Other anions that react with **1a** by the $S_{RN}1$ process are $(EtO_2C)_2CR^-$ (R = H, Me), PhS^-, and $PhSO_2^-$. With the malonate anions in Me_2SO only the $S_{RN}1$ process was observed to yield **5a** (49%) and **5b** (62%), whose formation was completely inhibited by 10 mol % $(t\text{-}Bu)_2NO\cdot$. With **1c** alkylation was not observed with $(EtO_2C)_2CMe^-$ and **4c** was the major product (62%). PhS^- and $PhSO_2^-$ with **1a** gave **5c** and **5d** by competing $S_{RN}1$ and ionic processes (the nitroxide retarded the photostimulated but not the dark reactions). Only ionic substitution was observed with **1c** to give **5e** and **5f**. $PhC{\equiv}CLi$ or $n\text{-}C_3H_7C{\equiv}CLi$ reacted (THF, -60 °C) with **1a** or **1c** to give the oxiranes **6** in nearly quantitative yields, whereas $(EtO)_2PO^-$ or $(EtO)_2PS^-$ reacted with **1a** or **1c** in a process unaffected by irradiation or free-radical scavengers to give the known enol phosphates[8] and thiophosphates in a Perkow-type reaction.[9,10]

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[8] Borowitz, I. J.; Anshel, M.; Firstenberg, S. *J. Org. Chem.* **1967**, *32*, 1723.

[9] Lichtenthaler, F. W. *Chem. Rev.* **1961**, *61*, 607.

[10] From **1c** the epoxy phosphonates (**5**, Y = H, A = $(EtO)_2P({=}O)$ and $(EtO)_2P({=}S)$) were also formed in Me_2SO or EtOH. The formation of both enol phosphates and epoxy phosphonates in the Michaelis–Becker reaction of α-halo ketones is a known process.[9]

Photoinduced Reductive Elimination of Iron Atoms and Methane from CH_3FeH

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In this communication we report on a novel photoreversible reductive elimination/oxidative addition reaction (1)

$$\mathrm{CH_3FeH} \underset{300\ \mathrm{nm}}{\overset{420\ \mathrm{nm}}{\rightleftharpoons}} \mathrm{Fe} + \mathrm{CH_4} \tag{1}$$

in the Fe/CH_4 system operating on a single iron atom site at 10–12 K and induced by 420- and 300-nm narrow-band irradiation, respectively.

Narrow-band irradiation into the intense 300-nm ($3d^74p^1$, $^5D_4 \leftarrow 3d^64s^2$, $^5D_4$) atomic resonance line of Fe atoms[1] in CH_4 under high dispersion ($1/10^4$) conditions at 12 K caused rapid bleaching of all Fe atom bands with concomitant growth of a weak, broad absorption around 415–420 nm (Figure 1A–C). The corresponding infrared experiments (Figure 2) clearly demonstrated the production of the CH_3FeH insertion product absorbing strongly at 2921, 2888, 2869, 1650, 1148, 1145, 547, 544, 519, 300, 293 cm^{-1}, which aside from slightly better resolution (see later) is in accord with the original observations of Billups et al.[2] The presence of a *single* intense ν_{FeH} and *three* ν_{CH} modes in the iron–hydrogen and –methyl stretching regions, respectively, together argue in favor of a CH_3FeH rather than a CH_2FeH_2 formulation for the Fe/CH_4 300-nm photoproduct.

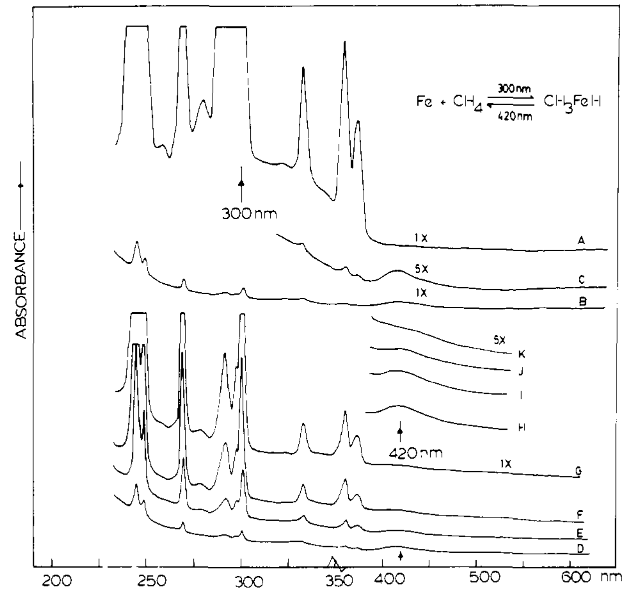

Figure 1. UV–visible spectra: (A) of Fe atoms isolated in solid CH_4 ($1/10^4$) at 10–12 K; (B) following 30 min of 300-nm photolysis (Oriel 450-W Xe lamp, Oriel monochromator 20-nm band pass, 10-cm water cell, intensity at the sample 85 $\mu W\ cm^{-2}$): (C) 5× ordinate expansion of B in the 300–600-nm region; (D–G) samples similar to B at 0, 2, 7, and 12 min of 420-nm photolysis (intensity at the sample 175 $\mu W\ cm^{-2}$); (H–K) 5× ordinate expansion of D–G in the 370–540-nm region.

The thermal reactivity of Fe atoms with respect to CH_4 was also examined in the accessible cryogenic range 10–50 K. Up to the temperature that the methane actually sublimed away from the sample window (around 50 K), no new infrared or optical bands, ascribable to an Fe atom–CH_4 reaction product, were ever observed.

Let us now focus attention on the 415–420-nm photoreactivity of the CH_3FeH insertion product, generated from 300-nm excitation of Fe atoms under rigorously monatomic conditions (Figure 1B,C). The outcome of these irradiations were probed by UV–visible and infrared spectroscopy. Both experiments showed the monotonic bleaching of the CH_3FeH absorptions with 420-nm irradiation time (Figure 1D–K). *Especially noteworthy was the concurrent and rapid generation of atomic iron*, clearly seen by the steady growth of the atomic resonance lines in the optical spectrum (Figure 1D–G). Infrared bands characteristic of new photoproducts were not observed at any time during the photoannihilation of CH_3FeH. The 420-nm photoproduction of Fe atoms from CH_3FeH is found to be highly efficient, and essentially quantitative, in terms of the ability to fully recover the Fe atoms consumed in the original 300-nm photogeneration of CH_3FeH. Furthermore, the atomic Fe produced in this photofragmentation process is identical in form (Figure 1D–G) with the originally deposited Fe atoms and moreover can be readily back-converted to CH_3FeH by further 300-nm excitation. These observations confirm that the photogenerated Fe atoms are not trapped in a special matrix site and/or in a different electronic state following their ejection from CH_3FeH.

Some information pertaining to the geometry of the ground electronic state of CH_3FeH can be derived from infrared spectroscopy. For CH_3FeH generated by 300-nm photoexcitation of Fe atoms in solid CH_4, one finds (Figure 2B) that the vibrational modes of CH_3FeH observed in the range 4000–250 cm^{-1} are comprised of two types, those arising from symmetrical stretching and bending motions of CH, FeH, and FeC bonds and those

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[1] Carstens, D. H. W.; Brashear, W.; Eslinger, D. R.; Gruen, D. M. *Appl. Spectros.* **1972**, *26*, 184. Moore, C. *Natl. Bur. Stand.* (*U.S.*) *Circ.* 1949, Vol. I, 467; 1952, Vol. II; 1958, Vol. III.

[2] Billups, W. E.; Margrave, J. L.; Hauge, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 7393.

J. Am. Chem. Soc. **1982**, *104*, 7352–7353

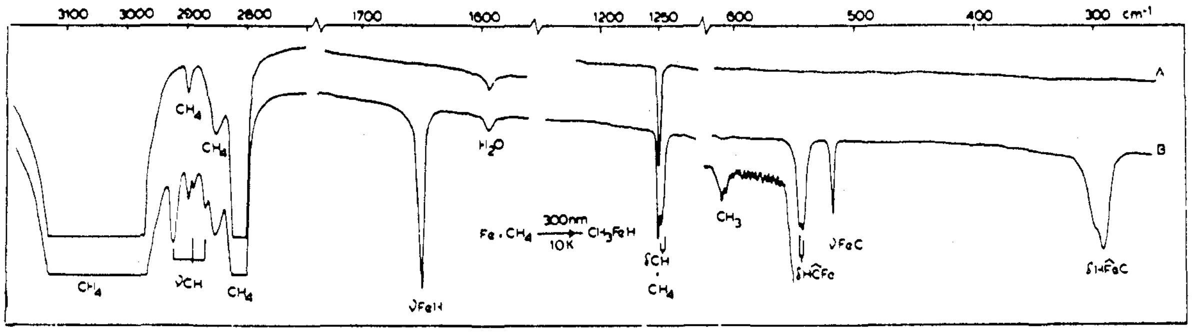
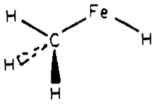


Figure 2. Infrared spectrum of Fe/CH_4 ($\simeq 1/10^4$): (A) following deposition at 10–12 K showing only CH_4 bands; (B) following 300 min of 300-nm photolysis (same experimental arrangement as used in Figure 2 showing CH_3FeH product bands (negligible amounts of CH_3 radicals are formed in the above processes as seen from high sensitivity scans in the 600–620-cm^{-1} region (10× ordinate expansions). Note that the total amount of Fe deposited in the UV–visible experiments required to obtain data of the type typified by those shown in Figure 1 is about 5 times less than that needed to obtain the corresponding infrared spectroscopic data).

deriving from modes that would be doubly degenerate (E) for a linear C_{3v} molecule while nondegenerate (A′ + A″) for a nonlinear C_s molecule. On the basis of the observation that the former modes appear in the IR spectra as sharp singlets whereas the latter modes are all split into doublets (Figure 2B), it can be tentatively concluded that a nonlinear geometry prevails for CH_3FeH in solid CH_4. It is also pertinent to note that no evidence was obtained for species such as CH_3Fe, FeH, CH_3, or H during the 420-nm photolysis of CH_3FeH. The observation of a single "normal" ν_{FeH} stretching mode without any sign of a "softened" ν_{CH} mode (expected to occur in the 2690–2420-cm^{-1} region[6]) argues in favor of the formal insertion product I rather than the plausible alternative activated species II. One can therefore surmise that 420-nm photoexcitation of nonlinear CH_3FeH populates a low lying electronic state having antibonding character with respect to the C–Fe–H framework, which in a nonlinear configuration leads to a facile and concerted reductive elimination of CH_4 in much the same way as that postulated to occur in the concerted, photoinduced reductive elimination of H_2 from $(\eta^5\text{-}C_5H_5)_2MoH_2$, $IrClH_2(PPh_3)_3$, and $IrH_3(PPh_3)_3$ complexes.[3]



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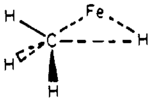

II

Finally, it is pertinent to note that the photoinduced reductive elimination of Fe atoms and CH_4 from CH_3FeH can be viewed as the microscopic reverse of the photoinsertion of Fe atoms into a CH bond of CH_4 to produce CH_3FeH. The system therefore provides the first "ligand free" model with which to experimentally probe the individual steps in a number of transition-metal-catalyzed processes,[4] as well as to theoretically evaluate which physically interpretable features of the local electronic structure of the metal determine chemical reactivity in the Fe/CH_4 and related M/alkane systems.[5]

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Registry No. CH_3FeH, 83615-51-4; Fe, 7439-89-6; CH_4, 74-82-8.

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Substrate Organometallic Chemistry of Osmium Tetraoxide: Formation of a Novel Type of Carbon Dioxide Coordination

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As part of our general interest in the chemistry available to oxidizing compounds we have begun to investigate the principal interactions available to osmium tetraoxide and related molecules with classical organometallic entities such as Vaska's complex, *trans*-$IrCl(CO)(PPh_3)_2$. In this communication we report on the result of the oxidative-addition reaction of osmium tetraoxide to Vaska's complex in the presence of pyridine bases, a reaction that yields a dinuclear carbon dioxide adduct. This result provides a first glimpse at the substrate organometallic chemistry of osmium tetraoxide. A new type of carbon dioxide coordination has been discovered here.[2]

When 1 equiv of Vaska's complex is added to osmium tetraoxide in toluene at −78 °C and the mixture is allowed to warm to room temperature, a gradual color change from yellow to orange-brown occurs. A brown powder can be isolated by precipitation with hexanes, and orange-brown crystals of the air stable compound I (see Scheme I) form upon recrystallization from dichloromethane–*tert*-butylpyridine–di-*n*-butyl ether. Compound I reacts readily at room temperature with *tert*-butyl isocyanide in dichloromethane to give the air-stable olive-green dinuclear salt, II, in high yield. We assume the coordination environment at iridium in II is as depicted in the scheme since treatment of II

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(1) Myron A. Bantrell Research Fellow, 1981–1983, the California Institute of Technology.

(2) Structurally characterized carbon dioxide complexes include $Ni(\eta^2\text{-}CO_2)(PCy_3)_2$ (Aresta, M.; Nobile, C. F.; Albano, V. G.; Forni, E.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1975**, 636. Aresta, M.; Nobile, C. F. *J. Chem. Soc., Dalton Trans.* **1977**, 708), $[Co(pr\cdot salen)K(\mu\text{-}CO_2)(THF)]_n$ (Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978**, *101*, 74). $[(Ph_3P)_2N][HOs_3(CO)_{10}\cdot O_2COs_6(CO)_{17}]$ (Guy, J. J.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1978**, B34, 1718), and $Nb(\eta^5\text{-}C_5H_4Me)_2\cdot(CH_2SiMe_3)(\eta^2\text{-}CO_2)$ (Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1145.

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