60 min and at intensities spanning a 20-fold range depending upon chalcogenapyrylium dye reactivity. In some cases, lower chalcogenapyrylium dye concentrations were also used to check the validity of eq 6 for determining $k(^1O_2)$. Photooxidation rates were measured at conversion levels of ≤10% to allow use of initial chalcogenapyrylium dye concentrations in eq 6. A k_{dec} value of 1.7×10^5 s^{-1} was used for 50% aqueous methanol.[31]

Methylene blue sensitized photooxidation efficiencies were also measured for **1j** in water and deuterium oxide. Solutions contained 3×10^{-6} M **1j** and 8×10^{-6} M methylene blue. A low dye concentration was used to minimize reduction of the relatively long singlet oxygen lifetime in deuterium oxide via reactive or physical quenching. A $k(^1O_2)$ value was calculated for **1j** in water with a k_{dec} of 2.4×10^5 s^{-1} and a value of $\Phi(^1O_2)$ for methylene blue of 0.50.[30b]

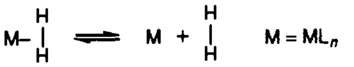
Molecular Hydrogen Complexes of the Transition Metals. 7. Kinetics and Thermodynamics of the Interconversion between Dihydride and Dihydrogen Forms of $W(CO)_3(PR_3)_2H_2$ Where R = Isopropyl and Cyclopentyl

G. Rattan K. Khalsa,[†] Gregory J. Kubas,* Clifford J. Unkefer, Lori Stepan Van Der Sluys, and Kimberly A. Kubat-Martin

Contribution from Los Alamos National Laboratory, Inorganic and Structural Chemistry Group (INC-4), MS-C346, Los Alamos, New Mexico 87545. *Received August 24, 1989*

Abstract: Kinetic and thermodynamic parameters have been obtained for the equilibrium system $H_2W(CO)_3(PR_3)_2 \rightleftharpoons W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$. The systems studied include a newly synthesized complex where R = cyclopentyl. ^{31}P NMR spin saturation transfer studies over a temperature range of 288–310 K afford values of $\Delta H^‡ = 10.1 \pm 1.8$ kcal/mol, $\Delta S^‡ = -19.9 \pm 6.0$ eu, and $\Delta G^‡ = 16.0 \pm 0.2$ kcal/mol (298 K) for the dihydrogen to dihydride exchange process where R = isopropyl. Exchange between nonequivalent hydrides in the seven-coordinate dihydride complex corresponds to $\Delta G^‡ \approx 11$ kcal/mol (253 K) derived from NMR coalescence data. ^{1}H{^{31}P} NMR equilibrium studies for the formation of the dihydrogen complex from the dihydride complex over the temperature range 265–309 K produce the following: $\Delta H° = -1.2 \pm 0.6$ kcal/mol, $\Delta S° = -1.2 \pm 2.1$ eu, and $\Delta G° = -0.80 \pm 0.12$ kcal/mol (298 K) for R = isopropyl; $\Delta H° = -1.5 \pm 0.4$ kcal/mol, $\Delta S° = -2.4 \pm 1.4$ eu, and $\Delta G° = -0.75 \pm 0.12$ kcal/mol (298 K) for R = cyclopentyl.

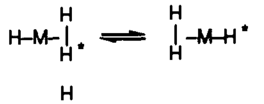
Although numerous η^2-H_2–transition metal complexes have now been characterized,[1] no comprehensive thermochemical studies have been reported concerning the stability and energetics of dihydrogen coordination relative to classical hydride binding. Metal-bound dihydrogen/hydride systems exhibit a greater variety of dynamic behavior than any other ligand systems. The η^2-H_2 ligand undergoes reversible dissociation (eq 1), rotation about the M–H_2 axis (eq 2), isotopic scrambling (eq 3), exchange with hydride coligands (eq 4), and reversible cleavage to hydride ligands (oxidative addition, eq 5), all of which essentially can occur simultaneously and as equilibrium processes. In regard to eq 4, activation parameters for intramolecular interchange of hydride and dihydrogen ligands have been measured for several cationic complexes.[2-4] From a fundamental standpoint, eq 5 is the most significant of the above transformations because it represents not only the key step in hydrogen activation but also *the breaking and re-forming of a metal-coordinated σ-bond as an equilibrium process*, a quite extraordinary situation. Such dynamic equilibria between dihydrogen and dihydride forms have been found to exist in solution for several complexes,[5-9] including $W(CO)_3(PR_3)_2H_2$,[5] $[CpRu(Me_2PC_2H_4PMe_2)H_2]BF_4$,[6] and $[(C_5Me_5)Re(CO)(NO)H_2]BF_4$,[7] with the H_2 form being predominant (essentially 100% in the *solid* state). Terminology-wise, "isomerism" or "tautomerism" seems inadequate to describe the situation here, since relatively large changes in metal–ligand geometry, coordination number, and formal oxidation state are involved. The seven-coordinate dihydride "tautomer" of the tungsten complex is stereochemically nonrigid on the NMR time scale, adding yet a further dimension to the already rich dynamics of this system.[5] The rate of oxidative addition of bound η^2-H_2 to produce the dihydride form of the Ru complex was reported to be considerably lower than that in the tungsten system (as estimated from pub-



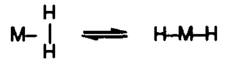
$$M{-}\overset{H}{\underset{H}{|}} \rightleftharpoons M + \overset{H}{\underset{H}{|}} \qquad M = ML_n \qquad (1)$$

$$M{-}\overset{H}{\underset{H^*}{|}} \rightleftharpoons M{-}\overset{H^*}{\underset{H}{|}} \qquad (2)$$

$$M{-}\overset{H}{\underset{H}{|}} + \overset{D}{\underset{D}{|}} \rightleftharpoons M{-}\overset{H}{\underset{D}{|}} + \overset{H}{\underset{D}{|}} \qquad (3)$$



$$H{-}M{-}\overset{H}{\underset{H^*}{|}} \rightleftharpoons \overset{H}{\underset{H}{|}}{-}M{-}H^* \qquad (4)$$



$$M{-}\overset{H}{\underset{H}{|}} \rightleftharpoons H{-}M{-}H \qquad (5)$$

[†] On leave of absence from the Department of Chemistry, Thiel College, Greenville, PA.

(1) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. Kubas, G. J. *Comments Inorg. Chem.* **1988**, *7*, 17.

(2) Morris, R. H.; Sawyer, J. F.; Shiralion, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581.

(3) Bautista, M. T.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780.

(4) Bautista, M. T.; Earl, K. A.; Morris, R. H. *Inorg. Chem.* **1988**, *27*, 1124.

(5) (a) Kubas, G. J.; Ryan, R. R.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339. (b) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000.

(6) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865.

(7) Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824.

(8) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548.

(9) (a) Arliguie, T.; Chaudret, B. *J. Chem. Soc., Chem. Commun.* **1989**, 155. (b) Mura, P.; Segre, A.; Sostero, S. *Inorg. Chem.* **1989**, *28*, 2853. (c) Cappellani, E. P.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Steel, M. R. *Inorg. Chem.* **1989**, *28*, 4437.

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lished NMR data for $W(CO)_3(PR_3)_2H_2)$,[6] indicating an opportunity for studying kinetic effects of metal–ligand variation. Other systems exhibiting evidence for interconversion between dihydrogen and dihydride forms of the same complex include $[MClH_2(R_2PC_2H_4PR_2)_2]^+$ (M = Fe, Ru, Os; R = Me, Ph),[9c] $RuH_2(OCOCF_3)_2(PCy_3)_2$,[9a] and air-stable, tripodal $[\{P(CH_2CH_2PPh_2)_3\}RhH_2]BF_4$, which is an octahedral dihydride complex in the solid state and in solution below 183 K, but which converts to a trigonal-bipyramidal dihydrogen form in solution above 183 K.[8] A novel temperature-dependent solution equilibrium between paramagnetic and diamagnetic species involving η^2-H_2 has been proposed for $IrH_2Cl_2(PR_3)_2$ (R = *i*-Pr, Cy).[9b] Examples of complexes that ostensibly are hydrides, but which contain small equilibrium or transient amounts of dihydrogen species, undoubtedly exist and have often been proposed to rationalize anomalous reactivity and NMR phenomena.[10] In contrast to the above dynamic situations, *irreversible* dihydrogen → dihydride conversions have been reported for $[CpRuL_2H_2]^+$ with $L_2 = (PPh_3)_2$, $Ph_2PC_2H_4PPh_2$.[11]

Using NMR methods, we have derived kinetic and thermodynamic parameters for the interconversion between dihydride and dihydrogen forms of $W(CO)_3(PR_3)_2(H_2)$. These data provide additional information on the energetics of transformation of η^2-H_2–transition metal complexes to dihydride oxidative addition products. Part of these studies have been carried out on a new complex where R = cyclopentyl (Cyp), the preparation and properties of which are also reported here.

Experimental Section

$W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$[5b] (I), $W(CO)_3(PCy_3)_2(H_2)$[5b] (III), $W(CO)_3(cht)$[12] (cht = η^6-cycloheptatriene), and $PCyp_3$[13] were prepared according to literature methods. The $PCyp_3$ prepared as starting material contained some minor impurities and was a liquid; when pure, it is a low-melting solid. Toluene-d_8 and benzene-d_6 from Aldrich were freeze–thaw degassed, dried over Na/Hg amalgam, and stored under Ar, He, or H_2. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on an IBM AF-250 spectrometer unless otherwise specified. ^1H chemical shift data are reported (ppm) relative to the residual proton resonance of benzene-d_6 at 7.15 ppm or that of the methyl group of toluene-d_8 at 2.09 ppm. ^{31}P chemical shifts are referenced to phosphoric acid, with positive shifts being downfield. IR absorption spectra were recorded as Nujol mulls between KBr plates on a Digilab FTS-40 spectrophotometer at 25 °C.

Preparation of $W(CO)_3(PCyp_3)_2(H_2)$ (II). The preparation was similar to that for the P-*i*-Pr_3 analogue.[5b] A mixture of $W(CO)_3(cht)$ (0.9 g, 2.5 mmol), $PCyp_3$ (1.6 mL, ca 5.5 mmol), and heptane (6 mL) was stirred under hydrogen (1 atm). The solution became orange; precipitation of the yellow microcrystalline product began within 10 min and was complete after 3 h. The product was collected on a frit, washed with heptane (2 × 4 mL), and dried, initially in a hydrogen stream and then by brief (~30-s) pumping in vacuo followed by readdition of a hydrogen atmosphere (yield ~60–75%). Yellow $W(CO)_3(PCyp_3)_2(H_2)$ (II) is slightly soluble in alkanes and moderately soluble in toluene and benzene. Nujol mull IR bands similar to those for $W(CO)_3(PCy_3)_2(H_2)$[5b] were observed at 1959 and 1843 cm^{-1} for $\nu(CO)$ and 1565 (br) and 938 cm^{-1} for $\nu_{as}(W\text{–}H_2)$ and $\nu_s(W\text{–}H_2)$. A W–H_2 deformation appeared at 462 cm^{-1}. ^1H NMR (25 °C, toluene-d_8): −4.49 (br, η^2-H_2), −3.57 (br, dihydride form), 2.17, 1.76, 1.50 ($PCyp_3$ ligands).

IR of the D_2 isotopomer (prepared by exposing the solid H_2 complex to a large excess of D_2 for 18 h at 25 °C) showed $\nu(CO)$ at 1959 and 1832 cm^{-1}, $\nu_s(W\text{–}D_2)$ at 700 cm^{-1}, and a $\delta(W\text{–}D_2)$ mode at 440 cm^{-1}.

Preparation of $W(CO)_3(PCyp_3)_2$. As the coordinatively unsaturated compounds $M(CO)_3(PCy_3)_2$ (M = Mo, W)[14] have been shown to be excellent precursors to molecular hydrogen species,[15] we attempted to synthesize the corresponding $W(CO)_3(PCyp_3)_2$ via the same reaction route. $W(CO)_3(cht)$ and a stoichiometric amount of $PCyp_3$ were combined in a dry, degassed 4:1 hexane/toluene mixture under argon and stirred at room temperature overnight. No identifiable products were isolated from this reaction mixture. However, the complex was easily isolated through removal of H_2 from $W(CO)_3(PCyp_3)_2(\eta^2\text{-}H_2)$. A yellow-orange solution of II in rigorously degassed nonane was stirred under a static vacuum at room temperature overnight, causing slow removal of H_2. The product precipitated in nearly quantitative yield as purple-black microcrystals.

The complex is extremely air and solvent sensitive and reacts irreversibly with N_2. As in the case of the η^2-H_2 complexes, this compound is much more soluble in nonpolar solvents than are the related complexes $W(CO)_3(PCy_3)_2$ and $Mo(CO)_3(PCy_3)_2$.[14]

Attempted Synthesis of Mo Analogues. Stirred heptane solutions of $Mo(CO)_3(cht)$ and $PCyp_3$ under either 1 or 3 atm of H_2 at room temperature did not produce the expected $Mo(CO)_3(PCyp_3)_2(\eta^2\text{-}H_2)$. IR spectra of the reaction mixtures after they were stirred overnight showed a considerable amount of the starting material $Mo(CO)_3(cht)$ along with some other unidentified products. The elevated pressure reaction gave a yellow precipitate showing IR bands at 1902 and 1746 cm^{-1} and no obvious bands due to $PCyp_3$.

Stirred solutions of $Mo(CO)_3(cht)$ and $PCyp_3$ in heptane under Ar also did not give rise to the five-coordinate $Mo(CO)_3(PCyp_3)_2$, and mixtures of $Mo(CO)_3(cht)$, $PCyp_3$, and N_2 in heptane did not produce an N_2 complex analogous to the one observed upon addition of N_2 to $W(CO)_3(PCyp_3)_2$. In each case, an IR spectrum of the reaction mixture after overnight stirring showed a considerable amount of starting material.

Spin Saturation Transfer Experiments. $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ (I), was prepared as a saturated toluene-d_8 solution (~0.5 M) under Ar/H_2 in a sealed 10-mm NMR tube. Variable-temperature $^{31}P\{^1H\}$ NMR (101.26-MHz) spectra were collected on an IBM AF-250 NMR spectrometer equipped with a Bruker VT-1000 temperature controller. Temperatures were determined to be constant within 0.5 °C by measuring the peak separation of a methanol calibration sample before and after each experiment. A Bruker BSV3 decoupler unit was used for single-frequency ^{31}P saturation. Saturation transfer experiments[16] were performed by saturating the ^{31}P resonance of the dihydride complex (IB) 189 Hz downfield of the observed resonance of the dihydrogen complex (IA) for a variable length of time (VD = 0.0100–3.00 s; 18 values) followed by a $\pi/2$ observation pulse and a relaxation delay of 15 s (~ $5T_1$). Each spectrum consisted of 32 pulses. A control spectrum was collected for each value of VD by ^{31}P saturation at a frequency 189 Hz upfield from the resonance of IA. No decrease in the intensity of resonance IA was observed in the control spectra. Absolute intensity values were determined by the Aspect 3000 computer relative to a constant resonance, $W(CO)_4(P\text{-}i\text{-}Pr_3)_2$, a noninteracting impurity in the sample tube. A three-parameter nonlinear least-squares fit of the intensity of the observed resonance as a function of saturation time (VD) produced values for M_{0A}, $M_{zA(\infty)}$, and τ_{1A}. T_{1A} was derived from the magnetization equation 16

$$M_{zA(\infty)}/M_{0A} = \tau_{1A}/T_{1A}$$

where M_{0A} and $M_{zA(\infty)}$ are the ^{31}P equilibrium z magnetizations (signal intensities) of site A without and with saturation of site B, respectively. T_{1A} is the spin–lattice relaxation time of the nucleus at site A, and $1/\tau_{1A} = 1/T_{1A} + 1/\tau_A$ is the mean lifetime of the nucleus at site A. The activation parameters, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$, were obtained from a nonweighted linear least-squares fit of ln (k_A/T) versus $1/T$ utilizing the Eyring equation: $k = (Kk_BT/h)e^{-\Delta G^{\ddagger}/RT}$ (assuming the transmission coefficient $K = 1$).[17] Error estimates represent 90% confidence limits.

Equilibrium Studies. Saturated solutions of I and II (~0.5 M) in toluene-d_8 were sealed under Ar/H_2 in 10-mm NMR tubes. Variable-temperature $^1H\{^{31}P\}$ NMR spectra were obtained at 200.13 MHz with a Bruker AM-200WB NMR spectrometer equipped with a Bruker VT-100 temperature controller. Temperature measurements were made with a thermocouple inserted into a temperature-equilibrated spinning tube of toluene to a fixed depth before and after each experiment. Temperatures were found to be constant to within ±1 °C. Protons were observed utilizing the ^1H-decoupler coil of an X-nucleus probe; the X-nucleus observe coil was used for ^{31}P decoupling. ^{31}P decoupling was carried out with an external frequency synthesizer (locked to the spec-

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(10) (a) Clark, H. C.; Hampden Smith, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 3829. (b) Rhodes, L. F.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 259. (c) Henderson, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 1670. (d) Vrieze, K.; van Koten, G. *Inorg. Chim. Acta* **1985**, *100*, 79. (e) Choplin, A.; Besson, B.; D'Ornelas, L.; Sanchez-Delgado, R.; Baset, J.-M. *J. Am. Chem. Soc.* **1988**, *110*, 2783.

(11) (a) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1675. (b) Amarasekera, J.; Rauchfuss, T. B. *Inorg. Chem.* **1989**, *28*, 3875. (c) Chinn, M. S. Ph.D. Dissertation, Yale University, 1989. (d) Heinekey, D. M. Private communication.

(12) Kubas, G. J. *Inorg. Chem.* **1983**, *22*, 692.

(13) Brainard, R. L.; Miller, T. M.; Whitesides, G. M. *Organometallics* **1986**, *5*, 1481.

(14) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294.

(15) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.

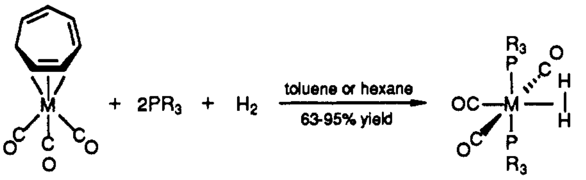
(16) Forsén, S.; Hoffman, R. A. *J. Chem. Phys.* **1963**, *39*, 2892.

(17) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, England, 1982.

trometer master clock), a 40-dB gain preamplifier, and a 10-W rf amplifier. The rf carrier was centered on the $W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$ ^{31}P signal and was modulated with a square wave (100 Hz). Spectra of I and II consisted of 3000 scans. Relative integrals were obtained by fitting the two broad overlapping dihydride and dihydrogen resonances as a sum of Lorentzian curves. The Lorentzian line-shape analysis was carried out on a VAX 11/780 computer with a modified Levenberg–Marquart algorithm implemented by the NMRI software package supplied by the National Institutes of Health Resource for NMR Data Analysis (Syracuse, NY). The line widths at half-intensity were determined from the NMR spectra prior to fitting. Best fits were deemed to be those with the closest match of line widths and shapes of the calculated spectra with those of the observed spectra. Thermodynamic parameters, $\Delta H°$, $\Delta S°$, and $\Delta G°$, were determined from a nonweighted linear least-squares fit of $-\ln K_{eq}$ versus $1/T$. Error estimates represent 95% confidence limits.

Results

Preparation, Properties, and Infrared Spectra of $W(CO)_3(PCyp_3)_2(H_2)$. The success of synthesizing the dihydrogen complexes $M(CO)_3(PR_3)_2(H_2)$ or their unsaturated precursors by displacement of cht from $M(CO)_3(cht)$ (M = Mo, W) is remarkably dependent on the nature of the trialkylphosphine reactants. The reaction in eq 6 has been found thus far to succeed only for $PR_3 = PCy_3$ and $PCy_2(i\text{-}Pr)$ (M = Mo, W) or $P\text{-}i\text{-}Pr_3$ (M = W). Use of an argon atmosphere gives the unsaturated precursor to the H_2 complexes, $M(CO)_3(PR_3)_2$, which contains an intramolecular *agostic* M···H–C interaction and, depending on temperature and H_2 pressure, can exist in equilibrium with the H_2 complex (eq 1). Phosphines with cone angles less than ~160° give $M(CO)_3(PR_3)_3$ regardless of stoichiometric ratios of reactants or reaction atmosphere, while a litany of bulky phosphines (e.g., *t*-Bu, *s*-Bu) produce only uncharacterized species. Even with such a limited range of phosphines, the stability and solubility of the H_2 complexes vary markedly. The $W\text{-}P\text{-}i\text{-}Pr_3$ complex, for example, loses H_2 under partial vacuum much more readily (~5 min, 25 °C, nonane, ~5 Torr) than the PCy_3 analogue (20–30 min, ~50 °C, toluene, 50–100 Torr). The $W\text{-}H_2$ species are stable in solution under 1 atm of H_2, but the Mo analogues partially dissociate to deep purple $Mo(CO)_3(PR_3)_2$. The PCy_3 complexes are only slightly soluble in toluene or benzene, making NMR studies difficult, while the $P\text{-}i\text{-}Pr_3$ species is very soluble even in hexane. Decomposition or substitution of $\eta^2\text{-}H_2$ occurs in most nonhydrocarbon solvents, with one exception being THF, which displaces little if any H_2 and binds only very weakly to $M(CO)_3(PR_3)_2$ because of steric repulsion by the phosphines.

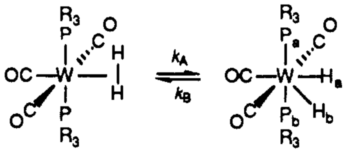


(6)

In order to determine whether a new analogue could be synthesized with more advantageous solubility/stability, spectroscopic, or even structural properties (the PCy_3 and $P\text{-}i\text{-}Pr_3$ complexes were crystallographically disordered), the reaction in eq 6 was carried out with tricyclopentylphosphine (hexane as solvent). The reaction proceeded similarly to those for R = Cy or *i*-Pr,[5b] and the yellow H_2 complex precipitated in good yield. $W(CO)_3(PCyp_3)_2(H_2)$ is readily studied by NMR since it is moderately soluble in toluene and is stable to H_2 dissociation under 1 atm of H_2. The X-ray structure[18] has the same molecular configuration as the other analogues[14,18] and unfortunately once again exhibits disorder between the H_2 ligand and the CO trans to it. Cone angles were calculated for the PCy_3, $PCyp_3$, and $P\text{-}i\text{-}Pr_3$ ligands (171°, 165°, and ~163°,[19] respectively) from the single-crystal X-ray structures (with hydrogens) of $W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$, I, II, and III.[15,18] The calculated values for PCy_3 and $P\text{-}i\text{-}Pr_3$ are close to those reported by Tolman (170° and 160°, respectively).[20] The order of decreasing cone angle parallels the order of decreasing stability and increasing solubility of the dihydrogen complexes. The Nujol mull IR of $W(CO)_3(PCyp_3)_2(H_2)$ was similar to that of the PCy_3 and $P\text{-}i\text{-}Pr_3$ congeners.[7] The positions of $\nu_{as}(WH_2)$ and $\nu_s(WH_2)$, 1565 and 938 cm^{-1}, were about 15 cm^{-1} lower than those of the PCy_3 derivative.

As was the case for the $P\text{-}i\text{-}Pr_3$ congener, the agostic complex $W(CO)_3(PCyp_3)_2$ could not be prepared directly from $W(CO)_3(cht)$ (eq 6, argon atmosphere). However, it could be isolated as a deep purple solid by removal of H_2 from $W(CO)_3(PCyp_3)_2(H_2)$ in solution in vacuo. Molybdenum–$PCyp_3$ analogues could not be prepared, once again paralleling the situation for the $P\text{-}i\text{-}Pr_3$ case.

Kinetic and Thermodynamic Studies of the Interconversion between Dihydride and Dihydrogen Forms of $W(CO)_3(PR_3)_2H_2$ (R = Cyp, *i*-Pr). In terms of an energy profile, oxidative addition of H_2 to a metal complex had been thought to give a shallow minimum corresponding to an unstable, transient metal–H_2 interaction, followed by a rapid, highly downhill process of H_2 cleavage to a dihydride. The observation[5] by NMR and IR that the dihydrogen complexes $W(CO)_3(PR_3)_2(H_2)$ can exist in dynamic solution equilibrium with their dihydride forms (eq 4) was thus quite surprising and revealing in that it demonstrated that in some cases there can be little energy difference between the two forms of coordination. The seven-coordinate dihydride form (~20–30%) has not as yet been isolated, but NMR evidence has shown that the hydrides H_a and H_b, as well as the phosphorus atoms P_a and P_b, are inequivalent at low temperature.



(7)

IA R = *i*-Pr IB
IIA = Cyp IIB
IIIA = Cy IIIB

In order to further understand and quantify the activation of H_2 on the tungsten complexes, we have carried out kinetic and thermodynamic studies of this dihydrogen–dihydride equilibrium.

$^{31}P\{^1H\}$ NMR spin saturation transfer studies[16] were carried out for $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ (I) in toluene-d_8 by saturating the resonance for the dihydride complex, IB, over a variable time range and monitoring the concomitant decrease in magnetization of the resonance of the dihydrogen complex, IA [k_A = 5.82 s^{-1} (288.4 K), 12.4 s^{-1} (300.2 K), 19.7 s^{-1} (309.6 K), 22.5 s^{-1} (309.9 K)]. Attempts to measure k_B by transferring saturation in the reverse direction (saturate IA, observe IB) were less successful ($k_B \approx 63$ s^{-1} at 298.6 K). The appreciably lower intensity of resonance IB relative to that of IA (6-fold lower) makes it considerably more difficult to measure reliable intensity values for IB without collecting a prohibitively large number of scans. The temperature range for ^{31}P saturation transfer studies at 101.26 MHz was limited to the region 268–310 K for this complex due to exchange broadening at surrounding temperatures. $^1H\{^{31}P\}$ NMR spin saturation studies were attempted in both forward and reverse directions of the equilibrium. The T_1 of the dihydrogen resonance was quite short compared to the lifetime for the exchange process; thus, the dihydrogen resonance could not be completely saturated relative to the time required for saturation transfer to take place. The Eyring plot of ln (k_A/T) versus $1/T$ for eq 7 is shown in Figure 1. Activation parameters for the conversion from the dihydrogen to the dihydride form of complex I are as follows: $\Delta H^{\ddagger}$ = 10.1 ± 1.8 kcal/mol, $\Delta S^{\ddagger}$ = −19.9 ± 6.0 eu, $\Delta G^{\ddagger}$ = 16.0 ± 0.2 kcal/mol (298 K). Exchange between nonequivalent hydrides in the seven-coordinate dihydride complex corresponds to $\Delta G^{\ddagger}$ = 11 kcal/mol (253 K) derived from NMR coalescence data.[5b]

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[18] Kubat-Martin, K. A.; Kubas, G. J.; Khalsa, G. R. K.; Stepan Van Der Sluys, L.; Wasserman, H. J.; Ryan, R. R. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, submitted for publication.

[19] This value is approximate due to the disorder of the $P\text{-}i\text{-}Pr_3$ ligands in the X-ray structure.

[20] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

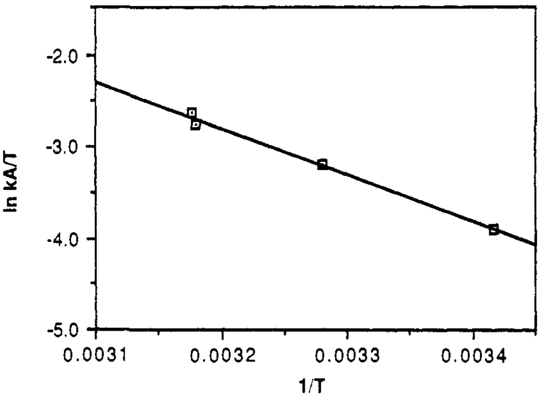

Figure 1. ln (k_A/T) vs $1/T$ for the conversion of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(\eta^2\text{-}H_2)$ to $WH_2(CO)_3(P\text{-}i\text{-}Pr_3)_2$.

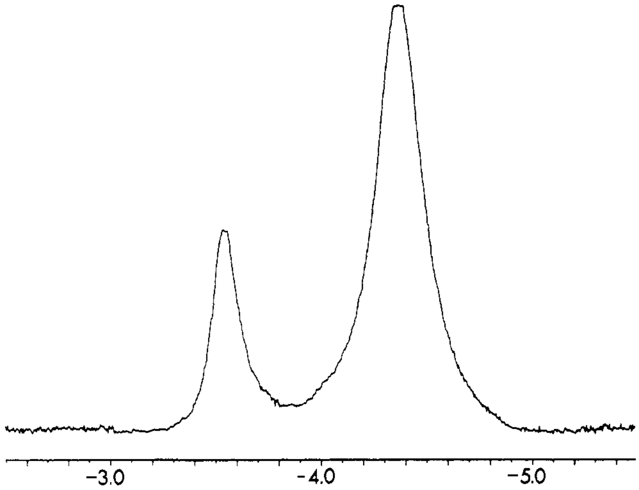

Figure 2. ^{31}P-decoupled ^{1}H NMR (200 MHz) spectrum of $W(CO)_3(PCyp_3)_2(\eta^2\text{-}H_2)$ obtained at 24 °C in toluene-d_8, showing signals due to dihydrogen (major) and dihydride (minor) tautomers.

$^1H\{^{31}P\}$ NMR equilibrium studies were performed over the temperature interval 263–309 K for the equilibrium system $H_2W(CO)_3(PR_3)_2 \rightleftharpoons W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$ for complexes I (R = *i*-Pr) and II (R = cyclopentyl). In order to increase the signal to noise ratio, simplify the line-shape analysis, and eliminate the complications that would arise from exchange broadening of the multiplet that results from ^{1}H–^{31}P coupling, ^{1}H NMR equilibrium studies were obtained under conditions of ^{31}P decoupling. Between 263 and 309 K, the magnetically nonequivalent dihydride resonances are undergoing fast exchange in the NMR time scale, thereby producing a single resonance. In this same temperature region, the dihydrogen and dihydride resonances are in the intermediate- to slow-exchange regime in their interconversion process and appear as two separate resonances (Figure 2). However, in this temperature range, the spin-lattice (T_1) relaxation times of the dihydrogen and the dihydride are exchange-averaged.[5b] The ^{1}H–^{1}H dipolar interaction is likely the dominant mechanism contributing to relaxation of both the dihydrogen and the dihydride even in the slow-exchange limit. Since the T_1's are exchange-averaged, the ^{31}P–^{1}H dipolar interaction will contribute equally to the relaxation of both species, and therefore, any NOE resulting from ^{31}P decoupling will contribute equally to the intensity of both resonances. Equilibrium constants were derived from line-shape analysis of the overlapping dihydrogen and dihydride resonances. The line widths of the dihydride and the dihydrogen resonances in the NMR spectra of I varied from minimum values of 33 and 38 Hz, respectively, at 291 K to maximum values of 58 Hz and 91 Hz at 305 K, respectively, over the temperature range examined. The line widths of the dihydride and the dihydrogen resonances in the NMR spectra of II varied from minimum values of 27 and 50 Hz, respectively, at 297 K to maximum values of 55 Hz at 273 K and 68 Hz at 305 K, respectively, over the temperature range investigated. The lower solubility and broader line widths of $W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$ (III) compared to those of I and II prevented our obtaining reliable values for thermodynamic parameters for the dihydride/dihydrogen equilibrium for III. The observed equilibrium constants for III varied from 1.5 at 298 K to 3.4 at 284 K. The broad line widths and low intensity of the dihydride/dihydrogen resonances relative to the phosphine proton resonances produce an inherent uncertainty of about 5% in the equilibrium constants. Van't Hoff plots for I and II, respectively, are shown in Figures 3 and 4. Equilibrium constants for I and II are given in Table I. Thermodynamic parameters for the formation of $W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$ from the dihydride complex are as follows: $\Delta H° = -1.2 \pm 0.6$ kcal/mol, $\Delta S° = -1.2 \pm 2.1$ eu, and $\Delta G° = -0.80 \pm 0.12$ kcal/mol (298 K) for R = isopropyl; $\Delta H° = -1.5 \pm 0.4$ kcal/mol, $\Delta S° = -2.4 \pm 1.4$ eu, and $\Delta G° = -0.75 \pm 0.12$ kcal/mol (298 K) for R = cyclopentyl.

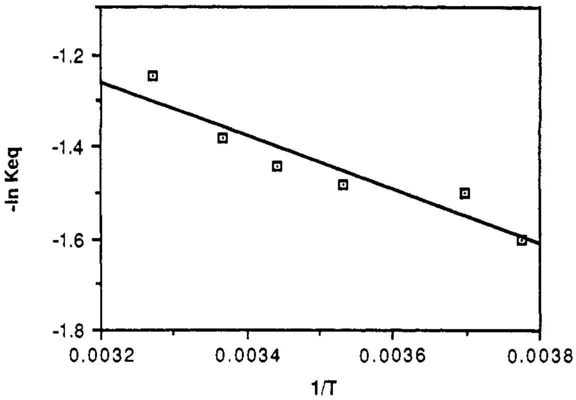

Figure 3. $-\ln K_{eq}$ vs $1/T$ for the equilibrium $WH_2(CO)_3(P\text{-}i\text{-}Pr_3)_2 \rightleftharpoons W(CO)_3(P\text{-}i\text{-}Pr_3)_2(\eta^2\text{-}H_2)$.

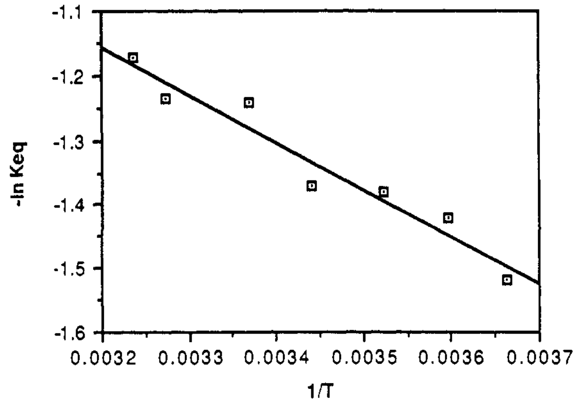

Figure 4. $-\ln K_{eq}$ va $1/T$ for the equilibrium $H_2W(CO)_3(PCyp_3)_2 \rightleftharpoons W(CO)_3(PCyp_3)_2(\eta^2\text{-}H_2)$.

Table I. Equilibrium Constants for the Dihydride–Dihydrogen Equilibrium $WH_2(CO)_3(PR_3)_2 \rightleftharpoons W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$

R = *i*-Pr		R = Cyp	
K_{eq}[a]	T (°C)	K_{eq}[a]	T (°C)
3.5	32	3.2	36
4.0	24	3.4	32
4.2	18	3.5	24
4.4	10	3.9	18
4.5	−3	4.0	11
5.0	−8	4.2	5
		4.6	0

[a] Estimated error in K_{eq} values is ±5%.

Discussion

The results of the thermodynamic studies are summarized in the reaction profile shown in Figure 5 beginning with H_2 addition to $W(CO)_3(PR_3)_2$. The latter contains an agostic interaction, and thus the true energy of the "naked" 5-coordinate precursor is ~10

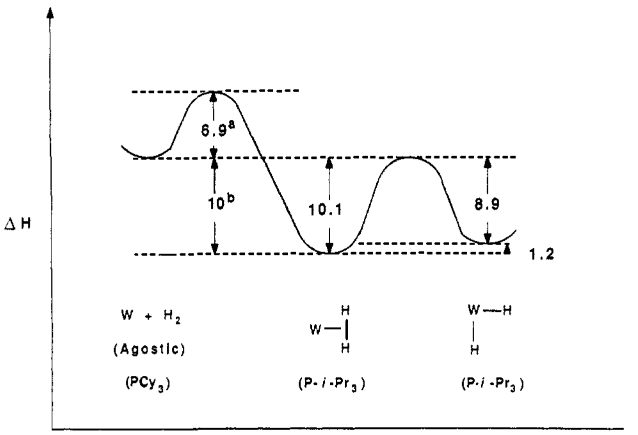

Figure 5. Reaction coordinate diagram for H_2 + $W(CO)_3(PR_3)_2$ (agostic) → $W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$ → $H_2W(CO)_3(PR_3)_2$. The data for the initial step were obtained from ref 21 and 27 (denoted by superscripts a[21,27] and b[21]) and were for the R = Cy analogue (the values for R = *i*-Pr should not differ significantly).

kcal/mol higher (the estimated[21] energy of the W–agostic interaction). The tungsten–dihydrogen complex resides in a much deeper potential energy well than could have been imagined from early conceptions of hydrogen activation on metal centers, including relatively recent theoretical studies.[22] An ab initio study of a model for our complexes, $W(CO)_3(PH_3)_2H_2$, found that the dihydride complexes with pseudo-pentagonal-bipyramid geometry formed by bending back either the OC–W–CO bonds or the P–W–P bonds during oxidative addition of H_2 were less stable in energy than the dihydrogen complex by 17 and 10 kcal/mol, respectively.[23] Our equilibrium studies for $W(CO)_3(PR_3)_2H_2$ (R = *i*-Pr, Cyp) show that the dihydrogen complex is actually only 1–2 kcal/mol lower in enthalpy than the dihydride tautomer in solution. Obviously, the model complex with PH_3 ligands does not adequately represent the electronic and steric features of the bulky phosphine ligands in the actual complexes. Also, NMR and IR studies of $W(CO)_3(PR_3)_2H_2$ suggest that the dihydride complex actually has a monocapped octahedral structure in solution, possibly with a CO or a hydride in the capping position.[5b] It is not clear to what extent these structural differences would aid in resolving the discrepancy between calculated and observed values. The important point, however, is that the energy differences and kinetic barriers between the dihydrogen and dihydride forms of these complexes are so low that they can be truly considered to be *tautomers* from these criteria. Hydrogen coordination to metals can thus be best described as an equilibrium system between the two tautomeric forms, with the electronics at the metal controlling where the equilibrium lies. Electron-rich metal centers or the presence of a donor rather than acceptor ligand trans to η^2-H_2 favors the dihydride tautomer by back-donation of electrons into the σ^* orbital of the η^2-H_2 form, promoting cleavage of the H–H bond. The energy difference between the dihydrogen and dihydride forms would then be much greater than the 1–2 kcal/mol observed for $W(CO)_3(PR_3)_2(H_2)$. An excellent example of this electronic control is the series $MoH_2(CO)(R_2PC_2H_4PR_2)_2$ in which spectroscopic and crystallographic data show that an octahedral dihydrogen complex exists for R = Ph (CO trans to η^2-H_2), but a pentagonal-bipyramidal *dihydride* results for the more electron-releasing phosphines with R = Et or *i*-Bu (CO cis to equatorial hydrides).[24] Because P-*i*-Bu_3 is similar to PPh_3 in cone angle,[20] differences in ligand bulk could be eliminated as a significant factor favoring either structure. Although clear evidence for the presence of dihydrogen–dihydride solution equilibria was not found in this system, higher H_2 lability and a lower NMR relaxation time, T_1, for the *i*-Bu species compared to the R = Et analogue indicated that a small concentration of the dihydrogen form may be present. It is also probable that many "classical" metal–polyhydride complexes,[10,25] especially those that can be induced to dissociate hydrogen photochemically or by other means, contain undetectably small quantities of dihydrogen tautomer. This labile dihydrogen form offers a ready pathway through H_2 loss to reactive, unsaturated species, and several catalytic hydrogenation systems based upon this strategy have recently been reported.[26]

The rate constant for oxidative addition of the dihydrogen ligand of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2H_2$ to produce the dihydride form was determined to be 12.4 s^{-1} (300 K) with a free energy of activation of 16.0 kcal/mol. The reductive elimination of the dihydride in IB to produce the dihydrogen complex is even more rapid ($k \approx 63\ s^{-1}$ at 299 K; $\Delta G^{\ddagger} = 15.2$ kcal/mol). Hoff and co-workers[27] have measured these rates for the PCy_3 analogue by stopped-flow kinetic techniques ($k = 18\ s^{-1}$ for dihydrogen → dihydride and 37 s^{-1} for the reverse, at 298 K); their results compare favorably to our values for the P-*i*-Pr_3 complex. An activation enthalpy barrier of 10.1 (1.8) kcal/mol and a standard enthalpy change of 1.2 (0.6) kcal/mol for the oxidative addition of η^2-H_2 to form the dihydride complex of I imply a barrier of 8.9 (2.4) kcal/mol for the reverse reductive elimination process for the P-*i*-Pr_3 complex. This value is somewhat lower than that measured by Hoff and co-workers for reductive elimination in the PCy_3 congener (14.4 ± 0.5 kcal/mol).

Comparison of the kinetic and thermodynamic results for the tungsten complexes can be made to those reported for ruthenium and rhenium species that also show dihydrogen/dihydride equilibria. As already noted by Chinn and Heinekey,[6] the oxidative addition process is considerably more facile for $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ than for $[CpRu(dmpe)(H_2)]BF_4$ [$k = 9.0 \times 10^{-3}\ s^{-1}$ (298 K); $\Delta G^{\ddagger} = 20.4$ kcal/mol]. They have also recently measured the rate of the reverse process, reductive elimination, for $[(\eta^5\text{-}C_5Me_5)Re(CO)(NO)H_2]BF_4$ → $[(\eta^5\text{-}C_5Me_5)Re(CO)(NO)(\eta^2\text{-}H_2)]BF_4$ to be 2.5 s^{-1} at 190 K from spin saturation transfer (7:93 ratio of tautomers at 225 K).[7] This latter system thus appears to be the most facile, with a significantly lower activation barrier $\Delta G^{\ddagger}$ of 10.2 kcal/mol for dihydrogen → dihydride conversion. A semiquantitative free energy diagram showed the energy difference ΔG° between the dihydrogen and dihydride tautomers to be 1.0 kcal/mol here, similar to that for $W(CO)_3(PR_3)_2(H_2)$.

Interconversion between dihydrogen and dihydride forms is not always reversible; Conroy-Lewis and Simpson[11a] have on protonation of the neutral hydrides observed exclusively the dihydrogen form for $[CpRu(Ph_2PCH_2PPh_2)(H_2)]^+$ while only the

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(21) Gonzalez, A. A.; Zhang, K.; Nolan, S. P.; de la Vega, R. L.; Mukerjee, S. L.; Hoff, C. D.; Kubas, G. J. *Organometallics* **1988**, *7*, 2429.

(22) (a) Sevin, A. *Nouv. J. Chim.* **1981**, *5*, 233. (b) Brandemark, U. B.; Blomberg, M. R. A.; Petterson, L. G. M.; Siegbahn, P. E. M. *J. Phys. Chem.* **1984**, *88*, 4617.

(23) Hay, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 705.

(24) Kubas, G. J.; Ryan, R. R.; Unkefer, C. J. *J. Am. Chem. Soc.* **1987**, *109*, 8113. See ref 5a for X-ray structure of the R = Ph complex.

(25) These especially include several polyhydrides (primarily Re) suspected to contain undefined amounts of η^2-H_2 ligand(s) which could not be unequivocally detected in recent NMR T_1, crystallographic, and other investigations in solution and/or solid states: (a) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126. (b) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 6, 2181. (c) Hamilton, D. G.; Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3198. (d) Luo, X.-L.; Crabtree, R. H. *Ibid.* **1989**, *28*, 3775. (e) Howard, J. A. K.; Mason, S. A.; Johnson, O.; Diamond, I. C.; Crennell, S.; Keller, P. A.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1988**, 1502. (f) Ammann, C.; Isaia, F.; Pregosin, P. S. *Magn. Res. Chem.* **1988**, *26*, 236. (g) Cotton, F. A.; Luck, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 5757.

(26) (a) Lundquist, E. G.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1165. (b) Marinelli, G.; Rachidi, I. E.-I.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1989**, *111*, 2346. (c) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sanchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431. (d) Bianchini, C.; Mealli, C.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 8725. (e) Morton, D.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1154. (f) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Zanobini, F.; Frediana, P. *Organometallics* **1989**, *8*, 2080. (g) Johnson, T. J.; Huffman, J. C.; Caulton, K. G.; Jackson, S. A.; Eisenstein, O. *Organometallics* **1989**, *8*, 2073.

(27) Zhang, K.; Gonzalez, A. A.; Hoff, C. D. *J. Am. Chem. Soc.* **1989**, *111*, 3627.

trans-dihydride form was observed in $[CpRu(Ph_2PCH_2CH_2CH_2PPh_2)H_2]^+$ and $[CpRu(PR_3)_2H_2]^+$. They also found that a 2:1 mixture of dihydride and dihydrogen cations could be obtained for $[CpRu(Ph_2PCH_2CH_2PPh_2)H_2]^+$ and claimed that they did not interconvert. Chinn and Heinekey[11c,d] observed irreversible isomerization of the dihydrogen form to the dihydride for $[CpRu(PPh_3)_2(H_2)]BF_4$ and suggest that protonation of $CpRuL_2H$ complexes always gives the dihydrogen form initially. The latter then, depending on the ligand set and thermodynamic factors, either remains as an H_2 complex, converts to an equilibrium system (L_2 = dmpe), or isomerizes all the way to the transoid dihydride form.

The low solubility and broad line widths of III relative to those of I and II prevented our examining the relative effect of the greater steric bulk and greater basicity of the PCy_3 ligand on the stability of the dihydrogen versus dihydride complexes. $PCyp_3$ has a similar cone angle as P-*i*-Pr_3 and is expected to have a slightly greater basicity than P-*i*-Pr_3. It is reasonable that the thermodynamic parameters are identical for I and II within estimated error.

The ΔS^* of −20 eu for the oxidative addition of η^2-H_2 in IA to form the dihydride tautomer is consistent with a well-ordered, late transition state. Theoretical calculations have shown that, in the concerted oxidative addition of dihydrogen to the d^8 metal system, $Pt(PH_3)_2$, the H–H bond is retained until late in the transition state when the H atoms suddenly separate.[28] The relatively high negative value of ΔS^* may partially be accounted for by a loss of the rotational degree of freedom of η^2-H_2 in the transition state as the metal–H bond strength increases. Inelastic neutron scattering[29] and solid-state NMR[5b] studies have shown that the H_2 ligand in $W(CO)_3(P$-*i*-$Pr_3)_2(H_2)$ undergoes rapid hindered rotation in a plane perpendicular to the W–H_2 axis with a barrier of only 2.4 kcal/mol.

The activation parameters for formation of the dihydride complex from the η^2-H_2 complex in I [ΔH^* = 10.1 (1.8) kcal/mol, ΔS^* = −20 (6) eu, ΔG^* = 16.0 (0.2) kcal/mol (298 K)] can be compared to the activation parameters obtained for intramolecular exchange in the d^6 cationic complexes *trans*-$[M(\eta^2\text{-}H_2)(H)(depe)_2]BPh_4$ (M = Fe, Ru, Os) [Fe, ΔH^* = 12.4 (0.4) kcal/mol, ΔS^* = −2 (1) eu, ΔG^* = 13.0 (0.2) kcal/mol; Os, ΔH^* = 9.0 (0.5), ΔS^* = −12 (4) eu, ΔG^* = 12.6 (0.2) kcal/mol].[3] In these complexes, the unique hydride is exchanged with the two equivalent hydrogen atoms of the coordinated η^2-H_2 and the H–H bond interaction decreases in the order Ru > Fe > Os. If the mechanism for exchange involves breaking of the H–H bond and formation of a fluxional seven-coordinate trihydride intermediate, the enthalpy of activation for the exchange would represent the energy of the conversion of the dihydrogen hydride complex to a trihydride complex. The stronger Lewis acid character of Os^{2+} (d^6) system compared to W^0 (d^6) in $W(CO)_3(P$-*i*-$Pr_3)_2(\eta^2$-$H_2)$ is expected to cause stronger $\sigma(H_2) \rightarrow M$ bonding in the Os^{2+} complex. This may be counterbalanced by the greater σ-donor ability of the ancillary ligands in the Os complex relative to the three π-accepting CO ligands in the W complex, in producing comparable values for activation enthalpies for the conversion of a dihydrogen into a dihydride ligand. Further work is in progress in defining the transition state in this process.

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Registry No. I, 104198-77-8; II, 125593-90-0.

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(28) Noell, J. O.; Hay, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4578.

(29) (a) Eckert, J.; Kubas, G. J.; Dianoux, A. J. *J. Chem. Phys.* **1988**, *88*, 466. (b) Eckert, J.; Kubas, G. J.; Hall, J. H.; Hay, P. J.; Boyle, C. M. *J. Am. Chem. Soc.* **1990**, *6*, 2324.

Cooperative Binding by Aggregated Mono-6-(alkylamino)-β-cyclodextrins

Russell C. Petter,* Jeffrey S. Salek, Christopher T. Sikorski, G. Kumaravel, and Fu-Tyan Lin

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260. *Received September 7, 1989*

Abstract: Mono-6-(hexadecylamino)-β-cyclodextrin (**5**) and mono-6-(octylamino)-β-cyclodextrin (**4**) have been titrated against organic guests (4-nitrophenol, 4-hydroxybenzoic acid, cyclohexanecarboxylic acid, etc.) in aqueous solution to give sigmoidal binding isotherms. Replotting of these data according to the Hill equation gives Hill coefficients > 1.0 (2.2 in the case of **5** and 4-nitrophenol). In contrast, both β-cyclodextrin (β-CD) and mono-6-amino-β-cyclodextrin (**3**) both exhibit hyperbolic binding isotherms, leading to Hill coefficients close to unity. Hill coefficients greater than one are the experimental hallmark of cooperativity, in which initial binding events render subsequent binding events more favorable. The degree of cooperativity is sensitive to the concentration of the hosts (**4** and **5**) and the solvent (cooperativity is suppressed in DMSO). These results are discussed in terms of the aggregation properties of the amphipathic hosts (cmc = 200 and 1.4 μM, for **4** and **5**, respectively), which were studied by conductivity, dynamic light scattering, and NMR. Two possible mechanisms to account for the observed cooperativity are presented and discussed.

Allosteric interaction between recognition sites is a ubiquitous regulatory mechanism in biological macromolecules, including enzymes,[1] receptors,[2] and ribosomes.[3] Allostery refers to the modulation of binding or catalysis at an active site as a consequence of binding at a remote effector site. When the active and effector sites are equivalent, the allostery is termed cooperativity (also "homotropic allostery"),[4] for which hemoglobin is the par-

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(1) (a) Fersht, A. *Enzyme Structure and Mechanism*, 2nd ed.; W.H. Freeman: New York, 1985; pp 39–41 and 263–292. (b) Hammes, G. G. *Enzyme Catalysis and Regulation*; Academic: New York, 1982; pp 152–186.

(2) Falke, J. J.; Koshland, D. E., Jr. *Science* **1987**, *237*, 1596.

(3) (a) Hausner, P.-P.; Geigenmüller, U.; Nierhaus, K. H. *J. Biol. Chem.* **1988**, *263*, 13, 103. (b) Gnirke, A.; Geigenmüller, U.; Rheinberger, H.-J.; Nierhaus, K. H. *J. Biol. Chem.* **1989**, *264*, 7291.

0002-7863/90/1512-3860$02.50/0