equipped with a wide-band, high-power probe and a Nicolet 1080 computer) 2588 ± 10 ppm upfield from aqueous permanganate, $\nu_{1/2} = 5742$ Hz (acetone-d_6 solution). [i] In pentane solution. [j] In cyclohexane solution. [k] Not measured. [l] $^3J_{H-CF_3} = 9.5$ Hz. [m] Poorly resolved spectrum owing to decomposition. [n] $^5J_{H_A-CF_3} \sim {}^5J_{H_B-CF_3} \sim 5$ Hz. [o] $^5J_{H-CF_3} = 1.3$ Hz. [p] $^5J_{H-CF_3} = 3.3$ Hz. [q] $^3J_{H-CF_3} = 9.2$ Hz.

assigned to the methine proton; its multiplicity derives from an overlapping doublet of quartets with both coupling constants about equal, $^3J_{H-H} \sim {}^3J_{H-CH_3} \sim 6.5$ Hz. This assignment was substantiated by proton decoupling experiments. Irradiation at τ 6.15 collapsed the τ 8.73 doublet ($J = 6.5$ Hz) of the CH_3 protons into a singlet whereas irradiation at τ 8.73 appeared to collapse the τ 6.15 quintet into a doublet ($J = 6.5$ Hz). In further support of structure II is the appearance of the resonance of the olefinic protons as a broad multiplet of intensity 3 at τ 3.9–5.1.

The reaction of η^5-$C_5H_5Fe(CO)_2CH_2CH=C(CH_3)_2$ with dicyanoacetylene gave a mixture of two compounds that could not be separated. The more abundant product is postulated on the basis of the infrared ν_{CO} bands at 2045 and 2001 cm^{-1} to be an insertion derivative analogous to I and II. The ^1H NMR spectrum of the mixture shows two equivalent CH_3 groups at τ 8.50 and olefinic protons at τ 3.76–4.96, thus supporting insertion of dicyanoacetylene with rearrangement of the allyl ligand for the major product. The structure of the minor product, also a dicarbonyl from the infrared spectrum, was not elucidated.

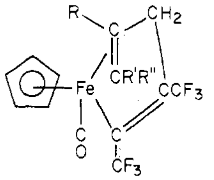
Photolysis of I afforded a monocarbonyl complex which is assigned structure III. Although this compound is unstable in solution, it was possible to obtain a poorly resolved ^1H NMR spectrum. An upfield shift of the olefinic protons on going



III

from I to III (Table II) is in accord with the proposed structure.

Reactions of the iron–η^1-allyl complexes in point with hexafluorobut-2-yne require temperatures of about 60–65 °C to give as major products compounds IV and V, formulated



IV, R = R' = H; R'' = CH$_3$
V, R = CH$_3$; R' = R'' = H

on the basis of elemental analyses and mass spectra. These compounds are red or red-orange crystalline solids and are quite soluble in organic solvents. Their structures have been assigned from spectroscopic data, furnished in Table II.

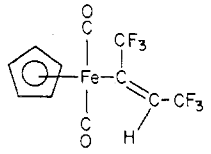
The infrared spectra of IV and V each show a single ν_{CO} absorption at 1995–1990 cm^{-1} and two $\nu_{C=C}$ absorptions at 1601 and 1501 cm^{-1}. The higher $\nu_{C=C}$ band is in the range expected for a vinyl group whereas the lower $\nu_{C=C}$ band is positioned right for a metal-bound, η^2 olefin.[19,20] Additionally, the intensity of the peak at 1601 cm^{-1} is higher than of that at 1501 cm^{-1}, in agreement with the assignment of the former to the CF$_3$-substituted double bond. Electronegative substituents are known to enhance the intensity of $\nu_{C=C}$ absorptions.[21]

In the ^{1}H NMR spectrum of V the two olefinic protons are observed as singlets at τ 7.12 and 7.93. By contrast, the spectrum of IV shows a multiplet of intensity 1 centered at τ 7.14; the other olefinic proton appears as a multiplet at τ 5.05–5.57 that overlaps the resonance of C$_5$H$_5$. The multiplet at τ 7.14 is interpreted as a first-order subspectrum with $^3J_{H-CH_3}$ = 6 Hz and $^3J_{CH=CH(trans)}$ = 12 Hz.[22] This assignment was substantiated by double resonance experiments. Irradiation at τ 7.14 collapsed the τ 8.49 doublet (J = 6.5 Hz) of the CH$_3$ group into a singlet whereas irradiation at τ 8.49 collapsed the τ 7.14 multiplet into a doublet with J = 12 Hz. These results are consistent only with the presence of an unrearranged allyl moiety, as in structure IV.

Each of IV and V shows two nonequivalent, mutually coupled (J = 13.7–14.1 Hz) CF$_3$ groups in its ^{19}F NMR spectrum. The lower field quartet is assigned to α-CF$_3$, in accord with the literature.[24] This α-CF$_3$ resonance is further split by interaction with the methylene protons. For V a $^5J_{H-CF_3}$ of 3.3 Hz is observed, whereas for IV a slightly second-order coupling is noted with the CH$_2$ protons, $^5J_{H_A-CF_3} \neq {}^5J_{H_B-CF_3} \sim 3$ Hz. The magnetic nonequivalence of the CH$_2$ protons of IV is also discernible in its ^{1}H NMR spectrum which shows a broad AB quartet with additional, unequal coupling of each hydrogen. Such nonequivalence of the methylene protons for metal–η^1,η^2-alkenyl complexes has been reported.[25] The ^{13}C NMR spectrum of IV, given in Table II, is also in accord with the assigned structure.[26]

The reaction of η^5-C$_5$H$_5$Fe(CO)$_2$CH$_2$CH=C(CH$_3$)$_2$ with hexafluorobut-2-yne yielded a monocarbonyl complex which showed a ν_{CO} absorption at ca. 1990 cm^{-1}, as expected for an analogue of IV and V. However, the compound could not be isolated and fully characterized because of instability.

Besides the aforementioned, main products, these reactions afforded a number of other complexes in low yields. Of these, compounds VI and XIV were obtained in sufficient quantities for isolation and full characterization. The assignment of a cis orientation of the CF$_3$ groups in VI is based on a comparison of the values of J_{H-CF_3} and $J_{CF_3-CF_3}$ for this and previously reported M-C(CF$_3$)=CHCF$_3$ complexes.[27-35] Accordingly, for the cis complexes $^4J_{H-CF_3(trans)}$ = 0 Hz, $^3J_{H-CF_3(gem)}$ = 9–11 Hz, and $^5J_{CF_3-CF_3}$ = 12–14.5 Hz whereas for the trans complexes $^4J_{H-CF_3(cis)}$ = 1.5–2.5 Hz, $^3J_{H-CF_3(gem)}$ = 8–9.5 Hz, and $^5J_{CF_3-CF_3}$ = 2–2.5 Hz. It is noteworthy that the trans isomer of VI was reported earlier by Clark.[35]



VI

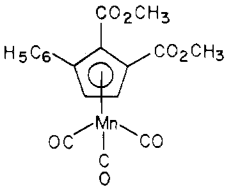
Complex XIV was synthesized more directly in this study by the reaction of η^5-C$_5$H$_5$Fe(CO)$_2$(η^1-C$_5$H$_5$) with hexafluorobut-2-yne and is considered later in the Results section.

Attempts at substitution of the coordinated double bond in IV by P(C$_6$H$_5$)$_3$ either thermally or photochemically have proved unsuccessful. This behavior contrasts with that of (CO)$_3$CoC(CF$_3$)$_2$CH$_2$CH=CH$_2$[36] and (CO)$_3$CoCF$_2$CF$_2$CH$_2$CH=CH$_2$,[24] which readily react with P(C$_6$H$_5$)$_3$ to replace the coordinated double bond of the η^1,η^2-alkenyl ligand.

Reactions of Metal–Propargyl Complexes with Acetylenes. Reaction of iron– and manganese–propargyl compounds with dicyanoacetylene and hexafluorobut-2-yne proceeded sluggishly and did not afford any adducts that could be fully characterized. The complex η^5-C$_5$H$_5$Fe(CO)$_2$CH$_2$C≡CC$_6$H$_5$ and dicyanoacetylene in ether at room temperature gave a trace amount of an unidentified brown powder with infrared ν_{CO} bands at 2036 and 1987 cm^{-1} (CH$_2$Cl$_2$) as the only isolated product. There was no reaction between Mn(CO)$_5$CH$_2$C≡CC$_6$H$_5$ and NCC≡CCN in ether at 25 °C.

Hexafluorobut-2-yne reacted with η^5-C$_5$H$_5$Fe(CO)$_2$CH$_2$C≡CC$_6$H$_5$ at 60 °C to give, among several low-yield products, a 2:1 adduct of the acetylene and the metal complex. The spectroscopic data of this orange solid (Experimental Section) indicate that both molecules of F$_3$C-C≡CCF$_3$ are bound to the propargyl fragment; however, the structure of the newly formed ligand has not been elucidated. The appearance of three ^{19}F NMR signals with different intensities does not fit any of the more obvious structural possibilities. Likewise, reaction of Mn(CO)$_5$CH$_2$C≡CC$_6$H$_5$ with hexafluorobut-2-yne in 1,2-dichloroethane at 65–70 °C afforded a product that has not been completely characterized. This yellow-brown powder showed infrared ν_{CO} absorptions at 2033 and 1961 cm^{-1} but a satisfactory ^{1}H NMR spectrum could not be obtained because of low stability.

In contrast to dicyanoacetylene and hexafluorobut-2-yne, the reaction of CH$_3$O$_2$CC≡CCO$_2$CH$_3$ with Mn(CO)$_5$CH$_2$C≡CC$_6$H$_5$ in 1,2-dichloroethane at 65–68 °C yielded a yellow solid that was characterized as a 1:1 adduct of the two reactants, VII.[37] The infrared spectrum of VII in the ν_{CO} region shows three terminal metal carbonyl (2041, 1982, and 1975 cm^{-1}) and one uncoordinated ester carbonyl[38] (1723 cm^{-1}) stretching absorptions, the former occurring in the range reported for various η^5-cyclopentadienylmanganese tricarbonyl complexes.[39,40] However, the most convincing evidence for structure VII is provided by the NMR data. The ^{1}H NMR



VII

spectrum shows separate singlet resonances for the two CH$_3$

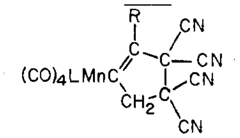
groups and the two cyclopentadienyl ring protons. The ^{55}Mn NMR spectrum exhibits a resonance with a chemical shift of 2588 ± 10 ppm upfield from aqueous permanganate with $\nu_{1/2}$ = 5742 Hz, in good agreement with the corresponding spectrum of η^5-$C_5H_5Mn(CO)_3$,[41] and in the ^{13}C NMR spectrum, three CO, two CO_2, two CH_3, five C_5H_2, and three C_6H_5 carbon signals are observed, all in the regions expected for the proposed structure.[26,42]

The complex $Re(CO)_5CH_2C{\equiv}CC_6H_5$ reacted with $CH_3O_2CC{\equiv}CCO_2CH_3$ to give what on the basis of the ν_{CO} spectrum[43] appears to be the rhenium analogue of VII. However, low yields and difficulties in purification prevented full characterization of this product.

The reaction of each of $Mn(CO)_5CH_2C{\equiv}CCH_3$, $Mn(CO)_4[P(C_6H_5)_3]CH_2C{\equiv}CCH_3$, and η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ with $CH_3O_2CC{\equiv}CCO_2CH_3$ in 1,2-dichloroethane or THF at 50 °C or above gave low yields of unstable or difficult to purify products. No attempt was made at their characterization. The reaction of $Mn(CO)_5CH_2C{\equiv}CCH_3$ afforded also the vinyl complex $Mn(CO)_5C(CH_2Br){=}CHCH_3$, characterized by infrared ν_{CO} and ^{1}H NMR spectroscopy. This compound, analogous to a series of iron–vinyl derivatives reported earlier,[18] likely resulted from protonation during chromatography of $Mn(CO)_5CH_2C{\equiv}CCH_3$ to give $Mn(CO)_5(\eta^2$-$CH_2{=}C{=}CHCH_3)^+$ followed by reaction with bromide. The bromide apparently originated from $BrCH_2C{\equiv}CCH_3$ used in the preparation of $Mn(CO)_5CH_2C{\equiv}CCH_3$. A similar hydroxy product, η^5-$C_5H_5Fe(CO)_2C(CH_2OH){=}CHCH_3$, was isolated after chromatography of the reaction mixture from η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ and $F_3CC{\equiv}CCF_3$.

Reactions of Metal–η^1-Allyl and –Propargyl Complexes with Olefins. Cycloaddition reactions of metal–η^1-allyl and –propargyl complexes with olefins bearing electronegative substituents have been the subject of a few investigations.[4,7,12] In extending these studies, some additional reactions of TCNE and the corresponding reactions of fumaronitrile were examined.

TCNE readily adds to the propargyl ligand of each of $Mn(CO)_5CH_2C{\equiv}CC_6H_5$, $Mn(CO)_4[P(C_6H_5)_3]CH_2C{\equiv}CC_6H_5$, and $Mn(CO)_4[P(C_6H_5)_3]CH_2C{\equiv}CCH_3$ to give (3 + 2) cycloaddition derivatives, VIII–X, respectively. The structures were inferred by comparison of the infrared ν_{CO} and ^{1}H NMR spectra of the products (Table II) with the spectra reported for similar compounds. Thus the values of ν_{CO} match well those found for $(CO)_4LMn\overline{C{=}C(R)S(O)OCH_2}$ (L = CO and $P(C_6H_5)_3$),[5] and the ^{1}H NMR chemical shifts compare satisfactorily with those observed for other, similar TCNE cycloadducts.[12]

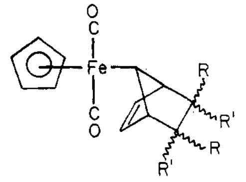


VIII, L = CO; R = C_6H_5
IX, L = *cis*-$P(C_6H_5)_3$; R = C_6H_5
X, L = *cis*-$P(C_6H_5)_3$; R = CH_3

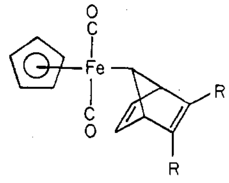
It was further of interest to ascertain whether fumaronitrile, with only two cyano groups, would be a sufficiently strong electrophile to undergo analogous cycloaddition reactions. Accordingly its behavior was investigated toward several metal–η^1-allyl and –propargyl complexes.

Little success was achieved, however, with these systems. When the metal complex was η^5-$C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$, $Mn(CO)_5CH_2C{\equiv}CC_6H_5$, $Mn(CO)_4[P(C_6H_5)_3]CH_2C{\equiv}CC_6H_5$, or $Mn(CO)_4[P(C_6H_5)_3]CH_2C{\equiv}CCH_3$ the reactions in CH_2Cl_2 or $CHCl{=}CCl_2$ at 25–55 °C produced very low yields of unstable and/or impure oils that could not be fully characterized. No observable reaction other than decomposition occurred in CH_2Cl_2 at room to reflux temperatures with the η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ where R = CH_3 and C_6H_5.

Reactions of η^5-$C_5H_5Fe(CO)_2(\eta^1$-$C_5H_5)$ with Olefins and Acetylenes. The complex η^5-$C_5H_5Fe(CO)_2(\eta^1$-$C_5H_5)$ reacted rapidly with each of fumaronitrile, *trans*- and *cis*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene, dicyanoacetylene, and hexafluorobut-2-yne to afford 1:1 adducts of the two reactants, XI–XIV, respectively. The corresponding reaction with TCNE was reported recently by Rosenblum et al.[7] By analogy with the reaction of metal–η^1-cyclopentadienyl complexes with electrophilic molecules,[44–46] these products are expected to possess norbornenyl (from the olefins) and norbornadienyl (from the acetylenes) ligands bonded to the iron. This is confirmed on inspection of the spectroscopic data in Table II.



XI, R = H; R' = CN
XII, R = CN; R' = CF_3

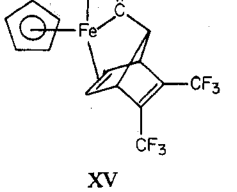


XIII, R = CN
XIV, R = CF_3

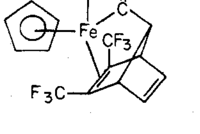
The infrared ν_{CO} absorptions fall in the ranges 2017–2013 and 1967–1958 cm^{-1} and are comparable to those for η^5-$C_5H_5Fe(CO)_2(\eta^1$-$C_5H_5)$ (2015 and 1964 cm^{-1}, CH_2Cl_2 solution). The ^{1}H NMR spectra show the resonance of η^5-C_5H_5 as a singlet between τ 5.19 and 5.31 and the resonances of the other protons at positions expected for norbornenyl and norbornadienyl fragments.[47] All four products are assigned structures that result from the addition of the electrophile to the ring on the side opposite the iron atom.[48] Such orientation of the metal was observed in the bicyclic products derived from iron–cycloalkenyl complexes and toluenesulfonyl isocyanate or TCNE.[6,7] Moreover, addition of hexafluorobut-2-yne to an η^1-cyclopentadienyl ring in two organoplatinum compounds has yielded products in which the platinum is anti to the added acetylene as determined spectroscopically and in one case crystallographically.[45]

Three diastereomers are possible for each of the bicyclic structures XI and XII: two meso diastereomers with the CN groups mutually cis and one pair of enantiomers with the CN groups trans. No attempt was made at determining which of the three is (are) present as XI; however, XII was examined by ^{19}F NMR spectroscopy with a view to ascertaining the stereochemistry of its norbornenyl ring. The observation of two singlets of equal intensity is consistent with the presence of the diastereomer with trans CF_3 groups or, less likely, equal amounts of the two meso diastereomers.[4] It is noteworthy that the stereochemistry of XII does not change when *trans*-$F_3C(CN)C{=}C(CN)CF_3$ is replaced with the cis isomer in the reaction with η^5-$C_5H_5Fe(CO)_2(\eta^1$-$C_5H_5)$.

Storage of a $CDCl_3$ solution of XIV leads to the formation of an orange isomer (from its P$^+$ in the mass spectrum) that shows a single infrared terminal ν_{CO} band at 1960 cm^{-1} and a bridging ν_{CO} band at 1657 cm^{-1}. This compound is assigned structure XV. Significantly, what appears to be the same

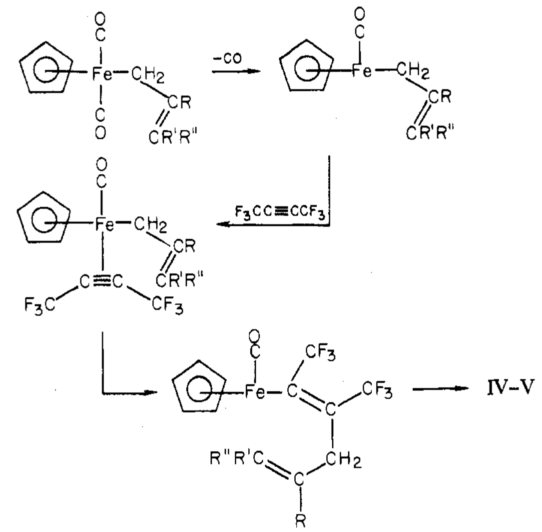


XV



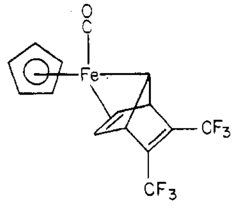
XVA

Scheme I



complex on the basis of the infrared ν_{CO} spectrum (1980 and 1668 cm^{-1} in CCl_4 solution) and the melting point (148–151 °C) was recently prepared by photolysis of η^5-$C_5H_5Fe(CO)_2(\eta^1$-$C_5H_5)$ and hexafluorobut-2-yne in hexane solution.[32,49] However, the authors assign to it the alternate structure, XVA, in which the CF_3-substituted double bond is coordinated to the iron. Assuming that the two preparations have yielded the same compound, we prefer formulation XV over XVA for two reasons. One, our complex is derived from XIV by the so-called carbon monoxide insertion, a reaction that proceeds with retention of configuration at the α carbon of the alkyl group.[50] Thus, provided that structure XIV is correct, the added hexafluorobut-2-yne should be in a position anti to the metal in XV. Two, the photochemically prepared complex shows ^{1}H NMR signals of the olefinic protons at τ 4.50 and 6.22. These signals occur at substantially higher fields compared to the corresponding resonance of XIV (τ 3.22) and, to us, suggest that the CH=CH rather than the F_3CC=CCF_3 double bond is bound to the metal.

Irradiation of XIV affords a red-orange, sublimable solid, XVI, which, from the mass spectrum, appears to be derived from XIV by loss of a molecule of CO. The infrared spectrum of this complex shows a single ν_{CO} band at 1960 cm^{-1} and a $\nu_{C=C}$ absorption at 1673 cm^{-1}. For the parent compound, XIV, $\nu_{C=C}$ absorptions occur at 1674 and 1563 cm^{-1}, with the more intense one at 1674 cm^{-1} being assigned to the CF_3-substituted double bond. Since the band at 1673 cm^{-1} for XVI is as intense as that at 1674 cm^{-1} for XIV, and since no absorption is observed around 1560 cm^{-1} for XVI, it is proposed that the CH=CH double bond is attached to the iron in XVI. Although XVI displays marginal stability in $CDCl_3$ solution, its poorly resolved ^{1}H NMR spectrum does show the resonances of the olefinic protons at higher fields than for XIV, in agreement with coordination of the CH=CH group to the metal.

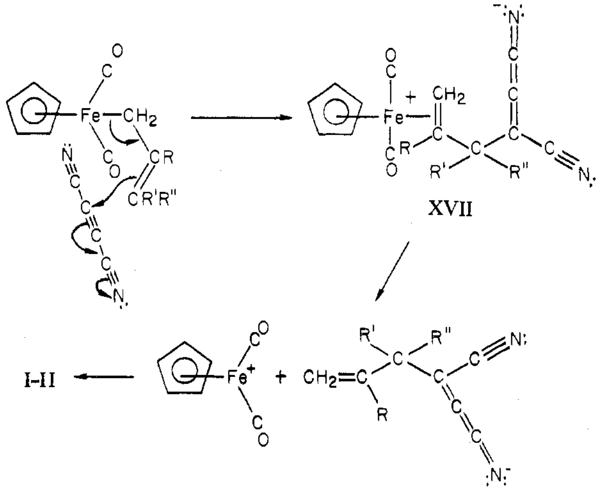


XVI

Discussion

Although reactions of η^5-$C_5H_5Fe(CO)_2CH_2C(R)$=$CR'R''$ have been carried out with a variety of electrophiles,[3-8] this investigation is the first one to utilize acetylenes in the latter capacity. The two acetylenes examined herein, dicyanoacetylene and hexafluorobut-2-yne, each afforded a different type of insertion product with the iron complexes, i.e., I–II and IV–V, respectively. The former are the dicarbonyls with an η^1-alkadienyl ligand containing a rearranged allyl fragment. The latter are monocarbonyls with an η^1,η^2-alkadienyl ligand containing an unrearranged allyl moiety. We now wish to address ourselves to possible mechanistic reasons for this difference.

The behavior of the iron–η^1-allyl complexes toward dicyanoacetylene can be readily rationalized on the basis of a mechanism analogous to that proposed for similar insertion reactions with SO_2, $ClSO_2NCO$,[3,6] or $SnCl_2$.[8] It is depicted below.



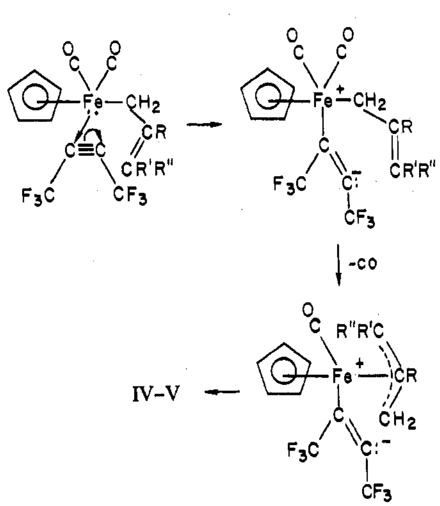
Cycloaddition of the acetylene to the η^1-allyl moiety appears to be prevented by the structure of the dipolar intermediate XVII which should contain a linear C=C=C=N fragment. Thus attack of the negative terminus at the =CH_2 carbon is precluded on steric grounds, and further reaction must occur by dissociation of the Fe–olefin bond and recombination of the ions to give I–II.

The more forcing reaction conditions required and the formation of a different type of product both indicate that the corresponding insertion of hexafluorobut-2-yne does not proceed via a parallel path. The observed lack of reactivity at ambient temperatures is ascribed to hexafluorobut-2-yne being a poorer electrophilic reagent than dicyanoacetylene toward the double bond of the η^1-allyl ligand. The reaction that occurs at higher temperatures likely proceeds via one of two pathways. The first path, Scheme I, comprises dissociation of a CO followed by attack of F_3CC≡CCF_3 at the iron, migration of the η^1-allyl onto bound F_3CC≡CCF_3, and coordination of the C(R)=CR'R'' double bond of the resultant η^1-alkadienyl ligand to the metal.

The second path is initiated by electrophilic attack of F_3CC≡CCF_3 at the metal, rearrangement of the η^1-allyl to η^3-allyl with loss of a carbonyl group and attack of the negative terminus of bound C_4F_6 at the sterically less hindered side of the η^3-allyl complete the reaction (Scheme II). Analogous mechanisms have been postulated for insertion of hexafluorobut-2-yne into metal–carbon bonds of η^3-allyl complexes.[24,25,31]

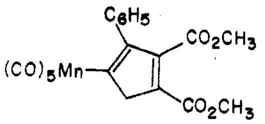
Both of the above paths are consistent with the nature of the products formed under the experimental conditions employed in this investigation, and both differ considerably from the path proposed for the corresponding reaction of dicyanoacetylene. In the absence of additional studies such as solvent effect on the rate we cannot favor one over the other.

Scheme II



Unlike the iron–η^1-allyl complexes discussed above, transition metal–propargyl complexes show little reactivity toward dicyanoacetylene. They are also less reactive than the η^1-allyl complexes and surprisingly nonselective in their behavior toward hexafluorobut-2-yne. All of these observations indicate that the propargyl triple bond is a much poorer site for attack by the electrophilic acetylenes than is the allyl double bond.

Similar general observations have been made on reactions of most of the metal–propargyl complexes with another electrophilic acetylene, dimethyl acetylenedicarboxylate. However, with $Mn(CO)_5CH_2C{\equiv}CC_6H_5$, $CH_3O_2CC{\equiv}CCO_2CH_3$ afforded on heating a ring-substituted η^5-cyclopentadienylmanganese tricarbonyl complex, VII, in moderate yield. What appears to be the rhenium analogue of VII was also prepared but could not be isolated pure. Compound VII may result from initial (3 + 2) cycloaddition of the acetylene to the propargyl ligand with concomitant 1,2 migration of the metal to yield XVIII. This intermediate, containing an sp^2 carbon of the cyclopentadienyl ring bonded to the manganese, would then undergo rapid rearrangement to VII with loss of two carbonyl groups.



XVIII

Although the above reaction path seems reasonable and bears complete analogy to (3 + 2) cycloaddition of various other electrophiles to coordinated propargyl ligands, it is proposed here with caution. The relative unreactivity of other electrophilic acetylenes toward metal–propargyl complexes and somewhat forcing reaction conditions employed in the synthesis of VII make other paths, e.g., those involving cleavage of the metal–carbon (propargyl) σ bond, viable as well.

The final point of discussion concerns the mechanism of the rapid addition of electrophilic olefins and acetylenes to the η^1-C_5H_5 ligand of η^5-$C_5H_5Fe(CO)_2(\eta^1$-$C_5H_5)$ to yield complexes XI–XIV. The two general paths that warrant special consideration are a dipolar one, possibly analogous to that for (3 + 2) cycloaddition involving metal–η^1-allyl complexes, and a concerted Diels–Alder one. In order possibly to distinguish between these two paths the stereochemistry of the reaction of η^5-$C_5H_5Fe(CO)_2(\eta^1$-$C_5H_5)$ with *trans*- and *cis*-$F_3C(CN)C{=}C(CN)CF_3$ to give XII was examined.

The formation of XII which most likely is the single diastereomer with trans CF_3 groups can be rationalized in terms of either mechanism. This is because a dipolar intermediate in a nonconcerted path can undergo rapid ring closure to preclude any loss of stereochemistry at the C–C bond of the added olefin. The isolation of the same diastereomer of XII using either *trans*- or *cis*-$F_3C(CN)C{=}C(CN)CF_3$ may be explained by a cis-to-trans isomerization and slow reaction of the cis olefin compared to the trans olefin. Previous studies on reactions of $F_3C(CN)C{=}C(CN)CF_3$ with transition metal complexes[4] have shown the above conditions indeed to be met.

Thus, the nature of these stereochemical results precludes distinguishing between the two types of mechanism in question. It is relevant, however, that similar cycloaddition reactions take place between silicon– or tin–η^1-cyclopentadienyl compounds and electrophilic olefins or acetylenes and are generally quite rapid.[46,52] This strengthens the possibility that the iron may not be involved in the reactions of η^5-$C_5H_5Fe(CO)_2(\eta^1$-$C_5H_5)$ and that the observed cycloaddition is different from that of the analogous η^1-allyl complexes.

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Registry No. I, 64082-03-7; II, 64082-02-6; III, 64082-01-5; IV, 64082-00-4; V, 64081-99-8; VI, 31832-97-0; VII, 59465-23-5; VIII, 63703-84-4; IX, 64081-98-7; X, 64081-97-6; XI, 64081-96-5; XII, 64081-95-4; XIII, 64081-94-3; XIV, 64081-93-2; XV, 64081-92-1; XVI, 64081-91-0; η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CH_2$, 38960-10-0; η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$, 31781-59-6; η^5-$C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$, 38905-70-3; η^5-$C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$, 31781-60-9; η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$, 33114-75-9; η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$, 34822-36-1; η^5-$C_5H_5Fe(CO)_2C(CH_2OH){=}CHCH_3$, 64070-53-7; $Mn(CO)_5CH_2C{\equiv}CC_6H_5$, 23626-46-2; $Re(CO)_5CH_2C{\equiv}CC_6H_5$, 59094-87-0; $Mn(CO)_4[P(C_6H_5)_3]CH_2C{\equiv}CC_6H_5$, 64070-52-6; $Mn(CO)_4[P(C_6H_5)_3]CH_2C{\equiv}CCH_3$, 64070-51-5; η^5-$C_5H_5Fe(CO)_2(\eta^1$-$C_5H_5)$, 12247-96-0; $NCC{\equiv}CCN$, 1071-98-3; $F_3CC{\equiv}CCF_3$, 692-50-2; η^5-$C_5H_5(CO)\overline{FeC(CF_3){=}C(CF_3)CH_2}CH{=}C(CH_3)_2$, 64082-23-1; $CH_3O_2CC{\equiv}CCO_2CH_3$, 762-42-5; TCNE, 670-54-2; *trans*-$NCCH{=}CHCN$, 764-42-1; *trans*-$F_3C(CN)C{=}C(CN)CF_3$, 2167-31-9; *cis*-$F_3C(CN)C{=}C(CN)CF_3$, 2167-32-0.

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Cyclopentadienylnitrosylmanganese Derivatives with Terminal and Carbon-Bridging Thiocarbonyl Groups[1]

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Reaction of $[RC_5H_4Mn(CO)(CS)(NO)]^+PF_6^-$ (R = H, CH_3) with KI gives the iodomanganese derivatives $RC_5H_4Mn(CS)(NO)I$. The reactions of these complexes with *trans*-perfluoro(1-methylpropenylate)silver, trifluoromethylthiosilver, and zinc dust yield $RC_5H_4Mn(CS)(NO)(\eta^1\text{-}C_4F_7)$, $RC_5H_4Mn(CS)(NO)SCF_3$, and $[RC_5H_4Mn(CS)(NO)]_2$ (cis and trans mixture), respectively. The reactions of several of the new complexes with Ph_3P are also described and discussed.

Introduction

Within the last decade, considerable attention has been given to the study of metal complexes containing coordinated thiocarbonyl.[3a] In contrast with metal carbonyls, the preparation of metal thiocarbonyl complexes requires the utilization of indirect synthetic routes since the free ligand is extremely labile. Despite the obvious resemblance between the coordinated carbonyl and thiocarbonyl ligands, their chemical properties differ substantially, and this can be attributed in part to the considerably greater polarity of the latter ligand. The carbon atom of a coordinated thiocarbonyl is significantly more electrophilic than that of a carbonyl ligand as evident by its higher susceptibility toward an attack by nucleophiles.[3] Furthermore, the nucleophilic character of the sulfur atom of a coordinated thiocarbonyl is evident from its facile reaction with electrophiles.[4] This specific feature suggests that the preparation of η^1-alkyl derivatives of metal thiocarbonyl complexes by synthetic routes involving strong nucleophiles is not likely to be straightforward. In fact, metal thiocarbonyl complexes of this type have not yet been reported.

In the majority of the currently known metal thiocarbonyl complexes, the coordinated thiocarbonyl behaves as a carbon-bonded terminal ligand. Recently, Dombek and Angelici reported[5] the preparation of some novel derivatives of tungsten which contain end-to-end bridging thiocarbonyl ligands. Carbon-bridging thiocarbonyl ligands were first proposed for the binuclear manganese complexes $[RC_5H_4Mn(CS)(NO)]_2$ (R = H, CH_3)[1] and have recently been confirmed by the x-ray crystal-structure analysis of *cis*-$[C_5H_5Fe(CS)(CO)]_2$.[6]

The present paper provides further details concerning the preparation of the above cited carbon-bridged thiocarbonyl derivatives of manganese and describes the syntheses and chemical properties of some novel mononuclear cyclopentadienylmanganese thiocarbonyl complexes.

Experimental Section

Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Infrared spectra were recorded on a Perkin-Elmer 225 grating spectrometer and calibrated against the 1601- and 1944-cm^{-1} bands of polystyrene film. Proton NMR spectra were recorded on a Jeol JHM-MH-100 spectrometer using TMS as an internal reference.

The solvents used during the course of this investigation were dried by conventional procedures as appropriate (e.g., tetrahydrofuran and diglyme were dried by boiling with $LiAlH_4$ and Na(spheres), respectively) and freshly distilled under nitrogen. Reactions and other manipulations involving organometallic solids and their solutions were carried out routinely under an atmosphere of dry nitrogen.

The cationic manganese complexes $[RC_5H_4Mn(CO)(CS)(NO)]^+PF_6^-$ (**1**, R = H, CH_3)[7] and the reagents trifluoromethylthiosilver[8] and perfluoro-1-methylpropenylsilver[9] were prepared according to published procedures.

Preparation of $RC_5H_4Mn(CS)(NO)I$ (2, R = H, CH_3). 2, R = H. A mixture of $[C_5H_5Mn(CO)(CS)(NO)]^+PF_6^-$ (6.0 g, 16.3 mmol) and KI (5.0 g, 30.1 mmol) was stirred in tetrahydrofuran (~180 mL) at ambient temperature for a period of 3 h. The solution was then filtered and the filtrate was dried under reduced pressure (25 °C (20 mm)). The crude green product was dissolved in a minimum amount of dichloromethane (~10 mL) and the solution obtained was diluted with pentane (~200 mL). The resulting solution was filtered and the clear green filtrate was cooled to −78 °C for ~5 h to afford, after separation, 2.0 g (38% yield) of the deep green crystalline product $C_5H_5Mn(CS)(NO)I$, mp 87–89 °C. The analytically pure sample of this compound was obtained by recrystallizations from pentane followed by sublimation at 50 °C (10^{-2} mm). Anal. Calcd for