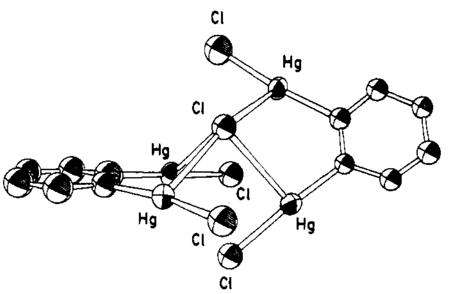

Figure 2. Crystal structure of the 2:1 complex 4 of dichloro-1,2-phenylenedimercury (1) and tetraphenylphosphonium chloride with tetraphenylphosphonium and all hydrogen atoms omitted for clarity.

distribution reaction. This result confirms that the formation of a stable halide complex requires a multidentate Lewis acid.

The far-infrared spectra of these halide complexes are similar to those of the uncomplexed 1,2-phenylenedimercury dihalides 1 and 2. For example, the strong band at 335 cm^{-1} in dichloride 1 (solid dispersed in polyethylene film), due predominantly to mercury–chlorine stretching, is shifted to 327 cm^{-1} in the 2:1 complex with tetrabutylammonium chloride. This shift to lower frequency indicates that additional coordination of chloride to mercury has occurred,[9] but the small magnitude of the shift suggests that the complex incorporates dichloro-1,2-phenylenedimercury units which are only slightly perturbed.[10]

The ^{199}Hg NMR spectra of the halide complexes also confirm that additional coordination of halide to mercury has taken place. For example, the ^{199}Hg chemical shift of dichloro-1,2-phenylenedimercury (1) is −1291 ppm in Me_2SO (0.1 M),[11] whereas the chemical shift of the 2:1 complex 4 with tetrabutylammonium chloride is −1220 ppm. The direction of this shift is persuasive evidence that additional chloride is complexed to mercury,[12] but its magnitude is small, presumably because the additional chloride is shared by four atoms of mercury. Figure 1 shows in detail how the ^{199}Hg chemical shift of dichloride 1 in Me_2SO increases as tetraphenylphosphonium chloride is added. The increase is steep and linear until a 1:1 ratio is reached, and subsequent changes are much smaller. This result suggests that although 2:1 complexes are isolated by precipitation, 1:1 complexes may be preferred in solution.

Study of complex 4 by X-ray crystallography,[13] summarized in Figure 2, confirms that the added chloride bridges two dichloro-1,2-phenylenedimercury units and is strongly coordinated to all four atoms of mercury. The four bonds from mercury to the central chloride average 3.02 Å in length, similar to the separation of mercury and the bridging chloride in $Hg_2Cl_5^-$.[6a]

The complexation of halides by 1,2-phenylenedimercury dihalides shows interesting selectivity. Initial tests of this selectivity have involved the competition of two 1,2-phenylenedimercury dihalides for an insufficient amount of halide, and the reaction of one 1,2-phenylenedimercury dihalide with two competing halides. For example, when dichloride 1, dibromide 2, and tetraphenylphosphonium chloride are mixed in the ratio 2:2:1, compound 2 can be recovered quantitatively by filtration, and complex 4 can be isolated in 73% yield after crystallization. These and similar results suggest that dichloride 1 is a stronger Lewis acid than bromide 2.[14] In addition, a 2:1:1 mixture of dichloride 1 and tetrabutylammonium chloride and bromide yielded complex 5 (mp 144–146 °C) in 72% yield after crystallization.[7] For a given 1,2-phenylenedimercury dihalide, the stabilities of complexes formed from added halide therefore appear to increase in the order $Cl^- < Br^- < I^-$.[15]

We are now studying the ability of 1,2-phenylenedimercury dihalides and related compounds to bind and activate organic substrates like thiocarbonyl compounds.

Acknowledgment. This work was financially supported by Research Corp., the Natural Sciences and Engineering Research Council of Canada, and le Ministère de l'Education du Québec. We are grateful to Dr. Jeffrey C. Hayes, who performed some preliminary experiments, and to Mr. Robert Mayer and Mr. Jean-Claude Bolduc, who skilfully recorded our ^{199}Hg NMR and far-infrared spectra.

Registry No. 1, 35099-05-9; 2, 89280-87-5; 3, 89487-90-1; 4, 93605-04-0; 5, 93605-06-2; $[(ClHgC_6H_4\text{-}o\text{-}HgCl)_2Cl]Bu_4N$, 93605-08-4; $[(ClHgC_6H_4\text{-}o\text{-}HgCl)Cl]PPh_4$, 93644-89-4; tetraphenylphosphonium tetrachloromercurate, 93605-07-3; diphenylmercury, 587-85-9; chlorophenylmercury, 100-56-1.

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[9] Clark, R. J. H. *Spectrochim. Acta* **1965,** *21,* 955–963.

[10] Such comparisons are deceptive if the mercury–halogen stretching frequencies in the solid dihalides 1–3 are themselves lowered by intermolecular interactions. Goggin, P. L.; Kemeny, G.; Mink, J. *J. Chem. Soc., Faraday Trans. 2* **1976,** 1025–1035.

[11] All $\delta(^{199}Hg)$ are reported in parts per million relative to external neat dimethylmercury. Negative values indicate upfield shifts.

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[13] (a) Beauchamp, A. L.; Olivier, M. J.; Wuest, J. D.; Zacharie, B., manuscript in preparation. (b) Crystals of complex 4, solvated with dichloromethane, belong to the triclinic space group $P\bar{1}$, with a = 13.35 (1) Å, b = 16.42 (1) Å, c = 20.20 (2) Å, α = 108.43 (6)°, β = 94.48 (6)°, and γ = 105.41 (6)°. An Enraf-Nonius CAD4 diffractometer was used to collect a limited set of intensity data ($2\theta \leq 70°$, Cu Kα, 3057 nonzero reflections). The structure was solved by direct methods and refined by full-matrix least-squares calculations to R = 0.041, R_w = 0.056, and goodness-of-fit ratio = 2.21. A complete set of three-dimensional intensity data is now being collected.

[14] Because the solubilities of compounds 1–3 are low, competitive complexation could not be studied conveniently in homogeneous solution. As a result, we cannot exclude the possibility that differential solubilities or rates of crystallization have important effects.

[15] For related observations, see: Ahrland, S.; Persson, I.; Portanova, R. *Acta Chem. Scand., Ser. A* **1981,** *A35,* 49–60. Giuashvili, I. I.; Katsman, L. A.; Vargaftik, M. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977,** 80–83. Schwarzenbach, G.; Schellenberg, M. *Helv. Chim. Acta* **1965,** *48,* 28–46. Pearson, R. G. *J. Am. Chem. Soc.* **1963,** *85,* 3533–3539. Ahrland, S.; Chatt, J.; Davies, N. R. *Q. Rev., Chem. Soc.* **1958,** *12,* 265–276.

Synthesis and Reactions of Bridging (Vinylcarbyne)diiron Complexes

Charles P. Casey* and Seth R. Marder

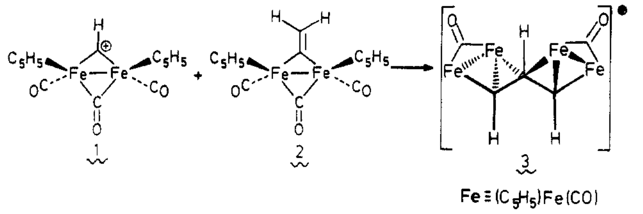
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received September 7, 1984

Summary: Reaction of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C{=}CH\text{-}(CH_2)_2CH_3]$ (**4**) with the hydride abstracting reagent $(C_6H_5)_3C^+PF_6^-$ leads to the vinylcarbyne complex $\{[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH{=}CHCH_2CH_3)\}^+PF_6^-$ (**5**). Conjugate addition of $P(CH_3)_3$ to **5** leads to $\{[(C_5H_5)(CO)\text{-}Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH[P(CH_3)_3]CH_2CH_3)\}^+PF_6^-$ (**13**). Deprotonation of **5** with $Li^+[(CH_3)_3Si]_2N^-$ leads to the dienylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH{=}CHCH_3)$ (**14**).

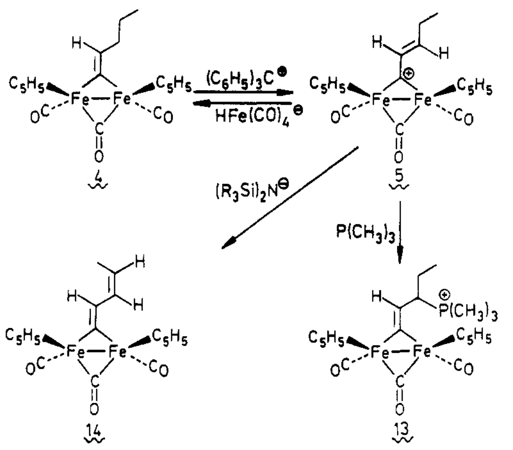
0276-7333/85/2304-0411$01.50/0

An increasing number of bridging alkenylidene transition-metal complexes have been synthesized,[1-6] but the reactivity of these complexes is largely unexplored. Only the protonation of bridging alkenylidene complexes has been extensively studied.[1-7] Since diiron-bridging alkenylidene complexes are now readily accessible either from hydrocarbation of alkenes with bridging methylidyne complex **1** followed by deprotonation of the intermediate μ-alkylidyne complex[8] or from reaction of selected lithium reagents with $[(C_5H_5)Fe(CO)_2]_2$ followed by treatment with strong acid[9] and neutralization, we have begun to explore their reactivity in greater depth. The high stability of the cationic bridging carbyne complexes produced upon protonation suggested that other electrophiles might add to bridging alkenylidene complexes. Recently we reported that electrophilic addition of bridging methylidyne complex **1** to the diiron ethenylidene complex **2** leads to the formation of the novel tetrairon complex **3**.[10]

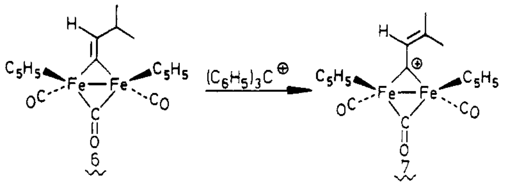


Fe ≡ $(C_5H_5)Fe(CO)$

In an attempt to extend this reaction to substituted alkenylidene complexes, the reaction of **1** with bridging pent-1-enylidene complex **4** was studied. However, instead of obtaining a 1:1 adduct of **1** and **4** analogous to tetrairon compound **3**, the bridging pent-2-enylidyne complex **5** was isolated in 28% yield. Since **5** is apparently the product of allylic hydride abstraction from **4**, the reaction of **4** with the excellent hydride abstracting reagent $(C_6H_5)_3C^+PF_6^-$ was studied. When pent-1-enylidene complex **4** (0.400 g, 1.02 mmol) and $(C_6H_5)C^+PF_6^-$ (0.385 g, 0.99 mmol) were stirred in CH_2Cl_2 for 1 h at 0 °C, pent-2-enylidyne complex **5** (0.428 g, 80.1%) formed as a red precipitate.[11] The IR spectrum of **5**, which exhibited three bands at 2037(s), 2005(w) and 1850(m) cm^{-1}, is similar to that of other cationic (μ-alkylidyne)diiron complexes.[12] In the ^1H NMR of **5**, the trans vinyl hydrogens give rise to resonances at δ 9.53 (dt, *J* = 14.6, 1.3 Hz, 1 H) and 7.35 (dt, *J* = 14.6, 6.6 Hz, 1 H). In the ^{13}C NMR, the carbyne carbon of **5** appears at δ 451 shifted 50 ppm upfield from the carbyne resonance of the pentylidyne complex $\{[(C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}C(CH_2)_3CH_3)\}^+PF_6^-$.[14] This upfield shift is probably related to the more diffuse nature of the allyl like LUMO of **5**.[15-16]



The reaction of $(C_6H_5)_3C^+PF_6^-$ with 3-methylbut-1-enylidene complex **6**[17] led to the abstraction of a tertiary hydrogen and the formation of 3-methylbut-2-enylidyne complex **7**[18] in 77% yield.



Reaction of $(C_6H_5)_3C^+PF_6^-$ with alkenylidene complex **8**, prepared from **1** in 81% yield by hydrocarbation of cyclopentene followed by deprotonation with aqueous $NaHCO_3$,[19,20] led to hydride abstraction and formation of cyclopent-1-enylmethylidyne complex **9** in 71% yield. The spectral properties[21] of **9** were in good agreement with those reported by Rosenblum who synthesized **9** by reaction of $(C_5H_5)Fe(CO)_2Li$ with cyclopentene oxide followed by treatment with acid.[9]

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[9] Nitay, M.; Priester, W.; Rosenblum, M. *J. Am. Chem. Soc.* **1978**, *100*, 3620.

[10] Casey, C. P.; Marder, S. R.; Rheingold, A. R., accepted for publication in *Organometallics.*

[11] For **5**: ^1H NMR (acetone-d_6, 270 MHz) δ 9.53 (dt, *J* = 14.6, 1.3 Hz, 1 H, μ-CCH), 7.55 (dt, *J* = 14.6, 6.6 Hz, 1 H, μ-CCH=*CH*), 5.62 (s, 10 H, C_5H_5), 2.66 (m, 2 H, CH_2), 1.33 (t, *J* = 7.5 Hz, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_3NO_2, 50.10 MHz, 0.07M Cr(acac)$_3$) δ 451.1 (μ-C), 253.8 (μ-CO), 208.2 (CO), 164.8 and 157.6 (μ-CCH=CH), 93.2 (C_5H_5), 30.0 (CH_2), 11.9 (CH_3). Anal. Calcd for $C_{18}H_{17}F_6Fe_2O_3P$: C, 40.19; H, 3.19. Found: C, 40.39; H, 3.39.

[12] For example, $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C(CH_2)_3CH_3)]^+PF_6^-$ exhibits bands at 2040 (s), 2004 (m), and 1870 (s) cm^{-1}.[13]

[13] Casey, C. P.; Marder, S. R.; Fagan, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 7197.

[14] The carbyne carbon of $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C(CH_2)_3CH_3)]^+PF_6^-$ appears at δ 502.5.[13]

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[16] A similar phenomenon is seen for $C_5H_5(CO)_2Fe{=}C(CH_3)_2^+$ (^{13}C NMR δ 406.5 for carbene carbon) and $C_5H_5(CO)_2Fe{=}CHCH{=}C(CH_3)_2^+$ (^{13}C NMR δ 316.7 for carbene carbon and δ 178.8 for terminal vinyl carbon). Casey, C. P.; Miles, W. H.; Tukada, H., submitted for publication in *J. Am. Chem. Soc.*

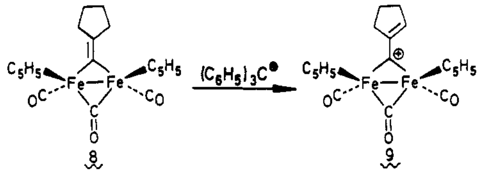
[17] Casey, C. P.; Fagan, P. J.; Meszaros, M. W.; Marder, S. R., unpublished results.

[18] For **7**: ^1H NMR (acetone-d_6, 270 MHz) δ 9.68 (m, 1 H, CH), 5.60 (s, 10 H, C_5H_5), 2.48 (d, *J* = 0.7 Hz, 3 H, CH_3), 2.34 (s, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_3NO_2, 50.10 MHz, 0.07 M Cr(acac)$_3$) δ 440.2 (μ-C), 254.3 (μ-CO), 208.7 (CO), 163.2 (*C*(CH_3)$_2$), 158.1 (μ-C*C*H), 93.7 (C_5H_5), 29.4 (CH_3), 23.4 (CH_3); IR (CH_2Cl_2) 2030 (s), 2000 (w), 1850 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{17}F_6Fe_2O_3P$: C, 40.19; H, 3.19. Found: C, 40.34; H, 3.33.

[19] Previously, we found that **1** reacts with 1,2-disubstituted alkenes to give rapidly equilibrating mixtures of μ-alkylidyne and μ-alkenyl complexes. When these equilibrating mixtures are treated with $NaHCO_3$, the alkylidyne complex is selectively deprotonated and the entire mixture is converted to a bridging alkenylidene complex.[13]

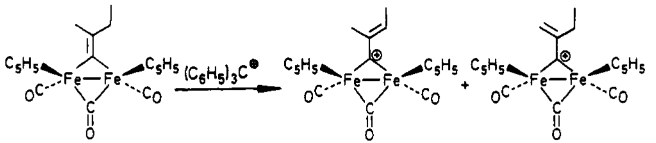
[20] For **8**: ^1H NMR (acetone-d_6, 270 MHz) δ 4.93 (s, 10 H), 3.25 (m, 2 H), 2.92 (m, 2 H), 1.84 (m, 4 H); $^{13}C\{^1H\}$ NMR (C_6D_6, 50.10 MHz, 0.07 *M* Cr(acac)$_3$) δ 270.2, 253.0 (μ-C and μ-CO), 211.7 (CO), 149.4 (μ-C=*C*), 86.7 (C_5H_5's), 38.3 (allylic C's), 28.7 (remaining C's); IR (CH_2Cl_2) 1985 (s), 1947 (w), 1780 (br) cm^{-1}; MS, significant high mass peaks (*m/e*) 406 (m^+), 378 (m^+ − CO), 350 (m^+ − 2CO), 322 (m^+ − 3CO).

[21] For **9**: ^1H NMR (acetone-d_6, 200 MHz) δ 7.55 (m, 1 H, CH), 5.64 (s, 10 H, C_5H_5's), 3.66 (m, 2 H, CH_2*CH*$_2$C=CH), 2.85 (m, 2 H, C=CH*CH*$_2$CH$_2$), 2.32 (m, 2 H CH_2*CH*$_2$CH$_2$); $^{13}C\{^1H\}$ NMR (CD_3NO_2, 50.10 MHz, 0.07 M Cr(acac)$_3$) δ 444.6 (μ-C^+), 254.1 (μ-CO), 208.3 (CO), 172.0 (μ-C*C*=CH), 163.2 (μ-CC=*C*H), 93.1 (C_5H_5), 40.3 (H_2*C*C=CH), 38.0 (C=CH*C*H$_2$), 25.7 (CH_2*C*H$_2$CH$_2$); IR (CH_2Cl_2) 2030 (s), 2000 (w), 1853 (m) cm^{-1}. Anal. Calcd for $C_{19}H_{17}F_6Fe_2O_3P$: C, 41.46; H, 3.12. Found C, 41.19; H, 3.58.



8

9



10

11

12

To determine the selectivity for the abstraction of primary vs. secondary allylic hydrogen atoms, the reaction of 2-methylbut-1-enylidene complex **10**[22] with $(C_6H_5)_3C^+PF_6^-$ was studied. The product of secondary allylic hydrogen abstraction was selectively formed, and a 3.8:1 mixture of **11** and **12** was isolated.[23]

The bridging vinylcarbyne group is a new kind of functional group, and we have begun to explore its reactivity. Nucleophiles undergo conjugate addition to the terminal vinyl carbon atom. Reaction of **5** with $P(CH_3)_3$ led to the formation of the phosphonium salt $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH[P(CH_3)_3]CH_2CH_3)]^+PF_6^-$ (**13**) as a mixture of a diastereomers in 87.6% yield.[24] Reaction of **5** with $(CH_3CH_2)_4N^+HFe(CO)_4^-$ led to hydride addition to the terminal vinyl carbon atom and regenerated complex **4** in 90% yield.

Deprotonation of **5** with $Li^+[(CH_3)_3Si]_2N^-$ led to the formation of a 3.8:1 mixture of two isomers of penta-1,3-dienylidene complex **14** in 66% yield.[25] In the major isomer, the cyclopentadienyl groups are cis relative to the central Fe_2C_2 ring system (as indicated by the observation of three IR bands at 1990 (s), 1955 (w), and 1787 (m) cm^{-1}) and the double bond in the bridging ligand is also cis (as indicated by a 10.6-Hz ^{1}H NMR coupling constant for the protons on the cis double bond).

Further investigations to define the scope of the hydride abstraction reaction leading to vinylcarbyne complexes and to explore the reactivity of vinylcarbyne complexes toward nucleophiles are in progress.

Acknowledgment. Support from the Department of Energy, Division of Basic Energy Sciences and the National Science Foundation is gratefully acknowledged.

Registry No. 1, 82660-13-7; 4, 87711-19-1; 5, 93842-64-9; 6, 93842-65-0; 7, 93842-66-1; 8, 93842-67-2; 9, 93921-99-4; 10, 87711-31-7; 11, 93842-68-3; 12, 93842-69-4; 13 (isomer 1), 93862-18-1; 13 (isomer 2), 93922-49-7; 14 (major isomer), 93842-70-7; 14 (minor isomer), 93922-00-0; $(C_6H_5)_3C^+PF_6^-$, 437-17-2; $(CH_3CH_2)_4N^+HFe(CO)_4^-$, 25879-01-0; $P(CH_3)_3$, 594-09-2.

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(22) Casey, C. P.; Meszaros, M. W.; Marder, S. R.; Fagan, P. J. *J. Am. Chem. Soc.* **1984,** *106,* 3680.

(23) The ^{1}H NMR (acetone-d_6, 270 MHz) of a mixture of **11** and **12** was assigned: for **11**, δ 7.67 (q, *J* = 7.2 Hz, 1 H), 5.65 (s, 10 H), 2.89 (s, 3 H), 2.25 (d, *J* = 7.2 Hz, 3 H), for **12** δ 6.38 (br s, 1 H), 6.25 (br s, 1 H), 5.69 (s, 10 H), 3.23 (q, *J* = 7 Hz, 2 H), 1.39 (t, *J* = 7 Hz, 3 H). At this point, we do not know whether the 3.8:1 mixture of **11**/**12** is a kinetically or thermodynamically controlled ratio.

(24) The ^{1}H NMR (acetone-d_6, 270 MHz) of the mixture of diastereomers of **13** was assigned: for the major isomer, δ 7.58 (dd, *J* = 10.7, 6.2 Hz, 1 H), 5.11 (s, 5 H), 5.07 (s, 5 H), 3.89 (m, 1 H), 2.00 (d, *J* = 13.9 Hz, 9 H), 1.48 (t, *J* = 7.3 Hz, 3 H) (CH_2 obscured by phosphine methyls), for the minor isomer, δ 6.97 (dd, *J* = 10.8, 6.6 Hz, 1 H), 5.11 (s, 5 H), 5.08 (s, 5 H), 3.89 (m, 1 H), 2.26 (d, *J* = 13.8 Hz, 9 H), 1.06 (t, *J* = 7.3 Hz, 3 H) (CH_2 obscured by phosphine methyls); $^{13}C\{^1H\}$ NMR (acetone-d_6, 50.10 MHz, 0.07 M $Cr(acac)_3$) major isomer, δ 277.7, 267.0 (μ-C and μ-CO), 212.7 (CO), 130.0 (=CH), 89.9 (C_5H_5), 88.9 (C_5H_5), 44.5 (d, *J* = 51 Hz, *C*P$(CH_3)_3$), 23.4 (CH_2), 13.2 (CH_3), 7.4 (d, *J* = 55 Hz, P*C*H_3), minor isomer, δ 277.5, 267.3 (μ-C and μ-CO), 213.5 (CO), 130.0 (=*C*(H)), 89.6 (C_5H_5), 88.5 (C_5H_5), 44.9 (d, *J* = 47 Hz, (*C*P$(CH_3)_3$), 23.8 (CH_2), 13.2 (CH_3), 7.6 (d, *J* = 55 Hz, $P(CH_3)_3$); $^{31}P\{^1H\}$ NMR (acetone-d_6, 80.76 MHz, 0.07 M $Cr(acac)_3$) δ 32.78 (major isomer), 3.65 (minor isomer), −141.00 (septet, *J* = 708 Hz, PF_6^-), major isomer:minor isomer = 2:1; IR (Nujol) 1996 (s), 1954 (m), 1813 (m), 1800 (m) cm^{-1}. Anal. Calcd for $C_{21}H_{26}F_6Fe_2O_3P_2$: C, 41.08; H, 4.27. Found: C 41.32; H, 4.57.

(25) For **14**: ^{1}H NMR (acetone-d_6, 270 MHz) cis, δ 8.23 (dd, *J* = 10.6, 1.3 Hz, μC=CH), 6.51 (ddq, *J* = 10.6, 10.6, 1.8 Hz, =CHC*H*=CH), 5.00 (s, C_5H_5), 4.98 (s, C_5H_5), 1.87 (dd, *J* = 7.1, 1.8 Hz, CH_3) (remaining vinylic hydrogen obscured by C_5H_5's), trans, δ 7.98 (d, *J* = 9.8 Hz, μ-C=C*H*), 6.51 (m, μ-CHC*H*=CH), 5.33 (m, C*H*CH_3), 5.00 (s, C_5H_5), 4.93 (s, C_5H_5), 1.85 (d, *J* = 7 Hz, CH_3); $^{13}C\{^1H\}$ NMR (CD_3NO_2, 50.10 MHz, 0.07 M $Cr(acac)_3$) δ 283.8, 272.3 (μ-C and μ-CO), 213.3 (CO), 139.7, 132.9, 116.7, (remaining vinyl carbons), 89.5 (C_5H_5), 88.9 (C_5H_5), 13.9 (CH_3); IR (CH_2Cl_2) 1990 (s), 1955 (w), 1787 (m) cm^{-1}; MS exact mass calcd for $C_{18}H_{16}Fe_2O_3$ 391.9797, found 391.9798.

Oxidative Addition Chemistry of a Photogenerated, Coordinatively Unsaturated Complex: Temperature Dependence of the Oxidative Addition of Triethylsilane to (Cyclobutadiene)iron Dicarbonyl

Ross H. Hill and Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received November 1, 1984

Summary: Near-UV irradiation of $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ at low temperature in alkane containing Et_3SiH or in neat Et_3SiH yields CO loss to give the IR detectable 16-electron $(\eta^4\text{-}C_4H_4)Fe(CO)_2$ which subsequently reacts thermally with the excess Et_3SiH to give $(\eta^4\text{-}C_4H_4)Fe(H)(SiEt_3)(CO)_2$. The rate of reaction is strictly first order in $(\eta^4\text{-}C_4H_4)Fe(CO)_2$ and depends on temperature; the Arrhenius activation energy is 46 ± 4 kJ/mol from rate measurements in the range 100–160 K.

We wish to report the temperature dependence of oxidative addition of Et_3SiH to a reactive, photogenerated intermediate, $(\eta^4\text{-}C_4H_4)Fe(CO)_2$ (eq 1 and 2). The light-

$$(\eta^4\text{-}C_4H_4)Fe(CO)_3 \xrightarrow{h\nu} (\eta^4\text{-}C_4H_4)Fe(CO)_2 + CO \quad (1)$$

$$(\eta^4\text{-}C_4H_4)Fe(CO)_2 + Et_3SiH \xrightarrow{k_2} (\eta^4\text{-}C_4H_4)Fe(H)(SiEt_3)(CO)_2 \quad (2)$$

induced loss of CO from $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ at low temperature is a known process.[1] The oxidative addition chemistry is not known but is an expected result, given that the isoelectronic analogues $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ and $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ are known to undergo similar photochemical reactions.[2,3] The significant new finding is that we show that it is possible to directly and quantitatively monitor the thermal reaction of a photogenerated intermediate. Light-induced chemistry of the sort represented by eq 1 and 2 is general, since many 18-electron organometallic complexes undergo light-induced loss of a 2-electron donor ligand.[4] Our objective is to learn about the thermal chemistry of the resulting 16-electron fragments.

It is true that there are numerous studies of the oxidative addition reactions involving isolable 16-electron compounds, including reactions with Si–H substrates.[5]

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