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Factors Influencing Coordination versus Oxidative Addition of C−H Bonds to Molybdenum and Tungsten: Structural and Spectroscopic Evidence That the Calixarene Framework Promotes C−H Bond Activation

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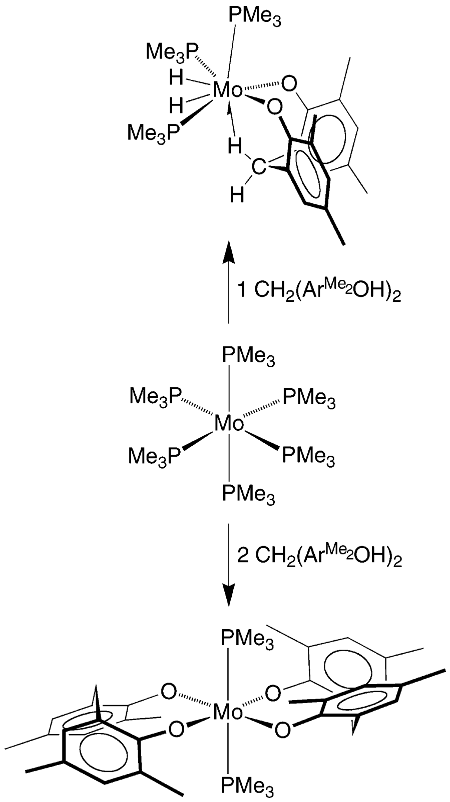
Summary: $Mo(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ react with the diphenol $CH_2(Ar^{Me_2}OH)_2$ ($Ar^{Me_2} = C_6H_2Me_2$) to yield $[\kappa^2,\eta^2\text{-}CH_2(Ar^{Me_2}O)_2]M(PMe_3)_3H_2$ (M = Mo, W), which possess agostic M−H−C interactions. NMR spectroscopic studies provide evidence that the tungsten compound is in facile equilibrium with the metalated trihydride $[\kappa^3\text{-}CH(Ar^{Me_2}O)_2]W(PMe_3)_3H_3$.

We have recently reported that *p-tert*-butylcalix[4]arene, $[Calix^{Bu^t}(OH)_4]$, reacts with $Mo(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ to yield compounds of composition $\{[Calix^{Bu^t}(OH)_2(O)_2]M(PMe_3)_3H_2\}$, resulting from the oxidative addition of two adjacent phenolic O−H bonds to the metal center.[1] Despite the common composition, however, X-ray diffraction studies indicate that there is a significant difference in the solid-state structures pertaining to the manner by which one of the calixarene methylene groups interacts with the metal center. Specifically, the molybdenum complex exists as the agostic[2] derivative $[Calix^{Bu^t}(OH)_2(O)_2]Mo(PMe_3)_3H_2$, whereas the tungsten derivative exists as the metalated trihydride $[Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3$.[3] In order to determine whether the calixarene framework is responsible for the differences between the molybdenum and tungsten compounds, we sought related compounds derived from non-macrocyclic phenols. Therefore, in this paper, we report the reactivity of the simple diphenol $CH_2(Ar^{Me_2}OH)_2$ (2,2′-methylenebis(4,6-dimethylphenol))[4] towards $Mo(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{−}CH_2PMe_2)H$. Significantly, the calixarene and diphenol systems proved to be distinct, with the latter showing a reduced interaction with the methylene C−H bond.

Scheme 1



The methylene-bridged diphenol $CH_2(Ar^{Me_2}OH)_2$, which may be viewed as a "half-calixarene", reacts with $Mo(PMe_3)_6$ at room temperature to give $[\kappa^2,\eta^2\text{-}CH_2(Ar^{Me_2}O)_2]Mo(PMe_3)_3H_2$ (Scheme 1).[5] Structural characterization by X-ray diffraction demonstrates that $[\kappa^2,\eta^2\text{-}CH_2(Ar^{Me_2}O)_2]Mo(PMe_3)_3H_2$ (Figure 1) possesses an agostic interaction akin to that of $[Calix^{Bu^t}(OH)_2(O)_2]Mo(PMe_3)_3H_2$.[1] Comparison of the respective Mo···C distances (Table 1), however, indicates that the magnitude of the interaction is greater for the calixarene complex.

Excellent evidence that the agostic interaction in $[\kappa^2,\eta^2\text{-}CH_2(Ar^{Me_2}O)_2]Mo(PMe_3)_3H_2$ is dictated by the electronic nature of the molybdenum center and is not a consequence of a required conformation of the $[CH_2(Ar^{Me_2}O)_2]$ ligand is provided by comparison with $[\kappa^2\text{-}CH_2(Ar^{Me_2}O)_2]_2Mo(PMe_3)_2$ (Figure 2), obtained via the reaction between a 2:1 ratio of $CH_2(Ar^{Me_2}OH)_2$ and $Mo(PMe_3)_6$ (Scheme 1). In particular, examination of the molecular structure of $[\kappa^2\text{-}CH_2(Ar^{Me_2}O)_2]_2Mo(PMe_3)_2$ shows that the ligand is capable of adopting a conformation in which the Mo···C distance (3.82 Å) is considerably longer than that for the agostic interaction in $[\kappa^2,\eta^2\text{-}CH_2(Ar^{Me_2}O)_2]Mo(PMe_3)_3H_2$ (2.91 Å).

The Mo−O bond lengths in $[\kappa^2\text{-}CH_2(Ar^{Me_2}O)_2]_2Mo(PMe_3)_2$ (1.945(2) and 1.970(2) Å) are shorter than those in $[\kappa^2,\eta^2\text{-}CH_2(Ar^{Me_2}O)_2]Mo(PMe_3)_3H_2$ (2.091(1) and 2.117(2) Å),[6] which may

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(1) Buccella, D.; Parkin, G. *J. Am. Chem. Soc.* **2006**, *128*, 16358−16364.

(2) (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395−408. (b) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1−124. (c) Brookhart, M.; Green, M. L. H.; Parkin, G. *Proc. Natl. Acad. Sci.* **2007**, *104*, 6908−6914.

(3) The abbreviation $[Calix\text{-}H^{Bu^t}(OH)_2(O)_2]$ is intended to indicate that a hydrogen atom has been removed from one of the methylene groups.

(4) Wiseman, P.; Fitton, F. *Educ. Chem.* **1979**, *16*, 180−181.

(5) For molybdenum and tungsten complexes of [RHC]-bridged diphenols, see, for example: (a) Chisholm, M. H.; Huang, J.-H.; Huffman, J. C.; Parkin, I. P. *Inorg. Chem.* **1997**, *36*, 1642−1651. (b) Takashima, Y.; Nakalama, Y.; Yasuda, H.; Harada, A. *J. Organomet. Chem.* **2002**, *651*, 114−123. (c) Lehtonen, A.; Sillanpää, R. *Polyhedron* **2002**, *21*, 1017−1022. (d) Redshaw, C.; Humphrey, S. M. *Polyhedron* **2006**, *25*, 1946−1954.

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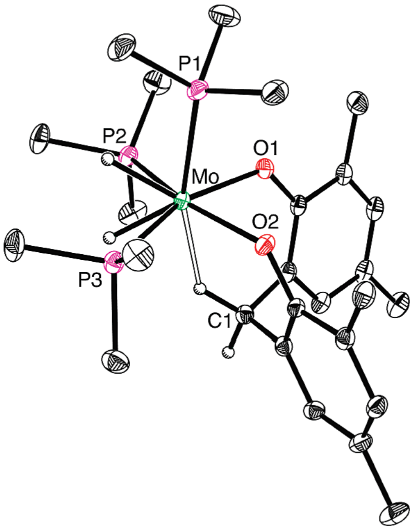

Figure 1. Molecular structure of $[\kappa^2,\eta^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{Mo(PMe}_3)_3\text{H}_2$.

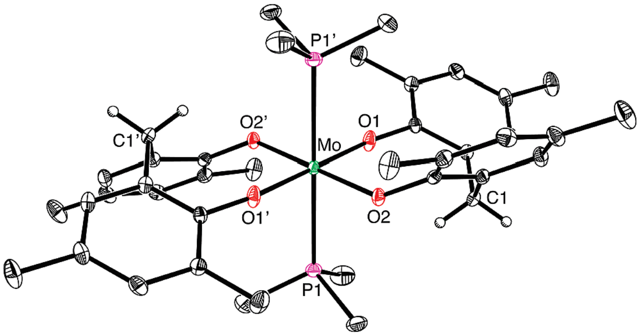

Figure 2. Molecular structure of $[\kappa^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]_2\text{Mo(PMe}_3)_2$.

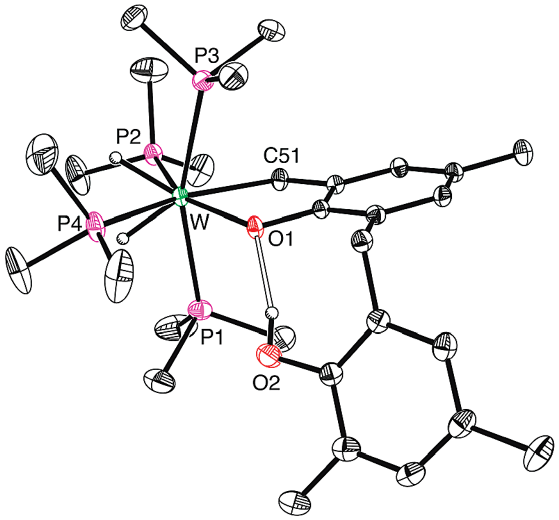

Figure 3. Molecular structure of $[\kappa^2\text{-}O,C\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{OH})\{(\text{C}_6\text{H}_2\text{Me})(\text{CH}_2)\text{O}\}]\text{W(PMe}_3)_4\text{H}_2$.

reflect the fact that oxygen-to-metal π donation is required to reduce the electron deficiency of the metal center in $[\kappa^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]_2\text{Mo(PMe}_3)_2$ in the absence of an agostic interaction. In this regard, evidence that an agostic interaction does indeed influence the Mo−O bond length is provided by density functional theory calculations on isomers of $[\kappa^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{Mo(PMe}_3)_3\text{H}_2$ both with and without an agostic interaction. Specifically, the Mo−O bond lengths in fully geometry optimized $[\kappa^2,\eta^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{Mo(PMe}_3)_3\text{H}_2$ with an agostic interaction (2.126 and 2.148 Å) are on average longer than the corresponding values for the species without an agostic interaction (2.050 and 2.158 Å) in which the Mo···C distance is constrained to be the same value as that in $[\kappa^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]_2\text{Mo(PMe}_3)_2$. The latter bond lengths are not, however, as short as those calculated for $[\kappa^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]_2\text{Mo(PMe}_3)_2$ (1.946 and 1.970 Å), which suggests that an ionic component to the bonding also plays a role in the latter compound.[7]

The reaction between $\text{W(PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ and $\text{CH}_2(\text{Ar}^{\text{Me}_2}\text{OH})_2$ follows a very different course to the corresponding reaction of $\text{Mo(PMe}_3)_6$. Thus, instead of reacting with both phenolic O−H groups, $\text{W(PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ yields initially $[\kappa^2\text{-}O,C\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{OH})\{(\text{C}_6\text{H}_2\text{Me})(\text{CH}_2)\text{O}\}]\text{W(PMe}_3)_4\text{H}_2$ (Figure 3), which is derived by reaction with an O−H bond and a C−H bond of an adjacent methyl group (Scheme 2). Such reactivity of the methyl group is analogous to the formation of $[\kappa^2\text{-}O,C\text{-OC}_6\text{H}_4(\text{CH}_2)]\text{W(PMe}_3)_4\text{H}_2$ upon treatment of $\text{W(PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ with 2-methylphenol.[8] It is, however, evident that cleavage of the C−H bond represents a kinetic preference because heating to 60 °C results in the formation of $[\kappa^2,\eta^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{W(PMe}_3)_3\text{H}_2$ derived from cleavage of the two O−H bonds.

Table 1. Comparison of M···C Distances (Å) in $[\kappa^2,\eta^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{M(PMe}_3)_3\text{H}_2$ and $\{[\text{Calix}^{\text{Bu}^t}(\text{OH})_2(\text{O})_2]\text{M(PMe}_3)_3\text{H}_2\}$

	d(Mo···C)/Å	d(W···C)/Å
$[\kappa^2,\eta^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{M(PMe}_3)_3\text{H}_2$	2.907(2)	2.917(2)
$\{[\text{Calix}^{\text{Bu}^t}(\text{OH})_2(\text{O})_2]\text{M(PMe}_3)_3\text{H}_2\}^a$	2.729(4)	2.256(4)

[a] Values taken from ref 1.

The molecular structure of $[\kappa^2,\eta^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{W(PMe}_3)_3\text{H}_2$ has been determined by X-ray diffraction (Figure 4),[9] thereby demonstrating that it possesses an agostic interaction similar to that in the molybdenum analogue. As such, $[\kappa^2,\eta^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{W(PMe}_3)_3\text{H}_2$ provides a marked contrast to its calixarene counterpart $[\text{Calix-H}^{\text{Bu}^t}(\text{OH})_2(\text{O})_2]\text{W(PMe}_3)_3\text{H}_3$, which exists as a metalated isomer in the solid state. For example, the W···C separation in $[\kappa^2,\eta^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{W(PMe}_3)_3\text{H}_2$ (2.917(2) Å) is significantly longer than the corresponding W−C bond length in $[\text{Calix-H}^{\text{Bu}^t}(\text{OH})_2(\text{O})_2]\text{W(PMe}_3)_3\text{H}_3$ (2.256(4) Å). Thus, consideration of the structures observed for the diphenoxide and calixarene systems, $[\kappa^2,\eta^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{M(PMe}_3)_3\text{H}_2$ and $\{[\text{Calix}^{\text{Bu}^t}(\text{OH})_2(\text{O})_2]\text{M(PMe}_3)_3\text{H}_2\}$ (M = Mo, W), as summarized in Table 1, demonstrates that the methylene group of the calixarene shows a greater propensity to interact with a metal center, via both coordination and oxidative addition, than does the methylene group of the $[\text{CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]$ ligand.

While the X-ray diffraction study indicates that $[\kappa^2,\eta^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{W(PMe}_3)_3\text{H}_2$ exists as an agostic complex in the solid state, NMR spectroscopic studies indicate that the metalated trihydride $[\kappa^3\text{-CH}(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{W(PMe}_3)_3\text{H}_3$ is accessible in solu-

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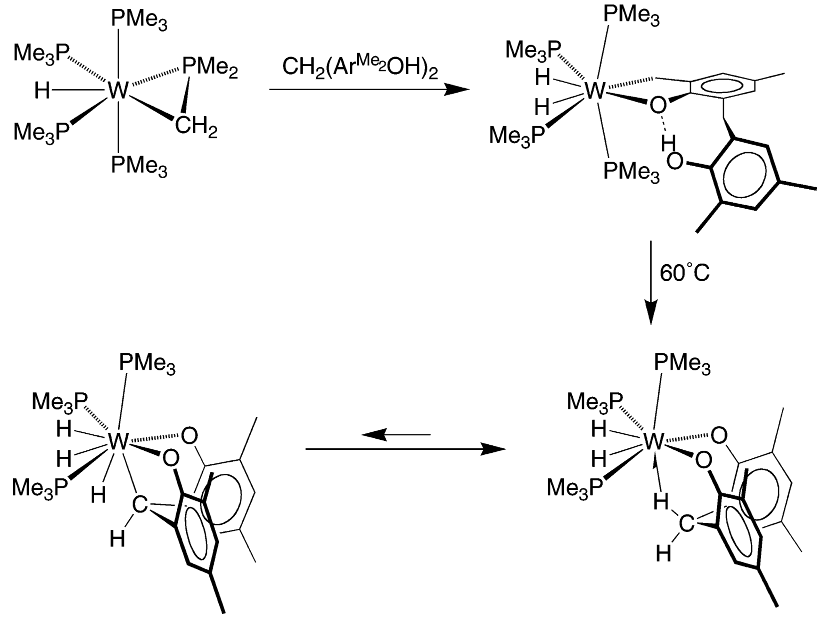
[6] Correspondingly, the Mo−O−C bond angles for $[\kappa^2\text{-CH}_2(\text{C}_6\text{H}_2\text{Me}_2\text{O})_2]_2\text{Mo(PMe}_3)_2$ (138.0(2)° and 164.8(2)°) are larger than those for $[\kappa^2,\eta^2\text{-CH}_2(\text{C}_6\text{H}_2\text{Me}_2\text{O})_2]\text{Mo(PMe}_3)_3\text{H}_2$ (127.1(1)° and 127.2(1)°).

[7] See, for example: (a) Howard, W. A.; Trnka, T. M.; Parkin, G. *Inorg. Chem.* **1995**, *34*, 5900−5909. (b) Howard, W. A.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *115*, 606−615. (c) Melnick, J. G.; Docrat, A.; Parkin, G. *Chem. Commun.* **2004**, 2870−2871. (d) Melnick, J. G.; Parkin, G. *Dalton Trans.* **2006**, 4207−4210.

[8] (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.

[9] The geometry about tungsten is similar to that for $[\kappa^3\text{-PhN-}(\text{C}_6\text{H}_4\text{O})_2]\text{W(PMe}_3)_3\text{H}_2$, derived from a phenylimino-bridged diphenol, with the principal difference being a dative nitrogen donor versus an agostic interaction. See: Kelly, B. V.; Tanski, J. M.; Janak, K. E.; Parkin, G. *Organometallics* **2006**, *25*, 5839−5842.

Scheme 2



tion (Scheme 2).[10] For example, the ^1H NMR spectrum of [κ^2,η^2-$CH_2(Ar^{Me_2}O)_2$]$W(PMe_3)_3H_2$ is highly temperature dependent, with J_{HH} for the nonagostic hydrogen atom of the methylene group varying from 15 Hz at 248 K to 0 Hz at 300 K (Figure 5). The reduction in J_{HH} upon increasing the temperature may be rationalized by invoking a temperature-dependent equilibrium between [κ^2,η^2-$CH_2(Ar^{Me_2}O)_2$]$W(PMe_3)_3H_2$ and [κ^3-$CH(Ar^{Me_2}O)_2$]$W(PMe_3)_3H_3$. Furthermore, when the temperature is increased from 300 to 328 K, the signal for the nonagostic methylene hydrogen sharpens and thereby reveals a quartet (J_{HH} = 4 Hz) due to coupling to the three hydride ligands of the metalated isomer.

In contrast to the marked temperature dependence for [κ^2,η^2-$CH_2(Ar^{Me_2}O)_2$]$W(PMe_3)_3H_2$, the nonagostic hydrogen atom of the methylene group of the molybdenum counterpart remains as a simple doublet with J_{HH} = 16 Hz over the temperature range 228−318 K. This observation indicates that the metalated trihydride [κ^3-$CH(Ar^{Me_2}O)_2$]$Mo(PMe_3)_3H_3$ is not accessible for the molybdenum system.

Density functional theory calculations support the notion that the agostic tungsten complex exhibits a greater tendency to undergo C−H bond cleavage than does the molybdenum counterpart. For example, whereas the metalated tungsten compound [κ^3-$CH(Ar^{Me_2}O)_2$]$W(PMe_3)_3H_3$ is 8.2 kcal mol^{-1} higher in energy than the agostic isomer [κ^2,η^2-$CH_2(Ar^{Me_2}O)_2$]-

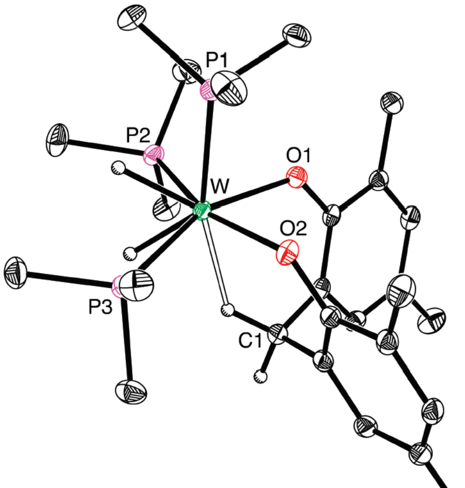


Figure 4. Molecular structure of [κ^2,η^2-$CH_2(Ar^{Me_2}O)_2$]$W(PMe_3)_3H_2$.

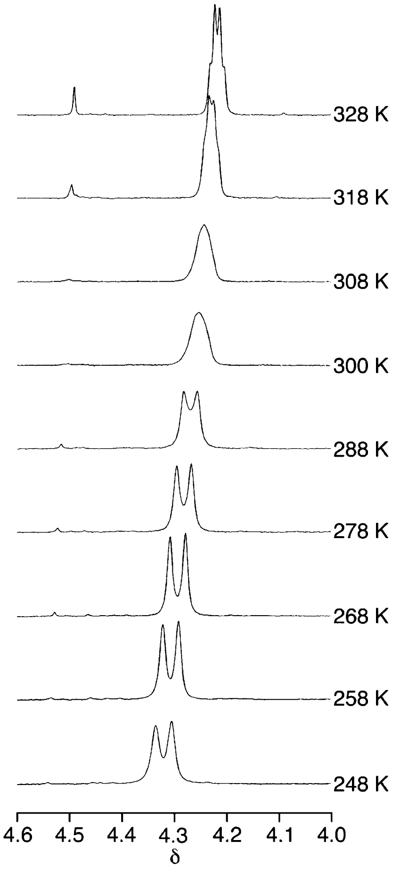


Figure 5. ^1H NMR spectrum of [κ^2,η^2-$CH_2(Ar^{Me_2}O)_2$]$W(PMe_3)_3H_2$ focusing on the nonagostic methylene hydrogen. J_{HH} is reduced upon increasing the temperature to 300 K, due to the equilibrium between [κ^2,η^2-$CH_2(Ar^{Me_2}O)_2$]$W(PMe_3)_3H_2$ and [κ^3-$CH(Ar^{Me_2}O)_2$]-$W(PMe_3)_3H_3$ shifting to the latter. When the temperature is increased from 300 to 328 K, the signal sharpens and thereby reveals a quartet due to coupling to the three hydride ligands of the metalated isomer.

Table 2. DFT Calculated Energies[a] of the Metalated Isomer Relative to the Agostic Isomer

	ΔE(Mo)/ kcal mol^{-1}	ΔE(W)/ kcal mol^{-1}
$[\kappa^2,\eta^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{M}(\text{PMe}_3)_3\text{H}_2$	21.0	8.2
$\{[\text{Calix}(\text{OH})_2(\text{O})_2]\text{M}(\text{PMe}_3)_3\text{H}_2\}^b$	19.9	5.4

[a] $\Delta E = H^{\text{SCF}}_{\text{metalated}} - H^{\text{SCF}}_{\text{agostic}}$. [b] Values taken from ref 1.

$\text{W}(\text{PMe}_3)_3\text{H}_2$, the corresponding value for the molybdenum system is 21.0 kcal mol^{-1} (Table 2).[11] A similar trend was also observed for the calixarene system, with access to the metalated form being less endothermic for tungsten (5.4 kcal mol^{-1}) than for molybdenum (19.9 kcal mol^{-1}).[1]

^{13}C NMR spectroscopic studies provide evidence that the methylene group of the calixarene ligand is more susceptible to participating in an agostic interaction and subsequent oxidative addition than is that of the $[\text{CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]$ ligand. Specifically, the J_{CH} coupling constant involving the agostic hydrogen of $[\text{Calix}^{\text{Bu}^t}(\text{OH})_2(\text{O})_2]\text{W}(\text{PMe}_3)_3\text{H}_2$ (65 Hz) is much lower than the corresponding value for $[\kappa^2,\eta^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{W}(\text{PMe}_3)_3\text{H}_2$ (94 Hz). Since these coupling constants correspond to the weighted average of $^1J_{\text{CH}}$ for the agostic interaction and $^2J_{\text{CH}}$ for the metalated derivative,[12] the reduced value for the calixarene system is consistent with (i) the agostic interaction in $[\text{Calix}^{\text{Bu}^t}(\text{OH})_2(\text{O})_2]\text{W}(\text{PMe}_3)_3\text{H}_2$ being greater than that in $[\kappa^2,\eta^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{W}(\text{PMe}_3)_3\text{H}_2$ and (ii) $[\text{Calix}^{\text{Bu}^t}(\text{OH})_2(\text{O})_2]\text{W}(\text{PMe}_3)_3\text{H}_2$ being in equilibrium with a greater concentration of its metalated isomer than is $[\kappa^2,\eta^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{W}(\text{PMe}_3)_3\text{H}_2$.

In summary, $\text{Mo}(\text{PMe}_3)_6$ and $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ react with $\text{CH}_2(\text{Ar}^{\text{Me}_2}\text{OH})_2$ to give $[\kappa^2,\eta^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{Mo}(\text{PMe}_3)_3\text{H}_2$ and $[\kappa^2,\eta^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{W}(\text{PMe}_3)_3\text{H}_2$, respectively. NMR spectroscopic studies demonstrate that the tungsten complex $[\kappa^2,\eta^2\text{-CH}_2(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{W}(\text{PMe}_3)_3\text{H}_2$ exists in facile equilibrium with the metalated trihydride $[\kappa^3\text{-CH}(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{W}(\text{PMe}_3)_3\text{H}_3$, whereas the molybdenum counterpart $[\kappa^3\text{-CH}(\text{Ar}^{\text{Me}_2}\text{O})_2]\text{Mo}(\text{PMe}_3)_3\text{H}_3$ is not readily accessible. Structural comparisons with the related calixarene compounds demonstrate that the methylene group of the calixarene ligand shows a greater propensity to undergo oxidative addition than does the methylene-bridged diphenoxide ligand.

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Supporting Information Available: CIF files giving crystallographic data for the four X-ray structure studies and text, tables, and figures giving experimental details, characterization data, and Cartesian coordinates for geometry-optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] In this regard, it is pertinent to note that reversible oxidative addition of a C−H bond of $[\text{CH}_2(\text{Ar}^{\text{Bu}^t,\text{Me}}\text{O})_2]$ to a dinuclear tungsten compound has been observed.[5a]

[11] B3LYP functional and cc-pVTZ(-f)/LACV3P basis sets. See the Supporting Information for further details.

[12] Typical values for $^1J_{\text{CH}}$ of the agostic complexes and $^2J_{\text{CH}}$ for alkyl hydrides are in the ranges ~75−100 and ~0−10 Hz, respectively.[2]