

Mononuclear and Dinuclear Molybdenum and Tungsten Complexes of *p*-*tert*-Butyltetra-thiacalix[4]arene and *p*-*tert*-Butyltetrasulfonylcalix[4]arene: Facile Cleavage of the Calixarene Ligand Framework by Nickel

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Received April 30, 2008; E-mail: parkin@columbia.edu

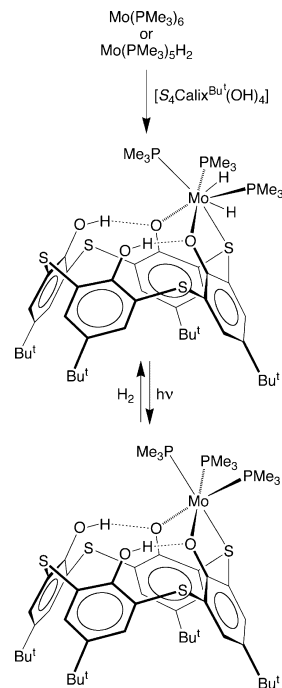
As part of our efforts to model species relevant to hydrodesulfurization (HDS) and hydrodenitrogenation (HDN),¹ we are particularly interested in synthesizing heterodinuclear complexes that incorporate combinations of molybdenum and tungsten with promoter metals such as cobalt and nickel.² Calixarenes are a class of multidentate macrocyclic phenols³ that offer considerable potential for achieving this objective, especially if the linker between the phenolic groups also contains donor atoms. For this reason, we have focused our attention on the applications of calixarenes that feature S and [SO₂] linkers, specifically *p*-*tert*-butyltetra-thiacalix[4]arene, [S₄Calix^{Bu^t}(OH)₄],^{4,5} and *p*-*tert*-butyltetrasulfonylcalix[4]arene, [(SO₂)₄Calix^{Bu^t}(OH)₄].⁶ An investigation of these calixarenes is also pertinent since we have recently demonstrated that the methylene linker of *p*-*tert*-butylcalix[4]arene, [Calix^{Bu^t}(OH)₄], can serve as a binding functionality in molybdenum and tungsten chemistry.⁷ Here we report that the nature of the linker has a profound effect on the chemistry of the system and influences the ability of the calixarene to coordinate a second metal center.

The *p*-*tert*-butyltetra-thiacalix[4]arene molybdenum dihydride complex [S₄Calix^{Bu^t}(OH)₂(O)₂]Mo(PMe₃)₃H₂ is conveniently obtained by treatment of the calixarene [S₄Calix^{Bu^t}(OH)₄] with either Mo(PMe₃)₆ or Mo(PMe₃)₅H₂ (Scheme 1). The molecular structure of [S₄Calix^{Bu^t}(OH)₂(O)₂]Mo(PMe₃)₃H₂ has been determined by X-ray diffraction, thereby demonstrating that the calixarene coordinates to the metal with a κ³-mode via one sulfur and two oxygen atoms. As such, the molybdenum coordination environment is similar to that of [Calix^{Bu^t}(OH)₂(O)₂]Mo(PMe₃)₃H₂,⁷ with the principal difference being that the thioether coordination replaces the agostic interaction involving the methylene linker of [Calix^{Bu^t}(OH)₂(O)₂]Mo(PMe₃)₃H₂. Evidence that the Mo–S interaction within [S₄Calix^{Bu^t}(OH)₂(O)₂]Mo(PMe₃)₃H₂ is stronger than the agostic interaction within [Calix^{Bu^t}(OH)₂(O)₂]Mo(PMe₃)₃H₂ is provided by the observation that the metal center of the latter migrates rapidly around the calixarene ring,⁷ whereas that of [S₄Calix^{Bu^t}(OH)₂(O)₂]Mo(PMe₃)₃H₂ appears static with respect to this process on the NMR time-scale at room temperature.⁸

The dihydride [S₄Calix^{Bu^t}(OH)₂(O)₂]Mo(PMe₃)₃H₂ is subject to photochemically induced reductive elimination of H₂, thereby generating the six-coordinate thiacalixarene complex [S₄Calix^{Bu^t}(OH)₂(O)₂]Mo(PMe₃)₃ (Scheme 1). The formation of [S₄Calix^{Bu^t}(OH)₂(O)₂]Mo(PMe₃)₃ is reversible and addition of H₂ regenerates [S₄Calix^{Bu^t}(OH)₂(O)₂]Mo(PMe₃)₃H₂ over a period of days at room temperature.

The sulfonyl calixarene [(SO₂)₄Calix^{Bu^t}(OH)₄] has so far been little exploited in transition metal chemistry.^{9,10} It is, therefore, noteworthy that [(SO₂)₄Calix^{Bu^t}(OH)₄] reacts with Mo(PMe₃)₅H₂ to yield [(SO₂)₄Calix^{Bu^t}(OH)₂(O)₂]Mo(PMe₃)₃H₂ (Scheme 2). As observed for [S₄Calix^{Bu^t}(OH)₂(O)₂]Mo(PMe₃)₃H₂, [(SO₂)₄Calix^{Bu^t}(OH)₂(O)₂]Mo(PMe₃)₃H₂ also undergoes photochemically induced reductive elimination of H₂ thereby generating 16-electron [(SO₂)₄Calix^{Bu^t}(OH)₂(O)₂]Mo(PMe₃)₃, a process that may be reversed under thermal conditions.

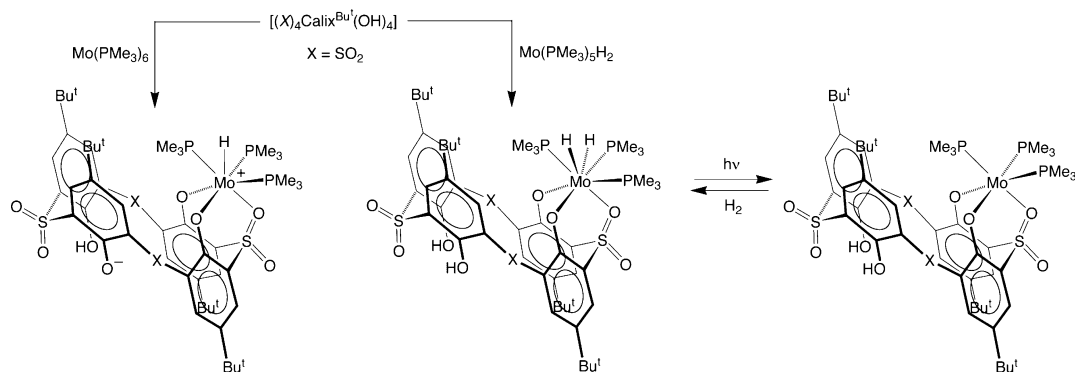
Scheme 1



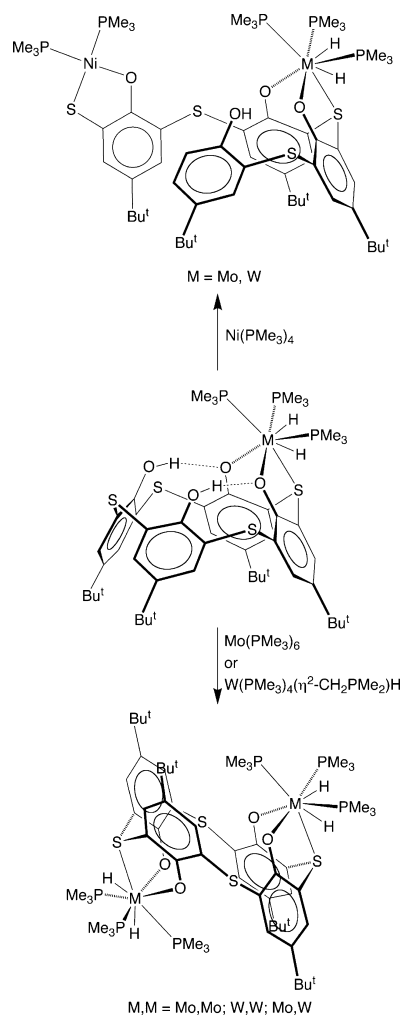
Interestingly, and in contrast to the reaction of Mo(PMe₃)₅H₂, treatment of Mo(PMe₃)₆ with [(SO₂)₄Calix^{Bu^t}(OH)₄] yields the zwitterionic monohydride, [(SO₂)₄Calix^{Bu^t}(OH)(O)₃]Mo(PMe₃)₃H (Scheme 2),¹¹ which is a tautomer of octahedral [(SO₂)₄Calix^{Bu^t}(OH)₂(O)₂]Mo(PMe₃)₃. The zwitterionic complex [S₄Calix^{Bu^t}(OH)(O)₃]Mo(PMe₃)₃H has not, however, been observed for the thiacalixarene system. In this regard, DFT calculations are in accord with the nature of the product being dependent on the calixarene linker. Thus, while [(X)₄Calix^H(OH)₂(O)₂]Mo(PMe₃)₃ and [(X)₄Calix^H(OH)(O)₃]Mo(PMe₃)₃H have comparable energies for X = SO₂ (ΔH = 1.6 kcal mol^{−1}), the zwitterion is strongly disfavored for X = S (ΔH = 29.5 kcal mol^{−1}).¹² As such, the nature of the calixarene linker has a profound effect.

The molecular structures of [(SO₂)₄Calix^{Bu^t}(OH)₂(O)₂]Mo(PMe₃)₃H₂ and [(SO₂)₄Calix^{Bu^t}(OH)(O)₃]Mo(PMe₃)₃H have been determined by X-ray diffraction, thereby demonstrating that the calixarene coordinates to the metal with a κ³-mode via two phenolic oxygen atoms and one oxygen of the [SO₂] linker. While both the thiacalixarene and sulfonylcalixarene ligands coordinate in a κ³-mode, a significant difference pertains to the conformations of the calixarenes. Specifically, the thiacalixarene ligands adopt a cone conformation that is supported by O–H⋯O hydrogen bonding interactions which span the rim of the calixarene, whereas the sulfonylcalixarene compounds adopt 1,2-alternate conformations in which the phenolic OH groups

Scheme 2



Scheme 3



participate in hydrogen bonding interactions with either the sulfonyl or phenoxide groups.

The tungsten counterparts, $[S_4\text{Calix}^{\text{Bu}'}(\text{OH})_2(\text{O})_2]\text{W}(\text{PMe}_3)_3\text{H}_2$, $[(\text{SO}_2)_4\text{Calix}^{\text{Bu}'}(\text{OH})_2(\text{O})_2]\text{W}(\text{PMe}_3)_3\text{H}_2$, and $[(\text{SO}_2)_4\text{Calix}^{\text{Bu}'}(\text{OH})(\text{O})_3]\text{W}(\text{PMe}_3)_3\text{H}$, have also been synthesized employing $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ and possess analogous structures to the molybdenum derivatives.

The metal centers in the mononuclear thiacalixarene complexes are readily derivatized. For example, the reactions of $[S_4\text{Calix}^{\text{Bu}'}(\text{OH})_2(\text{O})_2]\text{M}(\text{PMe}_3)_3\text{H}_2$ ($\text{M} = \text{Mo}, \text{W}$) with Ph_2C_2 give $[S_4\text{Calix}^{\text{Bu}'}(\text{OH})_2(\text{O})_2]\text{Mo}(\text{PMe}_3)_2(\text{Ph}_2\text{C}_2)$ and $[S_4\text{Calix}^{\text{Bu}'}(\text{OH})_2(\text{O})_2]\text{W}(\text{PMe}_3)(\text{Ph}_2\text{C}_2)_2$. The formation of the tungsten diphenylacetylene compound $[S_4\text{Calix}^{\text{Bu}'}(\text{OH})_2(\text{O})_2]\text{W}(\text{PMe}_3)(\text{Ph}_2\text{C}_2)_2$ is noteworthy because the corresponding reaction of $[(\text{Calix}^{\text{Bu}'}(\text{OH})_2(\text{O})_2)\text{W}(\text{PMe}_3)_3\text{H}_2]$ with Ph_2C_2 yields the alkylidene complex $[\text{Calix}^{\text{Bu}'}(\text{O})_4]\text{W}=\text{C}(\text{Ph})\text{R}$ [$\text{R} = \text{C}(\text{Ph})\text{C}(\text{Ph})\text{CH}_2\text{Ph}$].⁷ This observation provides a further illustration of how the nature of the calixarene linker (agostic C–H versus thioether S) may influence the reactivity of the metal center.

An interesting feature of the reactivity of $[S_4\text{Calix}^{\text{Bu}'}(\text{OH})_2(\text{O})_2]\text{M}(\text{PMe}_3)_3\text{H}_2$ pertains to the ability to functionalize the unused coordination sites of the calixarene with other metal centers. For example, the dinuclear complexes $\{[S_4\text{Calix}^{\text{Bu}'}(\text{O})_4]\text{M}(\text{PMe}_3)_3\text{H}_2\}_2$ may be obtained *via* reaction of $[S_4\text{Calix}^{\text{Bu}'}(\text{OH})_2(\text{O})_2]\text{M}(\text{PMe}_3)_3\text{H}_2$ with the respective low valent metal trimethylphosphine compound, $\text{Mo}(\text{PMe}_3)_6$ or $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ (Scheme 3). In addition, the sulfonylcalixarene ligand also enables isolation of the dinuclear complex $\{[(\text{SO}_2)_4\text{Calix}^{\text{Bu}'}(\text{O})_4]\text{M}(\text{PMe}_3)_3\text{H}_2\}_2$, but a corresponding dinuclear complex is yet to be isolated for the methylene-bridged calixarene.¹³ Complementing these homonuclear compounds $\{[S_4\text{Calix}^{\text{Bu}'}(\text{O})_4]\text{M}(\text{PMe}_3)_3\text{H}_2\}_2$, the heteronuclear counterpart $\{[S_4\text{Calix}^{\text{Bu}'}(\text{O})_4]\text{M}(\text{PMe}_3)_3\text{H}_2\}[\text{W}(\text{PMe}_3)_3\text{H}_2]$ may be synthesized by treatment of $[S_4\text{Calix}^{\text{Bu}'}(\text{OH})_2(\text{O})_2]\text{Mo}(\text{PMe}_3)_3\text{H}_2$ with $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ (Scheme 3).¹⁴

X-ray diffraction studies indicate that the dinuclear complexes $\{[S_4\text{Calix}^{\text{Bu}'}(\text{O})_4]\text{M}(\text{PMe}_3)_3\text{H}_2\}_2$ possess a 1,2-alternate conformation of the calixarene backbone, such that the two metal centers adopt an anti disposition. ¹H NMR spectroscopic studies also suggest this is the only conformation obtained in solution, presumably as a consequence of the steric requirements of the $[\text{M}(\text{PMe}_3)_3\text{H}_2]$ fragments.¹⁵ The observation that dinuclear $\{[S_4\text{Calix}^{\text{Bu}'}(\text{O})_4]\text{M}(\text{PMe}_3)_3\text{H}_2\}_2$ adopts a 1,2-alternate conformation of the calixarene provides a possible explanation for the fact that $[\text{Calix}^{\text{Bu}'}(\text{OH})_2(\text{O})_2]\text{M}(\text{PMe}_3)_3\text{H}_2$ compounds with methylene linkers do not form corresponding dinuclear complexes upon treatment with a second equivalent of $\text{Mo}(\text{PMe}_3)_6$ or $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ under comparable conditions. Specifically, the uncoordinated thiacalixarene $[S_4\text{Calix}^{\text{Bu}'}(\text{OH})_4]$ is known to (i) be more flexible than $[\text{Calix}^{\text{Bu}'}(\text{OH})_4]$ and (ii) exhibit a reduced tendency to adopt a cone conformation;¹⁶ as such, it is expected that

$[S_4\text{Calix}^{\text{Bu}'}(\text{OH})_2(\text{O})_2]\text{M}(\text{PMe}_3)_3\text{H}_2$ would be able to access more readily a non-cone conformation, thereby facilitating the formation of the dinuclear complex. In support of the notion that thiacalixarene metal compounds are more conformationally flexible, the mononuclear thiacalixarene complex $[S_4\text{Calix}^{\text{Bu}'}(\text{OH})_2(\text{O})_2]\text{W}(\text{PMe}_2\text{Ph})_3\text{H}_2$ has been isolated with both 1,2-alternate and partial cone conformations in the solid state.¹⁷

The unused coordination sites in $[S_4\text{Calix}^{\text{Bu}'}(\text{OH})_2(\text{O})_2]\text{M}(\text{PMe}_3)_3\text{H}_2$ may also be employed to bind metals other than molybdenum and tungsten. For example, $[S_4\text{Calix}^{\text{Bu}'}(\text{OH})_2(\text{O})_2]\text{M}(\text{PMe}_3)_3\text{H}_2$ incorporates nickel upon treatment with $\text{Ni}(\text{PMe}_3)_4$; however, rather than simply coordinate, the nickel cleaves one of the C–S bonds of the calixarene

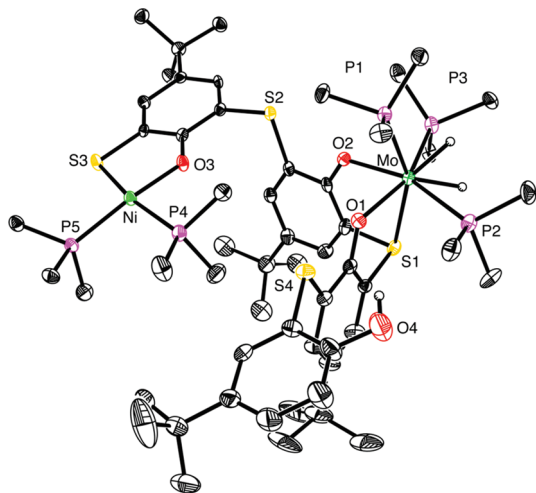


Figure 1. Molecular structure of $[(\text{SAr}^{\text{Bu}}\text{OH})(\text{SAr}^{\text{Bu}}\text{O})_3][\text{Mo}(\text{PMe}_3)_3\text{H}_2][\text{Ni}(\text{PMe}_3)_2]$.

to give $[(\text{SAr}^{\text{Bu}}\text{OH})(\text{SAr}^{\text{Bu}}\text{O})_3][\text{M}(\text{PMe}_3)_3\text{H}_2][\text{Ni}(\text{PMe}_3)_2]$ (Figure 1 and Scheme 3).¹⁸ Since this type of reactivity is not observed upon treatment of $[\text{S}_4\text{Calix}^{\text{Bu}}(\text{OH})_2(\text{O})_2]\text{M}(\text{PMe}_3)_3\text{H}_2$ with either $\text{Mo}(\text{PMe}_3)_6$ or $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$, the C–S bond cleavage achieved by nickel is of particular significance. Specifically, the observation supports the notion that the role of nickel in HDS may be concerned with the C–S cleavage step. In this regard, Jones has demonstrated that low valent tertiary phosphine compounds of nickel may cleave the C–S bond of thiophene derivatives,¹⁹ and García has reported that similar compounds are capable of achieving catalytic desulfurization of thiophenes in the presence of RMgX .²⁰

In summary, the nature of the calixarene linker can have a substantial impact on the chemistry of the system, as illustrated by the ability of the S and $[\text{SO}_2]$ linkers to facilitate coordination of a second metal center. Furthermore, the incorporation of nickel into $[\text{S}_4\text{Calix}^{\text{Bu}}(\text{OH})_2(\text{O})_2]\text{M}(\text{PMe}_3)_3\text{H}_2$ is accompanied by C–S bond cleavage of the calixarene ligand, an observation that is of relevance to the role that nickel plays in HDS catalysts.

Acknowledgment. We thank the U.S. Department of Energy, Office of Basic Energy Sciences (DE-FG02-93ER14339) for support of this research and the National Science Foundation for acquisition of the X-ray diffractometer (Grant CHE-0619638).

Supporting Information Available: Experimental details, computational data 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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- (12) X-ray diffraction studies provide evidence that $[(\text{SO}_2)_4\text{Calix}^{\text{Bu}}(\text{OH})_4]\text{Mo}(\text{PMe}_3)_3\text{H}$ adopts more than one possible conformation in the solid state, pertaining to different hydrogen bonding arrangements of the phenol/phenoxy groups. The different conformations were considered in the calculations, and the values reported here correspond to the lowest energy conformation in which the phenolic hydroxy group participates in hydrogen bonding with the uncoordinated phenoxy.
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JA803215X