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Co-complexation of Lithium Gallates on the Titanium Molecular Oxide $\{[\mathrm{Ti}(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$

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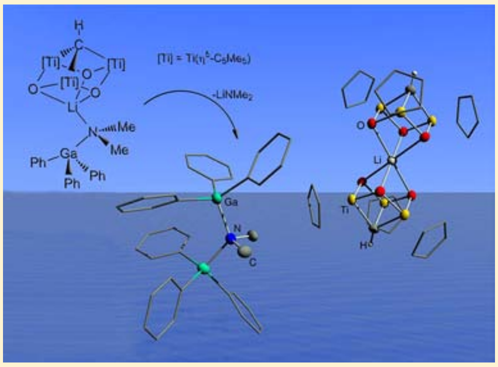
Supporting Information

ABSTRACT: Amide and lithium aryloxide gallates $[\mathrm{Li}^+\{\mathrm{RGaPh_3}\}^-]$ (R = NMe_2, O-2,6-$Me_2C_6H_3$) react with the μ_3-alkylidyne oxoderivative ligand $[\{\mathrm{Ti}(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ (**1**) to afford the gallium−lithium−titanium cubane complexes $[\{\mathrm{Ph_3Ga}(\mu\text{-}R)\mathrm{Li}\}\{\mathrm{Ti}(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ [R = NMe_2 (**3**), O-2,6-$Me_2C_6H_3$ (**4**)]. The same complexes can be obtained by treatment of the $[\mathrm{Ph_3Ga}(\mu_3\text{-}O)_3\{\mathrm{Ti}(\eta^5\text{-}C_5Me_5)\}_3(\mu_3\text{-}CH)]$ (**2**) adduct with the corresponding lithium amide or aryloxide, respectively. Complex **3** evolves with formation of **5** as a solvent-separated ion pair constituted by the lithium dicubane cationic species $[\mathrm{Li}\{(\mu_3\text{-}O)_3\mathrm{Ti}_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CH)\}_2]^+$ together with the anionic $[(\mathrm{GaPh_3})_2(\mu\text{-}NMe_2)]^-$ unit. On the other hand, the reaction of **1** with $\mathrm{Li}(p\text{-}MeC_6H_4)$ and $\mathrm{GaPh_3}$ leads to the complex $[\mathrm{Li}\{(\mu_3\text{-}O)_3\mathrm{Ti}_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CH)\}_2][\mathrm{GaLi}(p\text{-}MeC_6H_4)_2\mathrm{Ph_3}]$ (**6**). X-ray diffraction studies were performed on **1**, **2**, **4**, and **5**, while trials to obtain crystals of **6** led to characterization of $[\mathrm{Li}\{(\mu_3\text{-}O)_3\mathrm{Ti}_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CH)\}_2][\mathrm{PhLi}(\mu\text{-}C_6H_5)_2\mathrm{Ga}(p\text{-}MeC_6H_4)\mathrm{Ph}]$ **6a**.



INTRODUCTION

The chemistry of “ate” complexes[1] that contain a metallic center (magnesium, zinc, or aluminum), an alkaline metal (lithium or sodium), and a variable number of ligands has attracted the interest of many research groups for the last three decades. These species exhibit a large structural diversity and a distinctive and enhanced reactivity compared with that of their homometallic precursors.[2] Additionally, aluminum metalate derivatives are among the most widely used organometallic reagents in organic synthesis.[2e] A structural study about this family of complexes led to establishment of two general types of compounds, namely, solvent-separated ion pair and contact ion pair species.[3]

According to the literature, contact ion pair species require direct interaction between the positive and negative fragments. In most cases, a general bonding system $M(\mu\text{-}X)_n\mathrm{Li}$ (M = Al, Ga; X = O, N; n = 1, 2) is observed, although only few examples present a unique bridging ligand. Thus, the addition reaction of LiOH to the adduct $[\mathrm{M(Mes)_3(thf)}]$ (M = Al, Ga) led Roesky and co-workers[4] to isolate the compound $[\mathrm{Li(thf)_3}(\mu\text{-}OH)\mathrm{M(Mes)_3}]$ (M = Al, Ga), with only one M−O−Li moiety, while the M−N−Li bridging system could be obtained by Atwood and Rutherford[5] in the reaction of $[\mathrm{AlMe_2(NH\text{-}2,6\text{-}{}^iPr_2C_6H_3)}]$ with $\mathrm{Li}^t\mathrm{Bu}$ to give the adduct $[\mathrm{Li(thf)_3}(\mu\text{-}NH\text{-}2,6\text{-}{}^iPr_2C_6H_3)\mathrm{Al}^t\mathrm{BuMe_2}]$.

Reasonably, the presence of several coordinative ligands in the sphere of the metallate fragment should favor the formation of species containing more than one M−X−Li bridging unit. In this sense, the treatment of $[\mathrm{LiAlH_4}]$ with 2,6-${}^tBu_2C_6H_3OH$ in tetrahydrofuran (THF) produced the complex $[\mathrm{Li(thf)_2}(\mu\text{-}O^nBu)_2\mathrm{Al}(2,6\text{-}{}^tBu_2C_6H_3O)_2]$.[6] Also, Barron and co-workers[7] published the dinuclear complex $[\mathrm{Li(OEt_2)}(\mu\text{-}BHT)\{\mu\text{-}OC(Me)Ph_2\}\mathrm{AlMe(BHT)}]$ (BHT = O-2,6-${}^tBu_2$-4-MeC_6H_2) by addition of ethereal LiMe to the adduct $[\mathrm{AlMe(BHT)_2(OCPh_2)}]$.

In contrast with the aforementioned complexes, the existence of additional intramolecular interactions prevent the incorporation of solvent molecules, as has been reported for the aluminum derivatives $[\mathrm{Li}(\mu\text{-}BHT)_2\mathrm{AlMe_2}]$[8] and $[\mathrm{Li}(\mu\text{-}OC(Ph)(CF_3)_2)_2\mathrm{Al(OC(Ph)(CF_3)_2)_2}]$,[9] where the lithium metal center is stabilized by Me···Li or F···Li interactions.

Furthermore, the coordination number of the lithium atom can be affected by the presence of additional bridging bulky groups. In this sense, Wheatley and co-workers[10] have reported the complex $[\mathrm{Li(thf)}({}^i\mathrm{Bu})(\mathrm{TMP})\mathrm{Al}^i\mathrm{Bu_2}]$ (TMP = 2,2,6,6-tetramethylpiperidido) where the Li/Al bimetallic complex is bridged by the nitrogen atom of TMP and the α-carbon of a single isobutyl group, leading to a trigonal planar environment for the lithium atom. Even more curious is the complex $[\mathrm{Li}\{\mu\text{-}N(SiMe_3)_2\}\mathrm{MMe_3}]_\infty$ (M = Al, Ga) reported by Niemeyer and Power,[11] constituted by infinite chains that involve intermolecular Li···Me interactions to complete the tricoordinate geometry. Also, Power and co-workers[12] have published the complex $[\mathrm{Li}(\mu\text{-}NHCPh_3)_2\mathrm{Al}^t\mathrm{Bu_2}]$ in which in addition to bonding to two amide nitrogen the coordination sphere of Li has further close contacts to two of the phenyl rings.

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Finally, contact ion pair species containing only bridging alkyl ligands are rare. The first complex of this type, $[LiAlEt_4]$, published by Brown and co-workers,[13] consisted of open chains of alternating lithium and aluminum. Later, Wheatley and co-workers[14] reproduced a similar structural motif in the organometallic fragment, $[Li(Me_2Al^tBu_2)_2]^-$. More complex situations have been reported by Uhl and co-workers[15,16] in $[Li_2\{CH_2Al(CH_2SiMe_3)_3\}_2]$ with a "bowl" type structure, generated by reaction between $[(AlCl_2)_2CH_2]$ and $LiCH_2SiMe_3$, and one gallium derivative constituted by two units of $[Li\{(\mu\text{-}CH_2SiMe_3)_2Ga(CH_2SiMe_3)_2\}]$ linked through a dioxane molecule.

In contrast with the above-mentioned examples, in solvent-separated ion pair species[3] the direct electrostatic interaction between cation/anion centers is modified by intervention of one or more solvent molecules, ligands, etc., as observed in the derivatives $[Li(thf)_4][Al\{C(SiMe_3)_3\}(NHPh)_3]$,[17] $[Li(dioxane)_4][Al^iBu_4\}]$,[18] and $[Li(12\text{-crown-}4)(thf)][Ga\{[PhC{=}C(Ph)(Ph)C{=}CPh]_2\}_2]$.[19]

More generally, a solvent-separated ion structural disposition is favored by the presence of strong coordinative Lewis bases or bulky ligands. An illustrative example of this behavior can be found in the treatment of the alkyltrihydroaluminate $[Li(thf)_2\{AlH_3[C(SiMe_3)_3]\}]_2$ with tetramethylethane-1,2-diamine (tmen) to give $[Li(tmen)_2][Al\{C(SiMe_3)_3\}H_3]$,[17] which crystallizes as a solvent-separated ion pair. Also, Okuda and co-workers[20] synthesized solvent-separated lithium derivatives of the anion $[Al(CH_2SiMe_3)_4]^-$ by addition of 2 equiv of tmen or 12-crown-4 to $Li[Al(CH_2SiMe_3)_4]$. Finally, the presence of bulky ^{t}Bu instead of methyl groups linked to aluminum in the molecular framework $[Li(thf)_3(\mu\text{-}NH\text{-}2,6\text{-}^iPr_2C_6H_3)Al^tBuMe_2]$ led to the isolation of the anion/cation pair $[Li(thf)_4][Al^iBu_2{}^tBu(NH\text{-}2,6\text{-}^iPr_2C_6H_3)]$.[21]

Recently, we have communicated the capability of the molecular organometallic oxides $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CR)]$ (R = H, Me) to support heteroleptic lithium aryloxide aluminum "ate" fragments, identifying unambiguously the formation of both characteristic contact and solvent-separated ion pair structures containing titanium—lithium—aluminum.[22] In an attempt to gain insight into the chemistry of other group 13 metallates, we moved to the less-known chemistry of gallium. Herein we report the co-complexation reactions of lithium aryloxide, amide and aryl gallates on the μ_3-alkylidyne oxoderivative ligand $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ and describe the singular compounds obtained.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were performed with use of either glovebox or high vacuum line techniques. Toluene and hexane were freshly distilled under argon from sodium and sodium/potassium alloy, respectively. Benzene-d_6 was dried with sodium/potassium alloy, vacuum-distilled, and stored under argon. $GaPh_3$,[23] $Li(O\text{-}2,6\text{-}Me_2C_6H_3)$,[24] and $Li(p\text{-}MeC_6H_4)$[25] were prepared according to reported methods, while $LiNMe_2$ was purchased from Aldrich and used as received.

Elemental analysis (C, H, N) was performed with a Leco CHNS-932 analyzer and/or Perkin-Elmer 2400-Series II C, H, N, S/O. NMR spectra were obtained by using Varian NMR System spectrometers: Unity-300, Mercury-VX, or Unity-500 Plus. Trace amounts of protonated solvents or carbon of the solvent were used as references, and chemical shifts are reported relative to tetramethylsilane (TMS) or benzene-d_6 (^{1}H, δ 7.15; ^{13}C, δ 128.0).

Preparation of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ (1). $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)Me\}_3]$ (1.100 g, 1.71 mmol), placed in a 100 mL Carius tube, was dissolved in ~50 mL of toluene. The Carius tube was flame-sealed under vacuum and the solution was heated in an autoclave at 210 °C for 2 days. The Carius tube was opened in a glovebox, and the solvent was removed in vacuum to yield 0.860 g of a brownish-yellow solid (yield 82%). Suitable single crystals were obtained by slow evaporation of a saturated benzene-d_6 solution at room temperature over several days. IR (KBr, cm^{-1}) $\bar{\nu}$ = 2909 (s), 2857 (s), 1493 (w), 1434 (m), 1374 (s), 1165 (w), 1066 (w), 1024 (m), 788 (vs), 731 (s), 676 (vs), 627 (s), 430 (s), 395 (s); ^{1}H NMR (C_6D_6, 300 MHz, 298 K) δ = 12.59 (s, 1H, μ_3-C*H*), 1.96 (s, 45H, C_5Me_5); ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz, 298 K) δ = 383.9 (μ_3-CH), 119.9 (C_5Me_5), 11.8 (C_5Me_5); Elemental analysis (%) calcd for $C_{31}H_{46}O_3Ti_3$ (610.32): C, 61.00; H, 7.60. Found: C, 60.67; H, 7.30.

Preparation of $[Ph_3Ga(\mu_3\text{-}O)_3\{Ti(\eta^5\text{-}C_5Me_5)\}_3(\mu_3\text{-}CH)]$ (2). A suspension of $GaPh_3$ (0.148 g, 0.49 mmol) in toluene (10 mL) was added to a solution of **1** (0.300 g, 0.49 mmol) in 20 mL of the same solvent. The mixture was left at room temperature with stirring for 1 h. Then the solvent was removed under vacuum to give an orange solid identified as **2**. Yield 0.325 g (88%). IR (KBr, cm^{-1}) $\bar{\nu}$ = 3055 (m), 2979 (m), 2909 (s), 2857 (m), 1946 (w), 1880 (w), 1817 (w), 1563 (w), 1479 (w), 1424 (m), 1376 (m), 1253 (w), 1189 (w), 1165 (w), 1078 (m), 1023 (w), 791 (w), 729 (s), 702 (vs), 681 (vs), 659 (vs), 609 (vs), 460 (s), 435 (s), 392 (s). ^{1}H NMR (C_6D_6, 300 MHz, 298 K) δ = 12.89 (s,1H, μ_3-C*H*), 8.07 (6H, *o*-GaC_6H_5), 7.37−7.28 (9H, GaC_6H_5), 1.85 (s, 45H, C_5Me_5); ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz, 298 K) δ = 393.1 (μ_3-CH), 148.5, 138.9, 127.5, 128.2, (GaC_6H_5), 121.3 (C_5Me_5), 12.0 (C_5Me_5); Elemental analysis (%) calcd for $C_{49}H_{61}GaO_3Ti_3$ (911.30): C, 64.58; H, 6.75. Found: C, 64.55; H, 6.54.

Preparation of $[Ph_3Ga(\mu\text{-}NMe_2)Li(\mu_3\text{-}O)_3\{Ti(\eta^5\text{-}C_5Me_5)\}_3(\mu_3\text{-}CH)]$ (3). $LiNMe_2$ (0.023 g, 0.44 mmol) and $[Ph_3Ga(\mu\text{-}O)_3\{Ti(\eta^5\text{-}C_5Me_5)\}_3(\mu_3\text{-}CH)]$ (**2**) (0.400 g, 0.44 mmol) were suspended in approximately 20 mL of hexane, and then the suspension was stirred for 1 h at room temperature. The new compound was isolated by filtration as a yellow solid and dried under a flux of argon. Yield 0.336 g (78%). IR (KBr, cm^{-1}) $\bar{\nu}$ = 3051 (m), 2915 (s), 2859 (s), 2764 (w), 1946 (w), 1873 (w), 1816 (w), 1477 (m), 1422 (s), 1378 (s), 1250 (w), 1219 (w), 1188 (w), 1152 (w), 1126 (w), 1075 (m), 1023 (w), 916 (w), 885 (w), 803 (w), 728 (s), 704 (vs), 654 (s), 1126 (w), 916 (w), 885 (w), 803 (w), 679 (vs), 617 (vs), 440 (s), 401 (m); ^{1}H NMR (C_6D_6, 300 MHz, 298 K) δ = 13.07 (s, 1H, μ_3-C*H*), 8.13 (d, $^3J_{HH}$= 6.3 Hz, 6H, *o*-GaC_6H_5), 7.48−7.33 (m, 9H, GaC_6H_5), 2.85 (s, 6H, NMe_2), 1.74 (s, 45H, C_5Me_5); ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz, 298 K) δ = μ_3-CH (signal not detected), 154.3−125.9 (GaC_6H_5), 122.5 (br s, C_5Me_5), 45.2 (NMe_2), 11.8 (C_5Me_5); Elemental analysis (%) calcd for $C_{51}H_{67}GaLiNO_3Ti_3$ (962.31): C, 63.65; H, 7.02; N, 1.45. Found: C, 63.21; H, 6.52; N, 2.37.

Preparation of $[Ph_3Ga(\mu\text{-}O\text{-}2,6\text{-}Me_2C_6H_3)Li(\mu_3\text{-}O)_3\{Ti(\eta^5\text{-}C_5Me_5)\}_3(\mu_3\text{-}CH)]$ (4). The stoichiometric amount of $GaPh_3$ (0.100 g, 0.33 mmol) in hexane (10 mL) at −35 °C was added to a suspension of $Li(O\text{-}2,6\text{-}Me_2C_6H_3)$ (0.042 g, 0.33 mmol) in hexane (10 mL) at −35 °C. After the addition was completed, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. Then complex **1** (0.200 g, 0.33 mmol) was added to the previous mixture. After 1 h of stirring, a yellow microcrystalline solid was observed at the bottom of the Schlenk flask. The solid was obtained by filtration and dried under a flux of argon. Yield 0.190 g (56%). IR (KBr, cm^{-1}) $\bar{\nu}$ = 3053 (s), 2981 (s), 2912 (s), 2857 (m), 2277 (w), 1948 (w), 1874 (w), 1820 (w), 1590 (m), 1463 (vs), 1424 (vs), 1377 (s), 1329 (w), 1301 (w), 1267 (s), 1216 (s), 1159 (w), 1083 (s), 1024 (m), 981 (w), 947 (w), 916 (w), 915 (w), 846 (s), 792 (s), 758 (s), 730 (vs), 702 (vs), 687 (vs), 615 (vs), 558 (w), 530 (w), 499 (m), 451 (s), 399 (w); ^{1}H NMR (C_6D_6, 300 MHz, 298 K) δ = 12.94 (s, 1H, μ_3-C*H*), 7.80−7.22 (15H, GaC_6H_5), 7.00 (d, $^3J_{H-H}$ = 7.5 Hz, 2H, $O\text{-}2,6\text{-}Me_2C_6H_3$), 6.80 (m, 1H, $O\text{-}2,6\text{-}Me_2C_6H_3$), 2.34 (s, 6H, $O\text{-}2,6\text{-}Me_2C_6H_3$), 1.75 (s, 45H, C_5Me_5); ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz, 298 K) δ = μ_3-CH (signal not detected), 138.3−119.5 (GaC_6H_5 and $O\text{-}2,6\text{-}Me_2C_6H_3$), 122.4 (br s, C_5Me_5), 19.8 ($O\text{-}2,6\text{-}Me_2C_6H_3$), 11.7 ($C_5Me_5$); Elemental analysis (%) calcd for $C_{57}H_{70}GaLiO_4Ti_3$ (1039.39): C, 65.86; H, 6.79. Found: C, 65.85; H, 6.54.

Table 1. Crystal Data and Structure Refinement for **1**, **2**, **4**, **5**, and **6a**

	1	**2**·C_6D_6	**4**·C_6D_6	**5**·2C_6D_6	**6a**·2C_6D_6
empirical formula	$C_{31}H_{46}O_3Ti_3$	$C_{55}H_{67}GaO_3Ti_3$	$C_{63}H_{76}GaLiO_4Ti_3$	$C_{112}H_{140}Ga_2LiNO_6Ti_6$	$C_{105}H_{131}GaLi_2O_6Ti_6$
formula wt	610.38	989.51	1117.6	2030.03	1860.1
temp, K	200(2)	200(2)	200(2)	200(2)	200(2)
wavelength (Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
crystal system	orthorhombic	monoclinic	triclinic	monoclinic	triclinic
space group	*Pnma*	*P*2_1/*n*	*P*-1	*P*2_1/*c*	*P*-1
a, Å; *α*, deg	11.750(2)	11.129(1)	13.151(2);87.179(6)	26.272(3)	15.353(4);89.49(3)
b, Å; *β*, deg	19.208(3)	20.839(5);99.34(2)	13.637(2);81.662(7)	14.045(1);94.04(4)	17.205(7);85.67(2)
c, Å; *γ*, deg	13.722(4)	22.000(6)	17.017(1);73.24(1)	28.726(6)	18.504(7);83.94(2)
volume, $Å^3$; *Z*	3097(1); 4	5035(2); 4	2891.2(5); 2	10573(3); 4	4847(3); 2
ρ_{calcd}, g·cm^{-3}	1.309	1.305	1.284	1.275	1.275
μ, mm^{-1}	0.783	1.029	0.905	0.982	0.794
F(000)	1288	2072	1172	4256	1956
crystal size, mm^3	0.29 × 0.26 × 0.13	0.22 × 0.21 × 0.19	0.25 × 0.25 × 0.22	0.42 × 0.35 × 0.14	0.37 × 0.30 × 0.10
θ range, deg	3.12−27.54	3.01−25.24	3.08−27.50	3−25.4	3.02−27.5
index ranges	−15 to 15, −24 to 24, 0 to 17	−12 to 13, −25 to 25, −26 to 26	−17 to 17, −17 to 17, −20 to 22	−31 to 31, −16 to 16, 0 to 34	−19 to 19, −21 to 22, −24 to 24
collected reflcns	49 116	79 066	62 881	142 218	92 731
independent reflcns (R_{int})	3673 (0.067)	9106 (0.221)	13 251 (0.093)	19 329 (0.100)	21 908 (0.088)
goodness-of-fit on F^2	0.993	1.040	1.034	0.967	1.036
final *R* indices [$F > 4\sigma(F)$]					
R1	0.049	0.071	0.050	0.064	0.061
wR2	0.122	0.166	0.101	0.129	0.148
R indices (all data)					
R1	0.096	0.119	0.103	0.162	0.142
wR2	0.139	0.211	0.117	0.153	0.199
largest diff. peak/hole, e·$Å^{-3}$	0.785/−0.420	1.004/−1.183	0.463/−0.517	0.854/−0.87	0.823/−0.959

Preparation of [Li{(μ_3-O)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-CH)}$_2$][(Ph$_3$Ga)$_2$(μ-NMe$_2$)] (5). A toluene solution (25 mL) of **3** (0.336 g, 0.35 mmol) was left stirring for 1 day at room temperature. The orange solution was reduced to half volume under vacuum and cooled at −35 °C to give an orange microcrystalline solid identified as **5**·2C_7H_8. Yield 0.14 g (39%). IR (cm^{-1}) $\bar{\nu}$ = 3255 (w), 3054 (s), 2977 (m), 2910 (s), 2858 (s), 2764 (w), 1946 (w), 1874 (w), 1817 (w), 1494 (w), 1423 (s), 1376 (s), 1302 (w), 1251 (w), 1187 (w), 1152 (w), 1123 (w), 1078 (s), 1022 (w), 896 (w), 801 (m), 730 (s), 703 (s), 678 (vs), 618 (s), 565 (w), 522 (w), 458 (s), 436 (s), 395 (s); ^{1}H NMR (C_6D_6, 300 MHz, 333 K)[26] δ = 12.87 (s, 2H, μ_3-C*H*), 8.07−7.78 (12H, *o*-GaC$_6$*H*$_5$), 7.41−7.18 (18H, GaC$_6$*H*$_5$), 2.82 (s, 6H, N*Me*$_2$), 1.83 (s, 90H, C$_5$*Me*$_5$). Elemental analysis (%) calcd for $C_{100}H_{128}Ga_2LiNO_6Ti_6$·2$C_7H_8$ (2057.96): C, 66.53; H, 7.05; N, 0.68. Found: C, 66.53; H, 7.31; N, 1.78.

Preparation of [Li{(μ_3-O)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-CH)}$_2$][GaLi(*p*-MeC$_6$H$_4$)$_2$Ph$_3$] (6). Li(*p*-MeC$_6$H$_4$) (0.048 g, 0.49 mmol) in 10 mL of toluene at −35 °C were added over a suspension of GaPh$_3$ (0.074 g, 0.24 mmol) in toluene (10 mL) cooled at −35 °C. After 1 h of stirring, 0.300 g (0.49 mmol) of **1** was added and the resulting reaction mixture was stirred for 2 days at room temperature. After that, the solvent was removed by vacuum and the resulting brown solid was washed with hexane cooled at −35 °C. Finally, a yellow solid identified as **6** was obtained. Yield 0.131 (33%). ^{1}H NMR (C_6D_6, 300 MHz, 333 K)[26] δ = 12.61 (s, 2H, μ_3-C*H*), 8.15−7.23 (23H, GaC$_6$*H*$_5$/*p*-MeC$_6$*H*$_4$), 2.25 (s, 6H, *p-Me*C$_6$H$_4$), 1.90 (s, 90H, C$_5$*Me*$_5$); ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz, 333 K)[26] δ = μ_3-CH (signal not detected), 139.2−127.8 (GaC$_6$H$_5$/*p*-MeC$_6$H$_4$), 120.3 (br s, *C*$_5$Me$_5$), 21.5 (*p-Me*C$_6$H$_4$), 11.7 (C$_5$*Me*$_5$). Elemental analysis (%) calcd for $C_{94}H_{121}GaLi_2O_6Ti_6$ (1717.71): C, 65.72; H, 7.10. Found: C, 64.96; H, 6.25.

X-ray Structure Analysis of 1, 2, 4, 5 and 6a. Crystals were grown by slow evaporation at room temperature of saturated benzene-*d*$_6$ solutions. Then crystals were removed from the Schlenks and covered with a layer of a viscous perfluoropolyether (FomblinY). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 200 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data for all complexes are presented in Table 1. The structures were solved, by use of the WINGX package,[27] by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).[28]

Crystals of complexes **2** and **5** diffracted weakly, and only data collections up to θ = 25.4° could be performed. All the complexes except compound **1** crystallized with benzene solvent molecules (see Table 1). In order to characterize the weak C−H···π interactions, all hydrogen atoms involved were located in the Fourier difference map and isotropically refined. Also, the alkylidyne hydrogen atoms in complexes **1**, **4**, **5**, and **6a** and aromatic hydrogen atoms of the phenoxide ring in **4** were treated in the same way. The rest of the hydrogen atoms were positioned geometrically and refined by using a riding model. All non-hydrogen atoms were anisotropically refined.

Molecules of complex **1** presented disorder in one of the pentamethylcyclopentadienyl rings. By use of the corresponding SHELXL's PART command[28] and FVAR variable, two positions for each atom were refined with 56% and 44% occupancy, respectively.

■ RESULTS AND DISCUSSION

The μ_3-alkylidyne titanium organoderivative [{Ti(η^5-C$_5$Me$_5$)(μ-O)}$_3$(μ_3-CH)] (**1**) can be obtained as a brownish-yellow solid in high yield (82%) by thermal treatment of a toluene solution of [{Ti(η^5-C$_5$Me$_5$)Me(μ-O)}$_3$] at 210 °C for 2 days. Complex **1** exhibits only two resonances in the ^{1}H NMR spectrum, one at 1.96 ppm for the equivalent pentamethylcyclopentadienyl rings and other at 12.59 ppm assigned to the μ_3-

CH group, as was previously communicated.[29] The $^{13}C\{^1H\}$ NMR spectrum shows the corresponding signals at 11.8 and 119.9 ppm for the ancillary ligands and one at 383.9 ppm for the alkylidyne carbon atom. Further, a careful and lucky crystallization of complex **1** in benzene-d_6 gave us the opportunity, after numerous trials during the last years, to obtain a suitable single crystal for an X-ray diffraction study. Figure 1 shows how the μ_3-CH alkylidyne moiety is supported on the chair-conformation Ti_3O_3 organometallic oxide, the unique remarkable feature being the 0.04 Å shorter Ti−C(1) bond distances with respect to the ethylidyne analogue.[30]

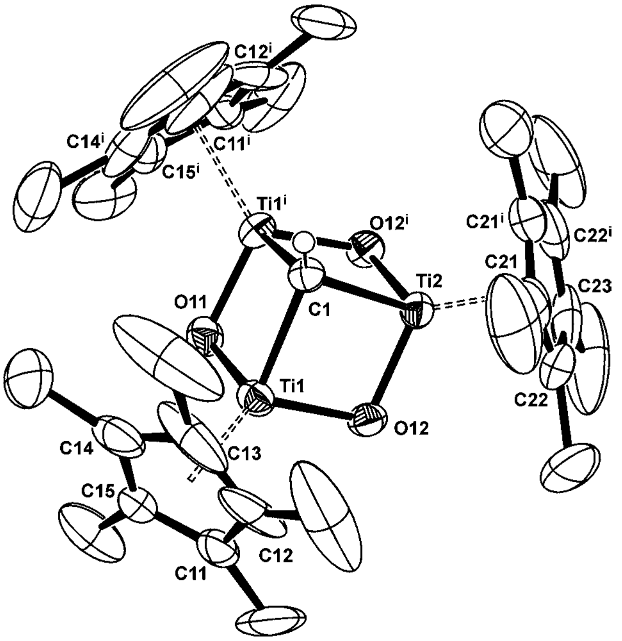
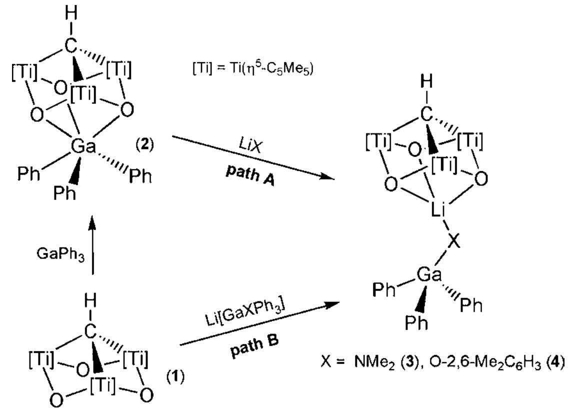


Figure 1. Molecular structure of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ (**1**) with thermal ellipsoids at the 50% probability level. Symmetry transformation (i) x, $-y + {}^1/_2$, z. Selected averaged distances (angstroms) and angles (degrees): Ti−C(1) 2.080(1), Ti−O 1.836(2), Ti···Ti 2.817(1), Ti−C(1)−Ti 85.2(1), Ti−O−Ti 100.2(1), O−Ti−O 104.3(5), C(1)−Ti−O 86.4(1).

Once the starting material was fully structurally characterized, the gallium−lithium−titanium species $[\{Ph_3Ga(\mu\text{-}X)Li\}(\mu_3\text{-}O)_3\{Ti(\eta^5\text{-}C_5Me_5)\}_3(\mu_3\text{-}CH)]$ [X = NMe_2 (**3**) or O-2,6-$Me_2C_6H_3$ (**4**)] could be obtained by treatment of adduct **2** with the corresponding lithium amide or aryloxide derivatives (path A) or by direct reaction of complex **1** with the in situ prepared lithium gallate (path B),[31] as shown in Scheme 1.

It is noticeable that only the treatment of adduct $[Ph_3Ga(\mu_3\text{-}O)_3\{Ti(\eta^5\text{-}C_5Me_5)\}_3(\mu_3\text{-}CH)]$ (**2**), obtained in high yield (88%) following the published procedure for the aluminum analogues,[32] with $LiNMe_2$ in hexane affords complex $[Ph_3Ga(\mu\text{-}NMe_2)Li(\mu_3\text{-}O)_3\{Ti(\eta^5\text{-}C_5Me_5)\}_3(\mu_3\text{-}CH)]$ (**3**) in a pure form (yield 78%) by this two-pot approach (Scheme 1, path A). On the other hand, yellow solid of $[\{Ph_3Ga(\mu\text{-}O\text{-}2,6\text{-}Me_2C_6H_3)Li\}(\mu_3\text{-}O)_3\{Ti(\eta^5\text{-}C_5Me_5)\}_3(\mu_3\text{-}CH)]$ (**4**) is isolated from both pathways, although only path B leads to acceptable yields (56%). Additionally, it always appears together with small amounts of redistribution products. Complexes **3** and **4** proved to be stable under argon at room temperature for long periods of time, insoluble in hexane, and partially soluble in aromatic solvents such as toluene or benzene.

Scheme 1. Synthesis of Complexes 2−4



Compounds **2**, **3**, and **4** were characterized by NMR and IR spectroscopy, and the structures of **2** and **4** were elucidated by single-crystal X-ray diffraction techniques. The NMR spectra in benzene-d_6 for **2** reveal the equivalence of the three C_5Me_5 ligands, consistent with a C_{3v}-symmetric structure. This behavior in solution is not in agreement with the solid-state structure of adduct **2**·C_6D_6 determined by single-crystal X-ray diffraction (Figure 2), but it could be understood if the existence of a fluxional process, like that reported for $[(I_3In)(\mu_3\text{-}NH)_3\{Ti(\eta^5\text{-}C_5Me_5)\}_3(\mu_3\text{-}N)]$,[33] is proposed. The expected signals for the μ_3-methylidyne group and those corresponding to the aryl ligands are also observed in the spectra.

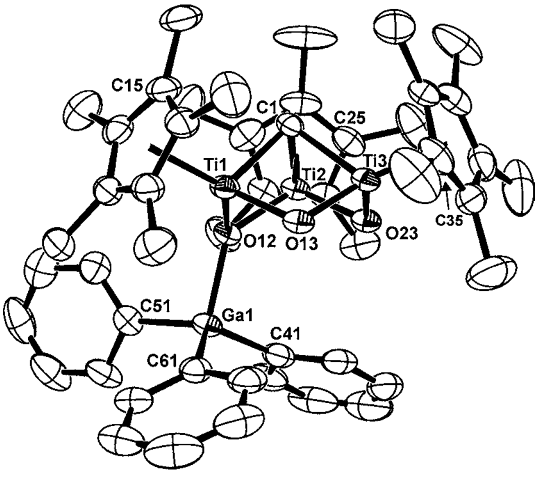


Figure 2. Molecular structure of **2** with thermal ellipsoids at the 50% probability level. The solvent molecule has been omitted for clarity.

The molecular structure of **2**·C_6D_6 reveals how the organometallic ligand **1** can coordinate to the incorporated gallium center in a monodentate way, as we had previously reported for the analogous aluminum derivative.[32] A selection of distances and angles is presented in Table 2. As can be seen in Figure 2, the gallium atom exhibits a distorted tetrahedral environment, with angles spanning from 103.8(2)° to 115.8(3)°. With that disposition, two of the three aromatic rings are located in an eclipsed conformation with respect to the pentamethylcyclopentadienyl ligands. Simultaneously, the C(41)−C(46) ring establishes a type III weak C−H···π interaction with the benzene solvent molecule, according with

Table 2. Selected Averaged Lengths and Angles for $2 \cdot C_6D_6$

Selected Averaged Lengths (Å)			
Ti−C(1)	2.071(9)	Ga(1)−O(12)	2.022(3)
Ti(1)−O(12)	1.907(4)	Ga(1)−C(41)	2.011(6)
Ti(2)−O(12)	1.927(4)	Ga(1)−C(51)	1.984(6)
Ti−O	1.827(5)	Ga(1)−C(61)	1.964(6)
Ti···Ti	2.84(4)		
Selected Averaged Angles (deg)			
Ti(1)−C(1)−Ti(2)	88.5(2)	O(12)−Ti(1)−O(13)	101.0(2)
Ti(1)−C(1)−Ti(3)	87.1(2)	O(12)−Ti(2)−O(23)	103.9(2)
Ti(2)−C(1)−Ti(3)	84.7(2)	O(13)−Ti(3)−O(23)	104.6(2)
Ti(1)−O(12)−Ti(2)	97.5(2)	C(41)−Ga(1)−O(12)	105.5(2)
Ti(1)−O(13)−Ti(3)	102.7(2)	C(51)−Ga(1)−O(12)	103.8(2)
Ti(2)−O(23)−Ti(3)	100.0(2)	C(61)−Ga(1)−O(12)	106.7(2)
Ga(1)−O(12)−Ti(1)	127.1(2)	C(41)−Ga(1)−C(51)	115.8(3)
Ga(1)−O(12)−Ti(2)	125.5(2)	C(41)−Ga(1)−C(61)	113.8(3)
O−Ti−C(1)	86(1)	C(51)−Ga(1)−C(61)	110.2(2)

the classification proposed by Malone and co-workers ($d_{\pi CH}$ = 2.78 Å, d = 0.66 Å, θ = 76.1°, α = 147°).[34]

The gallium−oxygen bond distance is ~0.1 Å longer than that found for $[Ph_3Al(\mu_3\text{-}O)(\mu\text{-}O)_2\{Ti(\eta^5\text{-}C_5Me_5)\}_3(\mu_3\text{-}CH)]$[32] indicating a weaker strength. Incorporation of the $GaPh_3$ moiety into the organometallic ligand **1** does not produce strong geometrical distortions; in fact, only the Ti(1)−O(12)−Ti(2) and O(12)−Ti(1)−O(13) angles are ~3° narrower.

On the other hand, the NMR spectra for complexes **3** and **4** show a single set of signals assigned to the $\eta^5\text{-}C_5Me_5$ ligands, indicating a local C_{3v} symmetry for the alkylidyne starting material **1**. This experimental fact suggests the existence of a fluxional process involving free rotation of the preorganized oxo derivative **1** around the lithium gallate fragment, as that observed in complexes $[\{(thf)(Me_3Si)_2NM\}(\mu_3\text{-}O)_3\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CCH_2)\}]$ (M = Ca, Sr)[35] and $[\{Cl_2(RN)Ti\}(\mu_3\text{-}NH)_3\{Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$ (R = CMe_3, 2,4,6-$Me_3C_6H_2$).[36] The $\mu\text{-}NMe_2$ and μ-O-2,6-$Me_2C_6H_3$ moieties show their characteristic signals, while the μ_3-CH units were not detected in the $^{13}C\{^1H\}$ NMR spectra, likely due to the aforementioned fluxional process.

The presence of the redistribution fragments $[Ga(O\text{-}2,6\text{-}Me_2C_6H_3)_2Ph_2]^-$ and $[GaPh_4]^-$, with a total contribution of 14% in the spectrum of **4**, is confirmed by an additional set of signals in the aromatic zone and a broadening of the resonance signals corresponding to the methyl groups of the aryloxide fragment, which were solved at −60 °C.

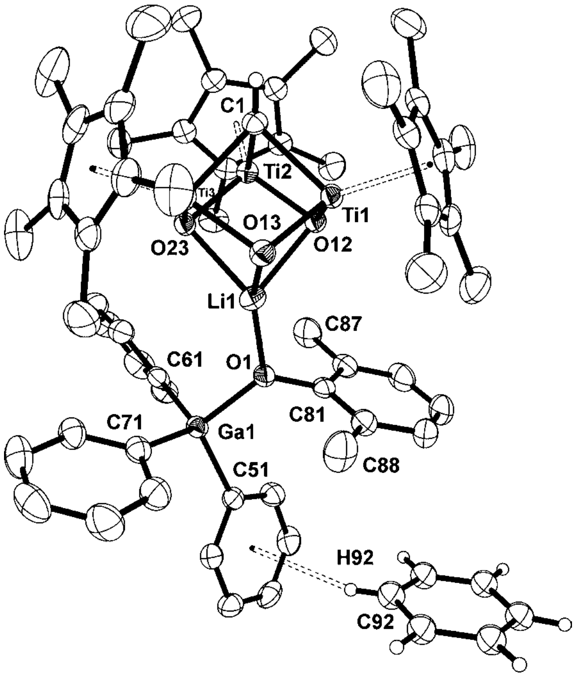


Figure 3. Molecular structure of $[Ph_3Ga(\mu\text{-}O\text{-}2,6\text{-}Me_2C_6H_3)Li(\mu_3\text{-}O)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CH)] \cdot C_6D_6$ ($\mathbf{4} \cdot C_6D_6$) with thermal ellipsoids at the 50% probability level.

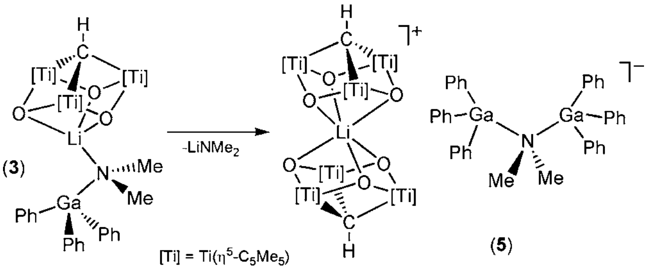
Table 3. Selected Averaged Lengths and Angles for $4 \cdot C_6D_6$

selected averaged lengths (Å)		selected averaged angles (deg)	
Ti−C(1)	2.077(6)	Ti−C(1)−Ti	85.9(1)
Ti−O	1.854(6)	Ti−O−Ti	99.8(1)
Ti···Ti	2.836(2)	Ti−O−Li(1)	90.5(5)
Li(1)−O(12)	2.155(6)	O−Ti−O	96.6(2)
Li(1)−O(13)	2.153(5)	O(12)−Li(1)−O(1)	122.2(3)
Li(1)−O(23)	2.108(5)	O(13)−Li(1)−O(1)	134.2(3)
Li(1)−O(1)	1.831(5)	O(23)−Li(1)−O(1)	137.2(3)
Ga(1)−O(1)	1.960(2)	Li(1)−O(1)−Ga(1)	123.3(2)
Ga−C	2.006(5)	Li(1)−O(1)−C(81)	113.2(2)
C(81)−O(1)	1.370(3)	Ga(1)−O(1)−C(81)	123.1(2)
C(81)−Li(1)	2.684(6)	O(1)−Ga(1)−C(51)	107.9(1)
		O(1)−Ga(1)−C(61)	105.7(1)
		O(1)−Ga(1)−C(71)	105.9(1)

Single crystals of $\mathbf{4} \cdot C_6D_6$ were grown after very slow evaporation of a benzene-d_6 solution. An analysis (Figure 3) of the structure shows how the μ_3-alkylidyne metalloligand $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ (**1**) stabilizes the lithium gallate through a tridentate coordination to the lithium atom, building a cube-type $[LiTi_3O_3C]$ core, and simultaneously a type III[34] weak C−H···π interaction ($d_{\pi CH}$ = 3.01 Å, d = 0.43 Å, θ = 81.8°, α = 144°) between the C(92)−H(92) bond of the benzene solvent molecule and the C(51)−C(56) phenyl ring is established. Those lithium−oxygen bond lengths are in the range 2.108(5)−2.155(6) Å (see Table 3). These distances are slightly shorter than those found for $[Et_3Al(\mu\text{-}O\text{-}2,6\text{-}Me_2C_6H_3)Li(\mu_3\text{-}O)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CMe)]$ [2.134(6)−2.273(6) Å].[22] On the other hand, the Li(1)−O(1) bond distance, 1.831(5) Å, is significantly shorter than those to the titanium organometallic ligand but similar to those reported for $[Li(OEt_2)(\mu\text{-}BHT)\{\mu\text{-}OC(Me)Ph_2\}AlMe(BHT)]$[7] [1.910(7) and 1.922(7) Å], $[Li(thf)_2(\mu\text{-}OCH_2Ph)_2Al(\{o\text{-}(C_5H_9)\text{-}NC_6H_4\}_2O)]$[37] [1.897(11) and 1.918(12) Å], $[Li(thf)_3(\mu\text{-}OH)Ga(Mes)_3]$[4] [1.831(15) Å], and $[Li(\mu\text{-}BHT)_2AlMe_2]$[8] [1.848(5) and 1.888(4) Å]. Thus, the spatial environment of Li(1) in $\mathbf{4} \cdot C_6D_6$ resembles the arrangements of other lithium atoms in $[In_2(SiMePh_2)_3(OH)_3Li_2(thf)_3]$ (1.86−2.27 Å)[38] and $[Li(\mu_4\text{-}O)(\mu_3\text{-}O)_2\{Ti(\eta^5\text{-}C_5Me_5)\}_3(\mu_3\text{-}C)]_2$[39] (2.057−2.386 Å). The gallium atom exhibits a distorted tetrahedral environment with a Ga(1)−O(1) bond length of 1.960(2) Å, slightly longer than that shown by $[Li(thf)_3(\mu\text{-}OH)Ga(Mes)_3]$[4] [1.936(9) Å] but shorter than those observed for the adducts $[GaMe_2(C(SiMe_3)_3)(thf)]$,[40] $[Ga(CH_2Ph)_3(thf)]$,[41] and $[Ga(o\text{-}MeC_6H_4)_3OEt_2]$,[42] with values in the range 2.069−2.182 Å. Similarly to the situation mentioned for **2**, incorporation of the lithium metallate into the starting material **1** modifies the O−Ti−O angles by approximately 8°.

Whereas complex **4** is stable in benzene-d_6 solutions for long periods of time, the analogous compound **3** undergoes a chemical rearrangement to give complex **5** as an orange microcrystalline solid (yield 39%) that owns the lithium dicubane fragment $[Li\{(\mu_3\text{-}O)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CH)\}_2]^+$ and the unusual dinuclear anion $[Ph_3Ga(\mu\text{-}NMe_2)GaPh_3]^-$ (see Scheme 2). Complex **5** proved to be stable in the solid state under argon atmosphere at room temperature, and it is scarcely soluble in benzene or toluene and insoluble in hexane.

Scheme 2. Synthesis of Complex 5



Due to the low solubility of **5**, only by heating at 60 °C could a satisfactory ^1H NMR spectrum be recorded. As a more remarkable feature, the spectrum shows a singlet at $\delta = 1.83$ for the methyl groups of the pentamethylcyclopentadienyl ligands, in agreement with the proposed structure depicted in Scheme 2 where the $[Li\{(\mu_3\text{-}O)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CH)\}_2]^+$ fragment exhibits C_{3v} symmetry. This resonance is approximately 0.1 ppm low-field-shifted with respect to the signal found for the monocubane species **3** (C_5Me_5, $\delta = 1.74$).

The solvent-separated ion pair nature of complex **5** was confirmed by a single-crystal X-ray diffraction study, as can be seen in Figure 4. The cationic fragment comprises two trinuclear $[Ti_3(\eta^5\text{-}C_5Me_5)_3O_3C]$ units that are joined to each other by a lithium metal atom, which lies on the center of symmetry. In that arrangement, the tridentate organometallic ligands situate the pentamethylcyclopentadienyl groups in a relative alternate disposition.

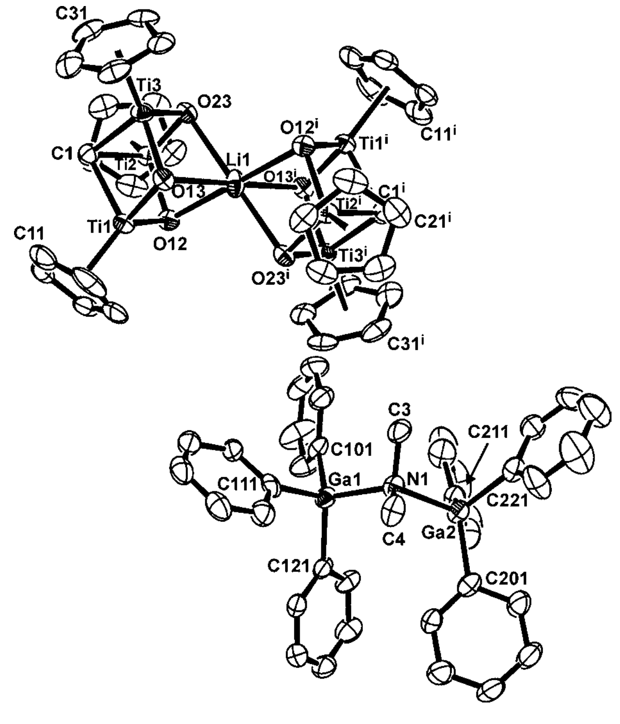


Figure 4. Molecular structure of $[Li\{(\mu_3\text{-}O)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CH)\}_2][Ph_3Ga(\mu\text{-}NMe_2)GaPh_3]$ ($5{\cdot}2C_6D_6$) with thermal ellipsoids at the 50% probability level. Symmetry transformation (i) $-x, -y + 1, -z$. Solvent molecules and methyl groups from the $\eta^5\text{-}C_5Me_5$ ligands have been omitted for clarity.

According to the values of the O–Li–O angles (see Table 4), the lithium atom shows a trigonal antiprism geometry with an averaged Li–O bond distance of 2.25(3) Å, which is almost identical to that found for the aluminum derivative $[Li\{(\mu_3\text{-}O)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CH)\}_2][Li\{(\mu\text{-}O\text{-}Me_2C_6H_3)AlPh_3\}_2]$[22] but approximately 0.1 Å longer than those found in different hexacoordinate lithium crown ether[43] and spiro complexes.[44] Geometrical parameters of the organometallic ligands are similar to those shown by the starting material **1**, except the O–Ti–O angles that are ~7° narrower to acquire the cube arrangement in **5**.

Table 4. Selected Averaged Lengths and Angles for $5{\cdot}2C_6D_6$

	Selected Averaged Lengths (Å)		
Ti–C(1)	2.075(5)	Ti–O	1.858(5)
Li–O	2.25(3)	Ga–N(1)	2.051(1)
Ti···Ti	2.842(6)	Ga–C	2.01(1)
N(1)–C	1.490(1)		
	Selected Averaged Angles (deg)		
Ti–(μ_3-C)–Ti	86.4(3)	Ti–O–Ti	99.8(3)
O–Li(1)–O[a]	76.5(9)	O–Ti–O	97.4(3)
O–Li(1)–O[b]	103.4(9)	N(1)–Ga–C	108(2)
Ti–O–Li	91.9(8)	C–Ga–C	111(2)
O–Ti–(μ_3-C)	86.6(3)	C(3)–N(1)–C(4)	106.7(4)
Ga(1)–N(1)–Ga(2)	120.8(2)	Ga–N(1)–C	107(1)

[a] Intracube. [b] Intercubes.

Figure 4 also shows how the anionic moiety in **5** consists of two $GaPh_3$ units linked by one dimethylamido group, resembling dizincate anions like $[Zn_2Et_5]^-$ and $[Zn_2(C_5H_5)_5]^-$.[45] It is noticeable that, to our knowledge, there is only one dinuclear structure in the literature where only one amido group is acting as a bridge between the two gallium metal centers, the complex $[Cl_2Ga\{(NEt_2)_2SiMe_2\}]\text{-}[(Cl_3Ga)_2(NEt_2)]$.[46] If we compare both anionic fragments, we can observe how complex **5** presents a Ga–N–Ga angle ~8° wider than that reported for the diethylamide derivative. This geometrical difference could be due to the existence of a type III weak C–H···π interaction ($d_{\pi CH} = 2.65$ Å, $d = 0.80$ Å, $\theta = 72.4°$, $\alpha = 134.8°$)[34] between C(202)–H(202) and the C(121)–C(126) phenyl ring and the steric hindrance of the aromatic substituents.

Each gallium atom adopts a distorted tetrahedral environment with averaged Ga–N bond distances of 2.051(1) Å, value slightly shorter than those found for the adducts $[GaMe_3\{NHMe(NH_2)\}]$ [2.114(2) Å],[47] $[Ga_2Me_6(14\text{-aza-crown-4})]$ [2.124(4) Å],[48] and $[Ga_2Me_6(dabco)]$ [2.154(9) Å],[49] in agreement with the stronger Lewis acid character of the phenyl gallium derivatives. Furthermore, the above-mentioned $[(Cl_3Ga)_2(NEt_2)]^-$ fragment, with more electronegative substituents linked to gallium, presents still shorter gallium–nitrogen distances [1.995(7) and 1.977(6) Å][46] than those of **5**.

Once the described results, about the capability of the titanium oxoligand **1** to develop co-complexation reactions with different lithium aryloxide/amide gallates, were known, we decided to extend this study to lithium alkyl derivatives. In this sense, treatment of adduct **2** with $Li(p\text{-}MeC_6H_4)$, in a similar fashion to path A in Scheme 1, afforded an intractable mixture of products. Fortunately, the equimolecular reaction in benzene-d_6 of complex **1** with $GaPh_3$ and Li(p-MeC_6H_4) (path B) apparently produced only one product, later identified as **6**. Slow evaporation of the solution led us to obtain single crystals, suitable for the corresponding X-ray diffraction study. Figure 5 shows the molecular structure of the new compound **6a**, while the averaged values of distances and angles are summarized in Table 5.

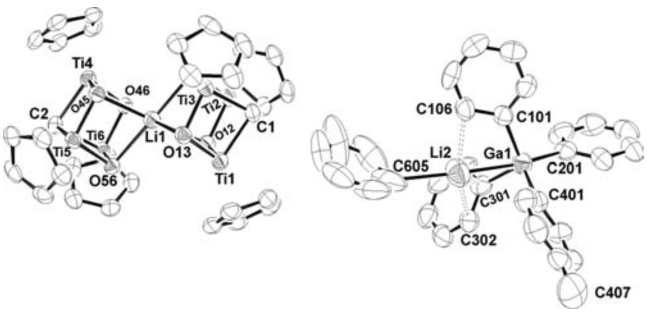


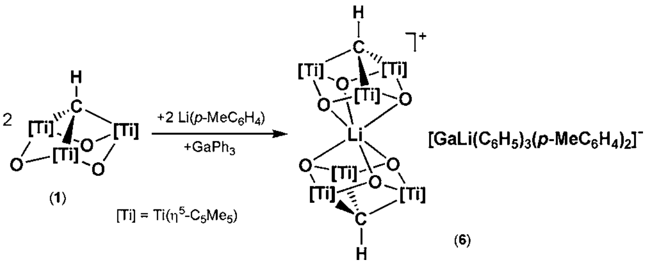
Figure 5. Molecular structure of [Li{(μ_3-O)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-CH)}$_2$] [PhLi(μ-Ph)$_2$Ga(p-MeC_6H_4)Ph] (**6a**·$2C_6D_6$) with thermal ellipsoids at the 50% probability level. Solvent molecules and methyl groups from the η^5-C_5Me_5 ligands have been omitted for clarity.

Complex **6a** presents a solvent-separated ion pair nature with a lower content in $GaPh_3$ units than expected. While the cation is identical to that formed in **5**, with similar values for the geometrical parameters, the anionic fragment consists of a [Ga(p-MeC_6H_4)Ph_3]$^-$ moiety linked to a LiPh unit.

The gallium atoms exhibits a distorted tetrahedral environment with Ga(1)−C bond distances [average 2.02(2) Å] analogous to those found in the [Ga(C_6F_5)$_4$]$^-$ gallate[50] [2.011(4) Å]. On the other hand, Li(2) is close enough to the [Ga(p-MeC_6H_4)Ph_3]$^-$ fragment to establish π interactions with the C(301) [2.14(1) Å] and C(302) [2.47(1) Å] carbon atoms of the C(301)−C(306) aromatic ring. The distance to C(301) is similar to the value of 2.129(4) Å reported for the lithium homocuprate [$Cu_2Li_2Mes_4$],[51] where a κC^1 lithium aryl interaction is suggested. However, the difference of 0.3 Å between the distances from Li(2) to C(301) and C(302) resembles the interaction reported by Power and co-workers[52] for the complex [LiO{2,6-(2,6-^{i}PrC_6H_3)$_2C_6H_3$}]$_2$ [2.390(3) and 2.647(3) Å], although these lengths are more similar to those from Li(2) to C(106) and C(101), being in this case the closer interaction to the carbon atom in ortho position. All these interactions between Li(2) and the [Ga(p-MeC_6H_4)-Ph_3]$^-$ fragment can be related to the enlargement of the Li(2)−C(605) bond distance [2.49(2) Å] with respect to that found for the solid structure of LiPh [2.242(14)−2.342(14) Å] determined by synchrotron powder diffraction.[53] Finally, a type III weak C−H···π interaction is established between one of the benzene solvent molecules and the phenyl ring of the p-MeC_6H_4 substituent ($d_{\pi CH}$ = 3.04 Å, d = 0.62 Å, θ = 78.3°, α = 132.8°).[34]

In accord with the contents shown by the crystal structure of **6a**, we proceeded to carry out the reaction of a mixture of Li(p-MeC_6H_4)/$GaPh_3$ in a 2:1 ratio with 2 equiv of complex **1** in toluene (see Scheme 3). After stirring at room temperature for 2 days and the solution workup, a yellow solid was obtained and characterized as **6** (yield 33%).

Scheme 3. Preparative-Scale Method to Obtain Complex 6



The ^{1}H and ^{13}C{^{1}H} NMR spectra of **6** at 333 K[26] show only one set of signals for the pentamethylcyclopentadienyl rings, in agreement with the C_{3v} symmetry of the shared vertex double cube structure. But the NMR spectra of this complex do not match with the anionic fragment of **6a**. Thus, the signals observed in the ^{1}H NMR spectrum confirm the presence of two p-MeC_6H_4 and three phenyl rings in the lithium gallate unit. The difference between the crystal structure of **6a** and the

Table 5. Selected Averaged Lengths and Angles for 6a·$2C_6D_6$

Selected Averaged Lengths (Å)			
Ti−(μ_3-C)	2.07(1)	Li(2)−C(101)	2.60(1)
Ti−O	1.85(1)	Li(2)−C(106)	2.31(1)
Ti···Ti	2.831(7)	Li(2)−C(301)	2.14(1)
Li(1)−O	2.24(3)	Li(2)−C(302)	2.47(1)
Ga(1)−C	2.02(2)	Li(2)−C(605)	2.49(2)
Ga(1)−Li(2)	2.46(1)		
Selected Averaged Angles (deg)			
Ti−(μ_3-C)−Ti	86.0(2)	O−Li(1)−O[a]	76.5(6)
Ti−O−Ti	100.0(4)	O−Li(1)−O[b]	103(1)
O−Ti−O	97.3(3)	Ga(1)−C(301)−Li(2)	72.7(4)
Ti−O−Li	91.9(6)	C(101)−Ga(1)−C(201)	108.5(2)
O−Ti−(μ_3-C)	86.7(4)	C(101)−Ga(1)−C(301)	109.2(2)
C(101)−Ga(1)−Li(2)	70.1(3)	C(101)−Ga(1)−C(401)	111.5(2)
C(201)−Ga(1)−Li(2)	163.2(4)	C(201)−Ga(1)−C(301)	110.9(2)
C(301)−Ga(1)−Li(2)	56.2(3)	C(201)−Ga(1)−C(401)	109.2(2)
C(401)−Ga(1)−Li(2)	86.2(4)	C(301)−Ga(1)−C(401)	107.4(2)

[a] Intracube. [b] Intercubes.

NMR spectra obtained for **6** could be explained by the existence of an interchange process involving the p-MeC_6H_4 linked to lithium and one of the phenyl groups of other $GaPh_3$ molecule, in excess during the crystallization process.

■ CONCLUSIONS

The molecular organometallic oxide $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}CH)]$ (**1**) is able to co-complex with different lithium gallates by direct reaction or formation of the $GaPh_3$ adduct in the first place, and subsequent treatment with the corresponding lithium amide, aryloxide, or aryl derivative. All these reactions lead to contact ion pair species. On the other hand, the stability of the $[Li\{(\mu_3\text{-}O)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CH)\}_2]^+$ dicubane fragments could be the driving force to afford solvent-separated ion pair species by evolution of the starting contact ion pair derivatives, leading to singular anionic gallate fragments.

Also, it is important to note that the existence of weak C−H···π interactions between the benzene solvent and phenyl rings of $GaPh_3$ has enabled us to obtain of suitable single crystals, a task that has not been achieved with the use of other solvents.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic information file (CIF) for **1**, **2**, **4**, **5**, and **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

†Dedicated to the memory of Professor Francisco Urbanos Urbanos, who died on May 28, 2011.

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