Metal Reactivity on Oxo Surfaces Modeled by Calix[4]arenes: Metal-Driven Reactions in an Oxo-Quasiplanar Environment

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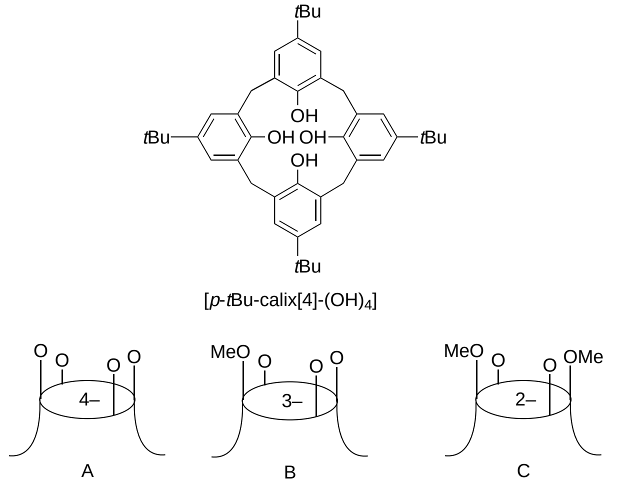
Abstract: A quite recent molecular approach to metal–oxo surfaces uses as a model the preorganised O_4 set of donor atoms derived from the calix[4]arene tetraanion and its alkylated forms. Metals bonded to such an environment assist: 1) the formation of $\mathrm{C{-}C}$ and $\mathrm{C{=}C}$ bonds by multiple migratory insertion reactions; 2) olefin rearrangement to $\mathrm{M{-}C}$, $\mathrm{M{=}C}$, $\mathrm{M{\equiv}C}$ occurring under very mild conditions; 3) the activation and reduction of dinitrogen with a complete $\mathrm{N{\equiv}N}$ triple bond cleavage.

Keywords: alkenes · alkylidenes · alkylidynes · calix[4]arene · dinitrogen · rearrangements



[p-tBu-calix[4]-(OH)$_4$]

[p-tBu-calix[4]-(O)$_4$]$^{4-}$ [p-tBu-calix[4]-(OMe)(O)$_3$]$^{3-}$ [p-tBu-calix[4]-(OMe)$_2$(O)$_2$]$^{2-}$

Figure 1. Anions derived from calix[4]arene.

Introduction

The use of molecular modeling studies of oxo surfaces[1] that bind metals appropriate to drive catalytic or stoichiometric reactions dates back a very long time.[2] An interesting approach foresees the use of a preorganised set of oxygen donor atoms in a quasiplanar arrangement for binding metal ions. In such a context, the calix[4]arene skeleton[3] comes into the game,[4] with a number of unique geometrical and electronic peculiarities. Calix[4]arenes have only recently been employed for binding metals,[5] and even more recently as ancillary ligands for supporting reactive metals in organometallic chemistry.[4] In such a role calix[4]arenes have quite a number of unique peculiarities. Let us first have a look at their geometrical properties. In the metalla-derivative, calix[4]arenes almost exclusively assume the cone conformation, thus keeping the oxygen set quasiplanar. They usually act as tetraanionic ligands, though the charge of the O_4 set can be tuned by a different degree of alkylation (Figure 1).

The oxygen alkylation enables us to control the functionalization degree of the metal and, at the same time, using appropriate R substituents, also the steric protection of the metal reactive site. The symmetry of the cone conformation is largely determined by the coordination number of the metal attached to it, and thus, indirectly, by the symmetry of the incoming substrate to the metal. Such geometrical features are revealed by the methylene bridging and the *t*Bu groups functioning as spectroscopic probes in a ^{1}H NMR spectrum.[4-d, e, j] What about the consequences for the frontier orbitals available at the metal thanks to its binding to the calix[4]arene skeleton? Although in metallacalix[4]arenes the metal anchoring groups are methylene-bridged phenoxo anions, the role of calix[4]arene is different from that played by the same number of monomeric phenoxo units.[2, 4]

The four oxygen donor atoms preorganised in a quasiplanar geometry, along with the partial alkylation of the phenoxo groups, have a major effect in determining the set and the relative energy of the frontier orbitals available at the metal for the substrate activation. How the metal–calix[4]arene fragments can assist the formation and the reactivity of organometallic functionalities, and particularly the $\mathrm{M{-}C}$ ones, is exemplified in the case of zirconium(IV) in Figure 2, showing a comparison between the frontier orbitals of the [ZrO_4] cores and the [Cp_2Zr] fragment.[6]

For all the Zr^{IV} fragments with a d^0 electron count, four low-lying metal-based orbitals have been identified. The $d_{x^2-y^2}$

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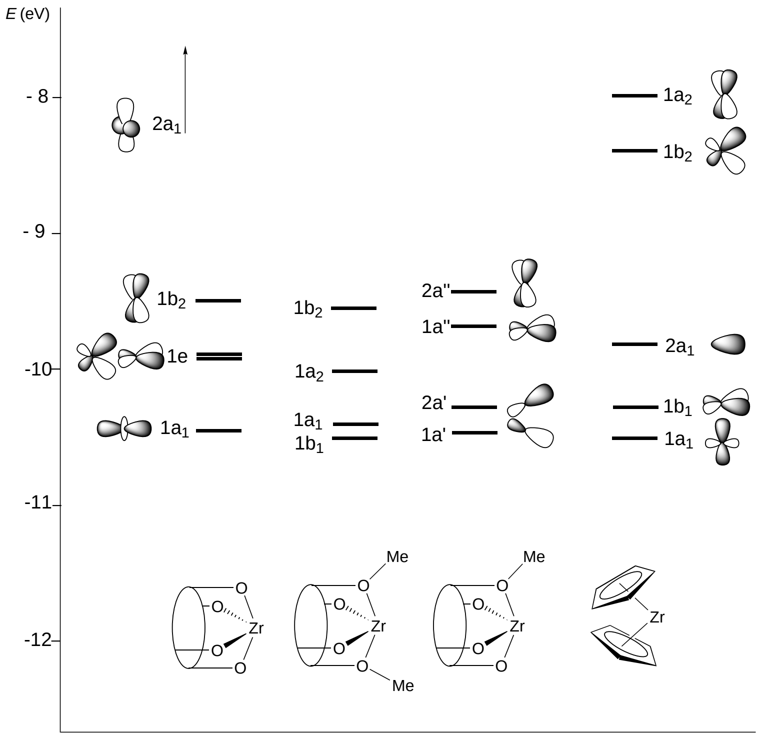


Figure 2. Frontier orbitals of metallacalix[4]arenes and the zirconacene fragment.

orbital, pointing more closely towards the oxygen ligands, is pushed high in energy, while the remaining four d orbitals are found within ca. 1 eV range. For the [calix[4]-(O)$_4$Zr] fragment the LUMO is $1a_1(d_z2)$ with a doubly degenerate $1e(d_{xz},d_{yz})$ approximately 0.5 eV higher. Due to the π interaction with the oxygen atoms, the $1b_2(d_{xy})$ orbital lies another 0.5 eV higher in energy. In the [calix[4]-(O)$_4$(OMe)$_2$Zr]$^{2+}$ fragment, owing to the reduced interaction with the methylated phenoxo ligands in the xz plane, the (d_{xz},d_{yz}) set splits by ca. 1 eV into the $1b_1(d_{xz})$, which becomes the LUMO, although almost degenerate with the $1a_1(d_{z^2})$ and the $1b_2(d_{yz})$, which is pushed slightly higher than the $1a_2(d_{xy})$. The frontier orbitals of the [calix[4]-(O)$_3$(OMe)Zr]$^+$ fragment are similar to those of the latter fragment. However, because of the lower molecular symmetry (C_s), the two lowest orbitals of d_{z^2} and d_{xy} character have the same a′ symmetry and mix strongly, giving rise to two hybridized 1a′ and 2a′ orbitals lying in the xz plane and tilted towards the (OMe) and (O) directions, respectively.

On the right of Figure 2 we display for comparison the well-known picture of the three low-lying empty orbitals of [Cp$_2$Zr]$^{2+}$ ($1a_1$, $1b_1$ and $2a_1$).[6] The main difference between the calix[4]arene-based fragments and [Cp$_2$Zr]$^{2+}$ is that, while the latter have only three low-lying empty orbitals available for bonding with additional ligands, all the three former fragments have four, and this fact has important consequences for its chemical behavior. Indeed, these four low-lying d orbitals can accommodate up to eight electrons, at variance with the case in [Cp$_2$Zr]$^{2+}$, which can accommodate up to a maximum of six electrons without violating the EAN rule. Moreover, while in [Cp$_2$Zr]$^{2+}$ all the three low-lying frontier orbitals lie in the symmetry plane bisecting the CpZrCp angle, in the calix[4]arene-based fragments the four lowest lying orbitals lie on two orthogonal planes, thus favouring a facial over a meridional structure when such a fragment is bound to three additional ligands. The facial compared to the meridional arrangement of the three low-lying frontier orbitals favours, among other things, the formation of a metal-substrate multiple bond,[4b, f, h] that is, stabilization of alkylidenes and alkylidynes, and affects the migration-insertion reactions.[4e]

The metal-oxo molecular models outlined above have a quite remarkable potential for studying the metal activity in a quite unusual environment. Some of the possibilities could be:

1) the generation and the chemistry of M−C, M=C, M≡C functionalities;
2) the interaction with hydrocarbons and hydrogen;
3) the activation of small molecules like N_2, CO, O_2, and CO_2.

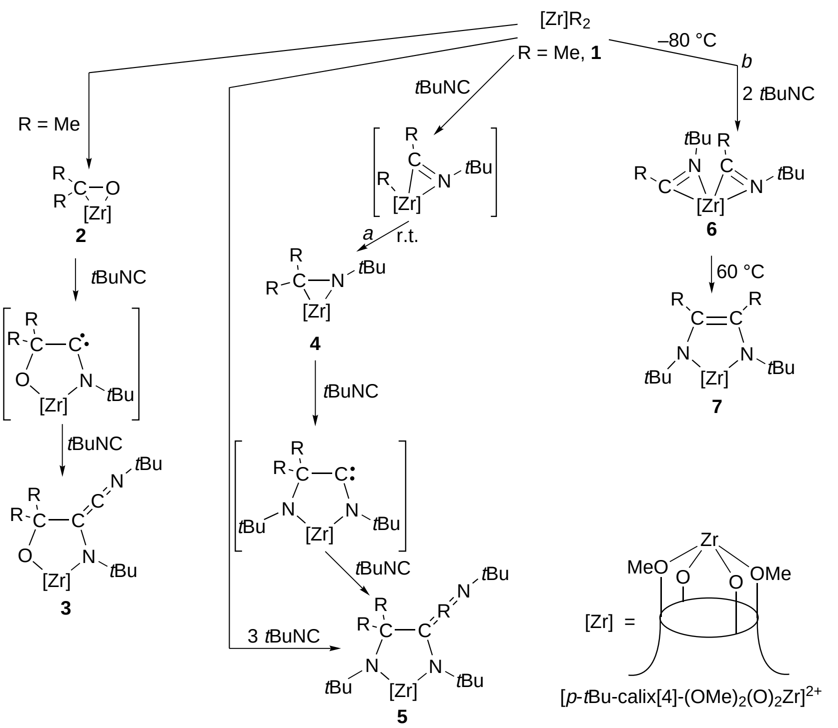
Some of the quite recent results and prospective applications will be summarized and emphasized in the following sections.

Discussion

A. Calix[4]arene metalation: A preliminary question is how to make the starting materials for entering organometallic and coordination chemistry in the area of calix[4]arenes. The main synthetic approaches include direct metalation using early transition metal halides;[4d, e, i] metathesis reaction between metal halides and the sodium or lithium derivative;[4] acid- or base-induced demethylation;[4i, k] and the use of homoleptic alkyl or aryl derivatives.[4f, m]

B. The chemistry of M−C functionalities bonded to a calix[4]arene matrix: Depending on the nature of the metal and the degree of its functionalization imposed by the alkylation of the oxygen donor atoms, the calix[4]arene skeleton allows entry into the vast area of the M−C, M=C, and M≡C[4a, b, d, e, f, h] functionalities anchored to a planar oxo surface. Significant comparisons can be made with many postulated intermediates occurring on the surface of heterogeneous oxo-catalysts,[1] or on supported organometallics.[2]

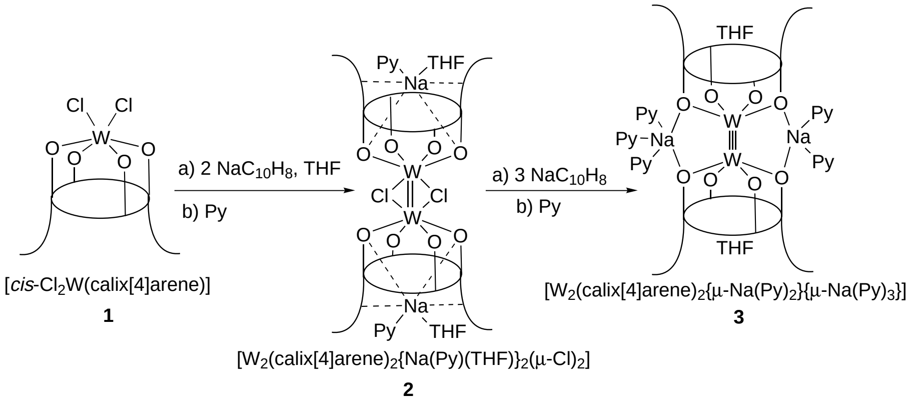
The first surprising feature is the very high thermal stability of the M−C functionalities bonded to a calix[4]arene skeleton, and the absence of significant β-elimination processes during their synthesis. A multiple migratory insertion reaction of carbon monoxide and isocyanides into the M−C bonds has been observed;[4e] the insertion is a consequence of the facial arrangement of the three frontier orbitals shown in Figure 2. Important, selected examples are in Scheme 1, showing metal-



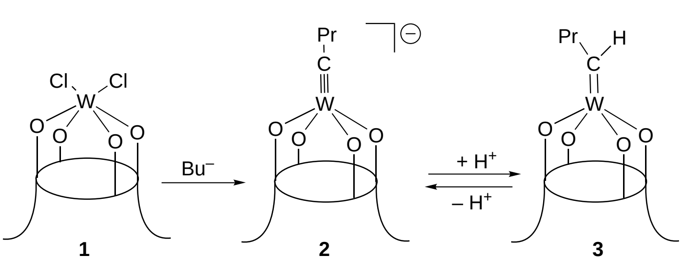
Scheme 1. Multiple migratory insertion reaction into Zr–C bonds.

assisted C–C and C=C bond formations. There is a prospect of using M–C functionalities bonded to calix[4]arenes 1) for assisting catalytic reactions, for example polymerization; 2) in H_2 activation and hydride chemistry; 3) in the σ-bond metathesis reaction.

The three frontier orbitals shown in Figure 2 are particularly suitable for establishing M–C multiple bonds. The one-step synthesis of anionic alkylidynes[4b] is exemplified in Scheme 2, along with the unusual reversible protonation to the corresponding alkylidenes. The stoichiometric and catalytic activity of interrelated alkylidyne – alkylidenes over an oxo surface looks particularly promising.



Scheme 3. Metal – metal bond formation between metallacalix[4]arenes.

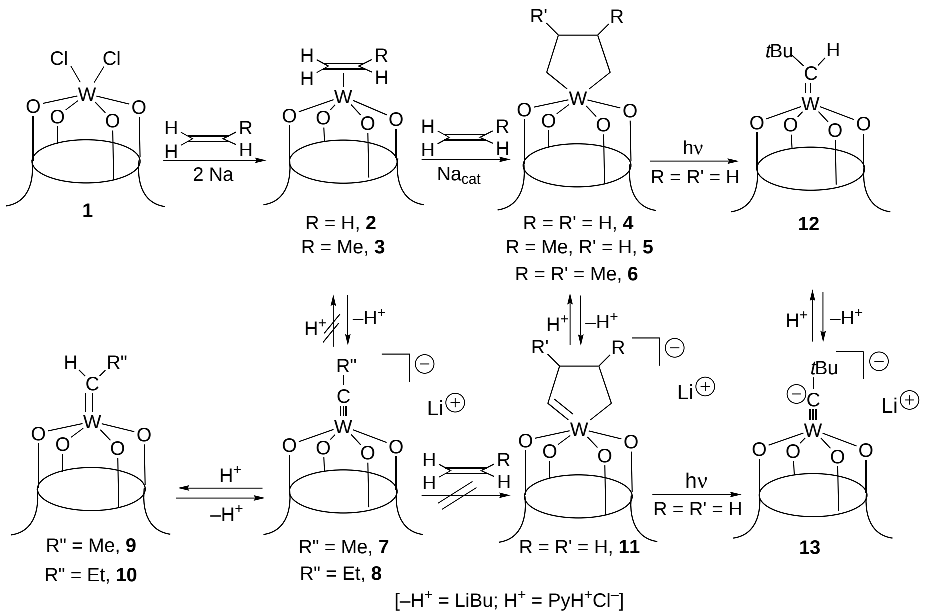


Scheme 2. One-step synthesis of a W alkylidyne and its reversible protonation reaction.

C. Generation of electron-rich metal centers: The generation of reactive species over an oxo surface seems, in principle, to be unlikely because of the nature of the chemical environment around the metal center. However, it has been found that metallacalix[4]arenes are particularly appropriate for electron-rich metal reactive sites.

C1. Formation of metal – metal bonded calix[4]arenes: In the absence of an appropriate substrate, a preliminary reaction occurring when a very reactive reduced metal is generated is, at least in the case of early transition metals, a metal – metal coupling, which leads to the dimeric species shown in Scheme 3.[4c] The reactivity of the metal – metal functionality[7] anchored to calix[4]arene moieties[4c, 8] is currently an open and so far unexplored field.

C2. Olefin rearrangements to M–C, M=C, and M≡C bonds over a metallacalix[4]arene oxo surface: Generation of M–C, M=C, and M≡C functionalities directly from hydrocarbons has been recognized for a long time as a superior feature of heterogeneous catalysts over homogeneous catalysts.[1] The ethylene rearrangements assisted by the d^2[{p-tBu-calix[4]-(O_4)}W][4h] fragment are very similar to those often supposed to occur on metal oxides or other active surfaces.[1, 2] Such rearrangements (Scheme 4) are driven by light, acids, or bases, or occur under reducing conditions. Scheme 4 gives the overall picture of the fundamental transformations undergone by ethylene and propylene on a W^{IV} oxocalix[4]arene surface.[4h] Although some of these transformations are known for different metal fragments, the occurrence both on a single fragment and on a metal – oxo surface is unprecedented and opens novel perspectives in the field.



Scheme 4. Olefin rearrangements over a W calix[4]arene oxo surface.

C3. Activation of small molecules by a metallacalix[4]arene oxo surface: The generation of highly reactive low-valent metals in an oxo environment may be quite an interesting avenue to explore, not only for hydrocarbon but also for small molecule activation. The latter case is exemplified by a quite recent report on the activation of dinitrogen, centered on the utilization of low-valent niobium bound to the calix[4]arene tetraanion.[4g] Such species can react to form metal–metal bonded dimers, or, under appropriate conditions, to reduce and cleave |N≡N| multiple bonds. Scheme 5 shows the stepwise reduction of dinitrogen to nitride assisted by niobium(III)–calix[4]arene.[4g]

Outlook

The preorganised oxo surface of calix[4]arene anions offers a unique opportunity for making molecular model compounds competitive with the well-known heterogeneous oxo-catalysts. They can challenge the heterogeneous systems in a range of reactions, from hydrocarbon rearrangements, to dinitrogen reduction and cleavage, and to oxo-transfer processes.

Acknowledgments

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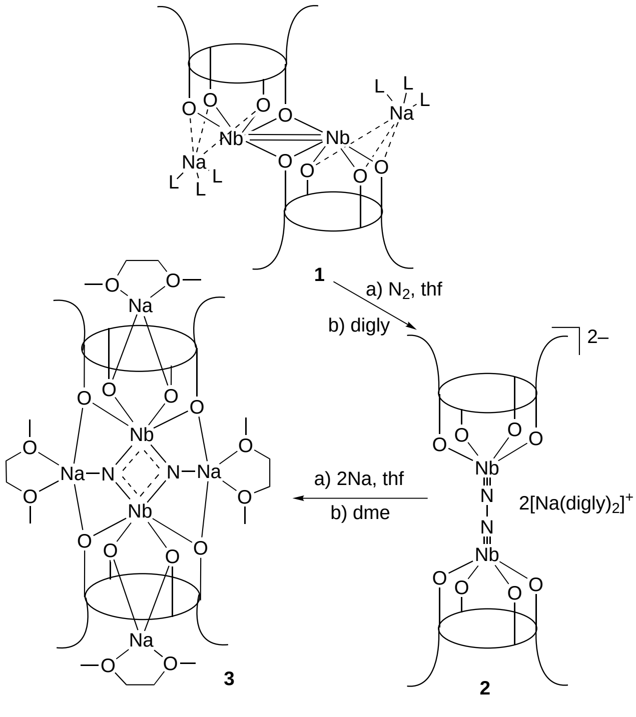

Scheme 5. Dinitrogen cleavage assisted by reduced forms of Nb calix[4]-arene moieties.

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