670 *Organometallics* 1988, 7, 670–675

Reactions of Heteroatom and Carbon Nucleophiles with the Cationic Bridging Methylidyne Complex $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)\}^+PF_6^-$

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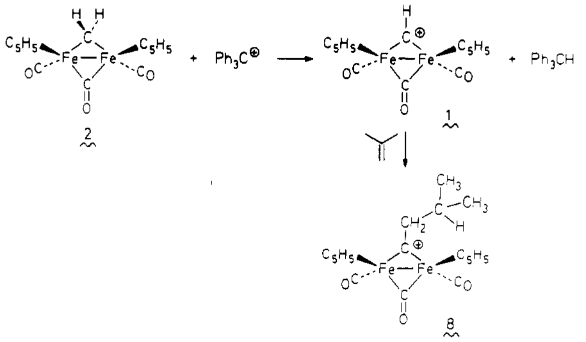
Received July 7, 1987

The reaction of the μ-methylidyne complex $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)\}^+PF_6^-$ (1) with NMe_3 and $(C_6H_5)_2C{=}NH$ gave the cationic 1:1 adducts $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHNMe_3)\}^+PF_6^-$ (3) and $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHNH{=}C(C_6H_5)_2]\}^+PF_6^-$ (9), respectively, arising from attack of nitrogen on the methylidyne carbon. The reaction of 1 with $KOC(CH_3)_3$ gave the neutral μ-carbene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHOC(CH_3)_3]$ (4). Reaction of 1 with water afforded a 1:1 mixture of μ-methylene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ (2) and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)_2$; these products are proposed to arise from disproportionation of an initially formed hydroxy carbene species. Reaction of 1 with $Et_4N^+Br^-$ gave the unstable μ-carbene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHBr)$ (6). Reaction of 1 with the carbon nucleophiles CH_3Li and $Li(C_6H_5CuCN)$ gave the μ-carbene complexes $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (11) and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHC_6H_5)$ (12), while reaction of 1 with $HFe(CO)_4^-$ afforded 2. 1 reacted with acetone via nucleophilic addition of the enol affording the neutral μ-carbene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_2COCH_3)]$ (13). 1 also reacted with cyclohexanone, 2-butanone, 4-methyl-2-pentanone, 2,4-pentanedione, 5,5-dimethyl-1,3-cyclohexanedione, ethyl acetoacetate, and the sodium salt of diethyl malonate to give similar μ-carbene products.

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. Work from a number of laboratories has shown that the Fischer–Tropsch reaction proceeds via successive addition of hydrogen to a surface carbide species.[2] Bridging methylidyne complexes are still rare; the short list of known dinuclear methylidyne complexes includes $\{[(C_5Me_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)\}^+$,[3] $\{(C_5H_5)(C_5Me_5)(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CH)\}^+$,[3] $\{[(C_5H_4Me)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)\}^+$,[4] $\{[(C_5H_5)(\mu\text{-}NO)\text{-}Fe]_2(\mu\text{-}CH)\}^+$,[5] $\{(C_5H_5)_2(dppm)Ru_2(\mu\text{-}CO)(\mu\text{-}CH)\}^+$,[6] and $\{[(C_5H_5)(CO)Ru]_2(\mu\text{-}CO)(\mu\text{-}CH)\}^+$.[7] Complexes such as $Co_3(CO)_9(\mu_3\text{-}CH)$,[8] $\{(C_5H_5)_3Rh_3(\mu\text{-}CO)_2(\mu_3\text{-}CH)\}^+$,[9] and $HOs_3(CO)_{10}(\mu_3\text{-}CH)$[10] in which a methylidyne group bridges three metals are well-known. Muetterties has reported a rare case in which the CH unit of $HFe_4(CO)_{12}(\mu_4\text{-}CH)$[11] bridges four metals. Mononuclear methylidyne complexes such as $W(CH)Cl(PMe_3)_4$[12] have also been reported.

The μ-methylidyne complex 1 is stable in the solid state but readily decomposes in solution. The best solvent for studying the reactions of 1 is methylene chloride; in this solvent, the half-life of 1 is about 2 h at room temperature. The kinetic instability of 1 is related to its potent electrophilic reactivity.

1 was prepared by hydride abstraction from $[Cp(CO)\text{-}Fe]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ (2) with $(C_6H_5)_3C^+PF_6^-$. This establishes that 1 is a thermodynamically more stable carbocation than $(C_6H_5)_3C^+$ and indicates that the two iron centers in 1 are better electron donors to the μ-CH unit than the three phenyl groups in $(C_6H_5)_3C^+$. Nevertheless, 1 remains a powerful electrophile and its reactions with alkenes and alkynes are initiated by an electrophilic attack of the μ-CH carbon on the alkene. Here we report the reactions of 1 with a wide range of heteroatom and carbon nucleophiles.



Results and Discussion

Reactions of Heteroatom Nucleophiles with 1. The addition of NMe_3 to a deep purple solution of μ-methylidyne complex 1 in CH_2Cl_2 at −78 °C produces an im-

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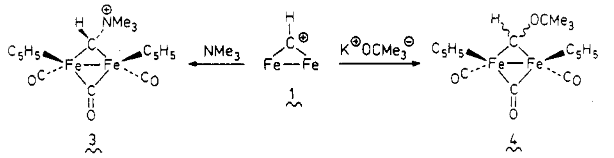
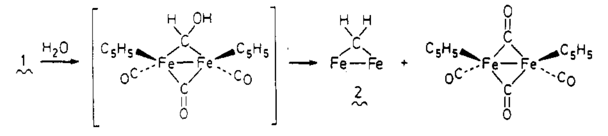
mediate color change to bright red. Evaporation of solvent and recrystallization from acetone–ether led to the isolation of the NMe_3 adduct $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHNMe_3)\}^+PF_6^-$ (**3**) as a bright red solid in 80% yield.

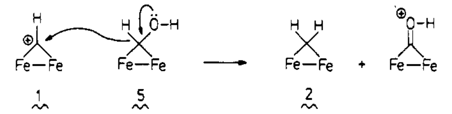


The structure of **3** was readily established spectroscopically. The presence of a μ-$CHNMe_3$ ligand is supported by the observation of a characteristic downfield singlet at δ 11.69 in the ^1H NMR spectra and by the observation of a downfield doublet (J_{CH} = 142 Hz) at δ 191.0 in the ^{13}C NMR spectrum. The resonance for the Me_3N protons appears as a singlet at δ 3.60. The cis arrangement of the Cp and terminal CO ligands of **3** is assigned on the basis of the observation of a single C_5H_5 resonance in both the ^1H (δ 5.27) and ^{13}C (δ 90.6) NMR spectra. This assignment was confirmed by the observation of a single terminal CO resonance at δ 213.6 in the ^{13}C NMR and by the appearance of infrared bands at 1998 (s) and 1962 (m) cm^{-1} consistent with cis terminal CO ligands. The bridging carbonyl ligand of **3** is assigned on the basis of an IR band at 1781 cm^{-1} and a ^{13}C NMR resonance at δ 270.0. Our spectral data do not allow an assignment of the relative geometry of the NMe_3 and Cp groups on iron. However, since both CO[13] and $C{\equiv}NR$[14] react with **1** to form adducts in which the nucleophile enters from the less hindered carbonyl face, we tentatively assign a similar geometry to **3**.

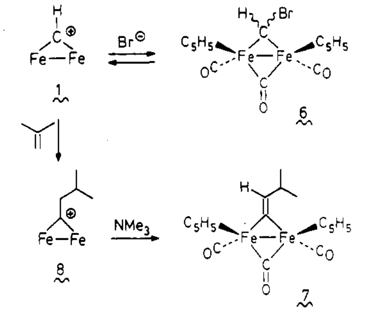
The reaction of potassium *tert*-butoxide in *tert*-butyl alcohol with **1** led to the formation of a 5:1 mixture of isomers of $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHOCMe_3)$ (**4a** and **4b**). Since each of the isomers exhibited a single Cp resonance in both the ^1H and ^{13}C NMR spectra, both isomers are assigned a cis relationship of the Cp rings. The two isomers differ in the relationship between the Cp ligands and the O-*tert*-butyl group on the bridging methylene carbon.



Since surface-bound bridging hydroxy carbenes are potential intermediates in heterogeneous Fischer–Tropsch reactions,[2] the reaction of **1** with water was examined as a possible route to a μ-CHOH complex. **1** was stirred with a 1:1 mixture of H_2O and CH_2Cl_2 for 24 h. Subsequent extraction with ether led to the isolation of a 1:1 mixture of $[Cp(CO)Fe]_2(\mu\text{-}CO)_2/[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ (**2**). We suggest that this mixture results from disproportionation of an initially formed intermediate $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHOH)$ (**5**). When the reaction of **1** with acidic, basic, or neutral water in CH_2Cl_2 was followed by ^1H NMR, several new peaks were observed between δ 11 and δ 14 at short reaction times. These peaks are indicative of new μ-CHX species. However, these new peaks were always much smaller than those arising from the μ-CH_2 protons of **2**, and it was not possible to unambiguously assign any of these signals to the proposed intermediate μ-CHOH compound **5**.



The disproportionation of **5** could occur by hydride transfer from **5** to **1** which would produce μ-CH_2 complex **2** and O-protonated $[Cp(CO)Fe]_2(\mu\text{-}CO)_2$. The disproportionation of α-hydroxy organometallic species is a common phenomenon.[15] For example, we have previously found that treatment of $Cp(CO)(NO)ReCH_2OH$ with acid leads to the formation of a 2:1 mixture of $Cp(CO)(NO)ReCH_3/Cp(CO)(NO)Re(CO)^+$.[16]



The reaction of **1** with $Et_4N^+Br^-$ in CH_2Cl_2 led to the isolation of the unstable neutral red adduct $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHBr)$ (**6**) in 22% yield ($t_{1/2} \approx$ 100 min in CH_2Cl_2 at 23 °C). The fact that bromide is covalently bound in **6** is shown by its ether solubility, by the upfield shift of the Cp protons of **6** (δ 4.83) relative to **1** (δ 5.39), and by the characteristic δ 11.60 chemical shift of the μ-CHBr unit. The thermal instability of **6** may be related to the fact that **6** can ionize to the thermally unstable methylidyne complex **1**.

Ionization of the bromide is apparently possible since **6** reacts with isobutylene at 25 °C in CH_2Cl_2 to produce the known compound $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCHMe_2)$ (**7**) in 16% yield after workup with NMe_3.[17] The formation of **7** is readily explained by ionization of **6** to regenerate cationic methylidyne complex **1** which is rapidly trapped by isobutylene in a hydrocarbation reaction that produces $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_2CHMe_2)^+$ (**8**). Deprotonation of **8** during workup with NMe_3 then produces **7**. Also observed in the ^1H NMR spectrum of the reaction mixture were resonances attributed to the vinyl-substituted μ-alkylidene complex $[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH{=}C(CH_3)_2]$ (8% yield). The formation of this product can be accounted for in terms of the rearrangement of **8**, via a 1,2-hydrogen shift, to the corresponding μ-vinyl complex which is then deprotonated to give the μ-alkylidene product. Such rearrangements in diiron complexes have been previously observed.[18] Alternatively, differences in the counterion of the methylidyne complex **1** (i.e., Br^- versus PF_6^-) might favor an alternative reaction pathway to hydrocarbation, namely, electrophilic addition of the methylidyne carbon to the isobutylene to generate a carbocation intermediate which then undergoes a 1,2-carbon migration[3] to produce the same μ-vinyl complex, which again can be deprotonated.

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(13) Casey, C. P.; Fagan, P. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7360.

(14) Casey, C. P.; Crocker, M., unpublished results.

(15) See, for example: (a) Wayland, B. B.; Woods, B. A.; Minda, V. M. *J. Chem. Soc., Chem. Commun.* **1982**, 634–635. (b) Van Voorhees, S. L.; Wayland, B. B. *Organometallics* **1985**, *4*, 1887–1888. (c) Vaughn, G. D.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1462–1473.

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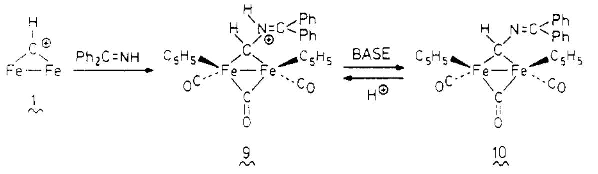
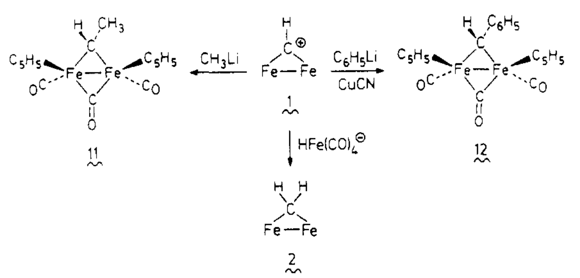
The reaction of **1** with $(C_6H_5)_2C{=}NH$ occurs via addition of the imine nitrogen to the methylidyne carbon of **1** to produce the adduct $\{[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CH\text{-}NH{=}C(C_6H_5)_2]\}^+PF_6^-$ (**9**) in 70% yield. Deprotonation of **9** with diisopropylethylamine or excess $(C_6H_5)_2C{=}NH$ led to the formation of the neutral derivative $[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHN{=}C(C_6H_5)_2]$ (**10**). Protonation of **10** with $HBF_4{\cdot}Et_2O$ in turn regenerated **9** in good yield as the BF_4^- salt.



Addition of Hydride and Alkyl Groups to 1. The addition of methyllithium to a slurry of **1** in CH_2Cl_2 at −78 °C led to the isolation of $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (**11**) in 91% yield. This ethylidene complex **11** had previously been prepared by hydride addition to the corresponding ethylidyne complex.[19]

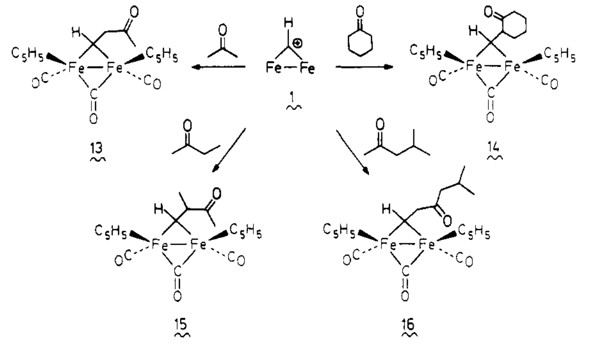


Similar treatment of **1** with PhLi produced the benzylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHC_6H_5)$ (**12**) in 25% yield. An improved yield of **12** was obtained by addition of the cuprate prepared from equimolar amounts of PhLi and CuCN to a THF slurry of **1**, affording **12** in 70% isolated yield. Hydride addition to **1** using $NEt_4^+HFe(CO)_4^-$ led to isolation of μ-methylene complex **2** in 67% yield.

Addition of Enols of Ketones to 1. Ketones were found to react readily with methylidyne complex **1** to afford new diiron complexes with a carbonyl group β to the bridging alkylidene group. The formation of these products is readily understood in terms of nucleophilic addition of the enol of the ketones to the methylidyne carbon.

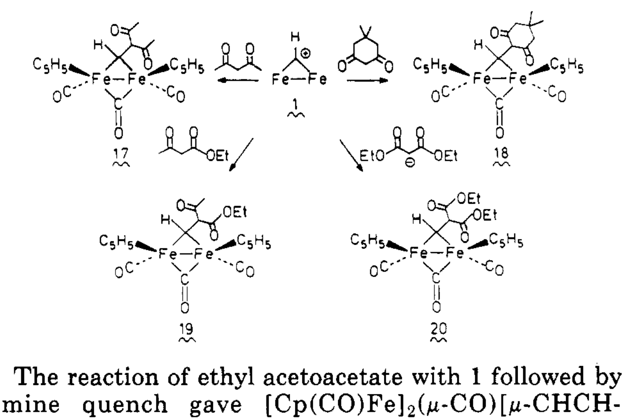
A mixture of methylidyne complex **1** and acetone was stirred for 15 min at room temperature and then quenched with diisopropylethylamine. The adduct $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_2COCH_3)$ (**13**) was isolated as a red-orange solid in 77% yield after chromatography. Also isolated were quantities of **2** and $[Cp(CO)Fe]_2(\mu\text{-}CO)_2$, these products presumably arising from the reaction of **1** with trace amounts of water present in the ketone. Similarly, reaction of cyclohexanone with **1** gave a 56% yield of $[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CH\overline{CHCO(CH_2)_3CH_2}]$ (**14**).

The reaction of 2-butanone with **1** resulted in regioselective formation of $[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH(CH_3)COCH_3]$ (**15**) in 59% isolated yield after chromatography. In the ^1H NMR of **15**, the proton on the bridging alkylidene carbon appears as a doublet ($J = 11.7$ Hz) at δ 11.25 coupled to the tertiary hydrogen α to the carbonyl group. The new asymmetric center in **15** renders the Cp groups diastereotopic and two Cp resonances are seen at δ 4.78 and 4.68. Examination of the crude reaction mixture prior to chromatography for traces of the other possible regioisomer by ^1H NMR revealed the presence of **15** together with side products **2** and $[Cp(CO)Fe]_2(\mu\text{-}CO)_2$. An additional unresolved multiplet possibly due to the other regioisomer was observed at δ 11.6 in the ^1H NMR spectrum; however, this was minor in comparison with that observed for the alkylidene proton of **15**. Furthermore, after chromatography the isolated product was found to consist of pure **15**.



The reaction of 4-methyl-2-pentanone with **1** led to the isolation of $[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH_2COCH_2CH(CH_3)_2]$ (**16**) in 7% yield. In contrast to the reaction of **1** with 2-butanone, the isolated product **16** from 4-methyl-2-pentanone results from reaction of the least substituted enol. Attempts to examine the crude reaction mixture for traces of the other possible regioisomer by ^1H NMR were prevented by the presence of paramagnetic side products formed in the reaction. However, again the isolated product was found to consist of a single regioisomer (**16**). Perhaps the more substituted enol of 4-methyl-2-pentanone is too sterically hindered to react with **1**, and only the less substituted enol reacts. However, in view of the low yield obtained, we are reluctant to claim that we understand why the reactions of **1** with 2-butanone and 4-methyl-2-pentanone exhibit opposite regioselectivities.

Reaction of β-Dicarbonyl Compounds with 1. The reaction of 2,4-pentanedione with **1** followed by quenching with diisopropylethylamine led to the isolation of $[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH(COCH_3)_2]$ (**17**) as an orange-red solid in 74% yield. Since this diketone adduct was partially deacetylated to the acetone adduct **13** upon chromatography on alumina, chromatography on silica gel was the preferred method of purification. The reaction of 5,5-dimethyl-1,3-cyclohexanedione with **1** under similar conditions led to the isolation of $[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CH\overline{CHCOCH_2C(CH_3)_2CH_2CO}]$ (**18**) in 59% yield.



The reaction of ethyl acetoacetate with **1** followed by amine quench gave $[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH(COCH_3)(CO_2CH_2CH_3)]$ (**19**) as an orange-red solid in 61% yield. **19** is a chiral molecule, and two diastereotopic Cp groups are observed in the ^1H NMR at δ 4.90 and 4.87. Similarly, the methylene protons of the ethyl ester are

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diastereotopic and appear as the AB portion of an ABX_3 spin system centered at δ 4.26.

The reaction of **1** with 1 equiv of the sodium salt of diethyl malonate in THF gave $[Cp(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH(CO_2CH_2CH_3)_2]$ (**20**) in 68% yield. While **20** possesses a plane of symmetry that renders the Cp groups equivalent (δ 4.89), the methylene protons of the ethyl group are nevertheless diastereotopic because of their prochiral relationship and appear as the AB portion of an ABX_3 system centered at δ 4.26.

Conclusion. The reaction of methylidyne complex **1** with nucleophiles provides access to a myriad of diiron-bridging methylene compounds with heteroatoms or functionalized carbon groups bonded to the bridging alkylidene carbon. In a subsequent paper, we will describe the reaction of **1** with CO that leads to an acylium complex $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCO)^+$ that is reactive toward nucleophiles and provides access to many additional μ-alkylidene complexes with functionalized side chains.

Experimental Section

^1H NMR spectra were normally obtained on a Bruker WP270 spectrometer or where indicated on a Bruker WP200 or AM500 spectrometer. $^{13}C\{^1H\}$ NMR spectra from samples containing 0.07 M $Cr(acac)_3$ as a shiftless relaxation agent were normally obtained on a JEOL FX 200 spectrometer (50.10 MHz) or where indicated on a Bruker AM 500 spectrometer (125 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 immediately prior to use from purple solutions of sodium and benzophenone. 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. Complex **1** was prepared as previously described.[17] Ketones used were dried over molecular sieves (4 Å) or B_2O_3 and were then distilled from anhydrous K_2CO_3 and freeze–pump–thaw degassed immediately prior to use. Dicarbonyl compounds were freshly distilled onto molecular sieves and were deoxygenated immediately prior to use by purging with nitrogen. $Et_4N^+Br^-$ was dried by heating at 110 °C under high vacuum for 6 h.

$\mathbf{\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHN(CH_3)_3]\}^+PF_6^-}$ **(3).** An excess of $(CH_3)_3N$ was condensed into a slurry of **1** (79 mg, 0.16 mmol) in CH_2Cl_2 (8 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature, and volatile material was evaporated under vacuum. The residue was extracted into acetone (3 mL) and the solution filtered. Diethyl ether (15 mL) was added, and the resulting precipitate was filtered, washed with ether (2 × 1 mL), and dried under vacuum to give **3** as a bright red solid (71 mg, 80%): ^1H NMR (acetone-d_6) δ 11.69 (s, μ-CH), 5.27 (s, 10 H, C_5H_5), 3.60 (s, $N(CH_3)_3$); ^{13}C NMR (acetone-d_6) δ 270.0 (μ-CO), 213.6 (CO), 191.0 ($J_{^{13}C\text{-}H}$ = 142 Hz, μ-CH), 90.6 ($J_{^{13}C\text{-}H}$ = 176 Hz, C_5H_5), 58.9 ($J_{^{13}C\text{-}H}$ = 142 Hz, $N(CH_3)_3$); IR (Nujol) 1998 (s), 1962 (m), 1781 (s) cm^{-1}. Anal. Calcd for $C_{17}H_{20}F_6Fe_2NO_3P$: C, 37.60; H, 3.71; P, 5.70. Found: C, 37.84; H, 3.75; P, 5.62.

$\mathbf{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHOC(CH_3)_3]}$ **(4).** *tert*-Butyl alcohol (3 mL, ~32 mmol) was condensed onto a solid mixture of **1** (216 mg, 0.45 mmol) and $KOC(CH_3)_3$ (610 mg, 5.45 mmol) cooled to −78 °C. The mixture was warmed to ambient temperature, and volatile material was evaporated under vacuum. The residue was extracted with toluene (10 mL), and the resulting solution was filtered and concentrated under vacuum to 0.5 mL. Addition of pentane (5 mL) then afforded a red precipitate which was isolated by filtration, washed with pentane (0.5 mL), and dried under vacuum to give **4** (79 mg, 43%, 5:1 mixture of cis Cp isomers): ^1H NMR (C_6D_6), major isomer, δ 12.62 (s, μ-CH), 4.17 (s, 10 H, C_5H_5), 2.30 (s, $OC(CH_3)_3$); ^1H NMR (C_6D_6), minor isomer, δ 12.04 (s, μ-CH), 4.34 (s, 10 H, C_5H_5), 2.10 (s, $OC(CH_3)_3$); ^{13}C NMR (C_6D_6), major isomer, δ 272.4 (μ-CO), 211.9 (CO), 205.3 ($J_{^{13}C\text{-}H}$ = 143 Hz, μ-CH), 86.6 ($J_{^{13}C\text{-}H}$ = 176 Hz, C_5H_5), 78.6 ($O\mathit{C}(CH_3)_3$), 28.0 ($J_{^{13}C\text{-}H}$ = 125 Hz, CH_3); IR (Nujol) 1973 (s), 1939 (m), 1743 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{20}Fe_2O_4$: C, 52.47; H, 4.89; Fe, 27.11. Found: C, 52.86; H, 4.89; Fe, 27.17.

Reaction of 1 with H_2O. **1** (250 mg, 0.53 mmol) was stirred in CH_2Cl_2 (7 mL) and H_2O (7 mL) under N_2 for 24 h. The mixture was extracted with diethyl ether (20 mL). The red diethyl ether phase was separated, filtered, and evaporated to dryness under vacuum affording a red solid (95 mg, 52%) determined by ^1H NMR spectroscopy to be a 1:1 mixture of **2** and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)_2$.

$\mathbf{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHBr)}$ **(6).** CH_2Cl_2 (20 mL) was condensed onto a solid mixture of **1** (290 mg, 0.60 mmol) and $Et_4N^+Br^-$ (175 mg, 0.83 mmol) cooled to −78 °C. The reaction mixture was stirred at −78 °C for 25 min and then warmed to room temperature. Solvent was evaporated under vacuum, and diethyl ether (20 mL) was added. The mixture was sonicated for 5 min and then rapidly filtered. Evaporation of solvent under vacuum from the resulting red solution afforded **6** as a red solid (55 mg, 22%, 3:1 mixture of cis Cp isomers) which was immediately stored at −78 °C: ^1H NMR (CD_2Cl_2), major isomer, δ 11.60 (s, CH) 4.83 (s, 10 H, C_5H_5); ^1H NMR (CD_2Cl_2), minor isomer, δ 10.80 (s, CH), 4.85 (s, 10 H, C_5H_5); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20 °C), major isomer, δ 210.3 (CO), 171.5 (CH), 87.4 (C_5H_5), μ-CO not observed; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20 °C), minor isomer, δ 210.6 (CO), 90.3 (C_5H_5), μ-CO, μ-CHBr not observed; IR (CH_2Cl_2) 1986 (s), 1945 (m), 1775 (s) cm^{-1}.

Decomposition of 6 in the Presence of Isobutylene. A solution of **6** (35 mg, 0.08 mmol) in CH_2Cl_2 (10 mL) was placed under an atmosphere of isobutylene (7.0 mmol). The mixture was stirred at room temperature for 5 h. Isobutylene was then removed under vacuum, the reaction mixture was cooled to −78 °C, and NMe_3 (1.0 mmol) was condensed in. The mixture was then warmed to room temperature. Volatile material was evaporated under vacuum. Diethyl ether (30 mL) was condensed in, the resulting solution was filtered, and solvent was evaporated under high vacuum affording a red oil (24 mg). ^1H NMR spectroscopy (acetone-d_6) showed the product to be a mixture containing **7** (16% yield by integration). Resonances in the mixture were also assigned to $(C_5H_5)Fe(CO)_2Br$ (13%), $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH{=}C(CH_3)_2]$ (8%), $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)_2$ (5%), and **2** (5%).

$\mathbf{\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHNH{=}C(C_6H_5)_2]\}^+PF_6^-}$ **(9-PF$_6$).** A solution of $Ph_2C{=}NH$[20] (100 mg, 0.55 mmol) in CH_2Cl_2 (5 mL) cooled to −78 °C was added by cannula to a slurry of **1** (260 mg, 0.54 mmol) in CH_2Cl_2 (10 mL) at −78 °C. After 15 min, the reaction mixture was warmed to room temperature and diethyl ether (10 mL) was added. The mixture was filtered, the filtrate was concentrated to 5 mL under vacuum, and diethyl ether (10 mL) was added. The resulting purple-red precipitate was isolated by filtration, washed with ether (3 × 10 mL), and dried under vacuum to give **9-PF$_6$** (249 mg, 70%): ^1H NMR (200 MHz, CD_2Cl_2) δ 10.92 (s, CH), 7.88–7.51 (m, 10 H, C_6H_5), 4.92 (s, 10 H, C_5H_5); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 259.8 (μ-CO), 211.6 (CO), 167.0 (μ-CHR), 150.4 ($={\mathit C}(C_6H_5)_2$), 140.6, 136.8, 130.8, 129.3, 128.8, 127.7, 126.8 (C_6H_5), 89.1 (C_5H_5); IR (CH_2Cl_2) 1994 (s), 1944 (w), 1815 (m) cm^{-1}.

$\mathbf{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHN{=}C(C_6H_5)_2]}$ **(10).** Diisopropylethylamine (0.04 mL, 0.25 mmol) was added by syringe to a solution of **9** (75 mg, 0.11 mmol) in CH_2Cl_2 (8 mL) at −78 °C. After 30 min, the reaction mixture was warmed to room temperature, and volatile material was evaporated under vacuum. The residue was extracted into CH_2Cl_2 (2 mL) and purified by column chromatography (alumina, diethyl ether). Evaporation of solvent from the resulting red solution afforded a dark red solid that was washed with hexane (2 × 5 mL) and dried under vacuum to give **10** (45 mg, 77%): ^1H NMR (200 MHz, CD_2Cl_2) δ 12.41 (s, CH), 7.56–7.41 (m, 10 H, C_6H_5), 4.56 (s, 10 H, C_5H_5); ^{13}C NMR (125.76 MHz, CD_2Cl_2) δ 270.7 (μ-CO), 211.4 (CO), 177.0 ($J_{^{13}C\text{-}H}$ = 141 Hz, μ-CH), 153.2 ($={\mathit C}(C_6H_5)_2$), 140.5 (ipso), 137.0 (ipso), 131.8–126.4 (m, C_6H_5), 86.6 ($J_{^{13}C\text{-}H}$ = 178 Hz, C_5H_5); IR (CH_2Cl_2) 1993 (s), 1953 (w), 1776 (m) cm^{-1}; HRMS calcd for M − 2CO $C_{25}H_{21}Fe_2NO$ 463.0289, found 463.0321. Anal. Calcd for

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[20] Pickard, P. L.; Tolbert, T. L. *J. Org. Chem.* **1961**, *26*, 4886–4888.

$C_{27}H_{21}Fe_2NO_3$: C, 62.47; H, 4.08; N, 2.70. Found: C, 61.97; H, 4.04; N, 2.60.

Protonation of 10. $HBF_4{\cdot}Et_2O$ (0.018 mL, 0.014 mmol) was added to a solution of **10** (65 mg, 0.013 mmol) in CH_2Cl_2 (5 mL) at −78 °C. The mixture was stirred at −78 °C for 10 min and was then warmed to room temperature. Diethyl ether (8 mL) was added at room temperature affording a purple solid which was filtered, washed with diethyl ether, and dried under vacuum to give **9-BF$_4$** (68 mg, 89%). Anal. Calcd for $C_{27}H_{22}BF_4Fe_2NO_3$: C, 53.43; H, 3.65; N, 2.31. Found: C, 53.46; H, 3.76; N, 2.22.

Reaction of 1 with CH_3Li. Methyllithium (0.88 mL, 0.12 mmol, 1.5 M in ether) was added via syringe to a slurry of **1** (60 mg, 0.124 mmol) in CH_2Cl_2 (1.2 mL) at −78 °C. When the solution was warmed to 0 °C, a bright red solution formed. After 1 h, solvent was evaporated under vacuum. The residue was extracted into diethyl ether and filtered. Evaporation of solvent under vacuum afforded **11** as a red solid[19] (40 mg, 91%, 5:2 mixture of cis Cp isomers): ^1H NMR (acetone-d_6), major isomer, δ 12.09 (q, J = 8.0 Hz, CH), 4.82 (s, 10 H, C_5H_5), 3.10 (d, J = 8.0 Hz, CH_3); ^1H NMR (acentone–d_6), minor isomer, δ 9.60 (q, J = 8.0 Hz, CH), 4.86 (s, 10 H, C_5H_5), 3.43 (d, J = 8.0 Hz, CH_3).

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHC_6H_5)$ (12). A solution of Li(C_6H_5CuCN) was prepared by adding C_6H_5Li (0.30 mmol) to CuCN (30 mg, 0.33 mmol) suspended in THF at −78 °C and stirring the suspension at −20 °C until a clear solution was formed. This solution was cooled to −78 °C and added by cannula to a stirred suspension of **1** (147 mg, 0.30 mL) in THF (8 mL) at −78 °C. After 30 min, the reaction was warmed to room temperature and volatile material was removed under vacuum. The residue was extracted into CH_2Cl_2 (2 mL) and chromatographed (alumina, diethyl ether). Evaporation of solvent from the resulting red solution afforded **12** as a red solid (88 mg, 70%): ^1H NMR (acetone-d_6) δ 12.36 (s, CH), 7.54–7.20 (m, C_6H_5), 4.94 (s, 10 H, C_5H_5); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 273.3 (μ-CO), 214.7 (CO), 167.6 (μ-CHR), 163.9 (ipso), 129.2, 128.6, 125.7 (C_6H_5), 89.3 (C_5H_5); IR (CH_2Cl_2) 1983 (s), 1946 (m), 1781 (s) cm^{-1}; HRMS calcd for $C_{20}H_{16}Fe_2O_3$ 415.9797, found 415.9775.[21]

Reaction of 1 with $(C_2H_5)_4N^+HFe(CO)_4^-$. **1** (200 mg, 0.41 mmol) and $(C_2H_5)_4N^+HFe(CO)_4^-$ (185 mg, 0.62 mmol) were stirred for 20 min in CH_2Cl_2 (5 mL) at −78 °C. The resulting red solution was stirred at room temperature for 40 min. Volatile material was evaporated under vacuum; neutral material was dissolved in diethyl ether and passed through an alumina plug. The filtrate was evaporated under vacuum to afford a red solid (94 mg, 67%) identified as **2**[19] by ^1H NMR.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_2COCH_3)$ (13). A suspension of **1** (175 mg, 0.36 mmol) in acetone (10 mL) was stirred for 5 min at 0 °C and then for an additional 15 min at room temperature. Diisopropylethylamine (0.08 mL, 0.46 mmol) was added, and volatile material was evaporated under vacuum. The residue was extracted into CH_2Cl_2 (2 mL) and loaded onto an alumina column (2 × 15 cm). Elution with 1:1 hexane/ether afforded a red band of **2** and $[Cp(CO)Fe]_2(\mu\text{-}CO)_2$. Subsequent elution with ether afforded an orange band which on evaporation of solvent gave an orange-red solid, **13** (110 mg, 77%): ^1H NMR (CD_2Cl_2) δ 11.60 (t, J = 8.5 Hz, CH), 4.88 (s, 10 H, C_5H_5), 4.20 (d, J = 8.5 Hz, CH_2), 2.29 (s, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 271.9 (μ-CO), 212.6 (CO), 207.9 ($COCH_3$), 162.2 (μ-CHR), 87.2 (C_5H_5), 68.0 (CH_2), 29.9 (CH_3); IR (CH_2Cl_2) 1982 (s), 1940 (w), 1778 (m), 1697 (w) cm^{-1}. Anal. Calcd for $C_{17}H_{16}Fe_2O_4$: C, 51.56; H, 4.07. Found: C, 51.47; H, 3.65.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CH\overline{CHCOCH_2(CH_2)_2CH_2}]$ (14). Addition of cyclohexanone (5 mL) to **1** (220 mg, 0.45 mmol) followed by workup as described for **13** gave **14** as a red solid (109 mg, 56%): ^1H NMR (CD_2Cl_2) δ 11.53 (d, J = 11.7 Hz, CH), 4.78 (s, C_5H_5), 4.76 (s, C_5H_5), 3.45 (ddd, J = 11.7, 7.5, 4.6 Hz, 1 H), 2.55 (m, 3 H), 2.07 (m, 5 H); $^{13}C\{^1H\}$ NMR (C_6D_6) 270.2 (μ-CO), 213.5 (CO), 212.2 (CO), 169.5 (μ-CHR), 87.9 (C_5H_5), 87.0 (C_5H_5), 74.8 (CH), 43.1 (CH_2), 42.5 (CH_2), 29.5 (CH_2), 25.7 (CH_2); IR (CH_2Cl_2) 1976 (s), 1936 (w), 1774 (m), 1692 (w) cm^{-1}; HRMS calcd for M − CO $C_{19}H_{20}Fe_2O_3$ 408.0110, found 408.0112. Anal. Calcd for $C_{20}H_{20}Fe_2O_4$: C, 55.09; H, 4.62. Found: C, 54.67; H, 4.60.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH(CH_3)COCH_3]$ (15). Addition of 2-butanone (10 mL) to **1** (175 mg, 0.36 mmol) followed by workup and chromatography as described for **13** gave **15** as a red solid (88 mg, 59%): ^1H NMR (CD_2Cl_2) δ 11.25 (d, J = 11.7 Hz, CH), 4.78 (s, C_5H_5), 4.69 (s, C_5H_5), 3.57 (dq, J = 11.7, 6.9 Hz, CH), 2.32 (s, CH_3), 1.65 (d, J = 6.9 Hz, CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 269.7 (μ-CO), 213.3 (CO), 213.0 (CO), 211.6 (CO), 173.7 (μ-CHR), 87.5 (C_5H_5), 87.2 (C_5H_5), 70.1 (CH), 29.8 (CH_3), 25.2 (CH_3); IR (CH_2Cl_2) 1978 (s), 1937 (w), 1778 (m), 1692 (w) cm^{-1}. Anal. Calcd for $C_{18}H_{18}Fe_2O_4$: C, 52.73; H, 4.43. Found: C, 52.53; H, 4.36.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH_2COCH_2CH(CH_3)_2]$ (16). Addition of 4-methyl-2-pentanone (8 mL) to **1** (203 mg, 0.42 mmol) followed by workup as described for **13** gave **16** as an orange-red solid (13 mg, 7%): ^1H NMR (CD_2Cl_2) δ 11.55 (t, J = 8.1 Hz, μ-CH), 4.75 (s, 10 H, C_5H_5), 4.21 (d, J = 8.1 Hz, CH_2), 2.48 (d, J = 7.0 Hz, CH_2), 2.25 (m, J = 7.0, 6.6 Hz, $C\mathit{H}(CH_3)_2$), 0.98 (d, J = 6.6 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ (125.76 MHz, C_6D_6) δ 269.9 (μ-CO), 213.3 (CO), 208.9 (CO), 162.8 (μ-CHR), 87.4 (C_5H_5), 68.2 (CH_2), 52.3 (CH_2), 24.6 (CH), 22.8 (CH_3); IR (CH_2Cl_2) 1979 (s), 1937 (m), 1776 (s), 1692 (w) cm^{-1}; HRMS calcd for M − CO $C_{19}H_{22}Fe_2O_3$ 410.0267, found 410.0264.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH(COCH_3)_2]$ (17). 2,4-Pentanedione (5 mL) and **1** (150 mg, 0.31 mmol) were stirred for 5 min at 0 °C and 10 min at room temperature. Diisopropylethylamine (0.07 mL, 0.38 mmol) was added at room temperature, and solvent was evaporated under high vacuum. The residue was extracted into CH_2Cl_2 (2 mL) and purified by column chromatography (silica gel, EtOAc). Evaporation of solvent from the resulting red solution afforded **17** as a red solid (100 mg, 74%): ^1H NMR (CD_2Cl_2) δ 11.03 (d, J = 12.5 Hz, μ-CH), 5.00 (d, J = 12.5 Hz, $CHC\mathit{H}$), 4.74 (s, 10 H, C_5H_5), 2.38 (s, 6 H, $COCH_3$); $^{13}C\{^1H\}$ NMR (125.76 MHz, CD_2Cl_2) δ 269.8 (μ-CO), 212.4 (CO), 202.9 ($\mathit{C}OCH_3$), 159.9 (μ-CHR), 91.6 (μ-CHCH), 87.7 (C_5H_5), 30.0 ($CO\mathit{C}H_3$); IR (CH_2Cl_2) 1975 (s), 1940 (w), 1790 (m), 1712 (m) cm^{-1}; HRMS calcd for M − CO $C_{18}H_{18}Fe_2O_4$ 409.9903 found 409.9906.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CH\overline{CHCOCH_2C(CH_3)_2CH_2CO}]$ (18). A mixture of **1** (150 mg, 0.31 mmol) and 5,5-dimethyl-1,3-cyclohexanedione (1000 mg, 7.13 mmol) in 40 mL of THF was stirred at 0 °C for 5 min. Diisopropylethylamine (0.07 mL, 0.38 mmol) was added, and solvent was evaporated under vacuum. The residue was extracted with CH_2Cl_2 (10 mL), filtered, and purified by column chromatography (alumina, EtOAc). Evaporation of solvent from the resulting red solution afforded **18** (88 mg, 59%) as an orange-red solid: ^1H NMR (acetone-d_6) δ 11.44 (d, J = 12.3 Hz, μ-CH), 4.82 (s, 10 H, C_5H_5), 3.82 (d, J = 12.3 Hz, μ-CHCH), 3.67 (d, J = 13.4 Hz, 2 H, $COC\mathit{H}HC(CH_3)_2$), 2.41 (d, J = 13.4 Hz, 2 H, $COCH\mathit{H}C(CH_3)_2$), 1.32 (s, $C(C\mathit{H}_3)(CH_3)$), 0.93 (s, $C(CH_3)(C\mathit{H}_3)$); $^{13}C\{^1H\}$ NMR (125.76 MHz, CD_2Cl_2) δ 269.9 (μ-CO), 211.5 (CO), 205 (CHCO), 158.1 (μ-CHR), 91.0 (μ-CHCH), 87.4 (C_5H_5), 51.9 ($CO\mathit{C}H_2$), 30.8 ($\mathit{C}(CH_3)_2$), 30.1 ($C(\mathit{C}H_3)(CH_3)$), 26.5 ($C(CH_3)(\mathit{C}H_3)$); IR (CH_2Cl_2) 1990 (s), 1952 (w), 1790 (m), 1700 (m) cm^{-1}; HRMS calcd for M − CO $C_{21}H_{22}Fe_2O_4$ 450.0216 found 450.0208.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH(COCH_3)(CO_2CH_2CH_3)]$ (19). Ethyl acetoacetate (2.5 mL) and **1** (190 mg, 0.39 mmol) were stirred at 0 °C for 5 min. Diisopropylethylamine (0.08 mL, 0.48 mmol) was added, and solvent was evaporated under high vacuum. The residue was extracted into CH_2Cl_2 (2 mL) and purified by column chromatography (alumina, 1:1 CH_2Cl_2/ether). Evaporation of solvent from the resulting red solution afforded **19** (113 mg, 61%) as an orange-red solid: ^1H NMR (acetone-d_6) δ 11.13 (d, J = 12.6 Hz, μ-CH), 4.90 (s, C_5H_5), 4.87 (s, C_5H_5), 4.52 (d, J = 12.6 Hz, μ-CHCH), 4.29 (qd, J = 7.2, 10.9 Hz, $C\mathit{H}HCH_3$), 4.23 (qd, J = 7.1, 10.9 Hz, $CH\mathit{H}CH_3$), 1.30 (t, J = 7.1 Hz, $CHHC\mathit{H}_3$); $^{13}C\{^1H\}$ NMR (125.76 MHz, acetone-d_6) δ 270.1 (μ-CO), 213.8, 213.3 (CO), 202.4 ($\mathit{C}OCH_3$), 170.3 ($\mathit{C}OCH_2CH_3$), 159.5 (μ-CHR), 88.7 (C_5H_5), 83.4 (μ-CHCH), 61.4 ($\mathit{C}H_2CH_3$), $CO\mathit{C}H_3$ obscurred by acetone-d_6, δ 29.8 in CD_2Cl_2, 14.6 ($CH_2\mathit{C}H_3$); IR (CH_2Cl_2) 1990 (s), 1950 (w), 1790 (m), 1740 (w), 1710 (w) cm^{-1}; HRMS calcd for M − CO $C_{19}H_{20}Fe_2O_5$ 440.0009, found 439.9985.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH(CO_2CH_2CH_3)_2]$ (20). A mixture of **1** (150 mg, 0.31 mmol) and sodium diethyl malonate (56 mg, 0.31 mmol) in 30 mL of THF was stirred at −78 °C for 25 min. Solvent was evaporated under vacuum. The residue was crystallized by dissolving in 5 mL of CH_2Cl_2, precipitating by

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[21] Although samples of **12** were pure by ^1H NMR and gave good hydrogen analyses, carbon analyses were consistently low.

addition of 10 mL of hexane, and filtering to give **20** as an orange-red solid. Evaporation of the mother liquor and treatment of the residue with CH_2Cl_2/hexane gave an additional quantity of **20** (105 mg total, 68%): ^1H NMR (500 MHz, acetone-d_6) δ 11.04 (d, $J = 12.7$ Hz, μ-CH), 4.89 (s, 10 H, C_5H_5), 4.33 (d, $J = 12.7$ Hz, μ-CHC*H*), 4.28 (qd, $J = 7.1$, 10.8 Hz, C*H*HCH$_3$), 4.24 (qd, $J =$ 7.1, 10.8 Hz, CH*H*CH$_3$) 1.30 (t, 6 H, $J = 7.1$ Hz, CHHC*H*$_3$); $^{13}C\{^1H\}$ NMR (125.76 MHz, acetone-d_6) δ 270.2 (μ-CO), 213.3 (CO), 169.9 (*C*OCH$_2$CH$_3$), 158.8 (μ-CHR), 88.7 (C_5H_5), 74.3 (μ-CH*C*H), 61.4 (*C*H$_2$CH$_3$), 14.6 (CH$_2$*C*H$_3$); IR (CH_2Cl_2) 1995 (s), 1950 (w), 1795 (m), 1750 (w), 1730 (w), 1650 (w) cm^{-1}; HRMS calcd for M − CO $C_{20}H_{22}Fe_2O_6$ 470.0114, found 470.0088.

Acknowledgment. Support from the Department of Energy, Division of Basic Energy Science, and the National Science Foundation is gratefully acknowledged. M.C. thanks the Science and Engineering Research Council (U.K.) for a NATO postdoctoral fellowship.

Registry No. **1**, 82660-13-7; **2**, 79839-80-8; **3**, 83681-74-7; **4a**, 83730-01-2; **4b**, 83681-78-1; **6** (isomer 1), 112172-84-6; **6** (isomer 2), 112318-69-1; **7**, 93842-65-0; **9-PF$_6$**, 112172-86-8; **9-BF$_4$**, 112318-70-4; **10**, 112172-85-7; **11** (isomer 1), 75811-60-8; **11** (isomer 2), 112318-71-5; **12**, 112172-87-9; **13**, 112172-88-0; **14**, 112172-89-1; **15**, 112172-90-4; **16**, 112172-91-5; **17**, 112172-92-6; **18**, 112172-93-7; **19**, 112172-94-8; **20**, 112172-95-9; $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)_2$, 12154-95-9; $(C_5H_5)Fe(CO)_2Br$, 12078-20-5; $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCH{=}C(CH_3)_2]$, 112172-96-0; $Ph_2C{=}NH$, 1013-88-3; $Li(C_6H_5CuCN)$, 41742-64-7; $(C_2H_5)_4N^+HFe(CO)_4^-$, 25879-01-0; diisopropylethylamine, 7087-68-5; acetone, 67-64-1; cyclohexanone, 108-94-1; 2-butanone, 78-93-3; 4-methyl-2-pentanone, 108-10-1; 2,4-pentanedione, 626-96-0; 5,5-dimethyl-1,3-cyclohexanedione, 126-81-8; ethyl acetoacetate, 141-97-9; sodium diethyl malonate, 51923-79-6.

Modeling Fischer–Tropsch Chemistry: The Thermochemistry and Insertion Kinetics of $ClRuH(CH_2)$

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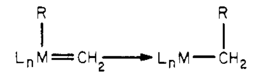
Received July 10, 1987

The insertions of metal-bound CH_x into M–H and M–CH_3 bonds have been proposed as the chain initiation and propagation steps, respectively, in the Fischer–Tropsch reductive polymerization of CO to form alkanes. As a model for this important elementary reaction, we have examined the properties and migratory insertion reactivity of a prototypical coordinatively saturated complex $ClRuH(CH_2)$ using ab initio methods (generalized valence bond + configuration interaction). The Ru=CH_2 double bond is covalent, with D_e(Ru=C) = 84.7 kcal/mol. The optimum geometry has the CH_2 plane perpendicular to the ClRuH plane, with a rotational barrier of ≥13.6 kcal/mol. The lowest energy conformer of the singlet state of $ClRuH(CH_2)$ has an in-plane π bond, which facilitates the insertion of the CH_2 ligand into the adjacent Ru–H bond. Using analytic gradient techniques combined with GVB-MCSCF wave functions to find the minimum energy pathway, we find that the insertion proceeds with a moderate barrier (11.5 kcal/mol) and is exothermic by 7.1 kcal/mol. From a thermodynamic cycle designed to probe basis set and electron correlation deficiencies, we estimate an actual barrier to insertion of 10.9 ± 1.7 kcal/mol and an exothermicity of 10.5 ± 1.0 kcal/mol.

I. Introduction

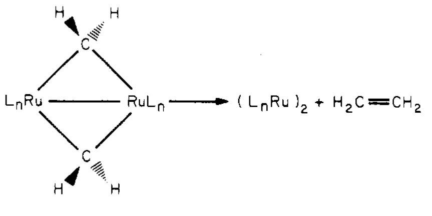
Ruthenium complexes containing hydrido, alkyl, alkylidene, and alkylidyne ligands have been proposed as intermediates in metal-catalyzed C–H and C–C bond-forming processes.[1-3]

In homogeneous reactions, both CH_2 insertion into M–H and M–R bonds to make new metal alkyls[1]



$$L_n\overset{R}{\overset{|}{M}}{=}CH_2 \longrightarrow L_nM{-}\overset{R}{\overset{|}{C}}H_2 \quad (1)$$

and intramolecular alkylidene coupling in binuclear Ru systems to make olefins



(2)

have been observed.[2] Catalytic reduction of CO to methanol, ethanol, and ethylene glycol by soluble Ru complexes have also been observed (eq 3).[3]

$$H_2 + CO \xrightarrow{Ru_3(CO)_{12}} CH_3OH + C_2H_5OH + HOCH_2CH_2OH \quad (3)$$

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[‡] Contribution No. 7583.

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