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Preliminary communication

Coordination of dihydrogen to transition metal complexes: ab initio investigation of $Cr(CO)_5(H_2)$ and $Cr(CO)_4(H_2)_2$

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Abstract

Carbonyl complexes of Cr-containing one- or two-coordinated H_2 molecules have been investigated by means of ab initio electronic structure calculations. Relative energy differences for various isomers of $Cr(CO)_5(H_2)$ and $Cr(CO)_4(H_2)_2$ complexes have been computed. Possible reaction paths for the H_2/D_2 intramolecular isotope exchange in the dihydrogen complex are discussed.

The recent discovery of a new class of compounds in which the H_2 molecule is stably coordinated to a transition metal complex [1–3] has stimulated several experimental and theoretical studies in this new area of organometallic chemistry. In 1984 Kubas [1] synthesized the first Mo and W complexes that react with H_2 to form complexes containing coordinated H_2 without dissociation of the H–H bond; schematically $LM + H_2 \rightarrow LM(H_2)$, where $L = CO$ and PR_3. The Kubas' complex $W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$ has been characterized in the solid state by both X-ray and neutron diffraction techniques [1–3]. Since then, other examples of metal-H_2 complexes have been reported [4], mainly on the basis of spectroscopic measurements. This is the case for the $Cr(CO)_5(H_2)$ complex [5,6], in which the H_2 molecule is weakly bound to the metal center as shown by the low-energy pathway for the H_2/D_2 exchange [5]. However, in contrast with the behaviour of the Kubas' compound, on which isotope exchange occurs to give a statistical mixture of H_2, D_2, and HD species, formation of HD occurs in the reaction of the complex $Cr(CO)_4(H_2)_2$ with D_2 [6], but interestingly has not been observed for mixtures of $Cr(CO)_5(H_2)$ and D_2 [5,6]. It is likely that H/D scrambling in $Cr(CO)_4(H_2)_2$ occurs through an intramolecular process, but the mechanism of the exchange is unknown.

The different behaviour of $Cr(CO)_5(H_2)$ and $Cr(CO)_4(H_2)_2$ towards isotope exchange is the subject of the present theoretical investigation. The electronic structure of the $Cr(CO)_5(H_2)$ and $Cr(CO)_4(H_2)_2$ complexes has been investigated

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Table 1

Geometries and relative energies of three isomers of the $Cr(CO)_5(H_2)$ complex

Complex	r(Cr–H) (Å)	r(H–H) (Å)	ΔE (kJ/mol)
dihydrogen, (η^2-H_2)	1.90	0.77	0
dihydrogen, (η^1-H_2)	2.26	0.75	30
dihydride, (H)(H)	1.58	1.77	156

by means of ab initio Hartree–Fock calculations. A preliminary qualitative search has been made for a possible low-energy reaction path for the H/D scrambling.

The calculations were carried out by using an ab initio effective core potential (ECP) [7] in place of the core electrons of the Cr atom. The $1s$ to $2p$ core is described by an ECP operator [7], while the $3s^2$ $3p^6$ $4s^1$ $3d^5$ valence electrons are treated explicitly. The Gaussian type orbital (GTO) basis set for Cr includes $5s$, $4p$ and $5d$ primitive functions contracted to $[3s1p2d]$ [7]. The CO ligands are treated at the all electron level with a minimal $[7s3p/2s1p]$ GTO basis set for C and O atoms [8]; the basis set for hydrogen is $[4s1p/2s1p]$ [9]. The Cr–C and C–O bond lengths are taken from X-ray data for $Cr(CO)_6$: d(Cr–C) 1.916 Å, d(C–O) 1.171 Å [10].

We find that the side-on η^2-H_2 form of $Cr(CO)_5(H_2)$ is preferred (Table 1 and Fig. 1); the energy of dissociation into $Cr(CO)_5$ and H_2 is 40 kJ/mol, a value consistent with the observed ready loss of H_2 upon thermal excitation [5,6]. In this complex the H–H bond is slightly elongated (0.03 Å) with respect to the free H_2 molecule. The bond can be regarded as an example of stable coordination of a σ bond with weak electron transfer from H_2 to the vacant metal orbitals. This bonding mechanism is accompanied by a mixing of a donor metal orbital and the σ^* (H_2) MO, with corresponding back donation of charge [11,12]. The Mulliken population analysis, although of limited validity, indicates a small population of the σ^* MO (0.07 electrons); this is, however, not enough to break the H–H bond to form the dihydride species. Indeed, the dihydride $Cr(CO)_5$(H)(H) form is 156 kJ/mol less stable than the dihydrogen complex (Table 1). The preference for η^2-H_2 over dihydride coordination is governed by the nature of the other ligands. It has been shown [13] that electron donor ligands such as phosphines favour the dihy-

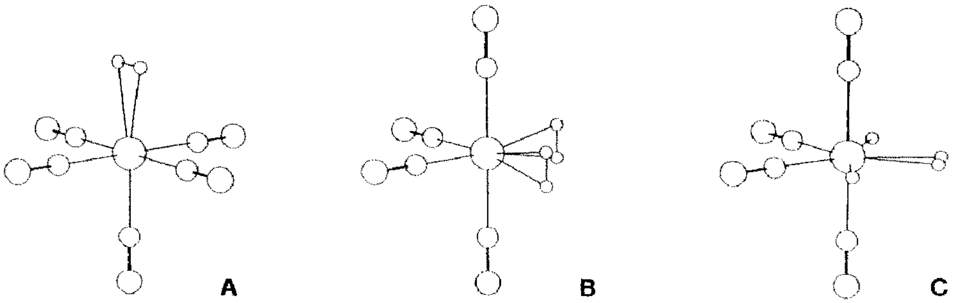

Fig. 1. (a) The preferred structure of $Cr(CO)_5(H_2)$; (b) the preferred structure of $Cr(CO)_4(H_2)_2$; (c) a possible intermediate dihydrogen-dihydride structure in the intramolecular H/D isotope exchange reaction observed for $Cr(CO)_4(H_2)(D_2)$.

Table 2

Relative stabilities of the geometrical isomers of the $Cr(CO)_4(H_2)_2$ complex

Complex		ΔE (kJ/mol)
$Cr(CO)_4(H_2)_2$	*cis*-dihydrogen upright	0
$Cr(CO)_4(H_2)_2$	*cis*-dihydrogen coplanar	20
$Cr(CO)_4(H_2)(H)_2$	dihydrogen-dihydride	120
$Cr(CO)_4(H)_4$	tetrahydride	293
$Cr(CO)_4(H_4)$	planar chain H_4	213
$Cr(CO)_4(H_3)(H)$	triangular H_3-hydride	557
$Cr(CO)_4(H_4)$	square H_4	546
$Cr(CO)_4(H_4)$	tetrahedral H_4	914

dride formation, while dihydrogen complexes are formed more readily in the presence of good π-acceptor ligands, such as CO, which reduce the electron density on the metal.

Several isomeric forms of the $Cr(CO)_4(H_2)_2$ complex have been considered (Table 2) and their total energies determined. Some of these structures are possible candidates for the molecular ground state geometry; other structures represent hypothetical intermediates in the H_2/D_2 isotope exchange reaction. Among these isomers are also those containing polyhydrogen ligands as recently suggested by Burdett et al. [14] on the basis of extended Hückel calculations.

In terms of our results, the most stable isomer of $Cr(CO)_4(H_2)_2$ contains two H_2 molecules oriented in an upright position with respect to the equatorial plane (Table 2 and Fig. 1), supporting the tentative assignment made on the basis of IR measurements [6]. This form is separated by only 20 kJ/mol from the orientational isomer with the two H_2 molecules lying in the equatorial plane. This low energy difference is indicative of a fluxional behaviour of the H_2 ligands around the $Cr-H_2$ axis. As found for the $Cr(CO)_5(H_2)$ complex, the dissociation of the H–H bond with formation of a dihydrogen-dihydride complex (Fig. 1) is unfavourable; the partially optimized $Cr(CO)_4(H_2)(H)_2$ structure is 120 kJ/mol less stable than the dihydrogen form (Table 2). As previously mentioned, H/D exchange has been observed for $Cr(CO)_4(H_2)_2$ but not for $Cr(CO)_5(H_2)$, in contrast with the Kubas' $W(CO)_3(PR_3)(H_2)$ complex for which the exchange is believed to proceed through a seven-coordinate hydridic species [1–3]. In the tungsten complex, the computed barrier for the fission of the H–H bond to give the hydridic intermediate, 46 kJ/mol [13], is relatively low because the presence of the PR_3 ligands increases the electron density on the metal. For the Cr complex, the calculated dihydrogen-dihydride barrier, 156 kJ/mol (Table 1), is more than three times as large as that for Kubas' complex [13]; in the case of $Cr(CO)_4(H_2)_2$, the replacement of a CO ligand by the weak π-acceptor H_2 ligand reduces the barrier for the H–H bond breaking to 120 kJ/mol (Table 2), thus favouring the isotope exchange. This helps to explain why in the Cr complex the scrambling occurs only when both H_2 and D_2 are coordinated to the metal.

We now consider the possible pathways for the intramolecular H/D exchange reaction. All isomers containing polyhydrogen (H_4) or $(H_3)(H)$ ligands, either open or cyclic, are highly unstable (Table 2). Simple theoretical arguments indicate that a basic requirement for the stabilization of coordinated H_n clusters is the net charge transfer of one electron (for H_3) or two electrons (for H_4) from the H_n unit to an empty metal orbital, a process very unfavourable for metal centers in formally zero oxidation state as in $Cr(CO)_4(H_2)_2$. Different coordinated polyhydrogen species can be formed under different conditions; our calculations indicate that a cationic $[Cr(CO)_5(H_3)]^+$ complex is stable toward dissociation into $Cr(CO)_5 + (H_3)^+$ or $Cr(CO)_5(H_2) + H^+$. Hence, protonation of $Cr(CO)_5(H_2)$ could give a stable trihydrogen complex.

To summarize, the present results, although obtained without introduction of correlation effects, rule out the possibility that polyhydrogen complexes can be readily formed in the H_2/D_2 exchange reaction. The pathway for the conversion of H_2 and D_2 into HD is more likely to imply the formation of a transient open polyhydrogen chain in $Cr(CO)_4$(HHDD) followed by the formation of the dihydrogen-dihydride complex $Cr(CO)_4$(H)(HD)(D) (Fig. 1). The latter can readily undergo rearrangement to form the more stable $Cr(CO)_4(HD)_2$, which in turn can lose an HD molecule and add a CO ligand to give $Cr(CO)_5$(HD) + HD. Preliminary results of ab initio calculations on $Cr(CO)_4(H_2)_2$, with some inclusion of electron correlation effects, are consistent with these conclusions [15].

Of course other mechanisms are possible, involving either coordinated H_2 and H atoms or radical intermediates, although paramagnetic species have not been detected so far during the reaction [5]. Some of these potential intermediates are at present under investigation, in particular a metallocyclo-H_3 hydride form or an unsymmetrical H_2/dihydride complex in which one hydride lies between the coordinated dihydrogen molecule and the other hydrido ligand [16]. In view of the complexity of the problem, there is no doubt that further experimental and theoretical work is necessary to provide a full understanding of the reactions of this novel class of compounds.

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