Contact and Solvent-Separated Ion Pair Aluminium 'ate Complexes on a Titanium Oxide Molecular Model.

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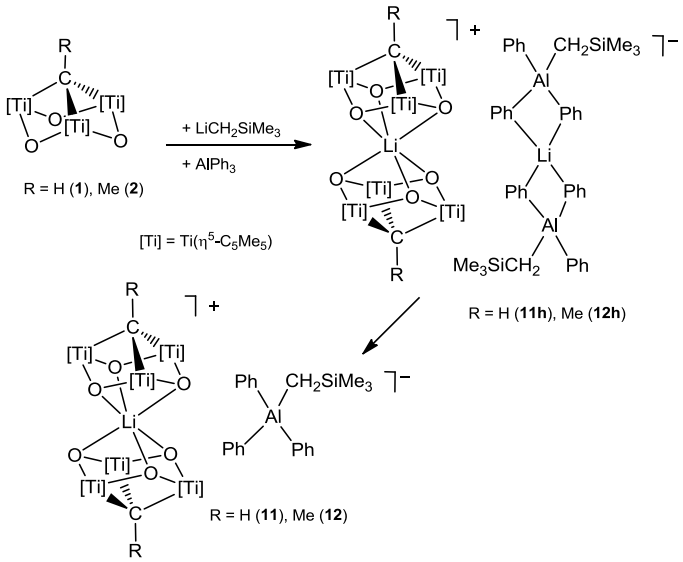
ELECTRONIC SUPPLEMENTARY INFORMATION

Reactions between 1 and 2 and the 'ate complex Li[Al(CH_2SiMe_3)Ph_3] prepared *in situ*

It was possible to synthesize two new complexes **11h** and **12h** in low-moderate yield (31-81%) by using the reaction of "[LiAl(CH_2SiMe_3)Ph_3]" prepared *in situ* with the oxoligands **1** or **2** (see Scheme SI1).



Scheme SI1.

In all cases the majority products [Li{(μ_3-O)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-CR)}$_2$][Li{(μ-Ph)$_2$Al(CH_2SiMe_3)Ph}$_2$] [R = H (**11h**), Me (**12h**)] appear together with the corresponding redistribution products of the alkyl groups between aluminium centres. The structure of these species could not be determined by X-ray diffraction studies, however their characterization by NMR spectroscopy and the existence in the bibliography of the fragment[1] $[Li(Me_2Al^tBu_2)_2]^-$ let us to propose a structural disposition as outlined in Scheme SI1. Complex **11h** is a yellow solid, soluble in aromatic solvents but scarcely soluble in hexane, while complex **12h** is an orange solid, hardly soluble in aromatic solvents and insoluble in hexane; both are stable for long periods of time under argon atmosphere.

The ^{1}H and ^{13}C NMR spectra of **11h** and **12h** show a single set of signals for the η^5-C_5Me_5 ligands and the corresponding of the μ_3-CR fragment. Moreover, different resonance signals for the Ph and $-CH_2SiMe_3$ groups linked to aluminium and/or lithium are observed. Karsch and coworkers[2] attribute these signals to redistribution products generated in heteroleptic aluminate species by formation of $[Li(\mu\text{-}R)_2AlR_2]$ fragments. By the other hand, the presence of alkyl bridges between aluminium and lithium metal centres has been reported for complexes $[LiAlEt_4]$[3] and $[LiN(SiMe_2CH_2P^iPr_2)_2LiAlMe_4]$.[4] Finally, the resonance signals of the $AlCH_2Si\mathit{Me}_3$ fragment in the $^{13}C\{^{1}H\}$NMR spectra for **11h** and **12h** are in the range found for other complexes as $[LiAl(CH_2SiMe_3)_4]$ [δ = 3.78 ($Si\mathit{Me}_3$)], $[Li(tmeda)_2][Al(CH_2SiMe_3)_4]$ [δ = 4.23 ($Si\mathit{Me}_3$)] or $[Li(12\text{-crown-}4)_2][Al(CH_2SiMe_3)_4]$ [δ= 4.23 ($Si\mathit{Me}_3$)].[5]

Experimental

Reaction of 1 with "[LiAl(CH$_2$SiMe$_3$)Ph$_3$]" in hexane. A suspension formed by 0.127 g (0.49 mmol) of $AlPh_3$, 0.046 g (0.49 mmol) of $Li(CH_2SiMe_3)$ and 20 mL of hexane was prepared and cooled at -35ºC. After one hour of stirring, 0.300 g (0.49 mmol) of **1** was added and the resulting suspension was left stirring for one hour. By filtration, 0.338 g (yield 81%) of complex $[Li\{(\mu_3\text{-}O)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CH)\}_2][Li\{(\mu\text{-}Ph)_2Al(CH_2SiMe_3)Ph\}_2]$ **(11h)** was isolated together with small amounts of the redistribution products $[Li\{(\mu_3\text{-}O)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}CH)\}_2][Li\{(\mu\text{-}Ph)_2Al(CH_2SiMe_3)_2\}_2]$ and $[Li\{(\mu_3\text{-}O)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}CH)\}_2][Li\{(\mu\text{-}Ph)_2AlPh_2\}_2]$.

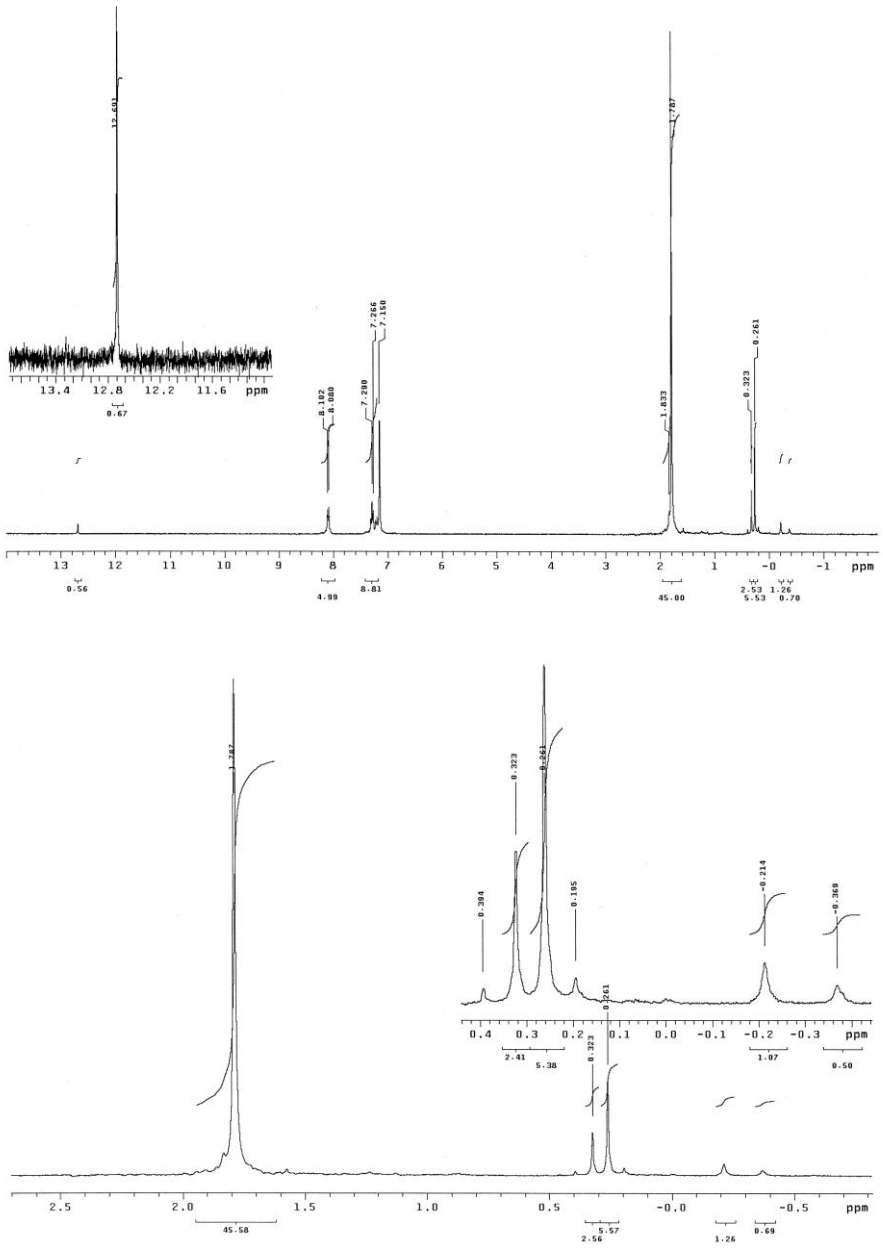


Table SI1.- NMR data for complex **11h** in benzene-d_6.

		^{1}H NMR	^{13}C{^{1}H} NMR
benzene-d_6 ***T* = 333K**	Al***C*$_6$*H*$_5$**	7.21 (6H), 7.29 (12H), 8.10 (12H)	126.6 - 139.6
	CH$_2$SiMe$_3$	-0.37,[a] -0.21 (s, 4H)	Not detected
	CH$_2$Si***Me***$_3$	0.26, 0.32[a] (s, 18H)	3.8
	C$_5$***Me***$_5$	1.79 (s, 90H)	11.8
	C$_5$Me$_5$		121.7
	μ_3–***CH***	12.69 (s, 2H)	Not detected

[a] Signal assigned to redistribution products.

Reaction of 2 with "[LiAl(CH_2SiMe_3)Ph_3]" in hexane. In a 100 mL-Schlenk 0.083 g (0.32 mmol) of $AlPh_3$, 0.030 g (0.32 mmol) of Li(CH_2SiMe_3) and 20 mL of hexane were placed and cooled at -35ºC. After one hour of stirring, a suspension of **2** (0.200g, 0.32 mmol) in 20 ml of hexane was added and the reaction mixture immediately turned to red colour. After one hour stirring an orange solid was filtered and washed with cooled hexane (-35ºC). This method let to obtain 0.098 g (yield 31%) of compound [Li{(μ_3-O)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ_3-CMe)}$_2$][Li{(μ-Ph)$_2$Al(CH_2SiMe_3)Ph}$_2$] (**12h**) together with the redistribution products [Li{(μ_3-O)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ-CMe)}$_2$][Li{(μ-Ph)$_2$ Al(CH_2SiMe_3)$_2$}$_2$] and [Li{(μ_3-O)$_3$Ti$_3$(η^5-C_5Me_5)$_3$(μ-CMe)}$_2$][Li{(μ-Ph)$_2$AlPh$_2$}$_2$].

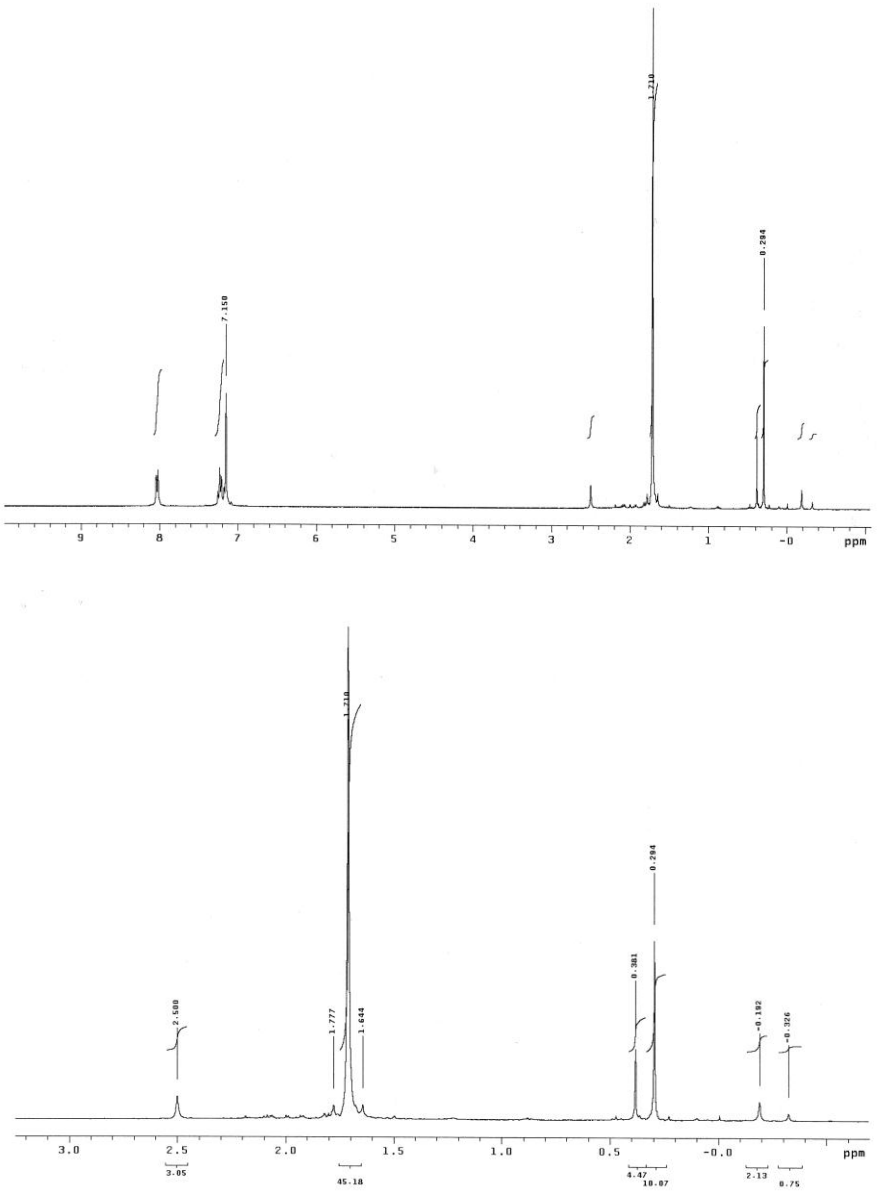


Table SI2.- NMR data for complex **12h in** benzene-d_6

		^{1}H NMR	^{13}C{^{1}H} NMR
benzene-d_6 r.t.	Al***C*$_6$*H*$_5$**	7.17 - 7.25 (18H), 8.03 (12H)	126.3 - 139.5
	CH$_2$SiMe$_3$	-0.33,[a] -0.19 (s, 4H)	Not detected
	CH$_2$Si***Me***$_3$	0.29, 0.38[a] (s, 18H)	3.6, 3.9
	C$_5$***Me***$_5$	1.71 (s, 90H)	11.3
	C$_5$Me$_5$		122.1 (bs)
	μ_3–C***Me***	2.50 (s, 6H)	40.1
	μ_3–***C***Me		Not detected

[a] Signals assigned to redistribution products.

Table SI3. Crystal data and structure refinement for **8**, **12** and **13**.

Compound	**8·C_6D_6**	**12·4C_7H_8**	**13**
empirical formula	$C_{52}H_{59}AlLiNO_3Ti_3 \cdot C_6D_6$	$C_{86}H_{122}AlLiO_6SiTi_6 \cdot 4C_7H_8$	$C_{41}H_{62}AlLiO_3Ti_3$
formula weight	1011.81	1969.78	780.53
temperature **[K]**	200(2)	200(2)	200(2)
wavelength **($Mo_{K\alpha}$) [Å]**	0.71073	0.71073	0.71073
crystal system	triclinic	monoclinic	Triclinic
space group	*P*-1	$P2_1$	*P*-1
a [Å]; α(°)	10.979(2);71.85(1)	13.803(2)	10.3218(7);88.66(1)
b **[Å];** β**(°)**	13.828(2);89.76(2)	27.796(9);98.392(6)	11.081(3);84.202(5)
c **[Å];** γ**(°)**	20.427(3);68.07(2)	14.222(1)	19.595(1);67.90(1)
volume **[Å^3];** ***Z***	2711.4(8); 2	5398(2); 2	2065.6(5); 2
ρ_{calcd} **[g·cm^{-3}]**	1.239	1.212	1.216
μ **[mm^{-1}]**	0.490	0.493	0.622
F(000)	1072	2096	828
crystal size **[mm^3]**	0.35 x 0.22 x 0.12	0.45 x 0.42 x 0.30	0.26 x 0.19 x 0.17
θ ***range***	3.06 to 27.50°	3.06 to 24.99°	3.14 to 25.00°
index ranges	-14 to 14, -17 to 17, -25 to 26	-16 to 15, -32 to 33, 0 to 16	-12 to 12, -13 to 13, -23 to 23
collected reflections	46054	56242	22974
independent reflections	12356 [R_{int}=0.090]	17265 [R_{int}=0.061]	7217 [R_{int}=0.096]
goodness-of-fit on F^2	1.063	0.969	0.934
final R indices **[F>4σ(F)]**	R1=0.066, wR2=0.159	R1=0.081, wR2=0.191	R1=0.052, wR2=0.105
R indices **(all data)**	R1=0.153, wR2=0.196	R1=0.142, wR2=0.224	R1=0.114, wR2=0.121
largest diff. peak/hole [eÅ^{-3}]	0.784/-0.607	0.582/-0.495	0.408/-0.345

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