



Kubas complexes extended to four centers; a theoretical prediction of novel dihydrogen coordination in bimetallic tungsten and molybdenum compounds

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ABSTRACT

A number of molybdenum and tungsten bimetallic compounds with carbonyl and phosphine ligands are investigated, using theoretical methods, with respect to their ability to bind molecular hydrogen in a Kubas type coordination. Some are found to give novel complexes, containing a four center metal–dihydrogen interaction.

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Introduction

Transition metal–dihydrogen complexes, also known as Kubas complexes, were first reported almost thirty years ago [1]. The significance, in terms of the beauty of the scientific breakthrough, is vividly described in a recent review [2]. The broader importance, both in the context of pure science, but also in the quest for efficient hydrogen storage, has been extensively reviewed [3–5]. The common features of Kubas complexes are:

- A three center interaction from the σ orbital of H_2 to an empty metal d-orbital
- A back-donation from occupied metal d orbitals towards the σ^* antibonding H_2 orbital
- A lengthening of the H–H bond to some extent, but not to the point of breaking. Lengths of less than 1.0 Å are generally accepted to constitute dihydrogen complexes, whereas for lengths of more than 1.3 Å the structure is characterized as a dihydride.

- A T-shaped structure and, generally speaking, low metal coordination

The numerous dihydrogen complexes that have been synthesized and characterized, or predicted theoretically, share one common feature; a *single* metal atom is bound to dihydrogen. In a recent letter [6], we reported the first theoretical prediction of *four-center* Kubas complexes, where *two* transition metal atoms bind to a single H_2 molecule *simultaneously*, with exactly the same characteristics as in the three-center Kubas complex. These will hereinafter be referred to as four-center Kubas (4cK) complexes.

In the general field of transition metal hydrides, the area of bridging hydrides carries special interest due to its importance in various chemical reactions. Many aspects are not definitively elucidated, as for example the extent of direct vs indirect metal–metal interaction. Numerous theoretical works address this and other issues; for example the works of Baik, Friesner and Parkin [7] and Richardson et al. [8] examine from a theoretical point of view a number of dibridging dihydrides of W, Re, Cr and Mo. Hoffmann and his coworkers [9] in a recent paper examine hydrogen binding to W clusters under pressure and mention that there are 85 reported polynuclear W complexes with Hydrogen bridges, and of these 14 involve two bridging hydrogens.

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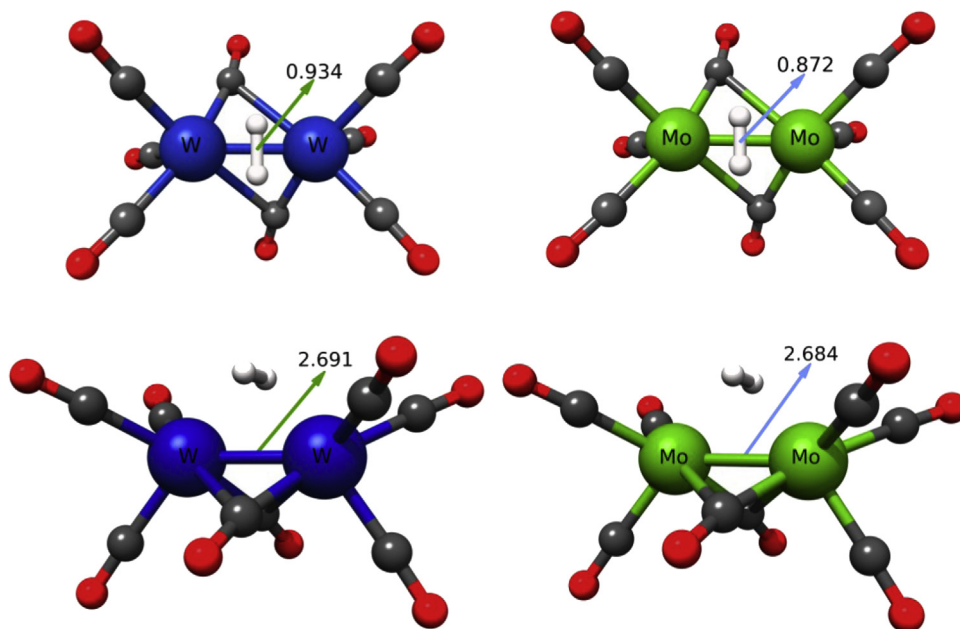


Fig. 1. The structure of $W_2(CO)_8(\mu-H_2)$ and $Mo_2(CO)_8(\mu-H_2)$ (side and top views, bond lengths from PBE data).

Summarizing the literature, no theoretical or experimental evidence has up to now been presented, where in a bridging dihydride the distance between the hydrogen atoms is so short that a dihydrogen interaction (Kubas type) can be recognized. For completeness, it is worth mentioning that in a work of Krasnov et al. [10] on H_2 adsorbed on Sc clustered on single wall carbon nanotubes, a similar four center interaction was predicted, as part of a number of hydrogen molecules attached to Sc atoms; this was however a part of a multi-metal cluster attached to a nanotube, and not an isolated molecule.

A systematic theoretical study of a number of 4cK complexes is presented here. It is reported that both W and Mo compounds with carbonyl and phosphine ligands are predicted from theory to form such complexes, and their binding is analyzed. In the first part of the results section, the pure carbonyl compounds are presented. The second part shows the results of investigations with phosphine ligands, and the third reports on the possibility of both three center and four center dihydrogen binding existing on the same molecule.

Computational details

The density functional theory (DFT) approach was used throughout, as implemented in the GAUSSIAN 09 suite of programs [11]. From experience from our previous work and the overall literature in the field, two functionals were chosen that best describe transition metal hydride computations. These are the Perdew, Burke and Ernzerhof (PBE) [12,13] functional, and the M06 of Zhao and Truhlar [14]. The basis set used is the def2-TZVPP of Weigend and Ahlrichs [15] including the relevant effective core potential for Mo and W [16] (basis sets retrieved from <http://www.cosmologic.de/basis-sets/basissets.php>). All structures were fully optimized using both functionals, and the potential energy minima were confirmed by a full second derivative calculation. Only geometrical data are reported here, but harmonic vibrational frequencies are also calculated; the stretching frequencies for H_2 for some of the complexes are given in the Supplementary material. Coordinates for all optimized structures are also given.

Results and discussion

Bimetallic carbonyls

Tungsten and molybdenum octacarbonyls are found to give stable 4cK complexes, as shown in Fig. 1. Both $W_2(CO)_8(\mu-H_2)$ and $Mo_2(CO)_8(\mu-H_2)$ are given here simultaneously for comparison, but the latter was first published previously by us [6].

The basic bond lengths of the optimized structure, calculated at both functional levels, are given in Table 1. The metal–metal bond length, as also confirmed by the molecular orbital picture, corresponds to a single bond, in agreement with other similar compounds [17,18].

The dihydrogen bond length is elongated with respect to the free molecule (approx 0.75 Å with both functionals), but remains below 1.0 Å as is expected for a true Kubas complex. Also, a good agreement is seen between the two functionals, with M06 giving shorter H–H and longer metal–metal bonds, meaning that the backbonding interaction is underestimated compared to PBE. In any case, however, both functionals support the same finding, namely the stability of the 4cK complex.

Attempts were made with other Mo and W complexes with different numbers of carbonyl ligands, but only the low coordination octacarbonyls are found to give dihydrogen complexes. Higher coordination compounds lead to dihydrides, in some cases unstable.

The bonding picture, similar for both functionals, is revealing of the true Kubas type nature of the metal dihydrogen interaction. A diagram of the occupied orbitals of interest for $W_2(CO)_8(\mu-H_2)$ are given in Fig. 2.

Table 1
Geometries of 4cK complexes of W and Mo (in Å).

Complex	Functional	M–M (M = W, Mo)	M–H	H–H
$W_2(CO)_8(\mu-H_2)$	PBE	2.691	2.035–2.042	0.934
	M06	2.721	2.072–2.087	0.877
$Mo_2(CO)_8(\mu-H_2)$ [6]	PBE	2.684	2.065–2.075	0.872
	M06	2.712	2.080–2.094	0.852

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