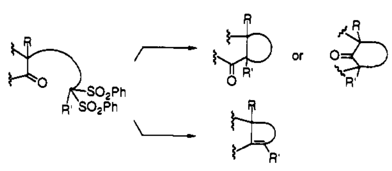

(9)

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Supplementary Material Available: Listings of characterization data for **4**, **5**, **8**, **10–12**, and **13–16** and X-ray data for **4a** and **5c** (4 pages). Ordering information is given on any current masthead page.

Spectroscopic Observation of a Thermal C–H Bond Insertion Reaction at 5 K: Intramolecular Rearrangement of Fe(CO)$_3$(η^2-C$_3$H$_6$) To Produce HFe(CO)$_3$(η^3-C$_3$H$_5$)

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We report direct observation of the rearrangement of a coordinatively-unsaturated (η^2-alkene)metal complex to yield a coordinatively-saturated (η^3-allyl)metal hydride complex. This observation is significant in two distinct mechanistic contexts: alkene isomerization[1] and C–H bond activation.[2] Although several (η^3-allyl)metal hydrides have been well characterized,[3,4] few of the corresponding coordinatively-unsaturated (η^2-alkene)metal complexes have been characterized[5] because of their rapid rearrangement to (η^3-allyl)metal hydrides. Recent studies of C–H bond activation resulted in the direct observation of *inter*molecular C–H bond insertion reactions.[2a,6] Our studies result in direct observation of an *intra*molecular C–H bond insertion reaction that is remarkably facile, occurring thermally at temperatures as low as 5 K.

Photolysis (260 ± 10 nm, 30 min) of Fe(CO)$_4$(η^2-CH$_2$=CHCH$_3$) (**1**),[7-9] matrix-isolated in either argon or methylcyclohexane (MCH) at 10 K,[10] results in a decrease in intensity of the carbonyl infrared absorptions of **1** with concomitant appearance of free CO (2132 cm^{-1}) and several new carbonyl infrared absorptions (Figure 1, Table I). The absorptions at 2064 and 1998 cm^{-1} are due to HFe(CO)$_3$(η^3-CH$_2$CHCH$_2$) (**4**), which has been previously characterized by IR spectroscopy in an MCH glass at 90 K[8] and by ^{1}H and ^{13}C NMR spectroscopy in fluid MCH-d_{14} at 160 K.[4] The absorption at 2046 cm^{-1} is due to $^{\bullet}$Fe(CO)$_3$(η^3-CH$_2$CHCH$_2$) (**5**).[11] The absorptions at 2038 and 1959 cm^{-1}

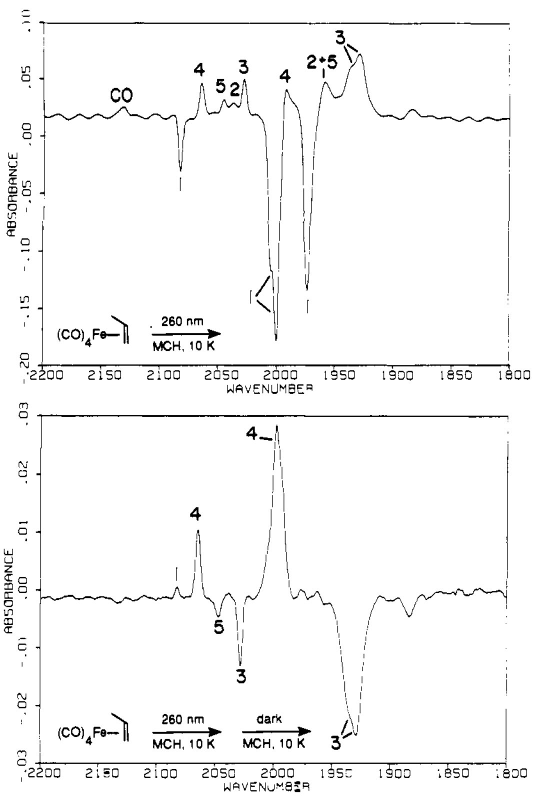
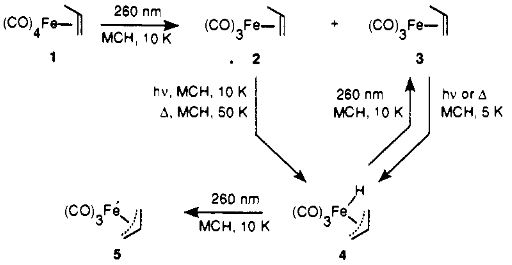


Figure 1. IR difference spectrum showing spectral changes observed upon photolysis (260 ± 10 nm, 30 min, 45% conversion) of Fe(CO)$_4$(η^2-CH$_2$=CHCH$_3$) (**1**) in MCH at 10 K (top). The spectrum shows the disappearance of **1** and the appearance of **2–5** and free CO. IR difference spectrum showing spectral changes observed on allowing the matrix to stand in the dark at 10 K (6 h) (bottom). The spectrum shows the disappearance of **3** and **5** and the growth of hydride **4**. (The absorption at 1884 cm^{-1} is tentatively identified as a trace amount of Fe(CO)$_2$(η^2-CH$_2$=CHCH$_3$)).



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[11] We confirmed this assignment by independently generating **5** from [Fe(CO)$_3$(η^3-CH$_2$CHCH$_2$)]$_2$ in MCH: Murdoch, H. D.; Lucken, E. A. C. *Helv. Chim. Acta* **1964**, *47*, 1517–1524. Muetterties, E. L.; Sosinsky, B. A.; Zamaraev, K. I. *J. Am. Chem. Soc.* **1975**, *97*, 5299–5300. Putnik, C. F.; Welter, J. J.; Stucky, G. D.; D'Aniello, M. J.; Sosinsky, B. A.; Kirner, J. F.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 4107–4116.

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Table I. IR Spectroscopic Data for Relevant Compounds

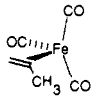
compound	medium (T, K)[a]	IR ν_{CO}, cm^{-1} (rel OD)
1	Ar (10)	2088 (1.0), 2014 (1.7), 2006 (3.7), 1986 (2.4), 1981 (1.0), 1977 (1.1)
	MCH (10)	2083 (1.0), 2004 (3.2), 2000 (4.5), 1974 (3.6)
2	Ar (10)	2047 (1.0), 1969 (2.1)[b,c]
	MCH (10)	2038 (1.0), 1959[b,c]
3	Ar (10)	2035 (1.0), 1940 (1.1), 1937 (2.9)
	MCH (10)	2028 (1.0), 1937 (1.4), 1929 (1.8)
4	Ar (10)	2070 (1.0), 2004 (2.9), 2001 (2.3)[d]
	MCH (10)	2064 (1.0), 1998 (1.8)[d]
5	Ar (10)	2053[e]
	MCH (10)	2046 (1.2), 1969 (1.0), 1960 (2.0)
	MCH (298)	2045 (1.3), 1968 (1.0)
$Fe(CO)_3(C_2H_4)$[f] (equatorial)	Ar (10)	2055 (1.0), 1975 (2.0), 1970 (1.6)
	MCH (10)	2043 (1.0), 1967 (1.6), 1961 (1.7)
$Fe(CO)_3(C_2H_4)$[f] (apical)	Ar (10)	2039 (1.0), 1960 (1.5), 1949 (2.0)
	MCH (10)	2033 (1.0), 1952 (2.0), 1942 (2.0)

[a] Ar, argon; MCH, methylcyclohexane. [b] OD is approximate, due to overlap with nearby absorptions. [c] Two low-frequency absorptions are expected, but they cannot be resolved due to broadening and overlap. [d] Possibly due to both exo and endo isomers. [e] Other absorptions obscured by **1**. [f] Reference 12.

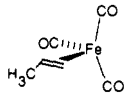
(**2**) and 2028, 1937, and 1929 cm^{-1} (**3**) were not previously observed upon photolysis of **1** in MCH at 77 K.[8] We assign these absorptions to two distinct species on the basis of their differing thermal behavior (vide infra). The ratio of **2**:**3** strongly depends on the photolysis conditions and on the matrix material. Monitoring the photolysis (260 nm) at low conversion of starting material reveals that **2** and **3** are formed in a constant ratio during the early stages of the reaction. This result implies that both **2** and **3** are primary photoproducts. In contrast, **4** and **5** appear as secondary photoproducts during sustained photolysis.

We formulate **2** and **3** as isomeric $Fe(CO)_3(\eta^2\text{-}CH_2{=}CHCH_3)$ complexes on the basis of the following chemical and spectroscopic information: (i) both are primary photoproducts formed upon loss of CO from **1**; (ii) both exhibit infrared carbonyl absorptions bearing striking similarities to the analogous $Fe(CO)_3(\eta^2\text{-}CH_2{=}CH_2)$ complexes;[12,13] (iii) both apparently exhibit long-wavelength electronic transitions[14] characteristic of coordinatively-unsaturated species;[8,15] and (iv) both rearrange thermally and photochemically to hydride **4** (vide infra). The similarities between the spectra of $Fe(CO)_3(\eta^2\text{-alkene})$ (alkene = ethene, propene) complexes suggest that agostic interactions[16] are not significant in $Fe(CO)_3(\eta^2\text{-propene})$, although we cannot state this conclusion with certainty. By analogy with $Fe(CO)_4$[17] and $Fe(CO)_3(\eta^2\text{-}CH_2{=}CH_2)$,[12,18] we expect $Fe(CO)_3(\eta^2\text{-}CH_2{=}CHCH_3)$ to possess a triplet ground state.

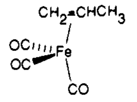
We previously suggested that geometric isomerism in triplet $Fe(CO)_3(\eta^2\text{-}CH_2{=}CH_2)$ occurs as a consequence of local C_{2v} symmetry at iron.[12] The similarities between the infrared spectra of the ethene and propene complexes (Table I) suggest that the structures of these complexes are analogous. The presence of the methyl substituent on the alkene ligand raises a further element of isomerism, beyond the equatorial/apical isomerism observed in the ethene complexes. In the equatorial isomer, the methyl substituent may now assume one of two possible orientations with respect to the other equatorial carbonyl ligand. We do not expect that these two equatorial isomers (**A** and **B**) would possess sufficiently different electronic structures to render their carbonyl groups distinguishable by IR spectroscopy. By analogy to the ethene complexes,[12] we suggest that the absorptions at 2038 and 1959 cm^{-1} are due to the equatorial propene complex (likely a mixture of **A** and **B**). Similarly, we suggest that the absorptions at 2028, 1937, and 1929 cm^{-1} are due to the apical complex **C** (with unspecified orientation(s) of the propene ligand).



A

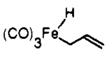


B

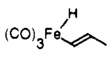


C

Other possible isomers of $Fe(CO)_3(\eta^2\text{-}CH_2{=}CHCH_3)$ include η^1-allyl hydride **6**, vinyl hydride **7**, and metallacyclobutane **8**. Our reasons for excluding these structures are based on chemical and spectroscopic evidence. First, we would not expect any of these species to be formed as primary photoproducts of **1**; such a scenario would require either CO loss and further isomerization to occur as a single-photon process or CO loss to occur as a photochemical process followed by rapid thermal isomerization at 10 K. Second, it is difficult to imagine that vinyl hydride **7** or metallacyclobutane **8** would thermally isomerize to hydride **4** at temperatures below 50 K (vide infra). Third, we cannot invoke **6**, **7**, or **8** without ignoring the concept of geometric isomerism in $Fe(CO)_3(\eta^2\text{-alkene})$ complexes, a concept which appears well founded in the case of the corresponding ethene complex.[12]



6



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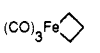

8

Long-wavelength photolysis (>420 nm) results in disappearance of the infrared absorptions of the primary photoproducts (**2** and **3**) and appearance of hydride **4**. Starting material **1** is unreactive under these photolysis conditions. Thus, the C–H bond insertion reaction in **2** and **3** occurs photochemically. Most remarkably, allowing a matrix containing **2** and **3** to stand in the dark at 5.0 ± 0.5 K results in thermal isomerization of **3**, but not **2**, to hydride **4** (Figure 1). *Thus, the C–H bond insertion reaction in* **3** *occurs thermally at 5 K.* Warming an MCH glass containing **2** to 50 K results in thermal isomerization to hydride **4**. Hydride **4** persists, even after the MCH glass melts ($T > 140$ K).[4] At $T > 170$ K, **4** rapidly recombines with CO to regenerate **1** in nearly quantitative yield.

We investigated the photochemistry of the hydride **4**, which itself is photosensitive under our irradiation conditions (260 ± 10 nm). Photolysis of **1** (>279 nm) in an MCH glass at 77 K produces 100% conversion to **4**, as described by Wrighton et al.[8] Further cooling the hydride to 10 K enables us to examine the photochemistry of the pure hydride **4** directly. Photolysis (260 ± 10 nm) of **4** produces a *single isomer* (**3**, apical) of the coordinatively-unsaturated propene complex, in addition to the radical **5**. This observation accounts for formation of the radical **5** in our initial photolysis mixture and demonstrates that reductive elimination of **4** to **3** can occur photochemically.

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(13) Comparison of the IR spectra of the coordinatively-unsaturated ethene and propene complexes reveals that the absorptions of the propene complexes are each shifted 5–15 cm^{-1} to lower energy, as expected for a metal carbonyl complex bearing a slightly better electron donor. (We observe a similar 5–7 cm^{-1} shift in comparing the IR spectra of $Fe(CO)_4(\eta^2\text{-}CH_2{=}CHCH_3)$ (**1**) and $Fe(CO)_4(\eta^2\text{-}CH_2{=}CH_2)$.

(14) We failed to observe these transitions by absorption spectroscopy, but we inferred their presence from the fact that **2** and **3** rearrange upon photolysis (>420 nm).

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