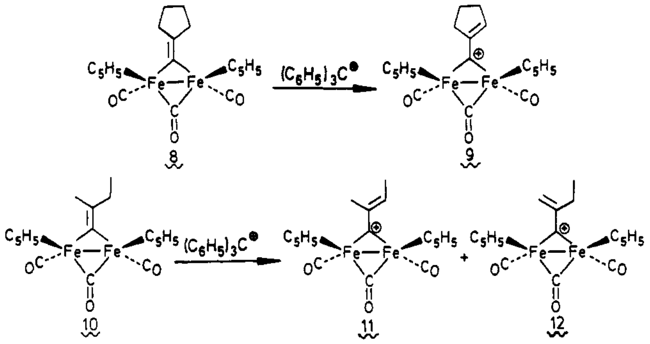

To determine the selectivity for the abstraction of primary vs. secondary allylic hydrogen atoms, the reaction of 2-methylbut-1-enylidene complex **10**[22] with $(C_6H_5)_3C^+PF_6^-$ was studied. The product of secondary allylic hydrogen abstraction was selectively formed, and a 3.8:1 mixture of **11** 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 ^1H 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 ^1H 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 ^1H 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, $\mathit{C}P(CH_3)_3$), 23.4 (CH_2), 13.2 (CH_3), 7.4 (d, J = 55 Hz, $P\mathit{C}H_3$), 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, ($\mathit{C}P(CH_3)_3$), 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**: ^1H 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, =CHCH=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=CH), 6.51 (m, μ-CHCH=CH), 5.33 (m, CHCH$_3$), 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

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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-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.

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

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

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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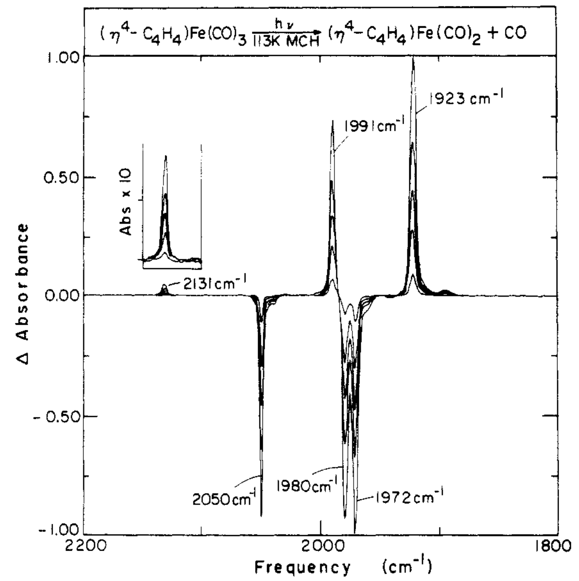

Figure 1. Difference FTIR spectra accompanying the near-UV irradiation of ~1 mM $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ in a methylcyclohexane glass at 113 K.

However, there are no such studies for fragments generated photochemically. The fragments from photoexcitation are expected to be more reactive than isolable 16-electron compounds, because in general, the fragments from photoexcitation are not isolable. Study of the oxidative addition of the Si–H group is important because this is a key step in photocatalyzed hydrosilation of olefins.[6]

Figure 1 shows the FTIR spectral changes accompanying the near-UV irradiation of ~1 mM $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ at 113 K in a methylcyclohexane glass.[7] The appearance of an absorption at 2131 cm^{-1} is associated with uncomplexed CO in the matrix[8] and the two, stronger, features at 1923 and 1991 cm^{-1} are attributable to the 16-electron $(\eta^4\text{-}C_4H_4)Fe(CO)_2$. The $(\eta^4\text{-}C_4H_4)Fe(CO)_2$ observed in a CH_4 matrix has nearly the same band positions, 1996 and 1928 cm^{-1}. Since we know[9] that the extinction coefficient for the released CO is ~400 M^{-1} cm^{-1}, we deduce that the spectral changes in Figure 1 are consistent with CO loss from the $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ as the only process responsible for consumption of the starting material. Essentially the same spectral changes shown in Figure 1 for the methylcyclohexane glass are found upon irradiation of $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ in 3-methylpentane or Et_3SiH glasses. The interesting findings relate to the chemistry of the $(\eta^4\text{-}C_4H_4)Fe(CO)_2$ in alkane solutions of Et_3SiH or in neat Et_3SiH. Reaction according to eq 2 is found to occur. Figure 2 illustrates the FTIR spectral changes that accompany reaction of $(\eta^4\text{-}C_4H_4)Fe(CO)_2$ with neat Et_3SiH at 133 K. The two bands due to the unsaturated species in Et_3SiH decline while two new bands appear at 2010 and 1950 cm^{-1}. The facts that there are two absorptions in the CO stretching region and these are at higher energies than the two bands for the 16-electron species are consistent with the formation of an oxidative addition product, $(\eta^4\text{-}C_4H_4)Fe(H)(SiEt_3)(CO)_2$. Further, the relative intensities of the bands suggest that the C–Fe–C angle for the two CO's is ~90 °[10] (the CO's are cis to each other). The spectral changes shown in Figure 2 are for neat Et_3SiH solvent, but essentially the same spectral changes occur when the solvent is methylcyclohexane or 3-methylpentane containing a modest concentration (~5×10^{-3} to 0.6 M) of Et_3SiH. In the absence of Et_3SiH, complete back-reaction of $(\eta^4\text{-}C_4H_4)Fe(CO)_2$ with CO is observed. The oxidative addition product is itself unstable above ~230 K and has not been isolated. However, irradiation of $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ in methylcyclohexane-d_{14}/Et_3SiH (9/1 by volume) at 196 K does yield the FTIR spectral changes illustrated in Figure 2, and the solution exhibits a singlet ^1H NMR resonance at −11.0 ppm, consistent with the formation of an Fe–H species. Warmup to temperatures exceeding 220 K leads to rapid loss of the hydride signal in the ^1H NMR, in accord with the loss of product measured in the FTIR spectrum. A final noteworthy feature of the oxidative addition product is that the reductive elimination of Et_3SiH can be effected photochemically at 100 K (eq 3). The reductive elimination of Et_3SiH is a

$$(\eta^4\text{-}C_4H_4)Fe(H)(SiEt_3)(CO)_2 \xrightarrow{h\nu} (\eta^4\text{-}C_4H_4)Fe(CO)_2 + Et_3SiH \quad (3)$$

photoreaction that has recently been discovered in this laboratory,[11] and the finding of reaction according to eq 3 is consistent with the cis disposition of the –H and –$SiEt_3$ groups.

Significantly, the oxidative addition reaction according to eq 2 can be monitored quantitatively as a function of temperature and Et_3SiH concentration. We find that the rate law given in eq 4 applies.[12] Data given in Figure 2 are typical of the kind of information that has been obtained; in excess Et_3SiH the reaction is pseudo-first-order in the loss of the 16-electron species and formation of the oxidative addition product. The second-order rate constant k_2 has been obtained at various temperatures, in various solvents and at various concentrations of the Et_3SiH. All experiments are in accord with the rate law given by eq 4, including experiments that are done at the lowest temperature, ~100 K, where the Et_3SiH solvent is extremely viscous. In calculating a value for k_2 we have used the concentration of the Et_3SiH and Fe species assuming the 298 K values. Figure 3 shows a summary of the data as an Arrhenius plot, ln (k_2) vs. $1/T$. The temperature range spanned yields a wide range of solvent viscosity, and yet all data points fall on one line, including data from the three different solvents. The fact that all measured values of k_2 fit on the same line indicates that the activation energy from the slope of the plot has relevance to the oxidative addition reaction and is not merely a reflection of the activation energy for diffusion. The activation energy, E_a, is +46 ± 4 kJ/mol, giving $\Delta H^* = +44 \pm 4$ kJ/mol and $\Delta S^* = +47 \pm 20$ J mol^{-1} K^{-1} at 273 K.

$$\text{rate} = k_2[Et_3SiH][(\eta^4\text{-}C_4H_4)Fe(CO)_2] \quad (4)$$

The large and positive value for ΔS^* is somewhat surprising for what would appear to be an associative reaction.

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(10) Based on arguments similar to those in: Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.

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(12) The rate of reactions of $(\eta^4\text{-}C_4H_4)Fe(CO)_2$ with Et_3SiH was measured by first photogenerating $(\eta^4\text{-}C_4H_4)Fe(CO)_2$ at a given temperature and in the presence of a given solvent and Et_3SiH concentration using, generally, a period of irradiation much smaller than the $t_{1/2}$ for reaction. The FTIR spectral changes were then monitored to obtain a pseudo-first-order rate constant, $k_2[Et_3SiH]$, for each set of conditions.

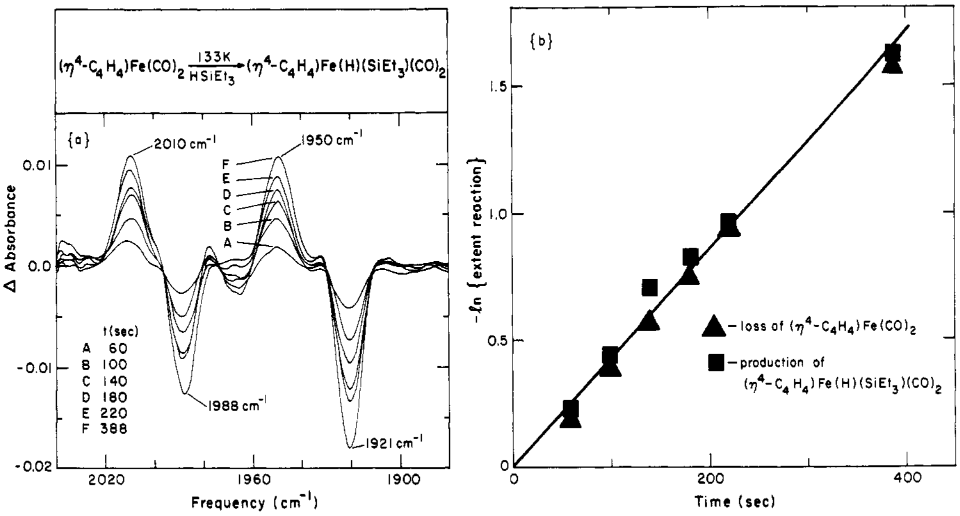

Figure 2. (a) Difference FTIR spectra accompanying the thermal reaction of photogenerated $(\eta^4\text{-}C_4H_4)Fe(CO)_2$ (1988, 1921 cm^{-1}) in neat Et_3SiH at 133 K to give an oxidative addition product, *cis*-$(\eta^4\text{-}C_4H_4)Fe(H)(SiEt_3)(CO)_2$ (2010, 1950 cm^{-1}). (b) First-order rate data for appearance of oxidative addition product and disappearance of 16-electron species.

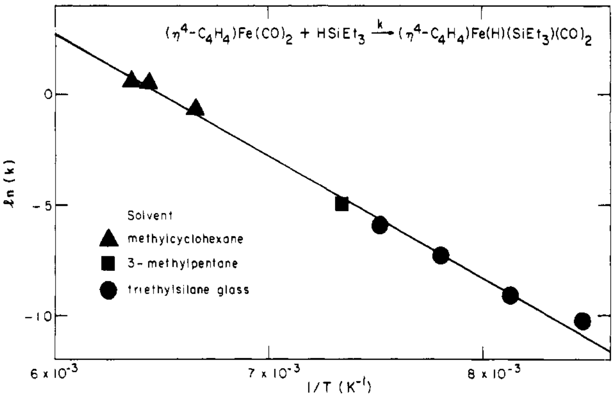

Figure 3. Arrhenius plot, ln (k_2) vs. $1/T$, for oxidative addition of Et_3SiH to photogenerated $(\eta^4\text{-}C_4H_4)Fe(CO)_2$. The raw data, i.e., Figure 2b, give $k_2[Et_3SiH]$. In determining each k_2 value for this plot the value of $[Et_3SiH]$ used was the concentration at 298 K. For neat Et_3SiH (●), $[Et_3SiH] = 6.3$ M, and from left to right in the figure the values of $[Et_3SiH]$ for the data points in the alkane solvent are 6.3×10^{-3}, 1.9×10^{-2}, 6.3×10^{-3}, and 6.3×10^{-2} M.

However, such is not unprecedented. The oxidative addition of CH_3I to *trans*-$RhCl(CO)(PPh_3)_2$ has an associated $\Delta S^{\ddagger}$ of +62 ± 23 J mol^{-1} K^{-1}.[13] However, for the analogous system involving the ligand $P(C_6H_4Bu)_3$ instead of the PPh_3 the value of $\Delta S^{\ddagger}$ was found[13] to be −122 ± 37 J mol^{-1} K^{-1}. In our system we favor the interpretation that the large, positive entropy change signals a large amount of solvation of the 16-electron complex. This is consistent with the the IR spectral differences for $(\eta^4\text{-}C_4H_4)Fe(CO)_2$ in various media:[1] Ar, 2005, 1936 cm^{-1}; Kr, 2000, 1931 cm^{-1}; CH_4, 1996, 1928 cm^{-1}; methylcyclohexane, 1991, 1923 cm^{-1}; and Et_3SiH, 1988, 1921 cm^{-1}. It is noteworthy that other workers have found[5a] that oxidative addition of Si–H groups to 16-electron Ir(I) complexes has a smaller $\Delta S^{\ddagger}$. Thus, the high reactivity of $(\eta^4\text{-}C_4H_4)Fe(CO)_2$ at low temperatures can be attributed to the large, positive $\Delta S^{\ddagger}$. Additional experimentation is underway in this laboratory to vary the silane and the nature of the metal center to completely define the parameters affecting the oxidative addition of silanes to photogenerated, coordinatively unsaturated intermediates.

Acknowledgment. We thank the National Science Foundation for support of this research. R.H.H. acknowledges support from the National Science and Engineering Research Council of Canada as a postdoctoral fellow, 1984–1985.

Cyclodimerization of Butadienes Catalyzed by Phosphine-Free Palladium Complexes

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Summary: Phosphine-free Pd(0) species produced from low-temperature decomposition of bis(allylic)palladium(II) complexes are efficient catalysts for diene cyclodimerization.

In discussions of butadiene dimerization procedures catalyzed by transition-metal complexes, standard textbooks highlight differences observed in reactivity of nickel compounds vs. those of palladium: whereas Ni(0) particpates in efficient cyclodimerization procedures, palladium complexes "behave somewhat differently, reacting with butadiene to give predominantly linear oligomers...the reaction is thought to proceed by a mechanism similar to the nickel-catalyzed [one], but the larger size of palladium (relative to nickel) prevents the final ring closure and leads to linear condensation instead".[1] An alternative explanation for observed differences in reactivity, however, may be that the presence of donor phosphine ligands, which are invariably used to stabilize common Pd catalysts, inhibits that very process which is necessary for *cyclodimerization* to occur: facile reductive elimination from a bis π-allylic intermediate. We have generated bis(allylic)palladium(II) complexes in the absence of phosphines and have shown that such species can eliminate biallylic products upon addition of the π-acidic ligand maleic an-

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