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A capped trigonal pyramidal molybdenum hydrido complex and an unusually mild sulfur-carbon bond cleavage reaction

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DFT calculations reveal that a reported molybdenum hydride complex has an unprecedented geometry with the molybdenum in the base of trigonal pyramid defined by three thiolate ligands with a phosphine ligand on the apex and a hydride capping a PS_2 face. This complex reacts with methanol to produce a sulfido complex by a new reaction: the protonation of an ipso carbon of a thiolate ligand by coordinated methanol.

Hydrodesulfurization (HDS) is an important step in the upgrading of petroleum to clean fuels, usually using catalysts based on molybdenum disulfide.¹ There is theoretical evidence for the formation of unstable molybdenum hydrides (MoH) and molybdenum hydrosulfide (MoSH) groups on the surface of the heterogeneous catalyst.^{2, 3} The MoSH groups are thought to be more stable under HDS conditions.³ The mechanism of carbon-sulfur bond cleavage is still under investigation. Inorganic chemists are studying the reactions of well-defined metal complexes to establish the mechanisms of carbon-sulfur bond cleavage.⁴ For example, low valent molybdenum complexes have been shown to cleave C-H and S-C bonds.⁵ The mechanisms of H₂ activation at sulfido-bridged dimolybdenum cyclopentadienyl complexes have been investigated computationally and found to occur either homolytically between sulfur ligands^{6a} or heterolytically across a Mo-S bond^{6b} depending on the complex.

Some of us were involved in the study of homogenous, diamagnetic molybdenum hydridoarylthiolato complexes $MoH(SAr)_3(PRPh_2)$, R = Me, Et, Ar = 2,4,6-iPr_3C_6H_2 and 2,4,6-Me_3C_6H_2 that underwent a spontaneous S-C cleavage event at a sulfur-aryl bond when their THF solutions were exposed to methanol.^{7, 8} When deuterated methanol (MeO²H) was employed, monodeuterated arene was detected along with non-deuterated free thiol and a dimeric molybdenum complex



Figure 1. The cleavage of sulfur-carbon bonds under mild conditions by reaction of $MeO^{2}H$ with $MoH(PMePh_{2})(SAr)_{3}$, $Ar = 2,4,6-Me_{3}C_{6}H_{2}$. The structure of the dimer was determined by single crystal X-ray diffraction^{7, 8} and a similar PMe₃ dimer (Mo_{2}) by DFT calculation (this work). The hydrogens and all carbons except those attached to the donor atoms have been removed for clarity. The level of theory for this calculation and the others shown in this article is M11-L with basis set SDD on Mo and 6-31G(d) on the other atoms with THF solvation applied using the PCM model unless otherwise specified.

 (Mo_2) with two bridging sulfido ligands (Figure 1).⁸ The Mo_2 product was characterized by single crystal X-ray diffraction but we were unable to obtain suitable crystals of the starting hydride complex.

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⁺ Electronic Supplementary Information (ESI) available: Computational details, coordinates and energies of the structures. See DOI: 10.1039/x0xx00000x

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Figure 2. The structure of MoH(PMe₃)(SAr)₃ with all of the hydrogens on the ligands and all of the carbons apart from the ipso carbons removed. Selected bond distances (Å) and angles (°): Mo(1)-H(12) 1.65, Mo(1)-P(6) 2.37, Mo(1)-S(2) 2.34, Mo(1)-S(4) 2.36, Mo(1)-S(8) 2.33; H(12)-Mo(1)-P(6) 54.1, H(12)-Mo(1)-S(2) 73.5, H(12)-Mo(1)-S(8) 84.6, P(6)-Mo(1)-S(2) 115.0, P(6)-Mo(1)-S(4) 84.6, P(6)-Mo(1)-S(8) 91.3, S(2)-Mo(1)-S(4) 112.9, S(4)-Mo(1)-S(8) 121.1, S(8)-Mo(1)-S(2) 121.6.

The molybdenum in MoH(SAr)₃(PRPh₂) was proposed to be in a trigonal bipyramidal geometry with the hydride *trans* to the phosphine ligand on the basis of the observation in the NMR spectra of a large ${}^{2}J_{HP}$ coupling constant ranging from 79 to 87 Hz between the hydride, detected at 3.3 ppm for one of the compounds, and the phosphorus nuclei.^{7, 8} However DFT calculations using a slightly simplified structure (Mo(PMe₃)(H)(SAr)₃, Ar = 2,6-Me₂C₆H₃) now provide strong evidence that the most stable isomer of these complexes has molybdenum in an unprecedented distorted capped trigonal pyramidal (CTP) geometry (Figure 2).

In this diamagnetic, five coordinate complex the molybdenum sits 0.3 Å above the middle of a distorted triangle defined by the three sulfur atoms (Figure 2). The phosphorus is at the vertex of the distorted S₃P trigonal pyramid with the short Mo-P bond (2.37 Å) at a 78° angle to the S_3 basal plane. The hydride ligand caps one PS2 face of this CTP with a small HMoP angle of 54.1°. Thus the large ${}^{2}J_{HP}$ is associated with this small angle between these nuclei. There are no distortions of the PMe₃ ligand that would indicate bonding favouring 5coordinate phosphorus. The HOMO is a lone pair with approximately $(d_{xz})^2$ (Mo) character, out of phase with a $(p_z)^2$ lone pair on S8 (see the SI) where the x direction is along the Mo-S8 bond and the z direction is between the Mo-H and Mo-None of the 620 five-coordinate complexes P bonds. containing a terminal hydride found in the Cambridge Structural Database has such a CTP geometry. Two isomers with the hydride approximately trans to the phosphorus in a distorted trigonal bipyramidal (TBP) geometry were located as stable minima at 10 and 13 kcal/mol higher in energy and a distorted trigonal bipyramidal complex in the triplet state was located at 5 kcal/mol higher in energy. Even the model complex $Mo(PMe_3)(H)(SMe)_3$ with much smaller substituents on the sulfurs adopts this CTP geometry. Apparently molybdenum is large enough to accommodate ligands cis to each other, thus avoiding trans H-Mo-P and H-Mo-S bond weakening. The ${}^{2}J_{HP}$ (unscaled) were calculated using the gauge-independent atomic orbital method as -70 Hz for the CTP geometry and -31 Hz for the TBP geometry. The former

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value agrees better with the range from experiment (79 to 87 Hz, \pm sign not determined).

This CTP geometry explains why the complex $MoH(PMePh_2)(SAr)_3$, $Ar = 2,4,6-iPr_3C_6H_2$ readily reacts with pyridine to give the complex $MoH(PMePh_2)(py)(SAr)_3$, $Ar = 2,4,6-iPr_3C_6H_2$,⁷ now known to have a capped trigonal bipyramidal (CTB) geometry⁹ with the pyridine across from the hydride and the phosphorus at a small angle to the hydride, producing a $^2J_{HP}$ of 87 Hz (eq 1).



The original proposal for the sulfur-carbon bond cleavage of Figure 1 was that the hydride would attack the carbon;⁸ however this would involve isotope exchange with the hydride



that was not observed and our DFT studies could not find a suitable transition state for the hydride attack. The methanol that is needed to trigger this cleavage reaction (Figure 1) can easily coordinate to give a formally Mo(IV) methanol complex as shown in eq 1. From this experimentally unobserved methanol adduct, the C-S bond is readily cleaved in an

Figure 3. (a) The methanol adduct MoH(PR₃)(OHMe)(SAr)₃ (Mo(1)-H(22) 1.66, Mo(1)-P(13) 2.39, Mo(1)-O(15) 2.21, Mo(1)-S(2) 2.36, Mo(1)-S(4) 2.33, Mo(1)-S(17) 2.36, O(15)-H(16) 0.97, S(4)-C(5) 1.78 Å; H(22)-Mo(1)-P(13) 52.1, H(22)-Mo(1)-O(15) 148.5, P(13)-Mo(1)-O(15) 158.7, Mo(1)-S(4)-C(5) 113.0°); (b) the hydrogen transfer transition state (OH...CSMO) (1635*i* cm⁻¹; Mo(1)-H(22) 1.66, Mo(1)-P(13) 2.45, Mo(1)-O(15) 2.07, Mo(1)-S(2) 2.37, Mo(1)-S(4) 2.20, Mo(1)-S(17) 2.38, O(15)-H(16) 1.21, S(4)-C(5) 2.14, H(16)-C(5) 1.33 Å; H(22)-Mo(1)-P(13) 54.3, H(22)-Mo(1)-O(15) 146.7, P(13)-Mo(1)-O(15) 157.7, Mo(1)-S(4)-C(5) 107.1°); (c) the sulfido product MoH(S)(PR₃)(OMe)(SAr)₂.HAr (Mo(1)-H(22) 1.65, Mo(1)-P(13) 2.46, H(22)-Mo(1)-O(15) 145.6, P(13)-MO(1)-O(15) 155.7° plus HAr (C(5)-H(16) 1.0 Å).

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Figure 4. A reaction coordinate diagram for the C-S bond cleavage reaction shown in Figure 1. Calculations were done with M11L/6-31G(d)/SDD on Mo/THF solvation.

unprecedented mechanism: the attack by the hydrogen of the methanol ligand on the ipso carbon of an aryl (Figure 3). The result of this transfer is the formation of a C-H bond in the arene product, consistent with the experimental observation that deuterium from MeO^2H ends up on this carbon (Figure 3b).

The hydrogen of the methanol ligand (Figure 3a) transfers to the aryl carbon 5 via a transition state with arenium character. Indeed the Mulliken positive charges on the carbons of the ring other than carbon 5 increase on going from the methanol adduct to the transition state. Atoms with increased negative charges include carbon 5, sulfur 4, hydrogen 16 and hydrogens on the methoxide methyl. The reaction has characteristics as described for other electrophilic aromatic substitution reactions.^{10, 11} The immediate metal-containing product of this reaction is a formally Mo(VI) CTB sulfido complex MoH(S)(PR₃)(OMe)(SAr)₂ with a short Mo-S bond of 2.14 Å (Figure 3c). The metal undergoes a formal two electron oxidation in this reaction, paradoxically indicating that the hydrogen transferred as a hydride.

The (OH...CSMo) transition state $(1635i \text{ cm}^{-1})$ is the highest energy point in the overall reaction shown in Figure 1 with a transition state energy of 21 kcal/mol above the energy of the methanol adduct MoH(PR₃)(OHMe)(SAr)₃ (Figure 4); the same TS energy was obtained for gas phase and liquid phase (THF) calculations. The use of higher basis sets on the central atoms (6-311++G(d,p)) resulted in an energy of 22 kcal/mol and the use of the PBE0 functional with dispersion correction D3 gave 24 kcal/mol. Little is known about the mechanism of protonolysis of carbon-sulfur bonds.^{12, 13}

Another interesting step in the overall reaction involves the transition state for the formal reductive elimination of the Mo(VI) CTB hydridosulfido complex MoH(S)(PR₃)(OMe)(SAr)₂ to produce the Mo(IV) hydrosulfido complex Mo(SH)(PR₃)(OMe)(SAr)₂ (Figure 5). This step has a barrier of 15 kcal/mol and is uphill thermodynamically by 7 kcal/mol but is likely driven by subsequent dimerization steps where HSAr is eliminated, a strongly downhill reaction (Figure 4). A similar transition state involving hydride migration to a bridging sulfido ligand in a formal hydride to proton conversion has been reported.^{6b} Molybdenum hydrido sulfido complexes can also readily eliminate dihydrogen.¹⁴

The details of the subsequent steps have not been established. The reaction may proceed via a singly bridged sulfido complex such as $Mo_2(\mu$ -S)(SH)(OMe)_2(PMe_3)_2(SAr)_3 (Figure 6) which might eliminate a further equivalent of thiol HSAr to give the observed dimeric product (PMe_3)(MeO)(ArS)Mo(μ -S)_2Mo(SAr)(OMe)(PMe_3) (Mo_2) of Figure 1 found at the zero energy point of the reaction coordinate diagram, Figure 4.

These unusual reactions and geometries highlight the rich redox chemistry of molybdenum in a sulfur environment. The chemistry has possible relevance to HDS catalysis but also the action of molybdenum enzymes.¹⁵

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Conflicts of interest

There are no conflicts to declare.



Figure 5. (a) Transition state structure MoH..S TS (959*i* cm⁻¹) for the hydride reductive elimination step (Mo(1)-H(27) 1.77, Mo(1)-P(9) 2.59, Mo(1)-O(11) 1.92, Mo(1)-S(2) 2.35, Mo(1)-S(8) 2.23, Mo(1)-S(15) 2.35, H(27)-S(8) 1.59 Å; H(27)-Mo(1)-P(9) 66.0, Mo(1)-H(27)-S(8) 82.7, P(9)-Mo(1)-O(11) 161.3, S(2)-Mo(1)-S(15) 119.8°, S(2)-Mo(1)-S(8) 122.3°) to give the (b) hydrosulfido complex Mo(SH)(PR₃)(OMe)(SAr)₂ (Mo(1)-P(9) 2.52, Mo(1)-O(11) 1.92, Mo(1)-S(2) 2.30, Mo(1)-S(8) 2.39, Mo(1)-S(15) 2.29, H(27)-S(8) 1.34 Å; P(9)-Mo(1)-O(11) 159.3, S(2)-Mo(1)-S(15) 117.1, S(2)-Mo(1)-S(8) 120.1, S(8)-Mo(1)-S(15) 122.8°).

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Figure 6. Structure of a possible intermediate in the reaction shown in Figure 1, a sulfido bridged dimer $Mo_2(\mu$ -S)(SH)(OMe)_2(PMe_3)_2(SAr)_3.

Notes and references

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- 1 V. C. Srivastava, *RSC Adv.*, 2012, **2**, 759-783.
- 2 P. Y. Prodhomme, P. Raybaud and H. Toulhoat, J. Catal., 2011, 280, 178-195.
- 3 S. J. Ding, S. J. Jiang, Y. S. Zhou, Q. Wei and W. W. Zhou, *J. Catal.*, 2017, **345**, 24-38.
- 4 L. Wang, W. He and Z. Yu, *Chem. Soc. Rev.*, 2013, **42**, 599-621.
- 5 (a) A. Sattler, K. E. Janak and G. Parkin, *Inorg. Chim. Acta*, 2011, **369**, 197-202; (b) K. E. Janak, J. M. Tanski, D. G. Churchill and G. Parkin, *J. Am. Chem. Soc.*, 2002, **124**, 4182-4183.
- 6 (a) A. G. Algarra, *Eur. J. Inorg. Chem.*, 2016, 1886–1894; (b) J.
 E. McGrady and J. Gracia, *J. Organomet. Chem.*, 2005, 690, 5206-5214.
- 7 T. E. Burrow, A. Hills, D. L. Hughes, J. D. Lane, N. J. Lazarowych, M. J. Maguire, R. H. Morris and R. L. Richards, J. Chem. Soc., Chem. Commun, 1990, 1757-1759.
- 8 T. E. Burrow, D. L. Hughes, A. J. Lough, M. J. Maguire, R. H. Morris and R. L. Richards, J. Chem. Soc., Dalton Trans., 1995, 2583-2589
- 9 R. H. Morris, Coord. Chem. Rev., 2017, DOI: <u>https://doi.org/10.1016/j.ccr.2017.06.019</u>.
- 10 B. Galabov, D. Nalbantova, P. V. Schleyer and H. F. Schaefer, Acc. Chem. Res., 2016, 49, 1191-1199.
- 11 S. L. C. Moors, X. Deraet, G. Van Assche, P. Geerlings and F. De Proft, *Chem. Sci.*, 2017, **8**, 680-688.
- 12 M. Rakowski DuBois, Polyhedron, 1997, 16, 3089-3098.
- 13 T. Y. Luh and Z. J. Ni, Synthesis, 1990, 89-103.
- 14 V. J. Murphy and G. Parkin, J. Am. Chem. Soc., 1995, 117, 3522-3528.
- 15 R. Hille, J. Hall and P. Basu, Chem. Rev., 2014, 114, 3963-4038.

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A five coordinate molybdenum hydride with an unprecedented CTP structure reacts with methanol, leading to the facile cleavage of a sulfur-carbon bond.