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η^2-ACRYLONITRILECYCLOPENTADIENYLDICARBONYLIRON(II) TETRAFLUOROBORATE: AN UNUSUAL HIGH-VALENT TRANSITION METAL COMPLEX

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Summary

Fp(η^2-vinyl ether)BF_4 complexes (**2a–d**) (Fp = η-$C_5H_5Fe(CO)_2$) are useful starting materials for the preparation of thermodynamically unstable Fp(η^2-acrylonitrile)BF_4 complexes (**3a–d**). Treatment of **2a–d** with tetraethylammonium cyanide at 0°C gave the neutral adducts **4a–d** which were transformed, in the presence of fluoroboric acid etherate at −78°C, to the acrylonitrile complexes **3a–d**. These salts are unstable at room temperature, but they add carbon and heteroatomic nucleophiles at −78°C to give (α-cyano-alkyl)Fp complexes **5a–c**, **6** and **7**.

Introduction

Cyano-substituted olefins have been used commonly as ligands in organometallic complexes for some time. Fumaronitrile, tetracyanoethylene [1] and perfluoromethyl substituted cyano-olefins [2] are well known for forming π-bonded olefin complexes. By contrast, few of the many complexes of acrylonitrile [3] involve metal coordination to the olefin. Iron tetracarbonyl forms complexes with this ligand in which the metal is bound to either the olefin or the terminal nitrogen, depending on the mode of formation [4], and π-bonded cinnamonitrile [5] and acrylonitrile [6] species have been identified spectroscopically and invoked as intermediates in catalytic hydrogenation cycles [6]. Much more common are complexes in which the acrylonitrile ligand is bound to the metal through the terminal nitrogen. These include complexes of Ru^{II} [7] and Rh^{III} [7], Rh^{I} [8], Pt^{II} [9], Ir^{I} [10] and Fe^{II} [11]. The latter is exemplified by the tetrafluoroborate and hexafluorophosphate complexes **1a** first reported by Fischer and Moser [11] in 1966 and shown by them to be bonded through the nitrogen.

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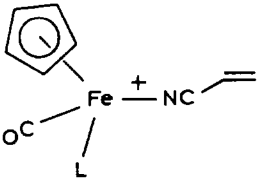
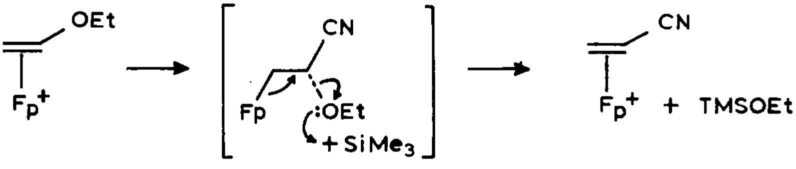


(**1a**, L = CO ;
1b, L = PPh_3)

More recently, Reger and Coleman have made the monocarbonyltriphenylphosphine analog **1b** [12]. In general, zero or low-valent transition metals would be expected to form a π-bonded complex with acrylonitrile, while high valent metals would be expected to preferentially bond to nitrogen. We wish now to report the synthesis of the first olefin-coordinated Fp-acrylonitrile tetrafluoroborate complex, as well as, a general route to other thermodynamically unstable, substituted acrylonitrile-Fp compounds (Fp = dicarbonyl-η-cyclopentadienyliron(II)).

Results and discussion

Fp-ethoxyethene tetrafluoroborate **2a** reacts with trimethylsilyl cyanide (TMSCN) at 0°C in methylene chloride to yield a bright yellow precipitate of Fp-(η^2-acrylonitrile)BF_4 (**3a**) (92%).



(**2a**) (**4a**) (**3a**)

The reaction presumably takes place via addition of cyanide to the activated double bond [13] to give **4a**, followed by trimethylsilyl cation assisted loss of trimethylsilyl ethyl ether. The dried solid product **3a** is stable in air for hours, but rearranges rapidly in solution ($t_{1/2}$ 0.25 h, CD_3NO_2, 37°C) to the known *N*-coordinated species.

The structure of the acrylonitrile complex was established by its infra-red spectrum (KBr), which shows the nitrile absorption as a doublet at 2228 and 2202 cm^{-1}. It has been well established that coordination of the double bond in unsaturated nitrile complexes causes small shifts of the nitrile band to lower frequency, while coordination through the nitrogen shifts the nitrile stretching absorption to higher frequency, relative to the free ligand at 2230 cm^{-1} [3]. Complex **3a** rearranges thermally to the *N*-bound species even in the solid state. KBr pellets used for a single scan (5 min, 4000–200 cm^{-1}) show a new band at 2330 cm^{-1} while the original CN bands have disappeared. The pellets also undergo a color change from yellow to orange-red, which on the basis of observations in our laboratories, is generally indicative of migration of the Fp group from an olefin center to a heteroatom (N or O).

More dramatic evidence for the π-bonded structure **3a** is the shift observed for the olefin carbons in the ^{13}C NMR spectrum. As shown in Table 1, the olefin

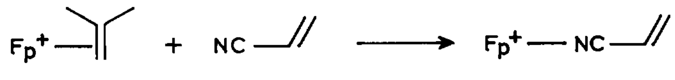
TABLE 1

^{13}C NMR DATA FOR ACRYLONITRILE COMPLEXES, **1a**, **1b** AND **3a**

Carbon	Free L	**1a**	**1b**	**3a**
C_α	107.8	107.5	106.7	44.0
C_β	137.5	143.5	140.8	59.7

carbons of **3a** are very strongly shielded by the π-bound Fp group relative to the free ligand [14] and to the *N*-bound complexes **1a** and **1b** [12]. This upfield shift is well documented for Fp-olefin complexes [15].

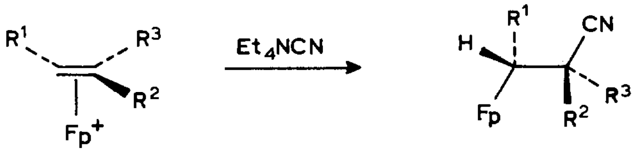
As anticipated, the ligand exchange reaction of Fp-isobutylene with acrylonitrile gave only **1a**; no sign of **3a** was observed. The Fp cation also appears to act as a catalyst for the polymerization of acrylonitrile, as a large amount of acetone insoluble solid was formed as a by-product (10 equiv of acrylonitrile were used in the exchange reaction).



(**1a**)

Attempts to prepare the analogous 1-methyl-, 2-methyl- and 2-methoxyacrylonitrile complexes by treatment of the requisite Fp-vinyl ether cation with TMSCN, failed. It appears that the synthesis of the parent compound was successful due to the fortuitous insolubility of the product **3a** in the reaction mixture. ^{1}H NMR spectroscopic evidence obtained in the attempted syntheses of the substituted acrylonitrile complexes with TMSCN indicates that the desired compounds were indeed formed, but remained in solution, where they decomposed rapidly.

Since the TMSCN reaction did not prove general for substituted acrylonitrile complexes, an alternative stepwise synthesis of these complexes was designed. Addition of tetraethylammonium cyanide to the Fp-vinyl ether complexes **2** at 0°C gave the neutral Fp-alkyl complexes **4** as yellow oils in high yield. These were purified by chromatography on basic alumina and were found to be stable indefinitely under N_2.

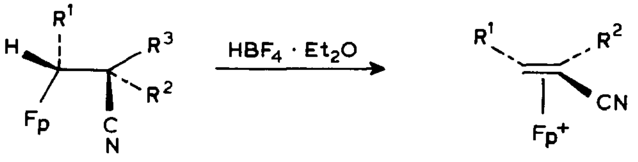


(**2**) (**4**)

	R^1	R^2	R^3	Yield (%)
a	H	H	OEt	99
b	H	Me	OEt	94
c	Me	H	OEt	93
d	OMe	H	OMe	92

The addition of nucleophiles to Fp-olefin complexes has been shown to be a stereospecific *trans*-addition [16], and indeed, complexes **4c** and **4d** were formed as single diastereomers as indicated by their ^{1}H and ^{13}C NMR spectra. These compounds are consequently assigned the relative stereochemistry shown.

Protonation of these complexes with $HBF_4 \cdot Et_2O$ and elimination of ethanol occurred readily at −78°C in Et_2O, and under these conditions the acrylonitrile complexes **3** precipitate immediately from solution. However, even when made by this procedure, these salts (**3b–d**) were not isolable at room temperature.



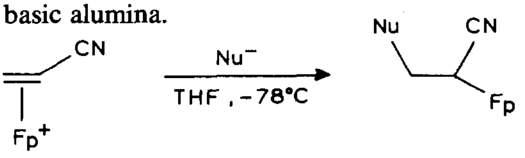
(**4**) (**3**)

	R^1	R^2	R^3	Yield [a] (%)
a	H	H	OEt	98
b	H	Me	OEt	74
c	Me	H	OEt	72
d	MeO	H	OMe	82

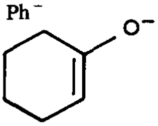
[a] Yields are based on total weight of partially rearranged material.

The compounds are bright yellow solids when isolated at −78°C, but undergo phase and color changes if they are allowed to warm to room temperature, indicating rearrangement to the *N*-coordinated compounds. Infrared spectra of the complexes, taken in CH_2Cl_2, show CN absorptions for complexes **3a–d** ranging from 2275 to 2360 cm^{-1}, in agreement with a rearrangement from the π-olefin complex to a nitrogen coordinated complex. The *trans* stereochemistry of **3c** is evidenced by the vinyl proton couplings (^3J 17 Hz), while that of **3d**, for which an NMR spectrum could not be obtained, is assigned on the basis of a preferred anti-periplanar arrangement of the Fp–C σ-bond and the C–O bond being broken in the conversion from **4** to **3**.

Although all of the π-bonded Fp-acrylonitrile complexes are unstable in solution at room temperature, their high reactivity makes them suitable substrates for nucleophilic addition at low temperature. A variety of nucleophiles add to **3a** including lithium dimethyl cuprate, phenylmagnesium bromide and lithium cyclohexanone enolate. As expected from the polarization of the double bond by the electron-withdrawing nitrile, nucleophiles add regiospecifically to the β-carbon giving the α-cyano Fp-alkyl compounds **5**. These compounds are bright yellow oils, stable in solution in the absence of O_2, and may be purified by chromatography on basic alumina.

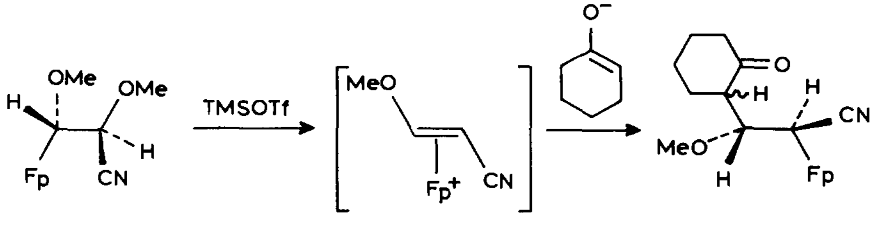


(**3a**) (**5**)

	Nu^-	Yield (%)
a	Me^-	71
b	Ph^-	45
c		68

With cyclohexanone enolate as the nucleophile, a 2/1 mixture of diastereomers is formed. This contrasts with the high diastereoselectivity observed in the addition of lithium cyclohexanone enolate to a number of Fp-vinyl ether cations [13,17]. The low diastereoselectivity observed in the reaction of **3a** with cyclohexanone enolate may be due to the fact that the chiral centers formed in the reaction with **2** are adjacent, while those derived from **3a** are not.

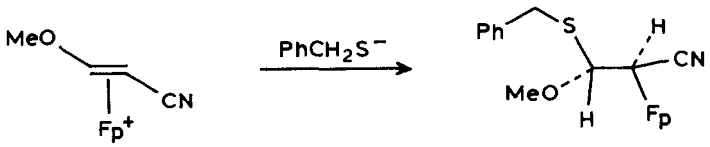
Like **3a**, the substituted acrylonitrile complexes (**3b–d**) may be trapped by reaction with nucleophiles at −78°C to form stable neutral species. Thus, 1-Fp-2-cyano-1,2-dimethoxyethane **4d**, on treatment with trimethylsilyl triflate at −78°C in ether, was converted to the *trans*-2-methoxyacrylonitrile complex **3d**. Addition of cyclohexanone enolate gave 2-Fp-3-(2′-oxocyclohexyl)-3-methoxypropanenitrile (**6**) in 42% overall yield after chromatography on basic alumina as a 2/1 mixture of diastereomers (based on ^{13}C NMR spectroscopic data).



(4d) (3d) (6)

We were surprised at the poor diastereoselectivity of this reaction. The Fp cation **3d** is not only an acrylonitrile, but a vinyl ether as well and the chiral sites in the reaction are adjacent. Presumably, the diastereomers are formed with respect to the chiral carbon in the cyclohexanone ring and the relative configurations of the carbons α and β to the Fp are fixed by the stereochemistry of **3d**.

To test this theory, complex **3d** was trapped with the achiral nucleophile, sodium benzylthiolate to produce the β-thio-β-methoxy compound **7**. As anticipated, **7** was formed as a single diastereomer as determined by ^{1}H and ^{13}C NMR spectra.



(3d) (7)

The use of complexes **3a–d** for organic synthesis is under further investigation. We are also exploring the factors that contribute to the low diastereoselectivity of the reactions of cations **3a,d** with cyclohexanone enolate compared with **2**.

Experimental

Reactions were carried out using standard Schlenk techniques under an argon atmosphere. THF and Et_2O were distilled under nitrogen from sodium/benzophenone. Methylene chloride was distilled under nitrogen from CaH_2. IR spectra were recorded on a PE-683 spectrophotometer in methylene chloride solution and referenced to polystyrene. ^1H NMR spectra were recorded on a Varian EM-390 or Varian XL300 (NIH-1-S10RR01493-01-Al) and referenced to internal TMS. ^{13}C NMR spectra were recorded on a Varian XL300 spectrometer and referenced to solvent. Alumina refers to basic alumina Brockman activity four unless otherwise noted. Petroleum ether refers to the fraction boiling 20–40°C. Methyllithium, phenylmagnesium bromide and n-butyllithium were purchased from Aldrich Chemical and used without further purification. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn.

Tetraethylammonium cyanide [18]

Sodium cyanide (5.0 g, 0.102 mmol) was dissolved in 150 ml of MeOH and added slowly via cannula to a stirred solution of tetraethylammonium chloride (10.0 g, 0.606 mmol) in 20 ml of MeOH. The mixture was stirred for 10 min, filtered through Celite and the solvent removed in vacuo. The resulting solid was extracted with 100 ml of acetonitrile and the solvent volume reduced to about 20 ml whereupon a precipitate became evident. The precipitate was collected, washed with 2 ml cold acetonitrile and dried under vacuum to give 2.3 g (24.4%) or product. THF (25 ml) was added to the filtrate to precipitate a second crop of product which was filtered, washed and dried to give 2.48 g (26.2%, 50.6% total). *Note*: This compound is very hygroscopic. It may be weighed in air if you work *rapidly*. On humid days it must be handled under a blanket of N_2. It may be stored at room temperature under N_2 or Ar indefinitely.

2-Cyano-2-ethoxyethyldicarbonyl-η-cyclopentadienyliron(II) (***4a***)

Fp-ethyl vinyl ether tetrafluoroborate (**2a**) (0.200 g, 0.596 mmol) was dissolved in 5 ml of CH_2Cl_2 and cooled to 0°C. Tetraethylammonium cyanide (0.098 g, 0.626 mmol, 5% xs) was added and the mixture stirred for 0.5 h. Addition of 10 ml of ether precipitated the tetraethylammonium tetrafluoroborate. The solution was filtered through a short plug of alumina and the solvent removed in vacuo to give a transparent yellow oil, 0.161 g (99%). *Note*: There is an obvious color change from orange to yellow on addition of the tetraethylammonium cyanide and it is thus apparent that the reaction is virtually instantaneous. The half-hour reaction times for this and similar syntheses are for convenience only. Times of 10 min to 1 h have been used with no apparent difference in yield as long as the reagents are dry. Occasionally, after removal of the solvent, traces of solid (Fp-salts or tetraethylammonium tetrafluoroborate) are seen. They may be removed easily by taking the oil up in ether and again filtering it through a short plug of alumina. IR (neat) 2250 (CN) 2020,1950 (C≡O) cm^{-1}; ^1H NMR ($CDCl_3$); δ 4.85 (s, 5H, Cp) 3.95 (app. t, 1H, J_{ave} 7.8 Hz, C*H*CN), 3.79, 3.47 (two d of q, 1H each, J_d 8.75, J_q 7.0 Hz, O-CH_2), 1.60 (d of AB q's, 2H, calc δ 1.65 and 1.56, calc. $\Delta\nu$ 26.1 Hz, J_{AB} 10.6 J_{AX} 7.35, J_{BX} 8.3 Hz, Fp-CH_2), 1.23 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$); δ 216.2, 215.9 (C≡O), 120.3 (CN), 85.2 (Cp), 74.4 (CH), 65.7 (OCH_2), 14.8 (CH_3), 1.7 (Fp-CH_2).

Anal. Found: C, 52.23; H, 4.54; N, 5.60. $C_{12}H_{13}FeNO_3$ calc: C, 52.39; H, 4.54; N, 5.09%.

2-Cyano-2-ethoxypropyldicarbonyl-η-cyclopentadienyliron(II) (***4b***)

Fp-2-propenyl ethyl ether tetrafluoroborate (**2b**) (0.30 g, 0.858 mmol) was dissolved in 5 ml of CH_2Cl_2 and cooled to 0°C. Tetraethylammonium cyanide (0.15 g, 0.945 mmol, 10% xs) was added and the mixture stirred 0.5 h. Addition of 10 ml of ether precipitated the ammonium salts. The mixture was filtered through a short plug of alumina and the alumina washed with 2 × 10 ml of ether. Removal of solvent in vacuo gave a clear yellow oil, 0.234 g (94%). IR (CH_2Cl_2) 2225 (CN) 2015,1955 (C≡O) cm^{-1}; ^1H NMR ($CDCl_3$); δ 4.85 (s, 5H, Cp), 3.6 (q, 2H, J 7.0 Hz, OCH_2), 1.72 (AB, calc δ 1.80 1.65, 2H, J 12 Hz, Fp-CH_2), 1.55 (s, 3H, CH_3), 1.20 (t, 3H, J 7.0 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$); δ 216.2, 215.9 (C≡O), 121.5 (CN), 88.8 (Cp), 77.4 (*C*-CN), 60.5 (OCH_2), 27.5 (CH_3), 14.6 (CH_2CH_3) 10.2 (Fp-CH_2).

Anal. Found: C, 54.25; H, 5.10; N, 4.60. $C_{13}H_{15}FeNO_3$ calc: C, 54.01; H, 5.23; N, 4.84%.

*2-Cyano-2-ethoxy-1-methylethyldicarbonyl-η-cyclopentadienyliron(II) (**4c**)*

Fp-1-propenyl ethyl ether hexafluorophosphate (**2c**) (0.35 g, 0.858 mmol) was dissolved in 5 ml of CH_2Cl_2 and cooled to 0 °C. Tetraethylammonium cyanide (0.15 g, 0.945 mmol, 10% xs) was added and the mixture stirred 0.5 h. Addition of 10 ml of ether precipitated the ammonium salts. The mixture was filtered through a short plug of alumina and the alumina washed with 2 × 10 ml of ether. The solvent was removed in vacuo to give a clear yellow oil, 0.231 g (93%). IR (CH_2Cl_2) 2230 (CN) 2018,1955 (C≡O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.80 (s, 5H, Cp), 4.10 (d, 1H, J 4.5 Hz, C*H*-CN), 3.80, 3.45 (two d of q, 1H each, J_d 8.5, J_q 7.5 Hz, O-CH_2), 2.55 (d of q, 1H, J_d 4.5, J_q 7.0 Hz, Fp-C*H*), 1.35 (d, 3H, J 7.0 Hz, CH_3CH-Fp), 1.25 (t, 3H, J 7.5 Hz, CH_3CH_2); ^{13}C NMR ($CDCl_3$); δ 216.8, 216.1 (C≡O), 118.9 (CN), 85.5 (Cp), 79.1 (CH-O), 66.0 (CH_2-O), 25.1 (CH_3-CH-Fp), 17.3 (Fp-CH), 14.6 (CH_3-CH_2O).

Anal. Found: C, 53.63; H, 4.82; N, 4.73. $C_{13}H_{15}FeNO_3$ calc: C, 54.01; H, 5.23; N, 4.84%.

*2-Cyano-1,2-dimethoxyethyl-dicarbonyl-η-cyclopentadienyliron(II) (**4d**)*

Fp-*cis*-1,2-dimethoxyethene tetrafluoroborate (**2d**) (0.300 g, 0.853 mmol) was dissolved in 5 ml of CH_2Cl_2 and cooled to 0 °C. Tetraethylammonium cyanide (0.146 g, 0.938 mmol, 10% xs) was added and the mixture stirred for 0.5 h. Addition of 10 ml of ether precipitated the ammonium salts. The mixture was filtered through a short plug of alumina and the alumina washed with 2 × 10 ml of ether. Removal of solvent in vacuo gave a clear yellow oil, 0.197 g (79%). Yields of 90–95% have been obtained for the preparation of this compound. IR (CH_2Cl_2): 2235 (CN), 2020,1960 (C≡O) cm^{-1}; ^1H NMR ($CDCl_3$): δ4.90 (s, 5H, Cp), 4.85 (d, 1H, J 5.0 Hz, Fp-CH), 4.10 (d, 1H, J 5.0, CH-CN), 3.55 (s, 3H, Me), 3.35 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): δ 216.2, 214.6 (C≡O), 117.7 (CN), 88.3 (Cp), 80.0, 79.0 (O-*C*H*C*H-O), 59.1, 57.8 (Me's).

Anal. Found: C, 49.20; H, 4.50; N, 4.81. $C_{12}H_{13}FeNO_4$ calc: C, 49.52; H, 4.50; N, 4.81%.

Dicarbonyl-η-cyclopentadienyliron(II)-η-acrylonitrile tetrafluoroborate (3a)

Method A. Fp-ethyl vinyl ether (**2a**) (7.15 g, 21.1 mmol) was dissolved in 30 ml of CH_2Cl_2 and cooled to −78 °C. Trimethylsilyl cyanide (3.16 ml, 2.32 g, 23.5 mmol, 10% xs) was added via syringe and the mixture allowed to warm to 0 °C during which time a bright yellow precipitate formed. Addition of 40 ml of ether completed the precipitation. The mixture was filtered and the precipitate washed with ether. Drying under vacuum gave a bright yellow powder, 5.80 g (88%).

Method B. 2-Cyano-2-ethoxyethyl-dicarbonyl-η-cyclopentadienyliron(II) (**4a**) (0.74 g, 2.54 mmol) was dissolved in 10 ml of CH_2Cl_2 and cooled to −78°C. $HBF_4 \cdot Et_2O$ (0.455 g, 2.80 mmol, 10% xs) was added dropwise via syringe with vigorous stirring, producing a copious yellow precipitate. After 10 min, addition of 10 ml of ether completed the precipitation. The mixture was filtered and the precipitate washed with ether. Drying under vacuum gave 0.80 g (98%). IR (KBr): 2228,2202 (CN), 2040,1985 (C≡O) cm^{-1}; ^1H NMR (acetone-d_6, −25°C) δ 6.18 (s, 5H, Cp), 4.86 (d of d, 1H, J 13.5 and 9.3 Hz, =CH), 4.51 (d, 1H, J 13.5 Hz, $=CH_{2trans}$), 4.50 (d, 1H, J 9.3 Hz, $=CH_{2cis}$); ^{13}C NMR (CD_3NO_2): δ 207.7, 206.2 (C≡O), 119.5 (CN), 93.2 (Cp), 59.7 (CH_2=), 44.0 (CH=).

Anal. Found: C, 37.85; H, 2.59; N, 4.57. $C_{10}H_8BF_4FeNO_2$ calc: C, 37.91; H, 2.55; N, 4.42%.

Note: The infrared spectrum must be taken on the *first* scan as the heat from the IR beam is sufficient to begin thermal decomposition of the compound. *Note*: The compound rearranges rapidly in acetone-d_6, CD_3NO_2 and CD_3CN at room temperature or above. The rearrangement may be followed by ^1H NMR and is complete in about 30 min at 37°C.

*Dicarbonyl-η-cyclopentadienyliron(II)-N-acrylonitrile tetrafluoroborate (**1a**)*

Fp-isobutylene tetrafluoroborate (1.00 g, 3.4 mmol) and acrylonitrile (2.0 ml, 1.62 g, 30.6 mmol) were dissolved in 20 ml of CH_2Cl_2 and refluxed for 5 h. The mixture was cooled to room temperature, filtered and 40 ml of ether added to give a yellow/brown gum. The gum was triturated with acetone which produced a yellow solution and light yellow solid. Filtration and removal of solvent from the filtrate in vacuo gave a yellow oil which crystallized on standing, 0.78 g (72%). The acetone insoluble portion appears to be polymeric material. ^1H NMR (acetone-d_6): δ 6.61 (d, 1H, J 17.5 Hz, $=CH_{2trans}$), 6.43 (d, 1H, J 11.4 Hz, $=CH_{2cis}$), 6.15 (d of d, 1H, J 17.5 and 11.4 Hz, =CH), 5.73 (s, 5H, Cp); ^{13}C NMR (acetone-d_6): δ 208.6 (C≡O), 143.5 (=CH_2), 134.4 (CN), 107.5 (=CH), 87.6 (Cp).

*Dicarbonyl-η-cyclopentadienyliron(II)-η-trans-2-butenenitrile tetrafluoroborate (**3c**)*

3-Fp-2-ethoxybutyronitrile (**4c**) (0.222 g, 0.77 mmol) was dissolved in 10 ml of ether and cooled to −78°C. $HBF_4 \cdot Et_2O$ (0.11 ml, 0.13 g, 0.80 mmol) was added dropwise via syringe and a bright yellow precipitate formed. The mixture was stirred 1 h to insure completion then the solvent was removed via cannula filtration and the precipitate washed with 2 × 5 ml of cold ether again via cannula filtration. Final drying under vacuum as the material warmed to room temperature gave a bright yellow powder, 0.187 g (72%). On standing at room temperature the solid turns to a brown oil, indicating decomposition and rearrangement to the *N*-coordinated species. The compound rearranges rapidly in solution or under the pressure of a KBr press. ^1H NMR (CD_3NO_2): δ 7.0 (d of q, 1H, J 17.0, 7.5 Hz, β=CH), 5.61 (q, 0.5H, J 1.5 Hz, half of α=CH), 5.46 (s, 5H, Cp), 1.97 (d of d, 3H, J 7.5, 1.5 Hz, CH_3).

The same procedure was used to prepare complexes **3b** and **3d** in 74 and 82% yield, respectively.

*1-Cyanopropyl-dicarbonyl-η-cyclopentadienyliron(II) (**5a**)*

Cuprous cyanide (0.565 g, 6.32 mmol, 2 eq) was slurried in 20 ml of THF and cooled to −78°C. MeLi (9.25 ml, 1.3 *M*, 12.00 mmol, 5% def) was added dropwise via syringe and then stirred for 45 min. Fp-acrylonitrile tetrafluoroborate **3a** (1.00 g, 3.16 mmol) was added as a single portion and stirred 2 h at −78°C. The mixture was then allowed to warm to room temperature (about 0.5 h). The reaction mixture was filtered through a short plug of alumina, the alumina washed with 3 × 10 ml of ether and the solvent removed in vacuo to give a dark yellow oil (0.73 g, 83% crude). Chromatography on alumina with 50% ether/petroleum ether gave a bright yellow oil, 0.65 g (71%). ^{1}H NMR ($CDCl_3$): δ 4.90 (s, 5H, Cp), 2.05 (t, 1H, J 7.5 Hz, Fp-CH), 1.55 (m, 2H, CH_2), 1.10 (t, 3H, J 6.5 Hz, CH_3); ^{13}C NMR ($CDCl_3$): δ 215.0, 214.7 (C≡O), 130.3 (CN), 86.4 (Cp), 32.1 (CH_2), 16.6 (CH_3), −4.2 (CH).

Anal. Found: C, 53.53; H, 4.21; N, 5.72. $C_{11}H_{11}FeNO_2$ calc: C, 53.91; H, 4.52; N, 5.72%.

1-Cyano-2-phenylethyl-dicarbonyl-η-cyclopentadienyliron(II) (5b)

Fp-acrylonitrile tetrafluoroborate (**3a**) (0.50 g, 1.58 mmol) was slurried in 15 ml of THF and cooled to −78°C. PhMgBr (0.55 ml, 3 *M*, 1.66 mmol, 5% xs) was added dropwise via syringe over a 20-min period and the reaction mixture stirred for 4 h. Slow addition is necessary to avoid crystallization of the PhMgBr. Ether (15 ml) was added and the mixture filtered through a short plug of alumina. Removal of solvent gave a red oil which was chromatographed on alumina with 20% ether/petroleum ether to give a clear yellow oil, 0.270 g (56%). IR (CH_2Cl_2): 2195 (CN), 2020,1972 (C≡O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.25 (m, 5H, pH), 4.95 (s, 5H, Cp), 2.25 (d of d, 1H, J 6.0 and 9.0 Hz, Fp-CH), 2.80,2.70 (six lines apparent, 2H, J_{AB} 14.5 Hz, Ph-CH_2) [19]; ^{13}C NMR ($CDCl_3$): δ 214.6, 214.3 (C≡O), 141.6 (*i*-Ph), 129.6 (CN), 128.5 (*m*-Ph), 128.3 (*o*-Ph), 126.3 (*p*-Ph), 86.6 (Cp), 44.3 (CH_2), −3.9 (Fp-CH).

Anal. Found: C, 61.36; H, 4.51; N, 4.48. $C_{16}H_{13}FeNO_2$ calc: C, 62.57; H, 4.27; N, 4.56%.

1-Cyano-2-(2′-Oxocyclohexyl)-ethyl-dicarbonyl-η-cyclopentadienyliron(II) (5c)

Lithium cyclohexanone enolate (1.66 mmol, 5% xs) was generated in 15 ml of THF from trimethylsilyl cyclohexenyl ether and n-BuLi at 0°C as previously described [20] and cooled to −78°C. Fp-acrylonitrile tetrafluoroborate **3a** (0.500 g, 1.58 mmol) was added as a single portion and stirred at −78°C for 2 h. Addition of 15 ml of ether, filtration through a short plug of alumina and removal of solvent in vacuo gave a red-yellow oil. Chromatography on alumina with 30% ether/petroleum ether gave a yellow oil, 0.345 g (68%) of a 2/1 mixture of diastereomers (A and B). IR (CH_2Cl_2): 2220 (CN), 2030,1960 (C≡O), 1700 (C≡O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.95 (s, 5H, Cp), 2.5–1.0 (broad overlapping lines, 12H, all other protons); ^{13}C NMR ($CDCl_2$); Diastereomer A: δ 214.7 (C≡O), 213.2 (C=O), 131.0 (CN), 86.2 (Cp), 52.7 (O=C-*C*H), 42.5 (O=C-*C*H_2), 39.6 (FpCH*C*H_2), 35.5, 28.4, 25.3 (*C*H_2*C*H_2*C*H_2), −8.6 (Fp-CH); Diastereomer B: δ 214.7, 214.3 (C≡O), 212.3 (C=O), 129.8 (CN), 86.5 (Cp), 51.4 (O=C-*C*H), 41.9 (O=C-*C*H_2), 373 (FpCH-*C*H_2), 32.3,27.6,24.9 (*C*H_2*C*H_2*C*H_2), −10.8 (FpCH).

Anal. Found: C, 58.92; H, 5.47; N, 4.40. $C_{16}H_{17}FeNO_3$ calc: C, 58.74; H, 5.24; N, 4.28%.

1-Cyano-2-methoxy-2-(2′-oxocylohexyl)-ethyldicarbonyl-η-cyclopentadienyliron(II) (6)

Compound **4d** (0.217 g, 0.746 mmol) was dissolved in 7 ml of THF, cooled to

−78°C and a standard solution of TMSOTf (1.20 ml, 0.80 *M* in CH_2Cl_2, 0.969 mmol) added. After 0.5 h, a solution of lithium cyclohexanone enolate (1.12 mmol, prepared as in the synthesis of **5c** above) in 1 ml of THF at −78°C was added via cannula. After 1.5 h, the reaction was allowed to warm to room temperature, the THF was reduced in vacuo to about 1 ml, 40 ml of ether was added and the mixture was filtered through a short plug of alumina. The solvent was removed in vacuo and the residue chromatographed (alumina, 30% ether/petroleum ether) to give two fractions, unreacted **4d** (79 mg, 36%) and **6** as a yellow oil, 71 mg (42% corrected for recovered **4d**, 2/1 mixture of diastereomers). IR (CH_2Cl_2): 2250 (CN), 2020,1975 (C≡O), 1705 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.95,4.89 (two s, 5H total, Cp's), 3.76 (d of d, 1H, *J* 9 and 1.5 Hz, CH_3O-C*H*), 3.30 (s, 3H, OCH_3), 2.5–1.3 (bm. 10H, Fp-CH and cyclohexyl ring); ^{13}C NMR ($CDCl_3$) Major diastereomer); δ 214.1 (C≡O), 211.1 (C=O), 128.8 (CN), 86.4 (Cp), 80.1 (OCH), 59.1 (OCH_3), 55.0 (O=C-*C*H), 41.9 (O=C-*C*H_2), 26.6, 26.1, 24.6 (*C*H_2*C*H_2*C*H_2), −0.7 (Fp-CH); Minor diastereomer); δ 214.4 (C≡O), 211.4 (C=O), 86.8 (Cp), 83.7 (O-CH), 58.9 (OCH_3), 52.5 (O=C-*C*H), 41.6 (O=C-*C*H_2), 25.2,24.8,24.3 (*C*H_2*C*H_2*C*H_2), −1.5 (Fp-CH).

Anal. Found: C, 57.54; H, 4.80; N, 3.84. $C_{17}H_{19}FeNO_4$ calc: C, 57.16; H, 5.36; N, 3.92%.

1-Cyano-2-methoxy-2-thiobenzyloxyethyldicarbonyl-η-cyclopentadienyliron(II) (7)

Compound **4d** (0.153 g, 0.53 mmol) was dissolved in 10 ml of ether, cooled to −78°C and a standard solution of TMSOTf (0.78 ml, 0.75 *M* in CH_2Cl_2, 0.58 mmol) was added. The resulting yellow precipitate was stirred at −78°C for 30 min. The yellow precipitate **3d** was then isolated via cannula filtration and washed with 2 × 20 ml of ether, keeping the precipitate at −78°C. The precipitate was then dissolved in 5 ml of THF at −78°C and a pre-cooled slurry of sodium benzyl thiolate (0.68 mmol), prepared by treatment of benzyl mercaptan (0.085 g, 0.68 mmol) with NaH was added. After 1.5 h the reaction mixture was warmed to room temperature and the solvent reduced to 1 ml in vacuo. Addition of 20 ml of ether precipitated sodium tetrafluoroborate which was filtered through a short plug of alumina. The solvent was removed in vacuo to give a red oil. Chromatography on alumina (50% ether/petroleum ether) gave three fractions: dibenzyldisulfide (**8**) (45.7 mg, 38%); Fp-SCH_2Ph (**9**) (12 mg, 10%) and **7** as a yellow oil, 105.7 mg (52%). IR (CH_2Cl_2): 2029,1977, 2204 cm^{-1} (C≡N); ^1H NMR ($CDCl_3$): δ 7.30 (s, 5H, Ph), 4.83 (s, 5H, Cp), 4.10 (d, 1H, *J* 4.5 Hz, O-CH), 3.85 (s, 2H, $PhCH_2$), 3.36 (s, 3H, OCH_3), 2.46 (d, 1H, *J* 4.5 Hz, Fp-CH); ^{13}C NMR ($CDCl_3$) δ 214.0 (C≡O), 138.6 (*i*-Ph), 128.9 (*m*-Ph), 128.4 (*o*-Ph), 127.2 (CN), 126.9 (*p*-Ph), 91.1 (O-CH) 86.2 (Cp), 55.7 (OCH_3), 34.7 (SCH_2), 3.2 (Fp-CH).

Anal. Found: C, 56.49; H, 4.05; N, 3.51. $C_{18}H_{17}FeNO_3S$ calc: C, 56.41; H, 4.47; N, 3.65%.

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