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Metal−Carbon and Carbon−Oxygen Related Reactivity in Tantalum *p-tert*-Butylcalix[4]arene Complexes Undergoing Organic Functionalization

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*Summary: [(Calix[4]OMe)TaCl$_2$] (**2**), formed from [calix[4](OMe)$_2$] (**1**) and TaCl$_5$ via a demethylation reaction, undergoes exhaustive alkylation to [(calix[4]OMe)TaR$_2$] (**3**−**5**), which give photochemically or thermally induced concerted dealkylation at the metal and at the methoxy group, to give [calix[4]TaR] (**6**−**8**). Double migration of alkyl groups has been observed in the reaction of **3**−**5** with CO and Bu^tNC to form the corresponding η^2-ketones [(calix[4]OMe)Ta(η^2-COR$_2$)] (**9**−**11**) and η^2-imines [(calix[4]OMe)Ta{η^2-N(Bu^t)CR$_2$}] (**12**−**14**).*

The use of calix[4]arenes[1] as ancillary ligands[2,3] in organometallic chemistry, though so far extremely limited,[4] is of growing interest in the area of early transition metals due to the nature of the donor atoms and their almost planar arrangement provided by the calix[4]arene skeleton. Such an arrangement mimics a planar oxo surface and leaves open a face to the metal for chemical reactivity. This report deals with the preliminary results in tantalum organometallic chemistry[5] based on the *p-tert*-butylcalix[4]arene skeleton.[6] It is particularly relevant that we mention the contributions of the Rothwell[7] and Wolczanski[8] groups on the use of alkoxotantalum organometallic chemistry.

The use of calix[4]arene derivatives adds significant novelties to alkoxotantalum chemistry, namely (i) forcing the metal into a quasi-planar O$_4$ environment, which results in a significantly different set of orbitals, and (ii) tuning the charge of the O$_4$ unit, *via* the methylation of the oxo groups, thus adapting it to the oxidation state and the functionalization degree desired by the metal.

We should anticipate that the methoxy group not only is a spectator fragment determining the overall charge of the O$_4$ set but also influences the metal reactivity patterns, *via* various demethylation pathways. This has been observed even in the synthesis of the parent compound **2**[9] obtained from the reaction of **1**[10] with TaCl$_5$ (Scheme 1), occurring with the demethylation of one of the two methoxy groups. The metal is bonded to the trianionic methoxy-*p-tert*-butylcalix[4]arene (calix[4]-OMe) residue. Complex **2** undergoes easy alkylation with either organomagnesium or organolithium derivatives, occurring with negligible concurrent reduction of the metal, to give the corresponding dialkyl derivatives (R = Me, **3**; R = PhCH$_2$,[11] **4**; R = p-MeC$_6$H$_4$, **5**). The synthesis is reported in detail for **4**. The dialkyl derivatives **3**−**5** are rather stable, but under different conditions, depending on the nature of the alkyl, they undergo photochemically (R = PhCH$_2$, **7**;[12] R = p-MeC$_6$H$_4$, **8**) or, in pyridine, thermally (R = Me, **6**; R = PhCH$_2$, **7**; R = p-MeC$_6$H$_4$, **8**) concerted dealkylation at one of the methoxy groups, as shown by NMR experiments (Scheme 1). The transformation of compound **4** to **7** was also achieved by reacting **4** with H$_2$.[12] The experimental conditions of this reaction are reported. Although all the demethylations accompanying both the synthesis of **2** and the conversion of **3**−**5** to **6**−**8** are mechanistically difficult to define at present, they are synthetically very important, since one of the methoxy substituents is masking an anionic site. This will intervene, when necessary, during the reaction

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(9) Procedure for **2**: TaCl$_5$ (20.95 g, 58.5 mmol) was added to a toluene (400 mL) solution of **1** (39.2 g, 58.0 mmol), and the yellow mixture was refluxed for 36 h. The solvent was removed *in vacuo*, and the yellow residue was washed with hexane (200 mL) and collected (43.2 g, 74%). Crystals suitable for X-ray analysis were grown in a saturated benzene−hexane (1/1) solution. Anal. Calcd for **2**·C$_7$H$_8$, C$_{45}$H$_{55}$Cl$_2$O$_4$Ta·C$_7$H$_8$: C, 62.20; H, 6.34. Found: C, 61.78; H, 6.12. ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ 0.67 (s, Bu^t, 9H), 0.73 (s, Bu^t, 9H), 1.34 (s, Bu^t, 18H), 2.1 (s, C$_7$H$_8$, 3H), 3.15 (d, CH$_2$-calix, 2H, J = 13.3 Hz), 3.3 (d, CH$_2$-calix, 2H, J = 13.8 Hz), 3.95 (s, OCH$_3$, 3H), 4.36 (d, CH$_2$-calix, 2H, J = 13.3 Hz), 4.97 (d, CH$_2$-calix, 2H, J = 13.8 Hz), 7.00 (m, H arom, 13H).

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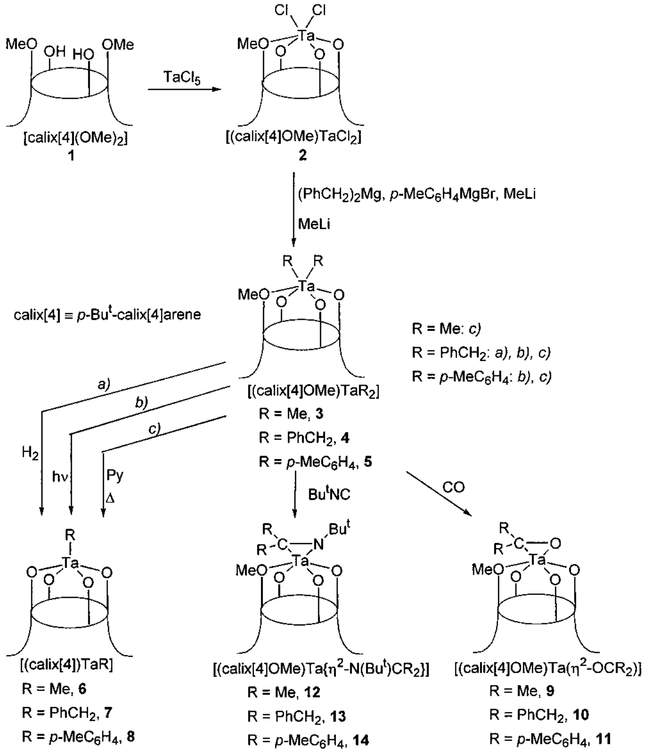
S0276-7333(96)00666-8 CCC: $12.00

Scheme 1



pathway of the metal. Among the preliminary explorations we chose to engage **3**−**5** into migratory insertion reactions with CO and RNC[5,13] (Scheme 1). In both cases we observed the migration of both alkyls to the inserting ligand, to give the corresponding η^2-ketones (**9**−**11**)[14] and η^2-imines (**12**−**14**) *via* the expected intermediacy of the corresponding η^2-acyl and η^2-iminoacyl, respectively.[13,15] Complexes **9**−**11** and **12**−**14** do not undergo, even under forced conditions, thermally, photochemically, or base (i.e. pyridine) induced demethylation of the methoxy group with concomitant migration of the methyl to the η^2-imino or η^2-ketone functionality, which allows us to make a direct comparison with reactions occurring on metal−oxo surfaces.

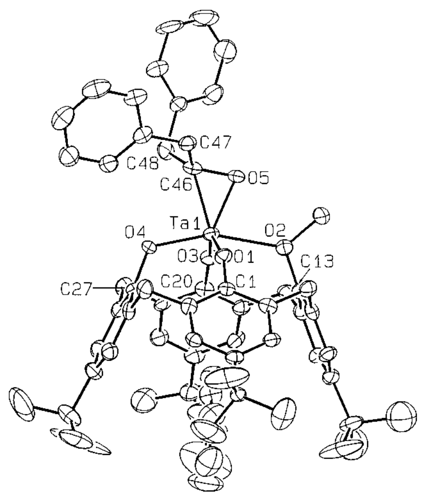


Figure 1. ORTEP drawing of complex **10**. Selected bond distances (Å) and angles (deg) are as follows: Ta1−O1, 1.895(5); Ta1−O2, 2.297(6); Ta1−O3, 1.900(5); Ta1−O4, 1.971(5); Ta1−O5, 1.942(5); Ta1−C46, 2.100(9); O5−C46, 1.405(11); C46−C47, 1.503(12); C46−C48, 1.553(11). O5−Ta1−C46, 40.4(3); O3−Ta1−O4, 90.0(3); O2−Ta1−O4, 157.8(3); O2−Ta1−O3, 81.1(2); O1−Ta1−O4, 91.0(2); O1−Ta1−O3, 136.0(3); O1−Ta1−O2, 81.8(2); Ta1−O5−C46, 75.8(4); Ta1−C46−O5, 63.7(4). For the disordered atoms only the A position is given for clarity.

Details are reported on the synthesis and X-ray structure of **10**, shown in Figure 1, along with selected structural parameters.[16] The calix[4]arene skeleton assumes an elliptical cone conformation, as determined by the distances between *para* carbon atoms: C4···C17, 9.181(11) Å; C10···C24, 7.306(11) Å. This is the conse-

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(11) Procedure for **4**: a THF solution (10.96 mL) of $(PhCH_2)_2Mg$ (0.34 M, 3.73 mmol) was added dropwise to a yellow toluene (150 mL) solution of **2** (3.74 g, 3.73 mmol) at room temperature. The mixture turned orange in seconds, and after 15 min dioxane (6 mL) was added. The reaction mixture was stirred for 1 h, salts were filtered off, and volatiles were removed *in vacuo*. The yellow residue was washed with *n*-hexane (100 mL), collected, and dried (1.6 g, 42%). Anal. Calcd for **4**, $C_{59}H_{69}O_4Ta$: C, 69.25; H, 6.81. Found: C, 69.35; H, 7.10. ^1H NMR (C_6D_6, 200 MHz): δ 0.67 (s, Bu^t, 9H), 0.72 (s, Bu^t, 9H), 1.39 (s, Bu^t, 18H), 3.12 (d, CH_2-calix, 2H, J = 13.3 Hz), 3.19 (s, OCH_3, 3H), 3.23 (d, CH_2-calix, 2H, J = 12.6 Hz), 3.6 (brd s, CH_2Ph, 4H), 4.31 (d, CH_2-calix, 2H, J = 13.3 Hz), 4.44 (d, CH_2-calix, 2H, J = 12.6 Hz), 7.16 (m, H arom, 18H). Solutions of the product are thermally stable (benzene, 100 °C, 24 h) but photosensitive. A sample in C_6D_6 exposed to light for 24 h gave, as shown by the NMR spectrum, a mixture of **7** (>80%) and another unidentified product (^1H NMR singlet at δ 9.63). A sample heated for 2 h at 80 °C in CD_5N gave quantitatively compound **7**.

(12) Procedure for **7**: a benzene (250 mL) suspension of **4** (5.1 g, 5.0 mmol) was saturated with H_2. Stirring at room temperature for 6 days resulted in the yellow mixture turning orange. The solvent was removed *in vacuo*, and the light yellow-brown residue was dissolved in *n*-hexane (60 mL). The solution was then kept at −30 °C for 36 h, yielding a light yellow-brown precipitate of **7**, which was collected and dried. Anal. Calcd for $C_{51}H_{59}O_4Ta$: C, 66.79; H, 6.49. Found: C, 66.66; H, 6.67. ^1H NMR (C_6D_5, 200 MHz): δ 1.09 (s, 36H, Bu^t), 3.28 (d, J = 12.2 Hz, 4H, CH_2-calix), 3.62 (bs, 2H, CH_2Ph), 4.98 (d, J = 12.2 Hz, 4H, CH_2-calix), 7.06 (s, 8H, H arom-calix), 7.37 (m, 5H, arom-CH_2Ph).

(13) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059. The review contains references also to the related Zr−alkoxo-based organometallic chemistry.

(14) Procedure for **10**: a toluene (120 mL) suspension of **4** (2.34 g, 2.3 mmol) was saturated with CO. Stirring at room temperature for 2 h resulted in a yellow solution. The solvent was removed *in vacuo* and the yellow residue was dissolved in *n*-hexane (50 mL). The solution was filtered and kept at −30 °C for 12 h, yielding a white precipitate which was then collected and dried *in vacuo* (1.37 g, 57%). Crystals suitable for X-ray analysis were obtained by cooling a saturated solution of **10** in hexane/benzene (10/1) from room temperature to 2 °C. Anal. Calcd for **10**, $C_{60}H_{69}O_5Ta$: C, 68.54; H, 6.63. Found: C, 68.62; H, 7.33. ^1H NMR (C_6D_6, 200 MHz): δ 0.67 (s, Bu^t, 9H), 0.83 (s, Bu^t, 9H), 1.38 (s, Bu^t, 18H), 3.1 (d, CH_2-calix, 2H, J = 12.5 Hz), 3.26 (d, CH_2-calix, 2H, J = 12.5 Hz), 4.06 (d, CH_2-calix, 2H, J = 12.5 Hz), 4.15 (d, CH_2Ph, 2H, J = 14.7 Hz), 4.32 (s, OCH_3, 3H), 4.42 (d, CH_2Ph, 2H, J = 14.7 Hz), 4.94 (d, CH_2-calix, 2H, J = 12.5 Hz), 7.02 (m, H arom, 14H), 7.70 (d, H arom, 4H, J = 8.28 Hz).

(15) Chamberlain, L. R.; Steffey, B. D.; Rothwell, I. P.; Huffman, J. C. *Polyhedron* **1989**, *8*, 341. Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L. M.; Latesky, S. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6068.

(16) Crystal data for **10**: $C_{60}H_{69}O_5Ta\cdot1.5C_6H_6\cdot0.5C_6H_{14}$, M_r = 1211.4, triclinic, space group $P\bar{1}$, a = 16.399(8) Å, b = 17.074(9) Å, c = 11.854(5) Å, α = 99.10(5)°, β = 107.92(3)°, γ = 88.70(4)°, V = 3117(3) Å^3, Z = 2, ρ_{calcd} = 1.291 g cm^{-3}, $F(000)$ = 1260, λ(Mo Kα) = 0.710 69 Å, μ(Mo Kα) = 17.88 cm^{-1}: crystal dimensions 0.22 × 0.52 × 0.64 mm. The structure was solved by the heavy-atom method and anisotropically refined for all non-hydrogen atoms except for those affected by disorder. Some Bu^t groups were affected by high thermal parameters, indicating the presence of disorder. The best fit was found by splitting the C35 and C36 atoms over two positions (A and B) isotropically refined with site occupation factors of 0.5. All the hydrogen atoms but those related to the disordered carbon atoms, which were ignored, were put in geometrically calculated positions and introduced as fixed contributors in the last stage of refinement (U_{iso} = 0.05 Å^2). For 8529 unique observed reflections ($I > 2\sigma(I)$) collected at T = 133 K on a Rigaku AFC6S diffractometer ($5 < 2\theta < 50$°) and corrected for absorption the final R is 0.061 (wR2 = 0.165 for the 9825 reflections having $I > 0$ used in the refinement). All calculations were carried out on a Quansan Personal Computer equipped with an Intel Pentium processor. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. See the Supporting Information for more details.

quence of the rather irregular trend in the Ta−O bond distances: they are quite close in the case of Ta−O1 and Ta−O3 (mean value 1.897(5) Å), significantly longer for Ta−O4 (1.971(5) Å), and much longer for the methoxy oxygen Ta−O2 (2.297(6) Å). The short Ta−O bond distances along with the wide Ta−O−C angles involving O1 and O3 (Ta−O1−C1, 152.4(5)°; Ta−O3−C20, 154.9(5)°) support a Ta−O multiple-bond interaction.[6]

The O_4 plane shows tetrahedral distortions varying within ±0.143(6) Å, the metal being displaced by 0.550(3) Å from the mean plane toward the η^2-ketone. The plane of the η^2-ketone is perpendicular to the O_4 mean plane, the dihedral angle being 90.6(3)°. The asymmetric η^2-bonding mode of dibenzyl ketone (Ta−O5, 1.942(5) Å; Ta−C46, 2.100(9) Å) and the O5−C46 distance (1.405(11) Å) are in agreement with other η^2-metal-bonded ketones.[13] The potential of the Ta−C, Ta−H bond chemistry over a calix[4]arene skeleton remains largely unexplored, along with the use of **2** as a starting material for accessing low-valent tantalum species. In addition, we can take advantage, in synthesis, of the controlled demethylation of one of the methoxy groups.

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Supporting Information Available: Tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles for complex **10** (10 pages). Ordering information is given on any current masthead page.

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