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Photoinduced Reactions of $(\eta^5\text{-}C_5H_5)_2MH_3$ and $(\eta^5\text{-}C_5H_5)_2M(CO)H$ (M = Nb, Ta) and the Molecular Structure of $(\eta^5\text{-}C_5H_5)_2Ta(CO)H$

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Abstract: The reaction of $(\eta^5\text{-}C_5H_5)_2TaCl_2$ with $NaBH_4$ followed by the addition of triethylamine and carbon monoxide yields $(\eta^5\text{-}C_5H_5)_2Ta(CO)H$. The molecular structure of $(\eta^5\text{-}C_5H_5)_2Ta(CO)H$ has been established by single-crystal X-ray diffraction methods. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 6.147$ (3) Å, $b = 13.864$ (6) Å, $c = 11.801$ (5) Å, $\beta = 100.53$ (3)°, and $\rho_{\text{calcd}} = 2.28$ g cm^{-3} for $Z = 4$. The structure was refined to an R value of 0.089 based on 1358 observed reflections. The tantalum-bound hydrogen atom was located on a difference electron density map and fixed at the observed Ta–H length of 1.45 Å. $(\eta^5\text{-}C_5H_5)_2Ta(CO)H$ is *not* isostructural with the earlier reported niobium analogue. Photolyses of $(\eta^5\text{-}C_5H_5)_2MH_3$ or $(\eta^5\text{-}C_5H_5)_2M(CO)H$ (M = Nb, Ta) in aromatic solvents lead to a common intermediate, $(\eta^5\text{-}C_5H_5)_2MH$, that can react with carbon monoxide, hydrogen, or triethylphosphine. These photogenerated species are also capable of inserting into the carbon–hydrogen bonds of benzene and catalyzing the photoassisted H/D exchange between molecular hydrogen and benzene.

While the photochemistry of metal carbonyl derivatives is well established,[2-5] reactions of transition-metal hydride complexes induced by light are much less documented.[6,7] Even less common are photochemical studies of group 5B metal hydride derivatives.[8-11] In this paper, we report on photoinduced reactions of $(\eta^5\text{-}C_5H_5)_2MH_3$ and $(\eta^5\text{-}C_5H_5)_2M(CO)H$ (M = Nb, Ta) in aromatic solvents. Formed in these photochemical reactions are the coordinatively unsaturated intermediates $(\eta^5\text{-}C_5H_5)_2NbH$ and $(\eta^5\text{-}C_5H_5)_2TaH$. These species have previously been suggested to be produced in the thermolysis of $(\eta^5\text{-}C_5H_5)_2MH_3$ (M = Nb, Ta) and related systems.[12-15] The photochemically generated 16-electron species undergo reactions similar to those found for the thermally generated complexes, including the activation of carbon–hydrogen bonds in benzene and the catalysis of H/D exchange between hydrogen and benzene. In connection with this study, a synthetic route to $(\eta^5\text{-}C_5H_5)_2Ta(CO)H$ has been developed, and the crystal and molecular structure of this compound has been determined from single-crystal X-ray diffraction data measured by counter methods.

Experimental Section

All reactions and manipulations were conducted under argon by using either quartz or Pyrex Schlenkware. Argon and solvents were purified as described previously[16] Photolyses were conducted with either a 450-W Hanovia photochemical lamp located in a quartz, water-cooled immersion well or with a 275-W General Electric sunlamp. The light source was placed 1–2 cm from the water-cooled vessel containing the solution to be photolyzed.

Gas chromatographic analyses were performed on an Aerograph A-700 gas chromatograph equipped with a thermal conductivity detector. Hydrogen and carbon monoxide analyses were made on a 10 ft × 0.25 in. silica gel column at ambient temperatures. Cyclohexane/benzene separation was accomplished on a 10 ft × $^1/_8$ in. column of 10% Bentone and 10% Apiezon-L on Chromosorb W 60–80. The compositions of various samples were identified by means of a Perkin-Elmer-Hitachi RMU-6L mass spectrometer interfaced with a Perkin-Elmer 990 gas chromatograph. IR spectra were obtained on either a Beckman IR-10 or a Perkin-Elmer 237-B infrared spectrophotometer. Ultraviolet/visible spectra were recorded on a Perkin-Elmer 202 ultraviolet/visible spectrometer. Proton NMR spectra were obtained on a Varian A-60 spectrometer. $(\eta^5\text{-}C_5H_5)_2NbCl_2$,[17] $(\eta^5\text{-}C_5H_5)_2TaCl_2$,[18] $(\eta^5\text{-}C_5H_5)_2NbH_3$,[19] and $(\eta^5\text{-}C_5H_5)_2TaH_3$[20,21] were prepared by known methods. Deuterated benzene was put through three freeze–thaw cycles, after which no gas evolved on melting.

Preparation of $(\eta^5\text{-}C_5H_5)_2Nb(CO)H$. The preparation of $(\eta^5\text{-}C_5H_5)_2Nb(CO)H$ was achieved by modifying an existing procedure.[19] To a slurry of 11.5 g (39.1 mmol) of $(\eta^5\text{-}C_5H_5)_2NbCl_2$ in 200 mL of benzene was added an excess (150 mmol) of 70% Vitride, sodium bis(2-methoxyethoxy)aluminum hydride, in benzene. The resulting homogeneous deep yellow-brown solution was stirred for 15 min and then cooled to 0 °C. Degassed, distilled water (40 mL) was carefully added to the mixture, resulting in vigorous bubbling. The dark yellow solution was decanted from the resulting precipitate and filtered through a 3 × 15 cm column of degassed, anhydrous sodium sulfate. The column was washed with benzene until the washings were nearly colorless. The filtrate and the washings were taken to dryness by vacuum. The resulting light brown solid was dissolved in 200 mL of benzene and heated in an 80 °C bath as carbon monoxide was gently bubbled through the mixture. After 1.5 h, the solution was cooled and the solvent removed under vacuum. The residue was sublimed at 100 °C and 10^{-3} torr to yield 4.17 g (42%) of purple crystalline $(\eta^5\text{-}C_5H_5)_2Nb(CO)H$: ^{1}H NMR ($C_6D_6$) τ 5.31 (d, 10 H, J = 1 Hz, C_5H_5), 16.43 (m, 1 H, Nb–H); IR (THF) ν_{CO} 1902, $\nu_{\text{Nb-H}}$ 1682 cm^{-1}; UV/visible (n-heptane) 538 (ϵ 48 cm^{-1} L^{-1}/mol), 297 (ϵ 3.63 × 10^3), 280 (ϵ 6.26 × 10^3), 272 (ϵ 7.62 × 10^{-3}) 252 nm (ϵ 8.33 × 10^3).

Preparation of $(\eta^5\text{-}C_5H_5)_2Ta(CO)H$. A slurry of 3.12 g (8.17 mmol) of $(\eta^5\text{-}C_5H_5)_2TaCl_2$ in 100 mL of DME was stirred at −50 °C. To the

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brown suspension was added 0.62 g (16.3 mmol) of $NaBH_4$. Gas was evolved, and the solution turned green. The mixture was warmed to room temperature and stirred for 1 h. The resulting red-brown mixture was filtered and the filtrate taken to dryness by vacuum. The residue was dissolved in 125 mL of THF. Dry triethylamine (2.0 mL, 16 mmol) was added to the mixture, and carbon monoxide was bubbled through the solution for 18 h. The solvent was then removed under reduced pressure and the residue dried at 50 °C under vacuum to remove traces of triethylamine. The dried residue was purified by sublimation at 100 °C and 10^{-3} torr. Purple crystals of $(\eta^5\text{-}C_5H_5)_2Ta(CO)H$ (0.48 g, 17%) were obtained: ^1H NMR (C_6D_6) τ 5.42 (d, 10 H, J = 1 Hz, C_5H_5), 16.88 (s, 1 H, Ta–H); IR (THF) ν_{CO} 1890, ν_{Ta-H} 1745 cm^{-1}; UV/visible (n-heptane) 550 (ϵ 13 cm^{-1} L^{-1} mol), 303 (ϵ 1.08 × 10^3), 285 nm (ϵ 4.42 × 10^3).

Photolysis of $(\eta^5\text{-}C_5H_5)_2NbH_3$ in Benzene. A solution of 1.7 g (7.5 mmol) of $(\eta^5\text{-}C_5H_5)_2NbH_3$ in 50 mL of benzene was photolyzed in a water-jacketed Schlenk tube for 48 h. The solution turned deep yellow during the photolysis with the Hanovia lamp. Gas chromatography revealed the presence of hydrogen above the reaction mixture. The solvent was removed under vacuum, leaving a yellow solid. ^1H NMR of this solid indicated it was a 2:1 mixture of $(\eta^5\text{-}C_5H_5)_2NbH_3$ and $[(C_5H_5)(C_5H_4)NbH]_2$.[13]

Photolysis of $(\eta^5\text{-}C_5H_5)_2NbH_3$ in Benzene-d_6. A solution of 0.25 g (1.1 mmol) of $(\eta^5\text{-}C_5H_5)_2NbH_3$ in 5 mL of benzene-d_6 (99.5% deuterated) was photolyzed for 36 h at 15 °C in a quartz Schlenk tube. The solution turned deep yellow. Analysis by mass spectrometry (20 eV) of the photogenerated gas above the reaction mixture revealed a mixture of H_2 (90%), HD (10%), and D_2 (<1%).

Another solution containing 25 mg (0.11 mmol) of $(\eta^5\text{-}C_5H_5)_2NbH_3$ in 1 g of benzene-d_6 (99.96% deuterated) was photolyzed for 36 h at 15 °C in a quartz Schlenk tube. The ^1H NMR spectrum of the photomixture revealed an increase in the absorption due to the aromatic protons of benzene (τ 2.8).

Photolysis of $(\eta^5\text{-}C_5H_5)_2TaH_3$ in Benzene-d_6. In a quartz Schlenk tube, 0.21 g (0.67 mmol) of $(\eta^5\text{-}C_5H_5)_2TaH_3$ in 5 mL of benzene-d_6 (99.5% deuterated) was photolyzed for 36 h at 15 °C with a Hanovia lamp. The solution turned blood red. Mass spectral analysis of the gas above the reaction mixture revealed a mixture of H_2 (60%), HD (33%), and D_2 (7%).

A solution of $(\eta^5\text{-}C_5H_5)_2TaH_3$ in benzene-d_6 (99.95% deuterated) was photolyzed for 36 h at 15 °C in a quartz Schlenk tube with a Hanovia lamp. The ^1H NMR spectrum of the photomixture revealed an increase in the resonance due to aromatic protons on benzene (τ 2.8). No new η^5-cyclopentadienyl proton resonances were observed.

In a related experiment, another solution of $(\eta^5\text{-}C_5H_5)_2TaH_3$ in benzene-d_6 (99.96% deuterated) was stirred in the dark for 1 h at 15 °C. The ^1H NMR spectrum indicated no absorption due to aromatic protons on benzene. The colorless solution was then photolyzed in a quartz Schlenk tube for 1 h at 15 °C with a Hanovia lamp. The resulting faint orange solution showed an absorption in its ^1H NMR spectrum due to protons on benzene (τ 2.8). The mixture was subsequently stirred for 18 h in the dark at 15 °C. The ^1H NMR spectrum was recorded again, and no change was observed. The solution was subsequently photolyzed again in a quartz Schlenk tube at 15 °C with a Hanovia lamp, this time for 18 h. The ^1H NMR spectrum of the resulting red solution revealed an increase in the resonance at τ 2.8.

Photolysis of $(\eta^5\text{-}C_5H_5)_2Nb(CO)H$ in Benzene-d_6. $(\eta^5\text{-}C_5H_5)_2Nb(CO)H$ was dissolved in benzene-d_6 (99.5% deuterated) and the solution photolyzed in a quartz Schlenk tube at 15 °C for 36 h with a Hanovia lamp. The gas above the reaction mixture was analyzed by mass spectrometry (20 eV). The photogenerated hydrogen was found to consist of H_2 (64%), HD (30%), and D_2 (6%). Carbon monoxide was also present in the gas phase.

A solution of $(\eta^5\text{-}C_5H_5)_2Nb(CO)H$ in benzene-d_6 (99.96% deuterated) was photolyzed for 36 h at 15 °C in a quartz Schlenk tube with a Hanovia lamp. The ^1H NMR spectrum of the reaction mixture revealed an increase in the resonance due to the aromatic hydrogens on benzene (τ 2.8). No new η^5-cyclopentadienyl proton resonances were observed.

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ta(CO)H$ in Benzene-d_6. $(\eta^5\text{-}C_5H_5)_2Ta(CO)H$ (40 mg, 0.12 mmol) was dissolved in 2 mL of benzene-d_6 (99.5% deuterated) in a quartz Schlenk tube. The purple solution was photolyzed for 36 h at 15 °C with a Hanovia lamp. The hydrogen generated by the photolysis was analyzed by mass spectrometry (30 eV) and was found to consist of H_2 (30%), HD (45%), and D_2 (25%). Carbon monoxide was also generated in the photoreaction.

A solution of $(\eta^5\text{-}C_5H_5)_2Ta(CO)H$ in benzene-d_6 (99.96% deuterated) was photolyzed for 36 h at 15 °C in a quartz Schlenk tube with a Hanovia lamp. The purple solution turned red-orange. The ^1H NMR spectrum of the photolyzed mixture revealed an increase in the resonance attributed to aromatic hydrogens on benzene (τ 2.8). No new η^5-cyclopentadienyl proton resonances were observed.

Table I. Analysis of Hydrogen Generated from the Photolysis of $(\eta^5\text{-}C_5H_5)_2NbH_3$, $(\eta^5\text{-}C_5H_5)_2TaH_3$, $(\eta^5\text{-}C_5H_5)_2Nb(CO)H$, and $(\eta^5\text{-}C_5H_5)_2Ta(CO)H$ in C_6D_6[a]

compound	% H_2	% HD	% D_2
$(\eta^5\text{-}C_5H_5)_2NbH_3$	90	10	<1
$(\eta^5\text{-}C_5H_5)_2TaH_3$	60	33	7
$(\eta^5\text{-}C_5H_5)_2Nb(CO)H$	64	30	6
$(\eta^5\text{-}C_5H_5)_2Ta(CO)H$	30	45	25

[a] Photolysis performed in all-quartz equipment with a 450-W Hanovia lamp for 36 h at 15 °C in 99.5% deuterated C_6H_6.

Table II. Photochemically Induced H/D Exchange between H_2 and C_6D_6[a]

organometallic species	quantity of organometallic species, mmol	C_6D_5H formed, mmol
$(\eta^5\text{-}C_5H_5)_2NbH_3$	0.19	0.038
$(\eta^5\text{-}C_5H_5)_2TaH_3$	0.080	0.095
$(\eta^5\text{-}C_5H_5)_2Nb(CO)H$	0.10	0.057
$(\eta^5\text{-}C_5H_5)_2Ta(CO)H$	0.088	0.076

[a] Photolysis performed in all-quartz equipment with a 450-W Hanovia lamp for 36 h at 15 °C; 1.9 mmol of benzene-d_6 in cyclohexane; 1 atm of H_2.

Table III. Photochemically Induced H/D Exchange between D_2 and C_6H_6[a]

organometallic species	quantity of organometallic species, mmol	C_6H_5D formed, mmol
$(\eta^5\text{-}C_5H_5)_2NbH_3$	0.17	0.042
$(\eta^5\text{-}C_5H_5)_2TaH_3$	0.12	0.084
$(\eta^5\text{-}C_5H_5)_2Nb(CO)H$	0.16	0.126
$(\eta^5\text{-}C_6H_5)_2Ta(CO)H$	0.11	0.063

[a] Photolysis performed in all-quartz equipment with a 450-W Hanovia lamp for 36 h at 15 °C; 2.1 mmol of benzene in cyclohexane; 1 atm of D_2.

Photolysis of $(\eta^5\text{-}C_5H_5)_2NbH_3$, $(\eta^5\text{-}C_5H_5)_2TaH_3$, $(\eta^5\text{-}C_5H_5)_2Nb(CO)H$, and $(\eta^5\text{-}C_5H_5)_2Ta(CO)H$ in the Presence of Hydrogen and Benzene-d_6. Approximately 0.1 mmol of the appropriate organometallic species was dissolved in 20.0 mL of cyclohexane in a 45-mL quartz Schlenk tube. Next, 0.20 mL (1.9 mmol) of benzene-d_6 (99.96% deuterated) was added. The system was saturated with hydrogen gas and then photolyzed for 36 h at 15 °C with a Hanovia lamp. The amount of benzene-d_6 converted to C_6D_5H was measured by GC/MS. The results of these photochemically induced H/D exchanges are summarized in Table II.

Photolysis of $(\eta^5\text{-}C_5H_5)_2NbH_3$, $(\eta^5\text{-}C_5H_5)_2TaH_3$, $(\eta^5\text{-}C_5H_5)_2Nb(CO)H$, and $(\eta^5\text{-}C_5H_5)_2Ta(CO)H$ in the Presence of Deuterium and Benzene. Approximately 0.1 mmol of the appropriate organometallic species and 0.20 mL (2.1 mmol) of benzene were dissolved in 20.0 mL of cyclohexane in a 45-mL quartz Schlenk tube. The mixture was saturated with deuterium gas and photolyzed for 36 h at 15 °C with a Hanovia lamp. The amount of benzene converted to C_6H_5D was analyzed by GC/MS. The results of these photochemically induced H/D exchanges are summarized in Table III.

Photolysis of $(\eta^5\text{-}C_5H_5)_2NbH_3$ in the Presence of Carbon Monoxide. $(\eta^5\text{-}C_5H_5)_2NbH_3$ (0.15 g, 0.66 mmol) was dissolved in 40 mL of toluene in a water-jacketed Schlenk tube and photolyzed for 4 h with a Hanovia lamp while carbon monoxide was bubbled through the mixture. The solvent was removed under vacuum and the resulting residue sublimed at 100 °C and 10^{-3} torr, yielding 30 mg (18%) of purple crystalline $(\eta^5\text{-}C_5H_5)_2Nb(CO)H$.

Photolysis of $(\eta^5\text{-}C_5H_5)_2TaH_3$ in the Presence of Carbon Monoxide. A solution of 0.30 g (0.96 mmol) of $(\eta^5\text{-}C_5H_5)_2TaH_3$ in 30 mL of toluene was photolyzed in a quartz Schlenk tube at 15 °C with a Hanovia lamp for 4 h as carbon monoxide was bubbled through the mixture. The solvent was removed under vacuum, leaving a 2:1 mixture of $(\eta^5\text{-}C_5H_5)_2TaH_3$ and $(\eta^5\text{-}C_5H_5)_2Ta(CO)H$.

Photolysis of $(\eta^5\text{-}C_5H_5)_2Nb(CO)H$ in the Presence of Hydrogen. A solution of 0.37 g (1.47 mmol) of $(\eta^5\text{-}C_5H_5)_2Nb(CO)H$ in 50 mL of toluene was photolyzed for 4 h in a water-jacketed Schlenk tube with a Hanovia lamp while hydrogen was bubbled through the mixture. The solvent was then removed under vacuum, yielding 0.26 g of a residue that consisted of a 50:50 mixture of $(\eta^5\text{-C}_5\text{H}_5)_2$Nb(CO)H and $(\eta^5\text{-C}_5\text{H}_5)_2\text{NbH}_3$.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2$Ta(CO)H in the Presence of Hydrogen. $(\eta^5\text{-C}_5\text{H}_5)_2$Ta(CO)H (0.40 g, 1.2 mmol) in 40 mL of toluene was photolyzed in a water-jacketed Schlenk tube for 4 h with a Hanovia lamp while hydrogen gas was bubbled through the mixture. The solvent was removed under vacuum, leaving only $(\eta^5\text{-C}_5\text{H}_5)_2\text{TaH}_3$.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{NbH}_3$ in the Presence of Triethylphosphine. $(\eta^5\text{-C}_5\text{H}_5)_2\text{NbH}_3$ (0.40 g, 1.77 mmol) and triethylphosphine (1.5 mL, 10.2 mmol) were dissolved in 250 mL of benzene in a water-jacketed Schlenk tube and photolyzed for 40 h with a Hanovia lamp. During the irradiation, the yellow solution turned orange, and hydrogen was evolved. The solvent was removed under vacuum and the residue recrystallized from pentane at −78 °C, giving 0.14 g (23%) or orange-red $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb[P(C}_2\text{H}_5)_3]\text{H}$:[13] ^{1}H NMR ($C_6H_6$) τ 5.50 (d, 10 H, J = 2 Hz, C_5H_5), 9.06 (m, 15 H, PC_2H_5), 17.83 (m, 1 H, Nb–H); IR (toluene) $\nu_{\text{Nb-H}}$ 1645 cm^{-1}.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{TaH}_3$ in the Presence of Triethylphosphine. In a quartz Schlenk tube, a solution of 0.18 g (0.57 mmol) of $(\eta^5\text{-C}_5\text{H}_5)_2\text{TaH}_3$ and 1.5 mL (10.2 mmol) of triethylphosphine in 30 mL of benzene was photolyzed at 15 °C for 24 h with a Hanovia lamp. The colorless solution became faintly orange in color with the formation of a precipitate. The reaction was filtered and the filtrate taken to dryness under vacuum, leaving an off-white solid that consisted of only $(\eta^5\text{-C}_5\text{H}_5)_2\text{TaH}_3$. No $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta[P(C}_2\text{H}_5)_3]\text{H}$[12,22] was detected.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2$Nb(CO)H in the Presence of Triethylphosphine. $(\eta^5\text{-C}_5\text{H}_5)_2$Nb(CO)H (0.63 g, 2.50 mmol) and triethylphosphine (1.5 ml, 10.2 mmol) were dissolved in 250 mL of benzene in a water-jacketed Schlenk tube. The purple solution was photolyzed for 16 h with a 275-W G. E. sunlamp. During the irradiation, carbon monoxide was evolved, and the solution turned deep orange. The solvent was then removed under vacuum and the residue recrystallized from pentane at −78 °C, resulting in 0.45 g (53%) of rust-orange air-sensitive $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb[P(C}_2\text{H}_5)_3]\text{H}$.[13]

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2$Ta(CO)H in the Presence of Triethylphosphine. A solution of 0.22 g (0.65 mmol) of $(\eta^5\text{-C}_5\text{H}_5)_2$Ta(CO)H and 1.5 mL (10.2 mmol) of triethylphosphine in 200 mL of benzene was photolyzed for 4 h in a water-jacketed Schlenk tube with a Hanovia lamp. During the photolysis, the solution changed from purple to orange, with the evolution of gas. The solution was filtered and the filtrate taken to dryness under reduced pressure, leaving a 50:50 mixture of $(\eta^5\text{-C}_5\text{H}_5)_2$Ta(CO)H and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta[P(C}_2\text{H}_5)_3]\text{H}$.[12,22]

X-ray Data Collection and Structure Determination for $(\eta^5\text{-C}_5\text{H}_5)_2$Ta(CO)H. Single crystals of $(\eta^5\text{-C}_5\text{H}_5)_2$Ta(CO)H were grown by slow sublimation at 80 °C and 10^{-4} torr. An appropriate single crystal was selected and sealed in a thin-walled glass capillary. Final lattice parameters as determined from 15 reflections ($2\theta > 30°$) carefully centered on an Enraf-Nonius CAD-4 diffractometer are given in Table IV. Intensity data were recorded on the diffractometer in the usual manner.[23] A summary of data collection and refinement parameters is presented in Table IV. The intensities were corrected for absorption by an empirical method similar to that described by Churchill.[24]

The structure was solved by conventional heavy-atom techniques. Subsequent difference-Fourier maps afforded the coordinates of all the non-hydrogen atoms. The hydrogen atoms of the cyclopentadienyl rings were placed at calculated positions 1.00 Å from the bonded carbon atoms, and their parameters were not refined. The tantalum-bound hydrogen atom was easily located on a difference-Fourier map, and its position was fixed. Unfortunately, the data suffered from a severe absorption problem that could not be adequately corrected. Attempts to refine the carbon and oxygen atoms with anisotropic thermal parameters always resulted in unrealistic values. The refinement is therefore not as good as desired, but adequate for the discussion given below.

Neutral atom scattering factors were taken from the compilations of Cromer and Waber[25] for Ta, O, and C, and that for Ta was corrected for the real and imaginary components of anomalous dispersion.[26] Scattering factors for H were from a literature source.[27] The final values of the positional parameters are given in Table V, and bond distances and angles in Table VI.[28]

Table IV. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compound	$(\eta^5\text{-C}_5\text{H}_5)_2$Ta(CO)H
M_r	340.16
space group	$P2_1/n$
cell constants: a, Å	6.147 (3)
b, Å	13.864 (6)
c, Å	11.801 (5)
β, deg	100.53 (3)
V, Å	988.8
molecules/unit cell	4
ρ_{calcd}, g cm^{-3}	2.28
μ_{calcd}, cm^{-1}	116.42
radiation	Mo Kα
max crystal dimensions, mm	0.23 × 0.38 × 0.78
standard reflections	(0012), (400)
variation of standards	±3%
reflections measured	2973
2θ range, deg	50
reflections collected	1358
no. of parameters varied	58
GOF	1.85
R	0.089
R_w	0.090

Results and Discussion

Synthetic and Spectral Studies. The preparation of $(\eta^5\text{-C}_5\text{H}_5)_2$Ta(CO)H could be accomplished by the addition of $NaBH_4$ to $(\eta^5\text{-C}_5\text{H}_5)_2\text{TaCl}_2$ followed by the addition of triethylamine and carbon monoxide. A similar synthetic route to $(\eta^5\text{-C}_5\text{H}_5)_2$Nb(CO)H has been reported.[29] The ^{1}H NMR spectra of $(\eta^5\text{-C}_5\text{H}_5)_2$Nb(CO)H and $(\eta^5\text{-C}_5\text{H}_5)_2$Ta(CO)H exhibit cyclopentadienyl proton resonances with doublet character. This result is most likely due to spin–spin coupling of the cyclopentadienyl protons with the metal hydride (J = 1 Hz). Previously reported ^{1}H NMR data for $(\eta^5\text{-C}_5\text{H}_5)_2$Nb(CO)H[19] and $(\eta^5\text{-C}_5\text{H}_5)_2$Ta(CO)H[30] make no mention of this coupling. In the solid state, the $(\eta^5\text{-C}_5\text{H}_5)_2$M(CO)H complexes are both purple, while the $(\eta^5\text{-C}_5\text{H}_5)_2\text{MH}_3$ derivatives are colorless. However, solutions of $(\eta^5\text{-C}_5\text{H}_5)_2\text{NbH}_3$ in hydrocarbon solvents are faintly purple, while solutions of $(\eta^5\text{-C}_5\text{H}_5)_2\text{TaH}_3$ remain colorless.[31]

Photochemical Studies. $(\eta^5\text{-C}_5\text{H}_5)_2\text{NbH}_3$, $(\eta^5\text{-C}_5\text{H}_5)_2\text{TaH}_3$, $(\eta^5\text{-C}_5\text{H}_5)_2$Nb(CO)H, and $(\eta^5\text{-C}_5\text{H}_5)_2$Ta(CO)H have been found to photodegrade when irradiated with polychromatic light. Hydrogen was detected in the photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{NbH}_3$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{TaH}_3$. Hydrogen and carbon monoxide were detected from the photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2$Nb(CO)H and $(\eta^5\text{-C}_5\text{H}_5)_2$Ta(CO)H in benzene. $(\eta^5\text{-C}_5\text{H}_5)_2\text{NbH}_3$, $(\eta^5\text{-C}_5\text{H}_5)_2\text{TaH}_3$, $(\eta^5\text{-C}_5\text{H}_5)_2$Nb(CO)H, and $(\eta^5\text{-C}_5\text{H}_5)_2$Ta(CO)H were photolyzed in benzene-d_6 for 36 h[32] to determine the source of the hydrogen generated in these photolyses. The photogenerated hydrogen was analyzed by mass spectrometry (20 eV). The results are summarized in Table I.

The presence of deuterium in the evolved gases clearly demonstrates that the carbon–deuterium bonds in benzene-d_6 have been cleaved. Detection of HD in the photogenerated gases also indicates that solvent deuterons are coupling with those on the organometallic species. It can be noted that increased deuterium content in the evolved gases was observed from the photolyses of $(\eta^5\text{-C}_5\text{H}_5)\text{TaH}_3$ and $(\eta^5\text{-C}_5\text{H}_5)_2$Ta(CO)H relative to their niobium counterparts. A greater percentage of H_2 was observed on photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{MH}_3$ relative to corresponding $(\eta^5\text{-C}_5\text{H}_5)_2$M(CO)H complexes, since H_2 elimination is a primary photoprocess in the former cases. Further, it has been observed

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(31) UV/visible data for $(\eta^5\text{-C}_5\text{H}_5)_2\text{NbH}_3$ (n-heptane): 570 (ϵ 843 cm^{-1} L^{-1} mol), 300 (ϵ 7.40 × 10^4), 279 (ϵ 1.86 × 10^5), 270 nm (ϵ 2.02 × 10^5). UV/visible data for $(\eta^5\text{-C}_5\text{H}_5)_2\text{TaH}_3$ (n-heptane): 280 (ϵ 3.78 × 10^3 cm^{-1} L^{-1} mol), 273 nm (ϵ 4.30 × 10^3). UV/visible data for $(\eta^5\text{-C}_5\text{H}_5)_2$Nb(CO)H and $(\eta^5\text{-C}_5\text{H}_5)_2$Ta(CO)H appear in the Experimental Section.

(32) ^{1}H NMR studies indicate that even after 36 h of photolysis, starting material was present in every case.

Table V. Final Fractional Coordinates and Thermal Parameters[a] for (η^5-C_5H_5)$_2$Ta(CO)H

atom	*x/a*	*y/b*	*z/c*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ta	0.9790 (2)	0.23869 (6)	0.1617 (1)	0.0203 (3)	0.00186 (5)	0.0081 (1)	−0.0001 (1)	0.0026 (1)	−0.00000 (6)
O	1.224 (6)	0.148 (2)	−0.025 (3)	8.8 (8)					
C(1)	1.124 (7)	0.180 (3)	0.046 (3)	6.0 (8)					
C(2)	1.102 (5)	0.380 (2)	0.085 (2)	4.0 (6)					
C(3)	0.937 (6)	0.406 (2)	0.137 (3)	5.4 (7)					
C(4)	0.975 (6)	0.390 (2)	0.252 (3)	4.5 (6)					
C(5)	1.196 (6)	0.353 (2)	0.269 (3)	4.9 (7)					
C(6)	1.273 (6)	0.348 (2)	0.168 (3)	5.3 (7)					
C(7)	0.885 (6)	0.075 (2)	0.166 (3)	5.2 (7)					
C(8)	0.708 (7)	0.122 (3)	0.194 (3)	5.8 (8)					
C(9)	0.755 (7)	0.165 (3)	0.283 (3)	6.2 (8)					
C(10)	0.987 (8)	0.148 (3)	0.330 (4)	7.1 (1)					
C(11)	1.063 (6)	0.090 (2)	0.253 (3)	5.3 (7)					
H(1)[Ta]	0.7590	0.2415	0.0929	5.5					
H(2)[C(2)]	1.1003	0.3857	−0.0003	5.5					
H(3)[C(3)]	0.7879	0.4358	0.0972	5.5					
H(4)[C(4)]	0.8845	0.3999	0.3150	5.5					
H(5)[C(5)]	1.2838	0.3306	0.3436	5.5					
H(6)[C(6)]	1.4185	0.3235	0.1548	5.5					
H(7)[C(7)]	0.8775	0.0366	0.0910	5.5					
H(8)[C(8)]	0.5564	0.1171	0.1430	5.5					
H(9)[C(9)]	0.6483	0.2123	0.3102	5.5					
H(10)[C(10)]	1.0668	0.1716	0.4070	5.5					
H(11)[C(11)]	1.2147	0.0639	0.2564	5.5					

[a] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table VI. Bond Distances (Å) and Angles (deg) for (η^5-C_5H_5)$_2$Ta(CO)H

atoms	distance	atoms	distance
C(1)-Ta	1.94 (4)	C(2)-Ta	2.34 (3)
C(3)-Ta	2.35 (3)	C(4)-Ta	2.36 (3)
C(5)-Ta	2.30 (3)	C(6)-Ta	2.35 (4)
C(7)-Ta	2.35 (3)	C(8)-Ta	2.40 (4)
C(9)-Ta	2.39 (4)	C(10)-Ta	2.34 (4)
C(11)-Ta	2.35 (3)	H(1)-Ta	1.45
C(1)-O	1.21 (4)	C(3)-C(2)	1.32 (4)
C(6)-C(2)	1.37 (4)	C(4)-C(3)	1.36 (4)
C(5)-C(4)	1.43 (5)	C(6)-C(5)	1.36 (4)
C(8)-C(7)	1.36 (5)	C(11)-C(7)	1.37 (5)
C(9)-C(8)	1.20 (5)	C(10)-C(9)	1.45 (6)
C(11)-C(10)	1.36 (5)	Ta-Cent 1	2.03
Ta-Cent 2	2.07		

atoms	angle	atoms	angle
H(1)-Ta-C(1)	97	O-C(1)-Ta	176 (3)
C(6)-C(2)-C(3)	108 (3)	C(4)-C(3)-C(2)	114 (3)
C(5)-C(4)-C(3)	100 (3)	C(6)-C(5)-C(4)	112 (3)
C(5)-C(6)-C(2)	105 (3)	C(11)-C(7)-C(8)	108 (3)
C(9)-C(8)-C(7)	112 (4)	C(10)-C(9)-C(8)	109 (4)
C(11)-C(10)-C(9)	106 (4)	C(10)-C(11)-C(7)	105 (4)
Cent 1-Ta-Cent 2	144.8	Cent 1-Ta-C(1)	106.2
Cent 1-Ta-H(1)	108.5	Cent 2-Ta-C(1)	102.3
Cent 2-Ta-H(1)	87.8		

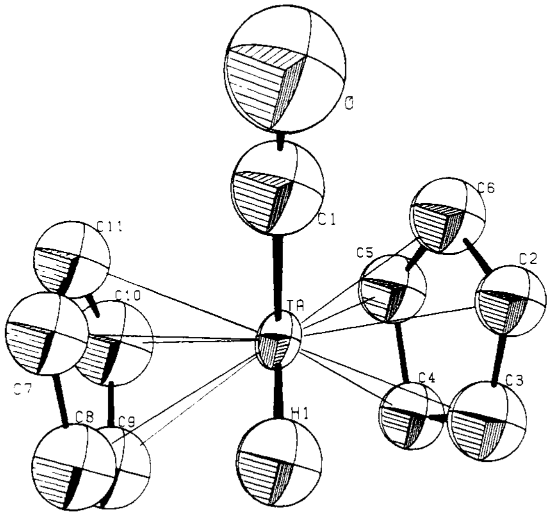

Figure 1. Molecular structure and atom numbering scheme for (η^5-C_5H_5)$_2$Ta(CO)H with the atoms represented by their 50% probability ellipsoids for thermal motion.

from ^{1}H NMR studies that photodegradations of the (η^5-C_5H_5)$_2$M(CO)H species are more facile than the corresponding (η^5-C_5H_5)$_2$MH$_3$ analogues.[33] For these reasons, the H$_2$/HD/D$_2$ distributions vary according to the respective organometallic precursor. (η^5-C_5H_5)$_2$NbH$_3$, (η^5-C_5H_5)$_2$TaH$_3$, (η^5-C_5H_5)$_2$Nb(CO)H, and (η^5-C_5H_5)$_2$Ta(CO)H were photolyzed in 99.96% deuterated benzene to determine if hydrogen was being transferred from the organometallic species to the solvent. ^{1}H NMR analysis of the reaction media from all four experiments indicated significant growth of the resonance at τ 2.8 attributed to protons on benzene. This exchange in the case of (η^5-C_5H_5)$_2$TaH$_3$ was conclusively demonstrated to be a photoassisted process at 15 °C. No exchange occurred without light, and continuous irradiation was required to maintain the process.

In view of this exchange process between the organometallic species and the solvent, exchange experiments between hydrogen in the atmosphere above the reaction mixture and benzene, mediated by the organometallic species, were attempted. H/D exchange reactions between H$_2$ and benzene-d_6 and between D$_2$ and benzene were examined by photolyzing the components in cyclohexane. The results, which are presented in Tables II and III, indicate that photochemically induced H/D exchange between molecular hydrogen and benzene is in fact successfully promoted by (η^5-C_5H_5)$_2$NbH$_3$, (η^5-C_5H_5)$_2$TaH$_3$, (η^5-C_5H_5)$_2$Nb(CO)H, and (η^5-C_5H_5)$_2$Ta(CO)H.[34]

The activation of carbon–hydrogen bonds by homogeneous transition-metal species is rare.[15,35-37] (η^5-C_5H_5)$_2$TaH$_3$,[12,14] (η^5-C_5H_5)$_2$NbH$_3$,[13,14] [(C_5H_5)(C_5H_4)NbH]$_2$,[14] and (η^5-$C_5H_4CH_3$)$_2$TaH$_3$[14] are reported to catalyze the H/D exchange between aromatic solvents and diatomic hydrogen at elevated

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[33] Foust, D. F. Ph.D. Dissertation, University of Massachusetts, 1981.

[34] While no attempt was made to optimize H/D exchange conditions, it can be seen from Table II that the amount of C_6D_5H formed is greater than the amount of (η^5-C_5H_5)$_2$TaH$_3$ photolyzed.

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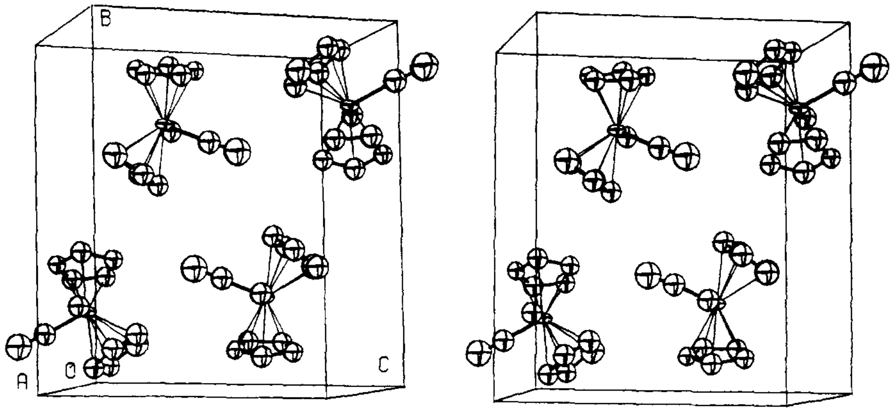

Figure 2. Stereoscopic view of the unit cell packing in (η^5-C_5H_5)$_2$Ta(CO)H.

temperature (107 °C). The mechanism proposed for this exchange is based on the intermediate (η^5-C_5H_5)$_2$MH (M = Nb, Ta).[15] In addition to generating this intermediate by thermally eliminating hydrogen from the trihydride derivatives of nibocene or tantalocene, we have now demonstrated that (η^5-C_5H_5)$_2$NbH and (η^5-C_5H_5)$_2$TaH can be formed by the photochemically induced loss of hydrogen from (η^5-C_5H_5)$_2$NbH$_3$ and (η^5-C_5H_5)$_2$TaH$_3$ and by photochemically induced loss of carbon monoxide from (η^5-C_5H_5)$_2$Nb(CO)H and (η^5-C_5H_5)$_2$Ta(CO)H, respectively. In a similar manner, the photochemical loss of hydrogen from (η^5-C_5H_5)$_2$WH$_2$[38] or carbon monoxide from (η^5-C_5H_5)$_2$WCO[39] has been reported to generate (η^5-C_5H_5)$_2$W. This intermediate is likewise capable of inserting into carbon–hydrogen bonds of benzene but is unable to effect the H/D exchange between hydrogen and benzene.

The photogenerated intermediates (η^5-C_5H_5)$_2$NbH and (η^5-C_5H_5)$_2$TaH could be trapped by the addition of two-electron ligands to the photomixture. Thus, the photolyses of benzene solutions of (η^5-C_5H_5)$_2$NbH$_3$ and (η^5-C_5H_5)$_2$Nb(CO)H in the presence of triethylphosphine produced (η^5-C_5H_5)$_2$Nb[P(C_2H_5)$_3$]H,[13] whereas the photolysis of (η^5-C_5H_5)$_2$Ta(CO)H in benzene in the presence of triethylphosphine afforded (η^5-C_5H_5)$_2$Ta[P(C_2H_5)$_3$]H.[12,22] The photolysis of (η^5-C_5H_5)$_2$TaH$_3$ in the presence of triethylphosphine, however, did not yield the corresponding hydrido–phosphine–metallocene derivative. Similar results have been recently reported for the photolysis of the group 6B complexes (η^5-C_5H_5)$_2$MH$_2$ (M = Mo, W) in the presence of two-electron-donating ligands.[40] While photolysis of (η^5-C_5H_5)$_2$MoH$_2$ in the presence of two-electron-donating ligands (L) gave (η^5-C_5H_5)$_2$MoL, similar photolyses involving (η^5-C_5H_5)$_2$WH$_2$ and L did not yield (η^5-C_5H_5)$_2$WL.[40]

The trihydride and carbonyl hydride derivatives of niobocene and tantalocene could be photochemically interconverted in toluene solution. Irradiation of (η^5-C_5H_5)$_2$NbH$_3$ and (η^5-C_5H_5)$_2$TaH$_3$ in the presence of carbon monoxide led to the formation of (η^5-C_5H_5)$_2$Nb(CO)H and (η^5-C_5H_5)Ta(CO)H, respectively. Likewise, photolysis of (η^5-C_5H_5)$_2$Nb(CO)H and (η^5-C_5H_5)$_2$Ta(CO)H while hydrogen was bubbled through the photomixture resulted in oxidative addition of hydrogen to the metal centers and the formation of (η^5-C_5H_5)$_2$NbH$_3$ and (η^5-C_5H_5)$_2$TaH$_3$, respectively.

Additional evidence for the intermediate (η^5-C_5H_5)$_2$MH comes from the photolysis of (η^5-C_5H_5)$_2$NbH$_3$ in benzene. Identified from this photomixture was the dimeric form of niobocene, [(C_5H_5)(C_5H_4)NbH]$_2$.[13] This species is reported to arise from the loss of hydrogen from (η^5-C_5H_5)$_2$NbH.[13]

X-ray Structural Studies. The molecular structure and atom numbering scheme for the title compound, (η^5-C_5H_5)$_2$Ta(CO)H, are illustrated in Figure 1. Figure 2 shows a stereoscopic view of the unit cell packing. It is interesting to note that (η^5-C_5H_5)$_2$Ta(CO)H is *not* isostructural with the niobium analogoue.[41] The former crystallizes in the monoclinic space group $P2_1/n$, while the latter belongs to the triclinic $P\bar{1}$. Since the structure of (η^5-C_5H_5)$_2$Nb(CO)H was only refined to $R = 16.9\%$, it certainly requires a reinvestigation.

The Ta–H unrefined distance of 1.45 Å in (η^5-C_5H_5)$_2$Ta(CO)H compares favorably with the 1.5 Å unrefined value found in TaH[P(C_6H_5)$_2$]$_2$[(CH_3)$_2$PC_2H_4P(CH_3)$_2$]$_2$.[42] The most reliable determination of a Ta–H length is 1.774 Å in the neutron diffraction study of (η^5-C_5H_5)$_2$TaH$_3$.[43]

Acknowledgment. We are indebted to the Nationl Science Foundation for support of this program and to E. Guzik for assistance in obtaining the mass spectra.

Registry No. (η^5-C_5H_5)$_2$Nb(CO)H, 11105-68-3; (η^5-C_5H_5)$_2$NbCl$_2$, 12793-14-5; (η^5-C_5H_5)$_2$Ta(CO)H, 11105-69-4; (η^5-C_5H_5)$_2$TaCl$_2$, 54039-37-1; NaBH$_4$, 16940-66-2; (η^5-C_5H_5)$_2$NbH$_3$, 11105-67-2; [(C_5H_5)(C_5H_4)NbH]$_2$, 11105-93-4; (η^5-C_5H_5)$_2$TaH$_3$, 12117-02-1; (η^5-C_5H_5)$_2$Nb[P(C_2H_5)$_3$]H, 11105-80-9; (η^5-C_5H_5)$_2$Ta[P(C_2H_5)$_3$]H, 11105-81-0; sodium bis(2-methoxyethoxy)aluminum, 22722-98-1.

Supplementary Material Available: A listing of least-squares planes, thermal parameters, and observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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