ORGANOMETALLICS

Volume 11, Number 12, December 1992

Communications

Formation of the Solvento Species upon Photodissociation of CO from $Mn_2(CO)_{10}$ in 3-Methylpentane

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Received August 7, 1992

Summary: The solvento species $Mn_2(CO)_9(solv)$, where solv is a solvent molecule, is shown to form upon photodissociation of CO from $Mn_2(CO)_{10}$ in 3-methylpentane glass at 93 K. The rate constant for its conversion to the semibridging species $Mn_2(CO)_8(\mu\text{-}\eta^1{:}\eta^2\text{-}CO)$ is $[4.9\ (3)] \times 10^{-3}\ s^{-1}$ at 93 K.

Formation of a solvento species upon photodissociation of CO from mononuclear metal carbonyl compounds in hydrocarbon solvents is well-established.[1] In the case of $Cr(CO)_6$, the process occurs within about 25 ps.[1d] An analogous solvento species following CO loss from dinuclear metal carbonyl compounds has only recently been unambiguously identified.[2] A recent ultrafast laser study of $Mn_2(CO)_{10}$[3] has prompted us to more fully characterize the solvento species $Mn_2(CO)_9(solv)$ (where solv represents a solvent molecule), formed upon photodissociation of CO from $Mn_2(CO)_{10}$ in 3-methylpentane glass at low temperature.

The photochemistry of $Mn_2(CO)_{10}$ has been much studied.[4] In earlier studies the emphasis was on Mn–Mn bond homolysis, producing a pair of $Mn(CO)_5$ radicals. However, Peters, Vaida, et al. showed that two absorbing species are present following 25-ps pulsed laser irradiation of $Mn_2(CO)_{10}$ in ethanol.[5] One was assigned to $Mn(CO)_5$ and the other, absorbing at 480 nm, to a solvento species, $Mn_2(CO)_9(EtOH)$, presumably involving oxygen coordination at the metal. Yesaka and co-workers also observed the absorbance at 480 nm and followed its decay upon reaction with CO, EtCN, or other ligands.[6a] Soon thereafter, Hepp and Wrighton showed that irradiation of $Mn_2(CO)_{10}$ in 3-methylpentane at 77 K leads to formation of the species $Mn_2(CO)_8(\mu\text{-}\eta^1{:}\eta^2\text{-}CO)$,[7] which we refer to as linear semibridged. Subsequent work has confirmed the existence of the semibridged species.[8]

Most recently, Zhang and Harris have studied the photodissociation of CO from $Mn_2(CO)_{10}$ using ultrafast techniques.[3] They observed transient absorbances at various wavelengths in the 480–830-nm range, at times as short as 2–3 ps following the laser pulse. They tentatively proposed that the initial photoproduct, $Mn_2(CO)_9$, does not have a bridging CO but isomerizes to the semibridging form in less than 2–3 ps. However, given that the semibridging form is stabilized by perhaps only 3–5 kcal mol^{-1} relative to a solvated species, it is not clear that the highly energized $Mn_2(CO)_9$ left upon photodissociation could lose sufficient excess energy to permit formation of the semibridge in such a short time. Taking a different approach, we have employed low-temperature flash methods with IR detection,[9] on a much slower time scale, in an effort to identify a solvento species and observe its conversion to the semibridged form.

When 0.45 mM $Mn_2(CO)_{10}$ in 3-methylpentane glass at

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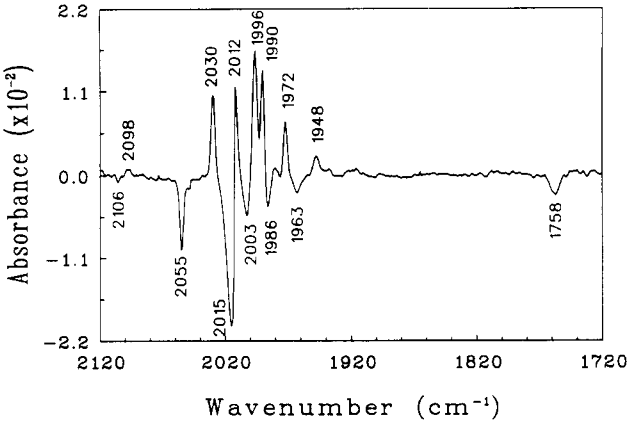

Figure 1. Difference IR spectrum in 3-methylpentane at 93 K, between 1 min following 6 flashes and 20 min following 6 flashes. The positive peaks are due to $Mn_2(CO)_9$(solv) and the negative peaks to $Mn_2(CO)_8(\mu\text{-}\eta^1{:}\eta^2\text{-}CO)$.

93 K is flashed with a conventional xenon flash lamp source, the IR spectrum following the flash reveals loss in absorbances due to $Mn_2(CO)_{10}$ and the appearance of bands ascribed to $Mn_2(CO)_8(\mu\text{-}\eta^1{:}\eta^2\text{-}CO)$, including a band at 1758 cm^{-1}. In addition, several new bands are seen at 2098, 2030, 2012, 1996, 1990, 1972, and 1948 cm^{-1}. At 93 K the new bands disappear over a period of about 10 min, with concurrent appearance of additional intensity in the bands ascribed to $Mn_2(CO)_8(\mu\text{-}\eta^1{:}\eta^2\text{-}CO)$. A difference spectrum in 3-methylpentane at 93 K, between 1 min following 6 flashes and 20 min following 6 flashes, is shown in Figure 1. The positive peaks are due to the new species, and the negative peaks are due to $Mn_2(CO)_8(\mu\text{-}\eta^1{:}\eta^2\text{-}CO)$. The band pattern of the new species is identical with that observed for several established instances of equatorially monosubstituted species.[10] We assign the new species to the solvento compound $Mn_2(CO)_9$(solv), which converts at 93 K to the semibridged species. The rate constant for its conversion to $Mn_2(CO)_8(\mu\text{-}\eta^1{:}\eta^2\text{-}CO)$, on the basis of the decay of the IR band at 2030 cm^{-1} or increase in intensity of the band at 2055 cm^{-1} due to $Mn_2(CO)_8(\mu\text{-}\eta^1{:}\eta^2\text{-}CO)$, is estimated as [4.9 (3)] × 10^{-3} s^{-1}. The changes in the absorbances vs time are illustrated in Figure 2.

Extrapolation of the intensities of the bands due to solvento and semibridged species back to zero time following the flash suggests that the solvento species is present in about 0.8:1.0 ratio relative to the semibridged species.[12] Because the xenon lamp flash is fairly prolonged, on the order of 30 μs at half-height, and with a trailing edge, it is possible that the semibridge form present at the end of the flash period has been formed via secondary photolysis of the solvento species. In any case, the solvento species is clearly a prominent initial product following CO loss.

Figure 3a shows the difference UV–visible absorption spectra of the solution at 93 K, 1 min after the flash and 15 min following the flash, taken with an HP8452 diode array spectrophotometer. The large negative absorption is due to the loss of $Mn_2(CO)_{10}$. Figure 3b shows an enlarged view of the region from 380 to 580 nm. The previously observed band at about 480 nm is evident, but there is, in addition, evidence for a previously unobserved band at about 410 nm. Previous evidence regarding the UV–visible spectrum of the $Mn_2(CO)_9$ intermediates is based on transient spectra.[5,6] For example, Kobayashi and co-workers reported the spectrum of the intermediate at 3 and 30 μs following a 355- or 266-nm laser flash.[6b] The spectra reveal absorption to wavelengths approaching 400 nm. However, the noise levels are high. Further, residual bleaching of absorption by starting dimer, due to formation of $Mn(CO)_5$ radicals, contributes to the absorption loss at short wavelength.[6b] In our low-temperature experiments,

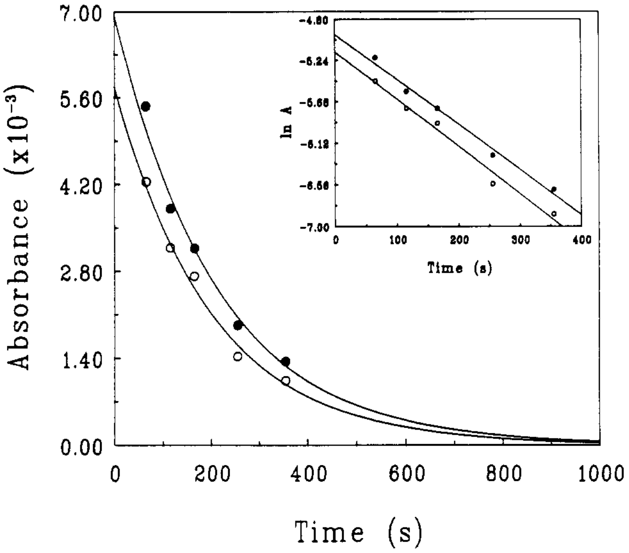

Figure 2. Changes in absorbances vs time due to conversion of $Mn_2(CO)_9$(solv) into $Mn_2(CO)_8(\mu\text{-}\eta^1{:}\eta^2\text{-}CO)$ at 93 K in 3-methylpentane. Data points correspond to $|A_t - A_\infty|$ for absorbances at 2030 cm^{-1} (●) and 2055 cm^{-1} (○), assigned to $Mn_2(CO)_9$(solv) and $Mn_2(CO)_8(\mu\text{-}\eta^1{:}\eta^2\text{-}CO)$, respectively. The inset shows linear ln *A* vs time plots, from which the first-order rate constant is estimated to be [4.9 (3)] × 10^{-3} s^{-1}.

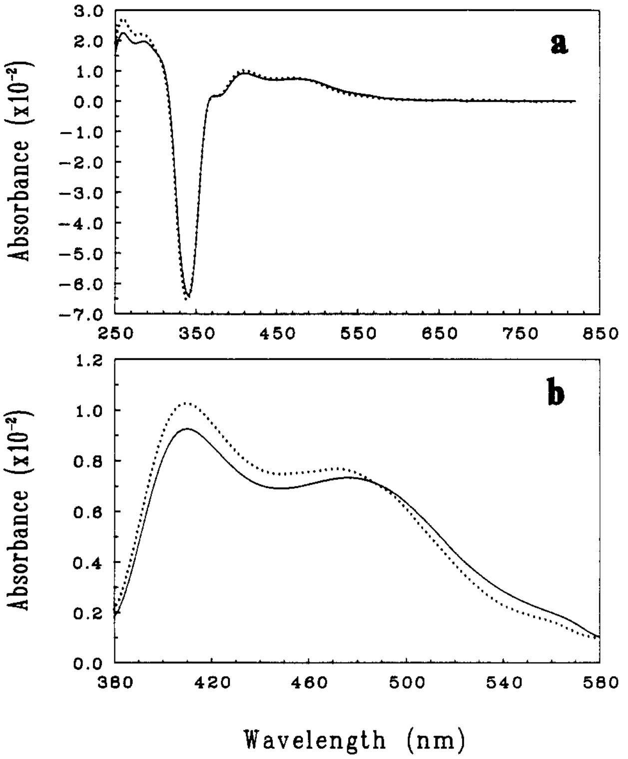

Figure 3. Difference UV–visible spectra of $Mn_2(CO)_{10}$ in 3-methylpentane glass at 93 K: (—) between 1 min after 6 flashes and before flashes; (···) between 15 min after 6 flashes and before the flashes.

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[10] For example, *eq*-$Mn_2(CO)_9$py: IR 2089 (w), 2016 (s), 2005 (m), 1980–1983 (s), 1962 (m), 1943 (m).[11]

[11] Koelle, U. *J. Organomet. Chem.* 1978, *155*, 53.

[12] The ratio of extinction coefficients of the bands at 2030 cm^{-1} due to $Mn_2(CO)_9$(solv) and that at 2055 cm^{-1} due to $Mn_2(CO)_8(\mu\text{-}\eta^1{:}\eta^2\text{-}CO)$ is estimated to be 1.2 from the time-dependent absorbance data, as $Mn_2(CO)_9$(solv) converts to $Mn_2(CO)_8(\mu\text{-}\eta^1{:}\eta^2\text{-}CO)$.

bleaching of the starting dimer due to formation of $Mn(CO)_5$ radicals is not a factor.

Examination of similar samples in the IR revealed the presence of substantial solvento form at the shorter time and its complete absence at the longer time. Most strikingly, the spectra in Figure 3 demonstrate that there is little difference in the absorption spectra of the solvento and semibridged forms. In particular, there is very little absorbance difference in the vicinity of 480 nm and virtually no absorbance due to either species at 580 nm or longer wavelength. Thus, the UV–visible absorbances at these wavelengths do not afford an effective means of determining whether the solvento or semibridged form is present.

The transient IR spectrum of $Mn_2(CO)_9$ following laser flash photolysis at room temperature has been reported by Church and co-workers.[8b] Bands due to $Mn_2(CO)_8(\mu\text{-}\eta^1{:}\eta^2\text{-CO})$ are observed at short times, on the order of 10 μs. Assuming from this result that the rate constant for semibridge formation from the solvento species is 1×10^6 s^{-1} or faster at room temperature, the enthalpy of activation for semibridge formation is on the order of 5 kcal mol^{-1} or larger. The estimated barrier to semibridge formation is similar to the rough estimate of 8 kcal mol^{-1} for the free energy barrier to formation of the semibridge in the phosphine-substituted CO-loss species $Mn_2(CO)_7[P(n\text{-}Bu)_3]_2$, on the basis of room-temperature kinetics behavior.[13] While these estimates are crude, they are reasonably consistent and suggest that formation of $Mn_2(CO)_8(\mu\text{-}\eta^1{:}\eta^2\text{-CO})$ following photodissociation of CO at room temperature could be fairly slow, in the time range of 0.01–1 μs. The most promising approach to determination of the time scale for semibridge formation at room temperature would seem to be time-resolved IR detection.

Acknowledgment. This research was supported by Grant No. NSFCHE89-12773 from the National Science Foundation.

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Migratory Insertion of Silyl and Thiocarbonyl Ligands on Ruthenium and Osmium To Give the η^2-Silathioacyl Complexes $M(\eta^2\text{-}C[S]SiMe_2X)Cl(CO)(PPh_3)_2$ (M = Ru, Os; X = Cl, OEt)

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Received August 19, 1992

Summary: The yellow, coordinatively unsaturated silyl thiocarbonyl complexes of ruthenium and osmium $M(SiMe_2Cl)Cl(CS)(PPh_3)_2$ (M = Ru (**1a**), Os (**2a**)) can be prepared by reaction of $HSiMe_2Cl$ with $MHCl(CS)(PPh_3)_3$ or $MPhCl(CS)(PPh_3)_2$. The Si–Cl bond in **1a** and **2a** is readily cleaved by ethanol, and the corresponding ethoxysilyl complexes **1b** and **2b** are formed. Addition of CO to **1a**, **1b**, and **2b** induces an immediate migratory insertion reaction involving the silyl and thiocarbonyl ligands, and the novel η^2-silathioacyl complexes $M(\eta^2\text{-}C[S]SiMe_2X)Cl(CO)(PPh_3)_2$ (M = Ru, X = OEt (**1c**), Cl (**1d**); M = Os, X = OEt (**2c**)) are formed. The single-crystal X-ray structure determination of **1c** is described.

Migratory insertion reactions involving coordinated alkyl and carbonyl ligands are well-known and have been studied extensively.[1] In contrast, the first examples of the analogous reaction involving silyl and carbonyl ligands have been reported only recently.[2] To date, all examples of this latter reaction have involved early transition metals of d^0 electron configuration with the resulting silaacyl ligands coordinating in a η^2 fashion through oxygen as well as carbon.[3] Although the known carbonyl silyl derivatives of the later transition metals are reluctant to undergo migratory insertion,[4] it appeared to us that the related thiocarbonyl derivatives would be much more likely to react in this way. The thiocarbonyl ligand generally undergoes migratory insertion reactions more readily than carbonyl (even hydride migration is easily induced), and for the later, thiophilic transition metals, coordination of the thioacyl ligand in a η^2 fashion might provide additional stability to the rearranged products.[5a,b] We therefore synthesized mixed silyl thiocarbonyl complexes of ruthenium and osmium (**1a**,**b** and **2a**,**b**) and now report the first examples of migratory insertion involving these ligands to give the corresonding η^2-silathioacyl derivatives.

We have previously reported that reaction of the silanes $HSiR_3$ (R = Cl, Me, Et) with the coordinatively unsaturated σ-aryl complexes $MPhCl(CO)(PPh_3)_2$ (M = Ru, Os) provides a simple and efficient route to the corresponding silyl derivatives $M(SiR_3)Cl(CO)(PPh_3)_2$.[6] In an extension

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[1] See for example: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 6, pp 356–376, and references therein.

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[3] A η^2-silaacyl complex of rhenium (fac-$Re(\eta^1\text{-}C[O]SiPh_3)(CO)_3$(diphos)) has been prepared by reaction of $[Re(CO)_4(diphos)]ClO_4$ with Ph_3SiLi: Anglin, J. R.; Calhoun, H. P.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 2281.

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