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p-tert-Butylcalix[4]arene Complexes of Molybdenum and Tungsten: Reactivity of the Calixarene Methylene C−H Bond and the Facile Migration of the Metal around the Phenolic Rim of the Calixarene

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Abstract: *p-tert*-Butylcalix[4]arene, $[\mathrm{Calix^{Bu^t}(OH)_4}]$, reacts with $\mathrm{Mo(PMe_3)_6}$ and $\mathrm{W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H}$ to yield compounds of composition $\{[\mathrm{Calix^{Bu^t}(OH)_2(O)_2]M(PMe_3)_3H_2}\}$ which exhibit unprecedented use of a C−H bond of a calixarene methylene group as a binding functionality in the form of agostic and alkyl hydride derivatives. Thus, X-ray diffraction studies demonstrate that, in the solid state, the molybdenum complex $[\mathrm{Calix^{Bu^t}(OH)_2(O)_2]Mo(PMe_3)_3H_2}$ exists as an agostic derivative with a Mo···H−C interaction, whereas the tungsten complex exists as a metallated trihydride $[\mathrm{Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3}$. Solution ^{1}H NMR spectroscopic studies, however, provide evidence that $[\mathrm{Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3}$ is in equilibrium with its agostic isomer $[\mathrm{Calix^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_2}$. Dynamic NMR spectroscopy also indicates that the $[\mathrm{M(PMe_3)_3H_2}]$ fragments of both the molybdenum and tungsten complexes $[\mathrm{Calix^{Bu^t}(OH)_2(O)_2]M(PMe_3)_3H_2}$ migrate rapidly around the phenolic rim of the calixarene on the NMR time scale, an observation that is in accord with incorporation of deuterium into the methylene *endo* positions upon treatment of the isomeric mixture of $[\mathrm{Calix^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_2}$ and $[\mathrm{Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3}$ with D_2. Treatment of $\{[\mathrm{Calix^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_2}\}$ with $\mathrm{Ph_2C_2}$ gives the alkylidene complex $[\mathrm{Calix^{Bu^t}(O)_4]W{=}C(Ph)Ar}$ [Ar = $\mathrm{PhCC(Ph)CH_2Ph}$].

Introduction

We are presently interested in the application of multidentate aryloxide ligands to prepare reactive metal complexes that may emulate aspects of heterogeneous catalyst surfaces. In this regard, calixarenes, a class of "chalice-like" macrocyclic phenols,[1] offer considerable potential for providing a platform that mimics oxygen rich surfaces.[2] With respect to molybdenum and tungsten, the synthetic entry to derivatives of *p-tert*-butylcalix[4]arene, $[\mathrm{Calix^{Bu^t}(OH)_4}]$, the most commonly employed calixarene, has been provided via reactions with high valent precursors such as $\mathrm{WCl_6}$, $\mathrm{WOCl_4}$, $\mathrm{MoOCl_4}$, $\mathrm{MoO_2Cl_2}$, $\mathrm{MoCl_4}$, $\mathrm{MCl_4L_2}$, $\mathrm{Mo(NMe_2)_4}$, $\mathrm{M(NBu^t)_2(NHBu^t)_2}$, $\mathrm{M(NMes)_2Cl_2(dme)}$, $\mathrm{Mo(NAr)(CHCMe_2Ph)(O_3SCF_3)_2(dme)}$ and $\mathrm{MoN(OBu^t)_3}$,[3] and dinuclear complexes such as $\mathrm{M_2(NMe_2)_6}$, $\mathrm{M_2(OBu^t)_6}$, $[\mathrm{Mo_2(OAc)_2(NCMe)_6}]^{2+}$, and $[\mathrm{Mo_2(DAniF)_2(NCMe)_4}]^{2+}$.[4,5] In contrast, the corresponding chemistry derived from mononuclear low valent electron rich metal centers is not well developed. We have previously demonstrated that low valent $\mathrm{Mo(PMe_3)_6}$ and $\mathrm{W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H}$ are useful for the synthesis of monodentate aryloxide compounds[6] and, in this paper, we describe this approach for the synthesis of calixarene compounds that feature novel binding modes.

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(5) In addition, high valent molybdenum and tungsten complexes of the larger *p-tert*-butylcalix[5]arene, *p-tert*-butylcalix[6]arene, and *p-tert*-butylcalix[8]arene derivatives have also been synthesized. See for example: (a) Fan, M.; Zhang, H.; Lattman, M. *Chem. Commun.* **1998**, 99−100. (b) Gibson, V. C.; Redshaw, C.; Elsegood, M. R. J. *Chem. Commun.* **2002**, 1200−1201. (c) Redshaw, C.; Elsegood, M. R. J. *Eur. J. Inorg. Chem.* **2003**, 2071−2074. (d) Redshaw, C.; Elsegood, M. R. J. *Inorg. Chem.* **2000**, *39*, 5164−5168. (e) Redshaw, C. *Coord. Chem. Rev.* **2003**, *244*, 45−70.

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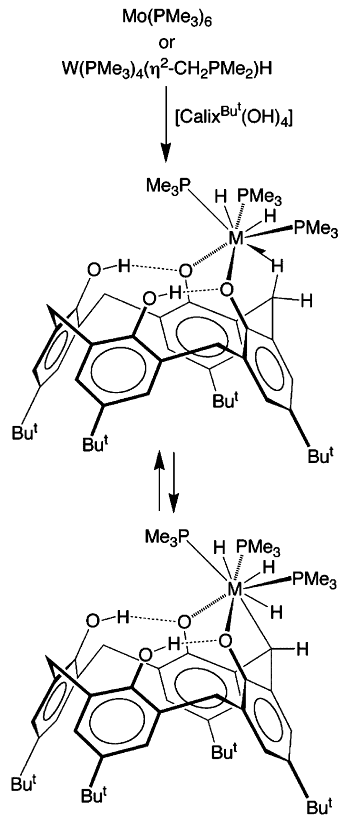
Scheme 1



Results and Discussion

$[\text{Calix}^{\text{Bu}^t}(\text{OH})_4]$ reacts with $Mo(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ to yield products with analogous composition, namely $\{[\text{Calix}^{\text{Bu}^t}(\text{OH})_2(\text{O})_2]\text{M}(\text{PMe}_3)_3\text{H}_2\}$, resulting from the oxidative addition of the O−H bonds of two adjacent phenol groups to the metal center (Scheme 1). In addition to the cleavage of the O−H bonds, ^{1}H NMR spectroscopy demonstrates that one of the methylene C−H groups also interacts with the metal center in both complexes (vide infra); however, detailed comparison of the molecular structures as determined by X-ray diffraction (Figures 1 and 2) demonstrates that there is an important difference with respect to the magnitude of interaction. Specifically, the W−C distance [2.256(4) Å][7] is considerably shorter than the Mo−C distance [2.729(4) Å]. These distances indicate that, for tungsten, the formally 16-electron fragment $\{[\text{Calix}^{\text{Bu}^t}(\text{OH})_2(\text{O})_2]\text{W}(\text{PMe}_3)_3\text{H}_2\}$ undergoes oxidative addition of the C−H bond to give a metallated trihydride $[\text{Calix-H}^{\text{Bu}^t}(\text{OH})_2(\text{O})_2]\text{W}(\text{PMe}_3)_3\text{H}_3$,[8] whereas for molybdenum the corresponding 16-electron fragment merely coordinates the C−H bond via an agostic interaction[9] to give $[\text{Calix}^{\text{Bu}^t}(\text{OH})_2(\text{O})_2]\text{Mo}(\text{PMe}_3)_3\text{H}_2$.[10]

The molecular structures of $[\text{Calix}^{\text{Bu}^t}(\text{OH})_2(\text{O})_2]\text{Mo}(\text{PMe}_3)_3\text{H}_2$ and $[\text{Calix-H}^{\text{Bu}^t}(\text{OH})_2(\text{O})_2]\text{W}(\text{PMe}_3)_3\text{H}_3$ are of particular interest because they provide the first evidence for the role of the calixarene methylene linker as a *binding functionality* via the formation of agostic and alkyl hydride derivatives.[11] As such, the compounds are a further illustration of the ability of calixarenes to afford a manifold of coordination modes. In this regard, it is pertinent to note that M···H−C interactions of varying degrees have been previously noted for several calixarene complexes with d^8 metal centers (Table 1),[12] but these are of a fundamentally different nature to the agostic interaction within $[\text{Calix}^{\text{Bu}^t}(\text{OH})_2(\text{O})_2]\text{Mo}(\text{PMe}_3)_3\text{H}_2$. Specifically, an agostic bond consists of a 3-center-2-electron interaction, whereas the M···H−C bond involving a d^8 metal center is best classified as an electrostatic interaction akin to that of a hydrogen bond.[13,14]

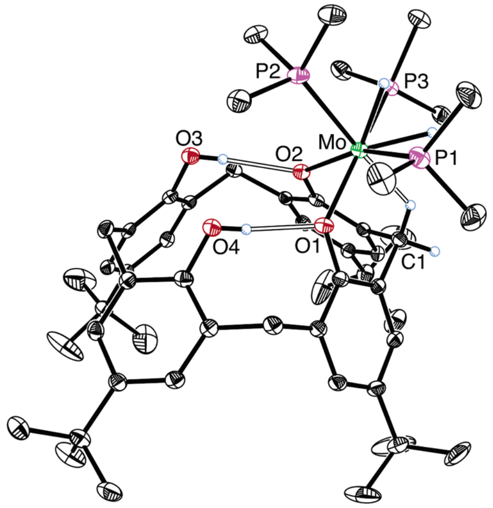


Figure 1. Molecular structure of $[\text{Calix}^{\text{Bu}^t}(\text{OH})_2(\text{O})_2]\text{Mo}(\text{PMe}_3)_3\text{H}_2$.

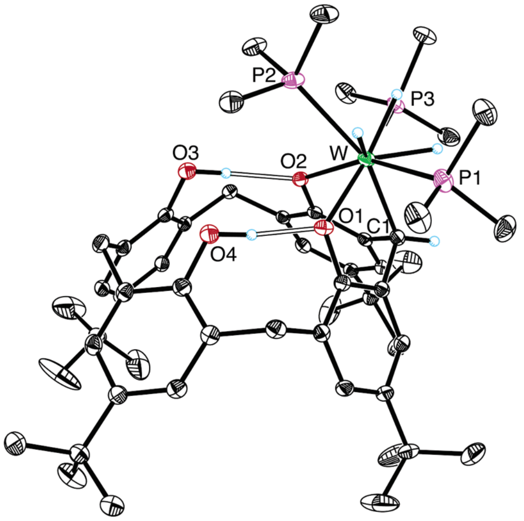


Figure 2. Molecular structure of $[\text{Calix-H}^{\text{Bu}^t}(\text{OH})_2(\text{O})_2]\text{W}(\text{PMe}_3)_3\text{H}_3$.

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(7) For comparison, the mean W−C (sp^3) distance for compounds listed in the Cambridge Structural Database is 2.23 Å. CSD Version 5.27. *3D Search and Research Using the Cambridge Structural Database*; Allen, F. H.; Kennard, O. *Chemical Design Automation News* **1993**, *8* (1), pp 1 and 31−37.

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

(9) (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.

(10) For other examples which show that tungsten has a greater ability to achieve C−H bond cleavage than does molybdenum, see ref 6.

(11) The reaction of $[\text{Cr}(\text{NBu}^t)_2\text{Cl}_2]$ with LiOBu^t and $[\text{Calix}^{\text{Bu}^t}(\text{OH})_4]$ yields a compound in which two calixarene units become linked via an ether function resulting from the coupling of a phenol group with a methylene group (ref 3m). While this transformation formally involves cleavage of a methylene C−H group, an alkyl hydride complex was not observed.

(12) (a) Kotzen, N.; Goldberg, I.; Lipstman, S.; Vigalok, A. *Inorg. Chem.* **2006**, *45*, 5266−5268. (b) Dieleman, C. B.; Marsol, C.; Matt, D.; Kyritsakas, N.; Harriman, A.; Kintzinger, J.-P. *J. Chem. Soc., Dalton Trans.* **1999**, 4139−4148. (c) Ishii, Y.; Onaka, K.-I.; Hirakawa, H.; Shiramizu, K. *Chem. Commun.* **2002**, 1150−1151. (d) Dieleman, C.; Jeunesse, C.; Matt, D. *Z. Kristallogr. - New Crystal Structures* **2001**, *216*, 435−438.

(13) (a) Yao, W.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chim. Acta* **1997**, *254*, 105−111. (b) Brammer, L. *Dalton Trans.* **2003**, 3145−3157. (c) Zhang, Y.; Lewis, J. C.; Bergman, R. G.; Ellman, J. A.; Oldfield, E. *Organometallics* **2006**, *25*, 3515−3519.

Table 1. Comparison of M···H and M···C Bond Lengths Involving Methylene Groups in Various Calixarene Complexes

compound	d(M···H)/Å	d(M···C)/Å	$r_{cov}(M)^a$/Å	ref
$[Calix^{Bu^t}(OH)_2(O)_2]Mo(PMe_3)_3H_2$	2.01	2.73	1.31	this work
$[Calix^{Bu^t}(OH)_2(O)_2]Pt(dppp)$	2.25	3.04	1.24	*b*
$[Calix^{Bu^t}(OH)_2(O)_2]\{Rh(cod)\}_2$	2.44	3.18	1.21	*c*
$[Calix^{Bu^t}(OCH_2PPH_2)_4]PtCl_2(AuPPh_3)_2$	2.61	3.49	1.24	*d*
$[Calix^{Bu^t}(OH)_2(OCH_2PPH_2)_2]PtCl_2$	2.67	3.55	1.24	*e*

[a] Batsanov, S. S. *Russ. Chem. Bull.* **1995**, *44*, 2245−2250. [b] Kotzen, N.; Goldberg, I.; Lipstman, S.; Vigalok, A. *Inorg. Chem.* **2006**, *45*, 5266−5268. [c] Ishii, Y.; Onaka, K.-I.; Hirakawa, H.; Shiramizu, K. *Chem. Commun.* **2002**, 1150−1151. [d] Dieleman, C.; Jeunesse, C.; Matt, D. *Z. Kristallogr. - New Crystal Structures* **2001**, *216*, 435−438. [e] Dieleman, C. B.; Marsol, C.; Matt, D.; Kyritsakas, N.; Harriman, A.; Kintzinger, J.-P. *J. Chem. Soc., Dalton Trans.* **1999**, 4139−4148.

3-Center-2-electron agostic and "electrostatic" M···H−C interactions are electronically distinct and, for the compounds listed in Table 1, the magnitude of the interaction, as judged by the M···H−C and M···C distances, is greatest for $[Calix^{Bu^t}(OH)_2(O)_2]Mo(PMe_3)_3H_2$ (Table 1). For example, the M···H−C and M···C distances in $[Calix^{Bu^t}(OH)_2(O)_2]Mo(PMe_3)_3H_2$ are approximately 0.25 Å shorter than the respective values in $[Calix^{Bu^t}(OH)_2(O)_2]Pt(dppp)$,[12a] the complex with the next shortest values. The 3-center-2-electron and "electrostatic" M···H−C interactions are also distinguished by ^1H NMR spectroscopy. Thus, the ^1H NMR spectroscopic signal for the methylene hydrogen involved in the agostic interaction of $[Calix^{Bu^t}(OH)_2(O)_2]Mo(PMe_3)_3H_2$ is shifted significantly to *high field* (−4.6 ppm) compared to that of its nonagostic counterpart (3.9 ppm), whereas those for the hydrogens involved in electrostatic interactions shift significantly to *low field*,[12] in accord with the "hydrogen bond" analogy of the interaction. For example, the methylene hydrogen involved in the M···H−C interaction of $[Calix^{Bu^t}(OH)_2(O)_2]Pt(dppp)$ is observed at 6.5 ppm.[12a,15]

Other than the details pertaining to the interaction of the C−H bond with the metal center, the overall structures of $[Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3$ and $[Calix^{Bu^t}(OH)_2(O)_2]Mo(PMe_3)_3H_2$ are similar, with both adopting a cone conformation of the calixarene that is stabilized by O−H···O hydrogen bonding interactions between intact O−H groups and the aryloxide oxygen atoms. In this regard, these structures are noteworthy because related molybdenum and tungsten complexes of *p-tert*-butylthiacalix[4]arene, $[S_4Calix^{Bu^t}(OH)_4]$, namely $[S_4Calix^{Bu^t}(OH)_2(O)_2]M(PMe_2Ph)_3H_2$, do not adopt a cone conformation but rather exhibit a 1,2-alternate conformation of the calixarene.[16,17]

While the X-ray diffraction study indicates that the tungsten complex $[Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3$ is a metallated trihydride in the solid state, variable temperature ^1H NMR spectroscopy provides convincing evidence that $[Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3$ exists in equilibrium with its agostic isomer $[Calix^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_2$ in solution (Figures 3 and 4).[18,19] For example, at room temperature, the *exo* hydrogen (H_A in Figure 5) of the interacting methylene group is observed as a doublet at δ 4.07 with $J_{HH} = 8$ Hz due to coupling to its *endo* counterpart (H_B in Figure 5). The magnitude of this coupling is highly temperature dependent, increasing from 0 Hz at 328 K to 12 Hz at 248 K (Figure 3), thereby indicating that the tungsten complex exists primarily as the agostic isomer $[Calix^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_2$ in solution at low temperature. For example, the 12 Hz coupling constant observed at low temperature is identical to $^2J_{HH}$ for other pairs of methylene groups in the complex and is comparable to the value for the agostic methylene group of $[Calix^{Bu^t}(OH)_2(O)_2]Mo(PMe_3)_3H_2$ ($^2J_{HH} = 16$ Hz). At room temperature, however, the coupling constant is reduced due to rapid equilibration with its metallated isomer $[Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3$, for which $^3J_{HH}$ is expected to be $\approx$ 0−5 Hz (Figure 5).[20]

Further evidence for the facile equilibration is provided by the observation that, at room temperature, the metallated/agostic carbon of the fluxional system exhibits $^1J_{CH}$ coupling constants of 126 and 65 Hz for the two "methylene" hydrogen atoms (H_A and H_B). The 126 Hz coupling constant for H_A is a typical value for an sp^3 hybridized carbon atom, and this value is observed because H_A is a component of a normal C−H bond in both agostic $[Calix^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_2$ and metallated $[Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3$ isomers. In contrast, the low 65 Hz coupling constant for H_B corresponds to the weighted average of $^1J_{CH}$ for the agostic interaction and $^2J_{CH}$ for the metallated derivative. $^1J_{CH}$ coupling constants for agostic alkyls are

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(14) For other examples where a metal serves the role as a hydrogen bond acceptor, see: (a) Martin, A. *J. Chem. Educ.* **1999**, *76*, 578−583. (b) Crabtree, R. H.; Eisenstein, O.; Sini, G.; Peris, E. *J. Organomet. Chem.* **1998**, *567*, 7−11. (c) Shubina, E. S.; Belkova, N. V.; Epstein, L. M. *J. Organomet. Chem.* **1997**, *536*, 17−29. (d) Brammer, L.; Zhao, D.; Ladipo, F. T.; Braddock-Wilking, J. *Acta Crystallogr., Sect. B* **1995**, *51*, 632−640. (e) Brammer, L. In *Implications of Molecular and Materials Structure for New Technologies*; Howard, J. A. K., Ed.; Kluwer Academic Publishers: Netherlands, 1999; pp 197−210. (f) Mareque, Rivas, J. C.; Brammer, L. *Coord. Chem. Rev.* **1999**, *183*, 43−80. (g) Braga, D.; Grepioni, F.; Tedesco, E.; Biradha, K.; Desiraju, G. R. *Organometallics* **1997**, *16*, 1846−1856. (h) Epshtein, L. M.; Shubina, E. S. *Organomet. Chem. in the U.S.S.R.* **1992**, *5*, 31−38. (i) Hascall, T.; Baik, M.-H.; Bridgewater, B. M.; Shin, J. H.; Churchill, D. G.; Friesner, R. A.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **2002**, 2644−2645. (j) Brammer, L. *Dalton Trans.* **2003**, 3145−3157.

(15) For calculations concerned with the ^1H NMR shifts of d^8 M···H−C species, see ref 13c.

(16) (a) Takemoto, S.; Otsuka, K.; Otsuka, T.; Seino, H.; Mizobe, Y.; Hidai, M. *Chem. Lett.* **2002**, 6−7. (b) Takemoto, S.; Tanaka, S.; Mizobe, Y.; Hidai, M. *Chem. Commun.* **2004**, 838−839.

(17) $[S_4Calix^{Bu^t}(OH)_2(O)_2]W(PMe_2Ph)_3H_2$ has also been reported to adopt a partial cone conformation. See ref 16.

(18) Density functional theory calculations are in accord with the agostic tungsten complex exhibiting a greater tendency to undergo C−H bond cleavage than does the molybdenum counterpart. Specifically, the calculations indicate that in each case the agostic complex $[Calix(OH)_2(O)_2]M(PMe_3)_3H_2$ is more stable than the metallated isomer $[Calix\text{-}H(OH)_2(O)_2]M(PMe_3)_3H_3$, but the difference is much greater for molybdenum (19.9 kcal mol^{-1}) than for tungsten (5.4 kcal mol^{-1}).

(19) In view of the fact that the agostic derivative is favored at low temperatures in solution, we repeated the X-ray diffraction study on a separate batch of crystals obtained from an independent reaction to determine whether the metallated trihydride $[Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3$ is actually representative of the solid state. The structure obtained corresponded to the metallated trihydride, $[Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3$. This observation suggests that the metallated trihydride is representative of the solid state because selecting crystals of the same minor component twice is an unlikely possibility, especially since $[Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3$ and $[Calix^{Bu^t}(OH)_2(O)_2]Mo(PMe_3)_3H_2$ are isomorphous. It is possible that the preferential crystallization of the metallated trihydride $[Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3$ could be due to crystal packing effects being sufficient to counter the small energy difference (5.4 kcal mol^{-1}) between the isomers for tungsten, but not the large energy difference (19.9 kcal mol^{-1}) for molybdenum.

(20) For example: (a) Churchill, D. G.; Janak, K. E.; Wittenberg, J. S.; Parkin, G. *J. Am. Chem. Soc.* **2003**, *125*, 1403−1420. (b) Mork, B. V.; Tilley, T. D. *J. Am. Chem. Soc.* **2004**, *126*, 4375−4385. (c) Baker, R. T.; Calabrese, J. C.; Harlow, R. L.; Williams, I. D. *Organometallics* **1993**, *12*, 830−841.

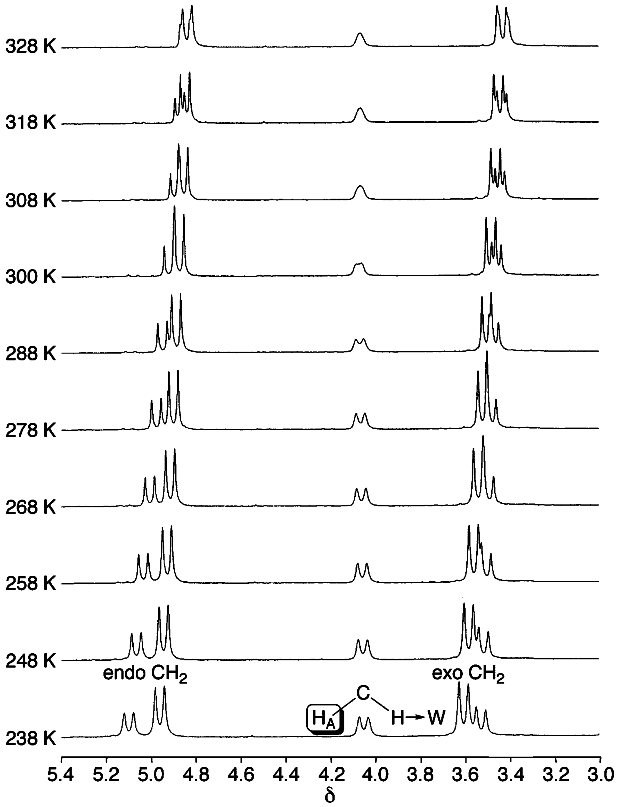

Figure 3. Variable temperature ^1H NMR spectra of a rapidly exchanging mixture of $[Calix^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_2$ and $[Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3$ in d_8-toluene (methylene region). Both molecules are characterized by three *endo* hydrogens in the ratio 2:1, three *exo* hydrogens in the ratio 2:1, and one *exo* hydrogen (H_A) that is attached to the agostic or metallated carbon atom. At each temperature, the signal corresponding to each hydrogen corresponds to the weighted average of the respective signals for the individual molecules, $[Calix^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_2$ and $[Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3$. The most important change is observed for H_A, for which the observed coupling constant decreases with temperature as the proportion of metallated derivative $[Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3$ increases.

typically in the range 75−100 Hz,[9,21] while $^2J_{CH}$ coupling constants for metal alkyl−hydride complexes are typically in the range 0−10 Hz.[9,22] Since the observed J_{CH} is a weighted average, its value depends on the equilibrium constant for the interconversion of the two isomers. In this regard, if $^1J_{CH}$ of the agostic complex $[Calix^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_2$ and $^2J_{CH}$ of the metallated isomer $[Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3$ are assumed to have representative values of ca. 100 and 5 Hz, respectively, the observed J_{CH} of 65 Hz would correspond to an equilibrium constant of ∼0.6 for the oxidative cleavage of the C−H bond of the agostic isomer at room temperature.

The hydride region of the ^1H NMR spectrum of the equilibrium mixture of $[Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3$ and $[Calix^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_2$ is also strongly temperature dependent. However, examination of Figure 4 illustrates that the spectral changes are more complex than those for the methylene region because the spectra not only reflect rapid interchange of $[Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3$ and $[Calix^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_2$, but also feature exchange between the agostic hydrogen and the hydride sites. Decisive evidence for the latter process is provided by the observation of magnetization transfer between the agostic hydrogen and the hydride sites (Figure 6).

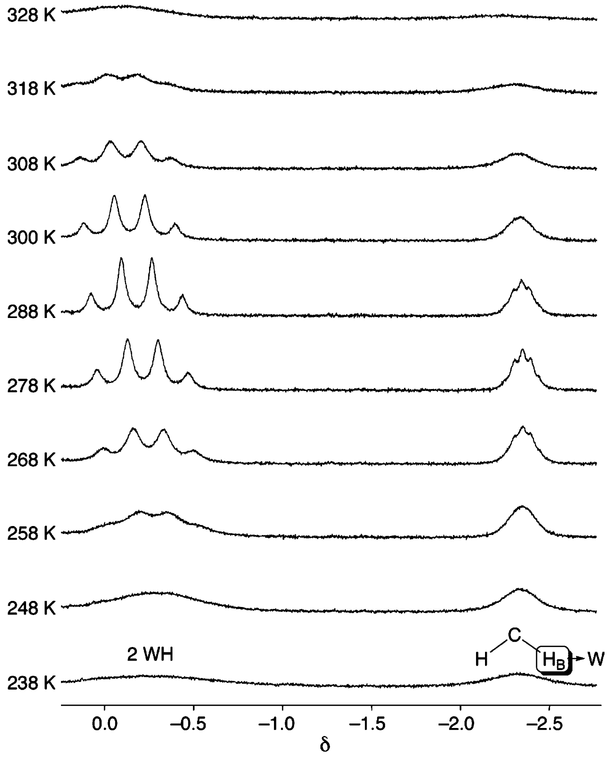

Figure 4. Variable temperature ^1H NMR spectra of a rapidly exchanging mixture of $[Calix^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_2$ and $[Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3$ in d_8-toluene (hydride region). The quartet pattern observed for the hydride ligands at intermediate temperature (e.g., 278 K) is due to phosphorus coupling, whereas the multiplet observed for the agostic hydrogen (H_B) is due to coupling to the hydride ligands and the nonagostic methylene hydrogen (H_A). A spectrum corresponding to a static structure of agostic $[Calix^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_2$, showing signals for three chemically inequivalent hydrogen atoms, was not obtained at the lowest temperature recorded.

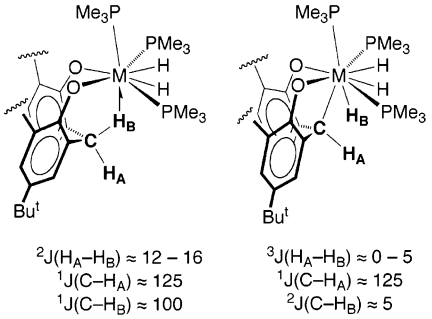

Figure 5. Anticipated NMR spectroscopic data for static structures.

In addition to the interconversion between agostic and metallated isomers, an interesting observation is that the $[M(PMe_3)_3H_2]$ fragments migrate rapidly around the phenolic rim of the calixarene.[23] For example, magnetization transfer and 2D EXSY studies demonstrate that adjacent pairs of methylene groups undergo site exchange that is rapid on the NMR time scale (Figure 7).[24] Thus, *endo* hydrogens exchange specifically with adjacent *endo* hydrogens, while *exo* hydrogens exchange

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[21] For example, $^1J_{CH}$ for the C−H group involved in the agostic interaction in $[Calix^{Bu^t}(OH)_2(O)_2]Mo(PMe_3)_3H_2$ is 99 Hz.

[22] For example, $^2J_{CH}$ for $Cp^*_2W(CH_3)H$ is 7 Hz. See: Parkin, G.; Bercaw, J. E. *Polyhedron* **1988**, *7*, 2053−2082.

[23] Evidence for migration has also been noted for a dinuclear rhodium calixarene derivative (ref 12c). Furthermore, an irreversible migration has been inferred from the formation of a 1,2-platinum compound from a 1,3-*bis*(trimethylsilyl)calixarene ether (ref 12a).

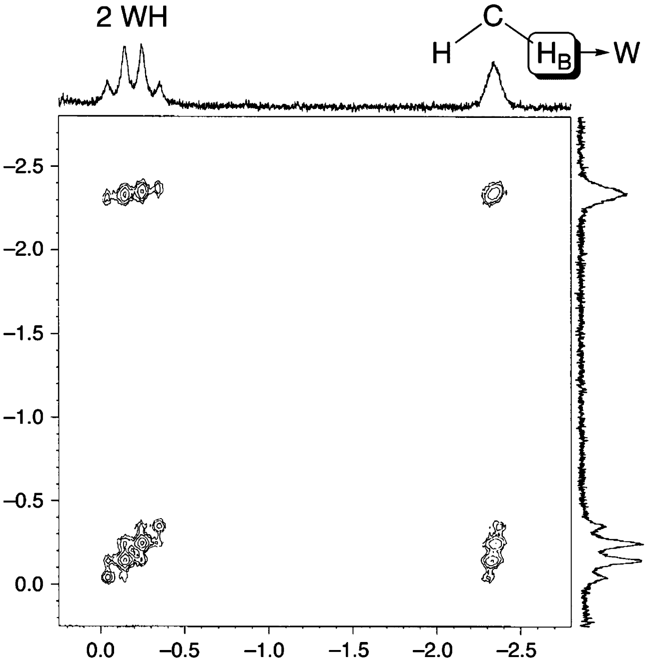


Figure 6. EXSY ^{1}H NMR spectra of $[\mathrm{Calix^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_2}$/$[\mathrm{Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3}$ in $\mathrm{C_6D_6}$ at room temperature (hydride region).

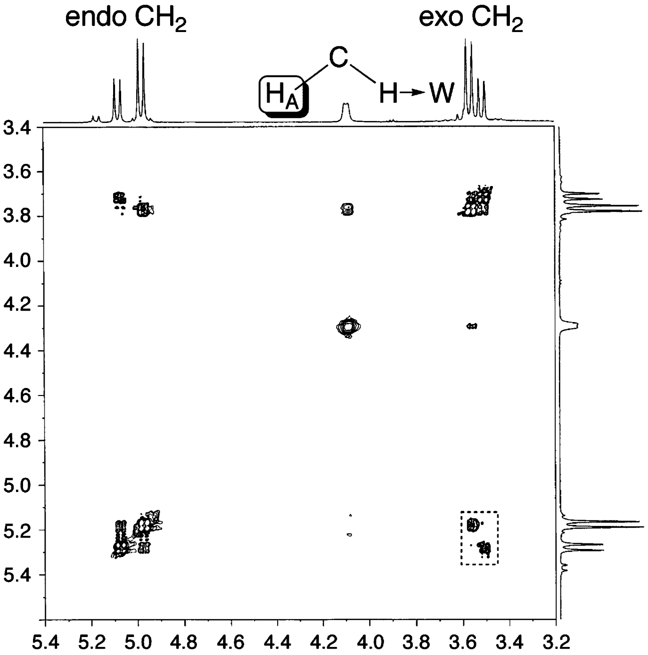
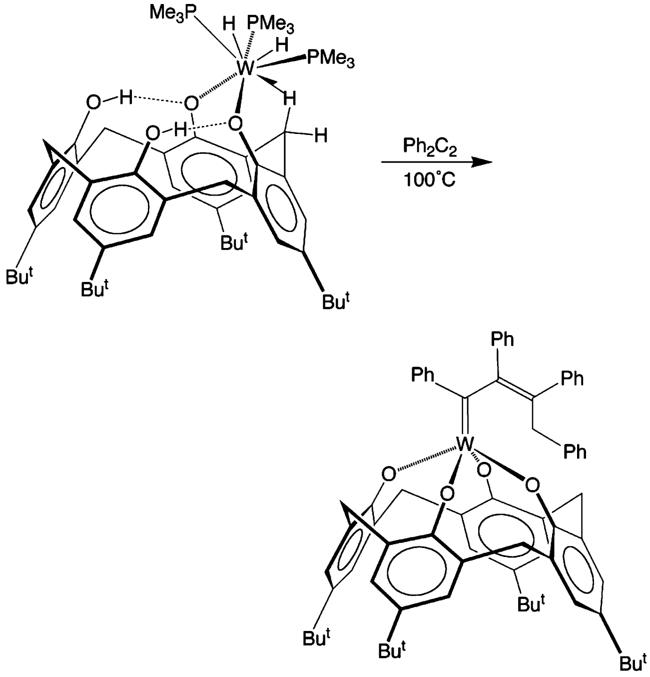


Figure 7. EXSY ^{1}H NMR spectra of $[\mathrm{Calix^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_2}$/$[\mathrm{Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3}$ in $\mathrm{C_6D_6}$ at room temperature (methylene region). The cross-peaks between *exo* and *endo* pairs (highlighted in a dotted box) are a zero quantum artifact resulting from *J* coupling and do not represent site exchange between *exo* and *endo* pairs.

specifically with adjacent *exo* hydrogens. Furthermore, the *exo* hydrogen attached to the agostic carbon ($\mathrm{H_A}$) also exchanges selectively with the two *exo* hydrogens of the adjacent methylene groups (Figure 7).[25]

In support of the proposed migration around the calixarene rim, treatment of the isomeric mixture of tungsten complexes $[\mathrm{Calix^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_2}$ and $[\mathrm{Calix\text{-}H^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_3}$ with $\mathrm{D_2}$ results in deuterium incorporation into all methylene *endo* sites, as well as hydride and phenolic groups. An interesting difference between the tungsten and molybdenum systems, however, is that although the latter incorporates deuterium into the O−H sites, there is no incorporation into the methylene sites over the same period at room temperature. This observation is in accord with the notion that the molybdenum center of $[\mathrm{Calix^{Bu^t}(OH)_2(O)_2]Mo(PMe_3)_3H_2}$ is incapable of cleaving the C−H bond under these conditions.

Scheme 2



While the agostic interactions within $[\mathrm{Calix^{Bu^t}(OH)_2(O)_2]M(PMe_3)_3H_2}$ provide stability for an otherwise 16-electron species, the rapid migration of the $[\mathrm{M(PMe_3)_3H_2}]$ fragment about the calixarene rim indicates that dissociation of the C−H bond and access to a 16-electron species are facile. As such, it raises the possibility that $[\mathrm{Calix^{Bu^t}(OH)_2(O)_2]M(PMe_3)_3H_2}$ could exhibit interesting reactivity. In this regard, treatment of $\{[\mathrm{Calix^{Bu^t}(OH)_2(O)_2]W(PMe_3)_3H_2}\}$ with $\mathrm{Ph_2C_2}$ gives the alkylidene complex $[\mathrm{Calix^{Bu^t}(O)_4]W{=}C(Ph)Ar}$ [Ar = $\mathrm{PhCC(Ph)CH_2Ph}$] (Scheme 2).[26] $[\mathrm{Calix^{Bu^t}(O)_4]W{=}C(Ph)Ar}$ has been structurally characterized by X-ray diffraction (Figure 8), thereby demonstrating that the calixarene coordinates via a κ^4-mode involving all four oxygen atoms.

Conclusions

In summary, $\mathrm{Mo(PMe_3)_6}$ and $\mathrm{W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H}$ react with *p-tert*-butylcalix[4]arene, $[\mathrm{Calix^{Bu^t}(OH)_4}]$, to yield compounds of composition $[\mathrm{Calix^{Bu^t}(OH)_2(O)_2]M(PMe_3)_3H_2}$ which employ a C−H bond of the calixarene methylene group as a binding functionality. In the solid state, X-ray diffraction studies demonstrate that the molybdenum complex exists as an agostic

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(24) Notably, there is no exchange between *endo* and *exo* hydrogen atoms of each methylene group indicating that the cone−cone interconversion observed for the free calixarene does not occur on a similar time scale. See: Gutsche, C. D.; Bauer, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 6052−6059.

(25) In principle, the agostic ($\mathrm{H_B}$) also exchanges sites with the *endo* hydrogen atoms. However, this process was not detected by the EXSY experiment because the agostic hydrogen preferentially exchanges with the hydride sites.

(26) Tungsten alkylidene complexes supported by $[\mathrm{Calix^{Bu^t}(O)_4}]$ are known. See: Giannini, L.; Solari, E.; Dovesi, S.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1999**, *121*, 2784−2796.

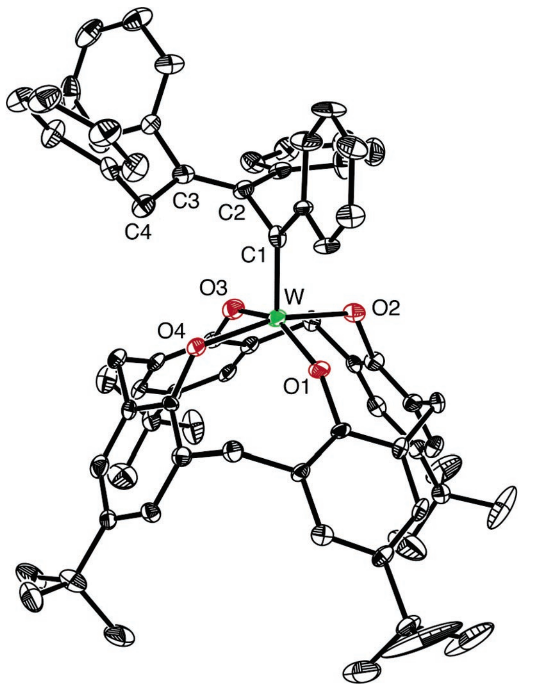

Figure 8. Molecular structure of $[\mathrm{Calix}^{\mathrm{Bu^t}}(\mathrm{O})_4]\mathrm{W}{=}\mathrm{C(Ph)C(Ph)}{=}\mathrm{C(Ph)}\text{-}\mathrm{CH_2Ph}$.

derivative, whereas the tungsten complex exists as a metallated trihydride $[\mathrm{Calix\text{-}H}^{\mathrm{Bu^t}}(\mathrm{OH})_2(\mathrm{O})_2]\mathrm{W(PMe_3)_3H_3}$. Solution ^{1}H NMR spectroscopic studies, however, demonstrate that $[\mathrm{Calix\text{-}H}^{\mathrm{Bu^t}}(\mathrm{OH})_2(\mathrm{O})_2]\mathrm{W(PMe_3)_3H_3}$ is in equilibrium with its agostic isomer and that the $[\mathrm{M(PMe_3)_3H_2}]$ fragments of both the molybdenum and tungsten complexes $[\mathrm{Calix}^{\mathrm{Bu^t}}(\mathrm{OH})_2(\mathrm{O})_2]\mathrm{M(PMe_3)_3H_2}$ migrate rapidly around the phenolic rim of the calixarene.

Experimental Section

General Considerations. All manipulations were performed using a combination of dry glovebox, high vacuum, and Schlenk techniques under an argon atmosphere unless otherwise specified.[27] Solvents were purified and degassed by standard procedures. ^{1}H NMR spectra were measured on Bruker 300 DRX, Bruker 400 DRX, and Bruker Avance 500 DMX spectrometers. ^{1}H chemical shifts are reported in ppm relative to $\mathrm{SiMe_4}$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for $\mathrm{C_6D_5H}$;[28] 2.09 for $\mathrm{C_6D_5CHD_2}$[29]). ^{13}C NMR spectra are reported in ppm relative to $\mathrm{SiMe_4}$ ($\delta = 0$) and were referenced internally with respect to the solvent (δ 128.06 for $\mathrm{C_6D_5H}$).[28] ^{2}H NMR spectra are reported with respect to $\mathrm{C_6H_5D}$ (δ 7.16). ^{31}P chemical shifts are reported in ppm relative to 85% $\mathrm{H_3PO_4}$ ($\delta = 0$) and were referenced using $\mathrm{P(OMe)_3}$ ($\delta = 141.0$) as an external standard. Coupling constants are given in hertz. Infrared spectra were recorded on a Nicolet Avatar 370 DTGS spectrometer and are reported in cm^{-1}. Mass spectra were obtained on a Micromass Quadrupole-Time-of-Flight mass spectrometer using fast atom bombardment (FAB). $\mathrm{Mo(PMe_3)_6}$,[30] $\mathrm{W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H}$,[31] and $[\mathrm{Calix}^{\mathrm{Bu^t}}(\mathrm{OH})_4]$[32] were prepared according to literature methods, and the latter was recrystallized from toluene and dried in vacuo prior to use.

Table 2. Crystal, Intensity Collection, and Refinement Data

	$[\mathrm{Calix\text{-}H}^{\mathrm{Bu^t}}(\mathrm{OH})_2\mathrm{O}_2]$-$\mathrm{WH_3(PMe_3)_3}\cdot$1.5$(\mathrm{C_6H_6})$	$[\mathrm{Calix}^{\mathrm{Bu^t}}(\mathrm{OH})_2\mathrm{O}_2]$-$\mathrm{MoH_2(PMe_3)_3}\cdot$1.5$(\mathrm{C_6H_6})$	$[\mathrm{Calix}^{\mathrm{Bu^t}}(\mathrm{O})_4]$-$\mathrm{W{=}C(Ph)Ar}\cdot$1$(\mathrm{C_5H_{12}})$
lattice	triclinic	triclinic	triclinic
formula	$\mathrm{C_{62}H_{92}O_4P_3W}$	$\mathrm{C_{62}H_{92}MoO_4P_3}$	$\mathrm{C_{77}H_{86}O_4W}$
formula weight	1178.12	1090.21	1259.31
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	13.0107(6)	13.042(1)	11.2558(11)
b/Å	13.9630(6)	14.113(1)	14.5191(17)
c/Å	18.9093(9)	19.0193(1)	21.579(2)
α/deg	85.0170(10)	86.228(2)	99.540(2)
β/deg	74.5210(10)	74.798(2)	91.222(4)
γ/deg	67.5780(10)	65.808(2)	110.178(2)
V/Å^3	3059.9(2)	3078.0(4)	3252.5(6)
Z	2	2	2
temperature (K)	243	243	243
radiation (λ, Å)	0.71073	0.71073	0.71073
ρ (calcd), g cm^{-3}	1.279	1.176	1.286
μ (Mo Kα), mm^{-1}	2.009	0.333	1.824
θ max, deg	26.37	25.03	26.37
no. of data	12365	10829	12227
no. of parameters	655	654	695
R_1	0.0382	0.0486	0.0768
wR_2	0.0686	0.1051	0.1555
GOF	1.051	1.031	1.030

X-ray Structure Determinations. X-ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector, and crystal data, data collection, and refinement parameters are summarized in Table 2. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (version 5.10).[33]

Computational Details. All calculations were carried out using DFT as implemented in the Jaguar 6.5 suite of ab initio quantum chemistry programs.[34] Geometry optimizations were performed with the B3LYP density functional[35] and the 6-31G** (C, H, O and P) and LACVP (Mo, W)[36] basis sets. Cartesian coordinates for geometry optimized structures are listed in the Supporting Information. The energies of the optimized structures were reevaluated by additional single-point calculations on each optimized geometry using the cc-pVTZ(-f) correlation consistent triple-ζ basis set for C, H, O, and P and LACV3P for Mo and W.

Synthesis of $[\mathbf{Calix}^{\mathbf{Bu^t}}(\mathbf{OH})_2(\mathbf{O})_2]\mathbf{W(PMe_3)_3H_2}$ and $[\mathbf{Calix\text{-}H}^{\mathbf{Bu^t}}(\mathbf{OH})_2(\mathbf{O})_2]\mathbf{W(PMe_3)_3H_3}$. A solution of $\mathrm{W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H}$ (217 mg, 0.39 mmol) in benzene (4 mL) was added to a solution of $[\mathrm{Calix}^{\mathrm{Bu^t}}(\mathrm{OH})_4]$ (250 mg, 0.39 mmol) in benzene (20 mL). The mixture was stirred for 3 h at 60 °C. After this period, the volatile components were removed by lyophilization, and the residue obtained was washed with pentane at −78 °C (3 × 3 mL) and dried in vacuo to give an isomeric mixture of $[\mathrm{Calix}^{\mathrm{Bu^t}}(\mathrm{OH})_2(\mathrm{O})_2]\mathrm{W(PMe_3)_3H_2}$ and $[\mathrm{Calix\text{-}H}^{\mathrm{Bu^t}}(\mathrm{OH})_2(\mathrm{O})_2]\mathrm{W(PMe_3)_3H_3}$ as a brown solid (321 mg, 79%). Red crystals of

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(27) (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 2, pp 6−23. (b) Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 4, pp 79−98. (c) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

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(29) "CIL NMR Solvent Data Chart", Cambridge Isotope Laboratories, Inc., Andover, MA 01810-5413, U.S.A.

(30) Murphy, V. J.; Parkin, G. *J. Am. Chem. Soc.* **1995**, *117*, 3522−3528.

(31) Green, M. L. H.; Parkin, G.; Chen, M.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1986**, 2227−2236.

(32) Gutsche, C. D.; Iqbal, M. *Org. Synth.* **1990**, *68*, 234−235.

(33) Sheldrick, G. M. *SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*; University of Göttingen: Göttingen, Federal Republic of Germany, 1981.

(34) *Jaguar 6.5*; Schrödinger, LLC: New York, NY, 2005.

(35) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100. (c) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789. (d) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200−1211. (e) Slater, J. C. *Quantum Theory of Molecules and Solids, Vol. 4: The Self-Consistent Field for Molecules and Solids*; McGraw-Hill: New York, 1974.

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[Calix-H$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]W(PMe$_3$)$_3$H$_3$ suitable for X-ray diffraction were obtained by slow evaporation of a solution in benzene. While the X-ray diffraction study indicates that the complex exists as a metallated species in the solid state, ^{1}H NMR spectroscopic studies demonstrate that the product exists as an equilibrium mixture of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]W(PMe$_3$)$_3$H$_2$ and [Calix-H$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]W(PMe$_3$)$_3$H$_3$ isomers in solution. ^{1}H NMR data (C$_6$D$_6$, room temperature): 10.35 [s, 2H of [Calix$^{\text{Bu}^t}$(O*H*)$_2$(O)$_2$]], 7.23 [d, $^4J_{\text{HH}} = 2$, 2 aromatic H of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 7.14 [d, $^4J_{\text{HH}} = 2$, 2 aromatic H of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 7.11 [d, $^4J_{\text{HH}} = 2$, 2 aromatic H of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 7.04 [d, $^4J_{\text{HH}} = 2$, 2 aromatic H of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 5.09 [d, $^2J_{\text{HH}} = 12$, 1 H of endo methylene in [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 4.98 [d, $^2J_{\text{HH}} = 12$, 2 H of endo methylene in [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 4.09 [broad d, $J_{\text{HH}} = 9$, 1 H of exo methylene in [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 3.57 [d, $^2J_{\text{HH}} = 12$, 2 H of exo methylene in [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 3.52 [d, $^2J_{\text{HH}} = 12$, 1 H of exo methylene in [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 1.33 [broad s, 27 H of W(P*Me*$_3$)$_3$], 1.24 [s, 18 H of 2 Bu^t of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 1.20 [s, 18 H of 2 Bu^t of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], −0.19 [broad q, $^2J_{\text{HH}} = 52$, 2 WH], −2.3 [broad s, 1 WH-(agostic)]. ^{13}C{^{1}H} (C$_6$D$_6$, room temperature): 163.5 [2 aromatic C of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 150.8 [2 aromatic C of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 142.2 [2 aromatic C of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 139.2 [2 aromatic C of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 130.9 [2 aromatic C of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 130.7 [2 aromatic C of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 129.9 [2 aromatic C of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 129.5 [2 aromatic C of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 126.0 [2 aromatic C of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 125.5 [2 aromatic C of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 124.6 [2 aromatic C of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 124.3 [2 aromatic C of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 50.7 [1 methylene C of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 34.2 [3 methylene C of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 33.9 [2 *C*(CH$_3$)$_3$ of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 33.6 [2 *C*(CH$_3$)$_3$ of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 31.9 [6 C(*C*H$_3$)$_3$ of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 31.7 [6 C(*C*H$_3$)$_3$ of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 23.4 [9 C of 3 P(*C*H$_3$)$_3$]. Analysis of a trace of a ^{13}C coupled heteronuclear single quantum correlation (HSQC) NMR spectrum gives $^1J_{\text{CH}}$ coupling constants of 126 and 65 Hz for the metalated/agostic carbon at 50.4 ppm in d_8-toluene at room temperature. ^{31}P{^{1}H} NMR data (C$_6$D$_6$, room temperature): −12.5 [broad s, 3 P of W(PMe$_3$)$_3$]. IR (KBr pellet, cm^{-1}): 3153 (br), 3043 (w), 2958 (s), 2918 (s), 2854 (m), 2602 (w), 1872 (w), 1741 (w), 1599 (w), 1478 (s), 1462 (s), 1424 (m), 1392 (w), 1360 (m), 1302 (s), 1282 (m), 1261 (w), 1203 (s), 1125 (w), 1105 (w), 1022 (w), 962 (m), 944 (s), 867 (w), 823 (w), 787 (w), 758 (w), 726 (w), 671 (w), 619 (w), 559 (w), 518 (w), 488 (w), 462 (w). Mass spectrum (FAB+): $m/z = 1060.9$ {M}$^+$.

Synthesis of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]Mo(PMe$_3$)$_3$H$_2$. A mixture of Mo(PMe$_3$)$_6$ (51 mg, 0.092 mmol) and [Calix$^{\text{Bu}^t}$(OH)$_4$] (60 mg, 0.092 mmol) was treated with benzene (2.5 mL) and heated at 60 °C for 3 days under an argon atmosphere. After this period, the solution was filtered and the volatile components were removed by lyophilization. The solid residue was washed with pentane at −78 °C (2 × 0.5 mL) and dried in vacuo to give a brown solid (34 mg) composed of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]Mo(PMe$_3$)$_3$H$_2$, accompanied by a paramagnetic unidentified species, and on occasions small amounts of unreacted calixarene. X-ray quality crystals were obtained from a concentrated sample in benzene using a slight excess of Mo(PMe$_3$)$_6$. The compound has limited stability in solution in the absence of dihydrogen. ^{1}H NMR data (C$_6$D$_6$, room temperature): 10.76 [s, 2H of [Calix$^{\text{Bu}^t}$(O*H*)$_2$(O)$_2$]], 7.22 [d, $^4J_{\text{HH}} = 2$, 2 aromatic H of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 7.19 [d, $^4J_{\text{HH}} = 2$, 2 aromatic H of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 7.16 (obscured by solvent) [2 aromatic H of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 6.99 [d, $^4J_{\text{HH}} = 2$, 2 aromatic H of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 5.23 [d, $^2J_{\text{HH}} = 12$, 1 H of endo methylene in [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 4.98 [d, $^2J_{\text{HH}} = 12$, 2 H of endo methylene in [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 3.89 [d, $^2J_{\text{HH}} = 16$, 1 H of exo methylene in [Calix$^{\text{Bu}^t}$(OH)$_2$O$_2$]], 3.62 [d, $^2J_{\text{HH}} = 12$, 2 H of exo methylene in [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 3.53 [d, $^2J_{\text{HH}} = 12$, 1 H of exo methylene in [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 1.23 [s, 18 H of 2 Bu^t of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 1.22 [s, 18 H of 2 Bu^t of [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], 1.21 [broad s, 27 H of Mo(P*Me*$_3$)$_3$H$_2$], −4.58 [d, $^2J_{\text{HH}} = 16$, 1 agostic H of methylene in [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]]; the hydride signals are not observed at room temperature but are observed at −35 °C in d_8-toluene: −0.76 [dt, $^2J_{\text{PH}}$(d) = 17, $^2J_{\text{PH}}$(t) = 67, 1 MoH], −4.74 [d, $^2J_{\text{HH}} = 17$, 1 agostic H of methylene in [Calix$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]], −6.34 [dt, $^2J_{\text{PH}}$(d) = 77, $^2J_{\text{PH}}$(t) = 57, 1 MoH]. Analysis of a trace of a ^{13}C coupled heteronuclear single quantum correlation (HSQC) NMR spectrum gives $^1J_{\text{CH}}$ coupling constants of 125 and 99 Hz for the agostic carbon at 46.1 ppm in C$_6$D$_6$ at room temperature. ^{31}P{^{1}H} NMR (C$_6$D$_6$): 20.3 [broad s, 3 P of Mo(PMe$_3$)$_3$]. Mass spectrum (FAB+): $m/z = 974.2$ {M}$^+$.

Synthesis of [Calix$^{\text{Bu}^t}$(O)$_4$]W=C(Ph)C(Ph)=C(Ph)CH$_2$Ph. [Calix-H$^{\text{Bu}^t}$(OH)$_2$(O)$_2$]W(PMe$_3$)$_3$H$_3$ (150 mg, 0.141 mmol) and diphenylacetylene (51 mg, 0.286 mmol) were mixed in benzene (8 mL). The mixture was heated to 100 °C in a sealed ampule for 24 h. After this period the solution was filtered and the volatile components were removed in vacuo. The solid residue obtained was washed with pentane (3 × 1 mL) at −78 °C and dried in vacuo to give [Calix(O)$_4$]W=C(Ph)C(Ph)=C(Ph)CH$_2$Ph as a brown solid (79 mg, 47%). X-ray quality crystals were obtained by slow evaporation of a solution in pentane. ^{1}H NMR data (C$_6$D$_6$): 7.93 [d, $^3J_{\text{HH}} = 8$, 2 aromatic H of W=C(Ph)Ar], 7.71 [d, $^3J_{\text{HH}} = 7$, 2 aromatic H of W=C(Ph)Ar], 7.44 [m, 3 aromatic H of W=C(Ph)Ar], 7.28 [d, $^3J_{\text{HH}} = 7$, 2 aromatic H of W=C(Ph)Ar], 7.09 [d, $^3J_{\text{HH}} = 8$, 2 aromatic H of W=C(Ph)Ar], 7.06 [s, 8 aromatic H of [Calix$^{\text{Bu}^t}$(O)$_4$]], 7.02−6.96 [m, 6 aromatic H of W=C(Ph)Ar], 6.87 [m, 3 aromatic H of W=C(Ph)Ar], 5.27 [s, 2 of C*H*$_2$Ph in W=C(Ph)Ar], 4.77 [d, $^2J_{\text{HH}} = 12$, 4 H of endo methylene in [Calix$^{\text{Bu}^t}$(O)$_4$]], 3.20 [d, $^2J_{\text{HH}} = 12$, 4 H of exo methylene in [Calix$^{\text{Bu}^t}$(O)$_4$]], 1.07 [s, 36 H of Bu^t in [Calix$^{\text{Bu}^t}$(O)$_4$]]. ^{13}C{^{1}H} NMR data (C$_6$D$_6$): 285.0 [1 C of W=*C*(Ph)Ar], 90.2 [1 vinyl C of W=C(Ph)*Ar*], 44.3 [1 methylene *C*H$_2$Ph in W=C(Ph)Ar], 34.1 [4 methylene C of [Calix$^{\text{Bu}^t}$(O)$_4$]], 34.0 [4 *C*(CH$_3$)$_3$ of [Calix$^{\text{Bu}^t}$(O)$_4$]], 31.4 [12 C(*C*H$_3$)$_3$ of [Calix$^{\text{Bu}^t}$(O)$_4$]]. Remaining 31 carbons from aromatic groups and vinyl carbon in W=C(Ph)Ar are observed in the region from 123 to 154 ppm with some being obscured by the solvent. IR (KBr pellet, cm^{-1}): 3080 (w), 3053 (w), 3020 (w), 2960 (s), 2925 (s), 2866 (m), 1596 (w), 1490 (m), 1475 (s), 1466 (s), 1459 (s), 1443 (m), 1392 (w), 1362 (m), 1301 (m), 1283 (m), 1262 (w), 1243 (m), 1209 (s), 1193 (s), 1124 (m), 1106 (s), 1078 (m), 1031 (m), 927 (w), 874 (m), 865 (w), 824(m), 798 (s), 757 (m), 693 (m), 567 (w), 545 (m), 504 (m), 468 (m), 419 (w). Mass spectrum (FAB): $m/z = 1187.2$ {M + H}$^+$.

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Supporting Information Available: Cartesian coordinates for geometry optimized structures and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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