Supporting Information for

Grafting trimethylaluminum and its halogen derivatives on silica: General trends for ^{27}Al SS-NMR response from first principles calculations

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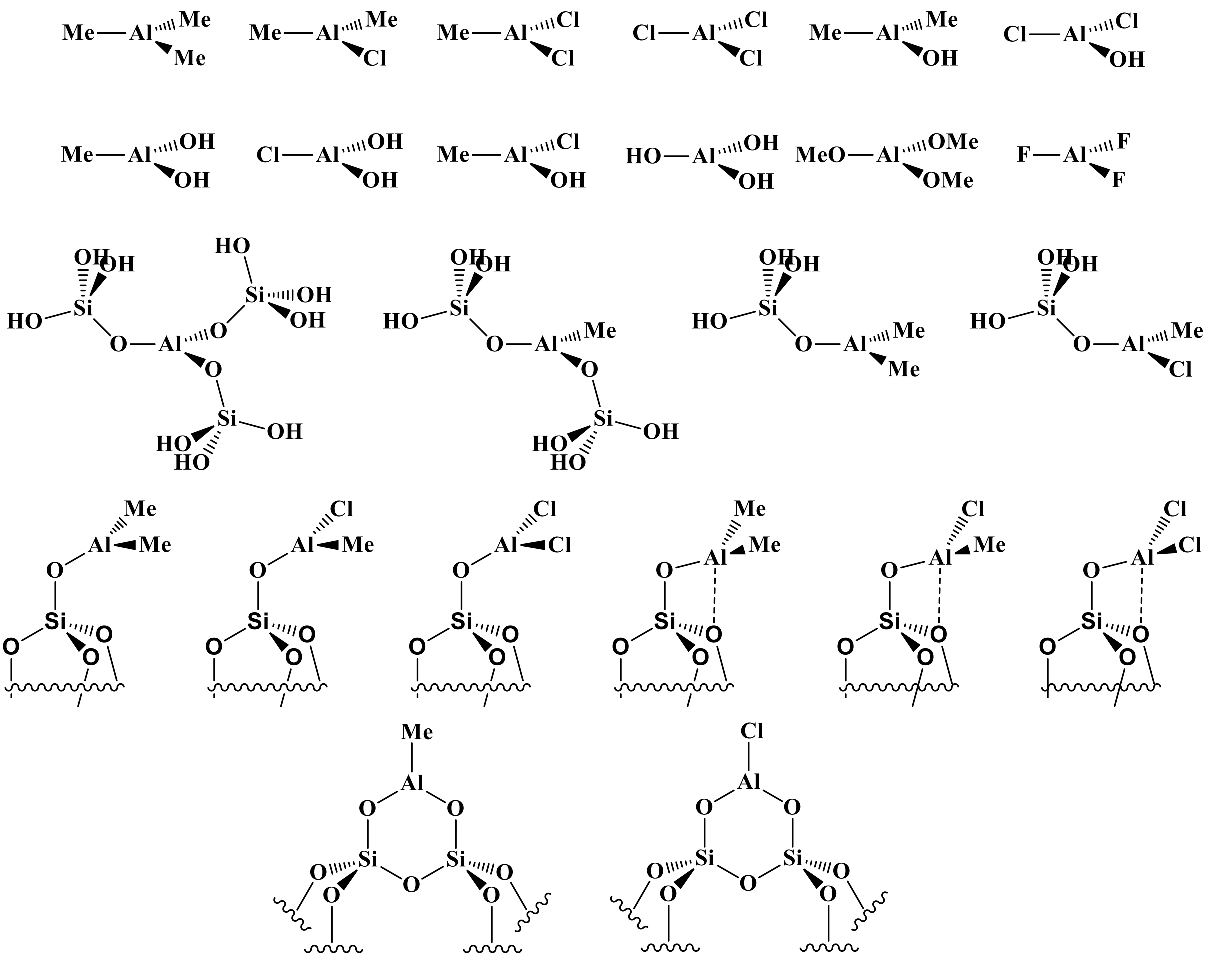
Monomers in gas-phase and grafted		
Species	**δ_{ISO} (ppm)**	**$\|C_Q\|$ (MHz)**
Gas-phase		
AlF_3	57	36
$AlCl_3$	149	29
$Al(OH)_3$	96	33
$Al(OH)_2Cl$	110	32
$Al(OH)Cl_2$	129	30
$Al(OH)_2Me$	143	36
$Al(OH)Me_2$	221	41
Al(OH)MeCl	165	35
$Al(OMe)_3$	70	32
$Al(Me)_3$	321	47
$AlMe_2Cl$	261	40
$AlMeCl_2$	197	34
Cluster models		
$Al(OSi(OH)_3)_3$	52	36
$AlMe(OSi(OH)_3)_2$	123	38
$AlMe_2(OSi(OH)_3)$	214	42
$AlMeCl(OSi(OH)_3)$	151	36
Surface models		
$O_{SURF}AlMe_2$	228	43
$(O_{SURF})_2AlMe_2$	174	34
$O_{SURF}AlMeCl$	165	37
$(O_{SURF})_2AlMeCl$	127	25
$O_{SURF}AlCl_2$	122	32
$(O_{SURF})_2AlCl_2$	95	18
$(O_{SURF})_2AlMe$	134	37
$(O_{SURF})_2AlCl$	103	33

Table S1. DFT-calculated ^{27}Al NMR parameters δ_{ISO} (ppm) and C_Q (MHz) for all monomeric species presented in Figure 1.



Scheme S1. Schematic representation of all models of Al monomers used in the 2D map: $AlMe_3$, $AlMe_2Cl$, $AlMeCl_2$, $AlMe_2OH$, $AlCl_2OH$, $AlMe(OH)_2$, $AlCl(OH)_2$, $AlMeClOH$, $Al(OH)_3$, $Al(OMe)_3$, AlF_3, $Al(OSi(OH)_3)_3$, $AlMe(OSi(OH)_3)_2$, $AlMe_2(OSi(OH)_3)$, $AlMeCl(OSi(OH)_3)$, $-O_{SURF}AlMe_2$, $-O_{SURF}$ $AlMeCl$, $-O_{SURF}$ $AlCl_2$, $-O_{SURF}AlMe_2$ O_{SURF}, $-O_{SURF}AlMeCl$ O_{SURF}, $-O_{SURF}AlCl_2$ O_{SURF}, $(O_{SURF})_2-AlMe$, $(O_{SURF})_2-AlCl$.

^{27}Al SS-NMR for dimeric species

Dimeric species in gas phase

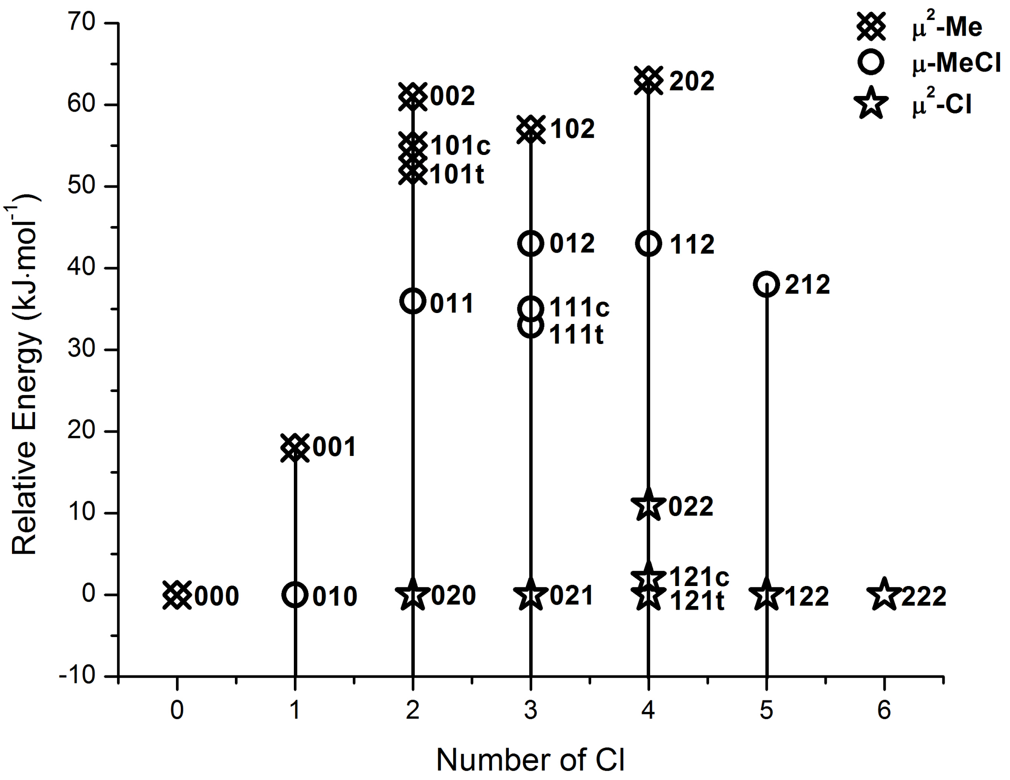


Figure S1 Relative energy as a function of the number of Cl for the dimers in gas phase with general formula $Me_nCl_{2-n}Al1(\mu^2\text{-}Me_nCl_{1-n})Al2Me_nCl_{2-n}$. The small c and t, stand for cis and trans isomers, respectively. The crossed diamond represents Me in bridge position, the circle corresponds to mixed MeCl bridge, and the star shows that in bridge we have Cl. The position of the Cl atoms is indicated as in the main text of the paper.

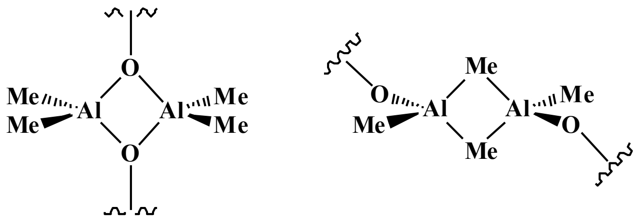
Species	Relative energies of gas-phase dimers							
	Cl position	Number of Cl atoms						
		0	1	2	3	4	5	6
Me2Al1(μ^2-Me)Al2Me_2	000	-	-	-	-	-	-	
Me_2Al1(μ-MeCl)Al2Me_2	010	-	**0**	-	-	-	-	
Me_2Al1(μ^2-Me)Al2MeCl	001	-	18	-	-	-	-	
Me2Al1(μ^2-Cl)Al2Me_2	020	-	-	**0**	-	-	-	
Me2Al1(μ-MeCl)Al2MeCl	011	-	-	36	-	-	-	
MeClAl1(μ^2-Me)Al2MeCl	101t	-	-	52	-	-	-	
MeClAl1(μ^2-Me)Al2MeCl	101c	-	-	55	-	-	-	
Me2Al1(μ^2-Me)Al2Cl_2	002	-	-	61	-	-	-	
Me2Al1(μ^2-Cl)Al2MeCl	021	-	-	-	**0**	-	-	
MeClAl1(μ-MeCl)Al2MeCl	111t	-	-	-	33	-	-	
MeClAl1(μ-MeCl)Al2MeCl	111c	-	-	-	35	-	-	
Me_2Al1(μ-MeCl)Al2Cl_2	012	-	-	-	43	-	-	
MeClAl1(μ^2-Me)Al2Cl_2	102	-	-	-	57	-	-	
MeClAl1(μ^2-Cl)Al2MeCl	121t	-	-	-	-	**0**	-	
MeClAl1(μ^2-Cl)Al2MeCl	121c	-	-	-	-	2	-	
Me_2Al1(μ^2-Cl)Al2Cl_2	022	-	-	-	-	11	-	
MeClAl1(μ-MeCl)Al2Cl_2	112	-	-	-	-	43	-	
Cl_2Al1(μ^2-Me)Al2Cl_2	202	-	-	-	-	63	-	
MeClAl1(μ^2-Cl)Al2Cl_2	122	-	-	-	-	-	**0**	
Cl_2Al1(μ-MeCl)Al2Cl_2	212						38	
Cl_2Al1(μ^2-Cl)Al2Cl_2	222	-	-	-	-	-	-	-

Table S2. Relative energy differences for the bigrafted dimers in gas phase as a function of the number of Cl with general formula Me_nCl_{2-n}Al1-(μ^2-Me_nCl_{1-n})Al2Me_nCl_{2-n}.

Species	Gas-phase dimers			
	Cl positions	**Al**	**δ_{ISO} (ppm)**	**$\|C_Q\|$ (MHz)**
Me_2Al1(μ^2-Me)Al2Me_2	000	Al1	152	25
		Al2	152	25
Me2Al1(μ2-Me)Al2MeCl	0’01	Al1	153	28
	00’1	Al2	134	18
Me2Al1(μ2-Me)Al2Cl2	0’02	Al1	155	31
	00’2	Al2	117	5
MeClAl1(μ2-Me)Al2MeCl c	101c	Al1	131	19
		Al2	131	19
MeClAl1(μ2-Me)Al2MeCl t	**101*t**	Al1	130	20
		Al2	130	20
MeClAl1(μ2-Me)Al2Cl2	1’02	Al1	128	20
	10’2	Al2	112	7
Cl2Al1(μ2-Me)Al2Cl2	202	Al1	107	9
		Al2	107	9
Me2Al1(μ-MeCl)Al2Me2	010	Al1	161	30
		Al2	161	30
Me2Al1(μ-MeCl)Al2MeCl	0’11	Al1	165	34
	01’1	Al2	133	21
Me2Al1(μ-MeCl)Al2Cl2	0’12	Al1	169	36
	01’2	Al2	110	11
MeClAl1(μ-MeCl)Al2MeCl c	111c	Al1	130	22
		Al2	130	22
MeClAl1(μ-MeCl)Al2MeCl t	111t	Al1	132	23
		Al2	132	23
MeClAl1(μ-MeCl)Al2Cl2	1’12	Al1	128	24
	11’2	Al2	107	12
Cl2Al1(μ-MeCl)Al2Cl2	212	Al1	103	12
		Al2	103	12
Me_2Al1(μ^2-Cl)Al2Me_2	**020***	Al1	180	36
		Al2	180	36
Me_2Al1(μ^2-Cl)Al2MeCl	0’21	Al1	183	38
	02’1	Al2	137	24
Me_2Al1(μ^2-Cl)Al2Cl_2	0’22	Al1	183	39
	02’2	Al2	104	13
MeClAl1(μ^2-Cl)Al2MeCl c	121c	Al1	136	25
		Al2	136	25
MeClAl1(μ^2-Cl)Al2MeCl t	121t	Al1	137	25
		Al2	137	25
MeClAl1(μ^2-Cl)Al2Cl_2	1’22	Al1	136	26
	12’2	Al2	103	14
Cl_2Al1(μ^2-Cl)Al2Cl_2	222	Al1	101	16
		Al2	101	16

Table S3. DFT-calculated ^{27}Al NMR parameters δ_{ISO} (ppm) and C_Q (MHz) for all dimeric species in gas-phase presented in Figure 2. Small c and t are indicating the cis and trans position of the substituent. Labels x’yz and xy’z indicate the position of the considered Al

(Al1(left) and Al2(right). In bold are the two dimer references used for the EFG calculations in terms of NBOs and NLMOs.



020 **101t**

Scheme S2. Representation of the two dimers with methyl and oxygen substituents used for the decomposition on localized molecular orbitals.

NLMO contributions	#	020	#	101
BD σ(Al-C)	2	-0.355	1	-0.473
BD σ(Al-O)	2	0.151	1	-0.103
Σσ(Al-X)		-0.408		-0.576
BD σ(C-H)	2	-0.040		-0.109
3C (Al_1-Al_2-C)		-	2	0.116
Al core		-0.396		-0.313
C core	2	-0.056	1	-0.072
O core	2	0.040		-
ΣAnalysis#		-0.916		-0.838
Total calculated ≡ $\|V_{33}\|$		0.773		0.552
NBO charges				
Al		1.829		1.709
Cl		-1.318		-1.314
C_t		-1.268		-1.267
C_{br}		-		-1.240

Table S4 NLMO analysis of aluminum V_{33} (in au) principal component for $Me_2Al1(\mu^2\text{-}OSiH_3)Al2Me_2$ and $Me(OSiH_3)Al1(\mu^2\text{-}Me)Al2Me(OSiH_3)$ dimers in gas phase. Here are presented the following labels: 2-center bond (BD), 3-center bond (3C), and 1-center core pair (CR). "Total calculated" is the actual $|V_{33}|$. ΣAnalysis corresponds to the sums of all terms shown here from NLMO analysis with >5% contribution.

Dimeric species grafted on silica

Monografted dimers

Species	Type / Cl position	Relative energies of monografted dimers					
		Number of Cl atoms					
		0	**1**	**2**	**3**	**4**	**5**
Me$_2$Al1(μ-MeO$_{SURF}$)Al2Me$_2$	2.1 / 000	**0**	-	-	-	-	-
O$_{SURF}$MeAl1(μ^2-Me)Al2Me$_2$	2.2 / 000	27	-	-	-	-	-
Me$_2$Al1(μ-ClO$_{SURF}$)Al2Me$_2$	2.1 / 010	-	**0**	-	-	-	-
Me$_2$Al1(μ-MeO$_{SURF}$)Al2MeCl	2.1 / 001	-	35	-	-	-	-
O$_{SURF}$MeAl1(μ-MeCl)Al2Cl$_2$	2.2 / 010	-	49	-	-	-	-
O$_{SURF}$ClAl1(μ^2-Me)Al2Cl$_2$	2.2 / 100	-	60	-	-	-	-
O$_{SURF}$MeAl1(μ^2-Me)Al2MeCl	2.2 / 001	-	75	-	-	-	-
Me$_2$Al1(μ-ClO$_{SURF}$)Al2MeCl	2.1 / 011	-	-	**0**	-	-	-
MeClAl1(μ-MeO$_{SURF}$)Al2MeCl trans	2.1 / 101t	-	-	8	-	-	-
O$_{SURF}$MeAl1(μ^2-Cl)Al2Me$_2$	2.2 / 020	-	-	14	-	-	-
Me$_2$Al1(μ-MeO$_{SURF}$)Al2Cl$_2$	2.1 / 002	-	-	19	-	-	-
MeClAl1(μ-MeO$_{SURF}$)Al2MeCl cis	2.1 / 101c	-	-	29	-	-	-
O$_{SURF}$ClAl1(μ-MeCl)Al2Me$_2$	2.2 / 110	-	-	48	-	-	-
O$_{SURF}$MeAl1(μ-MeCl)Al2MeCl	2.2 / 011	-	-	58	-	-	-
O$_{SURF}$ClAl1(μ^2-Me)Al2MeCl cis	2.2 / 101c	-	-	69	-	-	-
O$_{SURF}$MeAl1(μ^2-Me)Al2Cl$_2$	2.2 / 002	-	-	78	-	-	-
O$_{SURF}$ClAl1(μ^2-Me)Al2MeCl trans	2.2 / 101t	-	-	80	-	-	-
MeClAl1(μ-ClO$_{SURF}$)Al2MeCl trans	2.1 / 111t	-	-	-	**0**	-	-
Me$_2$Al1(μ-ClO$_{SURF}$)Al2Cl$_2$	2.1 / 012	-	-	-	14	-	-
MeClAl1(μ-ClO$_{SURF}$)Al2MeCl cis	2.1 / 111c	-	-	-	20	-	-
O$_{SURF}$ClAl1(μ^2-Cl)Al2Me$_2$	2.2 / 120	-	-	-	38	-	-
O$_{SURF}$MeAl1(μ^2-Cl)Al2MeCl	2.2 / 021	-	-	-	48	-	-
MeClAl1(μ-MeO$_{SURF}$)Al2Cl$_2$	2.1 / 102	-	-	-	57	-	-
O$_{SURF}$ClAl1(μ-MeCl)Al2MeCl cis	2.2 / 111c	-	-	-	82	-	-
O$_{SURF}$MeAl1(μ-MeCl)Al2Cl$_2$	2.2 / 012	-	-	-	89	-	-
O$_{SURF}$ClAl1(μ-MeCl)Al2MeCl trans	2.2 / 111t	-	-	-	90	-	-
O$_{SURF}$ClAl1(μ^2-Me)Al2Cl$_2$	2.2 / 102	-	-	-	109	-	-
MeClAl1(μ-ClO$_{SURF}$)Al2Cl$_2$	2.1 / 112	-	-	-	-	**0**	-
O$_{SURF}$ClAl1(μ^2-Cl)Al2MeCl cis	2.2 / 121c	-	-	-	-	25	-
O$_{SURF}$MeAl1(μ2-Cl)Al2Cl$_2$	2.2 / 022	-	-	-	-	31	-
O$_{SURF}$ClAl1(μ2-Cl)Al2MeCl trans	2.2 / 121t	-	-	-	-	32	-
Cl$_2$Al1(μ-MeO$_{SURF}$)Al2Cl$_2$	2.1 / 202	-	-	-	-	34	-
O$_{SURF}$ClAl1(μ-MeCl)Al2Cl$_2$	2.2 / 112	-	-	-	-	73	-
Cl$_2$Al1(μ-ClO$_{SURF}$)Al2Cl$_2$	2.1 / 212	-	-	-	-	-	**0**
O$_{SURF}$ClAl1(μ^2-Cl)Al2Cl$_2$	2.2 / 122	-	-	-	-	-	37

Table S4. Relative energy differences for the monografted dimers- grafted via terminal (GvT) and grafted via bridge (GvB) as a function of the number of Cl with general formula O$_{SURF}$Me$_n$Cl$_{1-n}$Al1-(μ^2-Me$_n$Cl$_{1-n}$)Al2Me$_n$Cl$_{2-n}$ and Me$_n$Cl$_{2-n}$Al1(μ-Me$_n$Cl$_{1-n}$O$_{SURF}$)Al2Me$_n$Cl$_{2-n}$, respectively.

Species	GvB			
	Cl position	Al	δ_{ISO} (ppm)	$\|C_Q\|$ (MHz)
$Me_2Al1(\mu\text{-}MeO_{SURF})Al2Me_2$	000	Al1	157	25
		Al2	157	25
$Me_2Al1(\mu\text{-}MeO_{SURF})Al2MeCl$	001	Al1	159	27
		Al2	128	19
$Me_2Al1(\mu\text{-}MeO_{SURF})Al2Cl_2$	002	Al1	169	33
		Al2	106	7
$MeClAl1(\mu\text{-}MeO_{SURF})Al2MeCl$ c	101c	Al1	126	20
		Al2	126	20
$MeClAl1(\mu\text{-}MeO_{SURF})Al2MeCl$ t	101t	Al1	127	21
		Al2	127	21
$MeClAl1(\mu\text{-}MeO_{SURF})Al2Cl_2$	102	Al1	126	20
		Al2	100	9
$Cl_2Al1(\mu\text{-}MeO_{SURF})Al2Cl_2$	202	Al1	99	11
		Al2	99	11
$Me_2Al1(\mu\text{-}ClO_{SURF})Al2Me_2$	010	Al1	171	30
		Al2	171	30
$Me_2Al1(\mu\text{-}ClO_{SURF})Al2MeCl$	011	Al1	172	31
		Al2	130	22
$Me_2Al1(\mu\text{-}ClO_{SURF})Al2Cl_2$	012	Al1	177	35
		Al2	97	11
$MeClAl1(\mu\text{-}ClO_{SURF})Al2MeCl$ c	111c	Al1	130	22
		Al2	130	22
$MeClAl1(\mu\text{-}ClO_{SURF})Al2MeCl$ t	111t	Al1	130	23
		Al2	130	23
$MeClAl1(\mu\text{-}ClO_{SURF})Al2Cl_2$	112	Al1	129	22
		Al2	97	13
$Cl_2Al1(\mu\text{-}ClO_{SURF})Al2Cl_2$	212	Al1	97	14
		Al2	97	14

Table S5. DFT-calculated ^{27}Al NMR parameters δ_{ISO} (ppm) and C_Q (MHz) for all GvB species ($Me_nCl_{2-n}Al1(\mu\text{-}Me_nCl_{1-n}O_{SURF})Al2Me_nCl_{2-n}$) in Figure 5 of the manuscript. Small c and t are indicating the cis and trans position of the substituent, respectively.

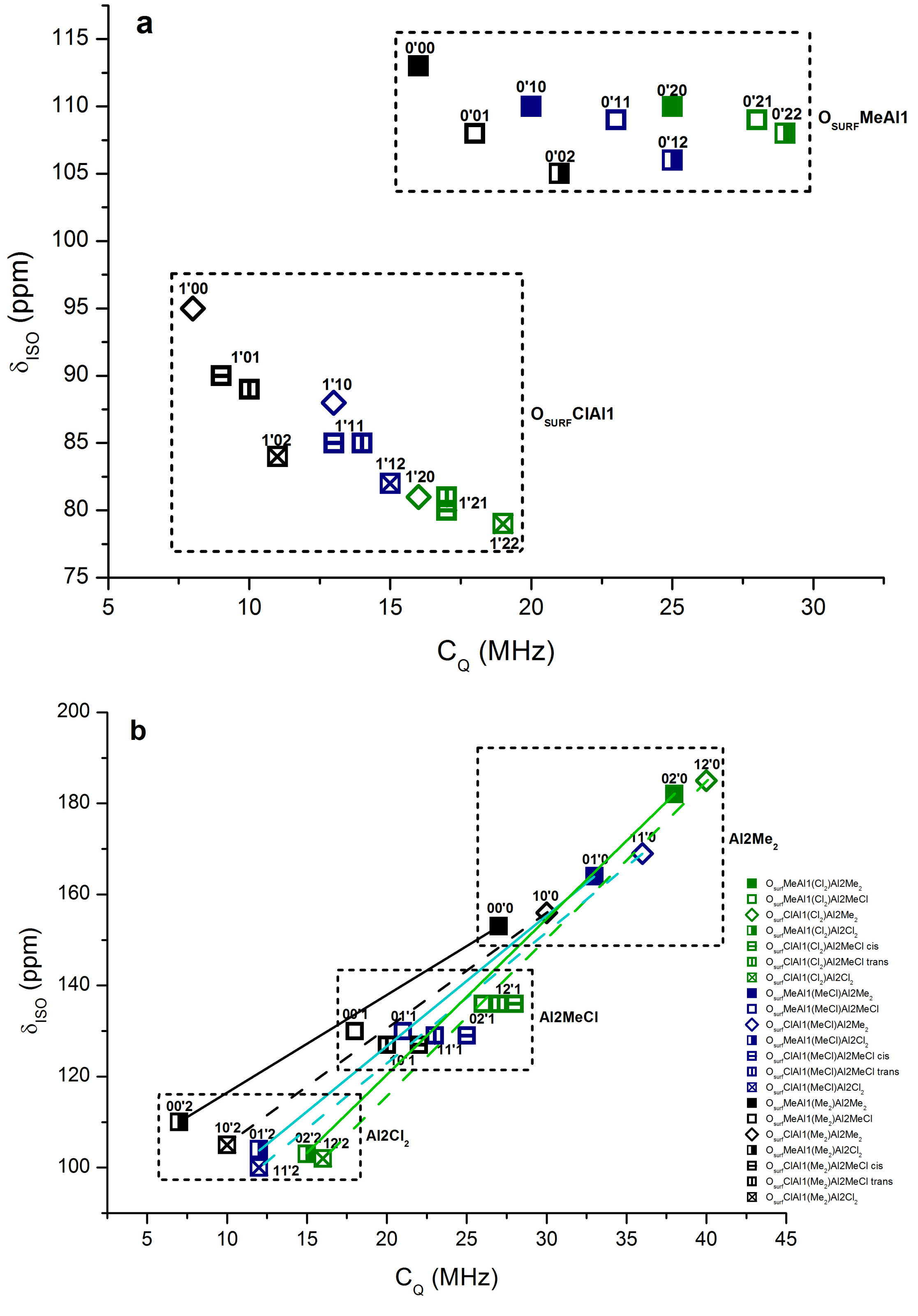


Figure S2. All methylaluminum monografted dimers via terminal (GvT) position are presented in two 2D plots, one for each Al (**a** for Al1 and **b** for Al2 environments), respectively together with their chloro derivatives grafted on the {001} silica surface.

Species	GvT			
	Cl position	Al	δ_{ISO} (ppm)	$\|C_Q\|$ (MHz)
$O_{SURF}MeAl1(\mu^2\text{-}Me)Al2Me_2$	000	Al1	113	16
		Al2	153	27
$O_{SURF}MeAl1(\mu^2\text{-}Me)Al2MeCl$	001	Al1	108	18
		Al2	130	18
$O_{SURF}ClAl1(\mu^2\text{-}Me)Al2Me_2$	100	Al1	95	8
		Al2	156	30
$O_{SURF}MeAl1(\mu^2\text{-}Me)Al2Cl_2$	002	Al1	105	21
		Al2	110	7
$O_{SURF}ClAl1(\mu^2\text{-}Me)Al2MeCl$	101c	Al1	90	9
		Al2	127	22
$O_{SURF}ClAl1(\mu^2\text{-}Me)Al2MeCl$	101t	Al1	89	10
		Al2	127	20
$O_{SURF}ClAl1(\mu^2\text{-}Me)Al2Cl_2$	102	Al1	84	11
		Al2	105	10
$O_{SURF}MeAl1(\mu\text{-}MeCl)Al2Me_2$	010	Al1	110	20
		Al2	164	33
$O_{SURF}MeAl1(\mu\text{-}MeCl)Al2MeCl$	011	Al1	109	23
		Al2	130	21
$O_{SURF}ClAl1(\mu\text{-}MeCl)Al2Me_2$	110	Al1	88	13
		Al2	169	36
$O_{SURF}MeAl1(\mu\text{-}MeCl)Al2Cl_2$	012	Al1	106	25
		Al2	104	12
$O_{SURF}ClAl1(\mu\text{-}MeCl)Al2MeCl$	111c	Al1	85	13
		Al2	129	25
$O_{SURF}ClAl1(\mu\text{-}MeCl)Al2MeCl$	111t	Al1	85	14
		Al2	129	23
$O_{SURF}ClAl1(\mu\text{-}MeCl)Al2Cl_2$	112	Al1	82	15
		Al2	100	12
$O_{SURF}MeAl1(\mu^2\text{-}Cl)Al2Me_2$	020	Al1	110	25
		Al2	182	38
$O_{SURF}MeAl1(\mu^2\text{-}Cl)Al2MeCl$	021	Al1	109	28
		Al2	136	26
$O_{SURF}ClAl1(\mu^2\text{-}Cl)Al2Me_2$	120	Al1	81	16
		Al2	185	40
$O_{SURF}MeAl1(\mu^2\text{-}Cl)Al2Cl_2$	022	Al1	108	29
		Al2	103	15
$O_{SURF}ClAl1(\mu^2\text{-}Cl)Al2MeCl$	121c	Al1	80	17
		Al2	136	28
$O_{SURF}ClAl1(\mu^2\text{-}Cl)Al2MeCl$	121t	Al1	81	17
		Al2	136	27
$O_{SURF}ClAl1(\mu^2\text{-}Cl)Al2Cl_2$	122	Al1	79	19
		Al2	102	16

Table S6. DFT-calculated ^{27}Al NMR parameters δ_{ISO} (ppm) and C_Q (MHz) for all GvT species ($O_{SURF}Me_nCl_{1-n}Al1\text{-}(\mu^2\text{-}Me_nCl_{1-n})Al2Me_nCl_{2-n}$) shown in Figure S2. Small c and t are indicating the cis and trans position of the substituent, respectively.

Bigrafted dimers

^{27}Al SS-NMR for bigrafted dimeric species on silica

Species	Type / Cl position	Relative energies of Number of Cl atoms				
		0	1	2	3	4
$O_{SURF}MeAl1(\mu\text{-}MeO_{SURF})Al2Me_2$	2.3/ 000	**0**	-	-	-	-
$Me_2Al1(\mu^2\text{-}O_{SURF})Al2Me_2$	2.4 / 000	26	-	-	-	-
$O_{SURF}MeAl1(\mu^2\text{-}Me)Al2MeO_{SURF}$	2.5 / 000	31	-	-	-	-
$(O_{SURF})_2Al1(\mu^2\text{-}Me)Al2Me_2$	2.6 / 000	57	-	-	-	-
$O_{SURF}Me_2Al1(\mu\text{-}ClO_{SURF})Al2Me_2$	2.3 / 010	-	**0**	-	-	-
$O_{SURF}Me_2Al1(\mu\text{-}MeO_{SURF})Al2MeCl$	2.3 / 001	-	33	-	-	-
$O_{SURF}ClAl1(\mu\text{-}MeO_{SURF})Al2Me_2$	2.3 / 100	-	38	-	-	-
$O_{SURF}MeAl1(\mu\text{-}MeCl)Al2MeO_{SURF}$	2.5 / 010	-	52	-	-	-
$MeClAl1(\mu^2\text{-}O_{SURF})Al2Me_2$	2.4 / 100	-	64	-	-	-
$O_{SURF}ClAl1(\mu^2\text{-}Me)Al2MeO_{SURF}$	2.5 / 100	-	73	-	-	-
$(O_{SURF})_2Al1(\mu\text{-}MeCl)Al2Me_2$	2.6 / 010	-	82	-	-	-
$(O_{SURF})_2Al1(\mu^2\text{-}Me)Al2MeCl$	2.6 / 001	-	94	-	-	-
$O_{SURF}MeAl1(\mu\text{-}ClO_{SURF})Al2MeCl$	2.3 / 011	-	-	**0**	-	-
$O_{SURF}ClAl1(\mu\text{-}ClO_{SURF})Al2Me_2$	2.3 / 110	-	-	11	-	-
$O_{SURF}MeAl1(\mu^2\text{-}Cl)Al2MeO_{SURF}$	2.5 / 020	-	-	24	-	-
$O_{SURF}ClAl1(\mu\text{-}MeO_{SURF})Al2MeCl$	2.3 / 101t	-	-	38	-	-
$O_{SURF}ClAl1(\mu\text{-}MeO_{SURF})Al2MeCl$	2.3 / 101c	-	-	40	-	-
$O_{SURF}MeAl1(\mu\text{-}MeO_{SURF})Al2Cl_2$	2.3 / 002	-	-	42	-	-
$(O_{SURF})_2Al1(\mu^2\text{-}Cl)Al2Me_2$	2.6 / 020	-	-	54	-	-
$O_{SURF}MeAl1(\mu\text{-}MeCl)Al2ClO_{SURF}$	2.5 / 011	-	-	63	-	-
$MeClAl1(\mu^2\text{-}O_{SURF})Al2MeCl$	2.4 / 101c	-	-	65	-	-
$Me_2Al1(\mu^2\text{-}O_{SURF})Al2Cl_2$	2.4 / 002	-	-	77	-	-
$(O_{SURF})_2Al1(\mu\text{-}MeCl)Al2MeCl$	2.6 / 011	-	-	85	-	-
$O_{SURF}ClAl1(\mu^2\text{-}Me)Al2ClO_{SURF}$	2.5 / 101	-	-	88	-	-
$(O_{SURF})_2Al1(\mu^2\text{-}Me)Al2Cl$	2.6 / 002	-	-	102	-	-
$O_{SURF}ClAl1(\mu\text{-}ClO_{SURF})Al2MeCl$	2.3 / 111t	-	-	-	**0**	-
$O_{SURF}ClAl1(\mu\text{-}ClO_{SURF})Al2MeCl$	2.3 / 111c	-	-	-	0	-
$O_{SURF}MeAl1(\mu\text{-}ClO_{SURF})Al2Cl_2$	2.3 / 012	-	-	-	4	-
$O_{SURF}ClAl1(\mu^2\text{-}Cl)Al2MeO_{SURF}$	2.5 / 120	-	-	-	23	-
$O_{SURF}ClAl1(\mu\text{-}MeO_{SURF})Al2Cl_2$	2.3 / 102	-	-	-	33	-
$(O_{SURF})_2Al1(\mu^2\text{-}Cl)Al2MeCl$	2.6 / 021	-	-	-	45	-
$O_{SURF}ClAl1(\mu\text{-}MeCl)Al2ClO_{SURF}$	2.5 / 111	-	-	-	64	-
$MeClAl1(\mu^2\text{-}O_{SURF})Al2Cl_2$	2.4 / 102	-	-	-	66	-
$(O_{SURF})_2Al1(\mu\text{-}MeCl)Al2Cl_2$	2.6 / 012	-	-	-	80	-
$O_{SURF}ClAl1(\mu\text{-}ClO_{SURF})Al2Cl_2$	2.3 / 112	-	-	-	-	**0**
$O_{SURF}ClAl1(\mu^2\text{-}Cl)Al2ClO_{SURF}$	2.5 / 121	-	-	-	-	30
$(O_{SURF})_2Al1(\mu^2\text{-}Cl)Al2Cl_2$	2.6 / 022	-	-	-	-	51
$Cl_2Al1(\mu^2\text{-}O_{SURF})Al2Cl_2$	2.4 / 202	-	-	-	-	69

Table S7. Relative energy differences for the bigrafted dimers- 2.3 ($O_{SURF}Me_nCl_{1\text{-}n}Al1(\mu\text{-}Me_nCl_{1\text{-}n}O_{SURF})Al2Me_nCl_{2\text{-}n}$), 2.4 ($Me_nCl_{2\text{-}n}Al1(\mu^2\text{-}O_{SURF})Al2Me_nCl_{2\text{-}n}$), 2.5 ($O_{SURF}Me_nCl_{1\text{-}n}Al1(\mu\text{-}Me_nCl_{2\text{-}n})Al2Me_nCl_{1\text{-}n}O_{SURF}$), and 2.6 ($(O_{SURF})_2Al1(\mu\text{-}Me_nCl_{2\text{-}n})Al2Me_nCl_{2\text{-}n}$.

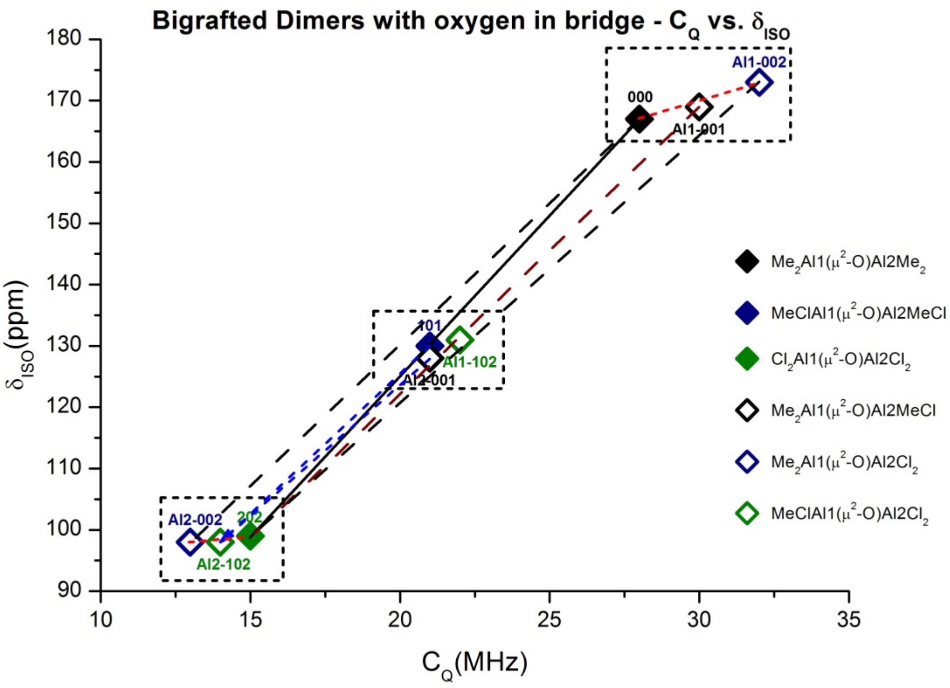


Figure S3. All methylaluminum bigrafted dimers and their chloro derivatives in which the Al-Al axis is parallel to the {001} silica surface.

For the 2.4 dimers ($Me_nCl_{2-n}Al1(\mu^2-O_{SURF})$ Me_nCl_{2-n}) we see clearly the effect of the number of the Cl atoms. Starting from $Me_2Al1(\mu^2-O_{SURF})$ Me_2 (where Al1 and Al2 are equivalent) we start from 167 ppm and 28 MHz, to 130 ppm and 21 MHz for the $MeClAl1(\mu^2-O_{SURF})$ MeCl, and ending with 99 ppm and 15 MHz for the $Cl_2Al1(\mu^2-O_{SURF})$ Cl_2. Along that linear correlation the δ_{ISO} and the C_Q both shift towards the small values with 68 ppm and 13 MHz respectively. This is exactly what we would expect based on the already observed trend for the monografted dimers.

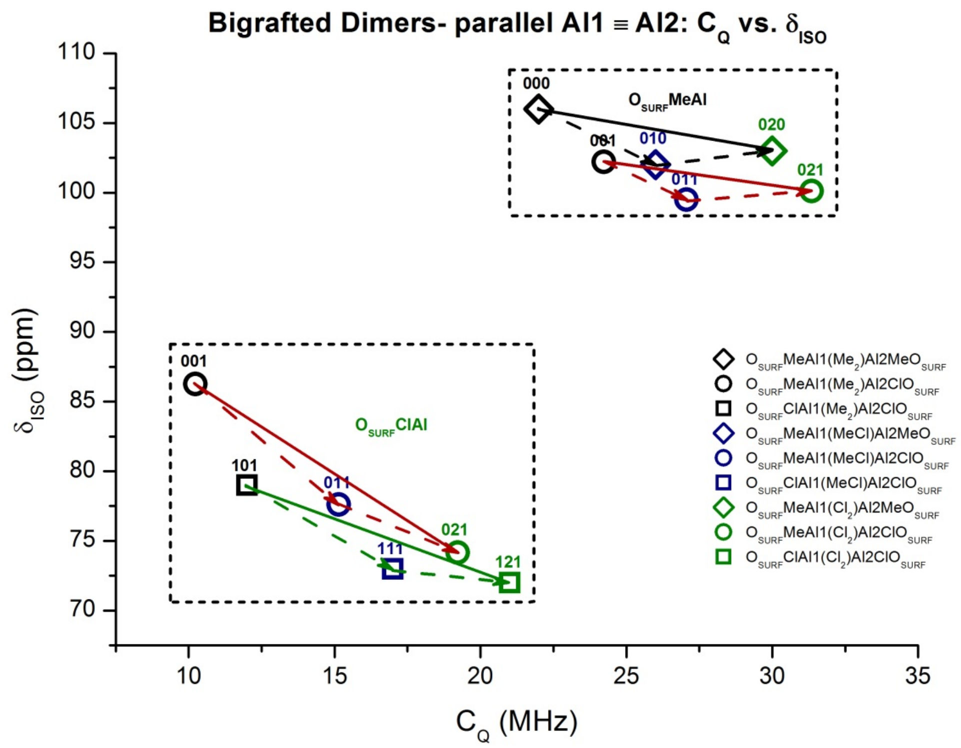


Figure S4. All methylaluminum bigrafted dimers and their chloro derivatives in which the Al-Al axis is parallel to the {001} silica surface.

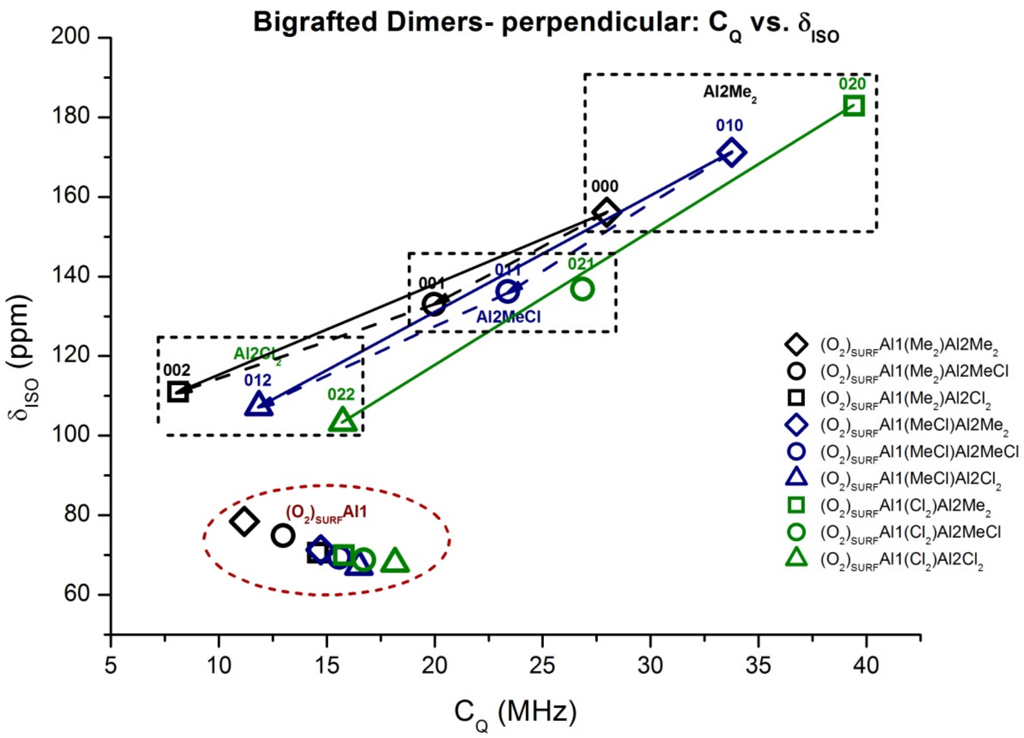


Figure S5. All methylaluminum bigrafted dimers and their chloro derivatives in which the Al-Al axis is perpendicular to the {001} silica surface.

Species	BG dimers			
	Cl position	Al	δ_{ISO} (ppm)	$\lvert C_Q \rvert$ (MHz)
	2.3			
O_{SURF}MeAl1(μ-O_{SURF}Me)Al2Me_2	000	Al1	116	19
		Al2	162	29
O_{SURF}MeAl1(μ-O_{SURF}Me)Al2MeCl	001	Al1	114	20
		Al2	128	20
O_{SURF}ClAl1(μ-O_{SURF}Me)Al2Me_2	100	Al1	92	13
		Al2	170	33
O_{SURF}MeAl1(μ-O_{SURF}Me)Al2Cl_2	002	Al1	112	22
		Al2	100	9
O_{SURF}ClAl1(μ-O_{SURF}Me)Al2MeCl c	101c	Al1	88	13
		Al2	127	23
O_{SURF}ClAl1(μ-O_{SURF}Me)Al2MeCl t	101t	Al1	89	13
		Al2	129	22
O_{SURF}ClAl1(μ-O_{SURF}Me)Al2Cl_2	102	Al1	86	14
		Al2	98	12
O_{SURF}MeAl1(μ-O_{SURF}Cl)Al2Me_2	010	Al1	111	22
		Al2	175	33
O_{SURF}MeAl1(μ-O_{SURF}Cl)Al2MeCl	011	Al1	111	24
		Al2	132	23
O_{SURF}ClAl1(μ-O_{SURF}Cl)Al2Me_2	110	Al1	82	14
		Al2	180	35
O_{SURF}MeAl1(μ-O_{SURF}Cl)Al2Cl_2	012	Al1	111	26
		Al2	99	14
O_{SURF}ClAl1(μ-O_{SURF}Cl)Al2MeCl c	111c	Al1	82	15
		Al2	132	25
O_{SURF}ClAl1(μ-O_{SURF}Cl)Al2MeCl t	111t	Al1	82	15
		Al2	133	24
O_{SURF}ClAl1(μ-O_{SURF}Cl)Al2Cl_2	112	Al1	81	16
		Al2	98	16
	2.4			
Me_2Al1(μ^2-O_{SURF})Al2Me_2	000	Al1	167	28
		Al2	167	28
Me_2Al1(μ^2-O_{SURF})Al2MeCl	001	Al1	169	30
		Al2	128	21
Me_2Al1(μ^2-O_{SURF})Al2Cl_2	002	Al1	173	32
		Al2	98	13
MeClAl1(μ^2-O_{SURF})Al2MeCl	101	Al1	130	21
		Al2	130	21
MeClAl1(μ^2-O_{SURF})Al2Cl_2	102	Al1	131	22
		Al2	98	14
Cl_2Al1(μ^2-O_{SURF})Al2Cl_2	202	Al1	99	15
		Al2	99	15
	2.5			
O_{SURF}MeAl1(μ^2-Me)Al2MeO_{SURF}	000	Al1	106	22
		Al2	106	22

$O_{SURF}MeAl1(\mu^2\text{-}Me)Al2ClO_{SURF}$	001	Al1	102	24
		Al2	86	10
$O_{SURF}ClAl1(\mu^2\text{-}Me)Al2ClO_{SURF}$	101	Al1	79	12
		Al2	79	12
$O_{SURF}MeAl1(\mu\text{-}MeCl)Al2MeO_{SURF}$	010	Al1	102	26
		Al2	102	26
$O_{SURF}MeAl1(\mu\text{-}MeCl)Al2ClO_{SURF}$	011	Al1	99	27
		Al2	78	15
$O_{SURF}ClAl1(\mu\text{-}MeCl)Al2ClO_{SURF}$	111	Al1	73	17
		Al2	73	17
$O_{SURF}MeAl1(\mu^2\text{-}Cl)Al2MeO_{SURF}$	020	Al1	103	30
		Al2	103	30
$O_{SURF}MeAl1(\mu^2\text{-}Cl)Al2ClO_{SURF}$	021	Al1	74	19
		Al2	100	31
$O_{SURF}ClAl1(\mu^2\text{-}Cl)Al2ClO_{SURF}$	121	Al1	72	21
		Al2	72	21
	2.6			
$(O_{SURF})_2Al1(\mu^2\text{-}Me)Al2Me_2$	000	Al1	78	11
		Al2	156	28
$(O_{SURF})_2Al1(\mu^2\text{-}Me)Al2MeCl$	001	Al1	75	13
		Al2	133	20
$(O_{SURF})_2Al1(\mu^2\text{-}Me)Al2Cl_2$	002	Al1	71	15
		Al2	111	8
$(O_{SURF})_2Al1(\mu\text{-}MeCl)Al2Me_2$	010	Al1	71	15
		Al2	171	34
$(O_{SURF})_2Al1(\mu\text{-}MeCl)Al2MeCl$	011	Al1	69	16
		Al2	136	23
$(O_{SURF})_2Al1(\mu\text{-}MeCl)Al2Cl_2$	012	Al1	67	16
		Al2	107	12
$(O_{SURF})_2Al1(\mu^2\text{-}Cl)Al2Me_2$	020	Al1	70	16
		Al2	183	39
$(O_{SURF})_2Al1(\mu^2\text{-}Cl)Al2MeCl$	021	Al1	69	17
		Al2	137	27
$(O_{SURF})_2Al1(\mu^2\text{-}Cl)Al2Cl_2$	121	Al1	68	18
		Al2	103	16

Table S6. DFT-calculated ^{27}Al NMR parameters δ_{ISO} (ppm) and C_Q (MHz) for all bigrafted dimeric species on silica surface some of which presented in Figure 5, S2-S5.