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TITLE AB INITIO STUDIES OF TRANSITION-METAL DIHYDROGEN CHEMISTRY

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AUTHOR(S) E. M. Kober
P. J. Hay

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Los Alamos, New Mexico 87545

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Ab Initio Studies of Transition-Metal Dihydrogen Chemistry

Edward M. Kober and P. Jeffrey Hay*
Los Alamos National Laboratory
Los Alamos, NM 87545

ABSTRACT

Examples of transition metal complexes containing dihydrogen ligands are investigated using ab initio electronic structure calculations employing effective core potentials. Calculated geometrical structures and relative energies of various forms of $WL_5(H_2)$ complexes (L = CO, PR_3) are reported, and the influence of the ligand on the relative stabilities of the dihydrogen and dihydride forms is studied. The possible intramolecular mechanisms for H/D scrambling are investigated in another d^6 complex, $Cr(CO)_4(H_2)_2$, where various polyhydride intermediates are possible.

Introduction

The recent discoveries[1,2] of a new class of metal complexes involving molecular hydrogen have spawned numerous experimental and theoretical investigations to understand the bonding and reactivity of these systems. In the first part of this article we review some of our recent theoretical calculations on W dihydrogen species and compare the results to available experimental information. In the second part mechanisms for scrambling of H_2/D_2 mixtures to HD by Cr dihydrogen complexes are investigated.

Tungsten Dihydrogen Complexes

In the molecular dihydrogen species $W(CO)_3(PR_3)_2(H_2)$ first characterized by Kubas et al.[2] in both X-ray and neutron diffraction studies, the dihydrogen is bonded in η^2 sideways fashion to the d^6 metal center. Over 50 compounds involving many of the transition metals have since been synthesized by various workers. In addition, existing hydrides such as $FeH_4(PR_3)_3$ have now been found[3] to be formulated as molecular hydrogen complexes, i.e., as $Fe(H_2)(H)_2(PR_3)_3$.

In this section we review briefly our previous theoretical calculations[4] on two prototypical dihydrogen complexes $W(CO)_3(PH_3)_2(H_2)$ and $W(PH_3)_5(H_2)$. The calculations employed a relativistic effective core potential (ECP) to replace the inner core electrons on W and a nonrelativistic ECP on P with a flexible gaussian basis to describe the valence electrons of the system.[5] Details of the calculation are given in Ref. 4.

Structures 1-3 exemplify the modes of H_2 bonding to a $W(CO)_3(PH_3)_2$ fragment: two sideways bonded (η^2-coordinated) forms (1 and 2) and the end-on bonded (η^2-coordinated) form (3). Using a rigid $W(CO)_3(PH_3)_2$ fragment, the geometries of these three forms of H_2 coordination 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 agreement with the experimental studies to date. Recent low-temperature neutron diffraction studies 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 Å. Although the calculations have correctly described the preferred mode of H_2 binding, there remain some quantitative differences (Table I) 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 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 fragments, (2) using model PH_3 ligands, and (3) neglecting electron correlation effects. Examination of the Mulliken population analyses for the fragment and the η^2 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 H_2 ligand and a lesser degree of π-back-donation from the metal.

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. The energies of these species are compared with the η^2-dihydrogen forms and the fragments in Figure 2. Both seven-coordinate dihydride species lie higher in energy than the dihydrogen from (17 and 11 kcal/mol, respectively) and are only slightly bound compared to WL_5 + H_2.

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. In contrast to $W(CO)_3(PH_3)_2(H)_2$, the seven-coordinate dihydride $W(PH_3)_5(H)_2$ lies 3 kcal/mol below the η^2 complex! 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. 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.

H_2-D_2 Exchange Involving Metal-Hydrogen Complexes

The gas phase reaction

$$H_2 + D_2 \longrightarrow 2HD$$

occurs only under severe conditions such as in shock tubes with an activation energy (~100 kcal/mole) comparable to the H-H bond energy. In fact, the kinetics have been interpreted in terms of a free radical mechanism involving H atoms rather than the biomlecular process indicated in the above equation. By contrast, several cases of facile H_2-D_2 exchange have been observed under thermal or low temperature conditions involving dihydrogen complexes

$$L_nMH_2 + D_2 \longrightarrow L_nMHD + HD$$

Upmacis, Poliakoff and Turner[6] observed HD exchange as in Eq. (2) for mixtures of $Cr(CO)_4(H_2)_2$ and D_2 but interestingly <u>not</u> for mixtures of $Cr(CO)_5(H_2)$ and D_2. Kubas <u>et al</u>. observe a similar phenomenon where HD is produced from reacting $W(CO)_3(PR_3)_2(H_2)$ with D_2 either in solution or in the solid state. In addition other cases of H-D scrambling occur readily with metal hydride complexes[6] as in the case of Cp^*_2ScH or Cp_2ZrH.

Since the work of Upmacis <u>et al</u>. on $Cr(CO_4)(H_2)_2$ complexes is suggestive of an intramolecular mechanism, Burdett <u>et al</u>.[7] have examined various polyhydride structures as possible intermediates in this process using extended Huckel theory. These studies have led us to pursue <u>ab initio</u> electronic structure calculations of $Cr(CO)_4(H_2)_2$ species and possible mechanisms leading to H_2-D_2 exchange. Implicit in these studies is the assumption that there is rapid equilibrium between

$$Cr(CO)_4(H_2)_2 + D_2 \rightleftarrows \underline{Cr(CO)_4(H_2)(D_2) + H_2}$$

which subsequently undergoes intramolecular exchange

$$Cr(CO)_4(H_2)(D_2) \longrightarrow Cr(CO)_4(HD)_2$$

although this is only inferred from the experimental studies. What is actually observed is $Cr(CO)_5(HD)$ formation in a mixture of $Cr(CO)_5(D_2)$ and $Cr(CO)_4(D_2)_2$ when reacted with H_2.

In Fig. 3 the results of ab inito calculations on stable structures of $Cr(CO)_4(H_2)_2$ or its fragments are presented. The calculations have been carried out at the Hartree-Fock level, where the structures have been optimized using gradient techniques with the modified GAUSSIAN 82 or the MESA electronic structure codes.[8] An effective core potential was used to replace the [Ne] core of Cr with a [3s 3p 2d] contracted Gaussian basis to describe the outer 3s, 4s, 3p, 4p and 3d orbitals. A flexible [3s 1p] basis was used for hydrogen and an STO-3G basis was employed for C and O.

Of the possible forms for the parent molecule cis-$Cr(CO)_4(H_2)_2$ the lowest geometrical structure is found to have the H_2 molecules oriented in an upright position relative to the equatorial plane. The structure with both H_2 ligands lying in the equatorial plane is 3.1 kcal/mole higher in energy, corresponding to a rotational barrier of 1.5 kcal/mole for the rotation of one H_2 about the metal-H_2 bond. Removal of one H_2 to form $Cr(CO)_4(H_2)$ requires 17.8 kcal/mole and removal of the second H_2 requires another 16.8 kcal/mole. At his level of calculation the dihydrogen-dihydride equilibrium

$$Cr(CO)_4(H_2) \rightleftarrows Cr(CO)_4(H)_2$$

is found to favor the dihydride by about 2 kcal/mole. The calculated Cr-H_2 and H-H bond lengths are 1.787 and 0.77 A respectively for the upright form. (Fig. 4).

Some of the possible polyhydride forms--having either a square H_4 or a H_3^+-H^- species coordinated to $Cr(CO)_4$--are found to be very high in energy (50 kcal/mole) and hence are unlikely intermediates in the H_2-D_2 exchange reaction.

Another pathway is shown schematically in Fig. 5, where the conversion of the bis-dihydrogen complex to a dihydrogen-dihydride complex. The process is symmetry allowed in the sense that the three relevant orbitals in the equatorial plane, the Cr $d_{x^2-y^2}$ and the two H_2 σ orbitals of the bis dihydrogen species transform into the Cr-H σ and H_2 σ bonds of the dihydrogen dihydride species. The dihydride form is calculated to lie 10 kcal/mole higher in energy with a Cr-H and Cr-H_2 bond lenghts of 1.729 and 1.923 A respectively.

The above reaction was investigated at the SCF level assuming C_{2v} symmetry and treating the H-Cr-H bond angle between the two central H atoms as the reaction coordinate. An activation barrier of 24 kcal/mole (see Fig. 6) was found for this process--a relatively low barrier compared to some of the other polyhydride species. A non-C_{2v}-pathway was also investigated where a similar barrier was also found (Fig. 6).

The calculated energies for the above process are considerably higher than the energy needed to remove a H_2 to form $Cr(CO)_4(H_2)$. It is premature to reject the above mechanisms, however, until calculations including electron correlation effects at a consistent level for all species involved along the reaction path. In addition, the possibilities of intermolecular reaction processes involving other H_2 molecules (or even H atoms inadvertantly produced in the matrix experiments) need to be considered.

In conclusion, while some relatively low energy pathways for the conversion of H_2-D_2 into HD in Eq. (4) have been found, it is unclear whether these intermediates are indeed responsible for the experimental observations of Upmacis, Poliakoff and Turner. A resolution will have to await more extensive theoretical calculations end experimental studies. In particular the current challenge to theorists in transition-metal chemistry is the development of reliable treatments of electron correlation effects which have not been included in SCF-level treatments of this sort but which are essential for chemically meaningful results.

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Figure Captions

Fig. 1. Structural forms of $W(CO)_3(PR_3)_2(H_2)$ species.

Fig. 2 Relative energies in kcal/mole of $W(CO)_3(PH_3)_2(H_2)$ species (above) compared to $W(PH_3)_5(H_2)$ species (below).

Fig. 3. Relative energies in kcal/mole of $Cr(CO)_4(H_2)_2$ species.

Fig. 4. Calculated structural parameters for $Cr(CO)_4(H_2)_2$ species.

Fig. 5. Correlation diagram for bis-dihydrogen to dihydrogen-dihydride forms of $Cr(CO)_4(H_2)_2$ species.

Fig. 6. Calculated energies from Hartree-Fock calculations for possible intermediates involved in H/D exchange.

TABLE 1. Calculated W-H and H-H bond lengths (in A) for $W(CO)_3(PR_3)_2(H_2)$ Species.

		R (W-H)	*R* (H-H)
$W(CO)_3(PH_3)_2(H_2)$ 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
dihydride complex	(8)	1.830	1.840
η^2-$W(CO)_3(PR_3)_2$ Complexes -- Experiment			
low-temp X-ray diffraction		1.95 ±0.23	0.75±0.16
room-temp neutron diffraction		1.75	0.84
low-temp neutron diffraction		1.89±0.01	0.82±0.01

Figure Captions

Fig. 1. Structural forms of $W(CO)_3(PR_3)_2(H_2)$ species.

Fig. 2 Relative energies in kcal/mole of $W(CO)_3(PH_3)_2(H_2)$ species (above) compared to $W(PH_3)_5(H_2)$ species (below).

Fig. 3. Relative energies in kcal/mole of $Cr(CO)_4(H_2)_2$ species.

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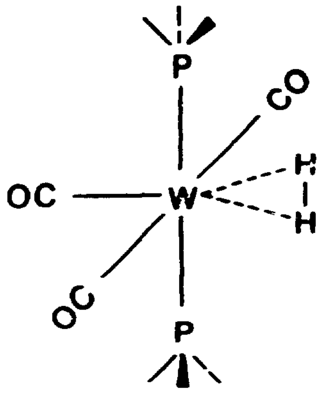
Fig. 6. Calculated energies from Hartree-Fock calculations for possible intermediates involved in H/D exchange.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W
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P

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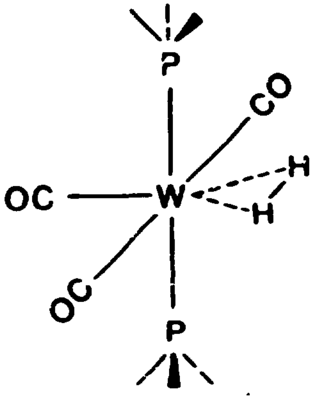
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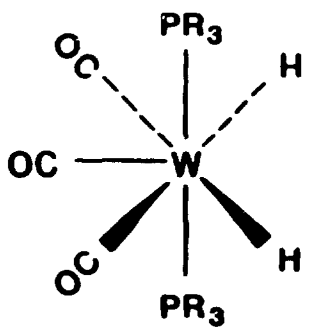
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PR$_3$

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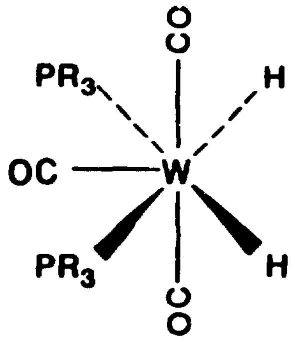
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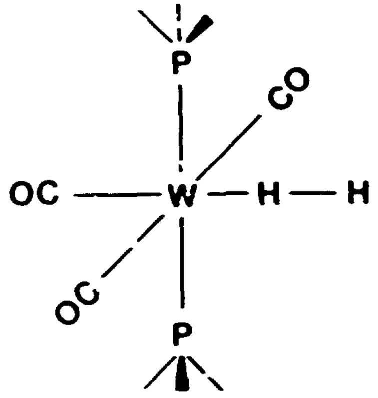
H
CO

8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OC
P

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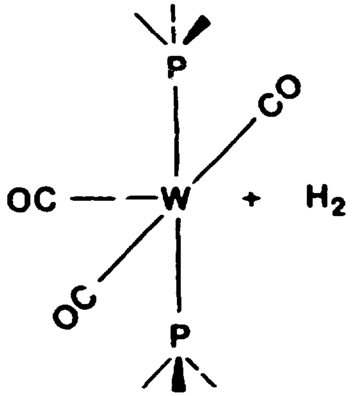
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H$_2$
OC
P

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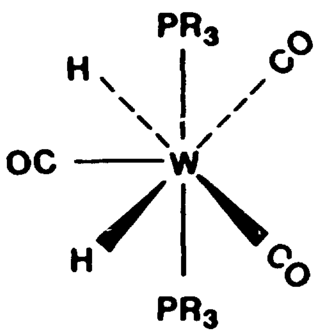
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OC
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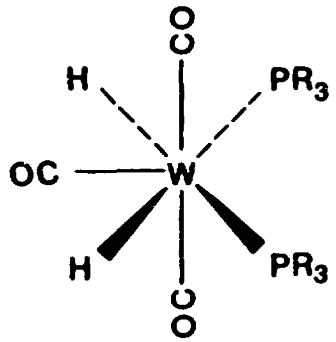
PR$_3$
CO

9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PR$_3$
OC
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H
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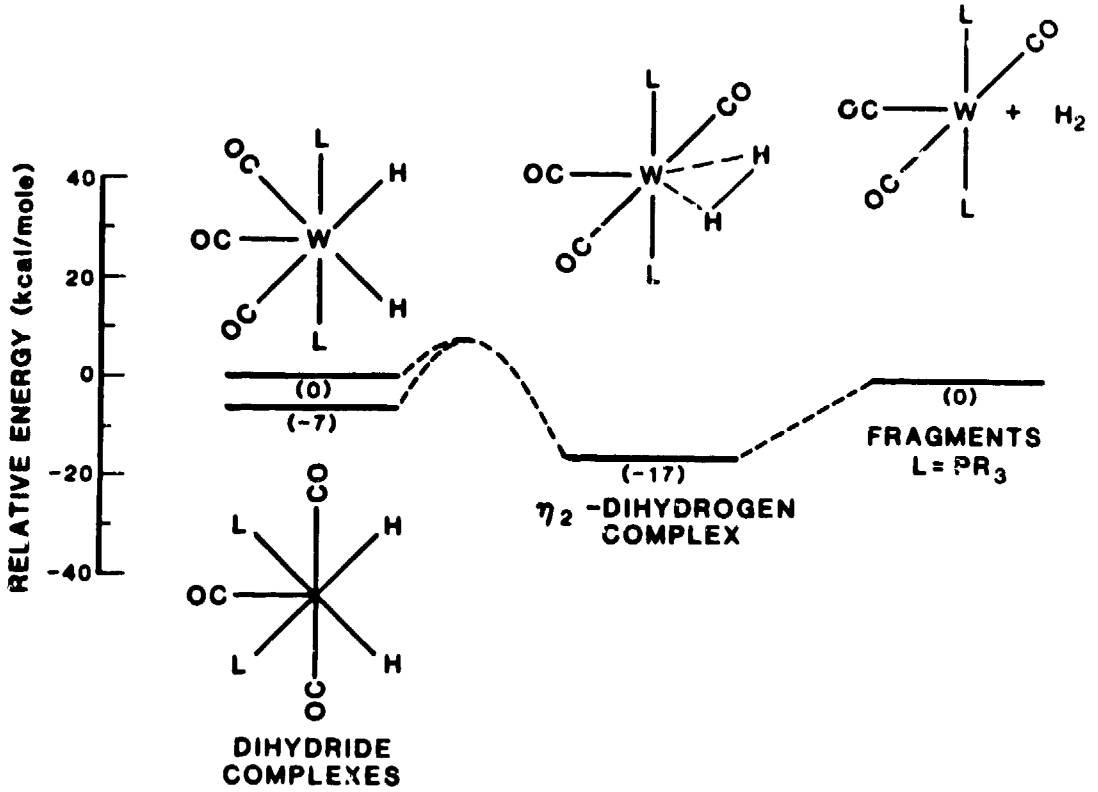
CO

10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-20
-40
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L
H
OC
W
OC
H
L
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(-7)
CO
L
H
OC
L
H
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DIHYDRIDE COMPLEXES
L
CO
OC
W
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H
OC
L
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η_2 -DIHYDROGEN COMPLEX
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+
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L
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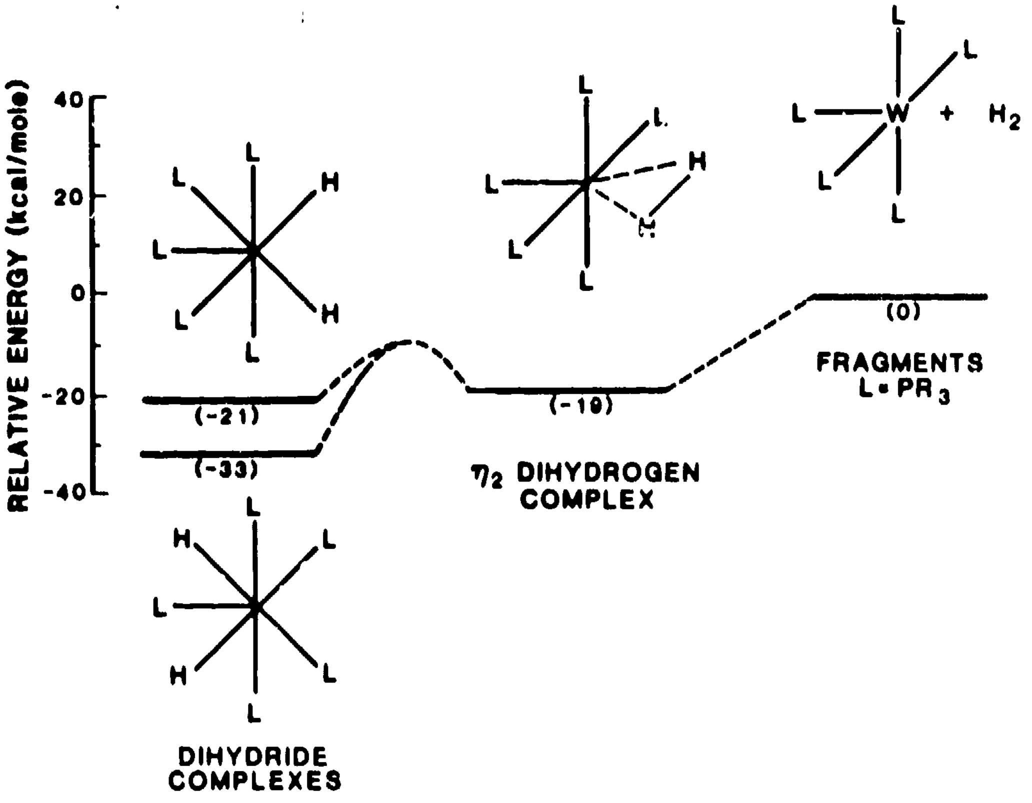
L = PR_3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20
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-20
-40
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L
H
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L
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(-33)
L
H
L
L
H
L
L
DIHYDRIDE COMPLEXES
L
L
L
H
H
L
L
(-19)
η_2 DIHYDROGEN COMPLEX
L
L
L
W
+
H_2
L
L
(0)
FRAGMENTS
L = PR_3

CHM-VG-9747

$Cr(CO)_4(H_2)_2$ Structures and Fragments

	E (kcal/mole)
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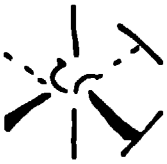
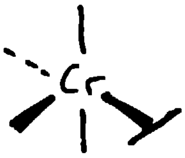
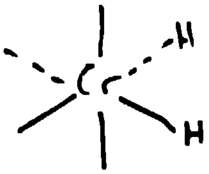
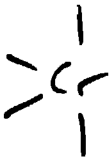
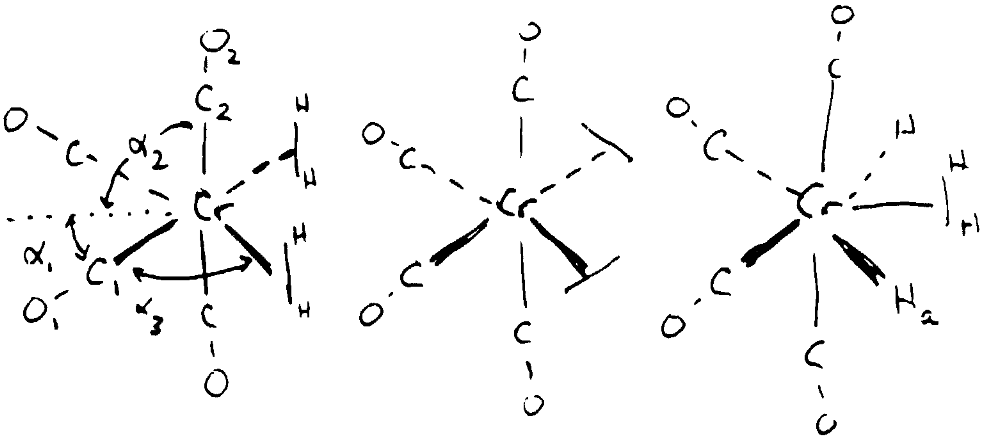
	+ 3.1
 $+ H_2$	+ 12.8
 $+ H_2$	+ 10.6
 $+ 2 H_2$	+ 29.4

Optimized Geometrical Parameters

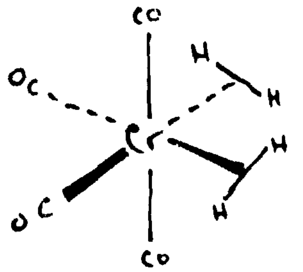


Bond lengths (Å)

Cr - H_2	1.787	1.772	1.923
H - H	0.772	0.779	0.764
Cr - H_f.			1.729
Cr - C_1	1.997	1.980	2.084
Cr - C_2	1.971	1.992	2.077
C_1 - O_1	1.147	1.148	1.143
Cl_2 - O_2	1.150	1.146	1.142

Bond angles (deg)

α_1	46.9	44.9	42.1
α_1	90.8	93.6	94.2
α_1	90.3	88.9	67.4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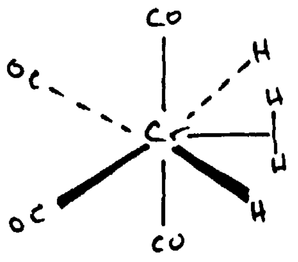
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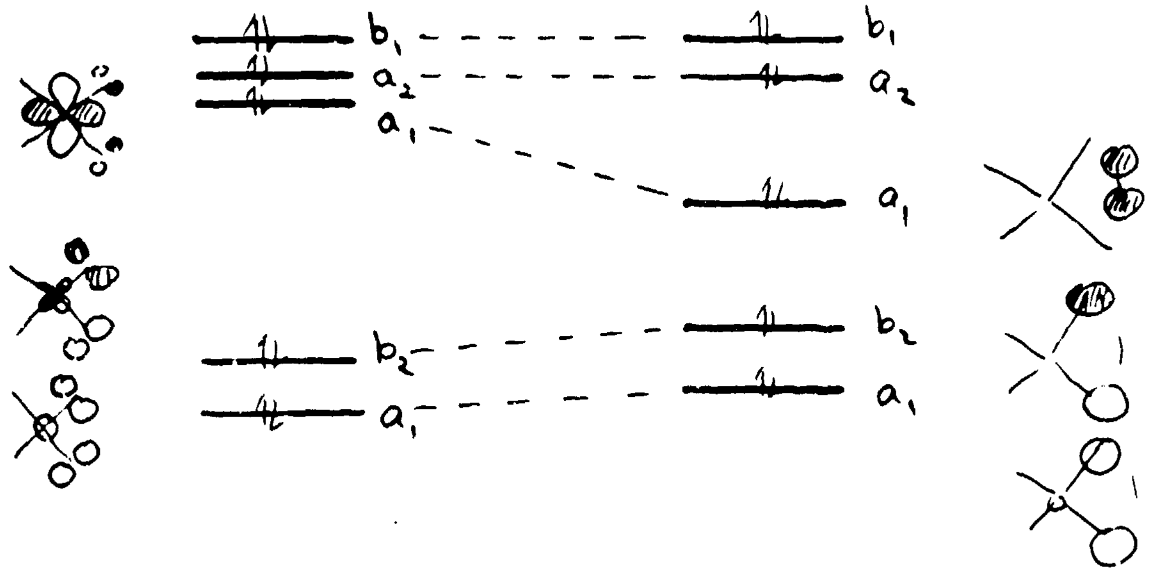
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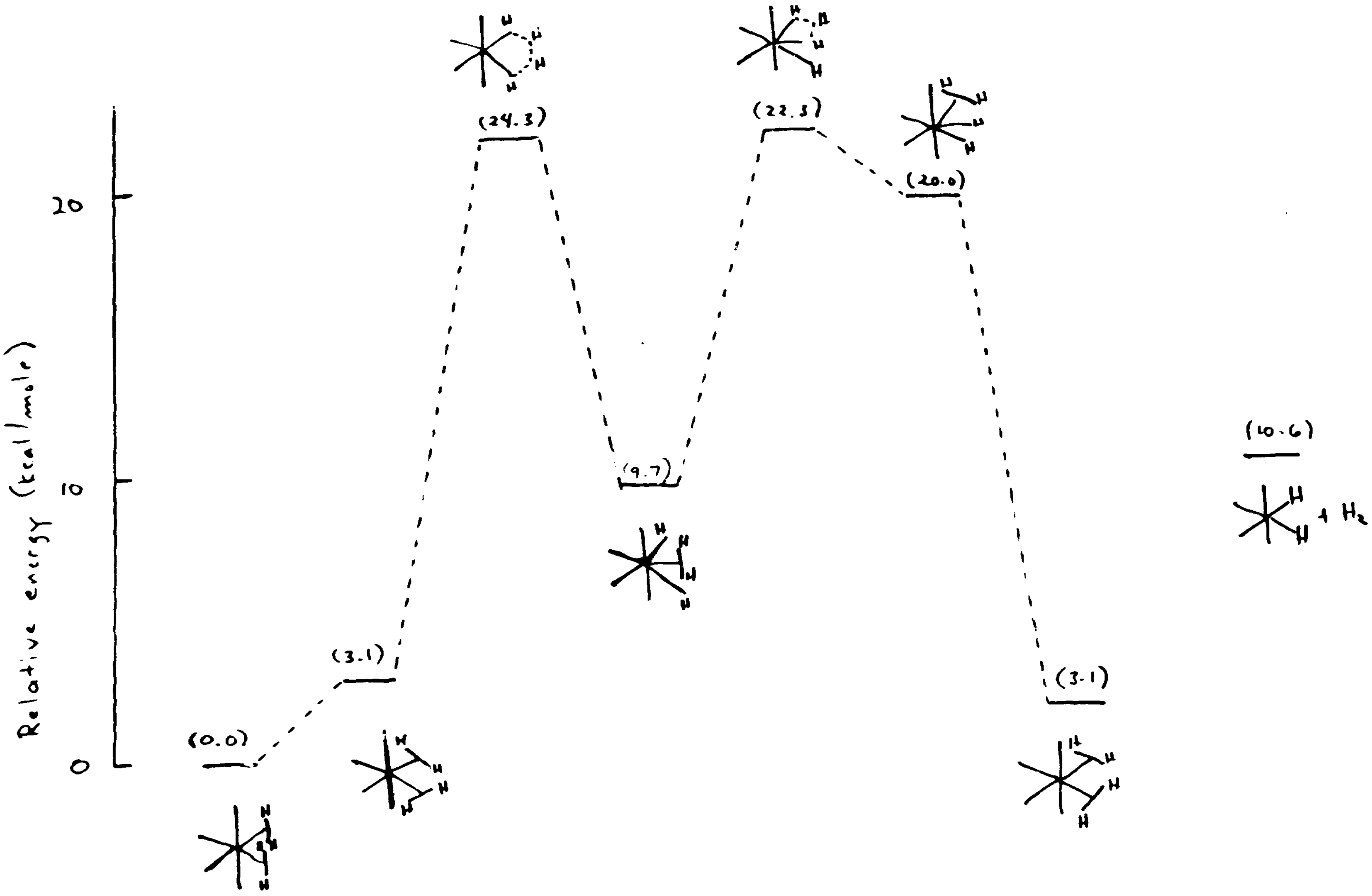
b$_2$
a$_1$


Relative energy (kcal/mole)
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20
(0.0)
(3.1)
(24.3)
(9.7)
(22.3)
(20.0)
(3.1)
(10.6)
H
+ H_2