diverts the preferred reaction pathway to 1,4 in this intramolecular case.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this work and to F. A. L. Anet and D. Farrelly for helpful discussions and assistance. Dr. M. D. Miller provided the graphics routines for Figures 4–13.

Registry No. 2,4-Cyclopentadienylcarbene, 65312-66-5; benzvalene, 659-85-8; methylene, 2465-56-7; butadiene, 106-99-0; allylmethylene, 90566-94-2; 2-cyclopropenylcarbene, 61281-66-1; 2-cyclobutenylcarbene, 112879-11-5; 2-cyclopentenylcarbene, 123811-71-2; 1-methyl-2,4-cyclopentadienylcarbene, 74130-26-0; 1-methylbenzvalene, 74130-27-1; 2-methylbenzvalene, 74130-29-3; cyclopentene, 142-29-0; vinylcyclopropane, 693-86-7; tricyclo[3.2.0.0^{2,6}]heptane, 30907-83-6; bicyclobutane, 157-33-5; tricyclo[1.1.1.0^{4,5}]pentane, 333-17-5; tetrahedrane, 157-39-1.

Supplementary Material Available: Structures and listings of bond lenths and bond angles (5 pages). Ordering information is given on any current masthead page.

Structure and Bonding in $Cr(CO)_5H_2$ and $Cr(CO)_4(H_2)_2$ Complexes

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Abstract: The electronic structure of $Cr(CO)_5(H_2)$ and $Cr(CO)_4(H_2)_2$ complexes has been investigated using ab initio electronic wave functions and effective core potentials. In $Cr(CO)_5(H_2)$ η^2-H_2 coordination is found to be energetically preferred, in agreement with experimental results. The formation of the dihydride form is an energy-demanding process; this explains why under D_2 pressure no isotope exchange is observed. $Cr(CO)_4(H_2)_2$ contains two coordinated hydrogen molecules; polyhydrogen forms are found to be highly unstable. A mechanism is proposed to explain the observed formation of $Cr(CO)_5(HD)$ during H_2/D_2 exchange in $Cr(CO)_4(H_2)_2$; it implies the formation of a dihydrogen–dihydride complex. The calculations predict also the possible existence of a stable open H_3 ligand in the hypothetical $[Cr(CO)_5(H_3)]^+$ complex.

The recent discovery of transition-metal complexes where the H_2 molecule is stably coordinated to a metal center[1] without giving oxidative addition has opened new opportunities to study one of the most fundamental molecular activations in organometallic complexes as well as in metal surfaces.[2] Since the first example of a stable dihydrogen complex, $W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$, where η^2-H_2 denotes side-on bonding, was reported by Kubas in 1984,[1a] an increasing number of similar compounds have been synthesized.[3] The original Kubas complex has been characterized in the solid state by both X-ray and neutron diffraction techniques,[1] showing an H–H distance of 0.75 Å (X-ray) and 0.84 Å (neutron); a similar H–H distance has been observed in the $[Fe(H)(H_2)(dppe)_2]^+$ complex.[3a,b] The existence of other η^2-H_2 complexes has been inferred mainly by spectroscopic measurements.[2,3]

This is the case of the $Cr(CO)_5H_2$ complex where the existence of coordinated molecular hydrogen has been deduced from ν_{H-H} IR data.[4,5] Simple theoretical arguments[6] as well as experimental evidence[4] support the view of an H_2 complex with low stability toward H_2 loss and low-energy pathways for the $H_2 \rightarrow D_2$ exchange. Indeed, under pressure of D_2, $Cr(CO)_5H_2$ thermally reacts to form $Cr(CO)_5D_2$.[5] However, different from Kubas' compound where isotope exchange occurs giving within a few days a statistical mixture of H_2, D_2, and HD species[1b,1c], under pressure of D_2, the only species observed with the Cr complex are $Cr(CO)_5H_2$ and $Cr(CO)_5D_2$ with no evidence for any $Cr(CO)_5HD$.[5] The latter is observed in a mixture of $Cr(CO)_5(D_2)$ and $Cr(CO)_4(D_2)_2$ under H_2 pressure.[5] This exchange is of considerable interest for the understanding of the interaction of H_2 with metal centers. A proposed mechanism for the exchange implies the simultaneous coordination of both H_2 and D_2 molecules according to the scheme $Cr(CO)_6 + 2H_2 - 2CO \rightarrow Cr(CO)_4(H_2)_2 + D_2 - H_2 \rightarrow Cr(CO)_4(H_2)(D_2) \rightarrow Cr(CO)_4(HD)_2 + CO - HD \rightarrow Cr(CO)_5(HD)$. The rate-determining step will involve the cleavage of H–H and D–D bonds and the formation of a new HD ligand, but the mechanism is not clear. It has been suggested that the exchange can occur through the formation of transient species where polyhydrogen "mass spectrometer molecules" like H_3 or H_4 are stabilized by bonding to the metal center.[7,8]

In this paper we present the results of an ab initio MO–LCAO study of $Cr(CO)_5(H_2)$ and $Cr(CO)_4(H_2)_2$ complexes. We will analyze the relative stabilities of η^1-H_2 and η^2-H_2 as well as the seven-coordinated dihydride forms of $Cr(CO)_5(H_2)$ and of a number of possible geometrical isomers of $Cr(CO)_4(H_2)_2$. The bonding of molecular hydrogen with transition-metal complexes has been already the subject of theoretical studies based on qualitative arguments.[6-9] However, ab initio approaches, different

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Table I. Computed Geometrical Parameters and Total Energies for Different Isomers of $Cr(CO)_5H_2$

system		r(Cr–H), Å	r(H–H), Å	α(H–Cr–H), deg	E_T, au	D_e,[a] kJ/mol	ΔE, kJ/mol
H_2			0.74		–1.1293		
$Cr(CO)_5$					–647.2829		
η^2-H_2	I	1.90	0.77	23	–648.4274	40.0	0.0
η^1-H_2	II	2.26	0.75		–648.4157	8.0	30.6
dihydride	III	1.58	1.77	68	–648.3679		156.0

[a] Dissociation energy with respect to $Cr(CO)_5 + H_2$

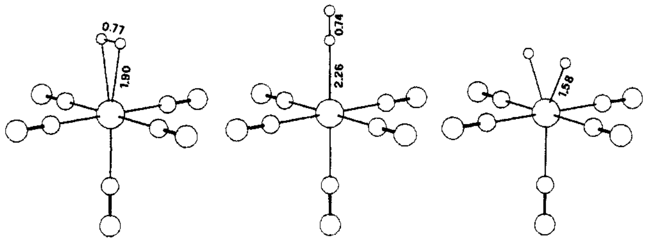
from semiempirical methods, provide more quantitative information about the relative stabilities of different structures, thus giving an indication of the possible reaction paths for the H_2/D_2 exchange reaction mentioned above.

Several ab initio studies were performed for single transition-metal atoms[10] or for coordinatively unsaturated complexes[11] interacting with H_2, while, to our knowledge, only two ab initio studies have been reported for real complexes: the work of Hay on Kubas' complex[12a,b] and, very recently, a preliminary investigation by Kober and Hay[12c] on the same $Cr(CO)_4(H_2)_2$ complex considered here. In the present study the computational scheme is the same adopted by Hay in his studies. The calculations have been performed at the Hartree–Fock level determining one-electron wave functions (details are given in the Appendix). Correlation effects have not been introduced; nevertheless, we believe that the present results provide reliable qualitative information on this novel class of metal dihydrogen complexes.

Bonding of H_2 to $Cr(CO)_5$. The factors governing the stability of nonclassical dihydrogen species versus the more common dihydride forms have been investigated experimentally[2] and theoretically.[6–12] H_2 complexes represent the first example of stable intermolecular coordination of a σ bond. In fact, the primary interaction in ML_5–H_2 complexes occurs when on the metal center is present a vacant, energetically accessible orbital, geometrically oriented so as to strongly interact with the $\sigma(H_2)$ MO. The overall result is electron transfer from H_2 to the metal with decrease of H–H bond strength. The second important mechanism is the mixing of a donor metal orbital of proper symmetry with the acceptor $\sigma^*(H_2)$ MO, with corresponding metal-to-hydrogen back-donation. This bonding interaction is absent for symmetry reasons in η^1-H_2 complexes where the H_2 molecules are bonded end-on.[6] The extent of the back-donation into the σ^* antibonding MO of η^2-H_2 is the key mechanism governing the formation of dihydride versus dihydrogen complexes. The presence on the metal of strong π acceptors like the CO ligands reduces the ability of the metal to back-donate charge and favors the formation of η^2-H_2 complexes. In particular, a carbonyl group trans to H_2 is more effective because the $2\pi^*$ MO of *trans*-CO can interact with the d orbital, which has the proper symmetry to populate the $\sigma^*(H_2)$ MO.[9] It has been suggested that d^6 complexes with all acceptor ligands, like $Cr(CO)_5H_2$, are thermally unstable to H_2 loss presumably because the back-bonding is too small,[2] while complexes where the π acceptors are replaced by PR_3 groups favor the oxidative addition of H_2 with formation of the dihydride species.[12]

This general view of the bonding in ML_5–H_2 complexes is confirmed by the present ab initio study. We have considered three forms of the $Cr(CO)_5H_2$ complex: η^2-H_2 (I), η^1-H_2 (II), and dihydride (III) (Chart I). In complex I, both the eclipsed form (where the H_2 axis is parallel to the CO–Cr–CO axis) and the staggered conformer (where H_2 is rotated by 45°) have been considered, and two geometrical parameters have been independently optimized in one dimension: the H_2 distance has been first fixed to the optimum SCF value of free H_2, 0.74 Å, and the Cr–H distance has been varied. Then, the H–H bond stretching was considered, keeping the Cr–H distance fixed to the minimum of the previous curve (Table I). An elongation of 0.03 Å indicates a weakened H–H bond with respect to the free molecule. The staggered conformer is bound with respect to dissociation into $Cr(CO)_5$ and H_2 by 40 kJ/mol. This can be considered as a real chemical bond (correlation effects are expected to increase this value) but nevertheless is consistent with the observed easy loss of H_2 by thermal excitation.[4,5] The eclipsed isomer is only 2.8 kJ/mol less stable than the staggered one. This value represents a rough estimate of the rotational barrier about the midpoint of Cr–H_2, and it indicates a fluxional behavior of the H_2 ligand in the Cr complex at room temperature. It can be compared with the barrier for rotational tunneling of H_2 in Kubas' complex, 9 kJ/mol, recently experimentally determined.[13]

Chart I



I II III

For the perpendicular approach of H_2 to $Cr(CO)_5$ (structure II) the same optimization procedure as in I was followed. As expected, the Cr–H bond distance (2.26 Å) is much longer than that in structure I, the H–H distance is virtually the same as in free H_2 molecule (Table I), and the complex is bound by 8 kJ/mol only; the lack of back-donation yields a weakly stable system where the bonding originates essentially from polarization effects.

Vibrational frequencies provide an indication of the nature of the metal–H_2 interaction. We calculated harmonic frequencies for the H–H and M–H_2 stretching modes of I using a polynomial fit of five points around the minimum of the potential energy curve. The computed H–H stretch in the dihydrogen complex I, 4193 cm^{-1}, is about 400 cm^{-1} lower than that in the free H_2 molecule, 4562 cm^{-1}; however, the experimentally observed ν_{H-H} decrease is significantly larger (from 4401 to 3030 cm^{-1}).[4,5] Apparently the calculations underestimate the amount of back-donation to coordinated H_2, a breakdown partly due to the lack of correlations and relativistic effects, which, given shorter metal–ligand bond lengths,[14] increase the d–σ* overlap; in principle, ignoring the ν_{H-H}–ν_{C-O} coupling constitutes an additional source of errors. For the same reasons, also the computed M–H_2 stretching frequency, 654 cm^{-1}, is too low with respect to the band observed at 1379 cm^{-1} in $Cr(CO)_5H_2$ and tentatively assigned to this vibrational mode.[5]

Without attributing too much physical meaning to the data of Mulliken population analysis, it is interesting to observe a small

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Chart II

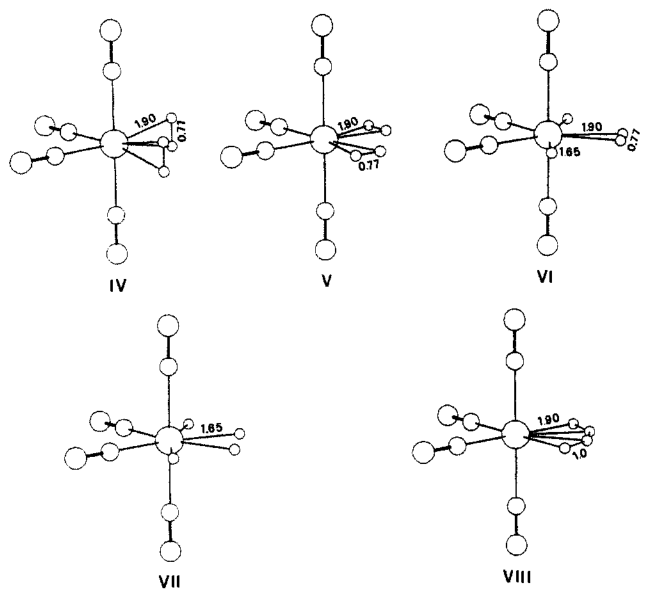
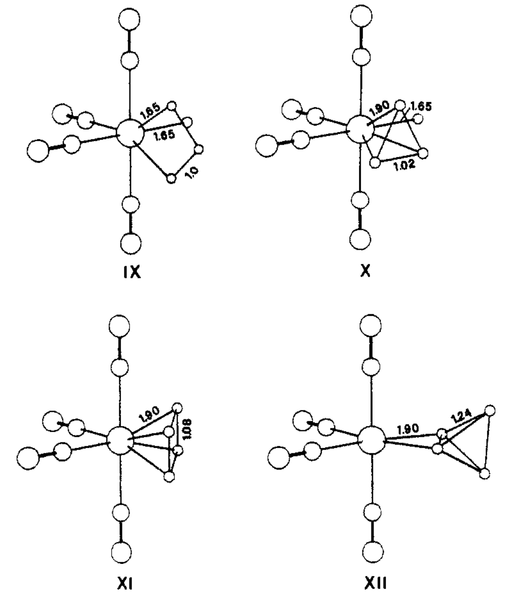


Chart III



but not negligible population of the $\sigma^*(H_2)$ MO in complex I (0.07 electrons). This is not enough however to break the H–H bond as shown by the total energy of the dihydride complex III (Table I). In this latter system the two CO ligands lying in the Cr–H_2 plane have been bent back by 10° as suggested by Hay for the analogous $W(CO)_3(PH_3)_2H_2$ complex.[12] Both the Cr–H distance and the H–Cr–H bond angle have been independently optimized (Table I). The structure represents a local minimum on the potential energy surface and is stable toward dissociation into $Cr(CO)_5$ + 2H by 178 kJ/mol but is unbound with respect to $Cr(CO)_5 + H_2$. In other words, the energy gain due to the formation of two Cr–H bonds is not enough to compensate the energy required to dissociate the H_2 molecule (338 kJ/mol according to our SCF calculations, 430 kJ/mol according to experimental measurements). The energy difference between η^2-H_2 (I) and dihydride (III) forms of $Cr(CO)_5H_2$ is therefore 156 kJ/mol; compared to the $W(CO)_3(PH_3)_2H_2$ complex, where the computed difference between the two structures is 46 kJ/mol,[12] the dihydride form of $Cr(CO)_5H_2$ is substantially less favored. This is consistent with the presence on the tungsten complex of two phosphine ligands, which increase the back-donation capability of the metal atom.

Structure of $Cr(CO)_4(H_2)_2$. $Cr(CO)_4(H_2)_2$ has been synthesized by prolonged ultraviolet photolysis of $Cr(CO)_6$ either in hydrogen-containing matrices[4] or in liquid Xe under H_2 pressure.[5] Under these conditions, $Cr(CO)_6$ loses two CO and adds two H_2 molecules. If the photolysis of $Cr(CO)_6$ is done under pressure of H_2/D_2 mixtures, the formation of $Cr(CO)_5(HD)$ is observed, via formation of $Cr(CO)_4(H_2)(D_2)$.[5]

The mechanism for the exchange is not known, and we have considered a few possible structures representing either candidates for the ground-state geometry or transient intermediates of the exchange reaction. IV and V are two isomers of $Cr(CO)_4(H_2)_2$ where the two H_2 molecules occupy two adjacent coordination sites; trans isomers have not been considered since the preference for the cis isomer has been proved experimentally.[5] The Cr–H and the H–H distances (Chart I) have been fixed to the optimum values found for $Cr(CO)_5H_2$. Structure VI is a seven-coordinated η^2-H_2, dihydride complex with distorted bipyramidal-pentagonal symmetry. Structure VII is an unusual example of an eight-coordinated tetrahydride intermediate. Structure VIII represents a possible transition state from V to VI via formation of a coordinated hydrogen chain. Strutures IX–XII (Chart III) contain polyhydrogen units as potential ligands.

The results are given in Table II. IV is the preferred structure; it is separated by only 20 kJ/mol from the orientational isomer V. As found for $Cr(CO)_5(H_2)$, the fission of the H_2 ligand with formation of two Cr–H bonds is energetically unfavorable. However, the substitution of a CO ligand in $Cr(CO)_5H_2$ with the weak acceptor H_2 molecule increases the electron density on the metal and reduces the energy separation between η^2-H_2 complex IV and dihydride complex VI from 156 kJ/mol (Table I) to 120 kJ/mol (Table II), a result of considerable importance for the explanation of the observed HD formation in $Cr(CO)_4(H_2)_2$ and not in $Cr(CO)_5(H_2)$. The dissociation of both H_2 molecules to form the tetrahydride isomer VII necessitates 293 kJ/mol, almost twice the energy required to dissociate a single H_2 molecule in $Cr(CO)_5H_2$, 156 kJ/mol, and clearly represents an unfavorable process. On the other hand, the energy cost for the formation of a coordinated tetrahydrogen chain (VIII) is about 213 kJ/mol (Table II); VIII represents therefore a possible intermediate in the H/D exchange reaction. All other structures are less stable (Table II).

Table II. Total Energies of Geometrical Isomers of $Cr(CO)_4(H)_4$

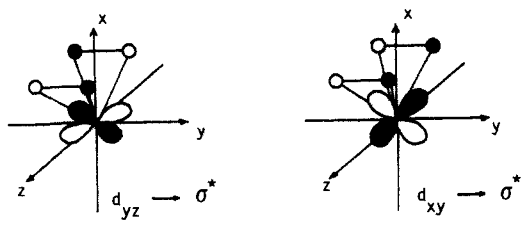
system		E_T, au	ΔE, kJ/mol
$Cr(CO)_4(H_2)_2$	IV	-537.1810	0.0
$Cr(CO)_4(H_2)_2$	V	-537.1733	20.2
$Cr(CO)_4(H_2)(H)_2$	VI	-537.1354	119.5
$Cr(CO)_4(H)_4$	VII	-537.0690	293.0
$Cr(CO)_4(H_4)$	VIII	-537.0997	213.0
$Cr(CO)_4(H_3)H$	IX	-537.0497	344.4
$Cr(CO)_4(H)(H_3)^a$	X	-536.9685	557.1
$Cr(CO)_4(H_4)^a$	XI	-536.9726	545.6
$Cr(CO)_4(H_4)^a$	XII	-536.8324	913.8

[a] H–H distance taken from optimized $(H_3)^+$ and $(H_4)^+$ free systems.

Therefore, these results support the formulation of the complex, based on IR measurements,[5] as $Cr(CO)_4(H_2)_2$ with two η^2-H_2 molecules coordinated to the metal center. The bonding can be interpreted in a similar way as in $Cr(CO)_5H_2$ (Figure 1). Besides the "σ-donation" from H_2 ligands to the metal center, in IV the metal-to-H_2 back-donation occurs through the interaction of the filled d_{xy} and d_{yz} orbitals and the $\sigma^*(H_2)$ MO (Figure 1) with a total net transfer of 0.06 electrons to each H_2 molecule. In V, the $d_{x^2-y^2}$ AO interacts more strongly with the σ^* (Figure 1) and back-donates 0.06 electrons to each H_2 molecule. Therefore, the overall charge back-donated is the same in IV and V and is virtually indistinguishable from that of $Cr(CO)_5H_2$. The tiny energy difference between the two structures, 20 kJ/mol, can be therefore attributed more to steric than to electronic effects and, in particular, to the shorter nonbonding H–H distance of V (2.30 Å) than that of IV (2.63 Å).

It is worth nothing that, according to the results recently obtained by Kober and Hay,[12c] the introduction of the correlation effects does not change the conclusion obtained at the Hartree–Fock level that the most stable form of $Cr(CO)_4(H_2)_2$ contains

STRUCTURE IV



STRUCTURE V

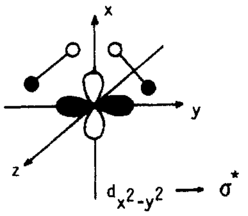


Figure 1. Orbital interaction in orientational isomers IV and V of the Cr(CO)$_4$(H$_2$)$_2$ complex.

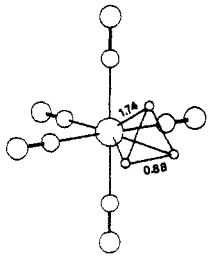
two H$_2$ molecules oriented in a position normal to the equatorial plane.

Polyhydrogen Ligands in Cr(CO)$_4$(H)$_4$. Recently, the possible existence of hydrogen-cluster ligands in metal complexes has been suggested.[7,8] Neutral gas-phase H$_n$ clusters have never been observed and the interaction of two ground-state hydrogen molecules has been extensively investigated either to study weak intermolecular forces[15] or in the attempt to rationalize the observed activation energy of the H$_2$/D$_2$ exchange reaction.[16] The existence of (H$_n$)$^+$ species has been observed in mass spectrometer experiments;[17] even masses have intensities about 50 times smaller than odd masses.[18a] However, although theoretically investigated,[19] no experimental results have demonstrated the existence of the (H$_4$)$^+$ species.[18b,19]

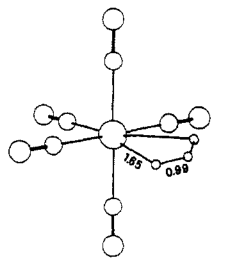
In metal complexes the basic requirement for the stabilization of coordinated polyhydrogen ligands is the net transfer of one (or two) electrons from the H$_n$ unit to an empty metal orbital, with formation of (H$_3$)$^+$ or (H$_4$)$^{2+}$ species (square and tetrahedral (H$_4$)$^+$ systems are Jahn–Teller unstable). A neutral H$_n$ ligand in fact will immediately dissociate into separate H$_2$ + H or H$_2$ + H$_2$ fragments.

In order to verify the possible occurrence and the energy cost of this charge transfer, we calculated the total energies of structures IX–XII assuming a singlet ground state for all of them since no evidence of paramagnetic dihydrogen complexes has been reported up to now.[4] In structures X–XII the H–H distances were initially taken from optimized (H$_n$)$^+$ clusters,[20] but distances taken from neutral H$_n$ and doubly charged (H$_4$)$^{2+}$ free systems have also been considered. Structures XI and XII, containing square and tetrahedral H$_4$ are clearly unstable (Table II), as predicted also by qualitative orbital energy arguments.[7] The population analysis shows that in the ground state the hydrogen cluster ligands are slightly negatively charged. Electronic configurations obtained by exciting an electron pair from H$_n$ to the metal 3d orbitals are highly unfavorable. The change of the H–H distance in the hydrogen ligand does not alter these conclusions; shorter H–H distances taken from optimized (H$_4$)$^{2+}$ systems further reduce the stability of the complexes. The most stable polyhydrogen complexes are obtained when the H–H distances are fixed to the value of the neutral free H$_4$ clusters, a result consistent with a basically covalent interaction between the metal complex and the H$_n$ ligands.

Chart IV



XIII

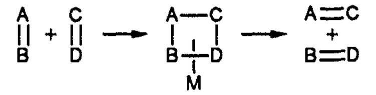


XIV

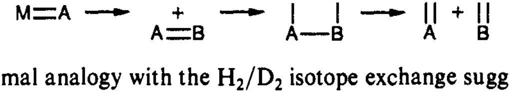
This result is not too surprising if one analyzes the one-electron orbital energies of the two subunits, neutral Cr(CO)$_4$ and, for instance, square H$_4$ ($^3A_{2g}$ ground state). The degenerate singly occupied e$_x$ and e$_y$ HOMOs in H$_4$ are at −0.384 au, i.e., slightly below the occupied 3d Cr orbitals, which in Cr carbonyls are in the region −0.15 to −0.35 au, and well below the Cr empty 3d orbitals. Hence, more than donor orbitals, the partially filled H$_4$ HOMOs act as weak acceptors of charge.

Structure X has been proposed not only as a possible transient species but also as a candidate for the ground-state structure.[7] This hypothesis, supported by extended Hückel type calculations, is based on the formation of a coordinated hydride (H$^-$) and a triangular (H$_3$)$^+$ ligand. The present total energy calculations, however, definitely rule out the possible existence of X as a stable species (Table II). If the M–H bond were totally ionic (M$^+$H$^-$), the metal would have been oxidized from d^6 (0) to d^5 (+I) and the H$_3$ ligand would have been bound by electron transfer to the metal reestablishing the d^6 configuration and leaving an (H$_3$)$^+$ unit. However, the Mulliken population analysis (although of limited validity) shows moderate charge flow from Cr to the H ligand. The Cr–H bond is essentially covalent with a small amount of Cr$^+$–H$^-$ character. Similar conclusions have been drawn also by localized descriptions of the M–H bonding based on the valence bond approach.[12] To the H$_3$ ligand are formally associated 2.75 electrons, and the system is unstable.

The idea that cyclic polyhydrogen units can form during H$_2$/D$_2$ scrambling is reminiscent of olefin metathesis, a reaction characterized by low activation barriers. In fact, originally a similar concerted four-center mechanism with formation of a coordinated cyclobutane intermediate was proposed:[21]



however, this pathway suffers from several difficulties, and the currently accepted mechanism is a one-carbene chain mechanism, proceeding through metallocyclobutane intermediates[21]



The formal analogy with the H$_2$/D$_2$ isotope exchange suggested to us to investigate the structure IX containing a "metallo-cyclo-H$_3$" unit characterized by short M–H bond lengths (Chart III); this latter form is about 130 kJ/mol less stable than the proposed transition state VIII but is clearly more favorable than all other polyhydrogen complexes considered (Table II). The geometry of IX was not optimized, but a calculation done with a longer Cr–H distance (1.90 Å) results in a less stable form. On

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(19) Borkman, R. F.; Cobb, M. *J. Chem. Phys.* **1981**, *74*, 2920. The most stable geometry for the H$_2$–(H$_2$)$^+$ complex is a planar T-shaped molecule, with the (H$_2$)$^+$ molecule lying on a line bisecting the H$_2$ bond axis; other orientations are also significantly bound, but in all cases the intermolecular distance between the two H$_2$ moieties are very large (1.50 and 1.85 Å).

(20) The computed geometries and total energies are the following: (H$_3$)$^+$ $^1A_1$, r = 0.88 Å, E_T = −1.2944 au; square, (H$_4$)$^+$ ^2E_u, r = 1.08 Å, E_T = −1.6683 au; tetrahedral, (H$_4$)$^+$ $^2T_2$, r = 1.24 Å, E_T = −1.6210 au.

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Table III. Total Energies of Open and Closed Forms of H_3 Coordinated to $[Cr(CO)_5]^+$

system		E_T, au	D_e,[a] kJ/mol
$[Cr(CO)_5(H_3)]^+$, closed H_3	XIII	−648.6052	73.2
$[Cr(CO)_5(H_3)]^+$, open H_3	XIV	−648.6653	230.6

[a] Dissociation energy with respect to $Cr(CO)_5$ + $(H_3)^+$.

the basis of these results, we cannot rule out the hypothesis that IX, or a related metallo-cyclo-polyhydrogen unit, is the transition state in the H/D exchange reaction.

From the present calculations it can be definitely concluded that polyhydrogen ligands do not easily form on Cr(0) complexes. Of course, coordinated polyhydrogen species can exist under different conditions. Indeed, a cationic trihydrogen complex of Ir, obtained by protonating $(\eta^5\text{-}C_5H_5)Ir(L)(H_2)$ with HBF_4, has been formulated as $[(\eta^5\text{-}C_5H_5)Ir(L)(H_3)]^+$ on the basis of large proton-proton NMR coupling.[22a] Very recently, however, it has been found that the large J_{HH} couplings in this and similar compounds are not magnetic in origin but are in fact exchange couplings;[22b] thus, the formulation of the molecule as a trihydrogen complex is still a matter of discussion. The presence of a coordinated H_3 unit has been suggested also as an intermediate in the H/H_2 exchange in $[Ir(H)(H_2)bqL_2]^+$.[3e,23]

In order to verify the possible existence of similar species, we computed the $[Cr(CO)_5(H_3)]^+$ complexes XIII and XIV (Chart IV) containing cyclic and open H_3 units, respectively. Very interestingly, both complexes are bound with respect to $Cr(CO)_5$ and $(H_3)^+$ (Table III). In XIII, the distance of H_3 from $Cr(CO)_5$ has been optimized (r_e(Cr–H) = 1.74 Å), and the resulting dissociation energy is 73 kJ/mol; in XIV, even with fixed Cr–H distances (Chart I), the stability of the complex is markedly larger, 231 kJ/mol (Table III). This considerable stability indicates that a stable $[Cr(CO)_5H_3]^+$ species could be obtained by protonation of $Cr(CO)_5(H_2)$.

The observed preference for open vs closed structures agrees with qualitative theoretical arguments.[7,8] The bonding in XIII is caused by the interaction of the degenerate nonbonding e levels of the H_3 equilateral triangular ligand with the d_{xz} and d_{yz} Cr orbitals; in XIV, however, the orientation of the open H_3 ligand allows a much stronger overlap between the b_1 H_3 MO and the d_{xz} Cr orbital giving rise to a strong stabilization.

This indicates that the stabilization of the H_3 ligand is connected to the formation of cationic species or, in general, to the presence of metal centers in positive oxidation states.

Mechanism of H_2/D_2 Exchange Reaction in $Cr(CO)_4(H_2)_2$. The identification of possible pathways for the H/D scrambling based on the previously reported results represents a very difficult and dangerous exercise. The first problem originates from the fact that the structures considered, chosen on the basis of the chemical intuition, are only partially optimized. An exact determination of the transition state and of the associated energy barrier requires the exploration of the entire potential energy hypersurface, a problem not easy to manage even considering the motion of the four H atoms only and the fixing of the rest of the molecule. The second problem arises from the Hartree–Fock approximation. It is well-known that correlation effects can significantly change the geometry and the stability of the optimal Hartree–Fock structures. For the specific case of $Cr(CO)_4(H_2)_2$, the effect of correlation has been taken into account by Kober and Hay[12c] who performed configuration interaction (CI) calculations on a few selected structures optimized at the SCF level. While correlation does not change the relative stabilities of the $Cr(CO)_4(H_2)_2$ structures IV and V and of the $Cr(CO)_4(H_4)$ structure VIII, they destabilize the $Cr(CO)_4(H_2)(H)_2$ complex VI by a considerable amount (75 kJ/mol).[12c] Although some care is necessary in the interpretation of these preliminary results, there is a clear indication that correlation effects can play an important role in determining the effective reaction path for the H_2/D_2 exchange reaction. Nevertheless, the SCF energy differences between some of the isomers considered are so large that it is unlikely that correlation will change the qualitative picture obtained here at the Hartree–Fock level. Thus, a possible, low-energy, reaction path for the HD formation can be formulated as follows (Figure 2).

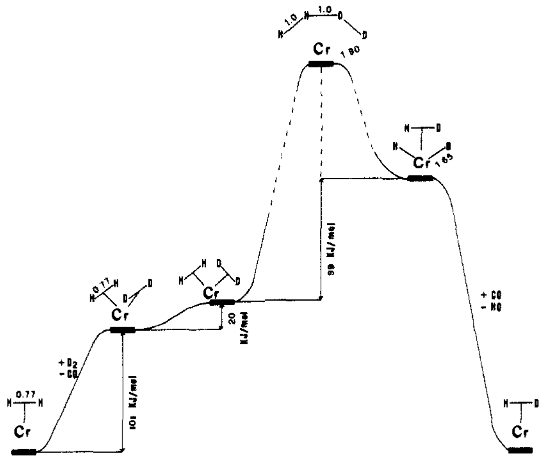

Figure 2. Qualitative energy profile for the H_2/D_2 exchange mechanism; bond distances are in angstroms.

Photolysis of $Cr(CO)_5(H_2)$ under D_2 pressure yields *cis*-$Cr(CO)_4(H_2)(D_2)$ (IV); the latter is about 100 kJ/mol less stable than I as the result of the replacement of a Cr–CO bond (about 140 kJ/mol) with a labile Cr–H_2 bond (40 kJ/mol). IV can easily rearrange to give the isomer V where the H_2 and D_2 molecules have the proper orientation to react and form a coordinated hydrogen chain. A mechanism based on the formation of a coordinated square H_4 unit (XI) directly from IV can definitely be excluded because the energy barrier for the exchange is too high (Table II); the formation of an intermediate open polyhydrogen unit VIII seems much more realistic. Whether this represents a real transition state (i.e., a saddle point on the potential energy surface) or not is a question that requires further work to be answered. In principle, metallo-cyclo-H_3 forms do also represent possible transition states.

The next step in the exchange reaction can be the linkage of the H–H and D–D bonds and the formation of a new H–D molecule as in VI (Figure 2). The complex can then easily lose HD and add a CO molecule to give $Cr(CO)_5(HD)$ or, considering the computed low rotational barrier and the reported fluxionality of the hydride-dihydrogen complexes,[3e,23] can form the $Cr(CO)_4(HD)_2$. The existence of this system however has been inferred but not proved.[5]

As previously mentioned, the H/D exchange has been observed in $Cr(CO)_4(H_2)_2$ but not in $Cr(CO)_5(H_2)$, at variance with Kubas' complex where the exchange is believed to occur through the formation of the seven-coordinated hydridic species.[1] In the tungsten complex the fission of the H–H bond to give the hydridic intermediate is a process characterized by a low activation barrier, 46 kJ/mol,[12] because of the presence of ligands increasing the electron density on the metal. In the Cr complex, the computed dihydrogen-dihydride barrier is more than 3 times larger than in Kubas' complex, but in $Cr(CO)_4(H_2)_2$ the substitution of a CO ligand with the poor π-acceptor H_2 molecule reduces the barrier for the H–H bond breaking favoring the isotope exchange. This contributes to the explanation of why in the Cr complex the scrambling occurs only when both H_2 and D_2 are coordinated to the metal.

Conclusions

The present study has confirmed the preference for η^2-H_2 coordination in $Cr(CO)_5(H_2)$ but has shown that the energy required for the dissociation of the H–H bond to give the dihydride complex is much larger than in $W(CO)_3(PR_3)(H_2)$; this rationalizes the

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different reactivity of the two complexes toward H_2/D_2 isotope exchange.

H/D scrambling is observed with $Cr(CO)_4(H_2)_2$; the calculations indicate that the ground-state geometry of this complex contains two-coordinated dihydrogen ligands oriented in an upright position relative to the equatorial plane and rule out the possibility that polyhydrogen forms are long-lived species. Cyclic polyhydrogen ligands are unlikely to exist even as transient intermediates.

The stabilization of H_n ligands is strictly connected to the possible formation of positively charged $(H_3)^+$ or $(H_4)^{2+}$ units. The charge transfer from the H_n unit to the metal is unlikely to occur in neutral complexes except in the presence of strong electronegative ligands leaving the metal center in a positive oxidation state. This is not the case of CO. On the other hand, stable H_n ligands, in particular H_3, can be obtained by protonation of preexisting dihydrogen or dihydride complexes. Considering the predicted stability of the hypothetical $[Cr(CO)_5(H_3)]^+$ complex, experimental effort in this direction could lead to the isolation of a new example of metal–H_3 coordination.

The pathway for the conversion of H_2 and D_2 into HD is likely to imply the formation of a polyhydrogen chain in $Cr(CO)_4$(H-HDD) (VIII) followed by the formation of the dihydrogen–dihydride complex $Cr(CO)_4$(H)(HD)(D) (VI). The low-energy barrier for H_2 rotation around the Cr–H_2 axis suggests an easy rearrangement of the complex to form the more stable $Cr(CO)_4(HD)_2$. The latter can easily lose an HD molecule and add a CO ligand to restore the $Cr(CO)_5$(HD) complex. All these mechanisms involve relatively low energy barriers as actually found in the low-temperature experiments of Upmacis et al.[5] As recently suggested by Kober and Hay,[12c] it is also possible that the mechanism is radical, involving either the presence of coordinated H atoms or a triplet ground state of some of the intermediates; however, no evidence for the existence of paramagnetic species has been reported so far,[4] providing indirect support in favor of a mechanism implying the formation of the dihydrogen–dihydride complex.

Appendix. Details of the Calculations

The calculations were done employing an ab initio effective core potential (ECP)[24] to replace the core electrons of the Cr atom. The 1s to 2p core is described by an ECP operator,[24c] while the $3s^23p^64s^13d^5$ valence electrons are treated explicitly. The Gaussian basis set for Cr includes 5s, 4p, and 5d primitive functions contracted to [3s1p2d].[24c] With this basis set the total energy for the ^7S ground state of the Cr atom is −85.630 83 au.

The CO molecule has been treated at all electron levels adopting a minimal Gaussian type orbital basis set[25] with an optimized contraction scheme [7s3p/2s1p].[26] (4s1p) primitive basis functions contracted to [2s1p][27] were used for H atoms and H_n molecules. With these basis sets, we computed the potential energy curve for the $^6\Sigma^+$ ground state of the Cr–H molecule. This represents an important test for the ECP and basis set used; we computed at the Hartree–Fock level for Cr–H an equilibrium bond distance, r_e = 1.68 Å, and a vibrational frequency, ω_e = 1722 cm^{-1}, in reasonably close agreement with the experimental data, r_e = 1.66 Å, ω_e = 1581 cm^{-1}.[28] Taking into account the limitations of the basis set and the lack of correlation effects, this can be considered as a satisfactory test.

The Cr–C and C–O bond lengths for the square-pyramidal $Cr(CO)_5$ complex and for the adducts with H_2 have been taken from X-ray data of $Cr(CO)_6$: d(Cr–C) = 1.916 Å, d(C–O) = 1.171 Å.[29] With these distances we computed for the dissociation of a CO ligand (E_T = −112.3355 au) from $Cr(CO)_6$ (O_h) (E_T = −759.6185 au) to give $Cr(CO)_5$ (C_{4v}) (E_T = −647.2830 au) a binding energy of 144 kJ/mol; this value is in close although fortuitous agreement with the experimentally measured value of 155 ± 22 kJ/mol.[30]

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