carbene **7**. Thus, it was necessary to explore the possibility that **10** arose from decomposition of the major product, silene dimer **9**. FVP of **9** at 750 °C produced only a trace of **10** (detectable only by GC MS), but at 850 °C the complex product mixture contained 9% of **10**. FVP of **9-2D** at 850 °C afforded **10-D** in which 66% was **10-2D**, 10% **10-3D**, 5% **10-1D**, and 18% deuterium incorporation into the methyl groups. Therefore, it appears that little, if any, of vinylsilane **10** originates from silene dimer decomposition, and the little that does almost certainly comes from reversion of dimer **9** to silene **8**, judging from the similarity of deuterium distribution.

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# Photoisomerization of the Ruthenium Cluster $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$, an Unprecedented Oxygen-to-Carbon Alkyl Migration

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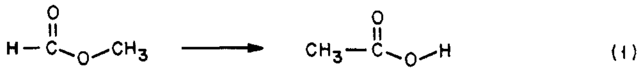
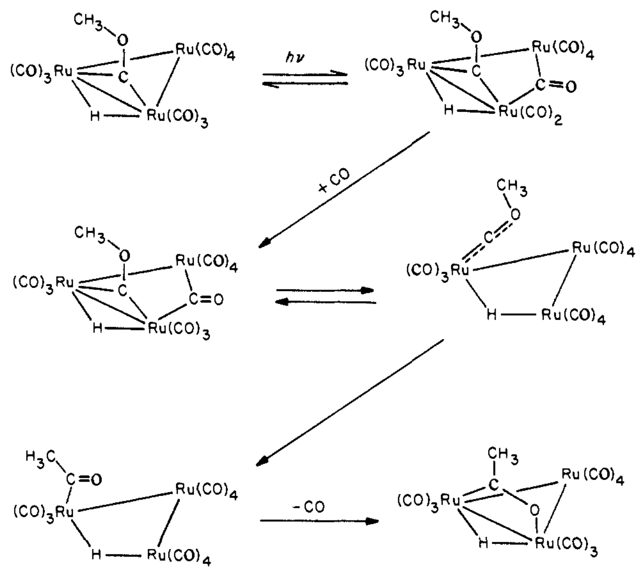
The formation of carbon-carbon bonds from simple $C_1$ precursors is a topic of major interest in both heterogeneous and homogeneous catalysis chemistry.[1] For example, a potentially important transformation is the isomerization of methyl formate (which can be formed by the base catalyzed methanolysis of carbon monoxide)[2] to acetic acid (eq 1). Although catalysts for this



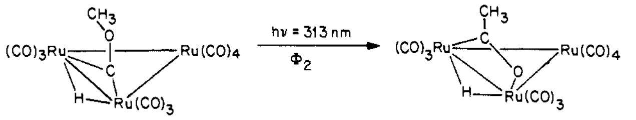
$$\mathrm{H{-}C(=O){-}O{-}CH_3} \longrightarrow \mathrm{CH_3{-}C(=O){-}O{-}H} \qquad (1)$$

transformation have been reported,[3] the conditions are relatively extreme and mechanisms are unknown. To our knowledge, simple molecular models for methyl migration from oxygen to carbon are unprecedented. Here we describe such a molecular transformation, in this case, the result of photochemical excitation of the bridging methylidyne triruthenium cluster $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$.[4]

Scheme I



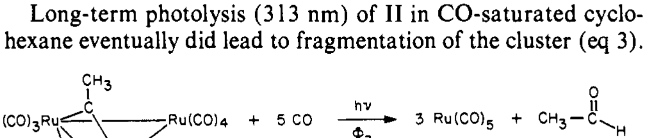
Photolysis ($\lambda_{irr}$ 313 nm)[5] of a $10^{-4}$ M solution of $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$ (I) in CO-saturated cyclohexane led to significant changes in the electronic spectrum. The absorption band characteristic of the starting cluster $\lambda_{max}$ 384 nm ($\epsilon$ = 6900 $M^{-1}$ $cm^{-1}$) diminished in intensity and underwent a shift to slightly lower wavelengths, accompanied by rising absorbance at longer wavelengths. Isosbestic points observed at 436 and 358 nm, for >40% reaction, clearly indicated that the initial cluster had undergone a clean transformation to a single product (or to several products in constant proportion), which is significantly less sensitive to secondary photolysis at 313 nm. Although the product infrared spectrum proved virtually identical with that of I, significant changes in the proton NMR spectra (300 MHz) were evident. The starting complex I, in CO-saturated benzene-$d_6$ solution, displayed singlets for the methylidyne $CH_3$– group at 3.64 ppm and for the hydride proton at –14.90 ppm in the expected 3:1 ratio. After several hours of photolysis (313 nm) these had significantly diminished and a new methyl resonance at 2.07 ppm and a new hydride resonance at –13.98 ppm in a 3:1 ratio had appeared. All three spectral properties (electronic, IR, and $^1$H NMR) are fully consistent with identification of the product as the $\mu$-$\eta^2$-acyl cluster $HRu_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C(O)CH_3)$ (II),[6] the result of overall oxygen-to-carbon migration of the methyl group (eq 2).



(2)

Quantum yields for eq 2 ($\Phi_2$), determined by using standard techniques,[5] were found to be notably dependent both on the CO concentration and on the irradiation wavelength $\lambda_{irr}$. Although the resulting optical changes were the same for different $\lambda_{irr}$, the quantum yields in CO-saturated cyclohexane varied from $<10^{-5}$ mol/einstein at $\lambda_{irr}$ = 405 nm to 4.9 × $10^{-2}$ at 313 nm. Furthermore, $\Phi_2$ was found to be strongly dependent on $P_{CO}$ and to vary linearly from 1.2 × $10^{-4}$ at $P_{CO}$ = 0 ($P_{N_2}$ = 1.0 atm) to 4.9 × $10^{-2}$ mol/einstein at $P_{CO}$ = 1.0 atm for 313-nm photolysis in cyclohexane.

Long-term photolysis (313 nm) of II in CO-saturated cyclohexane eventually did lead to fragmentation of the cluster (eq 3).



(3)

The products were the mononuclear $Ru(CO)_5$ (identified by IR) and the reductive elimination product acetaldehyde (identified by IR and $^1$H NMR), and the stoichiometry was confirmed by IR spectral techniques. This photoreaction was studied quantitatively by using authentic samples of $HRu_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C(O)CH_3)$ ($10^{-4}$ M), and the quantum yield at 313-nm irradiation was found to be 1.1 × $10^{-3}$ mol/einstein.

The mechanism of the unprecedented transformation shown in eq 2 is unclear from the present data. Of particular note is the promotion of this photoreaction by CO, although additional CO is not required by the stoichiometry of eq 2. In earlier studies of the photolytic fragmentation of the triangular cluster $Ru_3(CO)_{12}$,[7] a key step in the proposed mechanism[7c-f] was the heterolytic

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[1] *Catalysis in $C_1$ Chemistry*; Keim, W., Ed.; Reidel: Dordrect, Holland, 1983.

[2] Aguilo, A.; Horlenko, T. *Hydrocarbon Process.* **1980**, *59*, 120.

[3] Pruett, R. L.; Kacmarcik, R. T. *Organometallics* **1982**, *1*, 1693-1699.

[4] Keister, J. B.; Payne, M. W.; Muscatella, M. J. *Organometallics* **1983**, *2*, 219.

[5] Cyclohexane and benzene-$d_6$ were freshly distilled from $LiAlH_4$, freeze degassed, and then saturated with the appropriate gas. Photolyses were performed at $\lambda_{irr}$ 313, 334, 365, and 405 nm by using apparatus and procedures described previously (Hintze, R. E.; Ford, P. C. *J. Am. Chem. Soc.* **1975**, *97*, 2664-2671). Light intensities were measured by ferrioxalate or Actinochrome IR actinometry.

[6] Boag, N. M.; Kampe, C. E.; Lin, Y. C.; Kaesz, H. D. *Inorg. Chem.* **1982**, *21*, 1704-1708.

cleavage of a metal-metal bond with concomitant movement of a terminal CO to a bridging site. Such a transformation would open a coordination site for a two-electron donor such as CO. A similar mechanism, i.e., Scheme I, may be proposed here.[8] Further quantitative flash and continuous photolysis studies currently in progress should better illuminate the mechanism of this unusual transformation.

**Acknowledgment.** This work was supported by the National Science Foundation. Ruthenium used in these studies was provided on loan by Johnson Matthey, Inc.

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(7) (a) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979; and references therein. (b) Grevels, F.-W.; Reuvers, J. G. A.; Takats, J. *J. Am. Chem. Soc.* **1981**, *103*, 4096-4073. Desrosiers, M. F.; Ford, P. C. *Organometallics* **1982**, *1*, 1715-1716. (d) Desrosiers, M. F.; Wink, D. A.; Trautman, R.; Friedman, A. E.; Ford, P. C. *J. Am. Chem. Soc.* **1986**, *108*, 1917-1927. (e) Malito, J.; Markiewicz, S.; Poë, A. *Inorg. Chem.* **1982**, *21*, 4335-4338. (f) Bentsen, J. G.; Wrighton, M. S. *J. Am. Chem. Soc.*, in press. Private communication from M. S. Wrighton.

(8) According to this proposal the isomerization depicted in eq 2 should also be facilitated by other two-electron donor ligands. In this context, it is notable that at $P_{CO}$ = 0.0 the $\Phi_2$ has a value $1.4 \times 10^{-3}$ in THF solution, over an order of magnitude larger than under the same conditions in cyclohexane solution.

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## Thermochemical Study of the Lewis Acid Promoted Carbonyl Insertion Reaction

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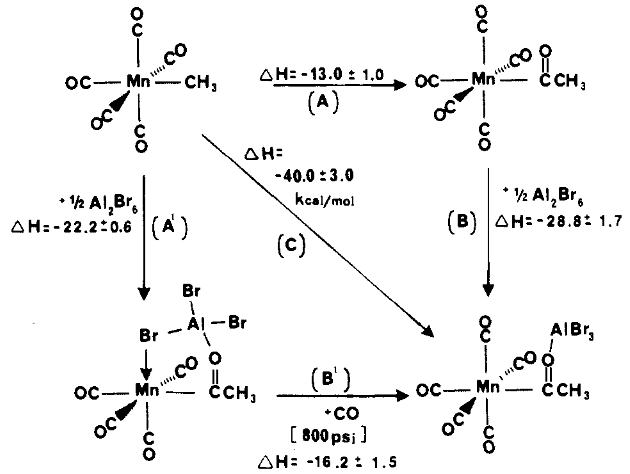
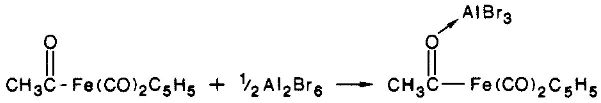
Interaction of Lewis acids with transition-metal alkyl carbonyl complexes has been shown to promote carbonyl insertion.[1] This effect combines both thermodynamic and kinetic factors. Since studies of homogeneous model systems can provide important information about heterogeneous catalysts, we have begun investigation of the thermodynamic effects of Lewis acids on carbonyl insertion. This is part of a general program of solution calorimetric studies of organotransition-metal complexes.[2]

Shriver and co-workers[1] have reported synthetic, structural, and kinetic details of the interaction of aluminum halides with methylmanganese pentacarbonyl. Cotton and Calderazzo previously determined the enthalpy of carbonylation of $CH_3Mn(CO)_5$ (reaction A in Scheme I) by measuring the temperature variation of the equilibrium constant ($\Delta H = -12.6$ kcal/mol in bis($\beta$-ethoxyethyl)ether[3]). Using calorimetric techniques similar to those reported earlier[2] and a newly developed high-pressure cell, we have repeated this measurement[4a] and completed the thermochemical cycle shown in Scheme I. To our knowledge this represents the first thermochemical assessment of the role of Lewis acids in the promotion of this important reaction.

Scheme I



Reaction of $H_3C(O)\text{-}Mn(CO)_5$ (reaction B) with $^1/_2Al_2Br_6$ in toluene solution at 25 °C is rapid and exothermic, $\Delta H = -28.8 \pm 1.7$ kcal/mol.[4b] In order to compare this result to the heat of adduct formation with other transition-metal complexes, we measured the enthalpy of reaction of the iron acyl complex shown in reaction 1. The enthalpy of this reaction ($\Delta H = -30.6 \pm 2.1$ kcal/mol (25 °C, toluene solution)) is similar to that for the analogous reaction with manganese acyl and suggests that the transition metal plays only a minor role in determining the stability of the aluminum bromide-carbonyl adduct. The heat of reaction 2 was measured in order to compare the stabilities of the organometallic aluminum bromide adduct with those of organic analogues. The enthalpy of reaction 2 at 25 °C, with all species



$$CH_3C(=O)\text{-}Fe(CO)_2C_5H_5 + {}^1/_2Al_2Br_6 \longrightarrow CH_3C(=O \rightarrow AlBr_3)\text{—}Fe(CO)_2C_5H_5 \quad (1)$$

$$(C_6H_5)_2C{=}O + {}^1/_2Al_2Br_6 \rightarrow (C_6H_5)_2C{=}O{\rightarrow}AlBr_3 \quad (2)$$

in toluene solution, is $-24.5 \pm 0.5$ kcal/mol, in agreement with previously reported values.[5]

Aluminum bromide adduct formation with more electron rich carbonyl compounds, such as $C_6H_5C(O)N(C_6H_5)_2$ is more exothermic ($\Delta H = -27.4$ kcal/mol[5]) and agrees, within 10%, with the values obtained for the transition-metal complexes. Thus, it appears that it may be possible to estimate the interaction of Lewis acids with transition-metal complexes by consideration of the interaction of an appropriate organic model compound with the relevant Lewis acid. It should also be noted that our data are based on reaction with $^1/_2Al_2Br_6$. Calculation based on reaction with the more powerful Lewis acid, $AlBr_3$, requires addition of $-13.3$ kcal/mol to the values reported herein.[6]

Reaction of $CH_3Mn(CO)_5$ with $^1/_2Al_2Br_6$, reaction A' in Scheme I, is exothermic by $22.2 \pm 0.6$ kcal/mol in toluene solution

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(1) (a) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219. (b) Butts, S. B.; Strauss, s. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. M.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093. (c) Richmond, T. G.; Basolo, F.; Shriber, D. F. *Inorg. Chem.* **1982**, *21*, 1272. (d) Richmond, T. G.; Basolo, F.; Shriver, D. F. *Organometallics* **1982**, *1*, 1624. (e) Shriver, D. F. *J. Organomet. Chem.* **1975**, *94*, 259. (f) Stimson, R. E.; Shriver, D. F. *Inorg Chem.* **1980**, *19*, 1141.

(2) (a) Hoff, C. D. *J. Organomet. Chem.* **1983**, *246*, C53. (b) Hoff, C. D. *J. Organomet. Chem.* **1985**, *282*, 201. (c) Nolan, S. P.; Hoff, C. D. *J. Organomet. Chem.* **1985**, *290*, 365. (d) Nolan, S. P.; Landrum, J. T.; Hoff, C. D. *J. Organomet. Chem.* **1985**, *282*, 357. (e) Nolan, S. P.; Lopez, de la Vega, R.; Hoff, C. D. *Organometallics*, in press. (f) Landrum, J. T.; Hoff, C. D. *J. Organomet. Chem.* **1985**, *282*, 215. (g) Nolan, S. P.; Lopez, de la Vega, R.; Mukerjee, S. L.; Hoff, C. D. *Inorg. Chem.* **1986**, *25*, 1160. (g) Nolan, S. P.; Lopez de la vega, R.; Hoff, C. D. *J. Organomet. Chem.*, in press.

(3) Calderazzo, F.; Cotton, F. A. *Inorg. Chem.* **1962**, *1*, 31.

(4) (a) The value we obtained, $-13.4 \pm 1.0$ kcal/mol at 30 °C in THF, agrees well with that reported earlier by others.[3] In Scheme I, we adopt an average value of $-13.0 \pm 1.0$ kcal/mol. Details of the high-pressure calorimetry will be published later. (b) In a typical reaction, a glass ampule containing approximately 0.1 g of the complex was broken into a solution of 25 g of $Al_2Br_6$ (purified by high-vacuum sublimination) in 400 mL of dry toluene by using the calorimetric system previously described.[2] (c) A similar value was obtained for the enthalpy of reaction B' (Scheme I) in toluene solution. However, due to formation of precipitate in some of the reactions, greater accuracy was obtained in $CH_2Cl_2$ solution where no precipitation was observed.

(5) (a) Ganyushin, L. A.; Romm, I. P.; Gur'yanova, E. N.; Isaeva, E. S.; Ryaboi, V. M.; Shcherbakova, E. S. *Zh. Obshch. Khim.* **1980**, *50*, 2159. (b) Ganyushin, L. A.; Romm, I. P.; Gur'yanova, E. N.; Shifrina, R. R.; Kopilov, V. V. *Zh. Obshch. Khim.* **1980**, *50*, 2755.

(6) Fischer, W.; Ralfs, O. *Z. Anorg. Allg. Chem.* **1932**, *205*, 1.

0002-7863/86/1508-7852$01.50/0