pounds studied, the degree of correlation between the first reduction potential of the ligand and that of the metal complex is impressive.

Acknowledgment. We thank the U.S. Department of Energy (DE-AC02-80ER10589) for support of this work. We are also indebted to Professors W. N. White and A. K. Rappé for helpful discussions.

Registry No. 2, 1134-35-6; **3**, 6813-38-3; **4**, 1762-42-1; **5**, 83605-42-9; **6**, 1762-34-1; **7**, 1802-30-8; **8**, 1762-46-5; **9**, 83605-43-0; **10**, 67994-94-9; **11**, 60804-74-2; **12**, 83605-44-1; **13**, 83605-45-2; **14**, 75324-94-6; **15**, 83605-47-4; **16**, 83605-48-5; **17**, 64189-98-6; **18**, 83605-49-6; **19**, 83605-83-8; $Ru(Bp5COOEt)_3^{3-}$, 83605-50-9; $Ru(Bp5COOEt)_3^{4-}$, 83605-51-0; $Ru(Bp4Me)_3^{3+}$, 47837-95-6; $Ru(Bp4Me)_3^{+}$, 65605-26-7; $Ru(Bp4Me)_3$, 83605-52-1; $Ru(Bp4Me)_3^{-}$, 83605-53-2; $Ru(Bp5Me)_3^{3+}$, 47837-83-2; Bpy, 37275-48-2; $Ru(Bp5Me)_3^{+}$, 83605-54-3; $Ru(Bp5Me)_3$, 83605-55-4; $Ru(Bp5Me)_3^{-}$, 83605-56-5; $Ru(Bp4CONEt_2)_3^{3+}$, 83615-44-5; 4,4′-diMediquat, 16651-71-1; $Ru(Bp4CONEt_2)_3^{+}$, 83605-57-6; $Ru(Bp4CONEt_2)_3$, 83605-58-7; $Ru(Bp4CONEt_2)_3^{-}$, 83605-59-8; $Ru((bpy)_2Bp4COOEt)^{3+}$, 83605-60-1; $Ru((bpy)_2Bp4COOEt)^{+}$, 83605-61-2; $Ru((bpy)_2Bp4COOEt)$, 83605-62-3; $Ru((bpy)_2Bp4COOEt)^{-}$, 83605-63-4; $Ru((bpy)_2Bp4COOEt)^{2-}$, 83605-64-5; $Fe(Bp4COOEt)_3^{3+}$, 83605-65-6; $Fe(Bp4COOEt)_3^{+}$, 83605-66-7; $Fe(Bp4COOEt)_3$, 83605-67-8; $Fe(Bp4COOEt)_3^{-}$, 83605-68-9; $Fe(Bp4COOEt)_3^{2-}$, 83605-69-0; $Fe(Bp4COOEt)_3^{3-}$, 83605-70-3; $Fe(Bp4COOEt)_3^{4-}$, 83605-71-4; $Ru(bpy)_3^{3+}$, 18955-01-6; $Ru(bpy)_3^{+}$, 56977-24-3; $Ru(bpy)_3$, 74391-32-5; $Ru(bpy)_3^{-}$, 56977-23-2; $Ru(Bp4COOEt)_3^{3+}$, 83605-72-5; $Ru(Bp4COOEt)_3^{+}$, 83605-73-6; $Ru(Bp4COOEt)_3$, 83605-74-7; $Ru(Bp4COOEt)_3^{-}$, 83605-75-8; $Ru(Bp4COOEt)_3^{2-}$, 83605-76-9; $Ru(Bp4COOEt)_3^{3-}$, 83605-77-0; $Ru(Bp4COOEt)_3^{4-}$, 83605-78-1; $Ru(Bp5COOEt)_3^{3+}$, 83615-45-6; $Ru(Bp5COOEt)_3^{+}$, 79374-05-3; $Ru(B5COOEt)_3$, 83605-79-2; $Ru(Bp5COOEt)_3^{-}$, 83605-80-5; $Ru(Bp5COOEt)_3^{2-}$, 83605-81-6; 5,5′-diMediquat, 16651-72-2; diethylamine, 109-89-7; 3-picoline, 108-99-6; 4-picoline, 108-89-4.

Photophysical and Photochemical Behavior of Tetrahydridobis(bis(1,2-diphenylphosphino)ethane)molybdenum and -tungsten: Optical Emission and Photoreduction of Alkenes

James L. Graff,[1a] Ted J. Sobieralski, Mark S. Wrighton,*[1a] and Gregory L. Geoffroy[1b]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and the Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802. *Received March 23, 1982*

Abstract: The complexes $H_4M(DPPE)_2$ and $D_4M(DPPE)_2$ (M = Mo, W; DPPE = bis(1,2-diphenylphosphino)ethane) exhibit emission of visible light upon photoexcitation at 77 K in 2-methyltetrahydrofuran. The emission lifetime at 77 K for the W species ($\sim$13 μs) is shorter than for the Mo species ($\sim$90 μs) and is independent of whether the substance is the ^1H or ^2H species. The shorter lifetime for the W species is consistent with an emissive triplet state that is antibonding with respect to $M-H_2$ interactions, since the solution photochemistry at 298 K is dominated by H_2 loss. While the lifetime of the ^1H and ^2H species is the same, the quantum yield for emission for M = Mo is higher for the ^2H species (0.28) than for the ^1H species (0.21). The data are consistent with an effect from ^2H that diminishes nonradiative decay from the singlet excited state reached by direct absorption. This diminished nonradiative decay allows intersystem crossing to be more competitive, yielding the emissive triplet with higher efficiency. Irradiation of the $H_4M(DPPE)_2$ species in the presence of an alkene (e.g., 1-pentene, *cis*-2-pentene, 3,3-dimethyl-1-pentene, cyclopentene) results in stoichiometric reduction to form an alkane; i.e., each $H_4M(DPPE)_2$ molecule yields two molecules of alkane. Irradiation of $H_4M(DPPE)_2$ in the presence of alkene and 10 psi of H_2 yields photoassisted alkane formation, yielding many alkane molecules per $H_4M(DPPE)_2$ initially present, as illustrated with the reduction of 1-pentene. The intriguing finding concerning the photoreduction of 1-pentene or *cis*-2-pentene is that the reduction occurs without detectable isomerization to *cis*- and *trans*-2-pentene or 1- and *trans*-2-pentene, respectively, an unprecedented result for such photoassisted alkene reactions using polyhydride precursors.

While studying the photophysical properties of $H_4Re_4(CO)_{12}$,[2] we discovered that $H_4W(DPPE)_2$ (DPPE = bis(1,2-diphenylphosphino)ethane) and $H_4Mo(DPPE)_2$ exhibit visible light emission when excited by ultraviolet or high-energy visible light. This afforded us an opportunity to further examine the effect of replacing ^1H with ^2H on the excited-state decay properties of transition-metal hydride complexes. As in earlier studies of hydrogen isotope effects on the excited-state decay of organic molecules and inorganic complexes,[2-4] the importance of these studies rests in the fact that replacement of ^1H by ^2H results in little change in the electronic structure or geometry of the molecules while the vibrational energies are altered significantly. Thus, the importance of high-energy vibrations on the rates of nonradiative excited-state decay can be probed by replacing ^1H with ^2H.

Often, the highest energy vibrations are found to be important in nonradiative decay, but for metal complexes where the excited

---

[1] (a) Massachusetts Institute of Technology. (b) Pennsylvania State University.

[2] Graff, J. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 2225.

[3] (a) Siebrant, W. *J. Chem. Phys.* **1967**, *47*, 2411. (b) Turro, N. J. "Molecular Photochemistry"; W. A. Benjamin: New York, 1967.

[4] (a) Petersen, J. D.; Watts, R. J.; Ford, P. C. *J. Am. Chem. Soc.* **1976**, *98*, 3188. (b) Bergkamp, M. A.; Brannon, J.; Magde, D.; Watts, R. J.; Ford, P. C. *Ibid.* **1979**, *101*, 4549. (c) Van Houten, J.; Watts, R. J. *Ibid.* **1975**, *97*, 3843. (d) Bergkamp, M. A.; Watts, R. J.; Ford, P. C.; Brannon, J.; Magde, D. *Chem. Phys. Lett.* **1978**, *59*, 125. (e) Kane-Maguire, N. A. P.; Kerr, R. C.; Walters. J. R. *Inorg. Chim. Acta* **1979**, *33*, L163. (f) Kane-Maguire, N. A. P.; Clonts, G. M.; Kerr, R. C. *Ibid.* **1980**, *44*, L157.

0002-7863/82/1504-7526$01.25/0

states can be regarded as "metal centered", the intraligand vibrations may not be crucial despite being the highest energy vibrations in the complexes. Rather, metal–ligand vibrations may be crucial in determining nonradiative decay rates for metal-centered excited states and of these vibrations the highest energy stretching modes might be the most critical. For $H_4M(DPPE)_2$ (M = Mo, W), the metal–hydrogen stretch is clearly the highest energy metal–ligand stretch. Of particular interest is the fact that the ^1H in $H_4M(DPPE)_2$ are terminal hydrides (ν_{Mo-H} = 1745 cm^{-1}; ν_{W-H} = 1770 cm^{-1}), whereas the ^1H in the previously studied $H_4Re_4(CO)_{12}$ and $[H_6Re_4(CO)_{12}]^{2-}$ are bridging hydrides ($\nu_{Re-H} \approx 1000$ cm^{-1}).[2,5] The structure of $H_4M(DPPE)_2$ has not been reported but is believed to be structurally similar to $H_4Mo(PPh_3Me)_4$ with the P donors and H atoms comprising interpenetrating tetrahedra.[6] The higher frequency ν_{M-H} stretch in the $H_4M(DPPE)_2$ complexes suggests the possibility of larger isotope effects on the excited-state decay properties being observed for the $H_4M(DPPE)_2$ complexes than for the $[H_6Re_4(CO)_{12}]^{2-}$ and $H_4Re_4(CO)_{12}$ complexes previously studied.[2]

For both $H_4Mo(DPPE)_2$ and $H_4W(DPPE)_2$ the emission establishes the energy and lifetime of the lowest energy, emissive excited state. These properties are important in understanding the nature of the excited state and the photochemistry of these systems. The only other transition-metal hydrides that are known to be emissive are $H_4Re_4(CO)_{12}$ and $[H_6Re_4(CO)_{12}]^{2-}$ where replacing ^1H with ^2H does significantly lower the rate of nonradiative decay.[2] Comparing the excited-state properties of $H_4W(DPPE)_2$ to $H_4Mo(DPPE)_2$ allows, additionally, an assessment of spin–orbit coupling effects on the excited-state properties of these species, since the heavier W would be expected to have larger spin–orbit coupling perturbation. Spin–orbit coupling effects on excited-state properties have been studied with many inorganic species including Ru(II), Os(II), Rh(III), and Ir(III) complexes.[7] In all cases either isotope studies or spin–orbit coupling studies on excited-state properties of luminescent complexes have been contributory to an understanding of the nature of the excited state.

Transition-metal hydrides have a rich photochemistry,[8] and though their use as catalyst precursors in photocatalytic reactions has been suggested often, few such studies have been done.[8d-h] We note especially the exciting result recently reported concerning the oxidative addition of alkanes to Ir(I) generated by photoinduced extrusion of H_2 from $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)H_2$.[8i] The room-temperature solution photochemistry of $H_4M(DPPE)_2$ involves the generation of a very reactive species from the photoinduced loss of H_2.[9] In light of our previous photocatalytic studies with $H_4Ru_4(CO)_{12}$[8d] and $H_2Os_3(CO)_{10}$,[8e] the reactive species generated via photolysis of $H_4M(DPPE)_2$ may serve as an active catalyst for olefin reactions.

Experimental Section

Materials. All solvents were reagent grade and were distilled under Ar from either CaH_2 or sodium benzophenone ketyl. The WCl_6 and $MoCl_5$, obtained from Alfa-Ventron, and the bis(1,2-diphenylphosphino)ethane (DPPE), obtained from Strem Chemicals, Inc., were used as received. The hydrogen (99.95%) and deuterium (99.5 atom % min) were obtained from Matheson and used as received. The methanol (absolute) and methanol-d_1 (Stohler Isotope Chemicals) were used as received. The 2-methyltetrahydrofuran was obtained from Aldrich Chemical Co. and passed through Al_2O_3, distilled under Ar from CaH_2, and again passed through Al_2O_3 prior to use. The $W(N_2)_2(DPPE)_2$ and $Mo(N_2)_2(DPPE)_2$ were prepared by known literature methods[10] and characterized by standard spectroscopic techniques.

Instrumentation. All vapor-phase chromatography was done with the use of Varian Series 1440 or 2440 gas chromatographs equipped with flame ionization detectors and a Hewlett-Packard 3380S integrator. Separations of the olefins and the corresponding alkanes from photoreduction were accomplished with a 30 ft × $^1/_8$ in. column of 20% propylene carbonate on Chromosorb P at 25 °C. All infrared spectra were recorded as KBr pellets or in matched path length (0.1 mm or 1.0 mm) NaCl solution cells with the use of a Perkin-Elmer Model 180 grating infrared spectrophotometer. Mass spectra were obtained with the use of a Varian MAT 122 mass spectrometer. High-resolution ^{13}C NMR spectra were obtained on the Bruker Model WM270 NMR spectrometer. High-resolution ^1H and ^2H NMR spectra were obtained on the Bruker Model WM250 NMR spectrometer. Since a deuterium probe was not readily available, ^2H NMR spectra were taken through the deuterium lock probe. The magnetic field was first shimmed with the ^2H lock probe as usual. Cables were then switched such that data was collected in an unlocked mode by pulsing through the deuterium lock probe.

Preparation of $H_4Mo(DPPE)_2$ and $D_4Mo(DPPE)_2$.[11] A stirred solution of 1.0 g of $Mo(N_2)_2(DPPE)_2$ in 250 mL of dry benzene was purged with H_2 for 20 min and then kept under 1 atm of H_2. After about 12 h the reaction mixture had gone from orange to golden yellow. The reaction mixture was filtered and reduced in volume. The $H_4Mo(DPPE)_2$ was precipitated from the reaction mixture by the slow addition of methanol. The yellow solid was filtered, recrystallized from benzene, and dried in vacuo for 4 h. The corresponding deuteride was prepared in an analogous manner with the use of D_2 in place of H_2 and MeOD in place of MeOH. The isotopic purity of $D_4Mo(DPPE)_2$ is >80% ^2H by infrared and mass spectral measurements. $H_4Mo(DPPE)_2$: ^1H NMR (C_6D_6) τ 13.65 quintet) and the resonances for the DPPE ligand; IR (KBr pellet) ν_{Mo-H} 1745 cm^{-1}; UV–Vis (2-methyltetrahydrofuran, 298 K) 380 nm (5000 M^{-1} cm^{-1}); cf. Figure 2. $D_4Mo(DPPE)_2$: IR (KBr pellet) ν_{Mo-D} 1250 cm^{-1}; UV–Vis (2-methyltetrahydrofuran, 298 K) 380 nm (5000 M^{-1} cm^{-1}).

Preparation of $H_4W(DPPE)_2$ and $D_4W(DPPE)_2$. A stirred solution of 1.0 g of $W(N_2)_2(DPPE)_2$ in 250 mL of dry benzene was purged with H_2 for 20 min and then kept under an atmosphere of H_2. The reaction mixture was heated to 55 °C for 36 h and by this time the orange solution had become yellow. After the reaction mixture was filtered and reduced in volume, $H_4W(DPPE)_2$ was precipitated by the slow addition of methanol. The yellow solid was filtered, recrystallized from benzene, and dried under vacuum for 4 h. The corresponding deuteride was prepared in an analogous manner with the use of D_2 in place of H_2 and MeOD in place of MeOH. The isotopic purity of $D_4W(DPPE)_2$ is >80% ^2H by infrared and mass spectral measurements. $H_4W(DPPE)_2$: ^1H NMR (C_6D_6) τ 13.65 (quintet) and the resonances corresponding to the DPPE ligand; IR (KBr pellet) ν_{W-H} 1770 cm^{-1}; UV–Vis (2-methyltetrahydrofuran, 298 K) 390 nm (5500 M^{-1} cm^{-1}); cf. Figure 3. $D_4W(DPPE)_2$: IR (KBr pellet) ν_{W-D} 1275 cm^{-1}; UV–Vis (2-methyltetrahydrofuran, 298 K) 390 nm (5000 M^{-1} cm^{-1}).

Emission Spectra and Quantum Yields. All emission spectra were recorded with the use of a Perkin-Elmer MPF-44 fluorescence spectrophotometer equipped with a Perkin-Elmer Model 150 xenon power supply and a Hamamatsu HR777 PMT detector. The relative sensitivity of the entire detection system and the PMT has been calibrated from 300 to 900 nm with the use of a standard lamp obtained from and calibrated by E, G, &G, Inc., Salem, MA. The standard lamp is a 200-W tungsten halogen lamp operated at 6.50 A (serial no. B115A) and calibrated from NBS standards Qm 197, Qm 198, Qm 199. All emission samples were placed in Pyrex tubes. The emission quantum yields of the complexes at 77 K were determined relative to rhodamine B (Φ = 0.69)[12] in ethanol by the following procedure. The absorbance of the complex whose quantum yield is to be measured is set equal to that of rhodamine B in ethanol (OD <0.10 in 1.00-cm path length cell) at 390 nm. The emission spectra of the complex and the standard were recorded exciting at 390 nm. The relative emission quantum yield of the complex is the integrated area under the corrected emission spectrum divided by that for the rhodamine B standard, after correction for differences in the index of refraction of the solvents.[13]

---

(5) (a) Kaesz, H. D.; Fontal, B.; Bau, R.; Kirtley, S. W.; Churchill, M. R. *J. Am. Chem. Soc.* **1969**, *91*, 1021. (b) Wilson, R. D.; Bau, R. *Ibid.* **1976**, *98*, 4687. (c) Lewis, J.; Johnson, B. F. G. *Gazz. Chim. Ital.* **1979**, *109*, 271.

(6) Meakin, P.; Guggenheimer, L. J.; Peet, W. G.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 1467.

(7) (a) Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 2841. (b) DeArmond, M. K.; Hillis, J. E. *J. Chem. Phys.* **1971**, *54*, 2247.

(8) (a) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979. (b) Geoffroy, G. L.; Bradley, M. G.; Pierantozzi, R. *Adv. Chem. Ser.* **1978**, *No. 167*, 181. (c) Geoffroy, G. L. *Prog. Inorg. Chem.* **1980**, *27*, 123. (d) Graff, J. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 2123. (e) Graff, J. L.; Wrigton, M. S. *Inorg. Chim. Acta*, in press. Wrighton, M. S.; Graff, J. L.; Kazlauskas, R. J.; Mitchener, J. C.; Reichel, C. L. *Pure Appl. Chem.* **1982**, *54*, 161. (f) Strohmeier, W. *J. Organomet. Chem.* **1973**, *60*, C60. (g) Strohmeier, W.; Csontos, G. *Ibid.* **1974**, *67*, C27. (h) Camus, A.; Cocevar, C.; Mestroni, G. *Ibid.* **1972**, *39*, 355. (i) Janowicz. A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352.

(9) (a) Pierantozzi, R.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 1821. (b) Pivovarov, A. P.; Gak, Y. V.; Doronina, T. N.; Makhaev, V. D.; Borisov, A. P.; Borod'ko, Y. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 1207.

(10) George, T. A.; Noble, M. E. *Inorg. Chem.* **1978**, *17*, 1678.

(11) (a) Aresta, M.; Sacco, A. *Gazz. Chim. Ital.* **1972**, *102*, 755. (b) Archer, L. J.; George, T. A. *J. Organomet. Chem.* **1973**, *54*, C25.

(12) Parker, C. A.; Rees, W. T. *Analyst (London)* **1960**, *85*, 587.

Emission Lifetimes. The emission lifetimes, τ, were measured with the use of a TRW Model 75A decay time fluorometer having a Hamamatsu R446UR PMT detector powered by a Kepco Model 2500 ABC regulated high-voltage supply. A Xenon Corp. nanopulser excitation source was used to excite the samples. Output from the PMT was monitored by a Tektronix 564B oscilloscope (type 2A63 differential amplifier and type 2B67 time base) and recorded with a Polaroid camera. Plots of log (emission intensity) vs. time were linear in every case over at least two lifetimes. The value of τ is taken as the time required for the emission intensity to decay to $1/e$ of its original intensity.

Absorption and Excitation Spectra. All UV–vis absorption spectra were recorded with the use of a Cary 17 and low-temperature spectra were obtained with an all quartz liquid N_2 Dewar equipped with optical quartz flats for windows. Excitation spectra were recorded with the use of a Perkin-Elmer MPF-44 fluorescence spectrophotometer equipped with a Hamamatsu HR77 PMT detector and a Perkin-Elmer Model 150 xenon power supply. The lamp output was calibrated with a rhodamine B quantum counter or internally by placing total white reflectance coating in the sample chamber, scanning the excitation and emission wavelengths simultaneously, and correcting for the PMT sensitivity throughout the wavelength region scanned.

Stoichiometric Photoreduction of Olefins. A toluene solution 10^{-3} M in $H_4M(DPPE)_2$ (M = Mo, W), 0.1 M in olefin, and 7×10^{-3} M in the internal standard, *n*-hexane, was prepared. Aliquots (1 mL) of this solution and 2×7 mm magnetic stir bars were placed into Pyrex test tubes (13×100 mm) with constrictions and degassed by five freeze–pump–thaw cycles, sealing hermetically. The stirred samples were irradiated with a 355-nm (width at half height is ~15 nm) light source (two 15-W General Electric blacklight bulbs). Thermal controls (foil-wrapped ampules containing the catalysis solutions) were placed side by side with the photolyzed samples during the reaction, and all samples were air-cooled, ensuring they remained at room temperature. Light intensities of 1.2×10^{-6} einstein/min were determined by ferrioxalate actinometry.[14] The solutions were analyzed by VPC following the photochemical or thermal reaction.

Photocatalyzed Olefin Hydrogenation Procedure. A toluene solution consisting of 10^{-3} M $H_4M(DPPE)_2$, the appropriate concentration (0.1–5.0 M) of olefin and the appropriate concentration of internal standard, *n*-hexane, was prepared. Aliquots (3 mL or 8 mL) and magnetic stir bars were placed into either demountable Pyrex reaction tubes (12-mm diameter), each equipped with a Teflon valve, or a 1×4 in. Kimax pressure reaction bottle attached to a stainless steel bombhead. The samples were degassed by five freeze–pump–thaw cycles. The reaction tubes were transferred to a gas manifold which was evacuated and backfilled with H_2 5 times. The appropriate pressure (10–50 psi) of H_2 was introduced to the reaction tube and allowed to saturate the solution. The solution was stirred and irradiated with a 355-nm (width at half-height is 15 nm) light source (two 15-W General Electric blacklight bulbs). The samples were analyzed by VPC following the reaction. The appropriate thermal controls showed little or no reaction on the same time scale as the photoreactions.

Photoreaction of $H_4Mo(DPPE)_2$ with Ethylene. $H_4Mo(DPPE)_2$ (300 mg) was placed into 200 mL of dry toluene, and the solution was purged with C_2H_4 for 30 min to remove air. The yellow, stirred solution was kept under 2 psi of C_2H_4 pressure and irradiated at 355 nm for 36 h. After irradiation the orange reaction mixture was concentrated by evaporation of solvent under vacuum at 25 °C and ~150 mL of reagent MeOH (purged with Ar for 30 min) was added via cannula. The solution was concentrated again at 25 °C, yielding an orange precipitate which was recrystallized from toluene/MeOH to give $(C_2H_4)_2Mo(DPPE)_2$ as established by ^1H NMR compared to material independently synthesized via the procedure used in ref 24.

Photoreaction of $H_4Mo(DPPE)_2$ with Propene. The procedure used in this photoreaction is identical with that for photoreaction with C_2H_4 described above except the irradiation was stopped after 18 h. The only Mo-containing product detected was the orange $(C_3H_6)Mo(DPPE)_2/(\eta^3\text{-}C_3H_5)HMo(DPPE)_2$. The ^1H NMR spectra in C_6D_6 at 32 °C and at 5 °C are the same as reported in ref 24 for these species.

Results and Discussion

Optical Emission and Absorption Behavior. The $H_4Mo(DPPE)_2$ and $D_4Mo(DPPE)_2$ complexes are emissive as solids or in organic glasses at 77 K. Figure 1 shows the corrected emission spectra recorded for the ^1H and ^2H complexes in 2-methyltetrahydrofuran at 77 K. As shown, the emission spectra are the same for the ^1H and ^2H species, a broad structureless peak with a maximum at 17 300 cm^{-1}. However, the emission quantum efficiency for the ^2H species is larger than that for the ^1H species. Quantitative emission data are collected in Table I. The absorption spectra of $H_4Mo(DPPE)_2$ at 298 and 77 K in 2-methyltetrahydrofuran solvent are shown in Figure 2. The onset of the band at 380 nm (~26 000 cm^{-1}) overlaps the onset of the emission and suggests

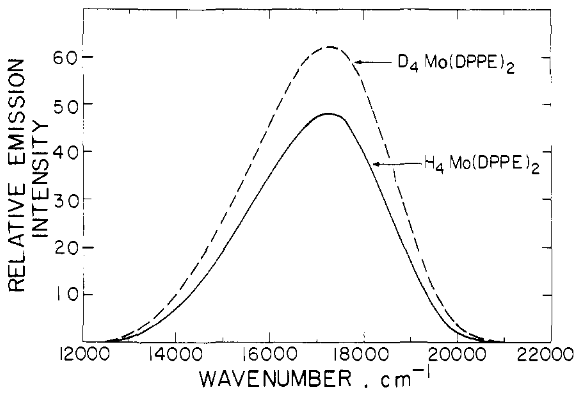


Figure 1. Corrected emission spectral distribution for $H_4Mo(DPPE)_2$ (–) and $D_4Mo(DPPE)_2$ (- -) in 2-methyltetrahydrofuran at 77 K. The excitation wavelength is 390 nm. See Table I for quantum yields.

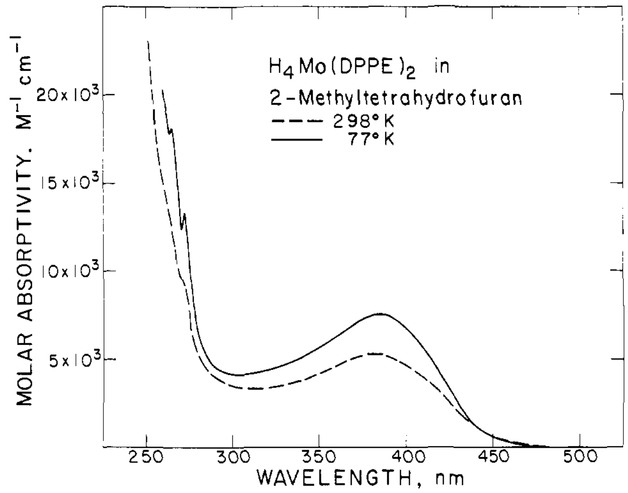


Figure 2. Electronic absorption spectra at 298 K (- -) at 77 K (–) in 2-methyltetrahydrofuran for $H_4Mo(DPPE)_2$. The spectral changes upon cooling have not been corrected for solvent contraction.

Table I. Emission Properties of Molybdenum and Tungsten Hydride Complexes[a]

complex	solvent T, K	Em Max, $\Delta\nu_{1/2}$ cm^{-1} ± 100 cm^{-1}	 cm^{-1} ± 100 cm^{-1} [b]	Φ^c ± 10%	τ, μs ± 10%
$H_4Mo(DPPE)_2$	pure solid 77	17 800	3000		99
	2-MeTHF 77	17 300	3400	0.21	87
$D_4Mo(DPPE)_2$	pure solid 77	17 800	2900		97
	2-MeTHF 77	17 300	3500	0.28	91
$H_4W(DPPE)_2$	pure solid 298	17 000	3800		<0.5
	77	17 900	2800		12
	2-MeTHF 77	16 900	3600	0.12	13
$D_4W(DPPE)_2$	pure solid 298	17 000	4000		<0.5
	77	17 900	2800		12
	2-MeTHF 77	16 900	3700	0.12	13

[a] All emission data shown are for 390-nm excitation; emission spectra and efficiency are independent of excitation wavelength. All emission data are corrected for variation in detector response. [b] Full width at half-height of emission band. [c] Quantum yield for emission relative to thodamine B (Φ = 0.69 in EtOH).[12] Error limit is on the absolute value of Φ. Relative $^1H/^2H$ quantum yield values have lower error, ±2%.

---

(13) Demas, J. .; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

(14) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

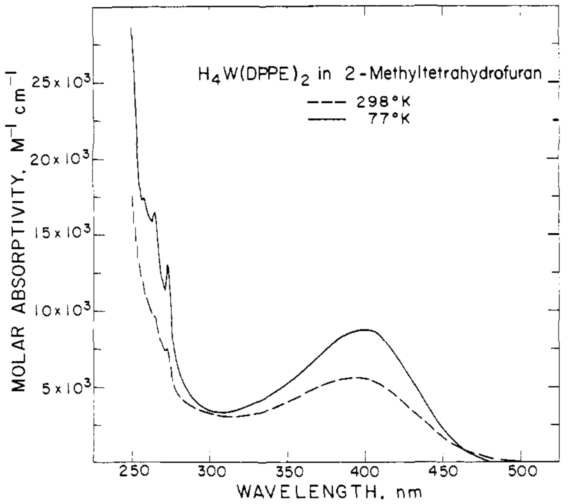


Figure 3. Electronic absorption spectra at 298 K (- -) and 77 K (–) in 2-methyltetrahydrofuran for $H_4W(DPPE)_2$. The spectral changes upon cooling have not been corrected for solvent contraction.

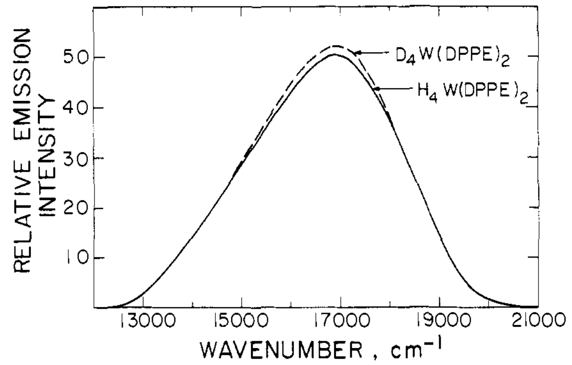
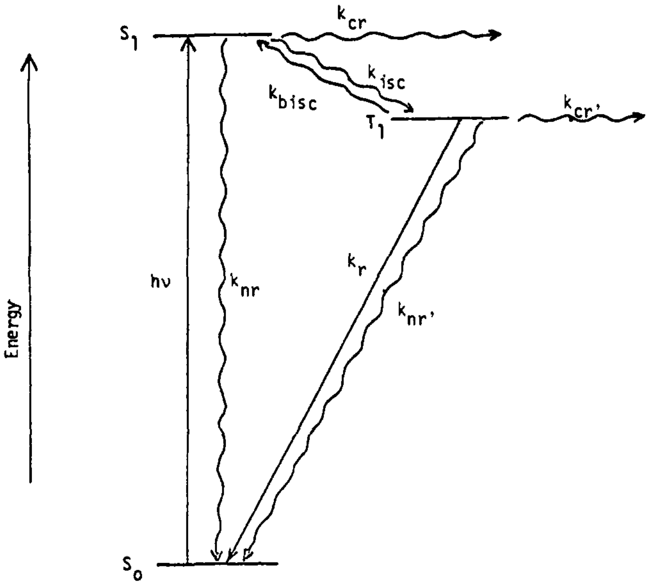


Figure 4. Corrected emission spectral distribution for $H_4W(DPPE)_2$ (–) and $D_4W(DPPE)_2$ (- -) in 2-methyltetrahydrofuran at 77 K. The excitation wavelength is 390 nm. See Table I for quantum yields.

that the 380-nm absorption corresponds to the photoexcitation of the ground state to produce the emissive state, but data to be developed below are most consistent with the production of a nonemissive singlet excited state that intersystem crosses to an emissive triplet. In the overlap region of absorption and emission, direct population of the triplet might be possible but quantitative experiments have not been performed. The spectral distribution of emitted light is independent of excitation wavelength, and the absorption spectrum in 2-methyltetrahydrofuran and the excitation spectrum of the emission (for $\lambda > 300$ nm) are the same when the optical density of the solution is <0.1. These data show that the emission quantum yield is independent of excitation wavelength, consistent with emission originating from the lowest excited state that is reached with equal efficiency at all exciting wavelengths. The data in Table I show that the lifetime, emission maximum, and emission width are all slightly sensitive to the medium and temperature. Note that only the emission quantum yield increases upon substitution of ^1H with ^2H; the excited-state lifetime remains unchanged. The $H_4Mo(DPPE)_2$ complex does not appear to be photoreactive upon visible or ultraviolet light excitation as a solid or in a solution at 77 K.

Emission is observed from $H_4W(DPPE)_2$ at 77 K as a solid or in an organic glass and at 298 K as a solid only. The absorption spectrum, Figure 3, and emission spectrum, Figure 4, of $H_4W(DPPE)_2$ are similar to those observed for $H_4Mo(DPPE)_2$ and have an absorption maximum at 390 nm and an emission maximum at 16 900 cm⁻¹. The onset of the absorption band at 390 nm (~25 500 cm⁻¹) overlaps the onset of emission, and the state produced in absorption is presumably a singlet as in the Mo species. The emission spectral distribution and emission quantum yield of $H_4W(DPPE)_2$ are independent of the excitation wavelength (for $\lambda > 300$ nm), consistent with emission from the lowest excited state that is achieved with equal efficiency at all exciting wavelengths. As shown in Figure 4 and by the data in Table I, there is little or no isotope effect on the excited-state properties of $H_4W(DPPE)_2$; i.e., the ^1H and ^2H species have essentially identical emission quantum yields and excited-state lifetimes. Note that the emission quantum yields and the excited-state lifetimes of $H_4W(DPPE)_2$ are less than those of $H_4Mo(DPPE)_2$, indicative of an increased spin–orbit coupling perturbation on the excited-state properties of the tungsten complex relative to that of molybdenum.[15]

Scheme I. State Diagram for the $H_4M(DPPE)_2$ (M = Mo, W) Complexes



The similarities in the absorption and emission spectra of $H_4Mo(DPPE)_2$ and $H_4W(DPPE)_2$ indicate that both complexes undergo the same transitions upon optical excitation and the same type of excited state is responsible for the observed emission. From the emission spectra of $H_4M(DPPE)_2$ (M = Mo, W) the energy of the emissive excited state is estimated to be ~56 kcal/mol above the ground state. The emission lifetimes of $H_4Mo(DPPE)_2$ and $H_4W(DPPE)_2$ (~90 μs and 13 μs, respectively) are in the range of lifetimes found for other second- and third-row transition-metal complexes in which the lowest excited state has considerable triplet character.[8a] Thus, we assign the emissive excited state for both complexes as principally triplet in character. The one-electron character of the excited state is unclear. As will be developed below, photoexcitation in solution at 298 K yields loss of H_2, consistent with a lowest excited state in solution that is antibonding with respect to $M-H_2$ interactions.

For the $H_4Mo(DPPE)_2$ species substitution of ^1H by ^2H results in an increase in the emission quantum yield but no change in the excited-state lifetime. On the surface this indicates that the rate constant of radiative decay increases while that of nonradiative decay remains unchanged. However, the theories of Robinson and Frosch[16] state that isotope substitution, changing only the vibrational energies and not the electronic structure or the geometry of the molecule, should result only in changes in the rate constant of nonradiative decay, not that of radiative decay. Within the confines of these theories,[16] the observed isotope effects on the excited-state properties of $H_4M(DPPE)_2$ are explained with the use of a Jablonski diagram, Scheme I, which involves two excited states, an emissive triplet state, and a nonemissive singlet

---

(15) (a) Ballhausen, C. J. "Introduction to Ligand Field Theory"; McGraw-Hill: New York, 1962. (b) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978.

(16) Robinson, G. W. *J. Mol. Spectrosc.* **1961**, *6*, 58. (b) Robinson, G. W.; Frosch, R. P. *J. Chem. Phys.* **1962**, *37*, 1962. (c) Robinson, G. W.; Frosch, R. P. *Ibid.* **1963**, *38*, 1187.

state. An analogous scheme has been used to explain the effects of deuterated solvents on the excited-state properties of Cr(III) complexes.[17] Optical excitation of the ground state, S_0, $H_4M(DPPE)_2$ species yields a nonemissive singlet excited state, S_1. The S_1 state can decay by various modes, chemical reactions with a rate constant of k_{cr}, intersystem crossing to the triplet excited state, T_1, with a rate constant of k_{isc}, or nonradiative decay to the singlet ground state, S_0, with a rate constant of k_{nr}. At 77 K no photoreaction is observed for the $H_4M(DPPE)_2$ species upon visible or ultraviolet light excitation; thus k_{cr} is negligibly small. The lifetime, τ_s, of the S_1 state is shown in eq 1. However, the

$$\tau_s = \frac{1}{k_{isc} + k_{nr}} \qquad (1)$$

experimentally measured excited-state lifetimes listed in Table I are those of the emissive, triplet excited state, T_1, not the nonemissive S_1 state. The T_1 state may decay by chemical reactions with a rate constant of $k_{cr'}$, back intersystem crossing to the S_1 state with a rate constant of k_{bisc}, nonradiative decay to the S_0 state with a rate constant of $k_{nr'}$, and radiative decay to the S_0 state with a rate constant of k_r. The lifetime of the T_1 state, τ_T, is represented in eq 2. Again, $k_{cr'}$ is negligible since no detectable

$$\tau_T = \frac{1}{k_{bisc} + k_{cr'} + k_{nr'} + k_r} \qquad (2)$$

photoreaction is observed at 77 K. At low temperatures (e.g., 77 K) any thermal back intersystem crossing is assumed to be very slow; therefore k_{bisc} is very small. Thus, the equation of the triplet lifetime reduces to eq 3, and the emission quantum yield of the

$$\tau_T = \frac{1}{k_{nr'} + k_r} \qquad (3)$$

T_1 state, Φ_T, is shown in eq 4. Substitution of ^1H by ^2H does

$$\Phi_T = \frac{k_r}{k_{nr'} + k_r} \qquad (4)$$

not change the lifetime of the emissive excited state for either $H_4Mo(DPPE)_2$ or $H_4W(DPPE)_2$, nor does it change the observed emission quantum yield of $H_4W(DPPE)_2$ at 77 K. It seems that the values of $k_{nr'}$ and k_r for the $H_4M(DPPE)_2$ species are independent of isotope substitution. However, the observed emission quantum yield for $H_4Mo(DPPE)_2$ in 2-MeTHF at 77 K increases from 0.21 to 0.28 upon substituting ^1H with ^2H. The observed emission quantum yield may be looked upon as the relative steady-state population of an emissive excited state.[17b] In Scheme I the emissive state, T_1, is populated by the nonemissive state, S_1; thus the observed emission quantum yield, Φ_{obsd}, is not simply the emission quantum yield of the T_1 state, Φ_T, in eq 4 but rather that shown in eq 5. Here, Φ_{isc} is the quantum yield for intersystem

$$\Phi_{obsd} = \Phi_{isc}\Phi_T \qquad (5)$$

crossing from the S_1 to the T_1 state, given in eq 6. Equation 6

$$\Phi_{isc} = \frac{k_{isc}}{k_{isc} + k_{nr}} \qquad (6)$$

gives the quantum efficiency for intersystem crossing, the number of molecules that intersystem cross per photon absorbed, for the case where radiative decay and chemical reactions from the state produced by absorption are both negligible. Since neither emission nor chemistry is detectable, this assumption appears valid. The increase in the Φ_{obsd} for $H_4Mo(DPPE)_2$ upon substitution of ^2H for ^1H is thus attributable to an increase in the Φ_{isc} not Φ_T. We expect this increase in Φ_{isc} results from a decrease in the rate constant, k_{nr}, not k_{isc}, because the S_1 and T_1, being relatively close in energy, should be little affected by the change in vibrational energy upon substitution of ^2H for ^1H.[16] Recall that $H_4W(DPPE)_2$ exhibits no change in the observed emission quantum yield upon substitution of ^2H for ^1H. Here, spin–orbit coupling affects the excited-state properties of $H_4W(DPPE)_2$, decreasing both its excited-state lifetime and observed emission quantum yield relative to $H_4Mo(DPPE)_2$. Similar effects have been reported for various emissive Ru(II) and Os(II) complexes.[6a] The lack of an observable isotope effect on Φ_{obsd} for $H_4W(DPPE)_2$ may be explained by the fact that spin–orbit coupling increases the rate constant of intersystem crossing from the S_1 to the T_1 state so that now $k_{isc} >> k_{nr}$. When this occurs, Φ_{isc} will approach unity and Φ_{obsd} will equal Φ_T, according to eq 5 and 6. Thus, in spite of any decrease in k_{nr} upon substitution of ^2H for ^1H, the observed emission quantum yields of the ^1H and ^2H species should be identical, as observed experimentally with $H_4W(DPPE)_2$.

The lack of any effect on the excited-state properties of $H_4W(DPPE)_2$ and the presence of a small effect on the excited-state properties of $H_4Mo(DPPE)_2$ upon isotope substitution is disappointing, since it is contrary to what we suspected, i.e., that the highest energy metal–ligand vibrations should be important pathways for nonradiative decay. Perhaps the important pathways involve the high-energy C–H stretches of the DPPE ligand and not the M–H vibrational modes. An alternative explanation would invoke the strong coupling mechanism used to explain the lack of isotope effect on excited-state properties when the ligands of Cr(III) complexes are deuterated.[4] In such a case, the emissive excited state is distorted from the ground state such that the vibronic overlap of the two states is always large and will be little affected by substitution of ^2H for ^1H. This latter explanation is more attractive since the lowest excited state is likely quite distorted leading to dissociative H_2 extrusion.

Photochemistry and Photocatalytic Activity. Photoexcitation of mononuclear polyhydrides generally results in the loss of H_2,[8,18] the exceptions being $ReH_5(PPh_2Me)_3$[19,20] and $ReH_3(PPh_2Me)_4$[20] in which photoinduced loss of PPh_2Me is observed. Geoffroy and co-workers[9a] find that UV photolysis of $H_4Mo(DPPE)_2$ in solution gives rise to 1.9 mol of H_2/mol of Mo and an orange solution containing a proposed "$Mo(DPPE)_2$" complex (eq 7). The

$$H_4Mo(DPPE)_2 \xrightarrow{h\nu} 2H_2 + \text{"}Mo(DPPE)_2\text{"} \qquad (7)$$

primary photoreaction is apparently loss of H_2 yielding $H_2Mo(DPPE)_2$ which subsequently forms the proposed "$Mo(DPPE)_2$". This proposed 14-e⁻ species should be extremely reactive, and indeed irradiation of $H_4Mo(DPPE)_2$ in the presence of CO or N_2 yields $Mo(CO)_2(DPPE)_2$ and $Mo(N_2)_2(DPPE)_2$, respectively. A similar "$W(DPPE)_2$" species has been detected by Diamantis[21] and Kisch[22] in flash photolysis studies of $W(N_2)_2(DPPE)_2$. Clearly, photolysis of $H_4M(DPPE)_2$ generates[9] reactive unsaturated species which may be active catalysts in olefin reactions.

Near-UV, 355 nm, irradiation of the $H_4M(DPPE)_2$ (M = Mo, W) complexes in the presence of 0.1 M 1-pentene results in efficient stoichiometric reduction of 1-pentene to *n*-pentane but *no* isomerization to 2-pentenes is found, even upon prolonged irradiation. No reduction or isomerization of 1-pentene occurs thermally at 25 °C, and heating 1-pentene in the presence of $H_4Mo(DPPE)_2$ to 100 °C results in only stoichiometric reduction to *n*-pentane. The particulars of the photoreduction chemistry are listed in Table II. The initial quantum yield for 1-pentene reduction (the number of 1-pentene molecules reduced per incident photon) is 0.09 and 0.006 for $H_4Mo(DPPE)_2$ and $H_4W(DPPE)_2$, respectively. Identical quantum yields for 1-pentene reduction are observed for the ^1H and ^2H species of $H_4W(DPPE)_2$. Although these quantum yields are not those for loss of H_2 from $H_4M(DPPE)_2$, it is of interest to note that they are in the same

---

(17) (a) Sriram. R.; Hoffman, M. Z.; Serpone, N. *J. Am. Chem. Soc.* **1981**, *103*, 997. (b) Walters, R. T.; Adamson, A. W. *Acta Chem. Acad. A* **1979**, *33*, 53.

(18) Geoffroy, G. L.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 3933.

(19) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 695.

(20) Roberts, D. A.; Geoffroy, G. L. *J. Organomet. Chem.* **1981**, *214*, 221.

(21) Thomas, R. J. W.; Laurence, G. S.; Diamantis, A. A. *Inorg. Chim. Acta* **1978**, *30*, L353.

(22) Caruana, A.; Kisch, H. *Int. Conf. Organomet. Chem. 9th*, **1979**, Abstr D10.

Table II. Photoreduction of Olefins Using $H_4M(DPPE)_2$ (M = Mo, W) Complexes[a]

A. Stoichiometric Photoreduction of 1-Pentene

M, 10^{-3} M	irrdn time, h	% redn to[b] n-pentane	% isomr[c] to 2-pentenes	Φ_{redn}[d]
Mo	0	0	0	
	0.13	33	<1	0.09
	0.28	50	<1	0.06
	0.77	100	<1	0.050
	thermal control	0	<1	
W	0	0	0	
	1	16	0	0.006
	3	29	0	0.004
	8	64	0	0.003
	30.5	70	<1	0.001
	48	87	<1	0.001
	thermal control	0	0	

B. Stoichiometric Photoreduction of Olefins

M, 10^{-3} M	irrdn time, h	olefin, 0.1 M	% conv[b]	product
Mo	0.77	1-pentene	100	*n*-pentane
	28.3	*cis*-2-pentene	13	*n*-pentane
	1.3	3,3-dimethyl-1-pentene	87	3,3-dimethylpentane
	24	cyclopentene	90	cyclopentane
W	48	1-pentene	87	*n*-pentane
	42	3,3-dimethyl-1-pentene	100	3,3-dimethylpentane
	44	cyclopentene	78	cyclopentane

C. Catalytic Photoreduction of Olefins (10 psi H_2)

M, 10^{-3} M	irrdn time, h	olefin, M	% isomer[c]	redn prod	turnover no.[e]
Mo	17.5	1-pentene, 0.1	<1	*n*-pentane	15.3
	15.5	1-pentene, 5.0	<1	*n*-pentane	151
	18	*cis*-2-pentene, 5.0	<1	*n*-pentane	1
	23.5	1-pentene, 0.1	<1	*n*-pentane	3.2

[a] All experiments were carried out in deoxygenated, dry toluene solutions of 10^{-3} M $H_4M(DPPE)_2$. Olefin concentration was 0.1 M unless otherwise noted. The light source was a 355-nm lamp, and the intensity measured for all stoichiometric reduction reactions was 1.2×10^{-6} ein/min. [b] Based on the assumption that $H_4M(DPPE)_2$ can transfer two molecules of H_2 ± 3%. [c] Conversion of 1-pentene to 2-pentenes and when the starting olefin is *cis*-2-pentene to the conversion of that to 1-pentene and *trans*-2-pentene. [d] Number of 1-pentene molecules reduced per incident photon. [e] Number of pentene molecules reduced per molecule of $H_4M(DPPE)_2$ initially present.

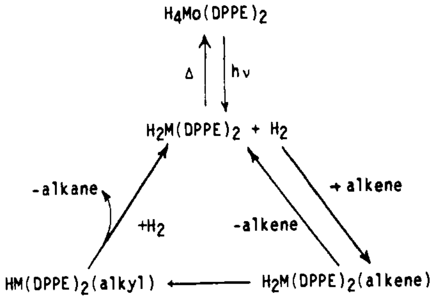
range as the quantum yields observed for loss of H_2 from Mo(η^5-$C_5H_5)_2H_2$ and W(η^5-$C_5H_5)_2H_2$, reactions 8 and 9.[23]

$$Mo(\eta^5\text{-}C_5H_5)_2H_2 \xrightarrow[\Phi_{366} = 0.1 + 0.02]{h\nu} Mo(\eta^5\text{-}C_5H_5)_2 + H_2 \quad (8)$$

$$W(\eta^5\text{-}C_5H_5)_2H_2 \xrightarrow[\Phi_{366} = 0.01 \pm 0.002]{h\nu} W(\eta^5\text{-}C_5H_5)_2 + H_2 \quad (9)$$

When the irradiations of $H_4M(DPPE)_2$ are done in the presence of H_2 and 1-pentene, catalytic reduction to *n*-pentane results, again without isomerization to the 2-pentenes. Turnover numbers (the number of pentene molecules reduced per molecule of $H_4M(DPPE)_2$ initially present) of >150 have been observed when photolyzing 10^{-3} M $H_4Mo(DPPE)_2$ in the presence of 5 M 1-pentene under 10 psi of H_2. Similar photoreductions are observed with internal olefins and olefins not possessing allylic hydrogens. The photoreduction of alkenes under 10 psi of H_2 requires continuous irradiation, and the quantum yield for reduction of 0.1 M 1-pentene is nearly the same as that for the stoichiometric reduction. These results indicate that irradiation does not generate a long-lived, active thermal catalyst. However, when the photoreduction of 1-pentene under 10 psi of H_2 is carried out at an alkene concentration of 5.0 M, the quantum yield increases by ~10-fold. These results are consistent with the mechanism represented in Scheme II, where the role of light is to accelerate the extrusion of H_2 to generate a dihydride that either thermally back reacts with H_2 or binds the alkene. The lack of a quantum yield that is greater than unity means that the thermal reaction of the dihydride with H_2 is very competitive with alkene reaction, since the catalytic cycle could continue in the dark if back reaction of the dihydride and H_2 did not occur. The thermal reaction of $H_2M(DPPE)_2$ with H_2 to regenerate $H_4M(DPPE)_2$ presumably has precedence, since a synthesis of $H_4M(DPPE)_2$ involves thermal reaction of $(N_2)_2M(DPPE)_2$ with H_2.[11]

Scheme II. Possible Mechanism for Alkene Hydrogenation



The clean formation of $(N_2)_2M(DPPE)_2$ or $(OC)_2M(DPPE)_2$ upon irradiation of $H_4M(DPPE)_2$ under a purge of N_2 or CO, respectively, strongly suggests that the M–P bonds are photoinert. If M–P cleavage occurs, thermally inert metal carbonyls such as $M(CO)_6$ and $M(CO)_4(DPPE)$ would result from irradiation under CO. The retention of the bulky P-donor groups in final products, of course, does not rule out a reversible loss of one M–P bond subsequent to photoexcitation. At this point, though, there is not evidence for such chemistry, and we will assume that it is unimportant in the photochemistry relative to the efficiency for loss of H_2.

Comparing the reduction of *cis*-2-pentene and 1-pentene, Table II, there is a marked difference in the rate to form *n*-pentane. We attribute this slower rate for the *cis*-2-pentene to the fact that the double bond is more hindered. The terminal double bond in 3,3-dimethyl-1-pentene is rapidly reduced and cyclopentene is photoreduced faster than *cis*-2-pentene. Thus, the ordering of photoreduction rates is 1-pentene ~3,3-dimethyl-1-pentene > cyclopentene > *cis*-2-pentene. This ordering is what would be expected for reduction by the sterically encumbered $H_2M(DPPE)_2$ formed by irradiation. Note that the relative ability to capture the dihydride by H_2 or the olefin can control the observed rate of alkane production according to Scheme II.

Consistent with the mechanism in Scheme II, we find that irradiation of $H_4Mo(DPPE)_2$ in toluene purged with C_2H_4 yields $(C_4H_4)_2Mo(DPPE)_2$, eq 10, where the "Mo(DPPE)$_2$" formed upon

$$H_4Mo(DPPE)_2 + C_2H_4 \xrightarrow{h\nu} (C_2H_4)_2Mo(DPPE)_2 \quad (10)$$

reductive elimination of alkane would be scavenged by C_2H_4. When irradiation of $H_4Mo(DPPE)_2$ is carried out under the same conditions but with C_3H_6 instead of C_2H_4, the species indicated in eq 11[24] are formed. The $(C_2H_4)_2Mo(DPPE)_2$ can be prepared

$$H_4Mo(DPPE)_2 + C_3H_6 \xrightarrow{h\nu} (C_3H_6)Mo(DPPE)_2 \rightleftarrows (H)(\eta^3\text{-}C_3H_5)Mo(DPPE)_2 \quad (11)$$

thermally or photochemically by reaction of $(N_2)_2Mo(DPPE)_2$ with C_2H_4, and the propene products can be prepared by reduction of $Cl_3Mo(THF)_3$ in the presence of DPPE and propene.[24] Irradiation of $H_4Mo(DPPE)_2$ in the 0.1 M 1-pentene solutions results in the growth of a UV–vis feature at ~430 nm whereas a feature

---

(23) (a) Geoffroy, G. L.; Bradley, M. G. *Inorg. Chem.* **1978**, *17*, 2410. (b) Geoffroy, G. L.; Bradley, M. G. *J. Organomet. Chem.* **1977**, *134*, C27.

(24) Byrne, J. W.; Blaser, H. U.; Osborn, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3871.

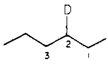
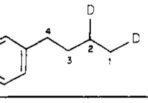
grows in at ~400 nm in the absence of the 1-pentene. The ~400-nm feature is presumably the uncharacterized "Mo(DPPE)$_2$" reported earlier[9a] and the ~430-nm feature is logically the C_5H_{10} analogue of the propene products shown in eq 11 that also shows absorption in this region. Unfortunately, the Mo-containing photoproduct from reaction with 1-pentene could not be isolated in a pure state, but the experiments with ethylene and propene would appear to umambiguously establish the ultimate fate of the Mo when irradiated in the presence of simple alkenes without and with allylic hydrogens, respectively.

Concerning the photoreduction, the intriguing finding is that the hydrogenation occurs without detectable isomerization of the alkenes. In the various metal complex photocatalyzed hydrogenation reactions of alkenes,[7a,d,e,25] there are no other examples of such a competitive reaction. Only in the $Cr(CO)_6$-photocatalyzed hydrogenation of 1,3-dienes have we seen an example of a catalyst that will not isomerize the starting olefin.[25] The result found for $H_4M(DPPE)_2$ is particularly surpising in view of the ability to observe the equilibrium represented in eq 11 for the products from reaction with C_3H_6.[24] Further, reaction of $H_4M(DPPE)_2$ with 1-pentene at 100 °C, where the C_3H_6 type products are labile,[24] does not give isomerization of 1-pentene; rather, *n*-pentane is slowly produced stoichiometrically. Irradiation of ~5×10^{-4} M $(C_3H_6)Mo(DPPE)_2/(H)(\eta^3\text{-}C_3H_5)Mo(DPPE)_2$ at 25 °C in the presence of 0.1 M 1-pentene gives no detectable isomerization or reduction of the 1-pentene in 20 h at a light intensity of 1.2×10^{-6} einstein (355 nm). The results suggest that alkane elimination, Scheme II, is very competitive with reverse β-hydrogen transfer to give an internal alkene dihydride species. The slow hydrogenation of *cis*-2-pentene, relative to 1-pentene, is consistent with a smaller tendency to bind internal alkenes compared to less-hindered terminal alkenes. Beginning with *cis*-2-pentene, we do not observe 1-pentene from isomerization either, despite the fact that the 1-pentene complex would be more thermodynamically stable than the *cis*-2-pentene complex. However, our data do not rule out formation of a 1-pentene complex followed by a reduction to *n*-pentane before loss of 1-pentene to form the uncomplexed isomerization product. The small amounts of alkane formed per unit time with *cis*-2-pentene (~stoichiometric reduction in 18 h) tends, however, to rule out rapid isomerization followed by reduction. We thus conclude the lack of isomerization activity to be due to the steric encumberance associated with the two DPPE ligands. Other studies in this laboratory have recently established very substantial effects of this kind on the photocatalyzed isomerization of 1-pentene and *cis*-2-pentene for catalyst precursors having P-donor ligands.[26]

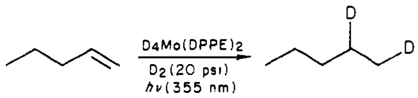
The fact that $H_4Mo(DPPE)_2$ photochemically catalyzes reduction of 1-pentene without formation of olefin isomerization products suggests that reducing equivalents (hydrogen atoms) are introduced specifically on the olefinic carbon atoms. Investigation into the regioselectivity of reduction was carried out with deuterium gas (D_2). Thus, the position of deuterium atoms on the resulting alkane can be detected by high-resolution NMR spectroscopy.

Photolysis of a degassed solution of 1-pentene (2.0 M) and $D_4Mo(DPPE)_2$ (4.0 mM) in toluene-d_8 with 355-nm light under 20 psig of deuterium gas gave 60% conversion to pentane after 5 days of continuous irradiation. Gas chromatography on the irradiated mixture showed that *n*-pentane was indeed the only product. In the proton-decoupled ^{13}C NMR spectrum, 1:1:1 triplets are observed at the base of intense methyl and methylene singlets at 14.4 and 22.7 ppm, respectively, Table III. These triplets arise from ^2H–^{13}C coupling. The strong singlets represent the perprotiomethyl and methylene ^{13}C absorptions. The absence of such coupling for the central methylene ^{13}C absorption of *n*-pentane at 37.6 ppm indicates that deuterium is present *only* at the two terminal carbon atoms. The ^2H spectrum of the solution shows two equally intense multiplets at 0.89 and 1.25 ppm, which occur in the expected region for methyl and methylene deuterium substitution. The absence of other deuterium absorption indicates that deuterium is not randomly incorporated into the starting alkene or reduction product, and that reduction is occurring primarily, if not exclusively, at the terminal olefinic carbon atoms, eq 12.

Table III. Nuclear Magnetic Resonance Data for the Photocatalytic Reduction of 1-Pentene and 4-Phenyl-1-butene under Deuterium Gas

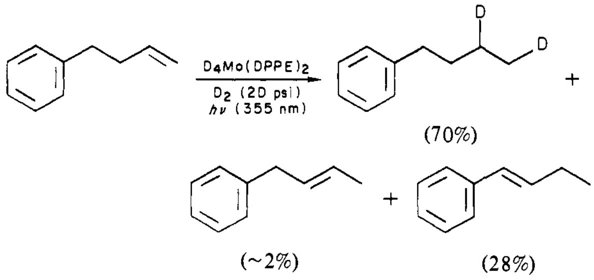
compd	nucleus	resonances,[a] ppm 1	2	3	4
	^{13}C	14.4[b]	22.7[b]	37.6[c]	
	^2H	0.89[d]	1.25[d]		
	^{13}C	13.9[b]	22.5[b]	34.1[c]	
	^2H	0.85	1.26		
	^1H	0.86[d]	1.23[d]	1.47[e]	2.48[e]

[a] All chemical shifts are reported in ppm relative to toluene-d_8 methyl for ^{13}C and ^2H spectra and relative to Me_4Si for ^1H spectra. [b] 1:1:1 triplet. [c] Singlet. [d] Multiplet. [e] Quartet.



(12)

Since 1,2-dideuteriopentane gives monodeuteromethyl and perprotiomethyl ^{13}C absorptions in the same position, the isotopic enrichment is not clearly shown. For this reasons, 4-phenyl-1-butene was reduced under the same conditions. The expected product, 1,2-dideuterio-4-phenylbutane, gives methyl and methylene ^{13}C peaks in a region free of other absorptions. Thus, deuterium substitution is clearly detected. After 4 days of irradiation, a surprisingly significant amount of olefin isomerization had occurred, eq 13. A 250-MHz ^1H NMR spectrum of the irradiated mixture gave near base-line resolution of each nonequivalent proton in the mixture of three products. Products were positively identified by comparison of spectral data with that of authentic samples. The distribution of products was calculated from ^1H NMR integration ratios. In particular, an integration ratio of 2:1 for adjacent methyl and methylene groups in the reduction product clearly shows the preferential formation of 1,2-dideuterio-4-phenylbutane. Deuterium and ^{13}C NMR data further support this conclusion, Table III. In the ^{13}C NMR spectrum, 1:1:1 triplets are observed for the methyl and adjacent methylene groups of the reduced product centered at 13.9 and 22.5 ppm, respectively. Two multiplets of equal intensity occur at 0.85 and 1.26 ppm in the ^2H NMR spectrum of the irradiated solution that are similar to the spectrum of 1,2-dideuteriopentane. Also, the absence of other absorptions in the ^2H NMR spectrum shows that deuterium was not introduced into either the benzylic and homobenzylic positions of the reduced product or the olefin isomerization products.



(13)

The absence of deuterium incorporation into the olefin isomerization products of 4-phenyl-1-butene indicates that two structurally different photogenerated species are responsible for reduction and isomerization. Reduction must occur from an intermediate containing reducing equivalents such as H_2Mo-

---

(25) Wrighton, M. S.; Graff, J. L.; Reichel, C. L.; Sanner, R. D. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 188.

(26) Graff, J. L.; Sanner, R. D.; Wrighton, M. S. *Organometallics* **1982**, *1*, 837.

(DPPE)$_2$ (see Scheme II), while isomerization could occur from a species void of hydrides, possibly through a π-allyl complex. But this point requires further study, since 1-pentene is not isomerized on the same time scale.

Mechanism aside, the photochemistry of $H_4M(DPPE)_2$ in the presence of olefins is unique both in terms of its relatively high quantum efficiency and selectivity toward reduction. The quantum efficiencies for the stoichiometric reduction of 1-pentene using $H_4Ru_4(CO)_{12}$[8d] and $H_2Os_3(CO)_{10}$[8e] are about 2 orders of magnitude less than that observed with $H_4Mo(DPPE)_2$. The cluster hydrides also isomerize 1-pentene to its internal isomers, even when irradiated under H_2. The rate of olefin isomerization far exceeds that of olefin reduction. The photoreduction of neat olefin solutions under 20 psi of H_2 with $Fe(CO)_5$ can occur with quantum efficiencies greater than 1.0, but again olefin isomerization occurs.[27] The experiments with $H_4M(DPPE)_2$ show no 1-pentene isomerization with or without H_2 present. Also, all well-known thermal olefin hydrogenation catalysts, though being selective catalysts for reducing olefins under H_2, isomerize olefins in the absence of H_2.

Conclusions

Replacement of ^1H by ^2H in $H_4M(DPPE)_2$ does not significantly alter the nonradiative decay rate from the emissive state that is triplet in character. Further, photoreduction of 1-pentene occurs at the same rate, using either $H_4W(DPPE)_2$ or $D_4W(DPPE)_2$. The loss of H_2 upon photoexcitation of $H_4M(DPPE)_2$ in solution is consistent with a lowest excited state that is M → P charge transfer in character that tends to labilize the H_2 with respect to reductive elimination, since the metal is partially oxidized in the excited state. Alternatively, the lowest excited state may involve population of an orbital that is antibonding with respect to the M–H_2 interaction that leads to a sufficiently distorted excited state that little isotope effect on nonradiative decay rate would be expected. All of the data seem to be best interpreted with the M–H_2 antibonding type of excited state as proposed for certain Ir(III) polyhydrides,[29] since strongly antibonding character in an excited state is usually responsible for efficient dissociative type processes in organometallic molecules.[8a] For $H_4M(DPPE)_2$ photoextrusion of H_2 leads to a reactive dihydride that will efficiently reduce, but not rapidly isomerize, alkenes. The photoreduction has good quantum efficiency for alkenes having a terminal double bond, and irradiation under H_2 leads to sustained conversion to alkane.

Acknowledgment. We thank the National Science Foundation for support of this research.

Registry No. $H_4Mo(DPPE)_2$, 32109-09-4; $D_4Mo(DPPE)_2$, 83632-65-9; $Mo(N_2)_2(DPPE)_2$, 41700-58-7; $H_4W(DPPE)_2$, 36352-27-9; $D_4W(DPPE)_2$, 83632-66-0; $W(N_2)_2(DPPE)_2$, 55954-53-5; D_2, 7782-39-0; ethylene, 74-85-1; propene, 115-07-1; 1-pentene, 109-67-1; *n*-pentane, 109-66-0; *cis*-2-pentene, 627-20-3; 3,3-dimethyl-1-pentene, 3404-73-7; cyclopentene, 142-29-0; 4-phenyl-1-butene, 768-56-9; 3,3-dimethylpentane, 562-49-2; cyclopentane, 287-92-3; 1,2-dideuteriopentane, 83615-82-1; 1,2-dideuteriobut-4-ylbenzene, 83615-83-2.

---

(27) Schroeder, M. A.; Wrighton, M. S. *J. Am. Chem. Soc. 1976*, *98*, 551.

(28) (a) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980. (b) James, B. R. *Adv. Organomet. Chem.* **1979**, *17*, 319. (c) James, B. R. "Homogeneous Hydrogenation"; Wiley-Interscience: New York, 1973.

(29) Geoffroy, G. L.; Pierantozzi, R. *J. Am. Chem. Soc.* **1976**, *98*, 8054.

Photochemistry of Divinylboranamines

Ted J. Sobieralski and Kenneth G. Hancock*

Contribution from the Department of Chemistry, University of California at Davis,
Davis, California 95616, and the Chemistry Division, National Science Foundation,
Washington, D.C. 20550. *Received February 19, 1982*

Abstract: The photochemistry of the divinylboranamines was explored in order to define structure–photoreactivity relationships for unsaturated organoboranes. Ultraviolet irradiation of the *N*,*N*-dimethyldivinylboranamines in cyclohexane gave cis–trans isomerization about the carbon–carbon double bonds to approximately statistical distributions of the three possible geometric isomers. Photolysis of the *N*-phenyldivinylboranamines gave nonoxidative photocyclization to azaboranaphthalenes in high yields. An investigation into the scope of cyclization revealed that chloro and bromo substitutents were tolerated on the aromatic ring, while compounds with methyl, ethyl, and *tert*-butyl groups on the vinyl moieties cyclized without difficulty. Quantum yields of cyclization ranged from 0.06 to 0.34 mol einstein^{-1}. Photoproduct structure determinations were accomplished from spectroscopic data and chemical degradation reactions. Cyclization was found to occur in a variety of solvents including pentane, cyclohexane, dioxane, and acetonitrile. In carbon tetrachloride, a carbon–boron bond-cleavage reaction occurred, giving an *N*-phenylvinylchloroboranamine as the only identifiable photoproduct. A new synthetic route for selective ortho-alkylation of anilines was developed via divinylboration, photocyclization, protonolysis, and hydrolysis. The alkylation is comparable in yields to known methods and tolerates introduction of a wide variety of alkyl groups.

The photochemical 1,2-boron shift and α-elimination processes, reported to date only in tetraarylborates[1] and trinaphthylborane,[2] are connected through the putative di-π-methane-type intermediate **1** (Scheme I). The unknown generality of these rearrangements in the photochemistry of di-π-borane systems suggested a systematic investigation into the governing structure–reactivity relationships. We, therefore, chose to study the photochemistry of various divinylboranamines.[3] The results to be discussed here indicate that rotational deactivation and nonoxidative photocyclization can occur in place of the di-π-methane-type rearrangement where structurally permitted.

---

* Address correspondence to Chemistry Division, National Science Foundation.

(1) Eisch, J. J.; Tamao, K.; Wilcsek, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 895–7.

(2) Ramsey, B. G.; Anjo, D. M. *J. Am. Chem. Soc.* **1977**, *99*, 3182–3.

(3) Current nomenclature practices of Chemical Abstracts Services designates boron–nitrogen compounds as boranamines. IUPAC uses the name aminoboranes as well.

0002-7863/82/1504-7533$01.25/0