Journal of Organometallic Chemistry, 134 (1977) C27—C31

Preliminary communication

Photoinduced Elimination of H_2 from $[Mo(\eta^5-C_5H_5)_2H_2]$. Generation of Molybdenocene.

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(Received February 28th, 1977)

Summary: Ultraviolet irradiation of deaerated solutions of $[Mo(\eta^5-C_5H_5)_2H_2]$ results in elimination of H_2 and generation of $[Mo(\eta^5-C_5H_5)_2]$. The transient molybdenocene can be trapped with substrates such as CO, C_2H_2, and PR_3 to yield stable adducts, but in the absence of substrate, oligomerization to the previously described $[Mo(\eta^5-C_5H_5)_2]_x$ occurs.

In a series of three communications, M. L. H. Green and coworkers reported that photolysis of $[W(\eta^5-C_5H_5)_2H_2]$ leads to apparent elimination of H_2 and generation of $[W(\eta^5-C_5H_5)_2]$.[1-3] Products isolated from the reactions are those resulting from insertion of the reactive tungstenocene into C-H bonds of solvent molecules. In our previous investigations[4,5] into the photochemical properties of metal hydride complexes, we have shown that photoinduced elimination of H_2 is a common photoprocess for dihydride complexes of iridium and ruthenium. We believe that this may be a general photoreaction for polyhydrides of all the transition elements and are now exploring its utility for generating otherwise unattainable, extremely reactive transition metal complexes. Accordingly, we have examined $[Mo(\eta^5-C_5H_5)_2H_2]$, and like the previous studies[1-3] of $[W(\eta^5-C_5H_5)_2H_2]$, find that photoinduced elimination

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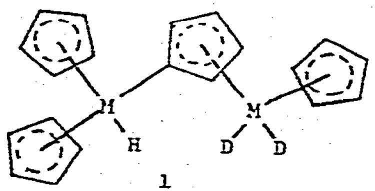
of H_2 occurs. Photolysis provides a convenient method for generating molybdenocene which can be readily trapped with added substrate. Unlike tungstenocene, however, solvent insertion does not occur.

Irradiation of a thoroughly degassed isooctane solution of $[Mo(\eta^5-C_5H_5)_2H_2]$ with 366 nm results in a rapid color change from yellow to brown, and a red-brown precipitate is obtained after prolonged photolysis. Accompanying the irradiation is a smooth decrease in intensity of the characteristic ν_{M-H} of $[Mo(\eta^5-C_5H_5)_2H_2]$ at 1847 cm^{-1}, and no new vibrations appear in the ν_{M-H} region. The ^1H NMR spectrum of the red-brown precipitate and its color suggest its identity as the "polymeric" $[Mo(\eta^5-C_5H_5)_2]_x$ species previously described by Thomas.[6,7] Mass spectral analysis of the gases above irradiated d_8-toluene solutions showed the presence of a considerable amount of H_2 but with little HD (<10%) present. Since toluene is an efficient hydrogen atom scavenger, the lack of a significant amount of HD indicates that free hydrogen atoms are not produced in the photolysis, and an intramolecular elimination process is suggested. Irradiation of $[Mo(\eta^5-C_5H_5)_2D_2]$ in C_6D_6, C_6H_6, or C_6D_6 solutions containing excess PPh_3 (see later) gave D_2/HD mixtures in an approximate 3/2 ratio. Since the toluene solution experiments showed that free hydrogen atoms are apparently not produced, and since heterolytic cleavage of a Mo-H bond is considered unlikely, the substantial production of D_2 must arise from concerted elimination of D_2 which generates molybdenocene, eq. 1.

$$[Mo(\eta^5-C_5H_5)_2D_2] \xrightarrow{h\nu} [Mo(\eta^5-C_5H_5)_2] + D_2 \qquad (1)$$

Such concerted elimination has been shown to be the mechanism by which photoinduced loss of H_2 occurs from $[IrClH_2(PPh_3)_3]$.[4] The HD presumably comes from secondary thermal reactions of photogenerated $[Mo(\eta^5-C_5H_5)_2]$ with unreacted $[Mo(\eta^5-C_5H_5)_2D_2]$. These reactions could give dimeric intermediates containing $\eta^1,\eta^5-C_5H_5$ rings (e.g., 1),



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which then could lose HD, eventually giving dimeric products similar to those described recently by Green and coworkers.[8] In contrast to $[W(\eta^5\text{-}C_5H_5)_2H_2]$, photolysis of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ in aromatic solvents produces no products arising from C-H insertion, and only the "polymeric" material is observed.

Further evidence for the initial generation of molybdenocene, eq. 1, comes from trapping experiments. Irradiation under a carbon monoxide or an acetylene purge, for example, leads to near quantitative formation of the previously characterized $[Mo(\eta^5\text{-}C_5H_5)_2CO]$[7] and $[Mo(\eta^5\text{-}C_5H_5)_2(C_2H_2)]$ adducts.[9] These can be separated and purified by fractional sublimation and have been identified by their infrared, NMR, and mass spectra.

Irradiation of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ in the presence of excess PPh_3 or PEt_3 leads to formation of the new tertiary phosphine adducts $[Mo(\eta^5\text{-}C_5H_5)_2PR_3]$. The electronic absorption spectral changes obtained when a 1.1×10^{-4} M hexane solution of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ is irradiated with 366 nm in the presence of excess PPh_3 are shown in Figure 1, and the isosbestic points at 285 and 270 nm (not shown) suggest a clean conversion. The phosphine adducts can be isolated from the photolysis mixture by fractional sublimation. $[Mo(\eta^5\text{-}C_5H_5)_2PPh_3]$ and $[Mo(\eta^5\text{-}C_5H_5)_2PEt_3]$ sublime at 90°C and 80°C (10^{-3} mm Hg), respectively, whereas unreacted $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ sublimes at 50-60°C. The PPh_3 adduct so obtained often contains small quantities of PPh_3 impurity, but the PEt_3 adduct can be isolated pure. Both adducts have been characterized by their

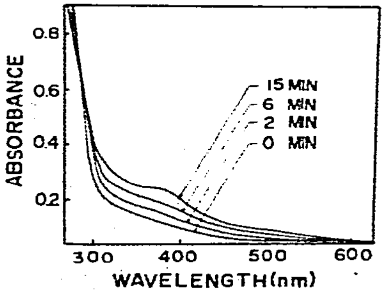

Figure 1. Electronic absorption spectral changes obtained during 366 nm irradiation of a 1.1×10^{-4} M hexane solution of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ and excess PPh_3.

NMR, infrared, and mass spectra. $[Mo(\eta^5-C_5H_5)_2PEt_3]$, for example, shows a doublet at 6.17 τ (J_{P-H} = 5Hz) in its ^1H NMR spectrum due to the $\eta^5-C_5H_5$ protons and a singlet at 34.9 ppm[10] in its ^{31}P NMR spectrum due to coordinated PEt_3. $[Mo(\eta^5-C_5H_5)_2PPh_3]$ shows corresponding resonances at 6.18 τ (J_{P-H} = 4Hz) and 18.9 ppm.

The phosphine complexes provide a thermal route to other molybdenocene adducts since the molybdenum-phosphorous bond appears to be quite labile. When solutions of $[Mo(\eta^5-C_5H_5)_2PEt_3]$ are allowed to react with CO or diphenylacetylene, formation of the corresponding adduct results, eq. 2.

$$[Mo(\eta^5-C_5H_5)_2PR_3] + L \xrightarrow{27°C} [Mo(\eta^5-C_5H_5)_2L] + PR_3 \qquad (2)$$

The quantum yield for elimination of H_2 from $[Mo(\eta^5-C_5H_5)_2H_2]$, measured at 366 nm in hexane solution in a degassed and sealed spectrophotometer cell, is 0.1. This value must be treated as a lower limit, however, since back reaction of H_2 with photogenerated molybdenocene was not prevented. This compares with a value of 0.01 which we obtained for elimination of H_2 from $[W(\eta^5-C_5H_5)_2H_2]$ under similar photolysis conditions.

Acknowledgement. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society and the National Science Foundation (Grant MPS-7505909) for support of this research.

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