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Reactions of nucleophiles with cationic bridging alkylidyne complexes *

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Abstract

The reaction of the μ-methylidyne complex $\{[Cp(CO)Fe]_2(\mu\text{-}CH)\}^+ PF_6^-$ (1) with $C_6H_5(CH_3)_2SiLi$ and CuI produced $[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHSi(CH_3)_2C_6H_5]$ (4). Reaction of *p*-tolyl carbyne complex $\{[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4\text{-}p\text{-}CH_3)\}^+ BF_4^-$ (13) with nucleophiles $NEt_4^+HFe(CO)_4^-$ and $Li(CH_3CuCN)$ gave μ-alkylidene complexes $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHC_6H_4\text{-}p\text{-}CH_3)$ (14) and $[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C(CH_3)C_6H_4\text{-}p\text{-}CH_3]$ (15), respectively. Treatment of ethylidyne complex $\{[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_3)\}^+ BF_4^-$ (7) with $Li(CH_3CuCN)\cdot BF_3$ produced μ-alkylidene complex $[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C(CH_3)_2]$ (17). Hydride abstraction from 17 by $Ph_3C^+ PF_6^-$ produced the μ-alkenyl complex $\{[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}C(CH_3){=}CH_2]\}^+ PF_6^-$ (18).

Several years ago we synthesized $\{[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)\}^+ PF_6^-$ (1) which was the first methylidyne complex in which a CH unit bridged between two metals [1]. This compound may be related to surface species in the heterogeneous Fischer–Tropsch reaction since work from a number of laboratories has shown that the Fischer–Tropsch reaction proceeds via a successive addition of hydrogen to a surface carbide species [2]. Complex **1** is a powerful electrophile which reacts with alkenes via addition of the methylidyne C–H bond across the carbon–carbon double bond of the alkene [3]. The reactions of **1** with carbon and heteroatom nucleophiles have been employed in the high yield syntheses of a variety of bridging alkylidene complexes [4]. For example, the reaction of **1** with one equivalent of the sodium salt of diethyl malonate gave $[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH(CO_2CH_2CH_3)_2]$ (2) in 68% yield and the addition of methyllithium to **1** led to isolation of $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (3) in 91% yield [4]. We have recently extended this

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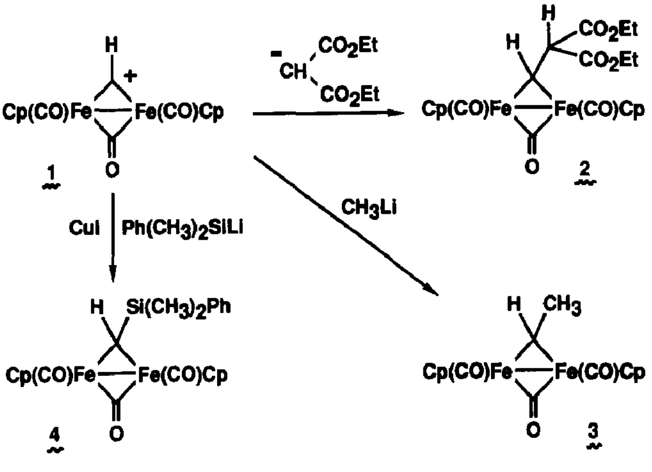
* Dedicated to Professor F.G.A. Stone on the occasion of his 65th birthday and in recognition of his pioneering work on the synthesis of hydrocarbyl bridged bimetallic compounds.



type of reaction to include silicon nucleophiles. Complex **1** reacted with $C_6H_5(CH_3)_2SiLi$ and CuI to produce μ-alkylidene complex $[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHSi(CH_3)_2C_6H_5]$ (**4**) in 58% yield. The trimethylsilyl analogue of **2**, $[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHSi(CH_3)_3]$ (**5**), had been prepared previously by the photolysis of $N_2CHSi(CH_3)_3$ and $[Cp(CO)Fe]_2(\mu\text{-}CO)_2$ (**6**) [5].

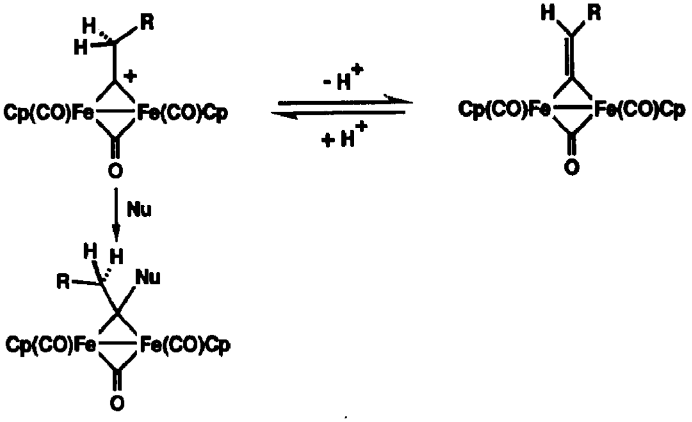
While formation of new carbon–carbon bonds to the $\mu\text{-}CH^+$ unit of **1** was extremely facile, we experienced great difficulty in forming new carbon–carbon bonds to substituted μ-alkylidyne complexes. For example, electrophilic addition of alkenes to **1** occurred at low temperature but alkenes were unreactive toward $\mu\text{-}CR^+$ complexes. Also, while CO readily formed a 1/1 adduct with **1**, it was totally unreactive towards $\mu\text{-}CR^+$ units. The addition of $CNCMe_3$ to $\{[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_3)\}^+ BF_4^-$ (**7**) was the only case in which we observed addition of a carbon nucleophile to a substituted μ-alkylidyne complex. Disubstituted μ-alkylidene complexes are relatively rare. Knox has prepared $[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C(CH_3)_2]$ by hydride addition to μ-alkenyl complex $\{[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}C(CH_3){=}CH_2]\}^+ PF_6^-$ [6].

In an effort to develop synthetic entries into disubstituted $\mu\text{-}CR_2$ complexes we have explored the reactions of μ-alkylidyne complexes with carbon nucleophiles.

Results and discussion

At the outset, we realized that deprotonation of the acidic hydrogens on the carbon α to the alkylidyne carbon of $\{[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_3)\}^+ BF_4^-$ (**7**) [7] might compete with the addition of nucleophiles to the bridging alkylidyne carbon. Previous work within our group established the acidic nature of these α-hydrogens; the acidity of complex **7** in CH_2Cl_2 was estimated to be approximately equal to that of trifluoroacetic acid [8].

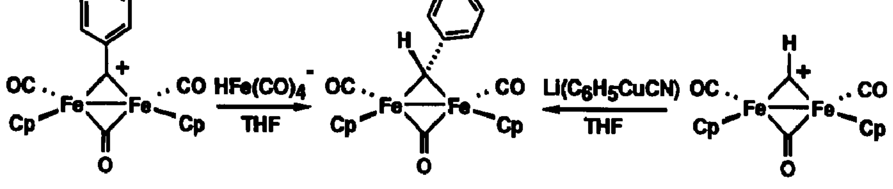
In fact, deprotonation of an α-hydrogen was the predominant reaction between some nucleophiles and μ-alkylidyne complexes. The reaction of a CD_2Cl_2 solution containing μ-ethylidyne complex **7** (0.02 *M*) and 1 equivalent of the sodium salt of diethyl malonate was monitored by ^1H NMR. Rapid deprotonation of **7** produced the neutral complex $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ (**8**) [9] and diethyl malonate.



Similarly, a CD_2Cl_2 solution of μ-propylidyne complex $\{[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_3)\}^+ PF_6^-$ (**9**) [3a] (0.04 *M*) and 1 equivalent of the sodium salt of diethyl malonate led to deprotonation of **9** and formation of $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_3)$ (**10**) [10] and diethyl malonate.

The bridging carbon of μ-methylidyne complex **1** was sufficiently electrophilic to be attacked by neutral 1,3-dicarbonyl compounds, presumably via an enol intermediate. However, when a CH_2Cl_2 solution of μ-ethylidyne complex **7** containing 20 equivalents of ethyl acetoacetate was monitored by IR spectroscopy, no disappearance of the terminal or bridging CO bands of **7** was observed over the course of 30 h. Examination of the diethyl ether soluble materials by ^1H NMR spectroscopy showed no signals which could be assigned to a 1/1 adduct.

We have pursued two strategies to obtain products from addition of nucleophiles to μ-alkylidyne complexes. First, we explored reactions of bridging alkylidyne compounds that did not contain acidic α-hydrogens. Second, we searched for nucleophilic reagents that would selectively add to the bridging alkylidyne carbon rather than deprotonate the acidic α-hydrogens.

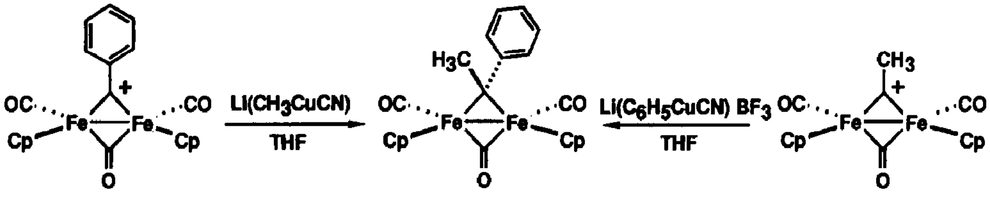


11 **12** **1**

Reactions of nucleophiles with bridging alkylidyne complexes that do not contain α-hydrogens

The reactions of nucleophiles with aryl-substituted μ-alkylidyne complexes were studied since these complexes do not have acidic α-hydrogens. Reaction of NEt_4^+ $HFe(CO)_4^-$ with the phenyl substituted alkylidyne complex $\{[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CC_6H_5)\}^+ BF_4^-$ (**11**) [7] produced the neutral μ-alkylidene complex $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHC_6H_5)$ (**12**) in 74% yield. The IR spectrum of **12** had two bands for the terminal CO ligands at 1983(s) and 1946(w) cm^{-1}. The greater intensity of the high energy band established a *cis* relationship of the terminal carbonyls. The ^1H NMR of complex **12** had one Cp resonance at δ 4.94, consistent with the presence of a single isomer with *cis* Cp ligands. A characteristic downfield singlet at δ 12.36 was assigned to the proton on the bridging carbon. The same isomer of complex **12** was previously obtained from addition of $Li(C_6H_5CuCN)$ to methylidyne complex **1** [4], and we have drawn **12** as the least sterically crowded structure with the phenyl group away from the *cis* Cp ligands. Since nucleophiles would be expected to attack the bridging carbon from the least hindered face away from the large *cis* Cp ligands, different isomers of **12** might have been expected from these two reactions. The fact that a single isomer was seen suggests that equilibration has taken place. Isomerization could occur by bridge opening and rotation about the Fe=CHPh group. Isomerization of *trans*- to *cis*-$[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ occurred at 17 °C with a $t_{1/2}$ of 1 h and has been suggested to occur by bridge opening followed by rotation and subsequent reclosure [11]. Reaction of *p*-tolyl carbyne complex $\{[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4\text{-}p\text{-}CH_3)\}^+ BF_4^-$ (**13**) [7] with NEt_4^+ $HFe(CO)_4^-$ produced a similar neutral complex $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHC_6H_4\text{-}p\text{-}CH_3)$ (**14**) in 60% yield.

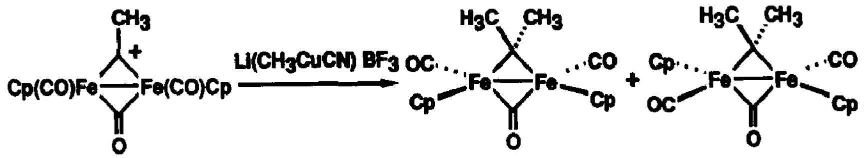
Reaction of **13** with $Li(CH_3CuCN)$ in THF produced $[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C(CH_3)C_6H_4\text{-p-}CH_3]$ (**15**) in 62% isolated yield as a single isomer after chromatography. In the absence of an added copper reagent, reaction of **13** with CH_3Li in THF at −78 °C produced **15** in only 13% yield. The presence of the μ-CRR′ ligand in **15** was supported by the observation of a downfield signal in the ^{13}C NMR at δ 170 assigned to the bridging carbon. The ^1H NMR spectrum of **15** showed a single resonance for the *cis* Cp ligands at δ 5.00. These spectral data do not allow us to distinguish between two isomers, in which the methyl group is *syn* or *anti* with respect to the *cis* Cp ligands. In the absence of definitive evidence, we have drawn **15** as the less hindered isomer in which the methyl group is *syn* to the Cp ligands.



11 **16** **7**

Reactions of nucleophiles with bridging alkylidyne complexes containing α-hydrogens

Since the use of alkylcuprate reagents gave increased yields in the reactions discussed above, we investigated the reactivity of these soft nucleophiles towards μ-alkylidyne complexes containing acidic α-hydrogens. The reaction of **7** with the arylcuprate $Li(C_6H_5CuCN) \cdot BF_3$ [12] gave a single *cis*-Cp isomer of $[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C(CH_3)C_6H_5]$ (**16**) in 26% yield as the sole isolated product. The same isomer of complex **16** was obtained from addition of $Li(CH_3CuCN)$ to a THF slurry of phenyl substituted alkylidyne complex **11**. That a single isomer of complex **16** was seen once again suggested that equilibration had taken place. We have drawn **16** as the least sterically crowded structure with the phenyl group away from the *cis* Cp ligands.

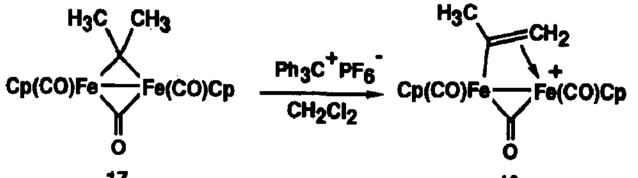


7 cis-17 trans-17

Treatment of μ-ethylidyne complex 7 with 1.1 equivalents of $Li(CH_3CuCN) \cdot BF_3$ in THF at $-78°C$, followed by warming to room temperature, afforded a 3.7/1 mixture of *cis*- and *trans*-$[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C(CH_3)_2]$ [6] (*cis*- and *trans*-**17**) in 24% yield as the sole isolated product [13*]. The major isomer was assigned as *cis*-**17** since its ^1H NMR had a Cp resonance at δ 4.83 and two associated methyl resonances at δ 3.31 and 2.90. The minor isomer was assigned as *trans*-**17** since its ^1H NMR had a Cp resonance at δ 4.69 and only a single methyl resonance for the symmetry equivalent methyl groups.

Reactions of $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_3R)$ with hydride abstraction reagents

Previous work by Pettit [14] established that hydride abstraction from the μ-ethylidene complex $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ resulted in the formation of the μ-alkenyl complex $\{[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CH)\}^+$. As an extension of this reaction, we studied the reaction of complex **17** with $Ph_3C^+\ PF_6^-$, which produced a 3/1 mixture of two isomers of $\{[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}C(CH_3){=}CH_2]\}^+PF_6^-$ (*cis*- and *trans*-**18**) in 63% yield.



17 18

There are three possible isomers **18**: two *cis* Cp isomers with CH_3 either *syn* or *anti* to the Cp ligands and one *trans* Cp isomer. Each of these isomers has inequivalent Cp ligands. A fluxional process involving oscillation of the μ-$C(CH_3){=}CH_2$ ligand between the two iron centers would interchange Cp environments of the *cis* isomers. However, such a process should be slow at room temperature in analogy with $\{[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CH_2)\}^+$ [15]. Therefore, each of the three isomers would be expected to have two Cp and one methyl resonance. In fact, the ^1H NMR of the major isomer of **18** had two Cp signals at δ 5.42 and 5.27 and that of the minor isomer also had two Cp signals at δ 5.78 and 5.58. Since at least one of the isomers must be a *cis* compound with 2 Cp resonances, the fluxional process of μ-vinyl oscillation for one of the *cis* Cp isomers of **18** must be slow. The IR spectrum of the 3/1 mixture of isomers of **18** in Nujol had two bands at 2003(s) and 1978(m) cm^{-1}. Based on these IR data, the major isomer was assigned a *cis* configuration and the minor isomer a *trans* configuration. The strong band at 2003 cm^{-1} must be due to the major isomer and was assigned to

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* Reference number with asterisk indicates a note in the list of references.

the symmetric stretch of *cis*-**18**. The medium intensity band at 1978 cm^{-1} was assigned as the superposition of the asymmetric stretches of the two isomers. The symmetric stretch of *trans*-**18** is IR inactive [16*].

In an attempt to observe an α-phenyl-substituted μ-alkenyl complex, the reaction of μ-alkylidene complex **16** with Ph_2CH^+ SbF_6^- was monitored by ^1H NMR which showed the disappearance of the starting material, but no formation of diamagnetic iron-containing products. Similar attempts to prepare a μ-alkenyl complex by hydride abstraction from the tolyl-substituted alkylidene complex **15** using a variety of reagents were unsuccessful.

Conclusion

New syntheses of disubstituted μ-alkylidene diiron complexes have been developed. Addition of organocuprates to aryl-substituted μ-alkylidyne complexes produced disubstituted μ-alkylidene complexes in good yield. The use of organocuprates in the presence of BF_3 allowed addition to occur to μ-alkylidyne complexes containing acidic α-hydrogens and produced disubstituted μ-alkylidene complexes without contamination with deprotonated products.

Experimental

^1H NMR spectra were obtained on Bruker WP200, WP270 or AM500 spectrometers. $^{13}C\{^1H\}$ NMR spectra from samples containing 0.07 *M* $Cr(acac)_3$ as a shiftless relaxation agent were obtained on a JEOL FX200 (50.10 MHz) or a Bruker AM500 spectrometer (126 MHz). In cases where indicated, proton-coupled ^{13}C NMR spectra were also obtained. Infrared spectra were measured on a Beckman 4230 or Mattson Polaris (FT) spectrometer. Mass spectra were determined on a KRATOS MS-80. Elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN) or by Schwarzkopf Laboratories (Woodside, NY).

Diethyl ether, THF, toluene, hexane and C_6D_6 were distilled from purple solutions of sodium and benzophenone immediately prior to use. CH_2Cl_2 and CD_2Cl_2 were dried over P_2O_5. CD_3CN and $(CD_3)_2CO$ were dried over CaH_2 and B_2O_3 respectively.

Air-sensitive materials were manipulated in an inert-atmosphere glovebox or by standard Schlenk techniques.

$[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHSi(CH_3)_2C_6H_5]$ (4). A solution of $Li[C_6H_5(CH_3)_2SiCuI]$, prepared by adding $C_6H_5(CH_3)_2SiLi$ (0.41 mmol) to CuI (78 mg, 0.41 mmol) in THF and stirring at 0 °C for 15 min, was added by syringe to a stirred suspension of **1** (200 mg, 0.41 mmol) in THF (20 ml) at −78 °C. The reaction mixture was stirred at 0 °C for 5 min, cooled to −78 °C, and quenched with methanol (10 ml). Solvents were evaporated under vacuum. The residue was extracted into CH_2Cl_2 (2 ml) and purified by column chromatography (alumina, diethyl ether), to give **4** (113 mg, 58%) as a red solid. ^1H NMR (270 MHz, acetone-d_6) δ 11.44 (s, μ-CHR), 7.8–7.4 (C_6H_5), 4.73 (s, 10 H, C_5H_5), 0.49 (s, 6 H, $SiCH_3$); IR (CH_2Cl_2): 1975(s), 1938(w), 1778(m) cm^{-1}; HRMS calcd. for $M-CO$ $C_{21}H_{22}Fe_2O_2Si$ 446.0087, found 446.0085.

$[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHC_6H_5)$ (12). THF (8 ml) was condensed onto a mixture of **11** (200 mg, 0.40 mmol) and Et_4N^+ $HFe(CO)_4^-$ (180 mg, 0.60 mmol) cooled to −78 °C. The reaction mixture was stirred at room temperature for 5 min.

Volatile material was evaporated under vacuum. The residue was dissolved in CH_2Cl_2 (2 ml) and chromatographed (alumina, diethyl ether) to give **12** (123 mg, 74%) as a purple-red solid identified by ^1H NMR [4].

$[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHC_6H_4\text{-}p\text{-}CH_3)$ (14). **13** (150 mg, 0.29 mmol) and $(C_2H_5)_4N^+$ $HFe(CO)_4^-$ (167 mg, 0.56 mmol) were stirred for 3 h in THF (30 ml) at room temperature. Solvent was evaporated under vacuum. Neutral material was dissolved in diethyl ether, filtered, and the ether evaporated under vacuum to yield **14** (75 mg, 60%) as a red solid. ^1H NMR (270 MHz, acetone-d_6) δ 12.36 (s, μ-CHR), 7.43 (d, J 8.1 Hz, 2H, C_6H_4), 6.98 (d, J 8.1 Hz, 2H, C_6H_4), 4.91 (s, 10H, C_5H_5), 2.25 (s, C_6H_4-CH_3); $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6, 0.07 M $Cr(acac)_3$) δ 272.1 (μ-CO), 214.3 (CO), 167.6 (μ-CHR), 161.1 (*ipso*-C_6H_4), 134.7 (p-C_6H_4), 128.9, 128.8 (o,m-C_6H_4), 89.1 (C_5H_5), 21.0 (CH_3); IR (CH_2Cl_2): 1982(s), 1946(w), 1786(m) cm^{-1}; HRMS calcd. for $M-CO$ $C_{20}H_{18}Fe_2O_2$ 402.0005, found 401.9927.

$[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C(CH_3)C_6H_4\text{-}p\text{-}CH_3]$ (15). A solution of $Li(CH_3CuCN)$, prepared from CH_3Li (0.32 mmol) and CuCN (31 mg, 0.35 mmol) in THF at −20 °C, was cooled to −78 °C and added to a stirred suspension of **13** (150 mg, 0.29 mmol) in THF (20 ml) at −78 °C. The reaction mixture was stirred at −30 °C for 0.5 h, and THF was evaporated under vacuum. The residue was extracted into CH_2Cl_2 (2 ml) and purified by column chromatography (alumina, diethyl ether) to give **15** (80 mg, 62%) as a red solid. ^1H NMR (270 MHz, acetone-d_6) δ 7.47 (d, J 8.6 Hz, 2H, C_6H_6), 6.90 (d, J 8.2 Hz, 2H, C_6H_4), 5.00 (s, 10H, C_5H_5), 3.20 (s, μ-CCH_3), 2.21 (s, CH_3); $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6, 0.07 M $Cr(acac)_3$) δ 273.6 (μ-CO), 213.0 (CO), 201.5 (μ-CRR′), 169.9 (*ipso*-C_6H_4), 133.1 (p-C_6H_4), 129.9, 127.5 (o,m-C_6H_4), 90.2 (C_5H_5), 59.4 (μ-CCH_3), 20.8 (CH_3); IR (CH_2Cl_2): 1990(s), 1945(w), 1775(m); HRMS calcd. for $M-CO$ $C_{21}H_{20}Fe_2O_2$ 416.0161, found 416.0086.

$[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C(CH_3)C_6H_5]$ (16). (A) A solution of $Li(CH_3CuCN)$ (0.42 mmol) in THF (3 mL) was added via cannula to a slurry of **11** (190 mg, 0.38 mmol) in THF (8 mL) at −78 °C. Evaporation of solvent and chromatography of the residue (alumina, diethyl ether) afforded **16** (85 mg, 52%) as a red solid. ^1H NMR (acetone-d_6) δ 7.60 (m, 2 H, o-C_6H_5), 6.98 (m, 3 H, m-, p-C_6H_5), 5.02 (s, 10 H, C_5H_5), 3.22 (s, CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 271.6 (μ-CO), 211.6 (CO), 199.9 (μ-$C(CH_3)C_6H_5$), 171.6 (*ipso*-C_6H_5), 129.5, 126.7, 124.6 (C_6H_5), 88.9 (C_5H_5), 59.1, (CH_3); IR (CH_2Cl_2): 1982(s), 1942(w), 1773(m) cm^{-1}; HRMS calcd. for $M-CO$ 402.0005, found 402.0001. Anal. Found: C, 58.58; H, 4.16. $C_{21}H_{18}Fe_2O_3$ calcd.: C, 58.65; H, 4.22%.

(B) A solution of $Li(C_6H_5CuCN)$, prepared by stirring CuCN (350 mg, 3.90 mmol) and C_6H_5Li (3.80 mmol) in THF (25 ml) at −20 °C until the solution became clear, was cooled to −78 °C and $BF_3 \cdot Et_2O$ (0.50 ml, 4.06 mmol) was added. The resulting slurry was added via cannula to a slurry of **7** (332 mg, 0.75 mmol) in THF (10 ml) at −78 °C. Work-up as described above afforded **16** (84 mg, 26%).

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C(CH_3)_2]$ (17). A solution of $Li(CH_3CuCN)$ (5.68 mmol) in THF (25 ml) was cooled to −78 °C and $BF_3 \cdot Et_2O$ (0.70 ml, 5.69 mmol) was added. The resulting slurry was added to a slurry of **7** (500 mg, 1.14 mmol) in THF (15 ml) cooled to −78 °C. The mixture was stirred at room temperature for 10 min and alumina (0.5 g) was added. Volatile material was evaporated under vacuum and the solid residue was chromatographed (alumina, diethyl ether) to afford **17**

(115 mg, 28%, 3/1 mixture of *cis/trans* Cp isomers) as a purple microcrystalline solid. ^{1}H NMR (acetone-d_6), *cis* isomer, δ 4.83 (s, 10H, C_5H_5), 3.31 (s, 3H, CH_3), 2.90 (s, 3H, CH_3); *trans* isomer, δ 4.69 (s, 10H, C_5H_5), 3.15 (s, 6H, CH_3); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6), *cis* isomer, δ 272.9 (μ-CO), 213.6 (CO), 198.8 (μ-$C(CH_3)_2$), 90.1 (C_5H_5), 55.8 (CH_3), 55.1 (CH_3); *trans* isomer, δ 271.8 (μ-CO), 213.9 (CO), 197.4 (μ-$C(CH_3)_2$), 88.6 (C_5H_5), 55.2 (CH_3); IR (CH_2Cl_2): 1977(s), 1938(s), 1768(m) cm^{-1}; HRMS calcd. for $M-$ CO $C_{15}H_{16}Fe_2O_2$ 339.9848, found 339.9824. Anal. Found: C, 51.82; H, 4.60. $C_{16}H_{16}Fe_2O_3$ calcd.: C, 52.22; H, 4.38%.

$\{[(C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^2\text{-}C(CH_3)=CH_2]\}^+\ PF_6^-$ *(18).* CH_2Cl_2 (8 ml) was condensed onto a solid mixture of **17** (245 mg, 0.67 mmol) and $Ph_3C^+\ PF_6^-$ (250 mg, 0.64 mmol) at −78°C. The reaction mixture was stirred at room temperature for 15 min. The resulting maroon-colored solution was cooled to −78°C and diethyl ether (5 ml) was condensed in to afford a maroon precipitate. The solid was isolated by filtration, washed with ether (3 × 5 ml), and dried under vacuum to give **18** (204 mg, 63% based on $Ph_3C^+\ PF_6^-$). ^{1}H NMR (acetone-d_6), major isomer, δ 5.42 (s, 5H, C_5H_5), 5.27 (s, 5H, C_5H_5), 4.82 (bs, 1H, H of CH_2), 3.79 (s, 3H, CH_3), 2.94 (bs, 1H, H of CH_2); minor isomer, δ 5.78 (s, 5H, C_5H_5), 5.58 (s, 5H, C_5H_5), 4.50 (bs, 1H, H of CH_2), 3.90 (s, 3H, CH_3), 2.15 (bs, 1H, H of CH_2); IR (Nujol): 2003(s), 1978(m), 1863(s) cm^{-1}. Anal. Found: C, 37.84; H, 2.78. $C_{16}H_{15}F_6Fe_2O_3P$ calcd.: C, 37.54; H, 2.95%.

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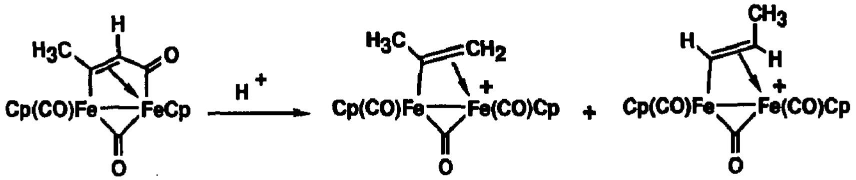

19 **18** **20**