Molybdenum(IV)-d^2 Reactivity in a Quasiplanar Oxo-Environment Modeled by Calix[4]arene: The Reductive Cleavage of N═N Double Bond and the Formation of 1-Metallacyclopropene from the Corresponding Alkyne Complexes

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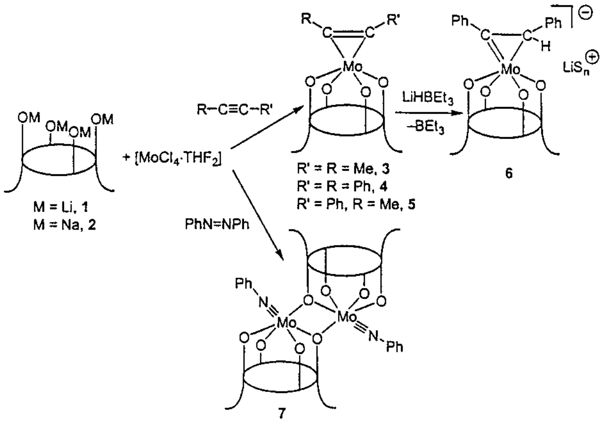
Summary: [p-Bu^t-calix[4]-(O)$_4$-Mo^{IV}], generated in situ from [MoCl$_4$·THF$_2$] and the alkali salts of p-Bu^t-calix[4]arene, displays the reactivity expected for a d^2-carbenoid metal. The reaction carried out in the presence of azobenzene led to the cleavage of the N═N bond and the formation of a dimeric Mo^{VI}-phenylimido derivative, [{μ-p-Bu^t-calix[4]-(O)$_4$}$_2${Mo^{VI}≡NPh}$_2$], while the reaction with acetylenes led to 2-metallacyclopropene complexes [{p-Bu^t-calix[4]-(O)$_4$-Mo}(η^2-C$_2$R$_2$)], which converted to 1-metallacyclopropenes, the precursor of alkylidene and alkylidyne functionalities, in the reaction with a hydride source.

Metalation of calix[4]arene addressed to generate reactive metal−ligand fragments,[1] rather than to make just new compounds, is an appropriate strategy for discovering unprecedented metal-assisted transformations. This has been the case in organometallic functionalization[2] and in the synthesis of low-valent metals[2f,3] in such an unusual environment, made up of only oxygen donor atoms. In the latter instance, the [Nb^{III}-d^2-calix[4]arene] moiety assists the reduction of dinitrogen and carbon monoxide to nitride[3d] and carbide,[3c] respectively. The high reactivity of W^{IV}-calix[4]arene[2f,4] and Nb^{III}-calix[4]arene[3b−d] derivatives does not have any counterpart in molybdenum-calix[4]arene chemistry, which is so far limited to unreactive M−M bonded dimers[5] or to Mo^{VI} derivatives, where the metal bears oxo,[6] arylimido,[7] and chloro ligands.[6] The Mo−C bond has never appeared in this scenario.

Scheme 1



The present report deals with the experimental procedure to generate in situ a very reactive Mo^{IV}-d^2-calix[4]arene entity, which can be captured by an appropriate substrate. This would be an ideal entry into calix[4]arene-based Mo organometallic chemistry. Reactions are performed by reacting a THF solution or suspension of [*p*-Bu^t-calix[4]-(OM)$_4$] (M = Li, Na) with [MoCl$_4$·THF$_2$] in the presence of the substrate. In the case of acetylenes, the reaction proceeds almost quantitatively to form the corresponding 2-metallacyclopropene (Scheme 1). Complexes **3**−**5** have been fully characterized including X-ray analysis. The structure of **4** recrystallized from acetonitrile, **4**·MeCN,[8] is displayed in Figure 1,[9] with some relevant structural parameters. The metallacalix[4]arene assumes the cone conformation with two long and two short M−O bond distances, according to the competition between the π-bonding of two oxygens to the metal and the presence of the alkyne at the metal.[2f,4] The Mo−C and C−C bond distances (see Figure 1) are consistent with the 2-met-

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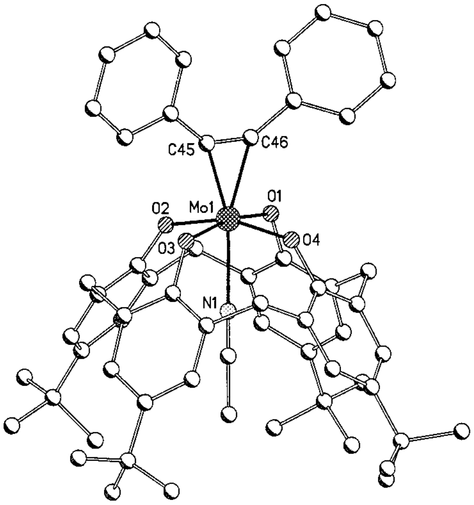

Figure 1. View of complex **4** (hydrogen atoms and external solvent molecule omitted for clarity). Selected bond distances (Å): Mo1−O1 = 2.020(3), Mo1−O2 = 1.895(3), Mo1−O3 = 1.999(3), Mo1−O4 = 1.901(3), Mo1−C45 = 2.057(4), Mo1−C46 = 2.058(4), Mo1−N1 = 2.317(3), C45−C46 = 1.270(5).

allacyclopropene formulation. Complex **3** is a quite relevant entry into the organometallic chemistry of molybdenum. Using a rather recent synthetic methodology,[4,10] it was converted to a 1-metallacyclopropene functionality, which paves the way to metallaalkylidynes or other related species.[2f,4,10] The addition of $LiHBEt_3$ to **4** led to the formation of the anionic 1-metallacyclopropene derivative, **6**.[11] This is a masked form of the corresponding anionic alkylidyne, to which it normally rearranges spontaneously in the case of hydrogen substituents at the carbon atoms.[2f,4,10] In addition, complex **6** is the potential precursor of dimetallic-dialkylidene,[4] to which it can be transformed upon one-electron oxidation. The proposed structure of **6** has been confirmed both in the solid state [Mo═C 1.871(10), Mo−C 2.232(12), C−C 1.435(16) Å] and in solution [^{13}C NMR, C-alkylidene, 303 ppm].

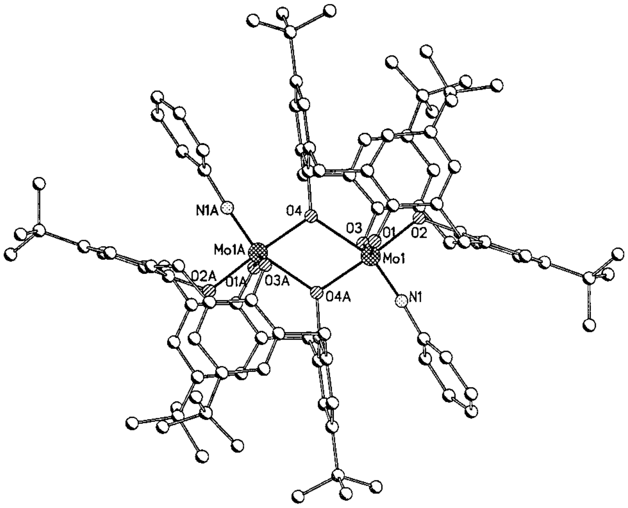

Figure 2. View of complex **7** (hydrogen atoms and solvent molecules omitted for clarity). Selected bond distances (Å) and angle (deg): Mo1−O1 = 1.924(5), Mo1−O2 = 1.948(5), Mo1−O3 = 1.924(5), Mo1−O4 = 2.251(5), Mo1−O4A = 2.046(5), Mo1−N1 = 1.713(6), N1−C45 = 1.390(11), C45−N1−Mo1 = 174.4(6). Letter A indicates the following symmetry transformation: $-x, -y, -z$.

When the reaction in Scheme 1 was carried out in the presence of azobenzene, the formation of the phenylimido derivative dimer, **7**,[12] was observed. The solid-state structure is shown in Figure 2.[13] The dimeric form derives from the sharing of one of the calix[4]arene

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(8) Procedure for **4**: $[MoCl_4\cdot(THF)_2]$ (4.67 g, 12.23 mmol) was added to a suspension of $[p\text{-Bu}^t\text{-calix[4]-(ONa)}_4]\cdot(THF)_2$ (10.76 g, 12.21 mmol) and diphenylacetylene (2.18 g, 12.23 mmol) in THF (250 mL) at −30 °C. The reaction mixture was stirred overnight while slowly warming to room temperature, giving a suspension of a white solid in a dark red solution. NaCl was filtered off, and volatiles were evaporated to dryness. The greenish brown residue was washed with *n*-hexane (70 mL) and dried in vacuo to yield 5.63 g (50.1%) of **4**. Anal. Calcd for **4**, $C_{58}H_{62}MoO_4$: C, 75.80; H, 6.80. Found: C, 75.56; H, 6.91. ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.36 (m, 4H, $C_2(C_6H_5)_2$); 7.58 (m, 4H, $C_2(C_6H_5)_2$); 7.51 (m, 1H, $C_2(C_6H_5)_2$); 7.32 (m, 1H, $C_2(C_6H_5)_2$); 7.10 (s, 8H, ArH); 4.31 (d, J = 12.4 Hz, 4H, *endo*-CH_2); 3.19 (d, J = 12.4 Hz, 4H, *exo*-CH_2); 1.22 (s, 36H, Bu^t). Crystals for X-ray analysis were grown from MeCN/*n*-hexane, and the analysis was carried out on the acetonitrile-solvated form **4**·MeCN.

(9) Crystal data for **4**: $(C_{60}H_{65}MoNO_4)\cdot0.5(C_6H_{14})$, M = 1003.16, triclinic, space group $P\bar{1}$, a = 12.245(2) Å, b = 14.947(3) Å, c = 16.339(3) Å, α = 78.32(3)°, β = 68.46(3)°, γ = 75.52(3)°, V = 2672.8(9) $Å^3$, Z = 2, D_{calcd} = 1.246 g/cm^3, $F(000)$ = 1062, λ(Mo Kα) = 0.71070 Å, μ = 0.293 mm^{-1}; crystal dimensions 0.28 × 0.22 × 0.20 mm. Diffraction data were collected on a mar345 Imaging Plate at 143 K. The structure was solved with direct methods and refined using full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. For 5752 observed reflections [$I > 2\sigma(I)$] and 623 parameters, the conventional R is 0.0561 (wR2 = 0.1597 for 7588 independent reflections).

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(11) Procedure for **6**: Complex **4** (3.31 g, 3.6 mmol) was added to a solution of $LiHBEt_3$ (3.5 mL, 1 N in THF, 3.5 mmol) in THF (120 mL) at −50 °C. The reaction mixture was stirred overnight while slowly warming to room temperature. The resulting red solution was filtered, and volatiles were evaporated to dryness to give a red residue, which was washed with pentane (30 mL) and dried in vacuo, yielding 2.62 g (63.6%) of **6**·$(C_4H_8O)_{2.5}\cdot(C_5H_{12})_{0.5}$. Anal. Calcd for **6**·$(C_4H_8O)_{2.5}\cdot(C_5H_{12})_{0.5}$, $C_{70.5}H_{89}LiMoO_{6.5}$: C, 74.06; H, 7.85. Found: C, 73.95; H, 7.75. ^1H NMR (THF-d_8, 400 MHz, 298 K, ppm): δ 8.63 (m, 2H, $C_2(H)(C_6H_5)_2$); 7.82 (m, 2H, $C_2(H)(C_6H_5)_2$); 7.51 (m, 1H, $C_2(H)(C_6H_5)_2$); 7.36−7.15 (m, 5H, $C_2(H)(C_6H_5)_2$); 6.86 (s, 8H, ArH); 4.76 (br, 1H, $C_2(H)(C_6H_5)_2$); 4.52 (d, J = 11.6 Hz, 4H, *endo*-CH_2); 3.62 (m, 10H, THF); 3.15 (d, J = 11.6 Hz, 4H, *exo*-CH_2); 1.77 (m, 10H, THF); 1.31 (m, 3H, pent); 1.18 (s, 36H, Bu^t); 0.90 (m, 3H, pent). ^{13}C NMR (THF-d_8, 100.6 MHz, 298 K, ppm): δ 303.06 (Mo*C*PhCHPh). Crystals suitable for a X-rays analysis were grown from a THF/diglyme solution.

(12) Procedure for **7**: $[MoCl_4\cdot(THF)_2]$ (0.98 g, 2.56 mmol) was added to a suspension of $[p\text{-Bu}^t\text{-calix[4]-(OLi)}_4]\cdot(DME)\cdot(C_6H_{14})_{0.5}$ (1.98 g, 2.46 mmol) and azobenzene (0.224 g, 1.23 mmol) in THF (120 mL) at −30 °C. The reaction mixture was stirred overnight while slowly warming to room temperature, giving a brown suspension, which was refluxed for 14 h. Then volatiles were evaporated to dryness, and toluene (120 mL) was added to the residue. The resulting brown suspension was refluxed overnight to give a suspension of a white solid in a dark red solution. The solid was filtered off, and volatiles were evaporated to dryness to give a dark brown residue, which was washed with pentane (40 mL) and dried in vacuo, yielding 1.2 g (56%) of **7**·(C_5H_{12}). Anal. Calcd for **7**·(C_5H_{12}), $C_{105}H_{134}Mo_2N_2O_8$: C, 72.31; H, 7.74; N, 1.61. Found: C, 72.10; H, 7.84; N, 1.56. ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.14 (m, 4H, ArH calix); 7.01 (m, 4H, ArH calix); 6.93 (m, 4H, ArH PhN); 6.84 (m, 2H, ArH PhN); 6.78 (m, 4H, ArH PhN); 6.73 (s, 4H, ArH calix); 6.60 (s, 4H, ArH calix); 5.57 (d, J = 12.2 Hz, 4H, *endo*-CH_2); 4.66 (d, J = 14 Hz, 4H, *endo*-CH_2); 3.37 (d, J = 12.2 Hz, 4H, *exo*-CH_2); 3.30 (d, J = 14 Hz, 4H, *exo*-CH_2); 1.26 (m, 6H, pent); 1.21 (s, 36H, Bu^t); 1.04 (s, 18H, Bu^t); 0.89 (s, 18H, Bu^t); 0.87 (m, 6H, pent).

(13) Crystal data for **7**: $(C_{100}H_{114}Mo_2N_2O_8)\cdot4(C_4H_8O)\cdot2(C_2H_3N)$, M = 2034.34, monoclinic, space group $P2_1/n$, a = 15.173(3) Å, b = 17.648(4) Å, c = 20.585(4) Å, β = 101.21(3)°, V = 5406.9(19) $Å^3$, Z = 2, D_{calcd} = 1.250 g/cm^3, $F(000)$ = 2160, λ(Mo Kα) = 0.71070 Å, μ = 0.294 mm^{-1}; crystal dimensions 0.27 × 0.20 × 0.15 mm. Diffraction data were collected on a mar345 Imaging Plate at 143 K. The structure was solved with direct methods and refined using full-matrix least-squares on F^2 with all non-H atoms anisotropically defined (except one THF molecule). For 3179 observed reflections [$I > 2\sigma(I)$] and 617 parameters, the conventional R is 0.0660 (wR2 = 0.1896 for 6516 independent reflections).

oxygens. The calix[4]arene ligand around Mo displays an elliptical conformation according to the hexacoordination of the metal.[2a,b] The most important structural parameters are in the caption of Figure 2. Although the arylimido functionality can be introduced in the Mo-calix[4]arene fragment using the preformed Mo-arylimido functionality, i.e., [$Cl_4Mo{=}NAr$],[7] the synthetic result in Scheme 1 has a completely different meaning and impact. Complex **7** is the result of a four-electron reduction of azobenzene. The other arylimido-Mo-calix[4]arenes[7] so far reported are exclusively monomeric, probably as a consequence of the steric hindrance at the aryl group, more than because of the different synthesis used. The formation of **3**, **4**, **5**, and **7** from the reactions in Scheme 1 reveals the presence in solution of either the precursor monomeric Mo^{IV}-d^2-carbenoid or the corresponding dimeric form containing a very reactive [Mo=Mo] fragment.[14] A quite similar scenario was found in the case of Nb^{III}.[3b,c,d]

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Supporting Information Available: ORTEP drawings and tables giving crystal data and structure refinement, atomic coordinates, bond lengths and angles, isotropic and anisotropic displacement parameters, and hydrogen coordinates for **4** and **7**. This material is available free of charge via the Internet at htpp://pubs.acs.org.

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[14] A very interesting analogy can be made with the very reactive [$W_2(OCH_2Bu^t)_8$], containing a W=W double bond: Chisholm, M. H.; Folting, K.; Lynn, M. A.; Streib, W. E.; Tiedke, D. B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 52, and references therein.