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RESEARCH ARTICLE

Protonation Behavior of a Tetrahydrido Molybdenum(IV) Complex with Organic and Inorganic Acids

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Abstract: The reaction of $[\text{MoH}_4(\text{depe})_2]$ (**1**) (depe = 1,2-bis(diethylphosphino)ethane) with different proton sources (HP^tBu_3^+ , $\text{C}_6\text{H}_5\text{COOH}$, $\text{C}_6\text{F}_5\text{COOH}$, H_2SO_4) was investigated. Whereas complete conversion of **1** into its protonated form is observed in the presence of the phosphonium salt, $[\text{MoH}_5(\text{depe})_2]^+$ only transiently forms upon treatment with the other acids. Further reactivity of the pentahydride complex is indeed noticed with the conjugated base, typically resulting in the formation of neutral ($\text{C}_6\text{F}_5\text{COOH}$, H_2SO_4) or cationic (PhCOOH) molybdenum dihydride complexes. The compounds were characterized by NMR spectroscopy and X-ray crystallographic studies were performed when suitable crystals were obtained.

Introduction

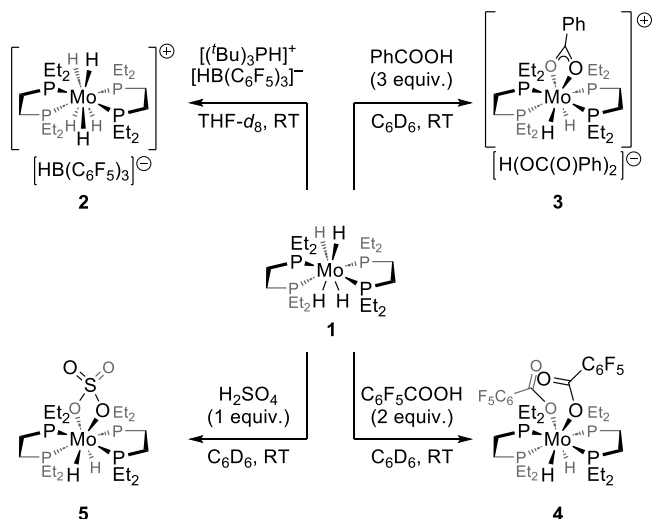
Due to the sometimes-ambiguous nature of their bonding and their rich and diverse reactivity, transition metal polyhydride complexes have been the subject of intense research effort.^[1] Compared to monohydride complexes, their ability to give rise to transient – or stable – $\sigma\text{-H}_2$ complexes expands the scope of reactivity that can be accessed.^[2] Polyhydride derivatives may indeed react through intermediates displaying unsaturated coordination sphere that form *via* reductive elimination of dihydrogen. Among the wide diversity of reactions transition metal polyhydride complexes can undergo, protonation is particularly interesting as it plays a major role in many catalytic processes. Protonation of hydrides is thus commonly invoked along proton reduction into molecular H_2 in biological or artificial systems.^[3] As simple as this acid-base reaction may appear, it usually reveals as a multistep, complex process.^[4] Typically, transient, unconventional hydrogen bonds between the acid-base partners have been evidenced to play a major role in facilitating the proton transfer.^[1e,5] A number of additional considerations may affect the overall protonation mechanism, sometimes making it uncertain and challenging to analyze. In a comprehensive review,^[4] Lledós *et al.* identified some of the key factors that trigger divergent pathways towards protonation. The strength of the proton source and its ability to engage in homoconjugation processes have to be considered, as well as the competition between the different basic sites of the transition metal (poly)hydride complex (hydride ligand vs metal vs ancillary ligand). Therefore, pK_a considerations,

though crucial, are often not enough when one aims at studying protonation of a metal hydride.

Beyond the few homoleptic molecular metal hydrides, such as the seminal ReH_9^{2-} complex,^[6] bulky, tertiary phosphines are typically encountered as ancillary ligands in a large body of polyhydride species.^[1h] Group 6 polyhydride complexes are significant contributors to the wide diversity of this class of compound. In particular, their neutral tetrahydride complexes featuring the general formula $[\text{M}(\text{R}_2\text{PCH}_2\text{CH}_2\text{R}_2)_2\text{H}_4]$ ($\text{M} = \text{Cr},^{[7]} \text{Mo},^{[8]} \text{W}^{[9]}$ and $\text{R} = \text{Me}, \text{Et}, \text{Ph}, ^i\text{Pr}$) have emerged as representative examples thank to their well-established and straightforward preparations. So far, two main approaches are reported, based either on the reduction of the corresponding halogenated precursors under a hydrogen atmosphere, or on the thermal or photo-assisted oxidative addition of H_2 to the parent bis-dinitrogen complexes. The behavior of some of those derivatives has previously been investigated towards acids. As examples, stopped-flow monitoring of the reaction of $[\text{MoH}_4(\text{dppe})_2]$ ^[10] (dppe = 1,2-bis(diphenylphosphino)ethane) or $[\text{WH}_4(\text{PMePh}_2)_4]$ ^[11] with HCl allowed the group of Henderson to suggest the existence of elusive $\sigma\text{-H}_2$ complexes *en route* to a spectroscopically-identified cationic pentahydride. UV-Vis and IR spectroscopies were used by the group of Shubina to evidence that protonation of the complex $[\text{WH}_4(\text{dppe})_2]$ was occurring through the assistance of unusual, but rather strong, hydrogen bonds.^[12] Alternatively, the addition of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ to $[\text{MoH}_4(\text{dppe})_2]$ or $[\text{MoH}_4(\text{PMe}_2\text{Ph})_4]$ has been shown to trigger new reactivities towards a large variety of small molecules.^[13]

Cationic pentahydride complexes of group 6 metals (Mo and W) have previously been isolated or proposed to act as relevant intermediates.^[13a,14] In 2020, the first structure of such a compound, namely $[\text{WH}_5(\text{dppe})_2]\text{Cl}$, was reported by the groups of Cundari and Yousufuddin.^[15] An analogous, depe-supported (depe = 1,2-bis(diethylphosphino)ethane) molybdenum derivative was recently identified and isolated in the context of the photo-assisted activation of N_2 .^[8c] In the present article, the reactivity of diverse proton sources, which pK_a s in MeCN range from 7.5 to 21.5, towards the complex $[\text{MoH}_4(\text{depe})_2]$ (**1**) has been evaluated with the aim of devising alternative syntheses of the $[\text{MoH}_5(\text{depe})_2]^+$ species. Our study shows that when the conjugated base carries oxygen, the intermediately formed $[\text{MoH}_5(\text{depe})_2]^+$ is not stable towards ligation of the oxyanion with concomitant hydrogen loss (Scheme 1).

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Scheme 1. Overview of the reactivity of the molybdenum tetrahydride **4** with inorganic and organic acids presented in this study.

Results and Discussion

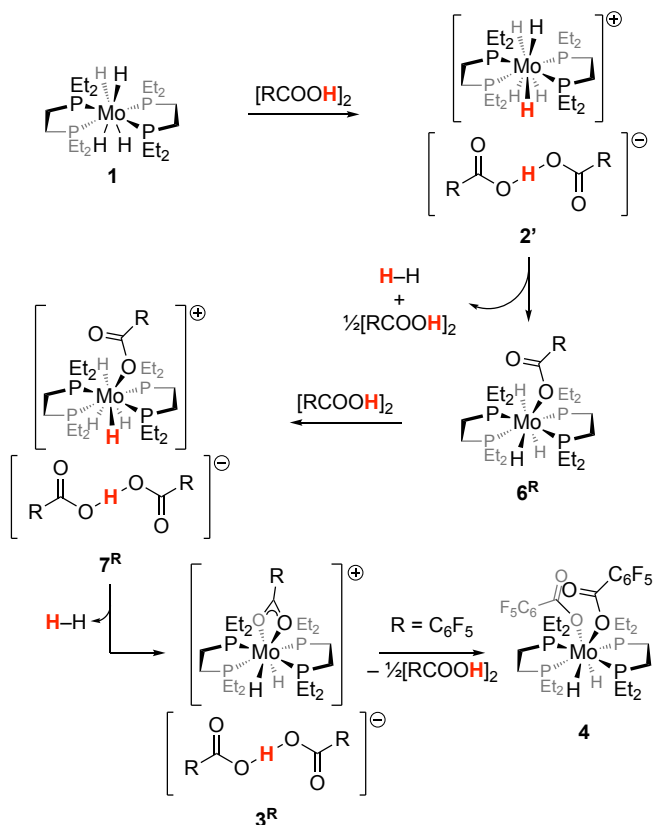
Reaction of **1** with $[(t\text{Bu})_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3]$, derived from dihydrogen activation by $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$,^[16] was first investigated (pK_a in THF = 10.7).^[17] Upon addition at room temperature of the phosphonium salt (1 equiv.) to a solution of **1** in THF- d_8 , a single product **2** formed along with free $(t\text{Bu})_3\text{P}$. This complex features a diagnostic high-field quintet at -5.0 ppm in the ^1H NMR spectrum ($^2J_{\text{P-H}} = 30.8$ Hz, see the Supporting Information), indicating the complete conversion of **1** into a new hydride species. Unambiguous determination of the number of hydride ligands was possible by ^{31}P NMR spectroscopy: the singlet observed at 73.8 ppm in broad-band ^1H -decoupled spectrum splits into a sextet upon selective decoupling of the aliphatic protons ($^2J_{\text{P-H}} = 30.6$ Hz, see Supplementary Information). ^{11}B NMR and ^{19}F NMR spectra are typical of $\text{HB}(\text{C}_6\text{F}_5)_3^-$.^[18] In accord, a pseudo-quadruplet can be found at 3.76 ppm in the ^1H -NMR spectrum, assigned to hydroborate resonance. Based on these spectroscopic data, the newly formed complex can be formulated as $[\text{MoH}_5(\text{depe})_2][\text{HB}(\text{C}_6\text{F}_5)_3]$ (**2**). Isolation of this cationic polyhydride complex is achieved in excellent yields (>95%), through precipitation of the off-white title compound in a large volume of cold pentane. The preparation of the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BAR^{F_4}) salt was also reported recently.^[8c] Complex **2** could be crystallized and submitted to a single crystal X-ray diffraction (sc-XRD) study, revealing the structure of this polyhydride species (Figure 1). The Mo atom in **2** is found in a distorted tricapped triangular prismatic environment, which is not uncommon for heteroleptic coordination compounds surrounded with 9 ligands.^[19] All five hydrides could be localized in the Fourier difference map, allowing for an estimation of the Mo–H bond lengths that range from 1.56 to 1.74 Å (averaging 1.65 Å with 0.08 Å standard deviation), in line with the reported Mo–H bond lengths for terminal hydrides (a mean value of 1.665 Å was found from an analysis of the CCDC database using the ConQuest software). Although discussing metal-hydride bond distances obtained from sc-XRD data remains subject to caution, the significant disparity found in those measurements may find a preliminary explanation when examining short contacts found

within the structure, since the longest Mo–H bonds interact with C–H ones in the lattice.

Addition of benzoic acid (1 equiv., pK_a in THF = 25.1^[20]) to a solution of **1** in C_6D_6 was monitored by NMR spectroscopy. Upon reacting at room temperature, a two-stage evolution of the spectra is observed. At short reaction time (< 2 h), the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows the emergence and the progressive disappearance of an ill-resolved signal at 73.8 ppm. In parallel, a broad resonance centred at -5.0 ppm was found to follow the same behaviour in the hydride region of the ^1H spectrum. These features are characteristic of the above-identified $[\text{MoH}_5(\text{depe})_2]^+$ (**2**) cationic complex (see the Supporting Information). Longer reaction time (> 2 h) allows further reactivity to be observed, with the appearance of two new singlets at 77.8 and 45.4 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. Upon selective decoupling of the aliphatic protons, these signals split into triplets ($^2J_{\text{P-H}} = 41.9$ and 33.7 Hz). Simultaneous formations of dihydrogen and a novel hydride derivative were also noticed in the ^1H spectrum, as a singlet at 4.47 ppm and a high-field pseudo-quintet located at -7.55 ppm ($^2J_{\text{P-H}}, \text{app} = 43.2$ Hz). After 24 h, the reaction mixture does not seem to evolve any further. If a second equivalent of benzoic acid triggers further reactivity, a third equivalent is required to reach full conversion of complex **1** into the new cationic complex **3**. Two main formulations – both cationic – may be envisioned according to the observed stoichiometry: a dihydride complex $[\text{MoH}_2(\text{depe})_2(\kappa^2\text{O-O}_2\text{CC}_6\text{H}_5)][\text{H}(\text{C}_6\text{H}_5\text{COO})_2]$ or a monohydride complex $[\text{MoH}(\text{depe})_2(\kappa^1\text{O-C}_6\text{H}_5\text{COO})_2][(\text{C}_6\text{H}_5\text{COO})]$. The IR transmission spectrum of the complex, recorded in C_6D_6 , displays transitions typical to Mo–H (1882 cm^{-1}) and OCO symmetric and antisymmetric bond vibrations at 1433 and 1378 cm^{-1} , respectively. Despite multiple crystallization attempts, only sticky solids were obtained. Therefore, certifying the mono- or bidentate character of the carboxylate ligand was not possible, but literature precedents^[14c,21] support the formulation of **3** as a Mo(IV) dihydride complex bearing a bidentate benzoate ligand. To further confirm the formulation of complex **3**, which ^1H NMR aromatic signal integrations did not allow us to definitively settle its formulation, anion metathesis was conducted in deaerated EtOH containing sodium tetraphenylborate (1 equiv.). The resulting complex was unambiguously assigned as $[\text{MoH}_2(\text{depe})_2(\kappa^2\text{O-O}_2\text{CC}_6\text{H}_5)][\text{BPh}_4]$, ^1H NMR analysis pointing to a 1:1 $\text{PhCOO}^-/\text{BPh}_4^-$ distribution.

A tentative mechanism is proposed to explain the reactivity in deuterated benzene, taking into account the identified intermediate **2** and the reaction stoichiometry (Scheme 2). Aprotic, low-polarity solvents have typically been shown to favour acid dimerization and homoconjugation of the conjugated base.^[22] This is most likely the case here. Association of benzoate anion with free benzoic acid after proton delivery is indeed expected to occur, resulting in the formation of the weakly acidic, homoconjugate anion $[(\text{C}_6\text{H}_5\text{COO})_2\text{H}]^-$.^[23] Whereas only two protons are required to account for the formation of **3**, three benzoic acid molecules are actually necessary to drive the transformation to completion. Involvement of homoconjugated forms of various acids (e.g. alcohols,^[24] anilinium^[25] or hydrogen halides^[14a,b,26]) have previously been evidenced in the protonation of transition metal hydrides. As postulated by Ito and co-workers on analogous systems,^[14c] the first step of the reaction of $[\text{MoH}_4(\text{depe})_2]$ (**1**) with the benzoic acid dimer is the protonation of **1** to intermediately form the pentahydride cation **2**.

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Scheme 2. Proposed mechanism explaining the reactivity of **1** with benzoic acid derivatives. Intermediates **6^R** and **7^R** could not be observed.

No evidence of the formation of a transient Mo(VI) σ -H₂ complex was found.^[10] Release of H₂ and η^1 -coordination of the benzoate counter-anion to the molybdenum centre yield a still-elusive neutral 18-electrons trihydride complex **6^{Ph}**. Protonation by a second equivalent of benzoic acid, followed by the liberation of a second H₂ molecule, results in the formation of complex **3^{Ph}**, presumably through a transient cationic benzoate-tetrahydride complex **7^{Ph}**. The failure to observe intermediates **6^{Ph}** and **7^{Ph}** between **2'** and **3^{Ph}** even at low temperature suggests that the first H₂ loss/benzoate ligation may be the rate determining state and that the subsequent protonation and H₂ loss are both very fast. If the reaction is performed in THF-*d*₆, only limited reactivity is noticed, with spectroscopic yields below 10% after 48 h at room temperature. It has been previously observed that solvent polarity had a deep impact on the thermodynamics of proton transfer from an acid to a metal hydride.^[24,27] Acid dimerization, anion homoconjugation and ion association through H-bonding are driving forces that become less favoured when polarity is increased. We believe here that the polar, H-bond acceptor THF solvent disfavours either of these associations within this equilibrated process, preventing protonation by the moderate acid to become complete.

Addition of the analogous pentafluorobenzoic acid on a solution of complex **1** was then investigated. Unlike the non-fluorinated analogue, only two equivalents are required to achieve full conversion of complex **1** to complex **4**. Similar NMR features were evidenced with a set of triplets at 75.2 and 44.3 ppm in the ³¹P{¹H} NMR spectrum and a new hydride signal in the ¹H

spectrum at -7.31 ppm displaying a complex multiplicity. ¹⁹F NMR reveals resonances at -144.6, -158.2 and -163.2 ppm, suggesting all pentafluorobenzoate anions to be equivalent. Isolation of **4** was achieved by addition of a concentrated solution of the complex in C₆D₆ into pentane. The resulting yellow solid was decanted off and washed with pentane affording the title compound in good yield (> 60%). Single crystals were grown from a concentrated solution of **4** in benzene, layered with hexamethyldisiloxane (HMDSO). Structural determination thus established the formulation of **4** as [MoH₂(depe)₂(κ^1 -O-C₆F₅COO)₂], a neutral Mo(IV) complex. This is a noticeable different situation than the one found for **3**. This result is somehow counter-intuitive as it is expected that the higher the strength of a carboxylic acid, the more stable the homoconjugated anion.^[28] Thus, we would have expected that **3^{C₆F₅}** is more stable than **3^{Ph}**. A more easily accessible open form (κ^1) due to decreased electron density of the carboxylate ligand in **3^{C₆F₅}** can favour an additional equivalent of perfluorobenzoate to interact with the Mo centre (Scheme 2), affording a more stable neutral complex **4**. The latter crystallizes as a monoclinic system, in the C 2/c space group. In the solid, **4** adopts a highly symmetric dodecahedral geometry due to a C₂ axis passing through the molybdenum centre, leaving all atoms undifferentiated in twos (Figure 1). As a result, the two Mo-H bond lengths are found identical with a value of 1.56 Å. The H-H distance (1.60 Å) determined in the structure lies at the arbitrary limit (1.60 Å) set up between hydrides and compressed hydrides.^[28] Variable-temperature (228–298 K) measurements were conducted in the hydride region of the ¹H NMR spectrum (see the Supporting Information). No change was observed for the explored temperatures. As expected, T₁ measurements on the same temperature range definitively ruled out the presence of any dihydrogen ligand (T_{1,min} of 303 ms at 278 K, 600 MHz, see Supplementary Information).

Addition of 1 equiv. of sulfuric acid (0.37 M in Et₂O, pK_a in MeCN = 7.5^[29]) to a solution of **1** in C₆D₆ triggers an immediate colour change from pale yellow to light brown. After 24 hours at room temperature, complex **1** was fully converted into a new species **5**. Two broad, unresolved resonances were observed at 75.7 and 33.5 ppm in the ³¹P{¹H} NMR spectrum. These signals remain unresolved upon selective decoupling of the aliphatic protons, preventing the determination of the precise number of hydride ligands surrounding the metal centre. These ligands are, however, characterized by the appearance of a new high-field pseudo-quintet at -6.46 ppm (²J_{(P-H)} = 46.7 Hz). When repeated in THF-*d*₆, similar reactivity is observed and single crystals spontaneously formed upon overnight standing of the solution in an NMR tube. Suitable for X-ray diffraction, they allowed the solid-state molecular structure of **5** to be revealed as a neutral Mo(IV) complex, bearing two hydrides and a κ^2 -sulfate ligand. Out of clusters, such denticity is very rare for sulfate anions as far as group 6 metals are considered. To the best of our knowledge, only a single structure was reported to date.^[30] Similarly to **4**, the complex adopts a distorted dodecahedron geometry (Figure 1). Surprisingly, the best fit found during resolution of the XRD data issues, after localization of the hydride in the Fourier difference map, a structure with highly divergent Mo-H bond lengths of 1.40 and 1.72 Å. The former measurement is rather short and again, the recorded Mo-H distances should be considered with caution. Yet, the difference may arise from one of the hydrides building a short intramolecular contact with an acidic PCH₂ proton, itself connected to an oxygen of a sulfate ligand from another molecule}

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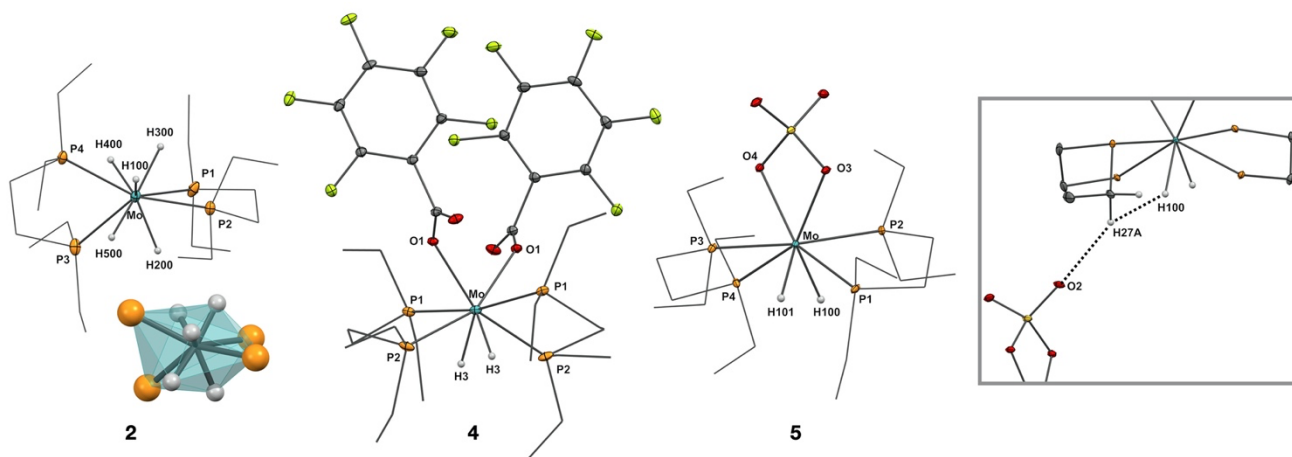


Figure 1. Molecular structures of complexes **2** (with highlight of the tricapped triangular prismatic geometry), **4** and **5** in the crystal. Thermal ellipsoids drawn at the 10% probability level. For clarity, all alkyl chains are represented as wireframes and counter anions and all non-hydridic hydrogens have been omitted. Selected bond lengths (Å) and angles (°) for **2**: Mo–H100 1.56(4), Mo–H200 1.67(6), Mo–H300 1.57(6), Mo–H400 1.70(6), Mo–H500 1.74(6), Mo–P1 2.473(1), Mo–P2 2.438(1), Mo–P3 2.494(1), Mo–P4 2.452(1). For **4**: Mo–O1 2.208(3), Mo–P1 2.512(1), Mo–P2 2.433(1), Mo–H3 1.56(5), O1–Mo–O1 75.78. For **5**: Mo–O3 2.223(3), Mo–O4 2.212(4), Mo–P1 2.419(2), Mo–P2 2.511(2), Mo–P3 2.504(2), Mo–P4 2.409(1), Mo–H100 1.72(8), Mo–H101 1.40(5), O3–Mo–O4 63.8(1). Box: Mo–H \cdots H \cdots O short contact network involving one of the hydride ligand in **5** observed in the unit cell.

of the unit cell (Figure 1, box). The relatively short H–H bond distance of 1.26 Å classifies this pair of ligands as compressed hydrides.^[31] Of note, the presence of a κ^2 -sulfate ligand suggests the sulfuric acid capability to act here as a diacid, providing the two protons necessary to drive the transformation with a single equivalent of acid.

Compounds **1–4** in solution after reaction with the acid decomposed when exposed to air. If most of them provided a complex mixture of dia- and paramagnetic degradation products, a few single crystals grew from the oxygen-exposed solution of **5** in C₆D₆ that allowed the structural determination of a decomposition product **8** after sc-XRD analysis. Unsurprisingly, **8** is an oxo complex (Figure 2) that adopts a distorted octahedral geometry. The equatorial plane is formed by the four phosphorus atoms of the depe ligands. The two axial positions are occupied by oxygen atoms from the oxo and bisulfate ligands. A Mo–O bond length of 1.68 Å is found that is typical of such bonds in phosphine-supported molybdenum complexes (a mean value of 1.728 Å was found from an analysis of CCDC database using the ConQuest software). The relatively long distance between the molybdenum centre and the bisulfate ligand (2.187 Å, a value 1.1

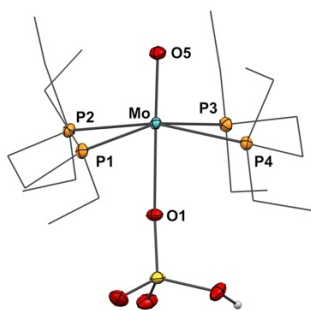


Figure 2. Solid-state molecular structure of complex **8**, with ellipsoids drawn at the 50% probability level. All hydrogen atoms except the one of the bisulfate ligand have been omitted for clarity. Similarly, a bisulfate counter-anion and a solvent molecule have been omitted for clarity. Selected bond lengths (Å) and angles (°): Mo–O1 2.187(1), Mo–O5 1.679(1), Mo–P1 2.5147(7), Mo–P2 2.5164(7), Mo–P3 2.5231(8), Mo–P4 2.5245(7), O1–Mo–O5 178.96(5).

times greater than the sum of the covalent atomic radii of molybdenum and oxygen) suggests a loosely coordinated ligand. Beyond first-row transition metals, and particularly copper,^[32] κ^1 -bisulfate ligands are relatively uncommon and are typically poorly coordinated to the metal centre.

Conclusion

In the present study, representative examples of different families of acids have been explored: a phosphonium salt, sulfuric acid and benzoic acid derivatives. The phosphonium salt results in the rapid and clean protonation of **1**. Remarkably, no further interaction of the free trialkyl phosphine with the cationic pentahydride **2** is observed, presumably due to the high steric hindrance provided by the *tert*-butyl substituents as well as the chelate and strong σ -donating effects of the diphosphine, conferring high stability of the Mo(depe)₂ platform towards substitution. Such acid-base only reactivity is reminiscent of the protonation of **1** by Brookhart's acid.^[8c] The scrutiny of a handful of oxyacids having a maximum pK_a in MeCN of 21.5 revealed that the release of the anionic, oxygenated conjugated bases upon protonation of **1** triggers consecutive reactivity. Expulsion of dihydrogen results in the net formal reduction of the metal center to access a Mo(IV) center that concomitantly builds a Mo–O bond with the oxyanion. The potentially bidentate character of some of these conjugated bases (benzoate and sulfate ions, namely) is also likely to play a role, as it saturates the coordination sphere of the associated complexes through chelation. In the case of benzoic acid, the weaker acid explored in this study, homoconjugation stabilizes ionic intermediates *en route* to the Mo(IV) compounds and makes the reaction between the anion and the pentahydride more sluggish. Due to the lack of pK_a data in benzene, correlating the observed reactivity to the strength of the acids employed could not be performed—we believe that this task may be complicated by the likely involvement of the conjugated bases, favored in non-polar, aprotic solvents, that

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strengthen the respective acid. Yet, these results provide a guide map on the nature of the proton source to be used in accessing nine-coordinate Mo polyhydride complexes, and specifically highlight the importance to consider further reactivity dictated by the nature of the conjugated base.

Experimental Section

General Information

All reactions were performed in oven-dried glassware with rigorous exclusion of air and moisture, using a nitrogen-filled *Jacomex* glove box ($O_2 < 1$ ppm, $H_2O < 1$ ppm) or an argon-filled MBraun glove box ($O_2 < 1$ ppm, $H_2O < 1$ ppm), both equipped with vacuum line. Solvents used were pre-dried (tetrahydrofuran, diethyl ether and *n*-pentane by passing through a Puresolv MD 7 solvent purification machine; benzene and hexamethyldisiloxane (HMDSO) by distillation over CaH_2), degassed by freeze-pump-thaw cycles, dried over molecular sieves and stored in the glove box. C_6D_6 and THF- d_8 (purchased from *Eurisotop*) were degassed by freeze-pump-thaw cycles, dried over molecular sieves and stored in the glove box. $[MoH_4(depe)_2]^{[8c]}$ and $[tBu_3PH][HB(C_6F_5)_3]^{[16]}$ were synthesized according to reported procedures and stored in the glove box. 1H , ^{11}B , ^{19}F and ^{31}P NMR spectra were recorded in C_6D_6 or THF- d_8 by using Wilmad quick pressure valve NMR tubes or J. Young high-vacuum valve NMR tubes on a *Bruker Avance III 400* spectrometer. Chemical shifts are in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual solvent resonances as the internal standard (C_6HD_5 : δ reported = 7.16 ppm; $C_4HD_7O_2$: δ reported = 1.72, 3.58 for 1H NMR). ^{11}B , ^{19}F and ^{31}P NMR spectra were calibrated according to the IUPAC recommendation using a unified chemical shift scale based on the proton resonance of tetramethylsilane as primary reference.^[33,34] Data are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet; m = multiplet), coupling constant (Hz), and integration. Infrared (IR) spectra were recorded in a nitrogen filled *Jacomex* glove box ($O_2 < 1$ ppm, $H_2O < 1$ ppm) on an *Agilent Cary 630 FT-IR* spectrophotometer equipped with a transmission module and are reported in wavenumbers (cm^{-1}).

Synthesis and characterization of $[Mo(depe)_2H_5][HB(C_6F_5)_3]$ (2)

$[MoH_4(depe)_2]$ (15.0 mg, 29.3 μ mol, 1.00 equiv.) was dissolved in THF (1 mL). A solution of $[HB(C_6F_5)_3][tBu_3PH]$ (21.0 mg, 29.3 μ mol, 1.00 equiv.) in THF (1 mL) was added. The reaction mixture was left at room temperature for 1h, under continuous stirring. The resulting pale-yellow solution was then dropwise transferred in a large volume (ca. 10 mL) of precooled pentane ($-40^\circ C$), triggering precipitation of a white solid. The solution was decanted off and the solid washed twice with cold pentane (2×5 mL). The white solid was then dried under an Ar atmosphere at room temperature yielding the desired compound (28.6 mg, 95%). Single crystals suitable for X-ray diffraction were obtained by storing at $-40^\circ C$ a concentrated THF solution of the complex layered by pentane over a few days. 1H -NMR (400 MHz, THF- d_8) δ 3.76 (br. q, $^1J_{B-H} = 94$ Hz, 1H), 1.72 (m, 24H), 1.11 (m, 24H), -5.00 (quin., $^2J_{P-H} = 30.6$ Hz, 5H). ^{11}B -NMR (128 MHz, THF- d_8) δ -25.8 (d, $^1J_{B-H} = 94.2$ Hz). ^{19}F -NMR (377 MHz, THF- d_8) δ -133.7 (d, $^3J_{F-F} = 23.8$ Hz, 6F), -167.0 (t, $^3J_{F-F} = 19.9$ Hz, 3F), -169.4 (m, 6F). ^{31}P -NMR (162 MHz, THF- d_8) δ 73.8 (s). ^{31}P -NMR (162 MHz, THF- d_8) δ 73.8 (sext., $^2J_{P-H} = 30.6$ Hz), upon 1H selective decoupling at 1.5 ppm.

Synthesis and characterization of $[Mo(depe)_2(C_6H_5COO)_2][C_6H_5COO)_2H_2]$ (3) and $[Mo(depe)_2(C_6H_5COO)_2][BPh_4]$

$[MoH_4(depe)_2]$ (15.0 mg, 29.3 μ mol, 1.00 equiv.) was dissolved in benzene (1 mL). A solution of benzoic acid (10.7 mg, 87.9 μ mol, 3.00 equiv.) in benzene (1 mL) was added. The reaction mixture was left at room temperature for 12h, under continuous stirring. Volatiles were removed

under reduced pressure, allowing an oily dark-red solid to be obtained. The residue was triturated and washed twice with cold pentane (2×5 mL). The red residue was then dried under reduced pressure (23.5 mg, 92%). 1H -NMR (400 MHz, C_6D_6) δ 15.25 (br. s), 8.57 (d, $J = 5.9$ Hz), 7.83 (d, $J = 7.5$ Hz), 7.28 – 7.18 (m), 7.06 (t, $J = 7.5$ Hz), 2.33 – 0.39 (m.), -7.55 (pseudo-quin., $J = 43.2$ Hz). Integrations are not provided, as inconsistencies are noticed probably due to ligand exchange. Attempts to adapt NMR experiments to limit exchange processes have been unsuccessful up to now. ^{13}C -NMR (100 MHz, C_6D_6) δ 179.2 (-COO-), 169.8 (-COO-), 135.8 (C_{quat}), 132.8, 132.2 (C_{quat}), 130.7, 130.3, 128.2, 127.9, 23.9 (m), 23.5, 21.4, 17.8, 14.2, 8.7, 7.9 (m). ^{31}P -NMR (162 MHz, C_6D_6) δ 77.8 (s), 45.4 (s). ^{31}P -NMR (162 MHz, C_6D_6) δ 77.8 (t, $^2J_{P-H} = 41.9$ Hz), 45.4 (t, $^2J_{P-H} = 33.7$ Hz) upon 1H selective decoupling at 1.5 ppm.

Anion metathesis can be performed by solubilizing the red residue in deaerated absolute ethanol (ca. 1 mL) containing NaBPh₄ (9.2 mg, 27.0 μ mol, 1.00 equiv.), triggering immediate precipitation of a red-orange solid. The powder was collected by filtration, washed with deaerated absolute ethanol (2×0.5 mL) and dried under an Ar flux (20.3 mg, 80%). When applying vacuum, the powder turns brown suggesting limited stability under vacuum. 1H -NMR (400 MHz, THF- d_8) δ 7.92 (d, $J = 7.1$ Hz, 2H, *ortho*- $C_6H_5COO^-$), 7.60 (t, $J = 7.5$ Hz, 1H, *para*- $C_6H_5COO^-$), 7.44 (t, $J = 7.7$ Hz, 2H, *meta*- $C_6H_5COO^-$), 7.27 (br. s, 8H, *ortho*-B(C_6H_5)₄), 6.84 (t, $J = 7.4$ Hz, 8H, *meta*-B(C_6H_5)₄), 6.69 (t, $J = 7.2$ Hz, 4H, *para*-B(C_6H_5)₄), 2.19-1.84 (br. m, 16 H), 1.62 (br. s, 6H), 1.42 (br. s, 6H), 1.19 (m, 8H), 1.06 (m, 12H), -7.55 (pseudo-quin., $J = 41.2$ Hz). Due to limited drying process, pentane is still present in the aliphatic region of the spectrum (triplet at 0.89 and multiplet at 1.31 ppm).

Synthesis and characterization of $[Mo(depe)_2(C_6F_5COO)_2H_2]$ (4)

$[MoH_4(depe)_2]$ (15.0 mg, 29.3 μ mol, 1.00 equiv.) was dissolved in benzene (1 mL). A solution of pentafluorobenzoic acid (12.4 mg, 58.6 μ mol, 2.00 equiv.) in benzene (1 mL) was added. The reaction mixture was left at room temperature for 12h, under continuous stirring. Hexamethyldisiloxane (HMDSO, 1 mL) was added to the yellow solution. Upon standing at room temperature overnight, small yellow needles formed and were collected by filtration. The crystals were dried at room temperature under a nitrogen atmosphere (12.3 mg, 45%). Among the crystallization crop, single crystals suitable for X-ray diffraction were found and analyzed. 1H -NMR (400 MHz, C_6D_6) δ 2.59 – 2.43 (m, 4H), 2.31 – 2.08 (m, 4H), 2.03 – 1.83 (m, 2H), 1.83 – 1.38 (m, 11H), 1.14 – 0.89 (m, 19H), 0.81 – 0.69 (m, 6H), 0.55 (t, $J = 14.7$ Hz, 2H), -7.31 (m, 2H). ^{13}C -NMR (100 MHz, C_6D_6) δ 162.1 (-COO-), 144.1, 141.7, 141.5, 138.6, 136.1, 24.9 (t, $J_{C-P} = 11.5$ Hz), 24.4 (t, $J_{C-P} = 19.1$ Hz), 23.9 (m), 20.8 (m), 20.5 (t, $J_{C-P} = 5.9$ Hz), 13.4 (t, $J_{C-P} = 5.9$ Hz), 8.9 (s), 8.4 (s), 8.3 (m), 7.6 (t, $J_{C-P} = 5.2$ Hz). ^{19}F -NMR (377 MHz, C_6D_6) δ -144.6 (dd, $J_{F-F} = 24.4$, 8.5 Hz, 4F), -158.2 (t, $J_{F-F} = 20.8$ Hz, 2F), -163.3 (td, $J_{F-F} = 22.5$, 8.7 Hz, 4F). ^{31}P -NMR (162 MHz, C_6D_6) δ 75.2 (t, $^2J_{P-P} = 14.3$ Hz), 44.3 (t, $^2J_{P-P} = 14.3$ Hz). ^{31}P -NMR (162 MHz, C_6D_6) δ 75.2 (tt, $^2J_{P-H} = 49.4$ Hz, $^2J_{P-P} = 14.2$ Hz), 44.3 (ddt, $^2J_{P-H} = 41.2$, 35.0 Hz, $^2J_{P-P} = 14.3$ Hz) upon 1H selective decoupling at 1.5 ppm.

Synthesis and characterization of $[Mo(depe)_2(SO_4)_2H_2]$ (5)

$[MoH_4(depe)_2]$ (15.0 mg, 29.3 μ mol, 1.00 equiv.) was dissolved in benzene (1 mL). An 80 μ L solution of H_2SO_4 (0.37 M, 1.00 equiv.) in Et₂O was added. The reaction mixture was left untroubled at room temperature for 24h. Dark red crystals spontaneously form from the resulting yellow solution. The solution was decanted off and the crystals washed twice with pentane (2×1 mL). The red crystals were then dried under an Ar atmosphere at room temperature yielding the desired compound (11.8 mg, 66%). Single crystals suitable were found in such batch and analyzed by X-ray diffraction. 1H -NMR (400 MHz, THF- d_8) δ 2.44 – 1.42 (m, 24H), 1.08 (m, 24H), -6.47 (p, $J = 46.7$ Hz, 2H). ^{13}C -NMR (100 MHz, THF- d_8) δ 21.9, 19.9, 18.7, 16.9, 7.7. ^{31}P -NMR (162 MHz, THF- d_8) δ 75.7, 33.5.

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Crystallographic data collection and refinement

Data for compounds (2), (4), (5) and (8) were collected at low temperature (100 K) either on a Bruker Kappa Apex II diffractometer using a Mo-K α radiation ($\lambda = 0.71073\text{\AA}$) micro-source or on a XtaLAB Synergy, Dualflex, HyPix diffractometer using micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray source. The structures have been solved using the new dual-space algorithm program SHELXT^[35] and refined by means of least-squares procedures using the SHELXL-2018,^[36] program included in the software package WinGX version 1.63^[37] or with the aid of the software package Crystal^[38]. The Atomic Scattering Factors were taken from International tables for X-Ray Crystallography^[39]. Hydrogen atoms were placed geometrically and refined using a riding model. All non-hydrogens atoms were anisotropically refined.

CCDC

Deposition Number(s) <url href="https://www.ccdc.cam.ac.uk/services/structures?id=doi:10.1002/ejic.20220XXX">2271268 (for 5), 2271269 (for 2), 2271270 (for 4), 2271271 (for 8)</url> contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe <url href="http://www.ccdc.cam.ac.uk/structures">Access Structures service</url>.

Supporting Information

The authors have cited an additional reference within the Supporting Information.^[40]

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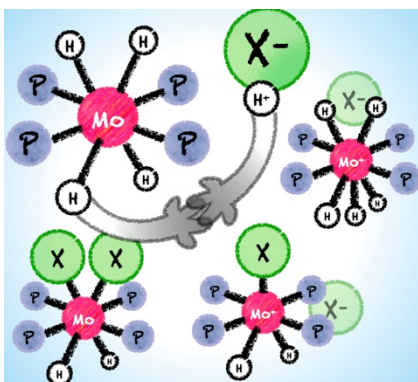
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Keywords: polyhydride complexes • protonation • acids • homoconjugation • molybdenum

RESEARCH ARTICLE

Entry for the Table of Contents



Protonation of polyhydride complexes: conjugated base matters! The protonation of a neutral molybdenum(IV) tetrahydride complex was investigated using a range of proton sources. Whereas simple acid-base process was achieved in the case of a phosphonium, subsequent reactivity of the resulting cationic pentahydride species with conjugated base was typically observed.

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