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Li-Intercalated Oxometallocubanes

Intercalation of Alkali Metal Cations into Layered Organotitanium Oxides**

José Gracia, Avelino Martín, Miguel Mena, María del Carmen Morales-Varela, Josep-M. Poblet, and Cristina Santamaría*

Dedicated to Professor Pascual Royo on the occasion of his 65th birthday

Species with a metallocubane structure constitute an interesting building block in inorganic solids, and considerable effort has been invested in selecting the composition and geometry of the precursor complexes to obtain specific characteristics and properties.[1] Some examples of the wide variety of inorganic materials whose structures are based on molecular cubane-like motifs are the molybdenum[2] and aluminum phosphates,[3] $M_yMo_xP_yO_z$ (M = metal cation), or various hydroxometalates $[M_xO_y(OH)_z]L$ (M = Ge, Ln,…).[4]

We have reported the formation and structure of the oxoheterometallocubanes $[\{(CO)_3Mo\}(\mu_3\text{-}O)_3\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CR)\}]$ (R = H, Me)[5], which were obtained from the preorganized organometallic oxides $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ (R = H (**1**), Me (**2**)).[6] Once we observed that the latter might be involved directly as macrocyclic tridentate ligands in encapsulation processes of different metals, we became interested in incorporating diverse metal complex fragments at the free vertex of the μ_3-alkylidyne oxo derivatives to build up the corresponding oxoheterometallocubanes.

As part of these ongoing studies, here we present the intercalation of alkali metal ions into layered organometallic titanium oxides by treatment of the alkylidyne complex **1** with different alkali metal alkyl and amide reagents.

The one-pot reaction of the tripodal starting material **1** with MR (M = Li, R = CH_2SiMe_3, CH_2CMe_3, *n*Bu; M = Na, R = *n*Bu; M = K, R = *n*Bu, CH_2Ph) in toluene/hexane at room temperature leads to the oxoheterometallodicubanes **3**–**5** in good yields. These compounds can be also obtained by

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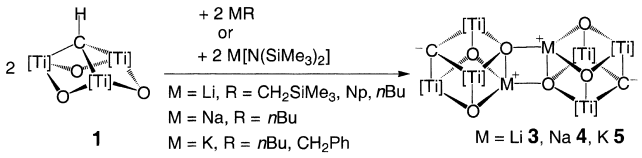
using $M[N(SiMe_3)_2]$ ($M = Li$, Na, K) in toluene or hexane at 60 °C (Scheme 1).

Crystallization of **3** from a double layer toluene/hexane at room temperature gave dark green crystals suitable for an X-ray diffraction study.[7–9] A simplified view of the unit cell of **3** showing the intercalation of the lithium atoms into the



Scheme 1. Synthesis of the oxoheterometallodicubanes **3**–**5**. [Ti] = $Ti(\eta^5\text{-}C_5Me_5)$.

organometallic titanium oxide layers is given in Figure 1, and the molecular structure of **3** is shown in Figure 2. The structure reveals two LiO_3Ti_3C cubane cores directly linked through two Li–O bonds. The ensuing Li_2O_2 rhomb is planar and has the dimensions Li···Li 2.61(2) Å, (close to the value of 2.67 Å, reported for the diatomic species Li_2[10]), Li–O 2.386(13) and 1.891(12) Å, and O-Li-O 105.7(5)°, consistent with a trigonal-pyramidal LiO_4 coordination of its lithium atoms, analogous to that found for $[M(\mu_3\text{-}N)(\mu_3\text{-}NH)_2\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]_2$ ($M = Li$, Na).[11]

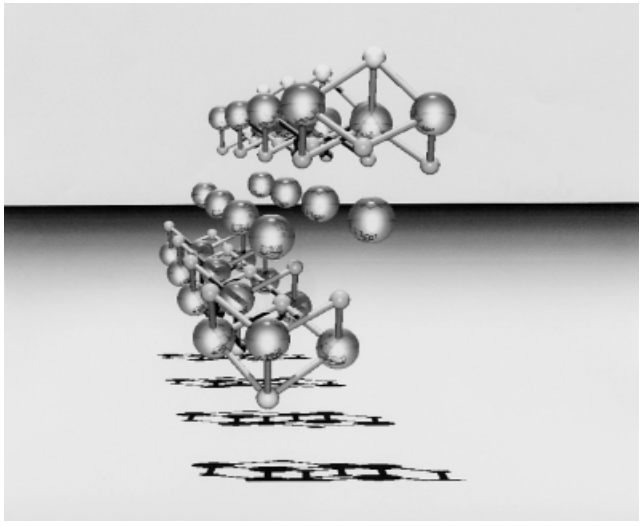


Figure 1. Simplified view of the unit cell of **3**, normal to the (100) plane.

The Ti_3O_3C subunits of **3** display several structural differences to that of the parent compounds **1** and **2**. The angles Ti-O-Ti (av 95.4°) and O-Ti-O (av 96.4°) in **3** are smaller than those in **1** and **2** (Ti-O-Ti av 100°, O-Ti-O av 104°).[6a,c] The Ti–C1 bond length (av 2.055 Å) lies between those in **1** (Ti–C1 2.10 Å),[6c] and **2** (Ti–C1 2.12 Å),[6a,c] and that in the zwitterionic derivative $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3\{\mu_3\text{-}\eta^2\text{-}C^-C(Me)N^+(2,6\text{-}Me_2C_6H_3)\}]$ (Ti–C$^-$ 2.017(5) Å).[12]

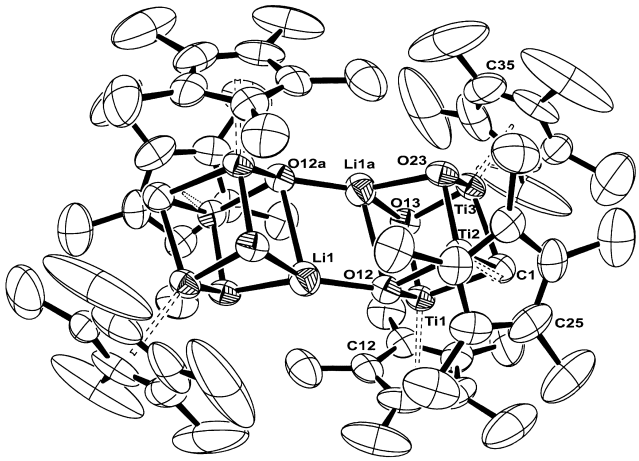


Figure 2. Structure of **3** (ORTEP drawing; 50% probability ellipsoids). The complex resides on an inversion center. Selected distances [Å] and angles [°]: Intercubane: Li···Li 2.61(2), Li-O 1.891(12); Li-(μ_4-O)-Li 74.3(5), (μ_4-O)-Li-(μ_4-O) 105.7(5), Ti-O(12)-Li(1) 130.2(4); intracubane: Ti···Ti 2.798(1) av, Li···Ti 2.885(11) av, (μ_4-O)-Li 2.386(13) av, (μ_3-O)-Li 2.057(12) av, Ti-O 1.891(4) av, Ti-C1 2.055(6) av; Ti-C1-Ti 85.8(2) av, C1-Ti-O 89.1(2) av, Ti-O-Ti 95.4(2) av, O-Ti-O 96.4(2) av, Ti-O12-Li1a 87.6(3) av, Ti3-O13-Li1a 86.1(4), Ti1-O13-Li1a 98.1(4), Ti3-O23-Li1a 87.5(4), Ti2-O23-Li1a 98.1(4).

DFT calculations reproduced quite well the X-ray geometry found for **3**.[13–17] However, for the central rhombic unit the optimization process yielded a structure with two short and two long Li–O bonds of 1.901 and 2.169 Å, respectively. Whereas the short bonds compare well with the experimental distance (1.891 Å), the discrepancy for the long bonds seems excessive (0.22 Å). In spite of this, we found that the energy difference between the complex optimized by keeping the central parallelepiped fixed at the experimental geometry and the fully optimized complex is only 12 kJ mol^{-1}.

The solid compounds **3**–**5** proved stable under argon at room temperature and practically insoluble in most common solvents (e.g. toluene, hexane, dichloromethane) with the exception of THF, which allowed the characterization of **4** and **5** by NMR spectroscopy. ^{1}H NMR spectra in [D$_8$]THF of **4** and **5** show only one signal at $\delta = 1.95$ and 1.94 ppm, respectively, which is assigned to the $\eta^5\text{-}C_5Me_5$ groups. The ^{13}C NMR spectra display signals with the appropriate multiplicity for the $\eta^5\text{-}C_5Me_5$ ligands, as well as a singlet for the apical μ_3-carbon atom ($\delta = 586.7$ (**4**) and 582.0 ppm (**5**)). These data indicate the removal of the proton of the μ_3-methylidyne fragment and are consistent with the formulation of these diamagnetic compounds as $[\{M(\mu_3\text{-}O)_3[Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}C)]\}_2]$ ($M = Li$, Na, K). Previously, Cummins et al. reported the formation of the carbidomolybdenum(VI) anions $[\{(Ar)RN\}_3Mo{\equiv}C]^-$ ($R = C(CD_3)_2CH_3$ or *t*Bu; $Ar = 3,5\text{-}Me_2C_6H_3$), which displayed a carbide chemical shift in the range $\delta = 474$–501 ppm.[18]

To clarify the magnitude of the chemical shifts found for the apical carbon atom in compounds **4** and **5**, we performed DFT-GIAO-based NMR calculations.[19] The computed δ value for the apical methylidyne-carbon atom in the precursor tridentate ligand model $[\{Ti(\eta^5\text{-}C_5H_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ (**1′**) was

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Table 1: Experimental and calculated ^{13}C chemical shifts (δ) for the apical carbon atom.

Molecule	δ	δ(DFT-GIAO)[b]	Shielding[a] σ_d[c]	σ_p[d]
$[\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ (**1**)	383.2			
$[\{TiCp(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ (**1′**)		385.3	241.2	−444.2
$[\{MeLi\}(\mu_3\text{-}O)_3\{Ti_3Cp_3(\mu_3\text{-}CH)\}]$		400.6	243.0	−461.3
$[Li(\mu_3\text{-}O)_3\{Ti_3Cp_3(\mu_3\text{-}C)\}]$		572.2	254.2	−644.1
$[\{Li(\mu_3\text{-}O)_3[Ti_3Cp_3(\mu_3\text{-}C)]\}_2]$(**3′**)		572.5	256.4	−646.6
$[\{Na(\mu_3\text{-}O)_3[Ti_3Cp^*_3(\mu_3\text{-}C)]\}_2]$ (**4**)	586.7			
$[\{K(\mu_3\text{-}O)_3[Ti_3Cp^*_3(\mu_3\text{-}C)\}_2]$ (**5**)	582.0			

[a] Shielding in ppm relative to TMS. [b] $\delta = \sigma(TMS) - (\sigma_d + \sigma_p)$ where the computed σ(TMS) is 182.3 ppm. For a detailed description of the implementation of the GIAO method in the ADF package as well as the calculation procedure of σ_d and σ_p see reference [19]. [c] Diamagnetic shielding. [d] Paramagnetic shielding.

385.3 ppm, a value that is almost identical to the experimental value found for **1** ($\delta = 383.2$ ppm). The formation of the carbido species induces an increase of the calculated δ value to 572.2 ppm, which is consistent with the experimental values measured for **4** ($\delta = 586.7$ ppm) and **5** ($\delta = 582.0$ ppm). These latter values can be explained in terms of a predominant paramagnetic contribution (Table 1), which could be attributed to the larger magnetic coupling between the σ carbon lone pair and the titanium orbitals. In the $[\{Ti(\eta^5\text{-}C_5H_5)(\mu\text{-}O)\}_3(\mu_3\text{-}C)]^-$ ionic fragment the HOMO orbital (−4.9 eV) is essentially the apical carbon lone pair, whereas in the corresponding nondeprotonated form $[\{Ti(\eta^5\text{-}C_5H_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ (**1′**), this orbital localizes very much lower in energy (at ~ −8 eV).

Because non-intermediates were detected during the course of this reaction, we used DFT calculations to propose the possible sequence leading to the formation of the oxometallodicubane model $[Li(\mu_3\text{-}O)_3\{Ti_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}C)\}]_2$ (**3′**; Figure 3). The initial step proceeds by coordination of the LiR unit to the oxomethylidyne ligand **1′** (Figure 3). The next step would consist in the CH_4 (or NH_3) elimination by deprotonation at the μ_3-methylidyne carbon atom, affording the monomer complex $[Li(\mu_3\text{-}O)_3\{Ti_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}C)\}]$. Finally, the assembly of two monomers leads to **3′**. All the processes are exothermic, especially those for the methane elimination.

The slow formation of the μ_3-ethylidyne complex $[Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}O)_3(\mu_3\text{-}CMe)]$ (**2**) from the reactions of **3–5** in $[D_6]$benzene with MeI confirmed unequivocally the existence of the μ_3-carbido group.

Herein we have focused on the reactions of the μ_3-methylidyne species **1** with alkali metal (Li, Na, K) alkyl or amide reagents. The process was analyzed by DFT calculations and the magnitude of the chemical shifts was determined for the apical μ_3-carbido groups in the products $[\{M(\mu_3\text{-}O)_3[Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}C)]\}_2]$ (M = Li, Na, K). As an extension of this work and to gain knowledge on the structural and electronic properties of this kind of compounds, we are currently investigating oxometallocubane-type systems containing the heaviest alkali metals as well as the incorporation of alkaline-earth metals into these sytems.

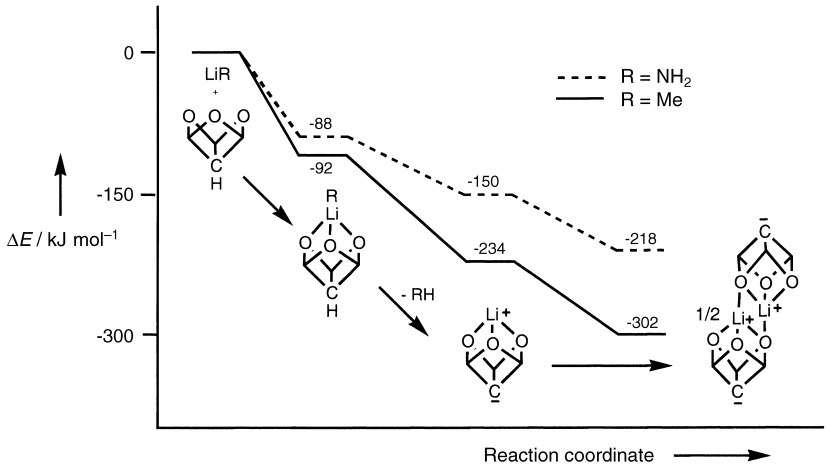

Figure 3. Computed ΔE (kJ mol^{-1}) values for the formation steps of the oxoheterometallodicubane model $[\{Li(\mu_3\text{-}O)_3[Ti_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}C)]\}_2]$ (**3′**).

Experimental Section

3: Treatment of **1** with $Li[N(SiMe_3)_2]$, NpLi, $Li[CH_2SiMe_3]$, or BuLi led to the formation of compound **3**. The reaction of **1** with BuLi is reported as an example. A solution of **1** (0.32 g, 0.52 mmol) in toluene (15 mL) and BuLi (0.3 mL, 0.52 mmol) in hexane (30 mL) was placed in a 100-mL Carious tube with a Young valve. The reaction mixture was left at room temperature overnight, after which a green microcrystalline solid was observed at the bottom of the flask. The solid was filtered and washed with hexane to yield **3** (0.30 g, 94%). This complex decomposed in THF precluding its characterization by NMR spectroscopy; IR (KBr): $\tilde{\nu} = 2907$ (vs), 2856 (vs), 1491 (w), 1437 (s), 1373 (s), 1023 (m), 801 (w), 681 (vs), 616 (vs), 464 (w), 416 cm^{-1} (s); elemental analysis calcd (%) for $Ti_6O_6C_{62}H_{90}Li_2$ (1232.50): C 60.41, H 7.36; found: C 60.40, H 7.34.

4: The treatment of **1** with BuNa or $Na[N(SiMe_3)_2]$ afforded compound **4**. The reaction of **1** with $Na[N(SiMe_3)_2]$ is reported as an example. A 100-mL Carious tube with a Young valve was charged with **1** (0.3 g, 0.49 mmol), $Na[N(SiMe_3)_2]$ (0.09 g. 0.49 mmol), and toluene (40 mL). The reaction mixture was heated at 60 °C overnight and the red solid formed was washed with hexane to give **4** (0.18 g, 58%); ^1H NMR (300 MHz, $[D_8]$THF, 25 °C, TMS): $\delta = 1.95$ ppm (s; C_5Me_5); ^{13}C NMR (300 MHz, $[D_8]$THF, 25 °C, TMS): $\delta =$ 11.7 ($C_5\mathit{Me}_5$), 115.4 (C_5Me_5), 586.7 ppm (μ_3-C); IR (KBr): $\tilde{\nu} = 2907$ (vs), 2850 (vs), 1493 (w), 1437 (s), 1372 (s), 1023 (m), 795 (w), 681 (vs), 621 (vs), 467 (w), 411 cm^{-1} (s); elemental analysis calcd (%) for $Ti_6O_6C_{62}H_{90}Na_2$ (1264.60): C 58.79, H 7.32; found: C 58.90, H 7.39.

5: Analogously to the preparation of **4, 1** (0.30 g, 0.49 mmol) and $K[N(SiMe_3)_2]$ (0.10 g, 0.49 mmol) were allowed to react in hexane (40 mL) to afford **5** as a red solid (0.21 g, 66%); ^1H NMR (500 MHz, $[D_8]$THF, 25 °C, TMS): $\delta =$

1.94 ppm (s, C_5Me_5); ^{13}C NMR (500 MHz, [D_8]THF, 25 °C, TMS): $\delta =$ 11.5 ($C_5\mathit{Me}_5$), 115.1 (C_5Me_5), 582.0 ppm (μ_3-C); IR (KBr): $\tilde{\nu} = 2910$ (vs), 2857 (vs), 1597 (w), 1495 (w), 1439 (s), 1375 (s), 1247 (w), 1067 (w), 916 (m), 899 (m), 852 (s), 784 (vs), 680 (s), 624 (m), 573 (m), 411 cm^{-1} (s); elemental analysis calcd (%) for $Ti_6O_6C_{62}H_{90}K_2$ (1296.82): C 57.42, H 6.99; found: C 56.99, H 7.10.

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[7] X-ray crystal structure determination of **3**: All data were collected on an ENRAF NONIUS CAD4 diffractometer at room temperature, $Mo_{K\alpha} = 0.71073$ Å. The structure was solved, using the WINGX[8] package, by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).[9] X-ray data for $C_{62}H_{90}Li_2O_6Ti_6$ (**3**): $0.45 \times 0.34 \times 0.30$ mm^3, triclinic, $P\bar{1}$, $a = 11.405(2)$, $b = 11.695(2)$, $c = 14.671(3)$ Å, $\alpha = 111.71(2)$, $\beta = 90.78(2)$, $\gamma = 116.39(3)$°, $V = 1590.9(5)$ Å^3, $\rho_{calcd} = 1.287$ Mg m^{-3}. Intensity measurements were performed by ω–2θ scans in the range $3° < \theta < 23°$, of the 4789 measured reflections, 4530 were independent; $R1 = 0.056$ and $wR2 = 0.138$ (for 2617 reflections with $F > 4\sigma(F)$). The values of $R1$ and $wR2$ are defined as follows: $R1 = \Sigma\,||F_o| - |F_c||/[\Sigma\,|F_o|]$; $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$. Largest difference peak and hole 0.380 and -0.318 e Å^{-3}. All non-hydrogen atoms were anisotropically refined. The hydrogen atoms were positioned geometrically and refined by using a riding model in the last cycles of refinement with a fixed value of $U(eq) = 0.08$. CCDC-190221 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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