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A non-classical hydrogen bond in the molybdenum arene complex [η^6-$C_6H_5C_6H_3(Ph)OH]Mo(PMe_3)_3$: evidence that hydrogen bonding facilitates oxidative addition of the O–H bond†

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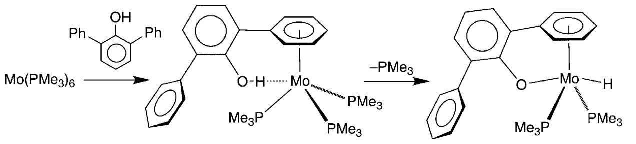
$Mo(PMe_3)_6$ reacts with 2,6-$Ph_2C_6H_3OH$ to give the η^6-arene complex [η^6-$C_6H_5C_6H_3(Ph)OH]Mo(PMe_3)_3$ which exhibits a non-classical Mo···H–OAr hydrogen bond; DFT calculations indicate that the hydrogen bonding interaction facilitates oxidative addition of the O–H bond to give [η^6,η^1-$C_6H_5C_6H_3(Ph)O]Mo(PMe_3)_2H$.

Hydrogen bonding interactions are pervasive in chemistry and biology. For example, having recently been described as the most important of all directional intermolecular interactions,[1] hydrogen bonds play critical roles in determining the structures of biological systems and are used extensively as control elements in crystal engineering,[1,2] While the proton acceptors of hydrogen bonds are most commonly electronegative atoms such as oxygen or fluorine, it has recently become recognized that there are several types of non-classical hydrogen bonds in which the acceptors are either electron rich metal centers, hydride ligands, or organic π-systems.[3] The full potential of these non-classical hydrogen bonds, however, is yet to be realized. Therefore, in this paper, we address structural and reactivity aspects of a complex that features a non-classical Mo···H–O hydrogen bond, and demonstrate that this interaction facilitates the oxidative addition of the O–H bond to the metal center.

$Mo(PMe_3)_6$ reacts rapidly with 2,6-$Ph_2C_6H_3OH$ at 70 °C to yield the η^6-arene complex [η^6-$C_6H_5C_6H_3(Ph)OH]Mo(PMe_3)_3$ (Scheme 1).

Although [η^6-$C_6H_5C_6H_3(Ph)OH]Mo(PMe_3)_3$ is not unusual in the sense that half-sandwich η^6-arene complexes of the type (η^6-ArH)ML_3 (*e.g.* L = CO, PR_3) have featured prominently in the organometallic chemistry of chromium, molybdenum and tungsten, the formation of [η^6-$C_6H_5C_6H_3(Ph)OH]Mo(PMe_3)_3$ by arene displacement of three PMe_3 ligands is unexpected in view of the fact that $Mo(PMe_3)_6$ reacts preferentially with the O–H bond of alkyl substituted phenols ArOH to give aryloxide derivatives $Mo(PMe_3)_4(OAr)H$ (Ar = 2,4,6-$C_6H_2Me_3$, 2,6-$C_6H_3Pr^i{}_2$).[4] The most important feature of the structure of [η^6-$C_6H_5C_6H_3(Ph)OH]Mo(PMe_3)_3$ is the presence of an intramolecular Mo···H–OAr hydrogen bond (Fig. 1), characterized by the following bond lengths and angle: *d*(Mo···H) = 2.76(3) Å, *d*(Mo···O) = 3.571(2) Å, and Mo–H–O = 172(3)°.[5,6]

In addition to the diffraction study, spectroscopic studies indicate that the hydrogen bonding interaction also persists in solution; thus, not only is the ^{1}H resonance of the OH group shifted substantially downfield from that of δ 5.2 for 2,6-$Ph_2C_6H_3OH$ to δ 8.2 in [η^6-$C_6H_5C_6H_3(Ph)OH]Mo(PMe_3)_3$, but the hydroxylic proton also exhibits coupling to the three phosphorus nuclei of the PMe_3 ligands [J_{P-H} = 2 Hz]. Variable temperature ^{1}H NMR spectroscopic studies indicate that the signal for the OH group is also temperature dependent, ranging from δ 8.0 at *ca.* 70 °C to δ 8.5 at −90 °C.



Scheme 1

It is important to emphasize that 3-center-4-electron M···H–X interactions are quite distinct from the 3-center-2-electron interaction present in, for example, agostic complexes, hydrocarbon σ-complexes and dihydrogen complexes.[7,8] Specifically, the metal center in M···H–X sigma bond complexes acts as a Lewis acid towards HX (*i.e.* M ← H–X), whereas the metal in a hydrogen bond complex acts as a Lewis base towards HX (*i.e.* M → H–X). In this regard, the linearity of the Mo···H–O interaction [172(3)°] is similar to that of other hydrogen bonds, and contrasts with the markedly bent geometries that are typically observed for 3-center-2-electron interactions.[7,8]

For a metal center to participate as the proton acceptor in a hydrogen bond, it is essential for it to be electron rich. Indeed, examples of such complexes have only previously been recognized for those with d^8 and d^{10} metal centers.[3e] Thus, the existence of a hydrogen bond interaction within [η^6-$C_6H_5C_6H_3(Ph)OH]Mo(PMe_3)_3$ is noteworthy since it only possesses a d^6 molybdenum center. The zerovalent nature of the molybdenum and the strong donor nature of the PMe_3 ligands are presumably the factors responsible for enhancing the basicity of the metal center in this complex.

Although stable at room temperature, [η^6-$C_6H_5C_6H_3(Ph)OH]Mo(PMe_3)_3$ is converted to the aryloxy-hydride species [η^6,η^1-$C_6H_5C_6H_3(Ph)O]Mo(PMe_3)_2H$ at 80 °C (Scheme 1). The molecular structure of [η^6,η^1-$C_6H_5C_6H_3(Ph)O]Mo(PMe_3)_2H$ has been determined by X-ray diffraction, as has that of the tungsten analogue [η^6,η^1-$C_6H_5C_6H_3(Ph)O]W(PMe_3)_2H$ which is obtained from the reaction of $W(PMe_3)_4$(η^2-$CH_2PMe_2)H$ with 2,6-$Ph_2C_6H_3OH$.[6,9]

Brammer has previously postulated that hydrogen bonded species may be intermediates for the oxidative addition of H–X to a metal center, but has noted that there are no definitive examples in which hydrogen bonded complexes undergo oxidative addition.[3b] The conversion of [η^6-$C_6H_5C_6H_3(Ph)OH]Mo(PMe_3)_3$ to [η^6,η^1-$C_6H_5C_6H_3(Ph)O]$-

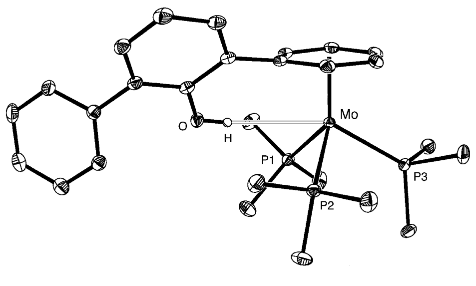


Fig. 1 Molecular structure of [η^6-$C_6H_5C_6H_3(Ph)OH]Mo(PMe_3)_3$.

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† Electronic supplementary information (ESI) available: synthesis of the Mo arene complex and its W analogue and of the respective aryloxy-hydride species. X-Ray structure determination, computational details and cartesian coordinates of optimized geometries. See http://www.rsc.org/suppdata/cc/b2/b208678f/

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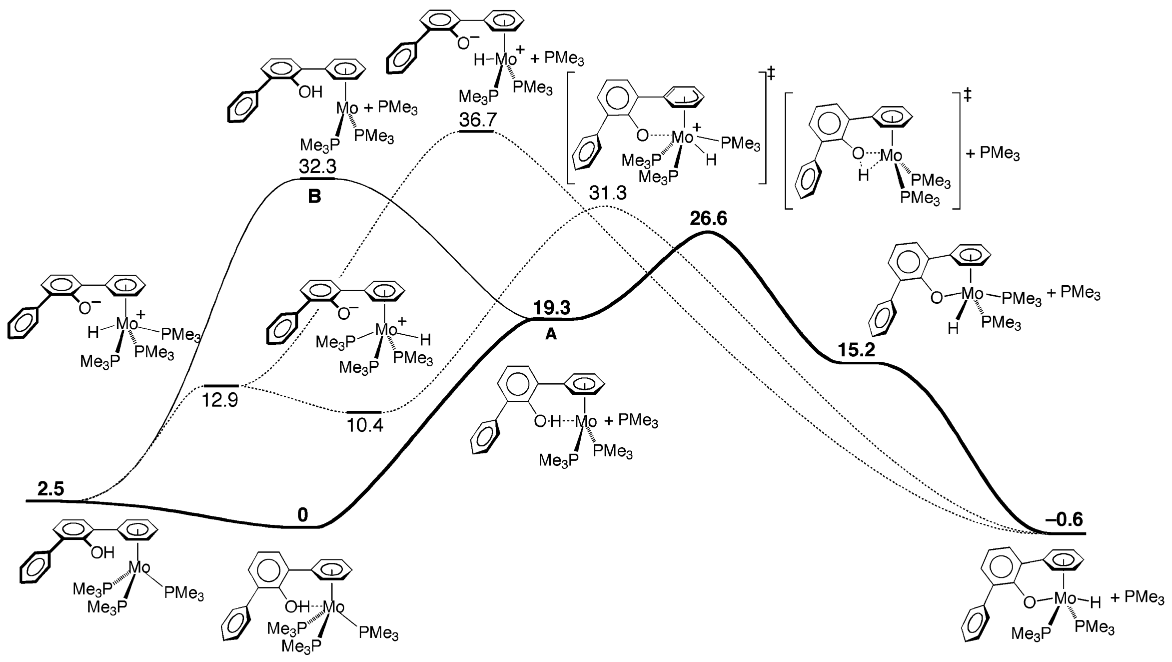

Fig. 2 Electronic energy surface for various mechanisms for oxidative addition of the O–H bond (values in kcal mol^{-1}).

$Mo(PMe_3)_2H$, therefore, provides the first well-defined example of a hydrogen bonded [M]···H–OAr system transforming to a product of overall oxidative addition, *i.e.* [M](H)(OAr). However, this observation does not address the issue of whether the hydrogen bonded [M]···H–OAr species is actually on the direct pathway to forming [M](H)(OAr) from reaction of [M] with H–OAr, or whether it represents an unproductive side reaction. This issue has been addressed by performing a series of DFT calculations (B3LYP)[10] to establish the feasibility of several mechanistic scenarios. Significantly, the calculations indicate that the [Mo]···H–OAr hydrogen bonding interaction[11] does indeed facilitate oxidative addition by providing a pathway that enthalpically stabilizes the intermediate $\{[\eta^6\text{-}C_6H_5C_6H_3(Ph)OH]Mo(PMe_3)_2\}$ resulting from dissociation of PMe_3;[12] specifically, intermediate **A** with a hydrogen bond (Fig. 2, bold line) is more stable than intermediate **B** without a hydrogen bond (Fig. 2, plain line).[13] We also considered the possibility that the oxidative addition could occur *via* a mechanism that involves initial protonation followed by internal nucleophilic attack (Fig. 2, dashed surface). However, although the initial protonation step is only 12.9 kcal mol^{-1} uphill enthalpically, the barrier for subsequent displacement of the PMe_3 ligand (both associatively and dissociatively) from $\{[\eta^6\text{-}C_6H_5C_6H_3(Ph)O]Mo(PMe_3)_3H\}$ is substantial and therefore not favored.[14]

In summary, the η^6-arene complex $[\eta^6\text{-}C_6H_5C_6H_3(Ph)OH]Mo(PMe_3)_3$ exhibits a non-classical Mo···H–O hydrogen bond. DFT calculations provide evidence that this interaction facilitates oxidative addition of the O–H bond, thereby resulting in the formation of $[\eta^6,\eta^1\text{-}C_6H_5C_6H_3(Ph)O]Mo(PMe_3)_2H$.

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Notes and references

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5 The tricarbonyl analogue, $[\eta^6\text{-}C_6H_5C_6H_3(Ph)OH]Mo(CO)_3$ also exhibits a Mo···O distance of 3.6 Å, but the possibility of a hydrogen bonding interaction was not discussed. See: J. L. Kerschner, E. M. Torres, P. E. Fanwick, I. P. Rothwell and J. C. Huffman, *Organometallics*, 1989, **8**, 1424.

6 CCDC reference numbers 193307–09. See http://www.rsc.org/suppdata/cc/b2/b208678f/ for crystallographic data in CIF or other electronic format.

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8 *Metal Dihydrogen and σ-Bond Complexes: Structure, Theory, and Reactivity*, ed. G. J. Kubas, Kluwer Academic/Plenum Publishers, New York, 2001.

9 The $PMePh_2$ analogues, $[\eta^6,\eta^1\text{-}C_6H_5C_6H_3(Ph)O]M(PMePh_2)_2H$ (M = Mo, W) have been reported. See ref. 5.

10 All calculations were carried out using DFT as implemented in the Jaguar 4.1 suite of *ab initio* quantum chemistry programs. Geometry optimizations were performed with the B3LYP functional and the 6-31G** basis set for C, H, O and P, while Mo was represented using the Los Alamos LACVP** basis set. The energies of the optimized structures were reevaluated by additional single point calculations on each optimized geometry using the cc-pVTZ(-f) basis set for C, H, O and P and the LACV3P** basis set for Mo.

11 For recent calculations on intramolecular M···H–O interactions, see: G. Orlova and S. Scheiner, *Organometallics*, 1998, **17**, 4362.

12 It should also be noted that the hydrogen bonded structure for $\{[\eta^6\text{-}C_6H_5C_6H_3(Ph)OH]Mo(PMe_3)_2\}$ is calculated to be 3.9 kcal mol^{-1} lower in energy than the structure in which the oxygen acts as a donor to the 16-electron molybdenum center (with a distance of 2.45 Å).

13 The calculations also indicate that the oxidative addition from the hydrogen bonded complex $[\eta^6\text{-}C_6H_5C_6H_3(Ph)OH]Mo(PMe_3)_3$ is significantly more exothermic for tungsten (−7.2 kcal mol^{-1}) than for molybdenum (−0.6 kcal mol^{-1}).

14 Further evidence which suggests that the mechanism does not involve internal proton transfer is that the rate constant for oxidative addition of the O–H bond is not strongly influenced by solvent polarity: $5.32(8) \times 10^{-5}$ s^{-1} (benzene) and $1.54(2) \times 10^{-4}$ s^{-1} (THF) at 100 °C.