complex is supported by very recent spectral studies of the change to absorbance after the addition of alkene to oxo-iron porphyrin. From this complex the epoxide is formed by a slipping displacement of the alkene toward the oxygen, which leads to a favorable interaction between the π^* of the alkene and the lone pair on the oxygen.

Appendix

All calculations were performed using transition metal INDO,[7] CNDO,[7] and extended Hückel[8] calculations. The parameters used in the INDO and CNDO calculations are given in Table I and in extended Hückel calculations in Table II.

Ab Initio Theoretical Studies of Dihydrogen Coordination vs. Oxidative Addition of H₂ to Five-Coordinate Tungsten Complexes

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Abstract: Various modes of H₂ bonding to d⁶ metal complexes are investigated using ab initio electronic wave functions and relativistic effective core potentials. The novel η^2 form in W(CO)₃(PR₃)₂(H₂) complexes, in which the H–H bond remains intact, is contrasted with seven-coordinate dihydride WL₅H₂ complexes, in which oxidative addition to the metal center has occurred. The influence of the electronic properties of the ligands in the relative stability of these forms is also discussed.
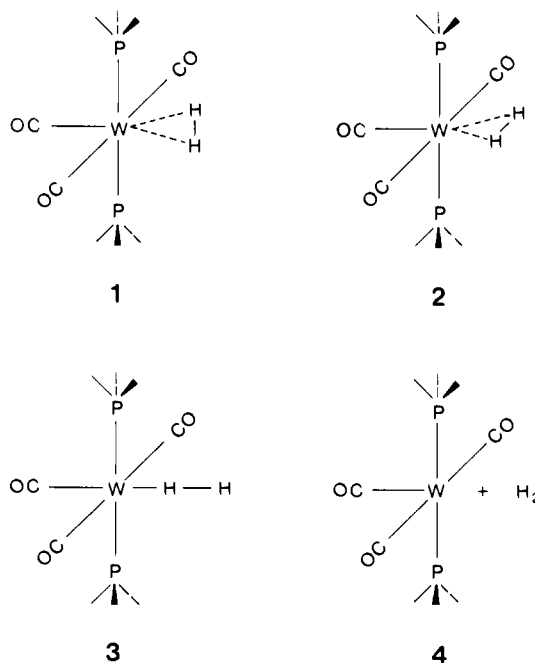
I. Introduction

Several compounds of a new class of dihydrogen metal complexes have recently been synthesized[1,2] in which the H–H bond remains essentially intact, in contrast to the traditional situation in oxidative addition[3] wherein the H–H bond is cleaved with the formation of two metal–hydrogen bonds or the analogous case of C–H activation.[4] In the dihydrogen compounds first characterized by Kubas et al.,[1a] the H₂ is bonded to five-coordinate d⁶ metal center in W(CO)₃(PR₃)₂(H₂) and its Mo analogue. The factors governing the stability of these dihydrogen species relative to their more familiar dihydride forms are being explored experimentally[1,2] and theoretically.[5,6]

In this study we present the first ab initio theoretical study of these species. We will analyze the relative stability of the two forms—the six-coordinate dihydrogen and the seven-coordinate dihydride—and we will explore the important role the ligand can play in stabilizing one form or the other. In particular, we present

results of ab initio calculations on model complexes W(CO)₃-(PR₃)₂(H₂) and W(PH₃)₅(H₂) where the effects of replacing the strongly π-accepting CO ligands by PR₃ groups can be probed. Using ab initio approaches, in contrast to semiempirical methods for metal complexes, one can optimize the bond lengths and other geometrical parameters and then compare the relative energies of the various geometrical forms of the molecule. The results of these studies are presented in the next sections, and the details of the calculation appear at the end.

II. Bonding of H₂ to WL₅ Fragments

A. W(CO)₃(PH₃)₂(H₂) Complexes. Structures 1–3 exemplify the modes of H₂ bonding to a W(CO)₃(PH₃)₂ fragment: two sideways bonded (η^2-coordinated) forms (1 and 2) and the end-on

(1) (a) Kubas, G. J; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. *J. Am. Chem. Soc.* **1984**, *106*, 451. (b) Kubas, G. J.; Ryan, R. R; Wrobleski, D. *Ibid.* **1986**, *108*, 1339. (c) Wasserman, H. J.; Kubas, G. J. Ryan, R. R. *Ibid.* **1986**, *108*, 2294. (d) Kubas, G. J; Unkefer, G. J.; Swanson, B. I.; Fukushima, E. *Ibid.* **1986**, *108*, 7000.

(2) (a) Sweany, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 2374. (b) Upmacis, R. K.; Gadd, G. E.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; Whyman, R. Simpson, A. F., *J. Chem. Soc., Chem. Commun.* **1985**, 27. (c) Church, S. P.; Grevels, F.-W.; Hermann, H.; Schaffner, K. *Ibid.* **1985**, 30. (d) Crabtree, R. H.; Lavin, M. *Ibid.* **1985**, 794. 1661. (e) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zublowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581. (f) Gadd, G. E.; Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *Ibid.* **1986**, *108*, 2547. (g) Ozin, G. A.; Garcia-Prieto, J. *Ibid.* **1986**, *108*, 3099. (h) Upmacis, R. K; Poliakoff, M.; Turner, J. J. *Ibid.* **1986**, *108*, 3645. (i) Clark, H. C.; Hampden Smith, M. J. *Ibid.* **1986**, *108*, 3829. (j) Crabtree, R. H.; Lavin, M.; Bonneviot, L. J. *Ibid.* **1986**, *108*, 4032. (k) Sweany, R. L. *Organometallics* **1986**, *5*, 387. (l) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1986**, 506. (m) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 3124.

(3) (a) Collman, J. P. *Acc. Chem. Res.* **1968**, *1*, 136. (b) Vaska, L. *Ibid.* **1970**, *3*, 386. (c) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973.

(4) For leading references on C–H activation, see, for example: Crabtree, R. *Chem. Rev.* **1985**, *85*, 245.

(5) Hay, P. J. *Chem. Phys. Lett.* **1984**, *103*, 466.

(6) (a) Saillard, J. Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006. (b) Bagatur'yants, A. A.; Anikin, N. A.; Zhidomirov, G. M.; Kazanskii, V. B. *Zh. Fiz. Khim.* **1981**, 55, 2035. (c) Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* **1977**, *16*, 511. (d) Sevin, A.; *Nouv. J. Chim.* **1981**, *5*, 233. (e) Sevin, A.; Chaquin, P. *Ibid.* **1983**, *7*, 353.

1

2

3

4

bonded (η^2-coordinated) form (3). Using a rigid W(CO)₃(PH₃)₂ fragment, the geometries of these three forms of H₂ coordination

Table I. Calculated Bond Lengths (Å) and Bond Angles for Tungsten Dihydrogen Complexes and Comparison with Experimental Studies

		R(W–H)	R(H–H)	bond angles (deg)
		W(CO)$_3$(PH$_3$)$_2$(H$_2$) Complexes—Theory		
η^2-dihydrogen complex	(1)	2.153	0.796	
η^2-dihydrogen complex	(2)	2.176	0.790	
η^1-dihydrogen complex	(3)	2.44	0.734	
fragment + H$_2$	(4)	∞	0.74	
dihydride complex	(7)	1.850	1.911	∠H–W–H = 62.2
				∠C$_{eq}$–W–C$_{eq}$ = 81.0
dihydride complex	(8)	1.830	1.840	∠H–W–H = 60.4
				∠P$_{eq}$–W–P$_{eq}$ = 81.9
		η^2-W(CO)$_3$(PR$_3$)$_2$ Complex (1)—Experiment		
low-temp X-ray diffraction[1a]		1.95 ± 0.23	0.75 ± 0.16	
room-temp neutron diffraction[1a]		1.75	0.84	
low-temp neutron diffraction[7a]		1.89 ± 0.01	0.82 ± 0.01	
		W(PH$_3$)$_5$(H$_2$) Complexes—Theory		
η^2-dihydrogen complex	(5)	2.043	0.836	
dihydride complex	(11)	1.838	1.843	∠H–W–H = 60.2
				∠P–W–P = 83.5
dihydride complex	(12)	1.838		∠P$_1$–W–H = 68[b]
				∠H–W–P$_2$ = 62[b]
				∠P$_2$–W–P$_2$ = 100[b]

[a] All angles refer to ligands in the equatorial plane containing the two H atoms and the three ligands. [b] Angles fixed at values from experimental structure for Mo complex (see text).
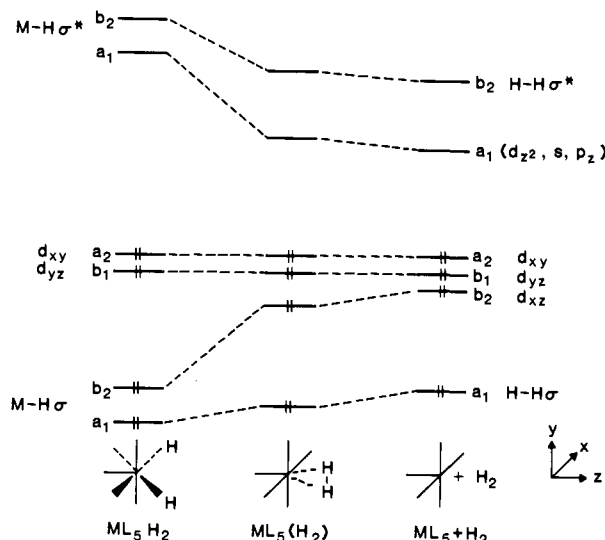
Table II. Calculated Relative Energies of Tungsten Dihydrogen Complexes

structure		rel energy (kcal/mol)
W(CO)$_3$(PH$_3$)$_2$(H$_2$) Complexes		
fragment + H$_2$	(4)	0.0
η^2-dihydrogen complex	(1)	−16.8
η^2-dihydrogen complex	(2)	−16.5
η^1-dihydrogen complex	(3)	−5.7
dihydride complex	(7)	−6.8
dihydride complex	(8)	0.0
W(PH$_3$)$_5$(H$_2$) Complexes		
fragment + H$_2$	(6)	0.0
η^2-dihydrogen complex	(5)	−19.1
dihydride complex	(11)	−22.2
dihydride complex	(12)	−32.7

have been optimized using Hartree–Fock wave functions. The sideways bonded species (Table I) are found to be stable with respect to the fragments **4** by 17 kcal/mol and more stable than the end-on form, which is bound by only 10 kcal/mol. Little difference in energy is observed between the two sideways bonded forms with the H$_2$ axis parallel either to the P–W–P axis or to the C–W–C axis. The former orientation is slightly favored, leading to a rotational barrier about the midpoint of the W–H$_2$ bond of 0.3 kcal/mol.

The calculated structure of the lower energy η^2 form (**1**) shows a slight lengthening (from 0.74 to 0.796 Å) of the H–H bond from uncomplexed H$_2$ with a W–H distance of 2.15 Å. This structure is in excellent agreement with the experimental studies to date (Table II). In the first report of the W(CO)$_3$(PR$_3$)$_2$(H$_2$) complex the X-ray and neutron diffraction studies had difficulty in ascertaining the positions of the hydrogen atoms because of crystal disorder and the small X-ray scattering cross sections for hydrogen.[1] The X-ray structure showed a H$_2$ moiety with H–H distance of 0.75 ± 0.16 Å and a W–H bond of 1.95 ± 0.23 Å; the room-temperature neutron diffraction structure showed H–H and W–H bond lengths of 0.84 and 1.75 Å, respectively. The H$_2$ also appeared to lie somewhat off the P–W–P and C–W–C axis of the five-coordinate fragment.

More recent low-temperature neutron diffraction studies[7a] clearly show two equal W–H bonds (1.89 ± 0.01 Å) and with the H$_2$ lying exactly parallel to the P–W–P axis as predicted by the present calculations and having a H–H separation of 0.82 ± 0.01

(7) (a) Vergamini, P. J.; Wasserman, H.; Keotzle, T.; Kubas, G. J., manuscript in preparation. (b) Kubas, G. J.; Private communication.

Figure 1. Orbital correlation diagram for ML$_5$ d^6 fragment interacting with H$_2$.

Table III. Orbital Population Analysis of W Complexes

		W				H
		s	p	d	tot	tot
		W(CO)$_3$(PH$_3$)$_2$(H$_2$) Complexes				
η^2-dihydrogen	(1)	0.302	0.781	5.817	6.900	0.981
η^2-dihydrogen	(2)	0.297	0.756	5.826	6.879	0.980
η^1-dihydrogen	(3)	0.287	0.689	5.829	6.805	1.116,[a]
						0.903[b]
dihydride	(7)	0.247	0.931	5.590	6.768	1.107
dihydride	(8)	0.356	1.025	5.499	6.880	1.086
fragments	(4)	0.319	0.650	5.805	6.776	1.000
		W(PH$_3$)$_5$(H$_2$) Complexes				
η^2-dihydrogen	(5)	0.017	−0.057	5.982	5.942	1.023
dihydride	(11)	0.144	0.219	5.720	6.083	1.118
dihydride	(12)	0.101	0.211	5.627	5.939	1.217
fragments	(6)	0.001	−0.071	5.950	5.884	1.000

[a] Inner H atom. [b] Outer H atom.

Å. Although the calculations have correctly described the preferred mode of H$_2$ binding, there remain some quantitative differences (Table II) between the theoretical and observed bond lengths. The most accurate experimental bond length is considerably shorter (by 0.26 Å) than the calculated value, and the H$_2$

Table IV. Comparison of Theoretical and Experimental Vibrational Frequencies for Tungsten Dihydrogen Complexes

	frequency (cm⁻¹)	
	H–H	M–H₂
W(CO)₃L₂(H₂) complexes		
calcd (L = PH₃)	2474	808
exptl (L = PCy₃)[a]	2690	1575
exptl (L = P-i-Pr₃)[a]	2695	1567
H₂ molecule		
calcd	4561	
exptl[b]	4401	

[a] Reference 1d. [b] Huber, K. P. Herzberg, G. *Constants of Diatomic Molecules*, Van Nostrand: New York, 1979.

bond length is underestimated by 0.024 Å in the calculations. These quantitative differences can arise from a combination of the following factors: (1) assuming a rigid five-coordinate fragment, (2) using model PH₃ ligands, and (3) neglecting electron correlation effects. A recent determination of the barrier to rotation[7b] indicates a larger barrier (∼2 kcal/mol) than the calculated barrier (0.3 kcal/mol).

The origin of the stabilization of the dihydrogen adduct is shown schematically in the orbital correlation diagram in Figure 1. The orbitals of the WL₅ fragment are quite familiar[9] and consist of the three filled 5d orbitals derived from the t₂g octahedral set and an unfilled σ orbital comprised of a 5d–6s–6p hybrid extending toward the vacant octahedral site. The filled H₂ σ orbital can delocalized into the empty WL₅ σ orbital in the formation of a weak dative bond. The other possible interaction arises from the filled $5d_{yz}$ orbital with the σ* orbital of H₂ which has the same symmetry. These dual mechanisms of σ-donation and π-back-donation are analogous to the features found in metal carbonyl complexes, where the extent of back-bonding is much more pronounced.

Examination of the Mulliken population analyses (Table III) for the fragment and the η² complex reveals an overall increase of 0.12 e on the W atom upon complexation and the total charge on each hydrogen has decreased slightly from 1.00 to 0.98 e. The σ-bonding orbitals of the W atom (6s, $6p_z$, and $5d_{z^2}$) show a net increase of 0.13 e, while the π-bonding orbitals ($6p_y$ and $5d_{yz}$) undergo a net loss of 0.03 e. Although the other five ligands also influence the amount of charge on the metal, the above trends are consistent with a mechanism involving some σ-donation from the H₂ ligand and a lesser degree of π-back-donation from the metal.

The origin of the small rotational barrier (0.3 kcal/mol) of H₂ about the M–H₂ axis is difficult to discern from the population analysis, since the amounts of σ-donation (+0.13 and 0.12 e) and π-back-donation (−0.03 and −0.03 e) are virtually indistinguishable in the two cases where the H₂ is parallel to the PH₃ and CO ligands, respectively. The slight preference for the former orientation is consistent with the fact that the dπ orbitals in the W(CO)₃(PR₃)₂ fragments have the ordering $d_{xz} < d_{yz}$ in Figure 1 if the PR₃ ligands are chosen to lie along the y axes. This ordering arises from the greater stabilization of the d_{xz} afforded by the CO π* orbitals relative to the d_{yz} orbitals. To the extent that back-bonding from the dπ orbitals into the H₂ σ* orbital can occur, the lower energy of d_{xz} relative to d_{yz} makes this back-bonding less favorable in the case when the H₂ σ* orbital is parallel to the CO ligands and more favorable when it is parallel to the PR₃ ligands.

Vibrational frequencies provide another measure of the metal-H₂ interaction in metal complexes. In Table IV we compare the calculated harmonic frequencies for the H–H stretch in the dihydrogen complex and in uncomplexed H₂ with the observed frequencies from IR and Raman studies. Both theory and experiment show a marked decrease in the H–H stretching frequency from free H₂ (4401 cm⁻¹ exptl, 4561 cm⁻¹ calcd) to the dihydrogen complex (2690 cm⁻¹ exptl, 2474 cm⁻¹ calcd). The calculations apparently underestimate the degree of M–H₂ bonding, however, as measured by the M–H₂ stretching frequency of 808 cm⁻¹ compared with 1575 cm⁻¹ observed experimentally. This is

consistent with the overestimate of the W–H bond length (by 0.2 Å) in the calculations compared to the experimental structures (Table I) discussed previously.

B. W(PH₃)₅(H₂) Complex. The dihydrogen complex in which the CO ligands were replaced by PH₃ groups was also examined and compared with the isolated fragments **5** and **6**. The geometry (Table I) for the H₂ ligands was similar to the W(CO)₃(PH₃)₂(H₂) complex with W–H and H–H distances of 2.043 and 0.836 Å, respectively; i.e., the H₂ is slightly longer than in the W(CO)₃-(PH₃)₂(H₂) complex. The H₂ molecule is bound to the rigid WL₅ fragment by 19.1 kcal/mol. The Mulliken population analysis indicates actually a slight (0.02 e) gain in charge on each H and much more donation (0.13 e) from the metal π-bonding orbitals upon complexation.

5   **6**
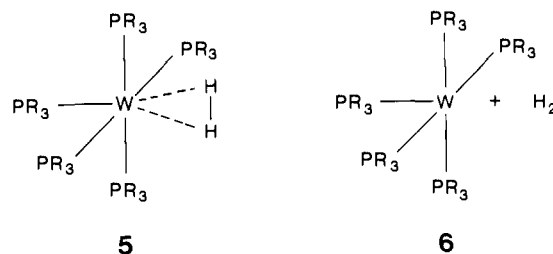
III. Oxidative Addition and Seven-Coordinate Dihydride Complexes

We now consider the question as to why the H₂ remains intact in the η²-dihydrogen complex W(CO)₃(PH₃)₂(H₂) instead of undergoing oxidative addition to form two W–H bonds and a seven-coordinate dihydride species. As we shall show, the electron-withdrawing or electron-donating characteristics of the ligands play a crucial role in influencing whether the oxidative addition will proceed or whether it will be arrested in the η² dihydrogen form. We will first investigate the possible seven-coordinate species W(CO)₃(PH₃)₂(H)₂ and again compare these complexes with the W(PH₃)₅(H)₂ species.
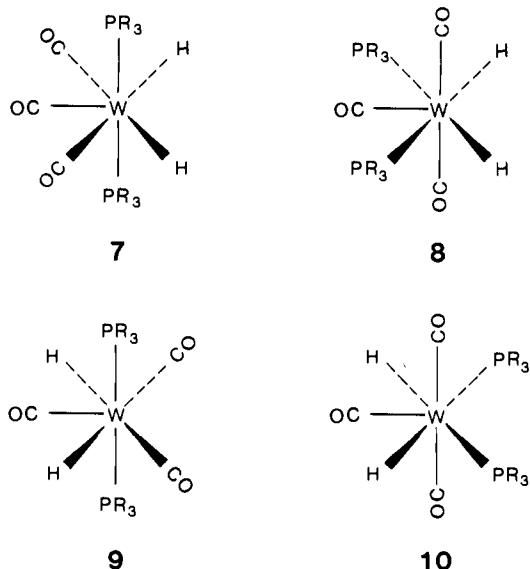
From the orbital correlation diagram (Figure 1) it is apparent that there is nothing to prevent concerted cis-addition of the H₂ to form the cis dihydride from orbital symmetry considerations, since the W–H bonding orbitals (a₁ and b₂) of the dihydride correlate with the H₂ σ orbital and the W $5d_{xz}$ orbital, respectively. These are the same set of orbitals involved in cis-addition of H₂ to d¹⁰ ML₂ and d⁸ ML₄ complexes to form ML₂H₂ and ML₄H₂ species, respectively. While the addition to ML₄ species has been studied extensively experimentally,[4] four-coordinate cis dihydrides are much less stable but have been observed in solution in equilibrium with the more stable trans dihydrides.[8a] Theoretical calculations on the model Pt(PH₃)₂ + H₂ reaction indicate a concerted addition of H₂ with barriers of 10–20 kcal/mol.[8b–d]

A. W(CO)₃(PH₃)₂(H₂) Species. Of the possible seven-coordinate dihydrides (**7–10**) let us consider the least motion reaction in which the two W–L bonds originally parallel to the H–H axis bend back as two W–H bonds are formed. In this pseudo-pentagonal bipyramid there are two possibilities depending on whether the OC–W–CO bonds bend back to form **7** or whether the P–W–P bonds bend back to form **8** (Table I). The optimized structures for **7** and **8** show shorter W–H bond lengths (1.83–1.85 Å) resembling metal–hydrogen single bonds. The L–W–L angles have decreased from 90° in the octahedral fragment to 60–62°. The H–H bond distances (1.84–1.91 Å) are sufficiently long that no trace of the H–H bond remains.

The energies of these species are compared with the η²-dihydrogen forms and the fragments in Figure 2. Both seven-coordinate dihydride species lie higher in energy than the dihydrogen form (17 and 11 kcal/mol, respectively) and are only slightly bound compared to WL₅ + H₂. These forms are in fact local

(8) (a) Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 1138. (b) Kitaura, K.; Obara, S.; Morokuma, K. *Ibid.* **1981**, *103*, 2891. (c) Noell, J. O.; Hay, P. J. *Ibid.* **1982**, *104*, 4578. (d) Low, J. J.; Goddard, W. A., III *Ibid.* **1984**, *106*, 6978.
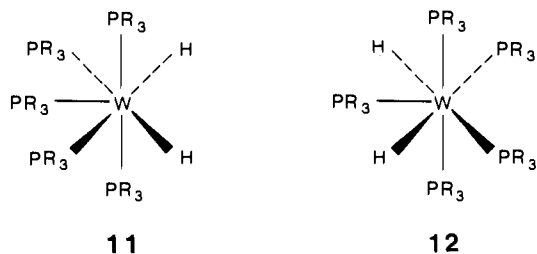
(9) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

7   **8**

9   **10**

Figure 2. Calculated relative energies for $W(CO)_3(PH_3)_2(H_2)$ species.

Figure 3. Calculated relative energies for $W(PH_3)_5(H_2)$ species.

minima, but the present calculations did not explore the reaction path to determine the magnitude of the barrier. It is interesting that it is preferable to bend the PH_3 ligands to accomodate the H_2 than it is to bend the CO ligands, since **8** is lower than **7** in energy. Bending the CO ligands to form **7** reduces the π-back-bonding from the metal d orbitals and the CO ligands, which is maximized at 90° bond angles. Since this loss of back-bonding stabilization is more severe for the CO ligands than the more weakly π-accepting PH_3 ligands, this would account for the preference of **8** to **7**. However, for realistic PR_3 groups with bulky R substituents, the steric effects may dominate these electronic effects as the P–W–P angle is compressed.

B. $W(PH_3)_5$ $(H)_2$ **Complexes.** For the case of having all PH_3 ligands in the $W(PH_3)_5(H)_2$ complexes, a much different situation prevails concerning the oxidative addition reaction. Before examining the results, let us consider the orbital correlation diagram in Figure 1. If the d_{xz} orbital is to interact with the σ^* H_2 orbital, the presence of the CO ligands will serve to decrease this interaction as the d levels are stabilized by back-bonding. Replacing the CO by PR_3 should destabilize the orbital and promote the activation of the H_2 bond. We note that the energies of the three highest filled levels (describing the 5d electrons) are –0.2066, –0.2034, and –0.1988 au for the $W(CO)_3(PH_3)_2(H_2)$ complex and –0.1440, –0.1426, and –0.1425 au for the $W(PH_3)_5(H_2)$ complex—a shift of 2 eV upward in energy (1 au = 27.2117 eV).

In contrast to $W(CO)_3(PH_3)_2(H)_2$, the seven-coordinate dihydride $W(PH_3)_5(H)_2$ (**11**) lies 3 kcal/mol below (Table II) the η^2 complex (**5**)! Replacing the CO ligands by PR_3 groups favors the oxidative addition reaction proceeding to completion rather than being arrested in the η^2-dihydrogen stage. The geometrical parameters of the $W(CO)_3(PH_3)_2(H)_2$ and $W(PH_3)_5(H)_2$ species are quite similar, despite the differences in their relative stabilities compared with the fragments.

11   **12**

While the proximal dihydride (**11**) represents the species initially formed in a least motion addition of H_2 to the WL_5 fragment, it appears that further polytopal rearrangements of the seven-coordinate complex can occur to yield even more stable forms. We investigated one such possibility for the distal form (**12**) $W(PH_3)_5(H)_2$ complex where two pairs of H and PH_3 ligands have been interchanged in the equatorial plane. In this form the hy-
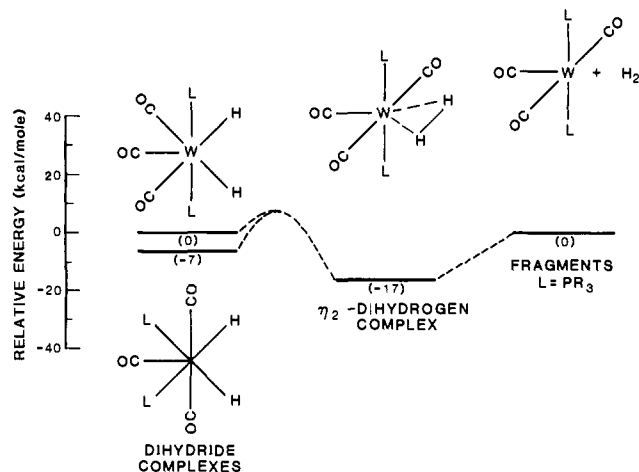
drogens are no longer cis to each other but have intervening phosphine ligands; in addition, the phosphines are less crowded in terms of steric interactions. This isomer is calculated to lie 10 kcal/mol lower than the cis form and 13 kcal/mol lower than the η^2 form.
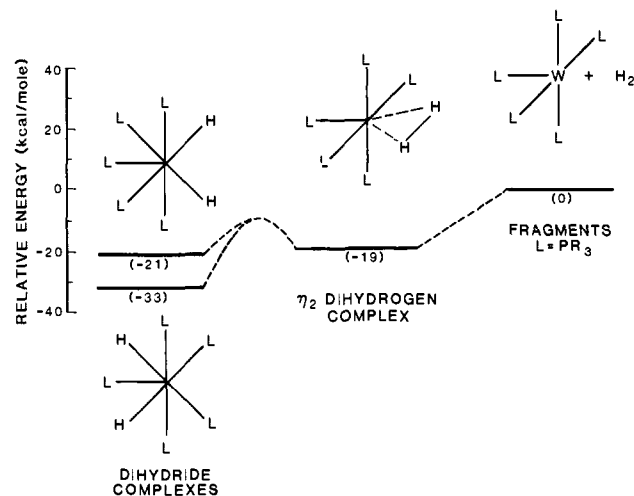
C. Dihydrogen vs. Dihydride Coordination. The calculations reported in the above sections show that, for the model compounds chosen for this study, the "sideways-bonded" η^2-coordination mode of dihydrogen is the preferred structure for $W(CO)_3(PH_3)_2(H_2)$ while the seven-coordinate dihydride is the most stable structure for $W(PH_3)_5(H_2)$. This preference for η^2-coordination in $W(CO)_3(PH_3)_2(H_2)$ correlates with the overall stabilization of the 5d orbitals, and the $5d_{xz}$ orbital in particular, by the back-bonding CO ligands. When these ligands are replaced by the less stabilizing PH_3 groups, the dihydride is the most favored form. Both of these observations are consistent with the experimental information to date. The calculated structure for $W(CO)_3(PH_3)_2(H_2)$ agrees well with the observed structure[1] of $W(PR_3)_2(CO)_3(H_2)$ where R = *i*-Pr.

A seven-coordinate dihydride complex of Mo analogous to form **12** of $W(PH_3)_5(H_2)$ has been reported by Lyons et al.[10] and characterized by X-ray diffraction. The $Mo(PMe_3)_5(H)_2$ complex has Mo–H bond lengths of 1.68 Å and a pseudo-pentagonal bipyramid structure. The bond angles in the equatorial plane are as follows: P_a–Mo–H (70 and 66°), H–Mo–P_b (59 and 66°), and P_b–Mo–P_b (99°). Above 190 K the complex is fluxional on the NMR time scale. Oxidative addition of H_2 has also been reported by Choi and Muetterties[11] to $W[P(OR)_3]_5$ and by Van-Catledge

(10) Lyons, D.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 695.

(11) Choi, H. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 153.

et al.[12] to Cr[P(OR)$_3$]$_5$ to form fluxional, seven-coordinate compounds in each case. The mechanistic analysis of the NMR line shapes by Van-Catledge et al.[12b] is most consistent with the assignment of the distal form (**12**) as the most stable species in solution.

The theoretical studies have arbitrarily chosen pentagonal-bipyramid-like structures (**7–10**) to represent seven-coordinate dihydrides, but these constitute but one of the many possible modes of seven-coordination.[13] Since full geometry optimizations were not feasible to be carried out for the model complexes discussed here, some of these other seven-coordinate dihydrides may have comparable energies to the dihydrides species (**7–10**). Recent experimental studies[8b] have detected the presence of a seven-coordinate dihydride in equilibrium with the η^2-dihydrogen species **1** previously isolated.[1]

The η^2-coordination mode still represents the less common mode of bonding of H$_2$ to metal centers. For W and Mo compounds, in addition to the "d^4" MH$_2$L$_5$ forms mentioned above, there are examples of "d^2" MH$_4$L$_4$ and "d^0" MH$_6$L$_3$ complexes with metal–hydrogen single bonds.[14] There have been an increasing number of η^2-dihydrogen complexes reported[2] since the initial work of Kubas et al.[1] The formation of Cr(CO)$_5$(H$_2$) and related species has been observed and detected using IR spectra by Sweany[2a] in low-temperature matrices and by Upmacis et al.[2b,h] and by Church et al.[2c] in solution.

An interesting parallel exists between the FeL$_4$H$_2$ complex—a "normal" d^6 six-coordinate dihydride—and the protonated form [HFeL$_4$(H$_2$)]$^+$, the crystal structure of which shows it to be a d^6 six-coordinate complex with a dihydrogen and a hydride ligand bound to the metal.[2e] This is also consistent with the trend noted earlier in which the proton, by stabilizing the d orbitals in the original FeL$_4$H$_2$ complex, can favor dihydrogen complexation in the η^2 form. Other examples[2d–m] of complexes of molecular-hydrogen have now been reported whic include Ir(III) d^6 complexes,[2d,j] a Pt(0) d^{10} complex,[2i] and a Mo(II) d^4 complex[2k]—HMoCp(CO)$_2$(H$_2$). Tetrahydrides ML$_4$H$_4$ have been found to actually exist as d^6 η^2-dihydrogen forms ML$_4$H$_2$(H$_2$) in the case of Fe and Ru but as the tetrahydride in the case of Os.[2m]

D. The Nature of Oxidative Addition. Let us consider in what sense the conversion from the dihydrogen complex to the dihydride form can be viewed as "oxidative addition". This will be examined from the standpoints of molecular orbital theory and of valence bond theory.

Hartree–Fock Approach. The HF orbitals for the seven-coordinate dihydride, which are schematically indicated in Figure 1, would be described by the configuration of doubly occupied orbitals

$$(d_{xy})^2 \ (d_{yz})^2(M\text{–}H, \ a_1)^2 \ (M\text{–}H, \ b_2)^2$$

where "M–H, a$_1$" and "M–H, b$_2$" represent the M–H σ bonds. If the M–H bonds were totally ionic (i.e., M$^+$H$^-$) the metal would have been oxidized from the d^6 M(0) to d^4 M(II) state. However, the Mulliken population analyses discussed above showed relatively little, if any, loss of electron charge from the metal in going from the dihydrogen to dihydride form. (Since such population analyses are notoriously difficult to interpret for transition metal species, especially for the more diffuse 6s and 6p components on the metal, it is difficult to ascribe too much physical interpretation to the numbers of Table III.) The 5d populations in these complexes are reduced by 0.2–0.3 e in the dihydride form compared to the dihydrogen form, and the total electron population on the metal decreased only 0.1–0.2 e. In the molecular orbital view, then, electron donation from the metal d$_{xz}$ into H$_2$ σ^* is nearly balanced
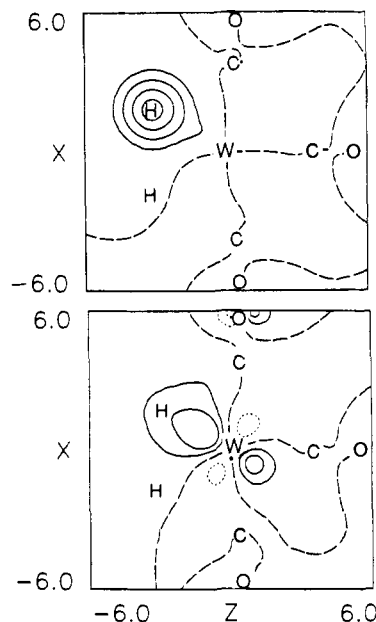
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Figure 4. Contour plot of GVB orbitals for the W–H bond in the W-(CO)$_3$(PH$_3$)$_2$(H)$_2$ dihydride complex. Each orbital contains one electron of the electron pair for the W–H bond. A symmetrically related pair of orbitals describes the other W–H bond.

by donation from the H$_2$ σ into the M dσ orbital.

The presence of π-accepting ligands prevent the oxidative addition from continuing on to the dihydride form. Conversely, σ-donating ligands should enhance the dπ–σ^* donation and favor dihydride formation.

Generalized Valence Bond Approach. Another interpretation of the bonding may be obtained by examining the generalized valence bond (GVB) orbitals,[15] in which each electron of the bond can occupy a spatially distinct orbital, in contrast to Hartree–Fock molecular orbital wave functions in which each electron pair is required to have the same spatial orbital. Typically the GVB orbitals give a localized description of the bonding, whereas canonical HF orbitals are more delocalized and maintain the symmetry of the molecule. In the GVB description each electron in the M–H bonds occupies a single orbital

$$(d_{xy})^2 \ (d_{yz})^2 \ (\phi_{1a}\overline{\phi_{1b}} + \phi_{1b}\overline{\phi_{1a}}) \ (\phi_{2a}\overline{\phi_{2b}} + \phi_{2b}\overline{\phi_{2a}})$$

where ϕ_{1a} and ϕ_{1b} represent the orbitals of one M–H bond. In Figure 4 the GVB orbitals ϕ_{1a} and ϕ_{1b} of the W–H bond in W(CO)$_3$(PH$_3$)$_2$(H)$_2$ are shown. One of the orbitals remains essentially a 1s orbital on H, while the other orbital is basically a pure 5d orbital on the W atom delocalized slightly onto the H atom, indicating a small amount of W$^+$–H$^-$ character in the bond. Overall, however, the bond remains essentially covalent. The other orbitals with significant involvement of metal orbitals are (1) the symmetrically related W–H bonding pair in the other W–H bond and (2) the essentially doubly occupied 5d$_{yz}$ and 5d$_{xy}$ orbitals. The net d electron count then remains six, just as in the η^2-dihydrogen form, except that two of the "d^6" electrons are involved in the W–H bond and the remaining four electrons are mainly nonbonding with some ligand back-bonding character. This picture qualitatively resembles a high-spin triplet d^6 configuration on the metal $(yz)^2(xy)^2(xz)^1(d\sigma)^1$ where one electron in the closed-shell d^6 configuration (Figure 1) has been promoted to the dσ orbital. Stabilization of the xz orbital by CO ligands in this picture would increase the excitation energy required to convert the low-spin d^6 configuration (which favors η^2-coordination) to the high-spin d^6 configuration (which favors dihydride formation). This argument is analogous to the discussion of Low and Goddard[8d] who described the "oxidative addition" of H$_2$ to d^{10} Pt complexes in

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Table V. Promotion Energies of WL$_5$ Fragments from Hartree–Fock Calculations

electronic configuration	rel energy (kcal/mol)	
	W(CO)$_3$(PH$_3$)$_2$	W(PH$_3$)$_5$
singlet—d$_{xy}$²d$_{yz}$²d$_{xz}$²	0^a	0^b
triplet—d$_{xy}$²d$_{yz}$²d$_{xz}$¹dσ¹	+1	−8
triplet—d$_{xy}$²d$_{yz}$¹d$_{xz}$²dσ¹	+12	−8

^{a}Total energy = −357.315 16 au. ^{b}Total energy = −47.851 59 au.

terms of exciting to a d⁹s¹ configuration which favors cis-dihydride formation.

Promotion Energies. As discussed in the preceding sections, the stability of the dπ orbital will reduce its propensity to form the dihydride. Examining the dπ → dσ promotion energy in the WL$_5$ fragment can provide an indication of this propensity. In Table V we show the results of SCF calculations on the low-spin d⁶ singlet state of the two WL$_5$ fragments—W(CO)$_3$(PH$_3$)$_2$ and W(PH$_3$)$_5$—and the high-spin d⁶ triplet state where the dπ orbital has been promoted to the dσ orbital (Figure 1). The promotion energies are 9–12 kcal/mol *larger* in the W(CO)$_3$(PH$_3$)$_2$ fragment compared to the W(PH$_3$)$_5$ fragments, which is consistent with the lower stability of the dihydrides in the former case relative to the η²-dihydrogen species. In the SCF calculations the triplet is actually predicted to lie below the singlet for the W(PH$_3$)$_5$ fragment, but electron correlation effects not included at the SCF level would stabilize the singlet relative to the triplet. These effects have been discussed for the electronic states of Cr(CO)$_5$, for example.[16] It is interesting that the promotion energy from the d$_{xz}$ orbital, which lies in the plane containing the phosphines, is lower than that for the d$_{yz}$ orbital, which lies in the plane of the CO ligands. This is consistent with the fact that formation of the cis dihydride by bonding back the phosphines (which will involve the d$_{xz}$ orbital in W–H bonding) is favored over the dihydride formed by bonding back the CO ligands (involving the d$_{yz}$ orbital).

IV. Summary

The η²-dihydrogen and dihydride forms of d⁶ ML$_5$–H$_2$ complexes have been investigated for the specific cases of H$_2$ bound to W(CO)$_3$(PR$_3$)$_2$ and W(PR$_3$)$_5$ fragments. Using optimized geometries from ab initio calculations, the six-coordinate η²-dihydrogen form is found to be the most stable species for the case of W(CO)$_3$(PR$_3$)$_2$(H$_2$) while the seven-coordinate dihydrides W(PR$_3$)$_5$(H)$_2$ are found to be most stable. The stability of η²-dihydrogen complexes can be traced to the stabilization of the d orbitals by the π-acceptor CO ligands which prevents the oxidative addition from continuing on to the dihydride complex.

V. Details of the Calculations

The calculations employed ab initio effective core potentials (ECP) on the P atoms[5] and relativistic ECP's (RECP) on the W atom[17] to replace the effect of the core electrons and, in the case of W, to incorporate the effects of the relativistic mass–velocity and Darwin terms on the valence electrons. A flexible primitive (3s 4p) and (3s 3p 3d) Gaussian basis set contracted to [2s 2p] and [2s 2p 2d] was used to represent the valence orbitals of P and W, respectively.[5] (4s) and (5s 1p) primitive bases contracted to [2s] and [3s 1p] were used for the hydrogens in PH$_3$ and H$_2$, respectively. The latter basis set provides a balanced description of the H$_2$ molecule and H atom. STO-3G minimal basis sets were used for C and O.

The bond lengths (Å) of the WL$_5$ fragment were fixed using the experimental values from the X-ray structure[1] of W(CO)$_3$(PR$_3$)$_2$(H$_2$) as follows (in Å): W–P (2.492), W–C$_{ax}$ (1.969), C$_{ax}$–O$_{ax}$ (1.119), W–C$_{eq}$ (1.989), and C$_{eq}$–O$_{eq}$ (1.148). The P–H distance of 1.421 Å was adopted with tetrahedral bond angles. For the W(PH$_3$)$_5$(H)$_2$ complex with the hydrogens staggered relative to each other in the equatorial plane, the following bond angles (in degrees) were taken from the Mo(PMe$_3$)$_5$(H)$_2$ structure of Lyons et al.[10]: P$_a$–M–H (68), H–M–P$_b$ (63), and P$_b$–M–P$_b$ (99).

Calculations were carried out using (1) the BIGGMOLI-GVBTWO programs of R. C. Raffenetti and F. W. Bobrowicz, respectively, and (2) the CRAY version of GAUSSIAN 82 by S. Binkley and R. L. Martin. Gradient optimization of the geometrical parameters not fixed in the ML$_5$ fragment was performed using the GAUSSIAN 82 program.

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Ab Initio Study of Hypervalent Sulfur Hydrides as Model Intermediates in the Interconversion Reactions of Compounds Containing Sulfur–Sulfur Bonds

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Abstract: Ab initio MO calculations involving the 4-31G* basis set have been used to predict the equilibrium geometries of the hypervalent sulfur hydrides H$_2$SS, (HS)$_2$SS, H$_2$S(SH)$_2$, H$_2$S(SSH)$_2$, and the cyclic H$_4$S$_4$. The energy changes in their formation from appropriate sulfanes H$_2$S$_n$ (n = 1–4) have been studied with the 6-31G* basis set including the correction for the electron correlation by the second- and third-order Møller–Plesset perturbation theory. The results are used to discuss the possible pathways in the interconversion reactions between various sulfur compounds containing cumulated SS bonds, for example, the formation of S$_7$ from S$_8$ for which hypervalent intermediates have been proposed recently. Comparison with experimental evidence is made whenever possible.

The structural features of the SS bonds in various environments are well-established.[2] It has also been observed that many compounds containing cumulated SS bonds easily undergo interconversion reactions. Some of the more common examples are