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Reversible C−H Bond Activation in Coordinatively Unsaturated Molybdenum Aryloxy Complexes, $Mo(PMe_3)_4(OAr)H$: Comparison with Their Tungsten Analogs

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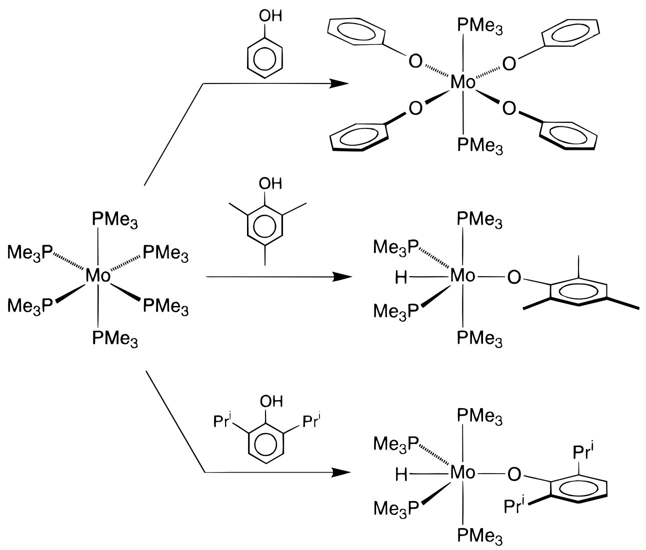
Summary: $Mo(PMe_3)_6$ reacts with ArOH (Ar = $C_6H_2Me_3$, $C_6H_3Pr^i_2$) to give aryloxy−hydride derivatives $Mo(PMe_3)_4(OAr)H$ in contrast to the cyclometalated derivatives that are obtained for the corresponding tungsten system. Deuterium labeling and magnetization transfer studies, however, demonstrate that the coordinatively unsaturated molybdenum complexes $Mo(PMe_3)_4(OAr)H$ are in fact kinetically capable of intramolecular oxidative addition of a C−H bond to yield cyclometalated derivatives but that the products so obtained are thermodynamically unstable with respect to the aryloxy−hydride derivatives.

The activation of carbon−hydrogen bonds by transition metal centers continues to be an important area of research, with the ultimate goal of achieving selective functionalization of hydrocarbons.[1] Of the most common nonradical mechanisms for C−H bond activation, namely *(i)* σ-bond metathesis, *(ii)* addition to metal−ligand multiple bonds, and *(iii)* oxidative addition, the lattermost is especially favored for electron-rich transition metal complexes. We have a particular interest in the chemistry of such complexes and have demonstrated that $W(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ are capable of selective intramolecular sp^2 and sp^3 C−H bond activation of phenol and its alkyl-substituted derivatives, thereby resulting in the formation of novel four- and five-membered oxametallacycles, *e.g.* $W(PMe_3)_4(\eta^2\text{-}OC_6H_4)H_2$ and $W(PMe_3)_4[\eta^2\text{-}OC_6H_2Me_2(CH_2)]H_2$.[2] Since an appreciation of the factors that promote C−H bond activation is important, we sought to compare analogous reactions of the molybdenum counterpart $Mo(PMe_3)_6$.[3] Significantly, the chemistry of these molybdenum and tungsten systems proved to be quite distinct with respect to their ability to achieve C−H bond activation.

Scheme 1



$Mo(PMe_3)_6$ reacts with an excess of phenol in benzene to give the orange paramagnetic tetrakis(phenoxy) complex $Mo(PMe_3)_2(OPh)_4$, accompanied by elimination of H_2 (Scheme 1).[4] $Mo(PMe_3)_2(OPh)_4$ has been characterized by X-ray diffraction,[5] identifying an octahedral geometry about the metal center, with *trans*-PMe_3 ligands.[6] $Mo(PMe_3)_2(OPh)_4$ provides a striking contrast to the product of the corresponding tungsten system which results from sp^2 C−H bond activation: specifically, both $W(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{-}PMe_2CH_2)H$ react with phenol to give the four-membered oxametallacycle $W(PMe_3)_4(\eta^2\text{-}OC_6H_4)H_2$.[2]

The formation of a tetrakis(aryloxy) derivative $Mo(PMe_3)_2(OAr)_4$ may be inhibited by increasing the steric demands of ArOH. Indeed, incorporation of substituents into both *ortho*-positions allows aryloxy−hydride complexes $Mo(PMe_3)_4(OAr)H$ to be isolated. For example, $Mo(PMe_3)_6$ reacts with 2,4,6-trimethylphenol and 2,6-diisopropylphenol to give the purple diamagnetic

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[1] (a) *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; John Wiley and Sons: New York, 1989. (b) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154−162. (c) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403−424. (d) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91−100. (e) Special issue: *J. Organomet. Chem.* **1996**, *504*(1,2).

[2] (a) Rabinovich, D.; Zelman, R.; Parkin, G. *J. Am. Chem. Soc.* **1990**, *112*, 9632−9633. (b) Rabinovich, D.; Zelman, R.; Parkin, G. *J. Am. Chem. Soc.* **1992**, *114*, 4611−4621.

[3] (a) Murphy, V. J.; Parkin, G. *J. Am. Chem. Soc.* **1995**, *117*, 3522−3528. (b) Brookhart, M.; Cox, K.; Cloke, F. G. N.; Green, J. C.; Green, M. L. H.; Hare, P. M.; Bashkin, J.; Derome, A. E.; Grebenik, P. D. *J. Chem. Soc., Dalton Trans.* **1985**, 423−433.

[4] The formation of aryloxy derivatives accompanied by elimination of H_2 has also been observed in a related tungsten system, namely the reactions of $W(PMePh_2)_4Cl_2$ with phenol or *p*-cresol to give $WCl_2(PMePh_2)_2(OAr)_2$. See: Jang, S.; Atagi, L. M.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 6413−6414.

[5] $Mo(PMe_3)_2(OPh)_4$ is monoclinic, $P2_1/c$ (No. 14), with a = 10.212(2) Å, b = 10.606(3) Å, c = 14.607(2) Å, β = 98.11(2)°, and Z = 2. $Mo(PMe_3)_4(OC_6H_2Me_3)$ is triclinic, $P\bar{1}$ (No. 2), with a = 9.514(2) Å, b = 12.220(2) Å, c = 12.820(3) Å, α = 87.24(2)°, β = 77.80(2)°, γ = 81.99(2)°, and Z = 2. $Mo(PMe_3)_4(OC_6H_3Pr^i_2)H$ is orthorhombic, *Pnma* (No. 62), with a = 20.055(5) Å, b = 17.076(5) Å, c = 9.400(3) Å, and Z = 4.

[6] The Mo−O bond lengths in $Mo(PMe_3)_2(OPh)_4$ [1.958(3) and 1.966(3) Å] are comparable to those in the related complex $Mo(NHMe_2)_2(O\text{-}2\text{-}C_6H_4Ph)_4$ [1.972(3) and 1.963(3) Å].[6a] For reference, the mean Mo−OAr bond length for complexes listed in the Cambridge Structural Database (version 5.11) is 1.99 Å. See, for example: (a) Bartos, M. J.; Kriley, C. E.; Yu, J. S.; Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1989**, *8*, 1971−1977. (b) Kerschner, J. L.; Yu, J. S.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1989**, *8*, 1414−1418. (c) Walborsky, E. C.; Wigley, D. E.; Roland, E.; Dewan, J. C.; Schrock, R. R. *Inorg. Chem.* **1987**, *26*, 1615−1621. (d) Kerschner, J. L.; Torres, E. M.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1989**, *8*, 1424−1431.

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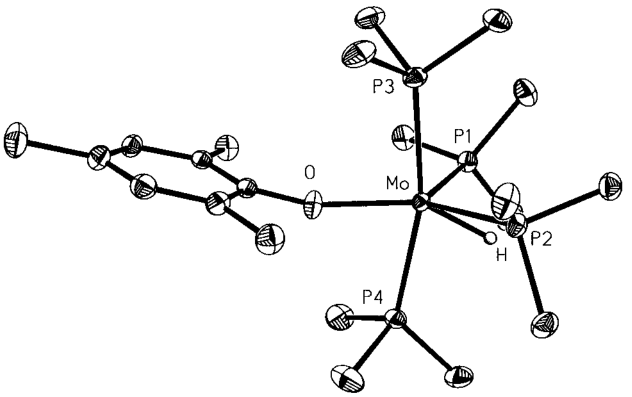


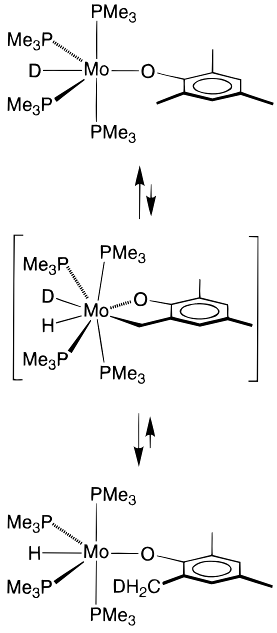
Figure 1. Molecular structure of $Mo(PMe_3)_4(OC_6H_2Me_3)H$.

complexes $Mo(PMe_3)_4(OC_6H_2Me_3)H$ and $Mo(PMe_3)_4(OC_6H_3Pr^i_2)H$, respectively (Scheme 1). Decisive characterization of the products as aryloxy–hydride complexes is provided by NMR spectroscopy.[7] For example, the ^1H NMR spectra of $Mo(PMe_3)_4(OC_6H_2Me_3)H$ and $Mo(PMe_3)_4(OC_6H_3Pr^i_2)H$ exhibit triplet of triplet resonances attributable to Mo–H ligands at δ −6.59 (J_{P-H} = 23, 84 Hz) and −6.53 (J_{P-H} = 22, 85 Hz), respectively. Furthermore, the observation of doublet resonances in the selectively decoupled $^{31}P\{^1H-P(CH_3)_3\}$ spectra provides convincing evidence that each complex contains only a single Mo–H ligand.[8]

The molecular structures of $Mo(PMe_3)_4(OC_6H_2Me_3)H$ and $Mo(PMe_3)_4(OC_6H_3Pr^i_2)H$ have been determined by X-ray diffraction (Figure 1).[5] Neglecting the hydride ligand, the coordination environment about molybdenum is based on a trigonal bipyramid, with axial PMe_3 ligands; the hydride ligand appears to be located close to the equatorial plane and *trans* to the aryloxy substituent.[9] As such, the *trans* arrangement of the aryloxy and hydride ligands contrasts with the *cis* geometries observed for the related 18-electron octahedral complexes $Ru(PMe_3)_4(OC_6H_4Me)H$[10] and $[Ir(PMe_3)_4(OMe)H][PF_6]$.[11] Moreover, consistent with the suggestion that the hydride ligands of $Mo(PMe_3)_4(OC_6H_2Me_3)H$ and $Mo(PMe_3)_4(OC_6H_3Pr^i_2)H$ are best described as *trans* to an aryloxy rather than a PMe_3 ligand, the hydride signals in the ^1H NMR spectra do not exhibit the large *trans* J_{P-H} couplings of *ca.* 100 and 145 Hz that are observed for $Ru(PMe_3)_4(OC_6H_4Me)H$[10] and $[Ir(PMe_3)_4(OMe)H][PF_6]$,[11] respectively.[12]

Since the aryloxy complexes $Mo(PMe_3)_4(OAr)H$ are formally 16-electron (d^4), lone pair π donation from oxygen is presumably operative.[13] Consequently, the Mo–OAr bond lengths in $Mo(PMe_3)_4(OAr)H$ [Ar = $C_6H_2Me_3$, 2.065(3) Å; Ar = $C_6H_3Pr^i_2$, 2.072(6) Å] are intermediate between those in the formally 14-electron complex $Mo(PMe_3)_2(OPh)_4$ [1.958(3) and 1.966(3) Å] and the 18-electron derivative $Mo(PMePh_2)_2(O\text{-}2,6\text{-}C_6H_3Ph_2)H$ [2.164(5) Å].[6d,14,15]

Scheme 2



The isolation of the molybdenum aryloxy–hydride complexes $Mo(PMe_3)_4(OAr)H$ is of particular significance since the tungsten analogues were postulated to be the intermediates responsible for the C–H bond activation reactions in the corresponding tungsten system. For example, the five-membered oxametallacycle $W(PMe_3)_4[\eta^2\text{-}OC_6H_2Me_2(CH_2)]H_2$ was proposed to be formed *via* intramolecular oxidative addition of one of the *ortho*-methyl C–H bonds to the tungsten center in the intermediate $[W(PMe_3)_4(OC_6H_2Me_3)H]$.[2] The ability to isolate molybdenum species that correspond to reactive intermediates for tungsten is presumably a consequence of the fact that a second-row transition metal typically forms weaker bonds to carbon and hydrogen than does the corresponding third-row metal.[16] Consequently, the energy required to break the C–H bond is not compensated by the formation of Mo–C and

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[7] See Supporting Information.

[8] Such data clearly exclude the possibility of the complexes being, in fact, 18-electron trihydride complexes $Mo(PMe_3)_4(OAr)H_3$.

[9] The location of the hydride ligands were observed in electron density difference maps; however, as with most hydrides coordinated to heavy metals, their location as determined by X-ray diffraction is subject to considerable uncertainty.

[10] (a) Osakada, K.; Ohshiro, K.; Yamamoto, A. *Organometallics* **1991**, *10*, 404–410. (b) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *Organometallics* **1991**, *10*, 1875–1887.

[11] Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387–6389.

[12] The hydride and thiolate ligands in $Mo(dppe)_2(SC_6H_2Pr^i_3)H$ have also been reported to adopt a *cis* disposition, but the geometry is grossly distorted from octahedral. The structure is also fluxional on the NMR time scale, and the hydride resonance appears as a quintet with J_{P-H} = 47 Hz. See: Henderson, R. A.; Hughes, D. L.; Richards, R. L.; Shortman, C. *J. Chem. Soc., Dalton Trans.* **1987**, 1115–1121.

[13] Consistent with the occurence of lone pair donation, the aryloxy–hydride complexes $Mo(PMe_3)_4(OAr)H$ are diamagnetic and provide a contrast to the paramagnetic nature of closely related $Mo(PR_3)_4X_2$ (e.g. X = Cl, I). See ref 3b and: Carmona, E.; Marín, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *Polyhedron* **1983**, *2*, 185–193.

[14] Rothwell has also noted a correlation between electron count and W–OAr bond length in a series of tungsten aryloxide complexes. See: Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1989**, *28*, 780–786.

[15] Furthermore, the bond angles at oxygen for $Mo(PMe_3)_4(OC_6H_2Me_3)H$ and $Mo(PMe_3)_4(OC_6H_3Pr^i_2)H$ are 159.7(3) and 145.9(6)°, respectively; however it should be noted that on its own such a parameter cannot be reliably used as an indicator of π-bonding. See ref 14 and: (a) Howard, W. A.; Trnka, T. M.; Parkin, G. *Inorg. Chem.* **1995**, *34*, 5900–5909. (b) Steffey, B. D.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1990**, *9*, 963–968. (c) Coffindaffer, T. W.; Steffy, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 4742–4749.

[16] (a) *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 1990; Vol. 428. (b) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629–688. (c) Eisenberg, D. C.; Norton, J. R. *Israel J. Chem.* **1991**, *31*, 55–66. (d) Skinner, H. A.; Connor, J. A. *Pure Appl. Chem.* **1985**, *57*, 79–88.

Mo—H bonds.[17] Thus, for molybdenum, the equilibrium between the aryloxy derivative and its cyclometalated counterpart lies in favor of the former species, while for tungsten the latter prevails. The relative energetics of these two equilibria resembles that of the cyclometalation equilibria involving $M(PMe_3)_6$ and $M(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$, for which the equilibrium constant for the tungsten system is a factor of *ca.* 2×10^3 greater than that for molybdenum at 30 °C.[3a]

Evidence that the molybdenum aryloxy—hydride complexes are indeed in equilibrium with their cyclometalated derivatives, and that C—H bond activation is kinetically feasible, is provided by magnetization transfer and deuterium exchange studies. For example, proton magnetization transfer is observed between the Mo—H ligands and the *ortho*-methyl substituents of the aryloxy group in $Mo(PMe_3)_4(OC_6H_2Me_3)H$. Likewise, scrambling of deuterium into the *ortho*-methyl groups is observed in the reaction of $Mo(PMe_3)_6$ with 2,4,6-$Me_3C_6H_2OD$. Both of these processes can be rationalized in terms of a mechanism that involves the reversible formation of a five-membered oxametallacycle—dihydride complex *via* sp^3 C—H bond activation, thereby permitting site exchange, as illustrated in Scheme 2.[18]

In summary, the reactions of $Mo(PMe_3)_6$ with phenol and its derivatives provide some interesting contrasts with the corresponding reactions of the tungsten complexes $W(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$. Specifically, the tendency to achieve C—H bond activation for a molybdenum center is reduced considerably from that for a tungsten center, so that the products of the molybdenum system are simple aryloxy derivatives, *e.g.* $Mo(PMe_3)_2(OPh)_4$ and $Mo(PMe_3)_4(OAr)H$, whereas cyclometalated derivatives, *e.g.* $W(PMe_3)_4(\eta^2\text{-}OC_6H_4)H_2$ and $W(PMe_3)_4[\eta^2\text{-}OC_6H_2Me_2(CH_2)]H_2$, are obtained for the tungsten system. Such differences are attributed to weaker M—C and M—H bond energies for molybdenum compared to tungsten.

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Supporting Information Available: Text giving experimental details, tables of spectroscopic data and crystal structure data, and ORTEP diagrams for $Mo(PMe_3)_2(OPh)_4$, $Mo(PMe_3)_4(OC_6H_2Me_3)$, and $Mo(PMe_3)_4(OC_6H_3Pr^i_2)H$ (26 pages). Ordering information is given on any current masthead page.

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[17] It must also be recognized that the oxidative addition of the C—H bond will be accompanied by loss of oxygen to metal π-donation.

[18] It is, of course, possible that the six-coordinate complexes $Mo(PMe_3)_4(OAr)H$ may dissociate PMe_3 prior to the C—H bond activation step; cf. the mechanism for oxidative addition of H_2 to $W(PMe_3)_4I_2$. See: Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 353—354.