Electronic Supplementary Information

Aluminum Complexes of Bidentate N,O- and N,N-Ligands Derived from Oxidative Functionalization of Amido Phosphines: Synthesis, Structure, and Reactivity

Lan-Chang Liang,*[,a] Feng-Yi Chen,[a] Mei-Hui Huang,[a] Liang-Chien Cheng,[a] Chun-Wei Li,[a] and Hon Man Lee[b]

[a]Department of Chemistry and Center for Nanoscience & Nanotechnology, National Sun Yat-sen University, Kaohsiung 80424, Taiwan
[b]Department of Chemistry, National Changhua University of Education, Changhua 50058, Taiwan
E-mail: lcliang@mail.nsysu.edu.tw

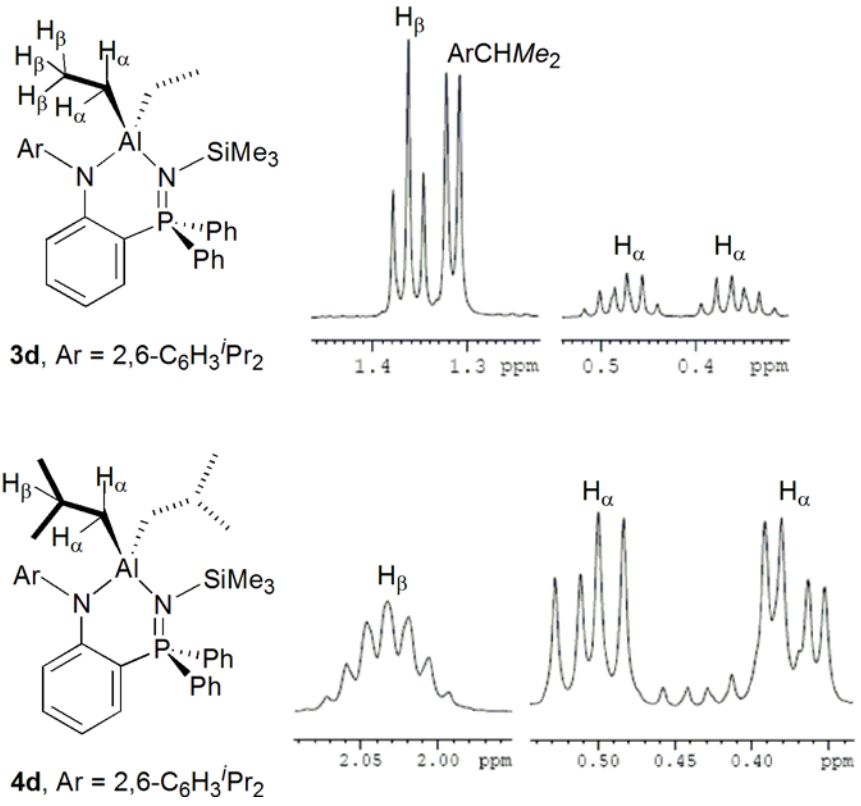

Figure S1. ChemDraw structures of **3d**-**4d** and their corresponding multiplet resonances of H_α and H_β atoms recorded in C_6D_6 at room temperature (500 MHz NMR).

Table S1. Crystallographic Data for **1a**, **1d**, **2c-d**, **3a**, **3d**, **4a**, and **4d**.

Compound	**1a**	**1d**

Formula	$C_{26}H_{24}NOP$	$C_{33}H_{41}N_2PSi$
Fw	397.43	524.74
crystal size (mm^3)	0.2 x 0.16 x 0.04	0.6 x 0.45 x 0.2
D_{calc} (Mg/m^3)	1.265	1.146
crystal syst	Triclinic	Monoclinic
space group	$P\bar{1}$	$P2_1/n$
a (Å)	8.5300(2)	18.4720(4)
b (Å)	15.1880(4)	9.3940(2)
c (Å)	16.6720(5)	19.4190(5)
α (deg)	92.563(1)	90
β (deg)	103.144(1)	115.508(1)
γ (deg)	95.943(2)	90
V ($Å^3$)	2086.82(10)	3041.24(12)
Z	4	4
T (K)	100(2)	200(2)
radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
2θ range (deg)	4.94≤2θ≤50.08	4.64≤2θ≤50.02
index ranges (h;k;l)	-10,9;-18,18;-19,19	-16,21;-11,10;-22,23
total no. of reflns	29156	15914
no. of indep reflns	7311	5325
R_{int}	0.1031	0.0700
absorp coeff (mm^{-1})	0.149	0.153
no. of data/restraints/ parameters	7311 / 0 / 524	5325 / 0 / 334
goodness of fit	1.021	1.007
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0596 wR2 = 0.1327	R1 = 0.0519 wR2 = 0.1354
R indices (all data)	R1 = 0.1025 wR2 =0.1516	R1 = 0.0709 wR2 = 0.1477
residual density ($e/Å^3$)	-0.529 to 0.564	-0.533 to 0.324

Table S1. (continued)

Compound	**2c**	**2d**
Formula	$C_{44}H_{54}AlN_2P$	$C_{35}H_{46}AlN_2PSi$
Fw	668.84	580.78
crystal size (mm^3)	0.23 x 0.21 x 0.14	0.15 x 0.12 x 0.08

D_{calc} (Mg/m^3)	1.109	1.157
crystal syst	Monoclinic	Triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	14.8344(3)	10.8710(2)
b (Å)	12.2348(2)	11.3320(3)
c (Å)	22.0762(4)	15.2670(4)
α (deg)	90	81.313(1)
β (deg)	91.695(1)	81.732(1)
γ (deg)	90	64.163(1)
V (Å^3)	4004.99(13)	1666.88(7)
Z	4	2
T (K)	200 (2)	293(2)
radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
2θ range (deg)	4.32≤2θ≤50.68	4.18≤2θ≤50.18
index ranges (h;k;l)	-15,17;-14,14;-26,23	-12,12;-13,13;-18,18
total no. of reflns	31022	23565
no. of indep reflns	7298	5885
R_{int}	0.0710	0.0754
absorp coeff (mm^{-1})	0.122	0.170
no. of data/restraints/ parameters	7298 / 0 / 434	5885 / 0 / 362
goodness of fit	1.172	1.116
final *R* indices (I> 2σ(I))	R1 = 0.1280 wR2 = 0.3391	R1 = 0.0689 wR2 = 0.1662
R indices (all data)	R1 = 0.1762 wR2 = 0.3698	R1 = 0.1101 wR2 = 0.2084
residual density (e/Å^3)	-1.019 to 0.737	-0.978 to 0.751

Table S1. (continued)

Compound	**3a**	**3d**
Formula	$C_{30}H_{33}$ Al N O P	$C_{37}H_{50}AlN_2PSi$
Fw	481.52	608.83
crystal size (mm^3)	0.15 x 0.08 x 0.05	0.36 x 0.32 x 0.16
D_{calc} (Mg/m^3)	1.195	1.175
crystal syst	Monoclinic	Triclinic
space group	*Cc*	$P\bar{1}$

a (Å)	12.617(1)	9.9164(1)
b (Å)	13.8230(11)	11.9278(2)
c (Å)	16.5600(14)	16.5097(3)
α (deg)	90	104.080(1)
β (deg)	112.033(4)	94.360(1)
γ (deg)	90	112.380(1)
V ($Å^3$)	2677.2(4)	1720.20(5)
Z	4	2
T (K)	150(2)	200(2)
radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
2θ range (deg)	5.3≤2θ≤49.96	4.52≤2θ≤50.08
index ranges (h;k;l)	-13,14;-16,15;-19,17	-11,11;-14,14;-19,19
total no. of reflns	7270	20810
no. of indep reflns	3927	6051
R_{int}	0.0597	0.0497
absorp coeff (mm^{-1})	0.158	0.168
no. of data/restraints/ parameters	3927 / 2 / 307	6051 / 0 / 379
goodness of fit	1.039	1.047
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0718 wR2 = 0.1613	R1 = 0.0422 wR2 = 0.1039
R indices (all data)	R1 = 0.0992 wR2 = 0.1783	R1 = 0.0550 wR2 = 0.1140
residual density ($e/Å^3$)	-0.321to 0.307	-0.550 to 0.350
Flack parameter	-0.3(2)	---

Table S1. (continued)

Compound	**4a**	**4d**
Formula	$C_{34}H_{41}AlNOP$	$C_{84}H_{122}Al_2N_4OP_2Si_2$
Fw	537.63	1375.94
crystal size (mm^3)	0.2 x 0.1 x 0.08	0.65 x 0.45 x 0.3
D_{calc} (Mg/m^3)	1.158	1.074
crystal syst	Monoclinic	Triclinic
space group	$P2_1/n$	$P\bar{1}$
a (Å)	18.5970(6)	11.2104(2)
b (Å)	8.8250(3)	12.4308(2)

c (Å)	19.4050(7)	16.5106(4)
α (deg)	90	98.669(1)
β (deg)	104.392(1)	100.727(1)
γ (deg)	90	105.668(1)
V (Å^3)	3084.78(18)	2126.92(7)
Z	4	1
T (K)	200(2)	200 (2)
radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
2θ range (deg)	3.50≤2θ≤50.08	4.34≤2θ≤50.80
index ranges (h;k;l)	-21,22;-8,10;-19,23	-13,13;-14,14;-19,19
total no. of reflns	20733	29583
no. of indep reflns	5446	7778
R_{int}	0.1218	0.0910
absorp coeff (mm^{-1})	0.144	0.143
no. of data/restraints/ parameters	5446 / 0 / 344	7778 / 0 / 437
goodness of fit	1.072	1.046
final *R* indices (I> 2σ(I))	R1 = 0.0811 wR2 = 0.1754	R1 = 0.0603 wR2 = 0.1628
R indices (all data)	R1 = 0.1629 wR2 = 0.2331	R1 = 0.0771 wR2 = 0.1760
residual density (e/Å^3)	-0.966 to 0.869	-0.582 to 0.744