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Synthesis and Reactions of New Organothallium(I) Compounds Derived from the Reactions of Cyclopentadienylthallium(I) with Electrophilic Olefins

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Received August 7, 1979

The reactions of cyclopentadienylthallium (TlCp) with several electrophilic olefins were investigated. Reaction of TlCp with tetracyanoethylene yields (tricyanovinyl)cyclopentadienide, $Tl^+[C_5H_4C(CN)C(CN)_2]^-$ (I), in 90% yield. Similarly the reaction of TlCp with 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene yields $Tl^+[C_5H_4C(CF_3)_2CH(CN)_2]^-$ (III). Protonation of I and III with anhydrous HCl results in the formation of the tricyanovinylcyclopentadiene, $C_{10}H_5N_3$, and both the linear and cross-conjugated isomers of 1,1-dicyano-2,2-bis(trifluoromethyl)-2-cyclopentadienylethane, $C_{11}H_6N_2F_6$, respectively. Compound I was found useful as a general reagent for production of tricyanovinyl-substituted metallocenes, including $[\eta^5\text{-}C_5H_4(CN)C(CN)_2]Mn(CO)_3$, $[\eta^5\text{-}C_5H_4C(CN)C(CN)_2]CuP(C_6H_5)_3$, and $[\eta^5\text{-}C_5H_4C(CN)C(CN)_2]Fe(\eta\text{-}C_5H_5)$. It has also been found that $[\eta^5\text{-}C_5H_4C(CN)C(CN)_2]Fe(\eta\text{-}C_5H_5)$ can be reacted with TlCp followed by addition of either $(\eta\text{-}C_5H_5)Fe(CO)_2I$ or $Mn(CO)_5Br$ to yield $[(\eta^5\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]_2C_2(CN)_2$ and $[(\eta^5\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]C_2(CN)_2[(\eta^5\text{-}C_5H_4)Mn(CO)_3]$, respectively. These latter two compounds are unusual examples of bridged metallocenes containing strongly electron-withdrawing groups on the bridging unit. The reaction of III with $(\eta\text{-}C_5H_5)Fe(CO)_2I$ was also investigated and found to yield $[(\eta^5\text{-}C_5H_4C(CF_3)_2CH(CN)_2]Fe(\eta\text{-}C_5H_5)$.

Introduction

The reactions of the half-sandwich complex cyclopentadienylthallium have been extensively investigated, and the compound is now in wide use as a synthetic reagent for the production of various metallocenes.[1] There have still been, however, no previous reports of reactions, involving cyclopentadienylthallium, resulting in products in which the thallium-ring interaction is retained. This fact has often been cited as evidence that the metal to ring bonding in cyclopentadienylthallium is predominately ionic in nature, and, indeed, other evidence supporting this interpretation has been obtained from infrared[2] and NMR studies[3] as well as an X-ray crystallographic determination of the solid-state structure.[4] On the other hand, data obtained from a gas-phase electron-diffraction investigation,[5] SCF calculations,[6] solution polarography, and conductivity studies[7] favor covalent bonding between thallium and the cyclopentadienyl group. These conflicting data are indicative, perhaps, of bonding of an intermediate nature, a conclusion which has gained support with the recent NMR work of Koridze et al.[8] which gave an estimated bond ionicity of 40–50%.

Because of the unusual nature of the bonding in cyclopentadienylthallium it was of interest to investigate its reactions with certain electron-deficient olefins. The reactions of such electrophiles with various metallocenes containing covalently η^5-bound cyclopentadienyl groups is well documented[9] and has been shown to result in the formation of either π complexes or charge-transfer salts, depending upon the extent of electron transfer. Either of these products might also be expected for cyclopentadienylthallium, if the thallium to ring bond has appreciable covalent character. The results presented in this paper detail the reactions of such olefins with cyclopentadienylthallium. Furthermore, it is also reported that several of the new organothallium compounds which are produced in these reactions are synthetically useful reagents and can be employed for the production of a variety of new substituted metallocenes.

Experimental Section

Reactions were performed under vacuum or dry nitrogen. Tetracyanoethylene (TCNE), Eastman Kodak Co., was vacuum sublimed at 50 °C prior to use. Cyclopentadienylthallium (TlCp) was purchased from the Alfa Division of Ventron Products and vacuum sublimed prior to use or prepared from Tl_2SO_4 and C_5H_6 in basic medium.[1] The bromopentacarbonylmanganese, chloromercuriferrocene, and cyclopentadienyliron dicarbonyl iodide were purchased from Strem Chemicals and used as received. (Triphenylphosphine)copper bromide[10] and 1,1-dichloro-2,2-dicyanoethylene[11] are prepared according to literature methods and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene was generously supplied by Dr. W. J. Middleton of E. I. DuPont Co. (Wilmington, DE). Acetonitrile and tetrahydrofuran were dried appropriately, stored under vacuum, and vacuum distilled immediately prior to use.

Infrared spectra were taken in chloroform or potassium bromide pellets and recorded on a Perkin-Elmer 521 in the range 4000–250 cm^{-1}, ^1H and ^{19}F (relative to $CFCl_3$, ϕ 0.00) NMR spectra were recorded on JEOL PS 100 or Varian HR-220 FT instruments, and elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN. Conductivity measurements were obtained by employing a Serfass bridge (Model RCM 15B1, A. H. Thomas, Co.) and a Fisher conductivity cell (cell constant at room temperature, 0.206). UV, visible, and near-infrared spectra were recorded on a Cary 14 spectrometer and mass spectra on a Perkin-Elmer Hitachi RMH-2 equipped with an AEI DS-50S data system. Differential pulse polarographs were obtained on a Princeton Applied Research Model 174A polarographic analyzer and controlled-potential electrolysis performed employing a PAR Model 173 galvanometer and Model 179 digital coulometer with a platinum-mesh working electrode and Ag/Ag^+ reference electrode. Electron paramagnetic resonance spectra were recorded as the first derivative on a Varian Model V-4502 X-band spectrometer.

Thallium(I) (Tricyanovinyl)cyclopentadienide (I). To 1.280 g (10.0 mmol) of TCNE dissolved in 200 mL of dry acetonitrile, was added, with a counterstream of N_2, 2.690 g (10.0 mmol) of TlCp, and the mixture stirred for 1 h. The solution was then filtered by suction and

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0020-1669/80/1319-1125$01.00/0

the residue washed with 25 mL of CH_3CN. The filtrate was evaporated to dryness with a rotary evaporator yielding 3.33 g (90% yield) of dark red crystalline material. Crystals were obtained by slowly cooling a saturated CH_3CN solution to 0 °C. The product was stored under vacuum to prevent formation of TlOH (mp 175 °C dec). Similar equimolar reactions on a smaller scale were carried out in a 5-mm quartz tube for EPR investigations. Spectra were recorded on frozen glasses which were warmed for short periods of time to allow the reaction to progress. A weak paramagnetic signal was observed approximately 2 min into the reaction. This signal then rapidly disappeared. The final product did not exhibit any signal.

Anal. Calcd for $(C_{10}H_4N_3)Tl$: C, 32.43; H, 1.08; N, 11.35. Found: C, 32.25; H, 1.11; N, 11.36.

^1H NMR (Me_2SO-d_6): δ 6.9 (complex multiplet, 1 H), 6.2 (complex multiplet, 2 H); 6.1 (complex multiplet, 1 H). IR (KBr, cm^{-1}): 2200 (vs), 2180 (sh, m), 1528 (s), 1491 (s), 1360 (s), 1342 (s), 1083 (w), 1022 (m), 912 (w), 824 (m), 758 (m), 750 (m), 661 (w), 544 (w), and 526 (w). Visible spectrum (CH_3CN): 448 nm (ϵ 24 700).

(Tricyanovinyl)cyclopentadiene (II). A 0.370-g sample (1.0 mmol) of I was placed in a 100-mL flask, and a large excess of anhydrous HCl was condensed in vacuo into the flask. After a stoichiometric amount of HCl had been consumed, the excess was removed resulting in the formation of a yellow solid, II. Purification of II was achieved by vacuum sublimation yielding a bright yellow, air-sensitive solid, $C_{10}H_5N_3$.

Mass spectrum: M^+ calcd 167.0483, M^+ found 167.0512 (82.76%); also major fragments at m/e 140.0372 [$(C_9H_4N_2)^+$ (100%)], 114.0338 [$(C_8H_4N)^+$ (54.31%)], and 91.0399 [$(C_6H_5N)^+$ (80.54%)]. ^1H NMR (CD_2Cl_2): δ 7.35 (m, 1 H), 6.63 and 6.43 ppm (m, 2 H, each). IR (KBr, cm^{-1}): 2200 (s), 1500 (s), 1438 (vs), 1380 (w), 1342 (w), 1032 (m), 1012 (w), 1000 (w), 955 (w), 886 (w), 810 (m), 800 (sh, w), and 710 (m).

Thallium(I) [1,1-Dicyano-2,2-bis(trifluoromethyl)ethyl]cyclopentadienide (III). To 1.070 g (5.0 mmol) of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene dissolved in 100 mL of dry CH_3CN was added 1.350 g (5.0 mmol) of TlCp. The solution immediately turned pink and then rapidly to orange. This orange solution was stirred for 1 h after which time all of the TlCp had dissolved. The solvent was then removed under vacuum yielding the air-sensitive pale orange product (approximately 100% yield). In order to facilitate characterization, we then protonated the product as indicated below.

1,1-Dicyano-2,2-bis(trifluoromethyl)-2-cyclopentadienylethane (IV). A 0.485-g sample (1.0 mmol) of III was placed in a 100-mL flask and a large excess of anhydrous HCl condensed in vacuo into the flask. After a stoichiometric amount of HCl had been consumed, the excess was removed resulting in the formation of a tan solid. Purification of IV was achieved by vacuum sublimation yielding a white, air-sensitive solid $C_{11}H_6N_2F_6$, mp 39–41 °C.

Mass spectrum: M^+ calcd 280.0435, M^+ found 280.0433 (11.69%); also major fragments at m/e 215.0218 [$(C_8H_5F_6)^+$ (100%)], 196.0296 [$(C_8H_5F_5)^+$ (14.52%)], 195.0229 [$(C_8H_4F_5)^+$ (26.61%)], 145.0261 [$(C_7H_4F_3)^+$ (41.94%)], and 127.0281 [$(C_8H_3N_2)^+$ (24.19%)]. ^1H NMR (100 and 220 MHz) ($CDCl_3$): IVa δ 7.00 (multiplet, 1 H), 6.68 (multiplet, 2 H), 3.22 (multiplet, 2 H), and 4.82 (singlet, 1 H); IVb δ 6.86 (multiplet, 1 H), 6.59 (multiplet, 2 H), 3.29 (multiplet, 2 H), and 4.79 (singlet, 1 H). IR (KBr, cm^{-1}): 2182 (sh, m), 2162 (m), 2115 (s), 2080 (s), 1658 (w), 1355 (w), 1240 (s, br), 1190 (s, br), 945 (m), 897 (m), 818 (w), 733 (m), and 708 (m).

[(Tricyanovinyl)cyclopentadienyl]tricarbonylmanganese (V). To 2.200 g (8.0 mmol) of bromomanganese pentacarbonyl dissolved in 200 mL of dry THF was added 2.960 g (8.0 mmol) of I. The mixture was stirred and refluxed for 3 h or until the disappearance of the $Mn(CO)_5Br$ as observed by TLC. Next the mixture was filtered by suction while still warm and the residue washed with 25 mL of THF. The solvent was removed and this crude material was initially purified by column chromatography (silica gel, 0.05–0.2 mm (70–270 mesh)) with CH_2Cl_2 as the eluent. Further purification was achieved by TLC (silica gel plates, $CHCl_3$ developing solvent, R_f 0.36). This yielded 150 mg (6.15% yield) of the red $Mn(CO)_3(C_{10}H_4N_3)$, mp 89.5–90 °C. Purification could also be achieved by sublimation of the column-eluted material.

Anal. Calcd for $Mn(CO)_3(C_{10}H_4N_3)$: C, 51.15; H, 1.31; N, 13.77. Found: C, 51.54; H, 1.87; N, 12.89.

Mass spectrum: M^+ calcd 304.9634, M^+ found 304.9686 (13.51%); also major fragments at m/e 220.9740 [$(C_{10}H_4N_3Mn)^+$ (100%)], 193.9657 [$(C_9H_3N_2Mn)^+$ (48.37%)], and 54.9352 [$(Mn)^+$ (68.68%)]. ^1H NMR ($CDCl_3$): δ 5.22 and 5.80 (poorly resolved triplets, 2 H each).

IR: (KBr, cm^{-1}) 2240 (sh, w), 2220 (m), 2030 (vs), 1950 (vs), 1930 (vs), 1515 (s), 1370 (s), 1295 (m), 1080 (m), 1050 (w), 850 (m), 812 (w), 652 (s), 610 (s); ($CHCl_3$, cm^{-1}) 2220 (m), 2050 (vs), 1975 (vs), 1550 (s), 1460 (m), 1385 (m), 1310 (m), 1080 (w), 1060 (w), 850 (m); (pentane, cm^{-1}) 2030 (s), 1962 (s), 1928 (s).

[(Tricyanovinyl)cyclopentadienyl](triphenylphosphine)copper (VI). To 1.280 g (5.0 mmol) of (triphenylphosphine)copper chloride dissolved in 125 mL of dry THF was added 1.850 g (5.0 mmol) of I. The mixture was stirred for 24 h and then filtered. The residue was washed with 25 mL of THF and the filtrate evaporated to dryness. This solid was dissolved in a minimum amount of CH_2Cl_2 and a large amount of pentane added. The resulting orange precipitate was recovered and further purified by TLC (silica gel plates, CH_2Cl_2 developing solvent, R_f 0.18). The product is moderately air sensitive but can be exposed to air for short periods of time: crude product yield 200 mg (8.1%), mp 140–141 °C dec.

Mass spectrum: M^+ calcd 493.0595, M^+ found 493.0682 [$(C_{28}H_{19}N_3P^{65}Cu)^+$ (10.39%)]; M^+ calcd 491.0598, M^+ found 491.0702 [$(C_{28}H_{19}N_3P^{63}Cu)^+$ (24.04%)]; major fragments at m/e 327.0298 [$(C_{18}H_{15}P^{65}Cu)^+$ (15.32%)], 325.0301 [$(C_{18}H_{15}P^{63}Cu)^+$ (34.46%)], 262.0846 [$(C_{18}H_{15}P)^+$ (92.52%)], and 183.0364 [$(C_{12}H_8P)^+$ (100%)]. ^1H NMR (Me_2SO-d_6): δ 7.37 (complex multiplet, 15 H), 6.20 and 6.12 (poorly resolved triplets, 2 H each). IR (KBr, cm^{-1}): 2195 (s), 2160 (sh, w), 1503 (s), 1343 (m), 1090 (w), 1025 (m), 915 (w), 825 (m), 765 (m), and 680 (w).

Ferrocenyltricyanoethylene (VII). I (1.67 g, 4.5 mmol) and cyclopentadienyliron dicarbonyl iodide (1.37 g, 4.5 mmol) were dissolved in 200 mol of dry THF. The mixture was refluxed with stirring for 24 h and then filtered by suction while still warm. The residue was washed with 25 mL of THF and the solvent removed. This crude material was chromatographed on a silica gel column (0.05–0.2 mm (70–270 mesh)). Methylene chloride eluted 51 mg (4.0% yield) of dark blue VII (mp 125–127 °C, lit. mp 133–134 °C),[12] R_f 0.71, and 53 mg (2.7% yield) of deep purple 1,1-dicyano-2,2-diferrocenylethylene (mp 270 °C, dec), R_f 0.52.

Mass spectrum: M^+ calcd 287.0145, M^+ found 287.0142 [$(C_{15}H_9N_3{}^{56}Fe)^+$ (100%)]; major fragments at m/e 221.9765 [$(C_{10}H_4N_3{}^{56}Fe)^+$ (10.62%)], 120.9749 [$(C_5H_5{}^{56}Fe)^+$ (61.86%)], and 55.9373 [$(^{56}Fe)^+$ (58.01%)].

1,1-Dicyano-2,2-diferrocenylethylene (VIII). To 0.400 g (1.4 mmol) of ferrocenyltricyanoethylene (prepared by literature methods)[12] in 125 mL of dry THF was added 0.276 g (1.4 mmol) of TlCp. The mixture was refluxed with stirring for 24 h at which time 0.427 g (1.4 mmol) of $C_5H_5Fe(CO)_2I$ was added. Reflux was continued for another 24 h, and the mixture was then filtered. After removal of the solvent the product was separated by column chromatography (silica gel, 0.05–0.2 mm (70–270 mesh)). Methylene chloride eluted 95 mg (15.7% yield) of the deep purple product, mp 270 °C dec.

Anal. Calcd for $C_{24}H_{18}N_2Fe_2$: C, 64.57; H, 4.04; N, 6.28; Fe, 25.11. Found: C, 64.66; H, 3.89; N, 6.12; Fe, 24.97.

Mass spectrum: M^+ calcd 446.0168, M^+ found 446.0142 (100%); major fragments at m/e 380.9761 [$(C_{19}H_{13}N_2{}^{56}Fe_2)^+$ (71.38%)], 353.9756 [$(C_{18}H_{12}N^{56}Fe_2)^+$ (17.02%)], 186.0110 [$(C_{10}H_{10}{}^{56}Fe)^+$ (43.16%)], 120.9738 [$(C_5H_5{}^{56}Fe)^+$ (32.11%)], 55.9370 [$(^{56}Fe)^+$ (24.48%)]. ^1H NMR ($CDCl_3$): δ 5.13 and 4.69 (poorly resolved triplets, 4 H each), 4.32 (singlet, 10 H). IR (KBr, cm^{-1}): 2204 (s), 2198 (sh, m), 1492 (s), 1445 (s), 1410 (w), 1380 (m), 1360 (sh, w), 1348 (w), 1317 (m), 1296 (m), 1050 (w), 1000 (w), 840 (m), 825 (m), 722 (m). Visible spectrum (CH_3CN): 565 nm (ϵ 3340). Polarography (10^{-3} M solution in CH_3CN with 0.1 M Et_4NClO_4): two reversible waves at +0.62 and +0.75 V vs. SCE.

Alternate Synthesis of VIII. Reaction of Lithioferrocene and 1,1-Dichloro-2,2-dicyanoethylene. An ethereal solution of $Cl_2C{=}C(CN)_2$[11] (250 mg, 1.7 mmol) was added dropwise to a stirred solution of lithioferrocene[13] (1.7 mmol) in ether at −78 °C. The solution was warmed to room temperature after addition of the olefin was complete, and the mixture was stirred overnight. Following filtration and

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evaporation of the solvent, the crude reaction mixture was purified by TLC (silica gel plates, CH_2Cl_2 developing solvent). This yielded several products including ferrocene (98 mg, 31.0% yield) and cyanoferrocene (82 mg, 23.0% yield) as identified by their melting points and mass spectra. 1,1-Dicyano-2,2-diferrocenylethylene (VIII) was isolated in 0.5% yield and was identified by its high-resolution mass spectrum, infrared spectrum, and chromatographic R_f. Other products isolated in low yield (<1%) include $[C_5H_4C(Cl)C(CN)_2]Fe(C_5H_5)$ (IX) and $[C_5H_4CHC(CN)_2]Fe(C_5H_5)$ (X). Reaction of chloromercuriferrocene and 1,1-dichloro-2,2-dicyanoethylene yielded IX and X in greater amounts but did not produce compound VIII, as described below.

To 0.760 g (5 mmol) of $Cl_2C{=}C(CN)_2$ in acetonitrile was added 2.105 g (5 mmol) of chloromercuriferrocene. The solution was refluxed for 3 h and then filtered. TLC (silica plates, CH_2Cl_2 developing solvent) yielded two purple products, the most mobile (R_f = 0.66) of which was isolated in 10.5% yield (350 mg) and identified as IX, mp 110–111 °C. The other purple product was identified as X (91 mg, 7.0% yield), mp 91–92 °C, R_f 0.52.

Anal. Calcd for $C_{14}H_9N_2ClFe$ (IX): C, 56.76; H, 3.04; N, 9.46. Found: C, 56.70; H, 2.94; N, 8.79.

Mass spectrum: M^+ calcd 297.9508, M^+ found 297.9520 [$(C_{14}H_9N_2{}^{37}Cl^{56}Fe)^+$ (28.37%)], and M^+ calcd 295.9803, M^+ found 295.9808 [$(C_{14}H_9N_2{}^{35}Cl^{56}Fe)^+$ (90.44%)]; also major fragments at m/e 157.9404 [$(C_5H_5{}^{56}Fe^{37}Cl)^+$ (49.79%)], 155.9430 [$(C_5H_5{}^{56}Fe^{35}Cl)^+$ (100%)], 120.9746 [$(C_5H_5{}^{56}Fe)^+$ (29.46%)], 55.9371 [$({}^{56}Fe)^+$ (37.45%)]. ^1H NMR ($CDCl_3$): δ 5.15 (singlet, 5 H), 5.11 and 4.74 (triplets, 2 H each). IR (KBr, cm^{-1}): 2210 (m), 1527 (s), 1423 (w), 1407 (w), 1377 (m), 1270 (m), 1098 (w), 1051 (w), 995 (w), 945 (m), 892 (w), 816 (m).

Anal. Calcd for $C_{14}H_{10}N_2Fe$ (X): C, 64.12; H, 3.82; N, 10.69. Found: C, 64.04; H, 3.98; N, 9.30.

Mass spectrum: M^+ calcd 262.0193, M^+ found 262.0195 (100%); also major fragments at m/e 196.9784 [$(C_9H_5N_2{}^{56}Fe)^+$ (44.81%)], 186.0110 [$(C_{10}H_{10}{}^{56}Fe)^+$ (75.96%)], 145.9694 [$(C_6H_4N^{56}Fe)^+$ (23.25%)], 120.9737 [$(C_5H_5{}^{56}Fe)^+$ (79.46%)], 55.9372 [$({}^{56}Fe)^+$ (79.55%)]. ^1H NMR ($CDCl_3$): δ 4.85 and 4.71 (poorly resolved triplets, 2 H each), 4.15 (singlet, 5 H), and 7.73 (singlet, 1 H). IR (KBr, cm^{-1}): 2218 (m), 1570 (s), 1445 (w), 1400 (w), 1350 (m), 1251 (m), 1100 (vw), 1039 (m), 994 (vw), 829 (w), 820 (w), 662 (m).

1,1-Dicyano-2-ferrocenyl-2-cymantrenylethylene (XI). To 0.400 g (1.4 mmol) of ferrocenyltricyanoethylene in 125 mL of dry THF was added 0.376 g (1.4 mmol) of TlCp. The mixture was refluxed with stirring for 24 h at which time 0.385 g (1.4 mmol) of $Mn(CO)_5Br$ was added. Reflux was continued until TLC showed that all of the $Mn(CO)_5Br$ had reacted (approximately 2 h), and then the solution was filtered. The filtrate was evaporated to dryness and the product obtained by column chromatography (silica gel, 0.05–0.2 mm (70–270 mesh)). Chloroform eluted 200 mg (31% yield) of the green product. Further purification was achieved by TLC (silica gel plates, $CHCl_3$ developing solvent, R_f 0.45) and finally crystallization from $CHCl_3$ at 0 °C under vacuum; mp 134–135.5 °C.

Anal. Calcd for $C_{22}H_{13}N_2O_3FeMn$: C, 56.90; H, 2.80; N, 6.03. Found: C, 56.13; H, 2.91; N, 5.79.

Mass spectrum: M^+ calcd 463.9656, M^+ found 463.9652 (16.12%); also major fragments at m/e 379.9832 [$(C_{19}H_{13}N_2{}^{56}FeMn)^+$ (100%)], 352.9556 [$(C_{18}H_{12}N^{56}FeMn)^+$ (9.22%)], 273.0369 [$(C_{17}H_{13}{}^{56}Fe)^+$ (10.49%)], 120.9676 [$(C_5H_5{}^{56}Fe)^+$ (16.51%)], 55.9370 [$({}^{56}Fe)^+$ (12.39%)], 54.9397 [$(Mn)^+$ (28.81%)]. ^1H NMR ($CDCl_3$): δ 5.49, 5.16, 4.96, and 4.79 (poorly resolved triplets, 2 H each), 4.38 ppm (singlet, 5 H). IR: (KBr, cm^{-1}) 2220 (s), 2215 (sh, m), 2020 (vs), 1960 (vs), 1920 (vs), 1526 (m), 1458 (m), 1400 (w), 1375 (m), 1315 (w), 1290 (m), 1255 (s), 1100 (m), 1030 (m), 925 (w), 845 (w), 828 (m), 794 (s) and 650 (s); ($CHCl_3$, cm^{-1}) 2223 (m), 2040 (vs), 1960 (vs), 1548 (m), 1460 (m), 1385 (m), 1310 (w), 1080 (w), 1040 (w), 830 (m).

1,1-Dicyano-2,2-bis(trifluoromethyl)-2-ferrocenylethane (XII). Method 1. To approximately 5.0 mmol of III dissolved in 100 mL of dry THF was added 1.620 g (5.0 mmol) of $C_5H_5Fe(CO)_2I$. The mixture was refluxed overnight and then filtered and the residue washed. The filtrate was evaporated to dryness, and the products were separated by column chromatography (silica gel, 0.05–0.2 mm (70–270 mesh)). Methylene chloride eluted 160 mg (8% yield) of XII (R_f 0.48) as well as some unreacted starting material. The product was further purified by repeated recrystallizations from pentane by cooling to 0 °C, yielding yellow crystals, mp 64.5–65 °C.

Method 2. 1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene (1.07 g, 5.0 mmol) and chloromercuriferrocene (2.110 g, 5.0 mmol) were dissolved in 100 mL of dry CH_3CN. The solution was refluxed for 1 h and then filtered. The filtrate was evaporated to dryness, and the products were separated by column chromatography as above. This yielded 40 mg (2% yield) of XII as well as some diferrocenylmercury and unreacted starting materials.

Anal. Calcd for $C_{16}H_{10}F_6N_2Fe$: C, 48.00; H, 2.50; N, 7.00; F, 28.50; Fe, 14.00. Found: C, 47.90; H, 2.57; N, 6.95; F, 28.35; Fe, 14.23.

Mass spectrum: M^+ calcd 400.0098, M^+ found 400.0071 (100%); also major fragments at m/e 334.9934 [$(C_{13}H_9F_6{}^{56}Fe)^+$ (60.85%)], 315.9965 [$(C_{13}H_9F_5{}^{56}Fe)^+$ (27.06%)], 241.0632 [$(C_{13}H_9F_4)^+$ (62.14%)], 221.0578 [$(C_{13}H_8F_3)^+$ (9.02%)], 201.0518 [$(C_{13}H_7F_2)^+$ (11.17%)], 195.0229 [$(C_8H_4F_5)^+$ (19.06%)], 176.0253 [$(C_8H_4F_4)^+$ (17.94%)], 139.9716 [$(C_5H_5FFe^{56})^+$ (32.49%)], 120.9747 [$(C_5H_5{}^{56}Fe)^+$ (63.92%)], 55.9366 [$({}^{56}Fe)^+$ (22.76%)]. ^1H NMR (CS_2/C_6D_6): δ 4.23 (multiplet, 2 H), 4.06 (singlet, 7 H), and 3.54 (singlet, 1 H). ^{19}F NMR (CS_2/C_6D_6): ϕ 62.66 (singlet). IR (KBr, cm^{-1}): 2908 (w), 1328 (w), 1308 (m), 1282 (m), 1255 (m), 1242 (m), 1230 (m), 1190 (s), 1165 (m), 1155 (w), 1058 (m), 960 (w), 820 (m), and 722 (m).

Electrochemistry of VIII. Electrochemical potentials were recorded by differential pulse polarography. The sample was 10^{-3} M in CH_3CN solution with 0.1 M Et_4NClO_4 as the supporting electrolyte. A Model 174A Princeton Applied Research (PAR) polarographic analyzer connected to a three-electrode cell with a glassy carbon working electrode, Ag/Ag^+ reference electrode, and platinum wire counter electrode was used to perform the experiment. All reported potentials were then standardized relative to the saturated calomel electrode (SCE). Two well-defined one-electron waves at +0.62 and +0.75 V vs. SCE were observed for VIII.

Similar solutions of VIII were also subjected to constant-potential electrolysis. These were performed with a PAR Model 179 digital coulometer and PAR Model 173 galvanometer. The solution was stirred vigorously during the experiment with a PAR Model 377 synchronous stirring motor. After oxidation by precisely 1 faraday/mol, at +0.7 V vs. SCE, the solution was transferred under N_2 to a quartz cell for spectrophotometric analysis. This solution exhibited only one absorption in the range 400–2000 nm, 600 nm (ϵ 2080). Transfer of this solution to a quartz EPR tube equipped with a vacuum stopcock enabled the EPR investigation of the monocation solution at 77 K, which did not reveal any signal.[14] The solution was then returned to the electrolysis cell and subjected to further exhaustive oxidation at +1.0 V vs. SCE. Subsequent similar spectrophotometric analysis of this solution showed only one absorption at 635 nm (ϵ 1490). Exposure of either solution to air resulted in decomposition.

Results

Reaction of an equimolar solution of TlCp and tetracyanoethylene (TCNE) at room temperature results in the formation of a 90% yield of thallium(I) tricyanovinylcyclopentadienide, I, according to the equation

$$TlCp + TCNE \xrightarrow[1\ h]{CH_3CN} Tl^+[C_5H_4C(CN)C(CN)_2]^- + HCN$$

This reaction is characterized by three color changes. Upon addition of the reactants, the solution immediately turns bright blue and then rapidly to green and finally the dark red color characteristic of I.

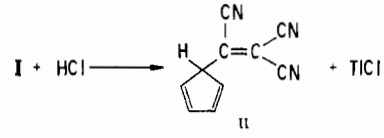
The composition of I was initially established by elemental analysis and its molecular structure deduced from the spectroscopic data. Thus the infrared spectrum of I exhibits a nitrile band in the region expected for a conjugated nitrile, along with absorptions at 1528 and 1360 cm^{-1} which can be assigned to the cyclopentadiene ring and are indicative of a σ-bonded diene type cyclopentadienyl ligand.[15] Additionally a band at 1491 cm^{-1} can be attributed to the carbon double

(14) This is not unexpected since it has been previously noted that EPR signals of ferrocenium systems can only be seen in the case of powdered pure solids at 10 K (see ref 32).

(15) H. P. Fritz, *Adv. Organomet. Chem.*, 1, 239 (1964).

bond absorption of the tricyanovinyl group, the intensity of which is slightly enhanced by the presence of the strongly electron-withdrawing groups.[16] The ^{1}H NMR is also indicative of a substituted cyclopentadiene with complex resonances at δ 6.9, 6.2, and 6.1 in a ratio of 1:2:1.

Further chemical structural elucidation of I was afforded by its protonation with anhydrous HCl. The product was assigned the elemental composition $C_{10}H_5N_3$, II, on the basis of the exact mass measurements on the parent ion. The



II

observation in the ^{1}H NMR of a multiplet of intensity 1 at δ 7.35 for the methine proton indicates that II is the unconjugated isomer since such a low-field methine resonance would not be expected if II were either the cross or linearly conjugated isomer. Final confirmation of the structure of I was achieved by a single-crystal X-ray investigation which is described elsewhere.[17]

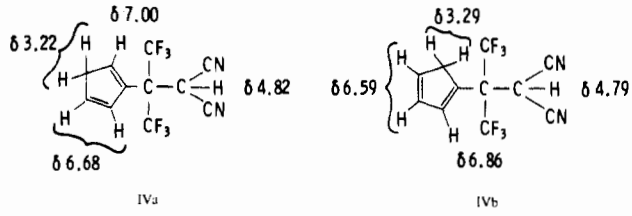
TlCp was also found to readily react with 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene in acetonitrile solution. Upon addition of the two reactants, the solution immediately turned pink and then rapidly orange. Completion of the reaction was then indicated after only 1 h by the disappearance of all undissolved TlCp. The final orange solution was extremely air sensitive, and the solvent was therefore removed in vacuo resulting in a pale orange solid, thallium(I) [1,1-dicyano-2,2-bis(trifluoromethyl)ethyl]cyclopentadienide (III), in essentially quantitative yield.

$$\text{TlCp} + (CF_3)_2C{=}C(CN)_2 \xrightarrow[1\text{ h}]{CH_3CN} Tl^+[C_5H_5C(CF_3)_2C(CN)_2]^-$$

Due to its extreme air sensitivity, compound III could not be definitely characterized, but its protonation with anhydrous HCl yielded IV. The structure of IV which was deduced from its spectroscopic data is consistent with the proposed formulation of III. High-resolution mass spectroscopy determined the elemental composition of IV as $C_{11}H_6N_2F_6$, and the fragmentation observed supports the proposed structure showing an initial loss of $-CH(CN)_2$ fragment followed by loss of $-HF$ and $-CF_2$. These data are consistent with the formulation of IV as the 1,1-dicyano-2,2-bis(trifluoromethyl)-2-cyclopentadienylethane isomer rather than the 1,1-bis(trifluoromethyl)-2,2-dicyano-2-cyclopentadienylethane.

The ^{1}H NMR (220 MHz) of IV indicates that the isolated compound is actually a 50:50 mixture of isomers corresponding to the linearly and cross-conjugated isomers of 1,1-dicyano-2,2-bis(trifluoromethyl)-2-cyclopentadienylethane. The spectrum consists of two unresolved multiplets each of intensity 1 at δ 7.00 and 6.86, two complex multiplets each of intensity 2 ($J \sim 1$ Hz) at δ 6.68 and 6.59, two singlets each of intensity 1 at δ 4.82 and 4.79, and two unresolved multiplets each of intensity 2 at δ 3.22 and 3.29 ppm. Consideration of the effects of the strongly electron-withdrawing groups allows the assignment of these resonances to structures IVa,b.

For example, the methylene protons in the cross-conjugated isomer, IVa, are further removed from the deshielding effects of the electron-withdrawing groups and would therefore be expected at slightly higher field (3.22 ppm) than in the linearly conjugated isomer, IVb (3.29 ppm). Similarly, the vinyl protons in IVa are closer to the deshielding groups and are

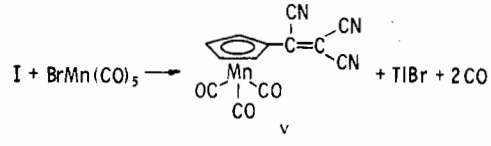


IVa IVb

consequently observed at slightly lower field (6.68 ppm) than in IVb (6.86 ppm). Similar guidelines allow the assignment of the remaining resonances. NMR evidence of this type has previously been used to distinguish between the isomers of nitrocyclopentadiene.[18] Additionally the appearance of singlets at δ 4.82 and 4.79 attributable to the ethyl protons substantiates the structure suggested from the mass spectral data. Not only are the chemical shifts indicative of a $-CH(CN)_2$ proton (as opposed to a $-CH(CF_3)_2$ formulation which would be observed at slightly higher field) but the lack of any proton–fluorine coupling completely rules out the possibility of a $-CH(CF_3)_2$ unit since coupling for this type system is on the order of 10 Hz[19] and easily observed.

The reactions of compounds I and III were explored with a number of different organometallic complexes and were found to result in the formation of new substituted metallocenes and cyclopentadienyl metal complexes.

The reaction of I and $Mn(CO)_5Br$ yielded an air-stable, sublimable red solid, $(C_{10}H_4N_3)Mn(CO)_3$ (V), in 6.2% yield.

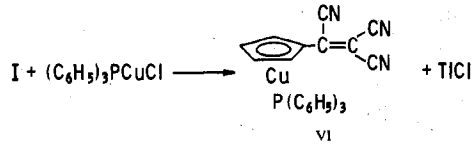


V

The composition of V was established by elemental analysis and high-resolution mass spectrometry. The mass spectrum exhibits a parent peak at m/e 304.9686 $(C_{13}H_4O_3N_3Mn)^+$ as well as the anticipated fragmentation pattern due to losses of the carbonyls and cyano groups. The ^{1}H NMR spectrum shows two poorly resolved triplets at δ 5.12 and 5.80 thus exhibiting a downfield shift of the cyclopentadienyl protons relative to unsubstituted $(\eta\text{-}C_5H_5)Mn(CO)_3$, δ 4.20, as was expected due to the presence of the strongly electron-withdrawing tricyanovinyl group. The solution infrared spectrum of V in chloroform exhibits two bands in the $\nu_{C\equiv O}$ region at 2030 and 1975 cm^{-1} as would be expected for a compound such as unsubstituted $(\eta\text{-}C_5H_5)Mn(CO)_3$ in which the local symmetry of the carbonyls is C_{3v}. Apparently anomalous behavior appears if the infrared spectrum is taken in a nonpolar solvent such as pentane or in the solid state due to the appearance of a third band in the $\nu_{C\equiv O}$ region at 1930 cm^{-1}. This is not without precedence, however, since a previous infrared study[20] of $(\eta\text{-}C_5H_5)Mn(CO)_3$ derivatives has shown that introduction of a polar substituent on the cyclopentadienyl ring leads to disruption of the C_{3v} symmetry thus making the carbonyls inequivalent and resulting in three absorptions. The third band is not noticeable in polar solvents, such as chloroform, due to broadening of the bands from solvent interactions.

Compound I reacts with $[ClCu(Ph_3P)]_4$ to give the air-sensitive compound, $(C_{10}H_4N_3)CuPPh_3$ (VI), in analogy to the synthesis of compounds of this type by Cotton and Marks.[21] The mass spectrum of VI supports the above formulation and

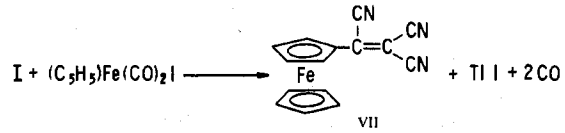
(16) J. K. Brown and K. J. Morgan, *Adv. Fluorine Chem.*, **4**, 253 (1965).
(17) M. B. Freeman, L. G. Sneddon, and J. C. Huffman, *J. Am. Chem. Soc.*, **99**, 5194 (1977).
(18) (a) R. C. Kerber and M. J. Chick, *J. Org. Chem.*, **32**, 1329 (1967); (b) T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc. A*, 106 (1974).
(19) R. Gregory, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. C*, 1750 (1970).
(20) A. N. Nesmeyanov, K. N. Anisimov, B. V. Lokshin, N. E. Kolobova, and Y. V. Makarov, *Dokl. Akad. Nauk SSSR*, **176**, 1082 (1967).
(21) F. A. Cotton and T. J. Marks, *J. Am. Chem. Soc.*, **92**, 5115 (1970).



VI

exhibits a parent copper isotope pattern at m/e 493.0682 and 491.0702 ($C_{28}H_{19}N_3PCu$) as well as fragments corresponding to $CuP(C_6H_5)_3^+$ and $P(C_6H_5)_3^+$. The downfield shift of the cyclopentadienyl protons due to the deshielding cyano groups was again observed in the NMR of VI. Infrared data were also in agreement with the proposed structure, showing absorptions attributable to the tricyanovinyl, cyclopentadienyl, and triphenylphosphine groups.

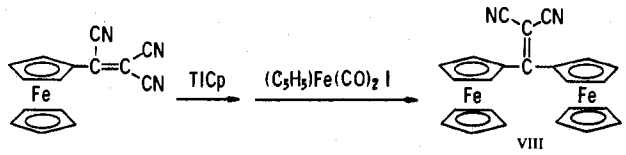
The reaction of I and $(\eta\text{-}C_5H_5)Fe(CO)_2I$ affords (tricyanovinyl)ferrocene (VII). This compound had previously



VII

been synthesized by the reaction of TCNE with chloromercuriferrocene in refluxing acetonitrile or with ferrocenyl(triphenylphosphine)gold in refluxing benzene.[12] The $(\eta\text{-}C_5H_5)Fe(CO)_2I$ reaction also yielded a small amount of a second compound, $[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]_2C_2(CN)_2$ (VIII), and it was subsequently found that the presence of additional TlCp increased its yield substantially.

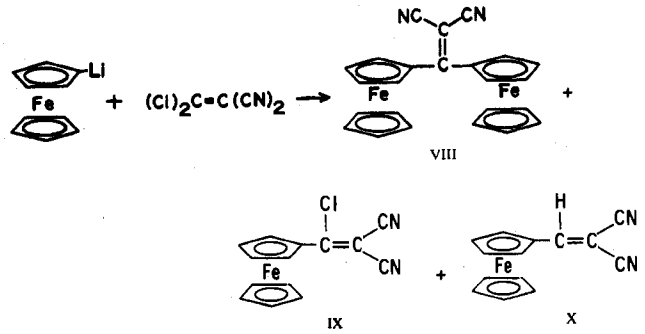
On the basis of this observation, a synthetic procedure was developed for the production of VIII in higher yields. That is, the reaction of VII with TlCp followed by addition of $(\eta\text{-}C_5H_5)Fe(CO)_2I$ and reflux produces VIII in 15.7% yield.



VIII

Elemental analysis and high-resolution mass spectroscopy established the composition of VIII as $C_{24}H_{18}N_2Fe_2$. The infrared spectrum of VIII indicated a ferrocene derivative substituted at one ring by a nitrile-containing substituent, due to the observation of absorptions at 1050 and 1000 cm^{-1} which are typical of substituted ferrocenes[22] as well as a band in the nitrile region. This conclusion is substantiated by the ^1H NMR spectrum which exhibits resonances due to both substituted and unsubstituted cyclopentadienyl rings. A conclusive structural confirmation was not possible, however, on the basis of the NMR and IR data, since these data would be in agreement with either the 1,1-dicyanovinylidene (as proposed) or the 1,2-dicyanoethylene isomer of VIII. The mass spectral fragmentation of this compound, however, did not support a 1,2-dicyanoethylene formulation since no peak due to loss of $(C_5H_5Fe)^+$ from the parent ion was observed. Fragmentation of this type has been previously reported[23] for 1,2-diferrocenyl-1,2-diphenylethylene. This fact was, however, not judged conclusive enough to completely eliminate the 1,2-dicyanoethylene structure, and a second synthetic route to VIII was therefore devised as chemical proof of the proposed structure.

Reaction of lithioferrocene with 1,1-dicyano-2,2-dichloroethylene resulted in a low yield of VIII, as confirmed by spectroscopic data, as well as the formation of two new products $[\eta^5\text{-}C_5H_4C(Cl)C(CN)_2]Fe(\eta\text{-}C_5H_5)$ (IX) and $[\eta^5\text{-}C_5H_4CHC(CN)_2]Fe(\eta\text{-}C_5H_5)$ (X).

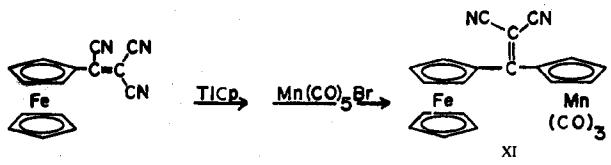


VIII IX X

The structures of compounds IX and X are consistent with the spectroscopic data presented in the Experimental Section. The formation of VII in this reaction provides strong support for the formulation of VIII as the 1,1-dicyanovinylidene isomer.

Final confirmation of the structure of VIII has recently been achieved through a single-crystal X-ray investigation.[24] This study confirmed the proposed 1,1-dicyanovinylidene structure and showed that the ferrocenyl units adopt a pseudo-trans configuration with respect to the plane of the dicyanovinylidene bridging unit. This configuration would be expected on the basis of steric factors and has been previously observed for other bridged ferrocenes.[25]

The basic reaction for the formation of VIII appears to be general, and a mixed-metal system bridged by the same type dicyanovinylidene unit $[(\eta^5\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]C_2(CN)_2[(\eta^5\text{-}C_5H_4)Mn(CO)_3]$ (XI) was similarly prepared by the

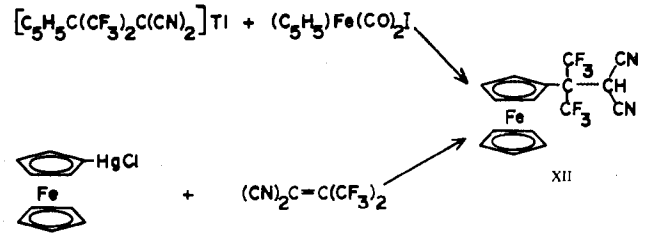


XI

addition of $BrMn(CO)_5$ instead of $(\eta\text{-}C_5H_5)Fe(CO)_2I$ in the second step of the reaction. The composition of XI was again established by elemental analysis and high-resolution mass spectroscopy. The mass spectral fragmentation pattern is similar to that of VIII with the exception of the initial loss which corresponds to the loss of all three carbonyls in one step. This type of fragmentation has previously been observed in bridged carbonyl complexes of this type.[26] As seen in the case of compound V, the chloroform solution infrared spectrum of XI exhibits only two bands in the carbonyl region, but three bands are observed in the solid state. The ^1H NMR spectrum also contains the resonances expected for the two inequivalent substituted cyclopentadienyls and the one unsubstituted cyclopentadienyl.

The preparation of 1,1-dicyano-2,2-bis(trifluoromethyl)-ethyl-substituted metallocenes was also explored through the use of compound III. Overnight reflux of $(\eta\text{-}C_5H_5)Fe(CO)_2I$ and III was found to yield $[(\eta^5\text{-}C_5H_4C(CF_3)_2CH(CN)_2]Fe(\eta\text{-}C_5H_5)$ (XII) in 8% yield. In analogy to the two methods of preparation of tricyanovinylferrocene, it was subsequently found that XII could also be prepared by the reaction of the original olefin, $(CN)_2C{=}C(CF_3)_2$, with chloromercuriferrocene followed by hydrolysis during reaction workup. The composition of XII was established by both elemental analysis and a high-resolution mass spectral study. The fragmentation observed in the mass spectrum was similar to that of IV and

(22) M. Rosenblum, "Chemistry of the Iron Group Metallocenes", Interscience, New York, 1965.
(23) H. Patin and R. Dabard, *Bull. Soc. Chim. Fr.*, 2413 (1973).
(24) Unpublished results of J. Gromek and J. Donohue.
(25) J. E. Gorton, H. L. Lentzner, and W. E. Watts, *Tetrahedron*, **27**, 4353 (1971).
(26) N. Maoz, A. Mandelbaum, and M. Cais, *Tetrahedron Lett.*, **25**, 2087 (1965).

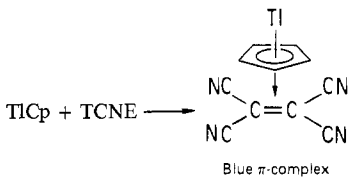


XII

the presence of a $-CH(CN)_2$ unit was indicated by the initial loss of 65.0135 amu. The ^1H NMR is similarly supportive of this formulation since the ethyl proton is again seen as a singlet with no evidence for proton–fluorine coupling. Additionally, the ^{19}F NMR of XII consists of only one singlet as expected for the uncoupled, equivalent trifluoromethyl groups.

Discussion

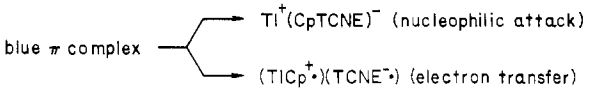
The various color changes observed in the reactions of electrophilic olefins with TlCp suggests that there are several intermediates in the reaction pathway. For the reaction with TCNE, the solution turns blue, then rapidly to green, and



Blue π-complex

finally the red color of I. The initial blue color suggests the possible formation of a π complex resulting from the interaction of a filled π orbital of the cyclopentadienyl ring of the TlCp with the empty olefin π^* orbital. This intermediate would be analogous to the π complex formed in the ferrocene–TCNE reaction, and such complexes have also been noted in the reactions of electrophiles with many aromatic compounds including benzene. Additionally π complexes of this type have been proposed as intermediates in other reactions such as the tricyanovinylation of *N,N*-dimethylaniline.[27]

A second step in the TCNE–TlCp reaction is indicated by the formation of a green color. Two different reaction pathways can be envisioned: (1) nucleophilic attack of the olefin as proposed in the tricyanovinylation reactions of aromatic compounds such as *N,N*-dimethylaniline[27] mentioned above and also in reactions of Grignard reagents with TCNE[28] or (2) electron transfer as proposed in the insertion of TCNE in alkyl metal compounds such as alkyl leads[29] and also in the reactions of certain metallocenes such as cobaltocene with electrophiles.[9]

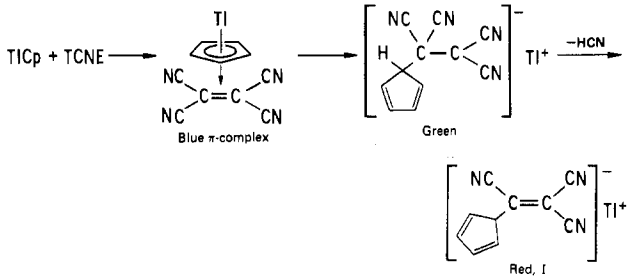


Either of the intermediates formed could then be envisioned to yield the final product obtained.

An EPR investigation of the TCNE–TlCp reaction revealed only a weak signal instead of the strong signal characteristic of the TCNE radical anion which is readily observed during the electron-transfer reaction of tetraethyllead and TCNE.[29] Thus electron transfer can be ruled out as the predominant mechanism and nucleophilic attack is strongly indicated.

The final step in the TCNE–TlCp reaction involves elimination of HCN from the green intermediate. Such elimination reactions are common and are observed in the tricyanovinylation reactions of aromatics[27] noted above.

To summarize, the data of the TCNE–TlCp reaction are consistent with the initial formation of a π complex, followed by nucleophilic addition at the olefin and finally elimination of HCN to give the final product, I. This is shown diagrammatically.



This proposed reaction mechanism is also supported by the results obtained from the reaction of TlCp with 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene. In this reaction two color changes are observed: initially a pink color forms which rapidly changes to the orange color characteristic of the final product. Again the initial color suggests the formation of a π complex and this complex can then undergo nucleophilic substitution which in this case yields the final product, III.

$$\text{TlCp} + (CN)_2C{=}C(CF_3)_2 \rightarrow \pi \text{ complex} \xrightarrow[\text{attack}]{\text{nucleophilic}} \text{III}$$

The attack of the TlCp occurs preferentially at the bis(trifluoromethyl)-substituted carbon due to the dissimilar electron-withdrawing abilities of the cyano and trifluoromethyl groups. The better electron-withdrawing cyano groups produce a partial positive charge at the trifluoromethyl-substituted carbon which results in nucleophilic attack at that carbon to yield III. It should be noted that III is analogous to the green intermediate proposed in the TCNE–TlCp reaction and provides further support for that proposed mechanism. Unlike that intermediate, however, III cannot readily eliminate HCN and is therefore the final product of this reaction.

Thus the reaction of TlCp with electrophilic olefins did not yield the type of final products (either π-complex or charge-transfer salt) as typically found in the reaction of these type electrophiles with covalent metallocenes. Instead, nucleophilic attack at the olefin was observed. This is a characteristic reaction of other nucleophilic reagents such as Grignard reagents which have predominantly ionic bonding. Some evidence was obtained, however, for the formation of a π-complex intermediate suggesting that some covalent bond character is also present in TlCp. These results are in agreement with a bond of intermediate nature for TlCp, that is, containing both ionic and covalent character.

While the bonding in TlCp appears to be of an intermediate nature, all of the data collected for I are indicative of ionic bonding. For example, I does not exhibit an absorption in its crystalline infrared spectrum attributable to the metal–cyclopentadienyl bond which would be expected in the case of covalent bonding. I also has a reasonable solubility in several polar organic solvents such as acetonitrile and tetrahydrofuran as would be expected for an ionic compound. Also in contrast to TlCp and indicative of ionic bonding is the solution conductivity of I (6.5×10^{-2} Ω^{-1} cm^2 equiv^{-1}) which is over 100 times greater than that of TlCp (5.1×10^{-4} Ω^{-1} cm^2 equiv^{-1}). Ionicity may also be indicated by the stability of I which is similar to that of TlCp and markedly more stable than most previous derivatives of TlCp. Thus the physical and spectroscopic data observed are consistent for ionic bonding in I as would be expected considering the effects of the strongly electron-withdrawing tricyanovinyl group.

(27) E. Ciganek, W. J. Linn, and O. W. Webster in "The Chemistry of the Cyano Group", Z. Rappoport, Ed., Interscience, New York, 1970, p 463.
(28) H. C. Gardner and J. K. Kochi, *J. Am. Chem. Soc.*, **98**, 558 (1976).
(29) H. C. Gardner and J. K. Kochi, *J. Am. Chem. Soc.*, **98**, 2460 (1976).

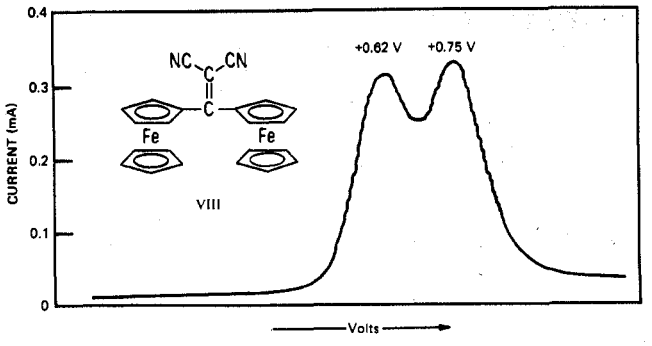


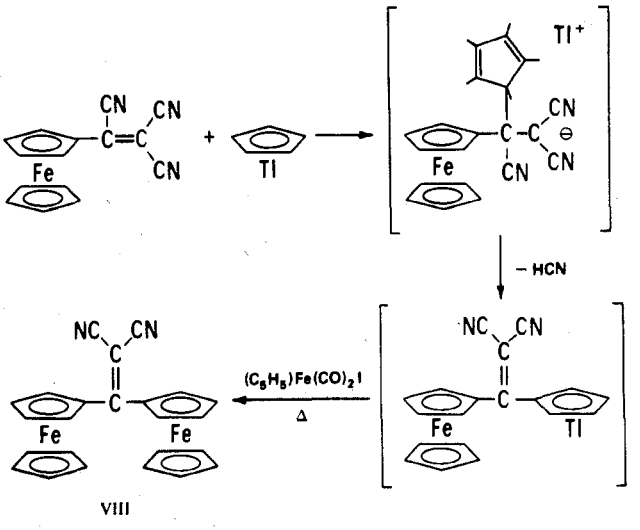
Figure 1. Differential pulsed polarogram of 1,1-dicyano-2,2-diferrocenylethylene (VIII).

Further evidence of ionic bonding is demonstrated by a low-temperature single-crystal X-ray investigation of I[17] which revealed a structure similar to that of unsubstituted TlCp consisting of zigzag chains of alternating cyclopentadienide units and thallium atoms with no evidence for delocalized covalent bonding between the cyclopentadiene ring and thallium.

TlCp has found extensive use as a mild reagent for the synthesis of metallocenes and transition-metal–cyclopentadienyl complexes as previously discussed. There was, however, no general method for the synthesis of metallocenes and cyclopentadienyl–metal complexes containing strongly electron-withdrawing substituents such as tricyanovinyl, and previously only one such metallocene, tricyanovinylferrocene, had been known. The use of I and III as synthetic reagents for the production of tricyanovinyl- and 1,1-dicyano-2,2-bis(trifluoromethyl)ethyl-substituted metallocenes and cyclopentadienyl metal complexes, respectively, was therefore explored.

The results presented in this paper demonstrate the success of these reagents, and a number of these substituted metallocenes including $(\eta^5\text{-}C_5H_4C(CN)C(CN)_2]Mn(CO)_3$, $[\eta^5\text{-}C_5H_4C(CN)C(CN)_2]Fe(\eta\text{-}C_5H_5)$, and $[\eta^5\text{-}C_5H_4C(CF_3)_2CH(CN)_2]Fe(\eta\text{-}C_5H_5)$ have been prepared. In general, these compounds were produced in 5–20% yields and have been found to be more oxidatively stable than their unsubstituted analogues due to the presence of the strongly electron-withdrawing groups. The effects of these groups are also seen in the colors exhibited by these substituted complexes which are shifted to longer wavelengths as previously observed in substitution of electron-withdrawing groups on metallocenes.[30]

The synthetic procedure has also been extended to include the synthesis of several bimetallic compounds such as $[(\eta^5\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]_2C_2(CN)_2$ and $[(\eta^5\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]C_2(CN)_2[(\eta^5\text{-}C_5H_4)Mn(CO)_3]$. These complexes were initially assigned a 1,1-dicyanovinylidene structure rather than a 1,2-dicyanoethylene on the basis of spectroscopic and chemical evidence, and this was subsequently confirmed by an X-ray study.[23] This structure is also consistent with a reaction mechanism which is an extension of the previously proposed mechanism to form I and III. That is, the following reaction pathway starting with tricyanovinylferrocene can be envisioned for the formation of both VIII and XI. The addition of TlCp would result in nucleophilic attack at the tricyanovinyl double bond to give the addition product shown below. In order to form the most stable carbanion, this attack would be expected to take place preferentially at the carbon substituted with the single cyano group and ferrocenyl moiety since it can be considered as having a partial positive charge. Elimination of HCN would then yield the next intermediate which could readily react with $(\eta\text{-}C_5H_5)Fe(CO)_2I$ to yield VIII or $Br\text{-}Mn(CO)_5$ to yield XI.



Although a number of bridged ferrocenyl systems are known, compounds VIII and XI appear to be unique since they are apparently the only examples of such a system containing strongly electron-withdrawing groups on the bridging unit. Bridged metallocenes in general have been an area of recent interest with respect to their unusual electrochemistry,[31] and therefore the electrochemistry of VIII was investigated. The differential pulsed polarogram of VIII exhibited two reversible one-electron waves at +0.62 and +0.75 V vs. SCE (Figure 1) resulting in the production of the corresponding mono- and diferrocenium cations of VIII. The effects of the strongly electron-withdrawing cyano groups are evident in the higher oxidation potentials of VIII as compared to unsubstituted ferrocene (+0.34 V vs. SCE) or diferrocenylmethane (+0.39 and +0.56 V vs. SCE). The appearance of two such consecutive one-electron oxidation steps has been previously shown[32] to be characteristic of two weakly interacting metal centers. Many compounds showing this general type of polarographic behavior have been found to also exhibit a band in the near-infrared spectra of their monocations,[31] which has been attributed to intervalence charge transfer. In order to examine the possibility of this behavior for the mixed valence monocation of VIII as well as investigate its dication, we generated 5×10^{-4} M solutions by controlled-potential electrolysis. Oxidation by precisely 1 faraday/mol yields a blue solution of the monocation while further oxidation and the addition of another faraday per mole results in the blue-green solution of the dication. Analysis of the polarographic data indicates that a solution of the monocation will disproportionate to the neutral and dicationic species. This precludes the isolation of the monocation, but spectroscopic analysis is still possible since the equilibrium mixture should contain approximately 90% of the monocation.[33]

The neutral VIII is deep purple and exhibits (Figure 2) an absorption band in the visible region at 565 nm (ϵ 3340) with no bands in the near-infrared region. The monocation has a visible region absorption at 600 nm (ϵ 2080) and also does not exhibit a band in the near-infrared region. Similarly the only band in the dication spectrum is at 635 nm (ϵ 1490). These bands in the visible region are typical of ferrocene and fer-

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(33) Differences in peak potentials in the polarogram are taken as representative of differences in redox potentials. The equilibrium constant is then calculated from the Nernst equation.

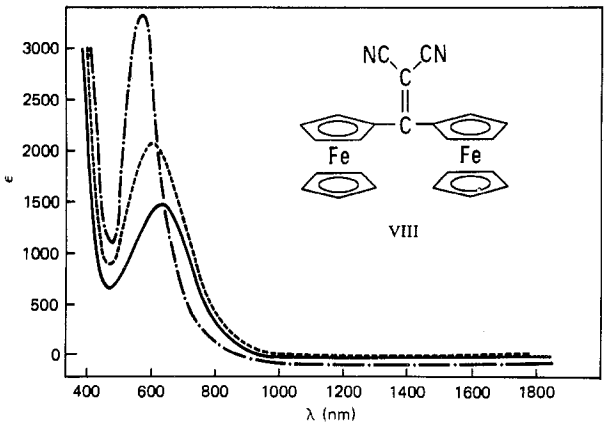

Figure 2. Visible and near-infrared spectra of 1,1-dicyano-2,2-diferrocenylethylene (VIII): neutral, ---; monocation, ---; and dication, —.

rocenium systems but are shifted considerably due to the highly electron-withdrawing substituents. Unsubstituted ferrocene has an absorption in the visible region at 440 nm (ε 91), and it has been noted that this absorption exhibits a bathochromic shift when electron-withdrawing substituents are placed on the ring.[30] It is important to note, however, that there are no absorptions in the near-infrared region for any of the spectra. This is particularly important in the case of the mixed-valence monocation since the lack of any bands in the near-infrared spectrum of the monocation of VIII indicates that no intervalence charge transfer is occurring in this compound. This is not unexpected upon consideration of the recently completed X-ray structural investigation of VIII.[24] If the monocation structure is similar to that of the neutral compound, then the observed iron–iron distance of 6.091 Å would be too large to permit direct metal–metal interaction. Electron transfer, if it were to take place, would then have to involve a ligand propagated exchange. No low-energy transitions are known for biferrocene type molecules bridged by saturated groups. In fact, diferrocenylacetylene is the only reported case[34] of intervalence charge transfer propagated through the bridging unit which in that case is a conjugated π system. Examination of the structure of VIII also eliminates this method of electron transfer. The cyclopentadienyl rings are tilted over 20° out of the plane of the bridging unit, and this results in an unconjugated system incapable of electron transfer through the π system. Thus since both known intervalence charge-transfer mechanisms are eliminated, the lack of evidence for this behavior is not unexpected.

Acknowledgment. We thank the National Science Foundation (Grant CHE-77-06793) and the University of Pennsylvania Materials Research Laboratory (Grant DMR-76-00678) for the support of this research.

Registry No. I, 64012-11-9; II, 72893-88-0; III, 72893-73-3; IVa, 72893-89-1; IVb, 72893-90-4; V, 64012-12-0; VI, 64023-21-8; VII, 38816-69-2; VIII, 64023-22-9; IX, 72893-74-4; X, 1271-88-1; XI, 72893-75-5; XII, 72893-76-6; TlCp, 34822-90-7; TCNE, 670-54-2; $(CN)_2C{=}C(CF_3)_2$, 1113-69-5; $BrMn(CO)_5$, 14516-54-2; $(C_6H_5)_3P$-CuCl, 22176-30-3; $(C_5H_5)Fe(CO)_2I$, 12078-28-3; $Cl_2C{=}C(CN)_2$, 10472-00-1; chloromercuriferrocene, 1273-75-2; lithioferrocene, 1271-15-4; cyanoferrocene, 1273-84-3; ferrocene, 102-54-5; $VIII^+$, 72985-64-9; $VIII^{2+}$, 72905-13-6.

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Metal Atom Reactions of Cobalt with Cyclopentadiene and Alkynes: Synthesis of Structurally Novel Organometallic Complexes

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Received August 17, 1979

The reactions of cobalt atoms and cyclopentadiene with various alkynes such as hexafluorobutyne, trifluoropropyne, and diphenylacetylene have been found to yield a variety of new organometallic compounds including both mono- and multimetal complexes. In general the products obtained fall into four categories: (1) complexes containing ligands resulting from dimerization or trimerization of the alkyne usually accompanied by hydrogen addition, i.e., $(\eta\text{-}C_5H_5)Co[C_4H_2(CF_3)_4]$, $(\eta\text{-}C_5H_5)_2Co_2[C_5H_2F(CF_3)_3]$, $(\eta\text{-}C_5H_5)_2Co_2[C_6H_5(CF_3)_3]$, $[\eta\text{-}C_5(CH_3)_5]Co[C_4H_2(CF_3)_4]$, $(\eta\text{-}C_5H_5)_2Co_2[C_2H_2(CF_3)]_2$, and $(\eta\text{-}C_5H_5)Co[C_4(C_6H_5)_4]$; (2) multimetal clusters containing cyclopentadienylcobalt units and alkynes, i.e., $(\eta\text{-}C_5H_5)_3Co_3[C_2(CF_3)_2]$, $(\eta\text{-}C_5H_5)_3Co_3[C_2(CF_3)_2](\mu_3\text{-}CO)$, and $[\eta\text{-}C_5(CH_3)_5]_2Co_2[C_2(CF_3)_2]_2$; (3) complexes containing ligands resulting from cycloadditions of cyclopentadiene and alkynes, i.e., $(\eta\text{-}C_5H_5)Co[C_7H_6(CF_3)_2]$ and $(\eta\text{-}C_5H_5)Co[C_9H_6(CF_3)_4]$; (4) complexes containing ligands resulting from simple additions of cyclopentadiene and alkynes, i.e., $(\eta\text{-}C_5H_5)_2Co_2$-$[C_7H_8(CF_3)_2]$, $(\eta\text{-}C_5H_5)_2Co_2[C_9H_4(CF_3)_4]$, $(\eta\text{-}C_5H_5)_2Co_2[C_9H_6(CF_3)_4]$, and $(\eta\text{-}C_5H_5)Co[C_9H_6(C_6H_5)_4]$. The nature of these products implies the formation of certain reactive cyclopentadienylcobalt intermediates in these metal atom reactions, and an appropriate reaction scheme is discussed.

Introduction

In recent years the reactions of metal atoms with various olefins have been an area of intense investigation and have yielded a number of new and unusual organometallic complexes.[1] It is therefore somewhat surprising that the corresponding reactions of metal atoms with alkynes have met with much less success. In fact until the recent work of Klabunde,[2] previous studies have shown that these reactions usually result in only the trimerization of the alkyne with little evidence for the formation of organometallic products.[3] Previously, we reported[4,5] that the reaction of cyclopentadiene and cobalt atoms with the various boranes and alkynes results in the

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