Supporting Information for:

"Masked" Lewis-acidity of an Aluminum α-Phosphino-Amide Complex

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Contents:

1. Single-crystal X-ray structure determinations

All crystal structures were solved using direct methods (SHELXT-2014)[1] and refined with SHELXL-2014[2] using OLEX2 software[3] All geometry calculations and graphics were obtained using PLATON.[4] The hydrogen atoms were placed on calculated positions and refined isotropically in a riding mode. Special features of the refinement are noted below. The crystal data have been summarized in Table S1.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1528561 $[Ph_2P(DIPP)NAlMe_2]_2$, 1528562 $Ph_2P(DIPP)NAlMe_2{\cdot}THF$, 1528563 $[(DIPP)N\text{-}Ph_2P\text{-}CH(CH_2SMe)CH_2]AlMe_2$, 1528564 $[(DIPP)N\text{-}Ph_2P\text{-}CH(C_4H_9)CH_2]AlMe_2$, 1528565 $[Ph_2P(DIPP)N(CO_2)Al(Me)_2]_2$, 1528566 $[(DIPP)N\text{-}Ph_2P\text{-}C(N\text{-}DIPP)O]AlMe_2$. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk)

Crystal structure determination of $Ph_2P(DIPP)NAlMe_2{\cdot}THF$

Complex $Ph_2P(DIPP)NAlMe_2{\cdot}THF$ crystallizes in the chiral space group $P2_12_12_1$ and the Flack parameter refined to 0.023(26).

Crystal structure determination of $[(DIPP)N\text{-}Ph_2P\text{-}CH(CH_2SMe)CH_2]AlMe_2$

Complex $[(DIPP)N\text{-}Ph_2P\text{-}CH(CHCH_2SMe)]AlMe_2$ crystallizes with two molecules in the asymmetric part of the unit cell. One of these molecules shows a thioether ligand that is disordered in the SMe group. This disorder was modeled and the atoms were refined anisotropically.

Table S1. Crystal structure data.

Compound	$[Ph_2P(DIPP)NAlMe_2]_2$	$Ph_2P(DIPP)NAlMe_2 \cdot THF$	$[(DIPP)N\text{-}Ph_2P\text{-}CH(CH_2SMe)CH_2]AlMe_2$
Formula	$C_{52}H_{66}Al_2N_2P_2$	$C_{30}H_{41}AlNPO$	$C_{30}H_{41}AlNPS$
M	834.97	489.59	505.65
Size (mm)	0.22 x 0.11 x 0.10	0.26 x 0.20 x 0.15	0.18 x 0.15 x 0.11
Crystal system	Triclinic	orthorhombic	Triclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$
a (Å)	9.7257(15)	9.8330(12)	9.296(2)
b (Å)	10.3432(17)	10.0370(6)	16.751(3)
c (Å)	12.758(2)	28.666(6)	18.941(5)
α	96.545(3)	90.0	88.25(2)
β	99.302(3)	90.0	89.542(16)
γ	109.982(3)	90.0	80.584(16)
V (Å³)	1170.3(3)	2829.2(7)	2908.3(11)
Z	1	4	4
ρ (g.cm^{-3})	1.185	1.149	1.155
μ (mm^{-1})	0.167 ($Mo_{K\alpha}$)	0.150 ($Mo_{K\alpha}$)	0.215 ($Mo_{K\alpha}$)
T (K)	150	150	150
Θ min – max (Deg)	1.7 - 29.6	2.9 - 27.5	2.7 - 26.5
Refl.total, independent R_{int}	24513, 6532 0.024	37996, 6328 0.0379	63838, 12047 0.142
Found refl. ($I > 2\sigma(I)$)	5753	5757	7292
Parameter	268	313	647
R_1	0.0341	0.0400	0.0743
*wR*2	0.0847	0.1022	0.1645
GooF	1.035	1.113	1.040
min/max remaining e-density (e/Å^3)	−0.33/0.45	−0.39/0.35	−0.40/0.50

Compound	[(DIPP)N-Ph_2P-$CH(C_4H_9)CH_2$]$AlMe_2$	[Ph_2P(DIPP)N(CO_2)$AlMe_2$]$_2$	[(DIPP)N-Ph_2P-C(N-DIPP)O]$AlMe_2$
Formula	$C_{32}H_{45}AlNP$, C_6H_6	$C_{54}H_{66}Al_2N_2O_4P_2$, C_6H_6	$C_{39}H_{50}AlN_2OP$
M	579.74	1001.10	620.76
Size (mm³)	0.2 x 0.3 x 0.4	0.16 x 0.23 x 0.25	0.24 x 0.26 x 0.30
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pca*2$_1$	*P*2$_1$/*c*	*P*2$_1$/*c*
a (Å)	9.2920(8)	14.0550(3)	13.7591(8)
b (Å)	17.6330(13)	12.3310(7)	16.2381(11)
c (Å)	20.6320(10)	19.9820(9)	18.7100(5)
α	90	90	90
β	90	126.651(4)	117.082(4)
γ	90	90	90
V (Å³)	3380.5(4)	2778.4(3)	3721.9(4)
Z	4	2	4
ρ (g.cm^{-3})	1.139	1.197	1.108
μ (mm^{-1})	0.133($Mo_{K\alpha}$)	0.157($Mo_{K\alpha}$)	0.128($Mo_{K\alpha}$)
T (K)	150	150	150
Θ min – max (Deg)	3.0, 27.5	2.9, 30.5	2.8, 30.0
Refl.total, independent R_{int}	43346, 7598 0.0441	93690, 8463 0.035	115146, 10840 0.041
Found refl. (*I* > 2σ(*I*))	7598	6890	8673
Parameter	377	322	407
R_1	0.0411	0.0372	0.0431
*wR*2	0.0977	0.1118	0.1306
GooF	1.119	1.11	1.15
min/max remaining e-density (e/Å³)	−0.30/0.43	−0.35/0.41	−0.37/0.42

2. Selected ^{1}H NMR spectra

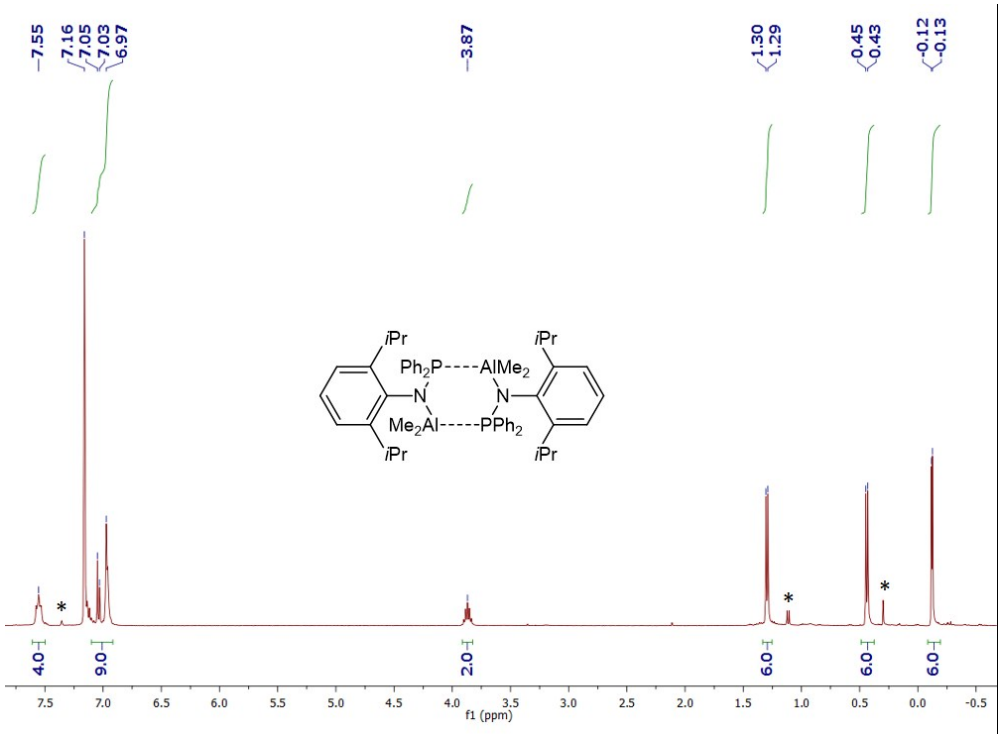

Figure S1. ^{1}H NMR spectrum of $[Ph_2P(DIPP)NAlMe_2]_2$ in C_6D_6. The complex is very poorly soluble in aromatic solvents. Impurities marked by * are due to DIPP-NH_2 and silicon grease.

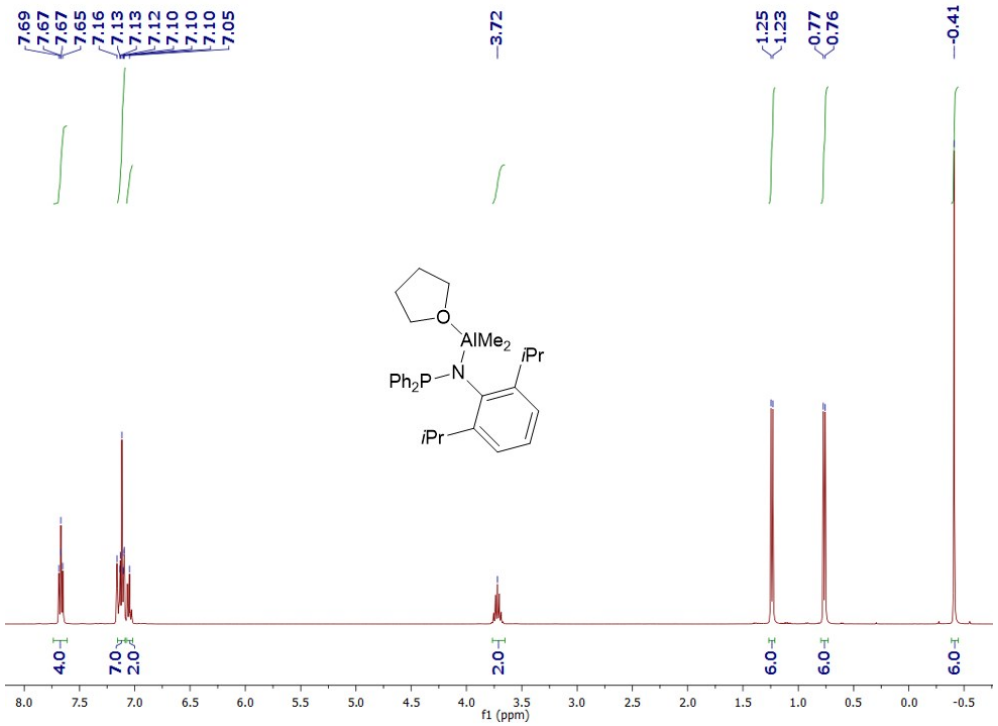

Figure S2. ^{1}H NMR spectrum of $Ph_2P(DIPP)NAlMe_2{\cdot}THF$ in C_6D_6.

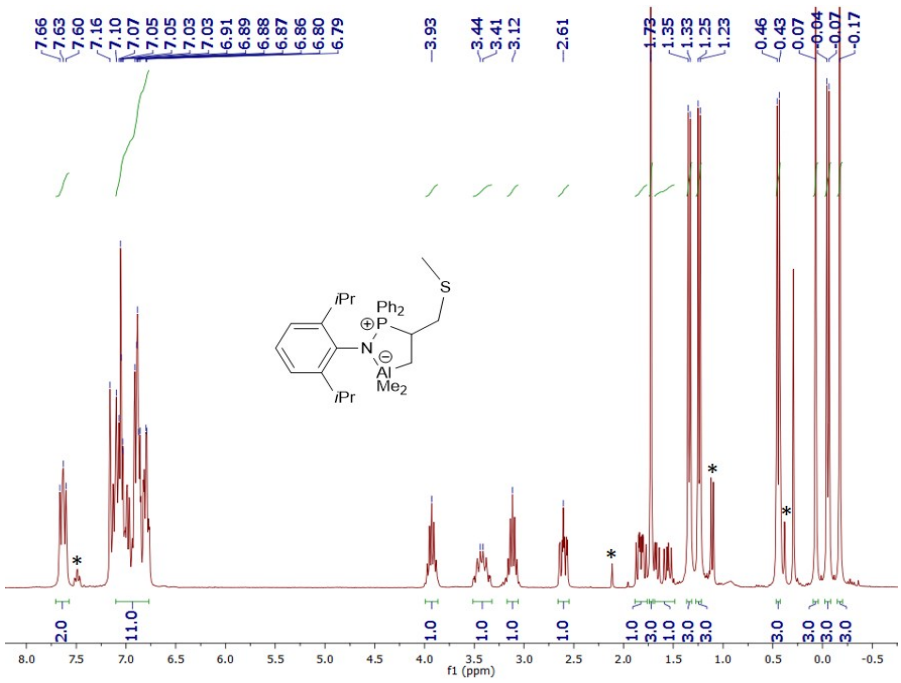

Figure S3. ^{1}H NMR spectrum of [(DIPP)N-Ph_2P-CH(CH_2SMe)CH_2]AlMe_2 in C_6D_6. Impurities marked by * are due to DIPP-NH_2, silicon grease and toluene.

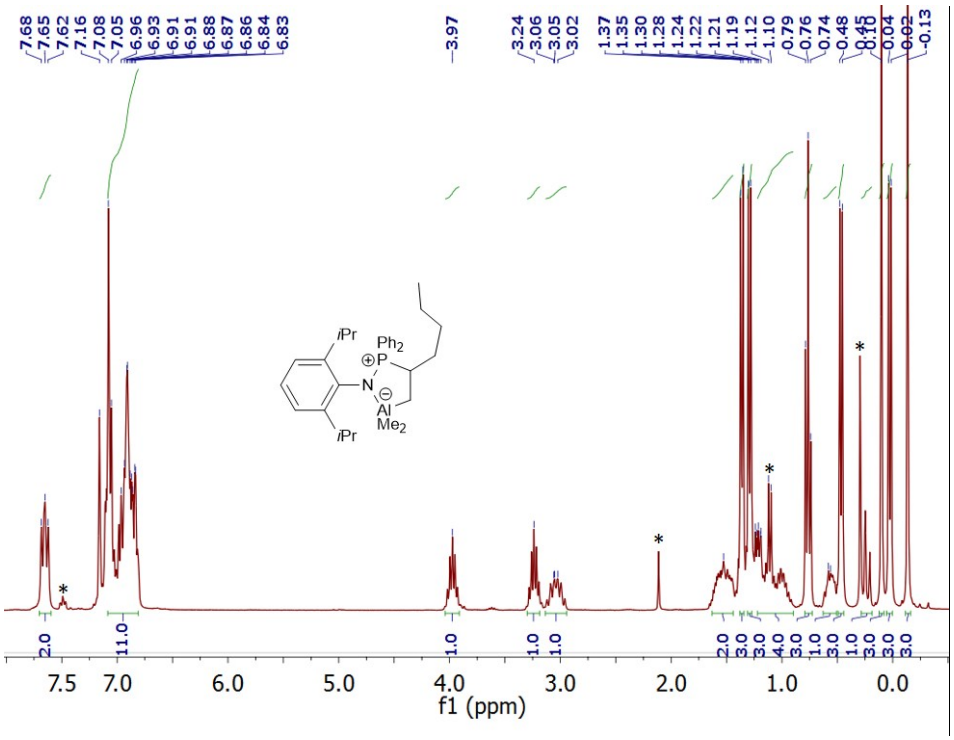

Figure S4. ^{1}H NMR spectrum of [(DIPP)N-Ph_2P-CH(C_4H_9)CH_2]AlMe_2 in C_6D_6. Impurities marked by * are due to DIPP-NH_2, silicon grease, and toluene.

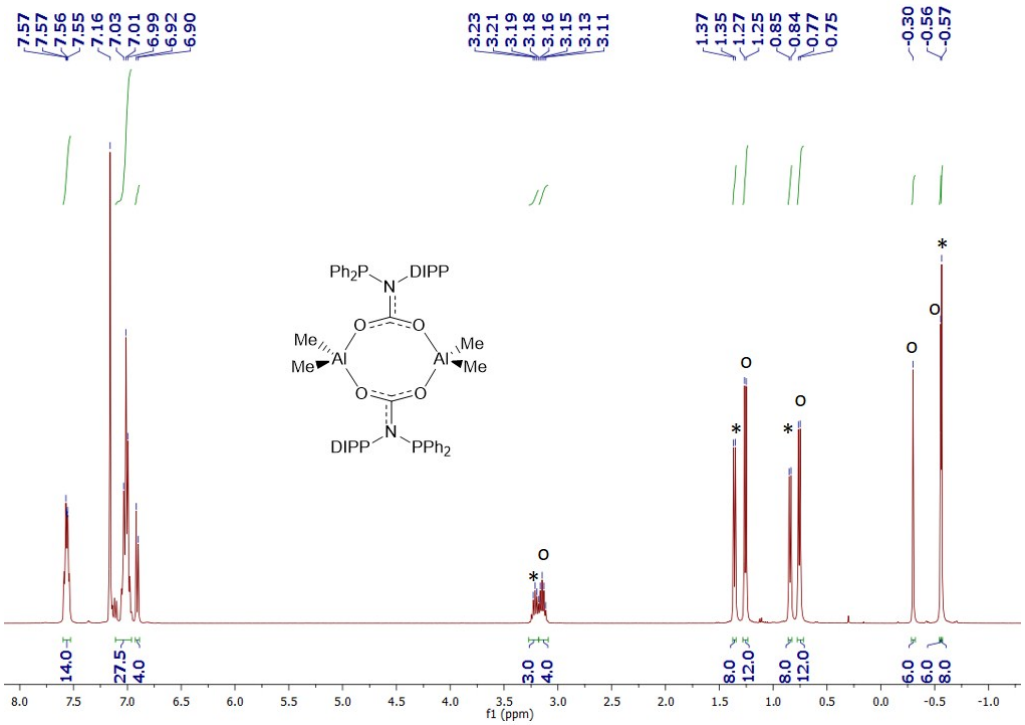

Figure S5. ^{1}H NMR spectrum of $[Ph_2P(DIPP)N(CO_2)Al(Me)_2]_2$ in C_6D_6. Two isomers marked with * and o are formed.

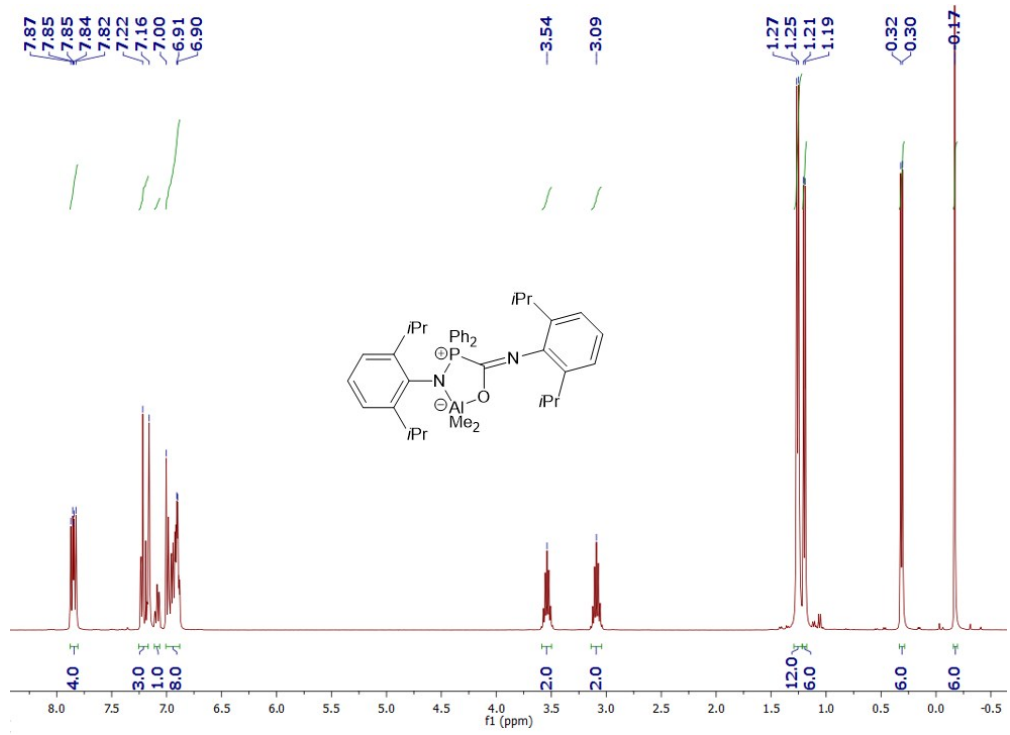

Figure S6. ^{1}H NMR spectrum of $[(DIPP)N\text{-}Ph_2P\text{-}C(N\text{-}DIPP)O]AlMe_2$ in C_6D_6.

3. References

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(2) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3-8.
(3) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2008, **64**, 112-122.
(4) A. L. Spek, PLATON, *A Multipurpose Crystallographic Tool* 2000, Utrecht University, Utrecht, The Netherlands.