



Formation and Structure of a Sterically Protected Molybdenum Hydride Complex with a 15-Electron Configuration: [(1,2,4-C₅H₂tBu₃)Mo(PMe₃)₂H]⁺

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Formation and structure of a sterically protected molybdenum hydride complex with a 15-electron configuration: [(1,2,4-C₅H₂tBu₃)Mo(PMe₃)₂H]⁺⁺⁺

Miguel Baya, Jennifer Houghton, Jean-Claude Daran, Rinaldo Poli*

Hydride complexes generally feature a closed shell configuration. They are implicated in a variety of catalytic cycles and are also intermediates of C-H oxidative addition processes. Open-shell, paramagnetic versions have not so far demonstrated broad utility, mainly because of their instability and multitude of decomposition pathways, including deprotonation,^[1] disproportionation,^[2] dihydrogen reductive elimination (for complexes containing at least two hydride ligands),^[3] atom transfer, etc.^[4] Yet, open-shell hydride complexes appear to play a role in enzymatic processes such as hydrogenase and nitrogenase,^[5-8] and their implication in a variety of electrocatalyzed transformation may be envisaged. Therefore, they are attracting renewed interest.

One-electron oxidation of compounds containing two 1-electron ligands, [M](X)(Y), may result in the reductive elimination of X-Y (oxidatively induced reductive elimination, OIRE). This has most clearly been demonstrated for dialkyl complexes, [M](R)₂, to give the organic product R-R plus products originating from [M]⁺.^[9-12] When X = Y = H, the process may lead to H₂ evolution, since the oxidation of a polyhydride complex [M]H_n is expected to favour the rearrangement to a nonclassical isomer, [M]H_{n-2}(H₂)⁺.^[4, 13, 14] In fact, the oxidation of polyhydride complexes often results in dihydrogen evolution,^[15] but the instability and the multitude of decomposition pathways of the intermediate oxidized polyhydride complexes often obscures the clean identification of OIRE.^[4] Indeed, the oxidation of complexes Cp^{*}Ru(PPh₃)H₃^[13] and Os(PiPr₃)₂H₆^[16] leads to hydrogen evolution, but this was shown to take place following proton transfer from the unstable oxidized complex to residual starting material, rather than from direct reductive elimination.

We have recently reported the first unambiguous case of H₂ OIRE for complex Cp^{*}Mo(dppe)H₃ (dppe = Ph₂PCH₂CH₂PPh₂), thanks to the characterization of the solvent-stabilized product, [Cp^{*}Mo(dppe)(S)H]⁺, by EPR (S = THF, CH₂Cl₂)^[3] and electrochemistry (S = MeCN),^[17] although the structure of the product could not be confirmed crystallographically. The oxidized trihydride complex, [Cp^{*}Mo(dppe)H₃]⁺, also decomposes simultaneously by deprotonation and disproportionation. All three pathways

occur via the nonclassical intermediate [Cp^{*}Mo(dppe)H(H₂)]⁺, although theoretical calculations and circumstantial evidence indicates that the oxidized complex adopts a classical structure.^[17] We have argued that both stronger electron donation and greater steric protection by the ligands stabilize paramagnetic hydride complexes by disfavoring, via different mechanisms, the various decomposition pathways.^[4] We have therefore turned our attention to a new Mo system, using the more donating PMe₃ ligand in place of dppe and the more sterically protecting 1,2,4-C₅H₂tBu₃ in place of Cp^{*}. This has allowed us to isolate and structurally characterize, for the first time, the starting and end products of the H₂ OIRE, [Cp^{tBu}Mo(PMe₃)₂H₃]⁺ and [Cp^{tBu}Mo(PMe₃)₂H]⁺ (Cp^{tBu} = 1,2,4-C₅H₂tBu₃).

The starting compound, Cp^{tBu}Mo(PMe₃)₂H₃, was prepared by adapting the procedure previously employed for Cp^{*}Mo(dppe)H₃,^[18] from Cp^{tBu}MoCl₄ and LiAlH₄ in the presence of PMe₃. Its X-ray structure shows a very similar geometry to that of Cp^{*}Mo(dppe)H₃,^[19] with the two PMe₃ ligands symmetrically disposed in adjacent coordination positions (P-Mo-P angle of 93.71(2)°) and far away from the Cp^{tBu} ligand, see Figure 1(a).^[20] When considering the Cp^{tBu} ring as occupying a single coordination position at the ring centroid, it can best be described as a distorted trigonal prism.

<insert Figure 1 here>

Figure 1. ORTEP views of (a) Cp^{tBu}Mo(PMe₃)₂H₃ and (b) the cation in [Cp^{tBu}Mo(PMe₃)₂H₃]PF₆. Ellipsoids are drawn at the 30 % probability level. All hydrogen atoms except the hydrides are not shown for clarity. Relevant parameters are listed in the order a/b (the parameters for the cation are averaged over two independent molecules in the asymmetric unit). Distances (Å): Mo-CNT, 2.0150(2)/2.002(2); Mo-P1, 2.3832(6)/2.473(2); Mo-P2, 2.3801(6)/2.473(2); Mo-H1, 1.58(3)/1.62(4); Mo-H2, 1.57(3)/1.54(4); Mo-H3, 1.58(3)/1.57(4); H2...H3, 1.63/1.40. Relevant angles (°): CNT-Mo-P1, 130.62(2)/127.0(8); CNT-Mo-P2, 132.14(2)/127.4(3); P1-Mo-P2, 93.71(2)/100.3(1); CNT-Mo-H1, 106(1)/104(2); CNT-Mo-H2, 107(1)/108(2); CNT-Mo-H3, 114(1)/108(2). CNT is the Cp^{tBu} ring centroid.

A preliminary electrochemical investigations shows a reversible one-electron oxidation process at E_{1/2} = -0.89 V in THF and -0.93 V in MeCN vs. ferrocene, suggesting that the oxidation product has a certain stability. The stoichiometric oxidation was accomplished by the use of Cp₂Fe⁺PF₆⁻ in THF, affording a product that was sufficiently stable to be isolated and crystallized.^[20] Its structure is closely related to that of the neutral precursor, see Figure 1(b). The Mo-Cp^{tBu}(centroid) separation shortens upon oxidation, whereas the Mo-P bonds lengthen. Not much significance should be attributed to the parameters involving the imprecisely determined hydride positions, but the most notable change is an apparent decrease of the H2...H3 contact (1.40 Å in the cation vs. 1.63 Å in the neutral complex), suggesting an increased H-H attraction in the oxidized complex. The complex, however, can still be described as a classical trihydride. In THF solution, the complex exhibits a rather broad EPR spectrum at ambient temperature, but sharpening occurs at lower temperatures allowing the identification of the expected quartet of triplet feature, due to coupling to three equivalent hydride ligands and to the P nuclei of two equivalent phosphine ligands, flanked by the ⁹⁵Mo and ⁹⁷Mo isotope satellites. Satisfactory simulation, see Figure 2, provides the hyperfine coupling constants a_P = 36.2 G, a_H = 11.4 G and a_{Mo} = 30.8 G, which compare with

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those of the analogous but less thermally stable $[\text{Cp}^*\text{Mo}(\text{dppe})\text{H}_3]^+$ complex ($a_P = 29.8$ G; $a_H = 11.8$ G).

<insert Figure 2 here>

Figure 2. EPR spectrum of compound $[\text{Cp}^{\text{Bu}}\text{Mo}(\text{PMe}_3)_2\text{H}_3]\text{PF}_6$ in THF solution ($T = 193$ K).

Although compound $[\text{Cp}^{\text{Bu}}\text{Mo}(\text{PMe}_3)_2\text{H}_3]\text{PF}_6$ is quite stable as a crystallized solid and in THF solution at low temperatures, it slowly decomposed at $T > 0^\circ\text{C}$, as indicated by a colour change from orange to green. Well formed green crystals were obtained by slow crystallization from THF/pentane at -20°C . The X-ray diffraction analysis revealed the identity of the compound as the H_2 elimination product, $[\text{Cp}^{\text{Bu}}\text{Mo}(\text{PMe}_3)_2\text{H}]^+\text{PF}_6^-$, see Figure 3.^[20] Its formation from $[\text{Cp}^{\text{Bu}}\text{Mo}(\text{PMe}_3)_2\text{H}_3]^+$ can be viewed as the collapse of the H2 and H3 atoms (Figure 1b) to yield a putative $[\text{Cp}^{\text{Bu}}\text{Mo}(\text{PMe}_3)_2\text{H}(\text{H}_2)]^+\text{PF}_6^-$ nonclassical intermediate, followed by H_2 dissociation. Although, once again, structural parameters involving the hydride position may be imprecise, the quality of the data set allowed the identification of a single hydride ligand with a high level of confidence. Therefore, the product is a 15-electron complex of Mo^{III} . When protected from air, the compound is stable over several months in the solid state and at least for several hours in THF solution at room temperature. This stability can be attributed to steric protection, since no additional electron density is available on the ligands for a π -stabilization mechanism.

<insert Figure 2 here>

Figure 3. ORTEP view of the cation in $[\text{Cp}^{\text{Bu}}\text{Mo}(\text{PMe}_3)_2\text{H}]\text{PF}_6$. Ellipsoids are drawn at the 30 % probability level. All hydrogen atoms except the hydride are not shown for clarity. Distances (Å): Mo-CNT, 2.0096(3); Mo-P1, 2.4801(8); Mo-P2, 2.4685(9); Mo-H1, 1.83(3).40. Relevant angles ($^\circ$): CNT-Mo-P1, 122.02(2); CNT-Mo-P2, 121.57(2); P1-Mo-P2, 109.55(3); CNT-Mo-H1, 125.2(9). CNT is the Cp^{Bu} ring centroid.

Although the 15-electron configuration is quite common in the coordination chemistry of Mo^{III} (associated without fail to a spin quartet state), it is extremely rare for organometallic compounds for reasons related to the lower cost of electron pairing in the presence of softer organic ligands.^[21, 22] Two examples, which also enjoy high steric protection and adopt a spin quartet ground state, are $[(\text{C}_5\text{Ph}_5)_2\text{Mo}]^{+[\text{23}]}$ and $\text{Mo}(\text{SPhMes}_2)_3$.^[24] Open-shell hydride complexes are also extremely rare. An example with a 15-electron configuration is $(\text{Tp}^{\text{Bu,Me}})\text{CoH}$.^[25]

The spin configuration for complex $[\text{Cp}^{\text{Bu}}\text{Mo}(\text{PMe}_3)_2\text{H}]^+$ could not be determined by magnetic methods, because of our inability to prepare a pure bulk sample (the compound crystallized together with other decomposition products, e.g. $[\text{Cp}^{\text{Bu}}\text{Mo}(\text{PMe}_3)_2\text{H}_4]^+$ obtained by proton transfer processes^[26]). However, we were able to confirm the spin quartet ground state by EPR spectroscopy. Unlike the spin doublet configuration, a spin quartet ground state is notoriously difficult to observe by EPR spectroscopy for 2nd and 3rd row transition metals with large zero-field splitting. According to theory, a slightly rhombically distorted tetragonal tensor should have g_x and g_y close to 4 and g_z close to 2 for the spin-allowed $\pm 1/2$ transition.^[27] In addition, a spin forbidden $\pm 3/2$ transition may also be accessible, yielding a weak feature at g ca. 6 for the z component. A rare example for Mo^{III} is given by $\text{Mo}(\text{acac})_3$, for which a relatively

broad spectrum can be observed between the liquid N_2 and the liquid He temperatures.^[28] Solutions of $[\text{Cp}^{\text{Bu}}\text{Mo}(\text{PMe}_3)_2\text{H}]\text{PF}_6$ in THF were EPR silent at room temperature and showed only a small resonance at the liquid nitrogen temperature, characteristic of residual $[\text{Cp}^{\text{Bu}}\text{Mo}(\text{PMe}_3)_2\text{H}_3]\text{PF}_6$. The solid sample, however, exhibited the features shown in Figure 4 at liquid He temperature. The g tensor x and y components ($\pm 1/2$ transition) are indeed visible at $g = 3.74$ and ca. 3.45, as well as a weak feature attributed to the $\pm 3/2$ transition (z component) at $g = 5.33$. The $g = 3.74$ peak appears to display a fine structure, possibly due to coupling to the two equivalent P nuclei. The g_z component of the $\pm 1/2$ transition is not visible because it is overshadowed by stronger resonances of residual 17-electron trihydride at $g = 2.009$.

<insert Figure 4 here>

Figure 4. Liquid He, X-band EPR spectrum of compound $[\text{Cp}^{\text{Bu}}\text{Mo}(\text{PMe}_3)_2\text{H}]\text{PF}_6$ (polycrystalline solid sample).

In summary, we have presented the first structural characterization of the starting and end products of an H_2 oxidatively induced reductive elimination. The end product is a rare example of a 15-electron hydride complex.

Experimental Section

All operations were carried out under an argon atmosphere with Schlenk line and dry box techniques. Solvents were dehydrated by standard methods and distilled under dinitrogen. Instrumentation used was: cyclic voltammetry, EG&G 362 potentiostat; ^1H and ^{31}P NMR, Bruker AC200; EPR, Bruker ESP300; X-ray diffraction, Oxford-Diffraction XCALIBUR and Stoe IPDS. Compound $\text{Cp}^{\text{Bu}}\text{MoCl}_4$ was obtained from $\text{Cp}^{\text{Bu}}\text{Mo}(\text{CO})_3(\text{CH}_3)$ and PhICl_2 , the carbonyl compound being obtained in turn from $\text{Mo}(\text{CO})_6$ and NaCp^{Bu} , by adapting the literature procedure used for the Cp^* analogue.^[29]

Preparation of $\text{Cp}^{\text{Bu}}\text{Mo}(\text{PMe}_3)_2\text{H}_3$: To compound $\text{Cp}^{\text{Bu}}\text{MoCl}_4$ (1.42 g, 3.00 mmol) in THF (20 mL) was added PMe_3 in THF (1 M, 8 mL, 8 mmol). After stirring for 30 min, a suspension of LiAlH_4 (ca. 650 mg) in THF (40 mL) was carefully added, resulting in gas evolution. After stirring for 5 h, MeOH (ca. 6 mL) was added dropwise causing vigorous gas evolution. After an additional 1 h stirring the suspension was vacuum-dried. The residue was then extracted with Et_2O (ca. 150 mL) and filtered through Celite. The final solution was vacuum-dried, and the pale yellow solid was washed with methanol and dried *in vacuo*. Yield: 727 mg (50 %). Anal. Calcd. for $\text{C}_{23}\text{H}_{50}\text{MoP}_2$: C, 57.01; H, 10.40. Found: C, 56.48; H, 10.88. ^1H NMR (C_6D_6): δ -5.20 (t, $J = 51.0$ Hz, 3 H, Mo-H), 1.37 (s, 9 H, 'Bu), 1.49 (br, 18 H, $\text{P}(\text{CH}_3)_3$), 1.58 (s, 18 H, 2 x 'Bu), 4.86 (s, 2 H, $\text{C}_5\text{H}_2\text{'Bu}_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 17.9 (s). A single crystal for the X-ray analysis was obtained by slow diffusion of a MeOH layer into a pentane solution at 5°C .

Synthesis of $[\text{Cp}^{\text{Bu}}\text{Mo}(\text{PMe}_3)_2\text{H}_3]\text{PF}_6$: A suspension of $[\text{Cp}_2\text{Fe}]\text{PF}_6$ (32 mg, 0.10 mmol) in THF (5 mL) was added dropwise to a cold solution (193 K) of $\text{Cp}^{\text{Bu}}\text{Mo}(\text{PMe}_3)_2\text{H}_3$ (53 mg, 0.11 mmol) in tetrahydrofuran (10 mL). The solution color immediately changed from pale yellow to dark blue and, within a few minutes, to orange. The reaction mixture was slowly warmed up to 253 K and then concentrated to ca. 1 mL. Addition of cold pentane (253 K, 10 mL) afforded a brown precipitate that was decanted and further washed with cold pentane (253 K, 3x10 mL) and finally vacuum-dried. Yield: 48 mg, 70 %. A single crystal for the X-ray analysis was obtained by diffusion of a pentane layer onto a THF solution at -80°C . EPR (THF, 193 K): $g = 2.016$ (triplet of quartets) $a_P = 36.2$ G, $a_H = 11.4$ G and $a_{\text{Mo}} = 30.8$ G.

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- [20] The structures were solved by direct methods (SIR97) and refined by full matrix least-squares (SHELXL97). H atoms were treated with the riding model except for the hydrides which were fully refined with isotropic thermal parameters. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 619352 – 619354. **X-ray data.** (a) **Cp^{Bu}Mo(PMe₃)₂H₃**: C₂₃H₅₀MoP₂, M_r = 484.51, monoclinic, space group P2₁/n, a = 16.2915(15), b = 17.4655(16), c = 9.2144(8) Å, β = 92.651(10)°, V = 2619.1(4) Å³, Z = 4, ρ_{calcd} = 1.229 g/cm³, μ = 0.629 mm⁻¹, MoKα radiation (λ = 0.71073 Å), T = 180 K, 2θ_{max} = 52.32, scan mode = φ (Stoe IPDS diffractometer), 20750 measured (5171 independent, R_{int} = 0.0337) reflection, 262 refined parameters. Absorption correction (Multi-scan), transmission factors 0.8299/0.7768. R = 0.0270, wR = 0.0657 refined against |F²|, GOF = 1.034, [Δρ]_{max} 0.514, [Δρ]_{min} -0.524 e.Å⁻³. (b) **[Cp^{Bu}Mo(PMe₃)₂H₃]PF₆**: C₂₃H₅₀F₆MoP₃, M_r = 629.48, monoclinic, space group P2₁/c, a = 14.0847(10), b = 26.216(2), c = 20.1855(15) Å, β = 99.221(8)°, V = 7357.2(10) Å³, Z = 8, ρ_{calcd} = 1.269 g/cm³, μ = 0.535 mm⁻¹, MoKα radiation (λ = 0.71073 Å), T = 180 K, 2θ_{max} = 50.00, scan mode = φ (Stoe IPDS diffractometer), 50093 measured (12934 independent, R_{int} = 0.0853) reflection, 763 refined parameters. Absorption correction (Multi-scan), transmission factors 0.8843/0.8674. R = 0.0488, wR = 0.1052 refined against |F²|, GOF = 0.835, [Δρ]_{max} 0.802, [Δρ]_{min} -0.441 e.Å⁻³. (c) **[Cp^{Bu}Mo(PMe₃)₂H]PF₆**: C₂₃H₄₈F₆MoP₃, M_r = 627.46, monoclinic, space group P2₁/c, a = 9.6185(5), b = 16.8699(10), c = 18.7489(12) Å, β = 90.441(5)°, V = 3042.2(3) Å³, Z = 4, ρ_{calcd} = 1.370 g/cm³, μ = 0.636 mm⁻¹, MoKα radiation (λ = 0.71073 Å), T = 180 K, 2θ_{max} = 52.74, scan mode = ω and φ (Oxford-Diffraction XCALIBUR diffractometer), 25511 measured (18993 independent, R_{int} = 0.0513) reflection, 317 refined parameters. Absorption correction (Multi-scan), transmission factors 0.8363/0.7206. R = 0.0507, wR = 0.1428 refined against |F²|, GOF = 1.070, [Δρ]_{max} 1.073, [Δρ]_{min} -0.981 e.Å⁻³.
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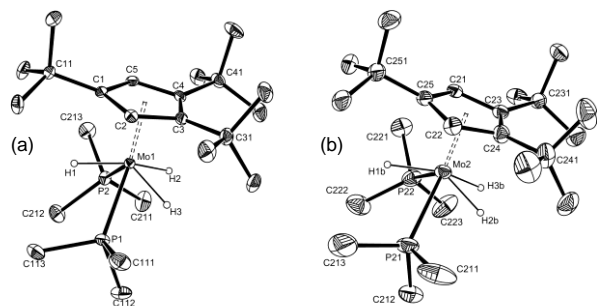


Figure 1

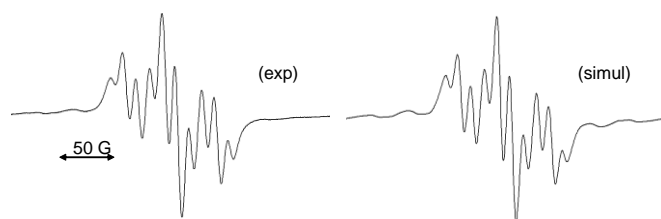


Figure 2

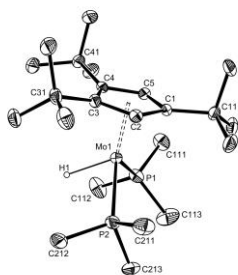


Figure 3

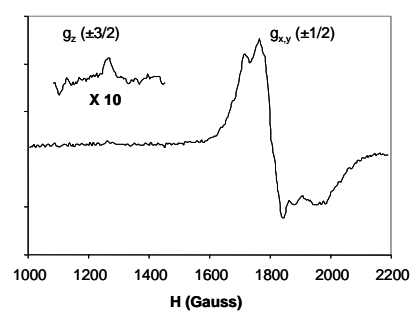


Figure 4

Sterically protected 15-electron molybdenum hydride

Miguel Baya, Jennifer Houghton, Jean-Claude Daran, Rinaldo Poli*

Formation and structure of a sterically protected molybdenum hydride complex with a 15-electron configuration: $[(1,2,4\text{-C}_5\text{H}_2\text{fBu}_3)\text{Mo}(\text{PMe}_3)_2\text{H}]^+$

Oxidation of $(1,2,4\text{-C}_5\text{H}_2\text{fBu}_3)\text{Mo}(\text{PMe}_3)_2\text{H}_3$ induces H_2 reductive elimination and yields the first stable 15-electron hydride complex, $[(1,2,4\text{-C}_5\text{H}_2\text{fBu}_3)\text{Mo}(\text{PMe}_3)_2\text{H}]^+$.

