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Why $[CpW(CO)_3]^+$ reduces H_2 to dihydride†

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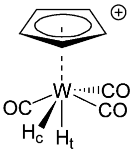
The $[CpW(CO)_3]^+$ complex, with three π acceptor ligands and a positive charge, is shown to have an unexpected reducing ability towards H_2 because of a low lying triplet state energy.

From the intensive experimental and theoretical work devoted to the H_2 interaction with transition metal complexes, the main electronic factors which govern dihydrogen $L_nM(\eta^2\text{-}H_2)$ *versus* dihydride $L_nM(H)_2$ bonding seem to be well known.[1] In particular, strong π acceptor ligands, such as CO, and positive charge(s) are believed to work in favour of the dihydrogen form by reducing the electron donating ability of the metal fragment which is required to achieve the oxidative addition process.[2] However, application of the well established rules to predict the dihydrogen or dihydride nature of a compound shows that there are several complexes which should be dihydrogen complexes when they are actually dihydrides.[2,3] Indeed a striking exception to these rules happens with the $[CpW(CO)_3]^+$ metal fragment, which by all accounts should give a dihydrogen complex. Nevertheless $[CpW(CO)_3(H)_2]^+$ has been characterized as a dihydride from NMR measurements.[4] In general, the family of half-sandwich complexes are "unpredictable in the way they coordinate hydrogen".[1]

In this communication, the behaviour of the $[CpW(CO)_3]^+$ metal fragment with H_2 is studied by means of CCSD(T)//B3LYP calculations. The structures of the dihydride and dihydrogen complexes as well as the whole oxidation process were studied by means of DFT calculations, the energies being recalculated at the more reliable CCSD(T) level (CCSD(T)//B3LYP).‡ All the energies given in this communication are CCSD(T) values.

In the most stable structure found for the dihydride form $[CpW(CO)_3(H)_2]^+$ one hydride (H_t) is nearly *trans* to the Cp while the other (H_c) is *cis* (**1**) with $W–H_t$ = 1.724 Å, $W–H_c$ = 1.719 Å and $H_t\cdots H_c$ = 1.911 Å. Such a structure is in agreement with the X-ray characterization of the related $[CpW(CO)_2(PMe_3)(H)_2]^+$complex which also exhibits one hydride *trans* to the Cp.[4b] A minimum was further located for the dihydrogen form $[CpW(CO)_3(\eta^2\text{-}H_2)]^+$ (**2**) with $H_1–H_2$ = 0.858 Å, $W–H_1$ = 1.879 Å and $W–H_2$ = 1.861 Å but **2** was found to be less stable than **1** by 9.7 kcal mol^{-1}. This value is large enough to conclude that the dihydride is the most stable form for this species, as was previously suggested from NMR measurements.[4]

The energy profile for the oxidative addition process (**2** → **1**) was calculated varying the $H\cdots H$ distance from 0.8 to 1.8 Å by steps of 0.2 Å, optimising the geometry of the complex for each fixed value of the $H\cdots H$ distance. The computed energy profile (CCSD(T)//B3LYP) shows that no energy barrier is associated with this reaction§ and thus confirms the high ability of the $[CpW(CO)_3]^+$ complex to break the H–H bond. Such a result is in marked contrast with what was found for other systems with π acceptor ligands. For instance, with $W(CO)_5$ as the metal fragment, the dihydrogen form is experimentally known[5] and has been calculated to be 14.6 kcal mol^{-1} more stable than the dihydride form (CCSD(T)//B3LYP level).[6] The possible existence of a dihydride form has however been recently suggested.[7]



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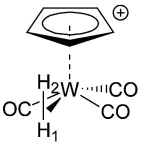

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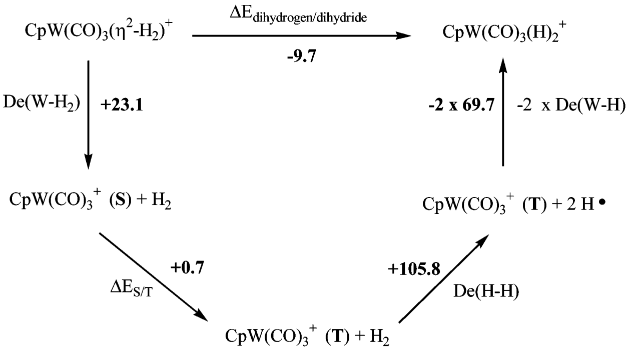
We have shown that the ability of a transition metal fragment to break the H–H bond can be rationalized by means of the thermodynamic cycle given in Scheme 1.[6] With the help of this cycle the dihydrogen–dihydride energy difference, which gives an indication of the thermodynamic viability of the oxidative addition process, can be broken down into some easily understandable terms: the bonding energy of H_2 in the dihydrogen complex ($De(W–H_2)$), the singlet–triplet energy difference in the $[CpW(CO)_3]^+$ metal fragment ($\Delta E_{S/T}$), the H–H bond dissociation energy (De(H–H)) and the W–H bond energy (2 × De(W–H)).

The values computed for these different terms are reported in Scheme 1 and in Table 1 for sake of comparison with that previously calculated for $[W(CO)_5]$.[6] To calculate the $\Delta E_{S/T}$ term, the geometry of $[CpW(CO)_3]^+$ was optimised in both electronic states within Cs constraints.¶ The opposite behaviour of these two metal fragments with respect to H_2 addition



Scheme 1

Table 1 Energy decomposition (kcal mol^{-1}), according to Scheme 1, of the dihydrogen–dihydride energy difference (ΔE) for $[CpW(CO)_3]^+$ and $[W(CO)_5]$ complexes

	$\Delta E_{S/T}$	De(W–H)	$De(W–H_2)$	ΔE
$[CpW(CO)_3]^+$	0.7	69.7	23.1	−9.7
$[W(CO)_5]$	30.8	70.6	19.1	+14.6

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† Electronic supplementary information (ESI) available: References for calculations. See http://www.rsc.org/suppdata/cc/b3/b301245j/

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(dihydride form favoured by 9.7 kcal mol^{-1} for $[CpW(CO)_3]^+$ and dihydrogen form favoured by 14.6 kcal mol^{-1} for $[W(CO)_5]$) can be explained neither by the W–H bond energies, which are almost equal, nor by the dissociation energies of the dihydrogen complex which differ by only 4 kcal mol^{-1} (Table 1). The electronic factor responsible for the change is the dramatic lowering, by about 30 kcal mol^{-1}, of *the singlet–triplet energy separation* in going from $[W(CO)_5]$ to $[CpW(CO)_3]^+$: the smaller $\Delta E_{S/T}$, the easier the oxidative addition process.

This trend for the $\Delta E_{S/T}$ term can be rationalized as follows. In $[W(CO)_5]$, a d^6-ML_5 complex with a square pyramidal geometry, it involves the excitation of an electron from a non-bonding d orbital (derived from the t_{2g} block of an octahedron) stabilized by bonding interactions with three π_{CO}* orbitals to the z^2 orbital, *antibonding* with the apical ligand. Therefore, the singlet–triplet energy separation is rather large. On the other hand, $[CpW(CO)_3]^+$can be seen as a distorted octahedral complex if the Cp is thought of as occupying three coordination sites. With a d^4 electronic configuration, the two orbitals involved in the singlet–triplet excitation belong to the set of the three orbitals derived from the t_{2g} block of an ideal octahedron. They are both non-bonding d orbitals, stabilized by bonding interactions with the π_{CO}* (Fig. 1), so that the energy required to form the triplet state is very small.

Finally, we have performed similar calculations on the $[CpW(CO)_2(PH_3)(H)_2]^+$ complex, the X-ray structure of the trimethylphosphine analogue having been reported.[4b] The dihydride form was found to be even more favoured (−10.9 kcal mol^{-1} with respect to the dihydrogen form). Since the W–H and W–H_2 bond energies remain almost unchanged (69.6 and 23.2 kcal mol^{-1}, respectively), this trend can be traced to a further lowering of the singlet–triplet separation (−0.6 instead of +0.7 kcal mol^{-1} for $[CpW(CO)_3]^+$).

In conclusion, the thermodynamic scheme developed to analyse the oxidative addition process accounts for the unexpected behaviour exhibited by $[CpW(CO)_3]^+$. Calculations to extend this analysis to the whole series of "unpredictable" half-sandwich complexes are in progress. Small or even negative values of $\Delta E_{S/T}$ are expected for all the d^4-$CpML_3$ fragments. However, the dihydrogen–dihydride energy difference is also related to the strength of the M–H bond (Scheme 1), a factor which has been shown previously to depend on the nature of the metal center.[6]

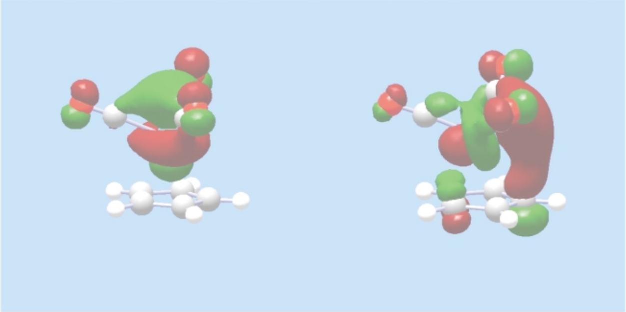

Fig. 1 Singly occupied MOs in the triplet state of $[CpW(CO)_3]^+$.

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Notes and references

‡ Calculations were performed with the Gaussian 98 series of programs. Geometry optimisations were done using the density functional theory (DFT) with the B3LYP functional. Effective core potentials and their associated double-ζ LANL2DZ basis set were used for W and P, augmented by a d polarisation function in the latter case. The hydrogen atoms directly attached to the metal were described with the 6-31G(d,p) basis. The 6-31G basis set was used for the other H atoms, as well as for C and O atoms. To obtain accurate values for the energies, they were recalculated with the highly-correlated CCSD(T) method using the B3LYP optimised geometries. The basis set influence was checked enlarging the basis set with the inclusion of the polarisation functions in the C and O atoms (6-31g(d) basis set). See ESI.† The energy difference between the dihydrogen and dihydride isomers of $[CpW(CO)_2(PH_3)\text{“}H\text{”}_2]^+$ complex was modified by less than 1 kcal mol^{-1}.

§ At the B3LYP level, a very small barrier of about 2 kcal mol^{-1} is found, a result which explains why the dihydrogen complex **2** is characterized as a minimum on the B3LYP potential energy surface.

¶ There is some geometrical reorganization in going from the singlet to the triplet state. In particular, the C–W–C angles vary from 80.5 (two angles) and 109.8° in the singlet state to 91.7 (two angles) and 112.1° in the triplet state. The values in dihydride **1** are 90.0 (two angles) and 135.1°.

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