Tungsten(VI) Hexahydride Complexes Supported by Chelating Triphosphine Ligands: Protonation To Give η^2-Dihydrogen Complexes and Catalytic Dehydrogenation of Cyclooctane to Cyclooctene

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Received September 2, 1992

Reactions of $WCl_4(PPh_3)_2{\cdot}CH_2Cl_2$ with the chelating triphosphine (triphos) ligands $PPh(CH_2CH_2PPh_2)_2$ (PP_2), $PPh(C_6H_4\text{-}o\text{-}PPh_2)_2$ (TP), and $MeC(CH_2PPh_2)_3$ (P_3) in refluxing benzene or toluene give WCl_4(triphos) (triphos = PP_2 (**1**), TP (**2**), P_3 (**3**)). Treatment of **1-3** with $LiAlH_4$ in Et_2O at room temperature followed by hydrolysis in THF at 0 °C affords WH_6(triphos) (triphos = PP_2 (**4**), TP (**5**), P_3 (**6**)), which are the first tungsten polyhydride complexes supported by a chelating triphosphine ligand. Variable-temperature ^1H NMR spectra and T_1 data of **4–6** are consistent with the formulation of them as classical hexahydride complexes containing no η^2-H_2 ligands. Reaction of **4** with Ph_3SiH in refluxing THF gives the rare silyl polyhydide complex $WH_5(SiPh_3)(PP_2)$ (**7**). Protonation of **4-6** with $HBF_4{\cdot}OEt_2$ in CD_2Cl_2 at 193 K affords the cationic nonclassical η^2-H_2 complexes $[WH_{7-2x}(\eta^2\text{-}H_2)_x(\text{triphos})]^+$ (triphos = PP_2 (**8**), TP (**9**), P_3 (**10**); x = 1–3). Deprotonation of **8–10** with NEt_3 regenerates the parent hexahydrides **4–6** quantitatively. The variable-temperature ^1H NMR T_1 data for the hydride resonances of **8–10** are consistent with the nonclassical η^2-H_2 coordination. The alternative formulation of **8–10** as classical heptahydride complexes (i.e., $[WH_7(\text{triphos})]^+$) containing no η^2-H_2 ligand can be ruled out because it would exceed the maximum oxidation state and coordination number of tungsten. In the presence of *tert*-butylethylene as a hydrogen acceptor, complexes **4** and $ReH_5(PP_2)$ (**11**) are active catalysts for the thermal dehydrogenation of cyclooctane to cyclooctene, whereas their analogues containing monodentate phosphine ligands are inactive under similar conditions.

Introduction

Recent studies have demonstrated that transition-metal polyhydride complexes supported by chelating polydentate phosphine ligands can have unusual chemical and structural properties by comparison with their analogues containing monodentate or bidentate phosphine ligands. For example, the complexes $[MH(\eta^2\text{-}H_2)\{P(CH_2CH_2PPh_2)_3\}]^+$ (M = Fe, Ru)[2] exhibit much higher stability toward hydrogen loss compared with their diphosphine analogues $[MH(\eta^2\text{-}H_2)(PPh_2CH_2CH_2PPh_2)_2]^+$.[3] The complexes $[ReH_6\{PPh(CH_2CH_2CH_2PCy_2)_2\}]^+$ [4a] and $[ReH_6\{PPh(CH_2CH_2PPh_2)_2\}]^+$ [4b] are shown by X-ray diffraction and ^1H NMR T_1 studies to contain an elongated η^2-H_2 ligand, and they are remarkably resistant to hydrogen loss in sharp contrast with their monophosphine analogues[5] which lose hydrogen spontaneously at room temperature.

Chelating polydentate phosphine ligands can offer certain advantages over mono- and bidentate phosphines.[6] For example, polydentate phosphine ligands may help slow down intra- and intermolecular exchange processes in the resulting complex, enabling one to obtain detailed structural and bonding information. They may also provide more control on the coordination number and stereochemistry of the complex and reduce the lability of the metal-phosphorus bonds (chelating effects), thus limiting the number of vacant coordination sites available at the metal center. This feature may contribute to the development of catalysts with increased lifetime by blocking decomposition pathways (e.g., dimerization, oligomerization or disproportionation) and with increased selectivity by limiting the number of substrate molecules that can reach the metal center.

Although the chemistry of tungsten polyhydride complexes that contain monodentate or bidentate phosphine ligands has been well developed,[7] to our knowledge, related species supported by chelating polydentate phosphine ligands are unknown. In this paper, we report the synthesis, characterization and reactivity of some tungsten(VI) hexahydride complexes supported by the three chelating triphosphine (triphos) ligands $PPh(CH_2CH_2PPh_2)_2$-(PP_2), $PPh(C_6H_4\text{-}o\text{-}PPh_2)_2$(TP), $MeC(CH_2PPh_2)_3$(P_3). A comparison of their structural and chemical properties is made with those of their analogues containing monodentate phosphine ligands. The catalytic activity of these new polyhydride complexes and the previously known rhenium pentahydride complex $ReH_5(PP_2)$[4b] toward alkane dehydrogenation is reported to demonstrate the importance of the chelating polydentate phosphine ligands in controlling the reactivity of polyhydride complexes.

Results and Discussion

Preparation of WCl_4(triphos) (triphos = PP_2 (1), TP (2), P_3 (3)). Complexes **1–3** are synthesized by the reaction of $WCl_4(PPh_3)_2{\cdot}CH_2Cl_2$[8] with the appropriate triphosphine ligand in refluxing benzene or toluene, and are isolated as green or grey solids in excellent yields (>85%). They are moderately air-stable

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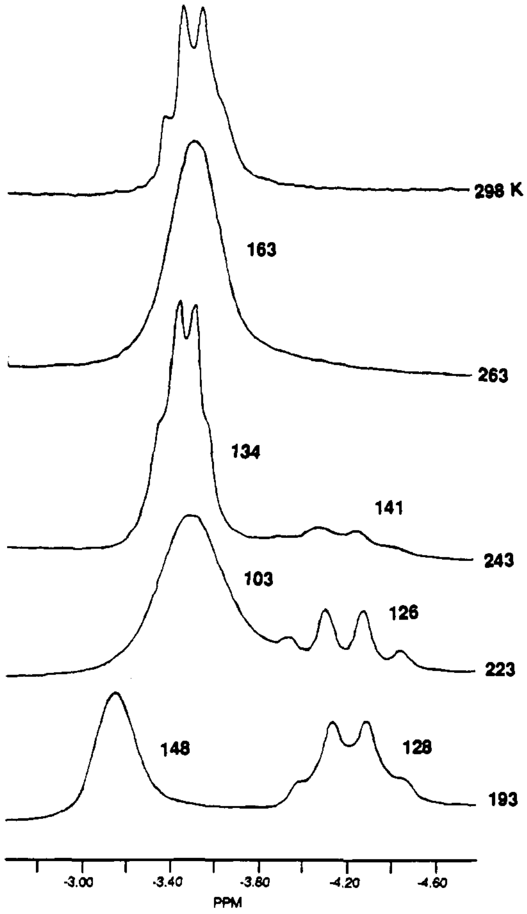


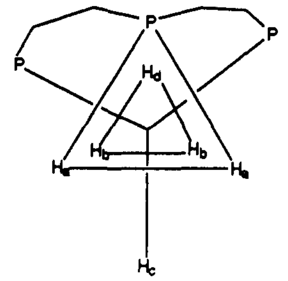
Figure 1. Variable-temperature ^1H NMR spectra of $WH_6(PP_2)$ (4) in CD_2Cl_2 at 250 MHz in the hydride region only. The T_1 values (ms) are also provided on the peaks.

in the solid state, but their solutions slowly decompose when exposed to air. They are characterized from their microanalytical data since meaningful NMR data cannot be obtained due to the paramagnetism of W(IV). Whether the triphosphine ligand acts as a bidentate or tridentate ligand in **1**–**3** is not clear. It is also possible that these two binding modes are in equilibrium,[9] considering the fact that $WCl_4(PMe_2Ph)_3$ is in equilibrium with $WCl_4(PMe_2Ph)_2$ and free PMe_2Ph.[10]

Preparation and Characterization of WH_6(triphos) (triphos = PP_2 (4), TP (5), P_3 (6)). Treatment of **1**–**3** with an excess of $LiAlH_4$ in Et_2O at room temperature followed by hydrolysis in THF at 0 °C affords the hexahydride complexes WH_6(triphos) (triphos = PP_2 (**4**), TP (**5**), P_3 (**6**)) in good yields as beige or off-white solids. To our knowledge, compounds **4**–**6** are the first tungsten polyhydride complexes supported by a chelating triphosphine ligand. The IR spectra of **4**–**6** in Nujol mulls show ν(W-H) bands in the region observed for analogous tungsten hexahydride complexes which contain monodentate phosphine ligands,[11] and no bands which can be assigned to the nonclassical $W(\eta^2\text{-}H_2)$ binding[12] are observed.

The hydride region of the variable-temperature ^1H NMR spectra of $WH_6(PP_2)$ (**4**) in CD_2Cl_2 at 250 MHz is shown in Figure 1. At 298 K, the six hydride ligands are almost equivalent, giving a broad distorted quartet resonance at δ −3.53 ($^2J_{PH}$ = 23.4 Hz, 6 H) without resolvable ^{183}W satellite peaks (^{183}W, $I = {}^1/_2$, natural abundance = 14.4%), while the $^{31}P\{^1H\}$ spectrum at 298 K shows two broad singlet resonances in an intensity ratio of 1:2. Upon cooling the hydride resonance becomes broad and then collapses at 243 K into two broad quartet resonances at δ −3.48 ($^2J_{PH}$ = 18.3 Hz) and δ −4.20 ($^2J_{PH}$ = 40.3 Hz) in an intensity ratio of 5:1. Upon further cooling, the resonance at δ −3.48 broadens and then at 193 K splits into a broad resonance at δ −3.15 (3 H) and another resonance (2 H) which overlaps with the quartet resonance at δ −4.20 (1 H). This results in a final low temperature hydride pattern which consists of a broad singlet (3 H) and a broad quartet ($^2J_{PH}$ = 41.5 Hz, 2 H + 1 H). The $^{31}P\{^1H\}$ NMR spectrum at 207 K shows an AB_2 splitting pattern ($^2J_{PP}$ = 15.2 Hz) with ^{183}W satellite peaks ($^1J_{WP}$ = 92.4 Hz for all phosphorus atoms).

Based on the variable-temperature NMR spectroscopic data and assuming the tricapped trigonal prismatic (TTP) geometry commonly observed for nine-coordinate polyhydride complexes,[7,13] the four structures **I**–**IV** are all possible for complex **4**. These structures should readily interconvert by pseudorotation.[14] However, other nine-coordinate geometries, e.g., the capped square antiprism, cannot be excluded. Structures **I**–**IV** all possess a symmetry plane (C_s) and should give a 2:2:1:1 hydride ratio (2 H_a:2 H_b:1 H_c:1 H_d) in the slow-exchange limit spectrum. Experimentally, we observe a 3:(2 + 1) ratio at the lowest accessible temperature (193 K). The broadness of the resonance at δ −3.15 (3 H) at 193 K suggests that it arises from two inequivalent sets of hydride ligands. The resonance at δ −4.20 (1 H) of the 5:1 pattern at 243 K is due to one of the unique hydride ligands H_c or H_d that is not yet rapidly participating in the averaging processes. A simple model which accommodates



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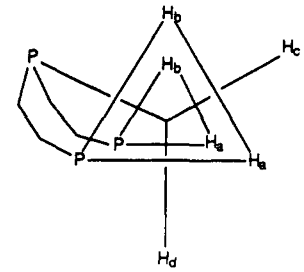

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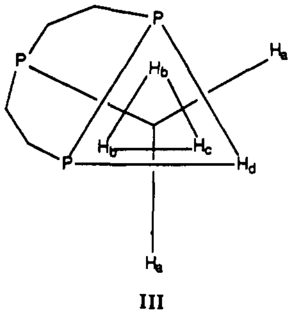

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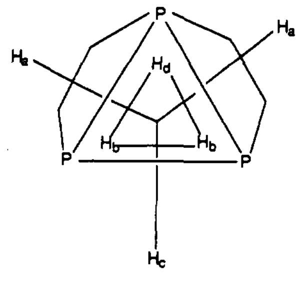

IV

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the observations assumes differential rates of rotation of the triangular faces containing hydrides in IV. Presumably H_b and H_d would resonate at approximately the same field (δ −3.15) and the others (H_a, H_c) at approximately another (δ −4.20). The rotations of the H_a–H_b–H_d triangles average the three δ −3.15 resonances with two of the δ −4.20 resonances to give the averaged δ −3.48 resonance and leave the remaining resonance from H_c at δ −4.20. As the remaining face rotates, H_c then averages with the others.

Because the barrier to inversion for coordinated phosphines is usually quite high,[15] each structure I–IV can have two isomers resulting from different orientations of the phenyl group on the central phosphorus atom of the PP_2 ligand.[16] However, only one isomer is observed in the variable-temperature ^{1}H and ^{31}P NMR spectra of complex **4** perhaps because the other isomer is thermodynamically much less favored. This observation is not very surprising since this kind of isomerization is not always observed for complexes of the PP_2 ligand. For example, we[17] have recently found only one isomer for some ruthenium complexes containing the PP_2 ligand, e.g., $[RuH(L)L')(PP_2)]^+$ ($L = \eta^2\text{-}H_2$, $L' = CO, P(OCH_2)_3CEt, PMe_2Ph$; $L = CH_3CN$, $L' = P(OCH_2)_3CEt, PMe_2Ph$), $RuCl_2(L)(PP_2)$ ($L = P(OCH_2)_3CEt, PMe_2Ph$), and $RuH_2(L)(PP_2)$ ($L = CO, P(OCH_2)_3CEt, PMe_2Ph$).

Nine-coordinate TTP structures are generally highly fluxional due to very low barriers for intramolecular rearrangements via pseudorotation.[18] Accordingly, the variable-temperature ^{1}H NMR spectra of $WH_6(PR_3)_3$ ($PR_3 = PMe_2Ph, PEt_2Ph$) show only one hydride resonance with no line shape changes even at the lowest accessible temperatures,[11] thus providing no stereochemical information. Clearly, the replacement of the three monophosphine ligands in $WH_6(PR_3)_3$ by the chelating triphosphine ligand PP_2 in complex **4** leads to an increase in the rearrangement barrier and so allow us to partially freeze out the fluxionality at low temperatures.

^{1}H NMR spin–lattice relaxation times (T_1) of hydride resonances have been shown useful in determining whether hydride complexes contain an $\eta^2\text{-}H_2$ ligand.[12,19–23] The variable-temperature ^{1}H NMR T_1 data of the hydride resonances of complex **4** are shown in Figure 1. The relatively high T_1(min) values of 103 and 126 ms observed for the two separate hydride resonances of **4** at 223 K are consistent with the formulation of $WH_6(PP_2)$ as a classical hexahydride complex containing no $\eta^2\text{-}H_2$ ligand.

The hydride region of the ^{1}H NMR spectrum of $WH_6(TP)$ (**5**) in CD_2Cl_2 at 298 K shows a slightly broad pseudoquartet at δ −2.86 ($^2J_{PH}$ = 23.8 Hz) with ^{183}W satellite peaks ($^1J_{WH}$ = 33.6 Hz), while the ^{31}P{^{1}H} spectrum shows two broad resonances in a ratio of 1:2. Upon cooling the hydride resonance becomes broad and then at 168 K splits into a broad resonance at δ −2.78 (3 H) partially overlapping with a quartet resonance at δ −3.32 ($^2J_{PH}$ = 37.2 Hz, 3 H). This low temperature hydride pattern is very similar to that of complex **4** at 193 K. Therefore, complex **5** probably adopts a structure similar to that of **4**. The ^{31}P{^{1}H} NMR spectrum of complex **5** at 207 K shows an AB_2 splitting pattern ($^2J_{PH}$ = 13.0 Hz) with ^{183}W satellite peaks ($^1J_{WP}$ = 101.4 and 98.7 Hz). The high T_1(min) value of 142 ms for the averaged hydride resonance of complex **5** at 213 K suggests that it is also a classical hexahydride complex containing no η^2-dihydrogen ligand.

The hydride region of the ^{1}H NMR spectrum of $WH_6(P_3)$ (**6**) in CD_2Cl_2 at 298 K shows a sharp binomial quartet resonance at δ −3.85 ($^2J_{PH}$ = 23.0 Hz) with ^{183}W satellite peaks ($^1J_{WH}$ = 29.0 Hz), while the ^{31}P{^{1}H} spectrum shows a sharp resonance with ^{183}W satellite peaks ($^1J_{WP}$ = 120.5 Hz). The variable-temperature ^{1}H NMR spectra of complex **6** provides no stereochemical information since they show no significant change in the temperature range 183–298 K. Clearly, change of the chelating triphosphine ligand in WH_6(triphos) complexes greatly affect the fluxional behavior of the complexes. The T_1(min) value for the averaged hydride resonance of complex **6** cannot be observed, but the high T_1 value of 211 ms measured at the lowest accessible temperature (183 K) suggests that like complexes **4** and **5**, complex **6** is also a classical hexahydride complex containing no $\eta^2\text{-}H_2$ ligand.

Preparation of $WH_5(SiPh_3)(PP_2)$ (7). Although transition-metal silyl dihydride or trihydride complexes (supported by either Cp* or Cp[24] or by phosphines[25]) are known, the only examples of silyl polyhydride complexes (i.e., containing more than three hydride ligands) are $ReH_6(SiR_3)L_2$ (L_2 = a chelating diphosphine or two monophosphines).[26] In this context, we decided to study the reaction of complexes **4**–**6** with Ph_3SiH. Complex **4** reacts with Ph_3SiH in refluxing THF to afford the silyl pentahydride complex $WH_5(SiPh_3)(PP_2)$ (**7**). Under similar conditions, complexes **5** and **6** give intractable products.

The hydride region of the ^{1}H NMR spectrum of complex **7** in $(CD_3)_2CO$ at 298 K shows a sharp binomial quartet resonance at δ −3.83 ($^2J_{PH}$ = 24.4 Hz) with ^{183}W satellite peaks ($^1J_{WH}$ = 27.5 Hz). The hydride resonance does not undergo decoalescence even at the lowest accessible temperature. This is in contrast with the case of $ReH_6(SiR_3)L_2$, where the replacement of a hydride ligand in ReH_7L_2 by a silyl group in $ReH_6(SiR_3)L_2$ leads to an increase in the barriers for the fluxional processes.[26] Either the silyl group has the opposite effect in complex **7**, or the apparent higher fluxionality of **7** compared with that of **4** may be a result of smaller chemical shift differences among the hydride ligands in complex **7**.

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Reaction of WH_6(triphos) (triphos = PP_2 (4), TP (5), P_3 (6)) with CO. Complex **4** reacts with CO in refluxing THF to give the known tricarbonyl complex *fac*-$W(CO)_3(PP_2)$ which was identified by comparison of its spectroscopic data with those reported in the literature.[27] Under similar conditions, complexes **5** and **6** react with CO but give a complicated mixture of carbonyl-containing products which could not be characterized.

Formation of $[WH_{7-2x}(\eta^2\text{-}H_2)_x(\text{triphos})]^+$ (triphos = PP_2 (8), TP (9), P_3 (10); x = 1–3). The protonation of **4–6** with $HBF_4{\cdot}OEt_2$ in CD_2Cl_2 at 193 K occurs rapidly without hydrogen evolution and affords the cationic nonclassical η^2-H_2 complexes $[WH_{7-2x}(\eta^2\text{-}H_2)_x(\text{triphos})]^+$ (triphos = PP_2 (**8**), TP (**9**), P_3 (**10**); x = 1–3). The alternative formulation of **8–10** as classical heptahydride complexes (i.e., $[WH_7(\text{triphos})]^+$) containing no η^2-H_2 ligand can be ruled out because it would exceed the maximum oxidation state and coordination number of tungsten. The compounds must therefore contain at least one η^2-H_2 ligand.

The protonation of **4–6** is reversible, and subsequent addition of NEt_3 results in immediate deprotonation of **8–10** and quantitative regeneration of the parent hexahydrides **4–6**. This represents a rare example of reversible protonation of d^0 transition-metal hydride complexes to give species of the general formula $[MH_x(\eta^2\text{-}H_2)_yL_z]^{n+}$, where the value of $(x + 2y + n)$ exceeds the maximum oxidation state of the metal and so the classical formulation $[MH_{x+2y}L_z]^{n+}$ must be excluded.

Previously, Shaw et al.[28] reported the first protonation of d^0 hydride complexes of the type $ReH_7(PR_3)_2$ to give η^2-H_2 complexes $[ReH_{8-2x}(\eta^2\text{-}H_2)_x(PR_3)_2]^+$ (x = 1–4). However, recent studies[29] have suggested that some $ReH_7(PR_3)_2$ complexes adopt a structure containing an elongated η^2-H_2 ligand and thus the rhenium center is better considered as having a d^2 configuration. Henderson[30] reported the double protonation of $MoH_4(dppe)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) to form a transient η^2-H_2 complex $[MoH_4(\eta^2\text{-}H_2)(dppe)_2]^{2+}$ with a lifetime of 0.75 s and suggested that initial protonation generates an intermediate $[MoH_5(dppe)_2]^+$ in rapid equilibrium with $[MoH_3(\eta^2\text{-}H_2)(dppe)_2]^+$, which upon further protonation generates $[MoH_4(\eta^2\text{-}H_2)(dppe)_2]^{2+}$.

Compounds **8–10** can be characterized spectroscopically, but attempts to isolate them have been unsuccessful due to facile and irreversible loss of dihydrogen at room temperature. The stability of $[WH_{7-2x}(\eta^2\text{-}H_2)_x(\text{triphos})]^+$ depends on the triphosphine ligand and decreases in the order $PP_2 > TP \approx P_3$. Thus, the temperature above which **8–10** decompose are 253, 238 and 240 K, respectively. A complicated mixture of decomposition products, which do not contain any hydride ligands, are formed and have not been characterized.

The hydride region of the ^1H NMR spectrum of each of complexes **8–10** in CD_2Cl_2 at 223 K exhibits a broad resonance (δ −3.0, $\omega_{1/2} \approx 65$ Hz (**8**); δ −2.1, $\omega_{1/2} \approx 50$ Hz (**9**); and δ −3.5, $\omega_{1/2} \approx 42$ Hz (**10**)), which integrates for 7 ± 0.3 protons and is assignable to rapidly exchanging η^2-H_2 and terminal hydride ligands. This hydride resonance does not undergo decoalescence even at the lowest accessible temperature due to rapid fluxionality.

The variable-temperature ^1H NMR T_1 measurements on the averaged broad hydride resonance of **8–10** in CD_2Cl_2 at 250 MHz are given in Table I. The very low T_1(min) values of 21 and 32 ms for **8** and **9**, respectively, suggest the presence of at least one η^2-H_2 ligand. The T_1 value of complex **10** does not reach a minimum at any accessible temperature, but the very low T_1 value of 15 ms observed at 183 K again suggests a nonclassical formulation.

Table I. Variable-Temperature ^1H NMR T_1 Measurements on the Averaged Hydride Resonance of $[WH_{7-2x}(\eta^2\text{-}H_2)_x(\text{triphos})]^+$ (triphos = PP_2 (**8**), TP (**9**), P_3 (**10**); x = 1–3) in CD_2Cl_2 at 250 MHz

	T_1, ms				T_1, ms		
T, K	**8**	**9**	**10**	T, K	**8**	**9**	**10**
253	38			213	27	32	29
243	31			203	35	37	22
233	26	40		193	39	41	17
223	21	36		183	45	46	15

The variable-temperature ^1H NMR spectra and T_1 data of **8–10** do not allow the determination of the value of x in $[WH_{7-2x}(\eta^2\text{-}H_2)_x(\text{triphos})]^+$. If x = 1, compounds **8–10** would be d^0 η^2-H_2 complexes. A certain degree of $M(d_\pi)$ to $H_2(\sigma^*)$ back-donation is usually thought to be necessary to stabilized the η^2-H_2 binding.[12] Accordingly, all d^0 η^2-H_2 complexes would be expected to be very unstable because of the lack of $M(d_\pi)$ to $H_2(\sigma^*)$ back-donation, and only two possible examples of d^0 transition-metal η^2-H_2 complexes have been reported, i.e., $[ReH_6(\eta^2\text{-}H_2)(PR_3)_2]^+$ [28] and $[MoH_4(\eta^2\text{-}H_2)(dppe)_2]^{2+}$,[30] both being labile. The existence of a labile lanthanide η^2-H_2 complex $(\eta^5\text{-}C_5Me_5)_2Eu(\eta^2\text{-}H_2)$ (formally a $4f^75d^0$ Eu(II) system) has been proposed on the basis of the line broadening and paramagnetic shift of the dissolved H_2 resonance in the presence of Cp'_2Eu.[31] If x = 2, compounds **8–10** would be d^2 bis(η^2-H_2) complexes, no examples of which are known although d^6 bis(η^2-H_2) complexes[32] and d^2 complexes containing one η^2-H_2 ligand[4,29] have been reported. If x = 3, compounds **8–10** would be d^4 tris(η^2-H_2) complexes, again no examples of which are known although d^4 systems containing one η^2-H_2 ligand have been reported.[33,34] There are also the possibilities that two or more species with different x values are in rapid equilibrium and even that compounds **8–10** are better formulated as η^3-H_3 complexes[33,35] $[WH_{7-3x}(\eta^3\text{-}H_3)_x(\text{triphos})]^+$ (x = 1, 2).

Several interesting mechanistic points arise from the protonation of complexes **4–6**. There are two general mechanisms that can be envisaged for the protonation of a transition-metal hydride complex: (a) protonation of a d-electron pair at the basic d^n ($n \geq 2$) metal center to give a classical hydride complex, which may or may not arrange to an η^2-H_2 complex, and (b) protonation of a terminal hydride ligand to give an η^2-H_2 complex, which may or may not rearrange to a classical hydride complex.[36] Both mechanisms are likely to operate for d^n ($n \geq 2$) hydride complexes. Oglieve and Henderson[36f] have recently reported that competitive protonation at the metal center and a hydride ligand occurs in $WH_4(PMePh_2)_4$ and that the more rapidly protonated site, i.e., a hydride ligand, is not the final residence of the proton. On the other hand, for d^0 hydride complexes such as **4–6**, the metal center cannot be the site or protonation due to the lack of any d-electron pair. Protonation must therefore occur at a hydride ligand, or the d^0 hydride complex must first undergo an intramolecular reductive coupling of two terminal hydride ligands

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to give an intermediate η^2-H_2 complex with a d^2 configuration which subsequently undergoes protonation at the metal center. We cannot distinguish these two possibilities for the protonation of **4**–**6**.

Reaction of $[WH_{7-2x}(\eta^2\text{-}H_2)_x(\text{triphos})]^+$ (triphos = PP_2 (8), TP (9), P_3 (10); x = 1–3) with CO. Many η^2-H_2 complexes readily undergo substitution reactions in which a labile η^2-H_2 ligand is displaced by a variety of other ligands.[12,37] When solutions of **8** and **10**, generated at low temperature, are allowed to warm up slowly to room temperature in the presence of CO, the previously known monohydride complexes $[WH(CO)_3(\text{triphos})]^+$ (triphos = PP_2, P_3)[27] are formed by displacement of dihydrogen with CO. These complexes were identified by comparison of their spectroscopic data with those reported in the literature.[27] Under similar conditions, complex **9** reacts with CO to give a mixture of carbonyl-containing products that we cannot characterize.

Catalytic Dehydrogenation of Cyclooctane to Cyclooctene by $WH_6(PP_2)$ (4) and $ReH_5(PP_2)$ (11). The activation and functionalization of alkanes by transition-metal complexes has been the object of much recent study.[38] One of the best studied reactions is catalytic dehydrogenation of alkanes to alkenes. A variety of transition-metal polyhydride complexes, notably $ReH_7(PR_3)_2$, $RuH_4(PR_3)_3$ and $IrH_5(PR_3)_2$, have been shown to be active catalysts in the presence of *tert*-butylethylene (tbe) as a hydrogen acceptor. Although the mechanism of the dehydrogenation is not entirely clear, the key step is generally thought to involve the oxidative addition of a C–H bond of the alkane to a highly reactive and coordinatively unsaturated intermediate which is generated thermally from the polyhydride complex by removal of two or more hydride ligands with the hydrogen acceptor.[38d]

The tungsten monophosphine hexahydride complexes such as $WH_6(PMe_2Ph)_3$ were previously found inactive for alkane dehydrogenation.[39] We were interested to see whether the new tungsten hexahydride complexes **4**–**6** that contain chelating triphosphine ligands might be active catalysts. Indeed, with tbe as a hydrogen acceptor, complex **4** is an effective catalyst for thermal dehydrogenation of cyclooctane to cyclooctene. The reaction was carried out in a glass vessel sealed with a Teflon stopcock. When cyclooctane (1.5 mL) containing tbe (0.070 mL, 0.53 mmol) and complex **4** (7.2 mg, 0.0099 mmol) was heated at 145 °C, ten turnovers of cyclooctene, as determined by GC, were obtained after 24 h (turnover frequency = 0.4 turnover h^{-1}). Under similar conditions, complexes **5** and **6** are inactive. To our knowledge, complex **4** is the first tungsten complex, and the first non-precious metal complex, to show catalytic activity for alkane dehydrogenation.

The catalytic activity of **4** for cyclooctane dehydrogenation encouraged us to study the closely related rhenium pentahydride complex $ReH_5(PP_2)$ (**11**),[4b] and it was indeed found to be a very active catalyst. At 180 °C and with the same cyclooctane/tbe/catalyst molar ratio as used for **4**, complex **11** gave seventy-one turnovers of cyclooctene after 24 h (turnover frequency = 3.0 turnover h^{-1}). By contrast, the pentahydride complex $ReH_5(PPh_3)_3$, which is supported by monodentate PPh_3 ligands, was found inactive under similar conditions.

In both catalytic systems involving **4** and **11**, the solutions were yellow and appeared to be perfectly homogeneous throughout the reaction. The homogeneity of both catalytic systems was examined by the mercury test.[40] We found that the yield of cyclooctene was not affected by the presence of a bead of liquid mercury, a well-known selective poison for heterogeneous catalysts. This suggests that metal colloids or bulk metal particles are not responsible for the catalytic dehydrogenation of cyclooctane. After the reaction, a small amount of free benzene was detected by GC in the product mixture. This suggests that catalyst deactivation may take place through cleavage of the P–C bonds of the triphosphine ligands.[41] After removal of all the volatiles from the reaction mixture, the organometallic residue, which is also soluble in acetone, dichloromethane and THF, was shown by ^1H and ^{31}P NMR spectroscopy to be a complicated mixture of metal phosphine complexes with no hydride ligands and thus was not further characterized.

The origin of the remarkable change in catalytic activity of these rhenium and tungsten polyhydride complexes on going from monodentate phosphine ligands to the chelating triphosphine ligand PP_2 is not yet understood. A possibility is that the PP_2 ligand prevents disproportionation of the complex. When $WH_6(PMe_2Ph)_3$ was used for alkane dehydrogenation, inactive $WH_4(PMe_2Ph)_4$ was detected in substantial amount in the reaction mixture and was probably formed by disproportionation of $WH_6(PMe_2Ph)_3$.[39] A even more intriguing observation is that changes in steric and electronic properties of the triphosphine ligand cause a large variation in the catalytic activity of tungsten hexahydride complexes **4**–**6** for cyclooctane dehydrogenation.

Conclusion

The compounds $WH_6(\text{triphos})$ (triphos = $PPh(CH_2CH_2PPh_2)_2(PP_2)$ (**4**), $PPh(C_6H_4\text{-}o\text{-}PPh_2)_2(TP)$ (**5**), $MeC(CH_2PPh_2)_3(P_3)$ (**6**)) represent the first tungsten polyhydride complexes which are supported by a chelating triphosphine ligand. The variable-temperature ^1H NMR spectra and T_1 data of **4**–**6** are consistent with the formulation of them as classical hexahydride complexes containing no η^2-H_2 ligand. The reaction of complex **4** with Ph_3SiH affords $WH_5(SiPh_3)(PP_2)$ (**7**), a rare silyl polyhydride complex. Protonation of **4**–**6** affords the cationic nonclassical η^2-H_2 complexes $[WH_{7-2x}(\eta^2\text{-}H_2)_x(\text{triphos})]^+$ (triphos = PP_2 (**8**), TP (**9**), P_3 (**10**); x = 1–3), whereas deprotonation of **8**–**10** with NEt_3 regenerates the parent hexahydrides **4**–**6**. This represents a rare example of reversible protonation of d^0 transition-metal hydride complexes. The variable-temperature ^1H NMR T_1 data for the hydride resonances of **8**–**10** are consistent with the nonclassical η^2-H_2 coordination. The alternative formulation of **8**–**10** as classical heptahydride complexes (i.e., $[WH_7(\text{triphos})]^+$) containing no η^2-H_2 ligand can be ruled out because it would exceed the maximum oxidation state and coordination number of tungsten. With *tert*-butylethylene as a hydrogen acceptor, complexes **4** and $ReH_5(PP_2)$ (**11**) are active catalysts for the thermal dehydrogenation of cyclooctane to cyclooctene, whereas their analogues containing monodentate phosphine ligands are inactive under similar conditions. Further work is needed to understand the origin of the effect of chelating triphosphine ligands on the structure and reactivity of polyhydride complexes.

Experimental Section

General Procedures. All manipulations were performed under a dry Ar atmosphere by standard Schlenk-tube techniques. Diethyl ether, hexane, heptane and tetrahydrofuran were distilled from Na/Ph_2CO; dichloromethane was distilled from CaH_2. All solvents were stored under N_2 over a 4-Å molecular sieves. Compounds $ReH_5(PP_2)$[4b] and $WCl_4(PPh_3)_2\cdot CH_2Cl_2$[8] and the triphosphine ligand $PPh(C_6H_4\text{-}o\text{-}PPh_2)_2$-

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(TP)[42] were prepared according to the literature methods. The triphosphine ligands $PPh(CH_2CH_2PPh_2)_2(PP_2)$ and $MeC(CH_2PPh_2)_3(P_3)$ were purchased from Strem Chemicals, Inc. All other chemicals were purchased from Aldrich Co. The cyclooctane used in the catalytic dehydrogenation experiments was purified by the literature procedure.[41b]

^{1}H and ^{31}P NMR spectra were recorded on Bruker WM 250 or WM 500 spectrometers; ^{1}H chemical shifts were measured with the residual solvent resonance as reference; ^{31}P chemical shifts were measured with external 85% H_3PO_4 as reference. ^{1}H NMR T_1 measurements were carried out at 250 MHz by the inversion–recovery method using a standard $180°–\tau–90°$ pulse sequence. IR spectra were recorded on a Nicolet 5-SX FT-IR spectrometer. Microanalyses were carried out by Desert Analytics Co. GC analyses were performed on a Varian Model 3700 gas chromatograph equipped with a flame ionization detector and a Varian 4270 integrator and using a 20-m Carbowax capillary column.

$WCl_4(PP_2)$ (1). To a suspension of $WCl_4(PPh_3)_2 \cdot CH_2Cl_2$ (1.00 g, 1.07 mmol) in benzene (40 mL) was added $PPh(CH_2CH_2PPh_2)_2$ (600 mg, 1.12 mmol), and the mixture was refluxed for 3 h. The solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2 (ca. 0.5 mL). Addition of ether (25 mL) resulted in the precipitation of a green solid, which was filtered off, washed with ether (3 × 5 mL), and dried in vacuo. Yield: 828 mg (90%). Anal. Calcd for $C_{34}H_{33}Cl_4P_3W$: C, 47.47; H, 3.87. Found: C, 47.18; H, 3.71.

$WCl_4(TP)$ (2). This complex was prepared analogously to **1** by using $WCl_4(PPh_3)_2 \cdot CH_2Cl_2$ (600 mg, 0.64 mmol) and $PPh(C_6H_4\text{-}o\text{-}PPh_2)_2$ (425 mg, 0.67 mmol) in benzene (25 mL) and was isolated as a green solid. Yield: 534 mg (87%). Anal. Calcd for $C_{42}H_{33}Cl_4P_3W$: C, 52.75; H, 3.48. Found: C, 52.91; H, 3.61.

$WCl_4(P_3)$ (3). This complex was prepared analogously to **1** by using $WCl_4(PPh_3)_2 \cdot CH_2Cl_2$ (450 mg, 0.48 mmol) and $MeC(CH_2PPh_2)_3$ (330 mg, 0.52 mmol) in refluxing toluene (25 mL) and was isolated as a grey solid. Yield: 390 mg (85%). Anal. Calcd for $C_{41}H_{39}Cl_4P_3W$: C, 51.81; H, 4.14. Found: C, 51.62; H, 4.01.

$WH_6(PP_2)$ (4). A suspension of $WCl_4(PP_2)$ (**1**) (500 mg, 0.58 mmol) and $LiAlH_4$ (264 mg, 6.97 mmol) in Et_2O (40 mL) was vigorously stirred at room temperature for 3 h. The mixture was filtered through Celite to give an orange filtrate which was evaporated to dryness in vacuo. The orange residue was dissolved in THF (20 mL), cooled to 0 °C, and hydrolyzed by dropwise addition of H_2O (0.50 mL) in THF (20 mL). The mixture was dried with anhydrous Na_2SO_4 (5 g) and filtered through Celite. The yellow filtrate was concentrated to ca. 0.2 mL. Addition of hexane (30 mL) resulted in the precipitation of an off-white solid. The precipitation was completed with the addition of heptane (10 mL). After cooling to 0 °C, the solid was filtered off, washed with heptane (3 × 5 mL), and dried in vacuo. Yield: 261 mg (62%). Anal. Calcd for $C_{34}H_{39}P_3W$: C, 56.36; H, 5.42. Found: C, 56.28; H, 5.51. IR (Nujol): ν(W–H) 1867, 1808, 1775 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 298 K): δ 8.0–7.2 (m, 25 H, Ph), 1.9–1.7 (m, 8 H, CH_2), –3.53 (br. q, $^2J_{PH}$ = 23.4 Hz, 6 H, W–H). ^{1}NMR (CD_2Cl_2, 173 K): δ 8.2–7.2 (m, 25 H, Ph), 2.0–1.6 (m, 8 H, CH_2), –3.18 (br. s, 3 H, W–H), –4.25 (br. q, $^2J_{PH}$ = 43.3 Hz, 3 H, W–H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 81.9 (br. s, 1 P), 49.8 (br. s, 2 P). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 207 K): δ 81.1 (t, $^2J_{PP}$ = 15.2 Hz, $^1J_{WP}$ = 92.4 Hz, 1 P), 48.1 (d, $^2J_{PP}$ = 15.2 Hz, $^1J_{WP}$ = 92.4 Hz, 2 P).

$WH_6(TP)$ (5). This complex was prepared analogously to **4** by using $WCl_4(TP)$ (**2**) (500 mg, 0.52 mmol) and $LiAlH_4$ (238 mg, 6.27 mmol) and was isolated as a beige solid. Yield: 236 mg (55%). Anal. Calcd for $C_{42}H_{39}P_3W$: C, 61.47; H, 4.79. Found: C, 61.60; H, 4.90. IR (Nujol): ν(W–H) 1875, 1810, 1779 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 298 K): δ 7.8–7.0 (m, 33 H, Ph), –2.86 (q, 6 H, $^2J_{PH}$ = 23.8 Hz, $^1J_{WH}$ = 33.6 Hz, W–H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 78.3 (br. s, 1 P), 50.5 (br. s, 2 P). ^{1}H NMR (CD_2Cl_2, 168 K): δ 7.9–7.0 (m, 33 H, Ph), –2.78 (br. s, 3 H, W-H), –3.32 (br. q, $^2J_{PH}$ = 37.2 Hz, 3 H, W–H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 190 K): δ 78.9 (t, $^2J_{PP}$ = 13.0 Hz, $^1J_{WP}$ = 101.4 Hz, 1 P), 51.1 (d, $^2J_{PP}$ = 13.0 Hz, $^1J_{WP}$ = 98.7 Hz, 2 P).

$WH_6(P_3)$ (6). This complex was prepared analogously to **4** by using $WCl_4(P_3)$ (**3**) (600 mg, 0.63 mmol) and $LiAlH_4$ (287 mg, 7.58 mmol) and was isolated as a beige solid. Yield: 411 mg (80%). Anal. Calcd for $C_{41}H_{45}P_3W$: C, 60.45; H, 5.57. Found: C, 60.31; H, 5.49. IR (Nujol): ν(W–H) 1866, 1824, 1770 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 298 K): δ 8.1–7.0 (m, 30 H, Ph), 2.51 (s, 6 H, CH_2), 1.72 (s, 3 H, CH_3), –3.85 (q, 6 H, $^2J_{PH}$ = 23.0 Hz, $^1J_{WH}$ = 29.0 Hz, W–H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 8.9 (s, $^1J_{WP}$ = 120.5 Hz).

$WH_5(SiPh_3)(PP_2)$ (7). A solution of $WH_6(PP_2)$ (**4**) (250 mg, 0.35 mmol) and Ph_3SiH (1.08 g, 4.14 mmol) in THF (20 mL) was refluxed for 50 min. The solution was concentrated in vacuo to ca. 0.2 mL. Addition of hexanes (20 mL) resulted in the precipitation of a beige solid, which was filtered off, washed with hexanes (3 × 4 mL), and dried in vacuo. Yield: 305 mg, (90%). Anal. Calcd for $C_{52}H_{53}P_3SiW$: C, 63.54; H, 5.44. Found: C, 63.61; H, 5.55. IR (Nujol): ν(W–H) 1961, 1890, 1826 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 298 K): δ 7.9–7.1 (m, 40 H, Ph), 2.2–1.8 (m, 8 H, CH_2), –3.83 (q, 5 H, $^2J_{PH}$ = 24.4 Hz, $^1J_{WH}$ = 27.5 Hz, W–H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 89.3 (t, $^2J_{PP}$ = 19.1 Hz, 1 P), 53.6 (d, $^2J_{PP}$ = 19.1 Hz, 2 P).

Reaction of WH_6(triphos) (triphos = PP_2 (4), TP (5), P_3 (6)) with CO. A stream of CO was bubbled for 45 min through a refluxing solution of **4** (200 mg, 0.28 mmol) in THF (20 mL). The yellow solution was concentrated in vacuo to ca. 0.1 mL. Addition of hexane (20 mL) resulted in the precipitation of *fac*-$W(CO)_3(PP_2)$ as a pale yellow solid, which was filtered off, washed with heptane (3 × 3 mL), and dried in vacuo. Yield: 152 mg (67%). The $^{31}P\{^1H\}$ NMR and IR spectroscopic data were identical to those reported in the literature.[27]

The reactions of complexes **5** and **6** with CO were run under similar conditions, but a mixture of carbonyl-containing products was obtained and not characterized.

$[WH_{7-2x}(\eta^2\text{-}H_2)_x(PPh_2)]^+$ (8; x = 1–3). $WH_6(PP_2)$ (**4**) (30 mg, 0.041 mmol) was dissolved in CD_2Cl_2 (0.4 mL) in a 5-mm NMR tube. The solution was cooled to 195 K (dry ice/acetone), and $HBF_4 \cdot OEt_2$ (85%, 7.2 μL, 0.041 mmol) was added via a microsyringe. The sample was shaken and then quickly introduced into a precooled NMR probe. ^{1}H NMR shows quantitative protonation of **4** to give **8**. ^{1}H NMR (CD_2Cl_2, 223 K): δ 8.2–7.4 (m, 25 H, Ph), 2.2–1.8 (m, 8 H, CH_2), –3.0 (br s, $\omega_{1/2} \approx$ 65 Hz, 7 H, W–H).

$[WH_{7-2x}(\eta^2\text{-}H_2)_x(TP)]^+$ (9; x = 1–3). This complex was prepared analogously to **8** by using $WH_6(TP)$ (**5**) (35 mg, 0.043 mmol) and $HBF_4 \cdot OEt_2$ (85%, 7.5 μL, 0.043 mmol). ^{1}H NMR (CD_2Cl_2, 223 K): δ 8.0–7.1 (m, 33 H, Ph), –2.1 (br s, $\omega_{1/2} \approx$ 50 Hz, 7 H, W–H).

$[WH_{7-2x}(\eta^2\text{-}H_2)_x(P_3)]^+$ (10; x = 1–3). This complex was prepared analogously to **8** by using $WH_6(P_3)$ (**6**) (32 mg, 0.039 mmol) and $HBF_4 \cdot OEt_2$ (85%, 6.8 μL, 0.039 mmol). ^{1}H NMR (CD_2Cl_2, 223 K): δ 8.3–7.2 (m, 30 H, Ph), 2.20 (s, 6 H, CH_2), 1.61 (s, 3 H, CH_3), –3.5 (br s, $\omega_{1/2} \approx$ 42 Hz, 7 H, W–H).

Deprotonation of $[WH_{7-2x}(\eta^2\text{-}H_2)_x$(triphos)$]^+$ (triphos = PP_2 (8), TP (9), P_3 (10); x = 1–3) with NEt_3. In a typical procedure, the above NMR tube containing a solution of **8** prepared in situ was quickly removed from the NMR probe and submerged in a dry ice/acetone bath. NEt_3 (5.7 μL, 0.041 mmol) was added via a microsyringe. The sample was shaken and transferred back to the NMR probe. The ^{1}H NMR spectrum was taken again and showed that the hydride resonance of **8** had been replaced by that of **4**. The deprotonation of **9** and **10** was carried out similarly.

Reaction of $[WH_{7-2x}(\eta^2\text{-}H_2)_x$(triphos)$]^+$ (triphos = PP_2 (8), TP (9), P_3 (10); x = 1–3) with CO. Complexes **8–10** were prepared in situ at 183 K (dry ice/acetone) as described above. A stream of CO was passed through the cold solutions which were allowed to warm up slowly to room temperature. In the case of **8** and **10**, complexes $[WH(CO)_3(PP_2)]^+$ and $[WH(CO)_3(P_3)]^+$ were formed, respectively. The ^{1}H NMR and IR spectroscopic data were identical to those reported in the literature.[27] Complex **9** gave a complicated mixture of carbonyl containing products, which were not characterized.

Cyclooctane Dehydrogenation with $WH_6(PP_2)$ (4) and $ReH_5(PP_2)$ (11). In a typical procedure, $WH_6(PP_2)$ (**4**) (7.2 mg, 0.0099 mmol), cyclooctane (1.5 mL), and *tert*-butylethylene (0.070 mL, 0.53 mmol) were placed in a resealable glass vessel (made of triple-thickness glass and equipped with an Ace glass Teflon stopcock). The solution was degassed by performing three freeze–pump–thaw cycles on a vacuum line. The vessel was filled with argon, sealed, and heated for 24 h at the reaction temperature (145 °C for **4**, 185 °C for **11**) in a thermostated oil bath. During the reaction, the solution was stirred with a small Teflon-coated stirring bar. After cooling to room temperature, the yellow solution was distilled in vacuo. All the volatiles were collected in a trap cooled in liquid N_2 and were analyzed by GC. The involatile organometallic residue was dissolved in CD_2Cl_2 and shown by ^{1}H and ^{31}P spectroscopy to be a mixture of metal phosphine complexes.

The procedure used for the mercury test for homogeneity of the catalytic system was identical with that described above except that a small drop of liquid mercury was added to the reaction mixture prior to degassing and heating.

Acknowledgment. We thank Yale University and the National Science Foundation for support.

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(42) Hartley, J. G.; Venanzi, L. M.; Goodall, D. C. *J. Chem. Soc.* **1963**, 3930.