Organometallics **2000,** *19,* 4915−4917

Notes

Dihydrogen as a Reactant in the Photochemistry of Bimetallic Cyclopentadienyl Carbonyl Compounds[⊥]

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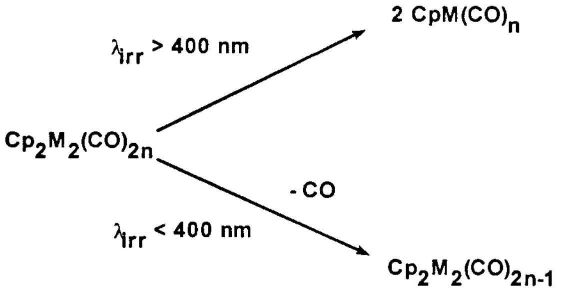
Received April 10, 2000

Summary: Dihydrogen has been found to react photochemically with bimetallic compounds of the form [(η^5-C_5H_5)M(CO)$_n$]$_2$, where M = Mo or W, n = 3, M = Fe or Ru, n = 2, to give the corresponding metal hydrides, (η^5-C_5H_5)M(CO)$_n$H. Hydride formation is only significant when the photolysis wavelengths are in the high-energy regions known to trigger CO loss from these compounds, and hydride formation is suppressed by added CO, making it likely that the reaction involves oxidative addition of H_2 to an electron-deficient, CO-loss intermediate.

The photochemistry of bimetallic compounds of general formula [(η^5-C_5H_5)M(CO)$_n$]$_2$, where M = Mo or W, n = 3, and M = Fe or Ru, n = 2, has been extensively studied, and the photochemistry of these group VI and group VIII compounds has recently been reviewed.[1,2] Photolysis of these compounds is characterized by two wavelength-dependent pathways. At low photon energy, typically in the visible portion of the spectrum, metal−metal bond breaking is almost exclusively observed, while at higher photon energies carbonyl ligand loss becomes the dominant reaction pathway. These pathways are illustrated in Scheme 1. At room temperature the group VI CO-loss intermediates, (η^5-C_5H_5)$_2$M$_2$(CO)$_5$, undergo thermal loss of a second CO to form the well-known tetracarbonyl species, (η^5-C_5H_5)$_2$M$_2$(μ-CO)$_4$,[3] while the group VIII compounds give rise to paramagnetic tricarbonyl derivatives, (η^5-C_5H_5)$_2$M$_2$(μ-CO)$_3$. In both cases the CO-loss species can react with ligands such as phosphines to give derivatives of the form (η^5-C_5H_5)$_2$M$_2$(CO)$_5$L and (η^5-C_5H_5)$_2$M$_2$(CO)$_3$L.

Scheme 1. Photolysis Pathways for Cyclopentadienyl Metal Carbonyl Compounds as a Function of Irradiation Wavelength



Brown and Zhang[4] have reported that (η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$ reacts photochemically with $HSnBu_3$ to give (η^5-C_5H_5)Fe(CO)$_2$H, (η^5-C_5H_5)Fe(CO)$_2$SnBu$_3$, and (η^5-C_5H_5)Fe(CO)H(SnBu$_3$)$_2$. Suppression of this reaction with CO led these workers to propose that the reaction was proceeding through a CO-loss intermediate by the mechanism in Scheme 2, X = $SnBu_3$. The key steps of this mechanism are the oxidative addition of $HSnBu_3$ to the CO-loss intermediate and the subsequent reductive elimination of (η^5-C_5H_5)Fe(CO)$_2$H. An analogous mechanism has been proposed in the photochemical reaction of $Mn_2(CO)_{10}$ with $HSnBu_3$.[5] Chalk and Harrod[6] postulated the addition of $HSiR_3$ to $Co_2(CO)_8$ via a CO-loss pathway to yield $HCo(CO)_4$ and $R_3SiCo(CO)_4$ as reactants in the cobalt carbonyl catalyzed hydrosilation of olefins. A mechanism involving CO loss has been proposed for the formation of $HCo(CO)_4$ from $Co_2(CO)_8$ and H_2.

To our surprise, a review of the extensive literature on the photolysis of the cyclopentadienyl metal carbonyl dimers of groups VI and VIII yielded no work on the reactions of these compounds with dihydrogen. Curtis[7] has noted a lack of reactivity of the unsaturated compounds (η^5-C_5H_5)$_2$M$_2$(μ-CO)$_4$, M = Mo and W, with H_2, but Alt and co-workers[8] have found that (η^5-C_5R_5)$_2$M$_2$(μ-CO)$_4$, M = Mo, R = CH_3, M = W, R = H or CH_3, do react photochemically with H_2 to give the bridging bimetallic compounds (η^5-C_5H_5)$_2$M$_2$(CO)$_4$(μ-H)$_2$.

[⊥] Dedicated to our dear friend and frequent collaborator Prof. Arnold Rheingold on the occasion of his 60th birthday.
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(4) Zhang, S.; Brown, T. L. *Organometallics* **1992**, *11*, 2122−2128.
(5) (a) Sullivan, R. J.; Brown, T. L. *J. Am. Chem. Soc.* **1991**, *113*, 9155−9161; (b) **1991**, *113*, 9162−9169.
(6) (a) Chalk, J. F.; Harrod, A. J. *J. Am. Chem. Soc.* **1969**, *89*, 1640−1647; (b) **1965**, *87*, 1133−1135.
(7) Curtis, M. D. *Polyhedron* **1987**, *6*, 759−782.
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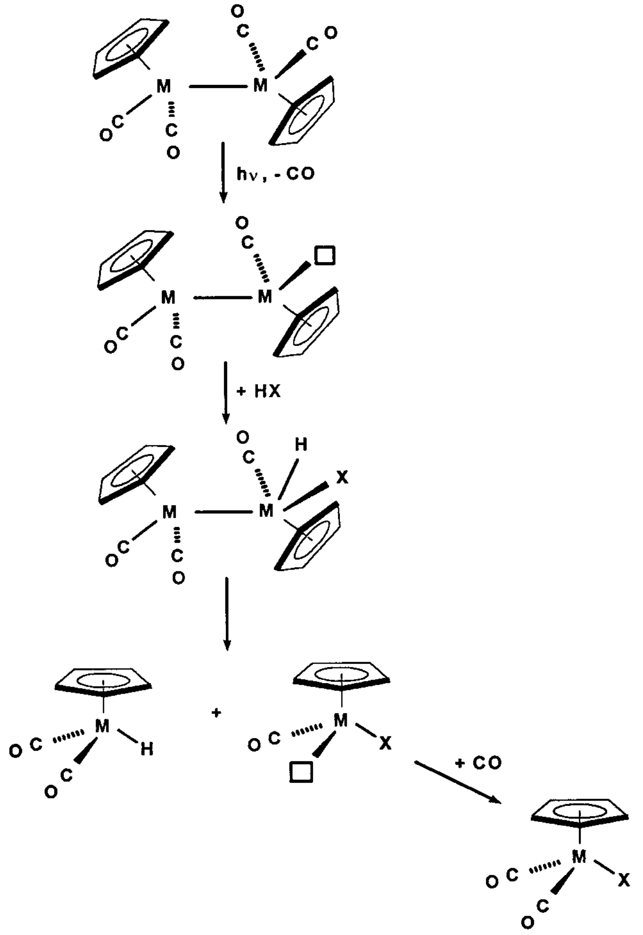
10.1021/om000292c CCC: $19.00

Scheme 2. Proposed Mechanisms for the Photochemical Reaction of HX, Where X = $SnBu_3$ or H, with Cyclopentadienyl Metal Carbonyl Compounds



Thermal reaction of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ with H_2 (150 bar) has been reported to give $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$, but no details are available.[9] In light of our long-term interest in the evolution of dihydrogen from bimetallic compounds and the reaction chemistry of metal hydrides, we undertook an investigation of this fundamental reaction. The results of this work are reported in this note.

Results and Discussion

Solutions of $[(\eta^5\text{-}C_5H_5)M(CO)_2]_2$, where M = Fe or Ru, and $[(\eta^5\text{-}C_5H_4Me)M(CO)_3]_2$, where M = Mo and W, in petroleum ether and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$, in benzene, were transferred under nitrogen to a high-pressure reaction vessel. Solutions were pressurized with dihydrogen or dihydrogen/CO mixtures and allowed to equilibrate for 1−6 h, with the longer times being needed for CO. Typical dihydrogen pressures were 10−20 bar, while CO pressures were 2−5 bar. Solutions were transferred under pressure to a high-pressure IR cell. Photolyses were carried out using a 350 W high-pressure mercury source. A water filter was used to remove infrared radiation, and optical filters were used to select photolysis wavelengths. Hydride formation was monitored by difference IR. All photolyses were carried out at room temperature.

Samples of each of the solutions before pressurization with hydrogen were subjected to photolysis with the same wavelength ranges used for the pressurized samples. Only in the case of $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4$ were significant metal hydride bands observed. It is known that bimetallic ruthenium hydride species, believed to be the result of metal-to-ring radical coupling in competition with the usual metal-to-metal recombination reaction, are formed upon photolysis;[10,11] therefore the observation of bands in this case was not unexpected.

Two minute photolyses in the visible region, $\lambda_{irr} = 450 \pm 70$ nm, of samples under dihydrogen results in the formation of traces of metal hydride, as determined by difference analysis of the spectra before and after photolysis. In contrast, UV photolyses, 340 nm $< \lambda_{irr} <$ 390 nm, of fresh samples under identical dihydrogen pressure results in extensive (50−80%) formation of the corresponding hydrides. IR spectra of authentic samples of the various metal hydrides confirmed the assignments. Yield of hydride increases with increased photolysis time and with increased dihydrogen pressure. In all cases, introduction of 2−5 bar of CO results in complete suppression of metal hydride formation. Because of the very small quantities involved in these photolyses, no attempt was made to isolate the product hydrides for further characterization.

In the case of $(\eta^5\text{-}C_5H_4Me)_2Mo_2(CO)_6$, spectra recorded two and four minutes after photolysis revealed the rapid decay of a species with IR bands at 1887 and 1867 cm^{-1}. These bands are consistent with the competitive formation of $(\eta^5\text{-}C_5H_4Me)_2Mo_2(\mu\text{-}CO)_4$ during photolysis. The subsequent decay of this species is almost certainly due to recapture of CO and not due to reactions with H_2. Attempts to carry out the reaction of H_2 with $(\eta^5\text{-}C_5H_4Me)_2Mo_2(CO)_6$ under normal Schlenk conditions under 1 bar of H_2 or even in Griffin-Worden tubes at 2 bar H_2 yielded only small amounts of the hydrides and $(\eta^5\text{-}C_5H_4Me)_2Mo_2(\mu\text{-}CO)_4$.

Following photolysis it was observed that bands of the iron, ruthenium, and molybdenum hydrides decreased over time, while bands of the metal dimers grew in. Attempts to obtain kinetic measurements of these thermal back-reactions yielded inconsistent rate values. Since it is known that these hydrides are typically stable over considerable periods in solution, we are carrying out additional studies to understand why they appear to be unstable under high pressures of dihydrogen.

The absence of significant hydride formation upon visible photolysis argues against radical involvement in these reactions. On the contrary, both the strong formation of hydrides at wavelengths where CO loss is known to occur and the effect of added CO to suppress hydride formation support a mechanism involving CO loss. A reasonable mechanism for these reactions, Scheme 2, X = H, is analogous to that proposed by Brown and Zhang.[3] UV photolysis of the metal carbonyl dimers results in CO loss and formation of an electron-deficient species. Oxidative addition of H_2 to this intermediate is followed by reductive elimination giving $CpM(CO)_nH$

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[9] Dub, M. *Organometallic Compounds*, 2nd ed.; Springer-Verlag: Berlin, 1966; Vol. 1.

[10] Bitterwolf, T. E.; Shade, J. E.; Hansen, J. A.; Rheingold, A. L. *J. Organomet. Chem.* **1996**, *514*, 13−21.

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and CpM(CO)$_{n-1}$H. The latter recovers CO to form the second molecule of CpM(CO)$_n$H. The reaction proceeds efficiently at high pressure but is not competitive with CO recapture at or near atmospheric pressure. Hydrogen addition products such as (η^5-C_5H_5)W(CO)H(H_2) and (η^5-C_5H_5)W(CO)H_3 observed to form in dihydrogen-doped gas matrixes are not observed under these conditions.[12]

These observations prompt us to offer an alternative interpretation to the mechanism of formation of (η^5-C_5H_5)$_2$$M_2(CO)_4$($\mu$-H)$_2$ upon photolysis of (η^5-C_5H_5)M(CO)$_3$H proposed by Alt and co-workers.[8] Gas matrix photochemical studies have established that the primary photochemical process of the group VI compounds (η^5-C_5H_5)M(CO)$_3$H, where M = Cr, Mo, and W, is loss of CO to form (η^5-C_5H_5)M(CO)$_2$H as a reactive intermediate.[13] It was proposed that direct dimerization of these intermediates results in formation of (η^5-C_5H_5)$_2$$M_2(CO)_4$($\mu$-H)$_2$. Considering that the concentrations of photochemical intermediates will almost always be too low to result in significant product formation through dimerization, we suggest that it is more likely that (η^5-C_5H_5)M(CO)$_2$H oxidatively adds (η^5-C_5H_5)M(CO)$_3$H to give (η^5-C_5H_5)$_2$$M_2(CO)_5(H)_2$ and that this species loses CO to give (η^5-C_5H_5)$_2$$M_2(CO)_4$($\mu$-H)$_2$. Under the conditions of our experiments free CO in the closed IR cell would reverse this reaction, but under the open photolysis conditions used by Alt CO loss becomes competitive.

Although the present studies have been conducted on a very small scale, it is reasonable that scale-up employing a high-pressure photolysis cell could easily result in the synthesis of preparative quantities of these metal hydrides. It is possible that reactions in which metal hydrides are stoichiometric reagents might be carried out under these photochemical conditions, and work is now underway in our laboratory to test this hypothesis.

Experimental Section

(η^5-C_5H_5)$_2$$Fe_2(CO)_4$,[14] ($\eta^5$-$C_5H_5$)$_2$$Ru_2(CO)_4$,[15] ($\eta^5$-$C_5H_4CH_3$)$_2$$M_2(CO)_6$, M = Mo and W,[16] ($\eta^5$-$C_5H_5$)M(CO)$_2$H, M = Fe or Ru,[17] ($\eta^5$-$C_5H_4CH_3$)Mo(CO)$_3$H,[18] and ($\eta^5$-$C_5H_4CH_3$)W(CO)$_3$H[19] were prepared by standard literature methods. IR spectra were recorded on a Perkin-Elmer Spectrum 1000 FTIR spectrometer at a resolution of 4 cm^{-1}. A 125 mL high-pressure O-ring seal reactor, OC-1 (High-Pressure Equipment Co., Erie, PA), was modified to allow gas inlet and liquid outlet and used to prepare gas-saturated solutions. A temperature-controlled/high-pressure IR cell, 118-1P (Wilmad, Buena, NJ), outfitted with CaF_2 windows was used for all IR measurements.

High-Pressure Photolyses. Cyclopentadienyl metal carbonyl dimers, ca. 100 mg, were placed in a Schlenk flask, which was evacuated and then back-filled with nitrogen. Petroleum ether, 50 mL, was added to the flask and the solution stirred until dissolution was complete. A sample of this solution was transferred to the IR cell for background IR and photolysis to establish a background for hydride formation in the absence of H_2.

The high-pressure reactor was evacuated and back-filled with nitrogen, after which the solution was transferred to the high-pressure reactor using nitrogen pressure. The reactor was connected to the gas manifold and flushed three times with H_2 (ca. 3 bar) before being pressurized to an operating pressure of 10−20 bar. Solutions were allowed to stand under pressure for 1−3 h to allow for equilibration of H_2 in the solution. Samples involving H_2/CO mixtures were allowed to stand for as much as 6 h to allow equilibration. After equilibration the solutions were transferred to the IR cell under pressure.

Photolyses were conducted using a 350 W high-pressure Hg lamp. Visible light photolyses were carried out using a band-pass filter, $\lambda_{\mathrm{irr}} = 450 \pm 70$ nm, while ultraviolet photolyses used a combination of filters. giving an effective photolysis range of 340 nm < λ_{irr} < 390 nm. Two minute photolyses were found to be optimal for the samples used, giving 50−80% conversion to the hydrides upon ultraviolet photolysis. Photolyses of longer than two minutes resulted in extensive secondary photolysis and decomposition. IR spectra were recorded immediately after photolysis, and difference spectra were used to identify the product bands resulting from photolysis. Because of the very small quantities involved, no effort was made to recover the hydrides.

Hydrides were identified on the basis of their characteristic carbonyl stretching bands. In some cases the carbonyl bands of the bimetallic complex overlap with or partially obscure the lower energy bands of the hydride. IR spectra of authentic samples of the metal hydrides were recorded in petroleum ether: (η^5-C_5H_5)Fe(CO)$_2$H, 2024, 1968 cm^{-1}; (η^5-C_5H_5)Ru(CO)$_2$H, 2032, 1973 cm^{-1}; (η^5-$C_5H_4CH_3$)Mo(CO)$_3$H, 2028, 1945 cm^{-1}; (η^5-$C_5H_4CH_3$)W(CO)$_3$H, 2032, 1940 cm^{-1}.

Acknowledgment. T.E.B. thanks Research Corporation for a Research Opportunity Grant that permitted the purchase of the FTIR and high-pressure equipment used in this research.

OM000292C

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