Supplementary Materials

Contents

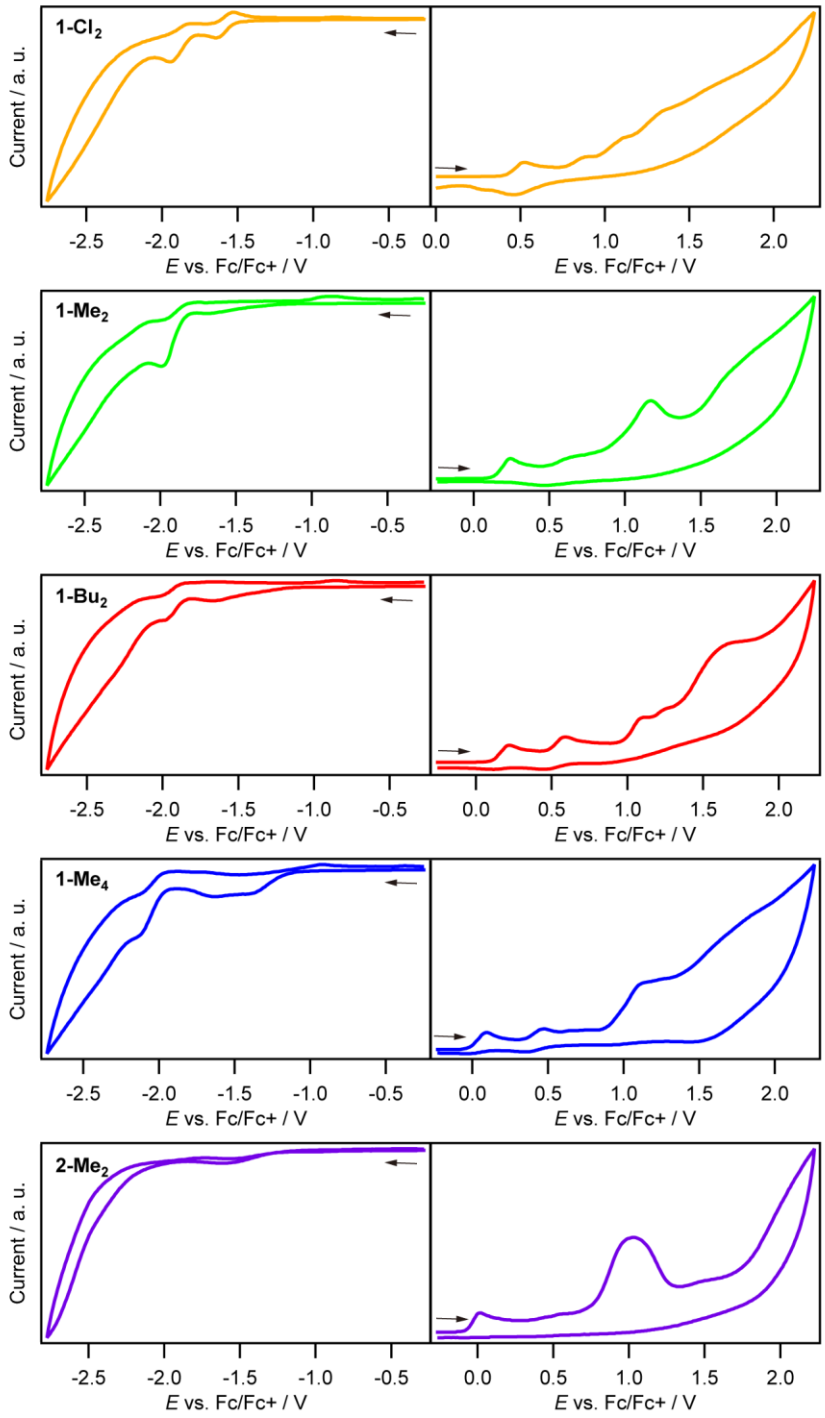


Figure S1. Cyclic voltammograms in the full potential range of the cathodic (left) and anodic (right) scans. Solvent: 0.1 M Bu_4NPF_6 solution of dichloromethane, Scan speed: 100 mV s^{-1}.

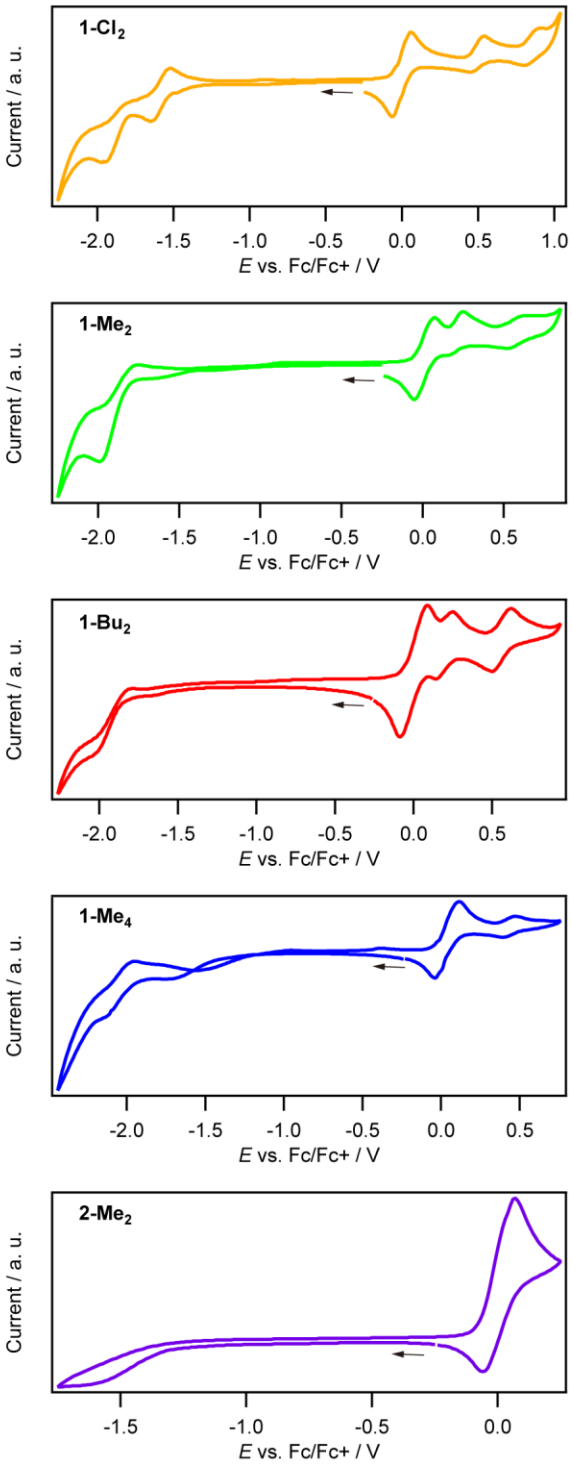
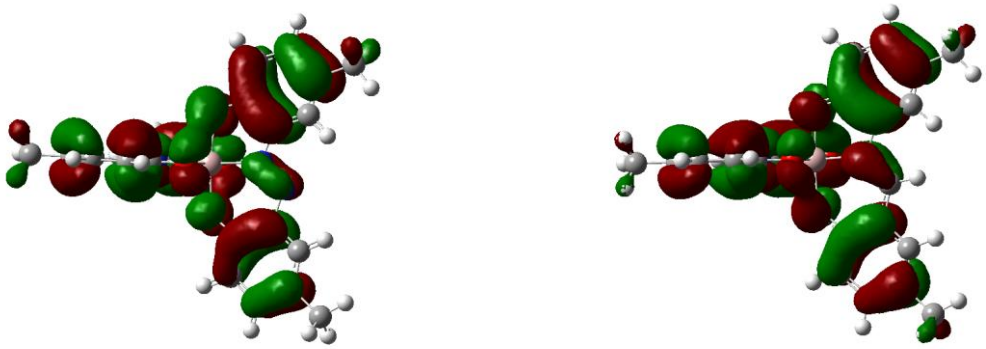


Figure S2. Cyclic voltammograms in the presence of an equivalent mole of ferrocene. For **1-Me**$_4$ and **2-Me**$_2$, the first oxidation waves of the Al^{III} complex anions overlapped with the oxidation wave of ferrocene.



(**a**) (**b**)

Figure S2. Molecular orbital surfaces of the SOMOs for the neutral Al^{III} complexes $[Al^{III}(L1^{Me2})_2]$ (**a**) and $[Al^{III}(L2^{Me2})_2]$ (**b**).

Table S1. Crystallographic data for the Al^{III} complexes **1** and **2**.

	1-Cl$_2$·solvent	**1-Me$_2$**·CH_3OH·H_2O	**1-Bu$_2$**	**1-Me$_4$**·1.5H_2O	**2-Me$_2$**·2CH_3CN
Formula	$C_{48}H_{32}AlCl_4N_4O_4P$	$C_{53}H_{48}AlN_4O_6P$	$C_{64}H_{68}AlN_4O_4P$	$C_{56}H_{55}AlN_4O_{5.5}P$	$C_{58}H_{52}AlN_4O_4P$
Formula Weight	928.52	894.90	1015.17	929.99	926.98
Color	black needle	red block	black platelet	black platelet	orange needle
Dimension / mm	0.40 × 0.05 × 0.01	0.30 × 0.17 × 0.12	0.40 × 0.40 × 0.10	0.15 × 0.10 × 0.05	0.30 × 0.07 × 0.07
T / K	90	90	293	90	273
Crystal System	orthorhombic	triclinic	triclinic	monoclinic	triclinic
Space Group	*Pna*2$_1$	*P*-1	*P*-1	*C*2/*c*	*P*-1
a /Å	13.424(2)	11.8738(19)	13.374(7)	21.806(4)	13.324(13)
b /Å	16.380(3)	13.224(2)	14.095(8)	21.822(4)	13.763(13)
c /Å	41.151(7)	16.406(3)	16.593(9)	20.800(4)	14.190(14)
α /°	90	81.934(2)	96.179(8)	90	91.243(14)
β /°	90	81.586(2)	106.731(7)	101.314(3)	104.039(13)
γ /°	90	64.230(2)	103.041(7)	90	101.050(12)
V /Å^3	9048(3)	2286.5(6)	2868(3)	9705(3)	2471(4)
Z	8	2	2	8	2
ρ_{calcd} / g cm^{-3}	1.363	1.300	1.176	1.273	1.246
μ (Mo-Kα)	0.365	0.136	0.113	0.130	0.125
$2\theta_{max}$ /°	54.96	53.46	50.06	50.06	50.06
No. Reflections (R_{int})	51060 (0.0591)	12543 (0.0173)	14118 (0.0167)	23418 (0.0507)	11791 (0.0228)
No. Observations ($I > 2.00\sigma(I)$)	19535 (14707)	9378 (7563)	10014 (7356)	8549 (5440)	8574 (5628)
No. Variables	1118	739	1125	987	947
$R1$ ($I > 2.00\sigma(I)$)	0.0460	0.0703	0.0562	0.0698	0.0581
R (all data)	0.0746	0.0843	0.0773	0.1110	0.0948
w$R2$ (all data)	0.0961	0.2036	0.1648	0.2098	0.1771
Residual Electron Density / e Å^{-3}	0.326 −0.318	1.873 −0.820	0.499 −0.412	0.998 −0.497	0.420 −0.282
Goodness of Fit	1.008	1.039	1.044	1.062	1.017
CCDC deposit. No.	2156173	2156174	2156175	2156176	2156177

Table S2. Cartesian coordinates of the [Al($L1^{Cl2}$)$_2$] anion.

Al	−0.00002	−0.00003	−0.23692
O	0.01343	1.35481	−1.57199
O	−0.33376	−1.28134	1.09085
N	−2.02071	0.32344	−0.31571
N	−2.98952	−0.21736	0.31022
C	−1.15993	1.82663	−1.90149
C	−1.34413	2.83438	−2.87509
H	−0.47378	3.23844	−3.37847
C	−2.61259	3.29864	−3.18111
H	−2.74393	4.07138	−3.92857
C	−3.73289	2.76893	−2.52281
C	−3.60769	1.78323	−1.56455
H	−4.46808	1.37235	−1.05419
C	−2.32382	1.31441	−1.25638
C	−1.44227	−1.71087	1.60743
C	−1.40719	−2.73237	2.59284
H	−0.43558	−3.12125	2.87392
C	−2.55409	−3.22356	3.18147
H	−2.49229	−4.00364	3.93041
C	−3.80630	−2.70849	2.80591
C	−3.90185	−1.72029	1.85782
H	−4.85872	−1.31326	1.55689
C	−2.73675	−1.20214	1.24055
O	−0.01357	−1.35506	−1.57178
O	0.33384	1.28148	1.09063
N	2.02067	−0.32352	−0.31583
N	2.98954	0.21734	0.30997
C	1.15976	−1.82692	−1.90133
C	1.34387	−2.83479	−2.87482
H	0.47347	−3.23892	−3.37807
C	2.61230	−3.29909	−3.18089

H	2.74358	−4.07193	−3.92826
C	3.73266	−2.76929	−2.52277
C	3.60755	−1.78347	−1.56462
H	4.46798	−1.37251	−1.05439
C	2.32370	−1.31461	−1.25639
C	1.44239	1.71103	1.60710
C	1.40740	2.73266	2.59239
H	0.43581	3.12160	2.87348
C	2.55434	3.22387	3.18091
H	2.49260	4.00404	3.92976
C	3.80652	2.70872	2.80534
C	3.90199	1.72042	1.85735
H	4.85884	1.31333	1.55642
C	2.73684	1.20223	1.24021
Cl	−5.34087	3.38587	−2.93708
Cl	5.26768	3.34878	3.56885
Cl	5.34061	−3.38627	−2.93710
Cl	−5.26741	−3.34851	3.56956

Table S3. Cartesian coordinates of the [Al($L1^{Me2}$)$_2$] anion.

Al	4.96191	3.16829	12.21311
O	3.66095	3.67899	10.91707
O	6.31659	2.43539	13.28545
N	5.47325	1.80937	10.77068
N	6.39101	0.92411	10.73161
C	3.68092	2.97932	9.80922
C	2.78536	3.19682	8.73772
H	2.04332	3.98172	8.83408
C	2.85797	2.42069	7.59287
H	2.15624	2.60965	6.78525
C	3.81336	1.39007	7.43964
C	4.69948	1.16460	8.48376
H	5.44919	0.38520	8.41464
C	4.64138	1.94023	9.65207
C	3.85628	0.56782	6.17263
H	4.04760	1.19373	5.29451
H	2.90676	0.05107	5.99733
H	4.64296	−0.18813	6.21999
C	7.18927	1.50400	13.03845
C	8.16034	1.17165	14.01824
H	8.13467	1.72520	14.95046
C	9.10472	0.18787	13.80471
H	9.82737	−0.02599	14.58728
C	9.15912	−0.54811	12.59765
C	8.22180	−0.24216	11.63192
H	8.21136	−0.77183	10.68464
C	7.23604	0.76293	11.80934
C	10.20683	−1.61602	12.39125
H	10.09454	−2.09489	11.41631
H	10.14008	−2.39605	13.15679
H	11.21835	−1.19967	12.44417

O	6.16010	4.50945	11.58235
O	3.70014	2.06008	13.05264
N	4.44678	4.63541	13.54386
N	3.60657	4.64819	14.50382
C	6.08430	5.65755	12.21003
C	6.87162	6.78100	11.87096
H	7.57317	6.69292	11.04881
C	6.74393	7.96701	12.57486
H	7.36097	8.81497	12.29095
C	5.83656	8.11226	13.64893
C	5.05750	7.01674	13.99458
H	4.34652	7.07996	14.80991
C	5.17340	5.80605	13.29397
C	5.72522	9.42718	14.38506
H	5.40862	10.23529	13.71697
H	6.68522	9.72690	14.81835
H	4.99829	9.36361	15.19753
C	2.91637	2.27617	14.06638
C	2.05288	1.24546	14.52071
H	2.08405	0.30115	13.98829
C	1.20584	1.42442	15.59562
H	0.56629	0.60195	15.90363
C	1.14659	2.64614	16.30683
C	1.97576	3.66309	15.87936
H	1.97511	4.62451	16.38291
C	2.86219	3.52109	14.78034
C	0.21108	2.81149	17.48074
H	−0.83224	2.65689	17.18637
H	0.29155	3.81213	17.91056
H	0.43175	2.08865	18.27321

Table S4. Cartesian coordinates of the [Al(L1^{Me4})$_2$] anion.

Al	0.00002	0.00003	−0.22933
O	0.01644	1.35458	−1.56800
O	−0.33489	−1.28276	1.09927
N	−2.01691	0.32484	−0.31200
N	−2.98543	−0.22426	0.31159
C	−1.16196	1.82801	−1.89450
C	−1.32781	2.84294	−2.87678
C	−2.61108	3.28963	−3.15841
H	−2.73300	4.06606	−3.91004
C	−3.76689	2.78613	−2.51695
C	−3.60609	1.79605	−1.56076
H	−4.46065	1.37902	−1.04145
C	−2.32218	1.31917	−1.25024
C	−5.13180	3.32590	−2.87698
H	−5.35446	3.17885	−3.93926
H	−5.20345	4.40118	−2.68078
H	−5.91580	2.82963	−2.30096
C	−1.44809	−1.72033	1.60965
C	−1.39835	−2.75349	2.59611
C	−2.57193	−3.22850	3.15440
H	−2.50535	−4.01549	3.90185
C	−3.85141	−2.73974	2.79837
C	−3.90576	−1.74283	1.84881
H	−4.85624	−1.32578	1.53210
C	−2.73779	−1.21511	1.23922
C	−5.09432	−3.30312	3.44579
H	−5.99349	−2.81727	3.06094
H	−5.07862	−3.16474	4.53211
H	−5.19043	−4.37832	3.26096
O	−0.01612	−1.35523	−1.56728
O	0.33465	1.28347	1.09872

N	2.01697	−0.32480	−0.31143
N	2.98536	0.22457	0.31212
C	1.16236	−1.82876	−1.89337
C	1.32844	−2.84418	−2.87512
C	2.61178	−3.29089	−3.15634
H	2.73387	−4.06769	−3.90757
C	3.76746	−2.78698	−2.51497
C	3.60644	−1.79646	−1.55929
H	4.46089	−1.37910	−1.04006
C	2.32245	−1.31954	−1.24917
C	5.13247	−3.32679	−2.87458
H	5.35529	−3.18011	−3.93688
H	5.20416	−4.40200	−2.67799
H	5.91634	−2.83025	−2.29862
C	1.44773	1.72117	1.60924
C	1.39779	2.75463	2.59537
C	2.57125	3.22981	3.15377
H	2.50451	4.01704	3.90097
C	3.85080	2.74092	2.79819
C	3.90535	1.74370	1.84898
H	4.85589	1.32651	1.53263
C	2.73751	1.21578	1.23931
C	5.09358	3.30452	3.44570
H	5.18975	4.37964	3.26051
H	5.99283	2.81850	3.06123
H	5.07763	3.16651	4.53207
C	0.05115	3.29655	2.99684
H	−0.47647	3.72158	2.13746
H	−0.59247	2.50456	3.39184
H	0.15466	4.07203	3.75861
C	0.11363	−3.39547	−3.57340
H	−0.59979	−3.81520	−2.85696
H	−0.42120	−2.61011	−4.11747

H	0.39130	−4.17759	−4.28327
C	−0.05180	−3.29529	2.99801
H	0.47594	−3.72070	2.13889
H	0.59180	−2.50316	3.39278
H	−0.15545	−4.07045	3.76009
C	−0.11283	3.39378	−3.57512
H	0.60034	3.81413	−2.85879
H	0.42223	2.60801	−4.11839
H	−0.39033	4.17532	−4.28570

Table S5. Cartesian coordinates of the [Al($L2^{Me2}$)$_2$] anion.

Al	−0.00017	−0.00090	−0.25688
O	0.06823	1.35692	−1.59666
O	−0.31257	−1.29113	1.09507
N	−2.00070	0.37115	−0.35442
C	−1.09450	1.86686	−1.93283
C	−1.24253	2.88117	−2.90184
H	−0.35348	3.25626	−3.39775
C	−2.49755	3.38678	−3.21505
H	−2.57968	4.16730	−3.96646
C	−3.66417	2.91698	−2.58567
C	−3.52900	1.91203	−1.62801
H	−4.42246	1.54212	−1.13584
C	−2.27428	1.38519	−1.29818
C	−5.01675	3.49985	−2.92745
H	−5.18734	3.51201	−4.00860
H	−5.11134	4.53361	−2.57613
H	−5.82364	2.92262	−2.46992
C	−1.40319	−1.75325	1.62988
C	−1.33023	−2.77928	2.60929
H	−0.34575	−3.14906	2.87474
C	−2.46379	−3.29302	3.20814
H	−2.35569	−4.07731	3.95261
C	−3.75871	−2.83044	2.88171
C	−3.84683	−1.83227	1.92897
H	−4.82432	−1.44770	1.64870
C	−2.71050	−1.27655	1.28981
C	−4.98056	−3.41154	3.55339
H	−5.89445	−2.93967	3.18568
H	−4.94723	−3.27142	4.63907
H	−5.06547	−4.48814	3.37136
O	−0.06998	−1.36495	−1.59007

O	0.31378	1.29593	1.08834
N	2.00007	−0.37466	−0.35362
C	1.09203	−1.87869	−1.92299
C	1.23876	−2.89891	−2.88594
H	0.34927	−3.27567	−3.37979
C	2.49316	−3.40797	−3.19612
H	2.57433	−4.19294	−3.94299
C	3.66034	−2.93602	−2.56945
C	3.52645	−1.92515	−1.61783
H	4.42039	−1.55347	−1.12783
C	2.27243	−1.39471	−1.29124
C	5.01206	−3.52363	−2.90651
H	5.17742	−3.55616	−3.98799
H	5.10970	−4.55043	−2.53599
H	5.82040	−2.93693	−2.46379
C	1.40504	1.76030	1.62000
C	1.33326	2.79108	2.59448
H	0.34913	3.16250	2.85897
C	2.46749	3.30719	3.19004
H	2.36027	4.09506	3.93085
C	3.76197	2.84250	2.86486
C	3.84894	1.83972	1.91687
H	4.82604	1.45327	1.63783
C	2.71189	1.28145	1.28121
C	4.98457	3.42626	3.53285
H	5.06990	4.50191	3.34551
H	5.89797	2.95214	3.16681
H	4.95193	3.29145	4.61922
C	−2.92769	−0.24097	0.32095
H	−3.97135	0.03185	0.15971
C	2.92788	0.24063	0.31773
H	3.97126	−0.03371	0.15731

Table S6. Cartesian coordinates of the neutral [Al($L1^{Me2}$)$_2$] complex.

Al	−0.00000	−0.00001	−0.19549
O	0.07972	1.36923	−1.52516
O	−0.38056	−1.28381	1.10435
N	−1.99154	0.39020	−0.30295
N	−2.99240	−0.12751	0.31626
C	−1.06115	1.87751	−1.85548
C	−1.19961	2.92209	−2.80687
H	−0.30295	3.31106	−3.27330
C	−2.44852	3.40022	−3.12243
H	−2.54114	4.19146	−3.86021
C	−3.63396	2.89532	−2.51546
C	−3.51974	1.88785	−1.57431
H	−4.39168	1.47728	−1.08120
C	−2.25809	1.37767	−1.23576
C	−4.97394	3.46371	−2.90500
H	−5.16883	3.32250	−3.97350
H	−5.01976	4.54060	−2.71093
H	−5.78399	2.98743	−2.35035
C	−1.50273	−1.68736	1.59099
C	−1.51409	−2.74510	2.54189
H	−0.55661	−3.17710	2.80674
C	−2.68370	−3.18866	3.10582
H	−2.64611	−3.99361	3.83404
C	−3.94733	−2.62891	2.76798
C	−3.96480	−1.61443	1.84140
H	−4.89598	−1.15108	1.53534
C	−2.78247	−1.11727	1.22901
C	−5.20565	−3.14989	3.41421
H	−6.08766	−2.62453	3.04378
H	−5.17444	−3.02727	4.50198
H	−5.34273	−4.21786	3.21477

O	−0.07970	−1.36923	−1.52517
O	0.38055	1.28379	1.10436
N	1.99154	−0.39021	−0.30294
N	2.99239	0.12751	0.31627
C	1.06117	−1.87751	−1.85548
C	1.19965	−2.92209	−2.80687
H	0.30299	−3.31106	−3.27330
C	2.44856	−3.40022	−3.12242
H	2.54119	−4.19147	−3.86019
C	3.63399	−2.89533	−2.51543
C	3.51975	−1.88785	−1.57428
H	4.39168	−1.47728	−1.08116
C	2.25810	−1.37768	−1.23574
C	4.97398	−3.46371	−2.90496
H	5.16888	−3.32246	−3.97345
H	5.01978	−4.54060	−2.71093
H	5.78401	−2.98745	−2.35028
C	1.50272	1.68735	1.59100
C	1.51406	2.74510	2.54190
H	0.55658	3.17709	2.80675
C	2.68366	3.18867	3.10583
H	2.64607	3.99362	3.83404
C	3.94730	2.62893	2.76799
C	3.96478	1.61444	1.84141
H	4.89597	1.15110	1.53536
C	2.78246	1.11727	1.22903
C	5.20561	3.14992	3.41423
H	5.34267	4.21789	3.21481
H	6.08763	2.62458	3.04377
H	5.17442	3.02727	4.50199

Table S7. Cartesian coordinates of the [Al($L2^{Me2}$)$_2$] anion.

Al	0.00000	−0.27358	−0.00003
O	0.02213	−1.67543	1.30736
O	0.23069	1.02977	−1.31761
N	2.01033	−0.37052	0.27659
C	1.19087	−2.02243	1.73322
C	1.38841	−3.06038	2.67896
H	0.51564	−3.58673	3.04541
C	2.65649	−3.36351	3.11809
H	2.79253	−4.15208	3.85165
C	3.79761	−2.67335	2.63888
C	3.62217	−1.66585	1.69691
H	4.49678	−1.14343	1.32619
C	2.34651	−1.32940	1.23111
C	5.16786	−3.03828	3.14958
H	5.39538	−4.09211	2.95752
H	5.24085	−2.88743	4.23194
H	5.94553	−2.43650	2.67556
C	1.27486	1.64326	−1.76415
C	1.12367	2.66302	−2.74350
H	0.11608	2.88742	−3.07210
C	2.20983	3.32968	−3.25628
H	2.04966	4.09845	−4.00705
C	3.53735	3.04869	−2.83904
C	3.70406	2.06993	−1.88670
H	4.70459	1.82711	−1.53865
C	2.61402	1.35158	−1.32611
C	4.70019	3.80628	−3.42980
H	5.64832	3.47414	−3.00195
H	4.61098	4.88231	−3.24689
H	4.75785	3.66798	−4.51461
O	−0.02226	−1.67544	−1.30744

O	−0.23059	1.02983	1.31751
N	−2.01035	−0.37039	−0.27662
C	−1.19103	−2.02237	−1.73326
C	−1.38868	−3.06033	−2.67896
H	−0.51595	−3.58675	−3.04542
C	−2.65678	−3.36338	−3.11806
H	−2.79290	−4.15196	−3.85160
C	−3.79785	−2.67312	−2.63884
C	−3.62231	−1.66562	−1.69690
H	−4.49688	−1.14314	−1.32616
C	−2.34662	−1.32924	−1.23113
C	−5.16812	−3.03791	−3.14956
H	−5.39547	−4.09189	−2.95811
H	−5.24129	−2.88641	−4.23182
H	−5.94580	−2.43651	−2.67507
C	−1.27471	1.64335	1.76411
C	−1.12345	2.66309	2.74346
H	−0.11583	2.88745	3.07202
C	−2.20956	3.32979	3.25628
H	−2.04933	4.09856	4.00705
C	−3.53710	3.04886	2.83910
C	−3.70389	2.07011	1.88675
H	−4.70445	1.82734	1.53875
C	−2.61390	1.35172	1.32612
C	−4.69990	3.80646	3.42994
H	−4.75777	3.66777	4.51469
H	−5.64802	3.47466	3.00180
H	−4.61044	4.88254	3.24744
C	2.89731	0.36678	−0.34265
H	3.95223	0.23282	−0.10177
C	−2.89728	0.36695	0.34266
H	−3.95221	0.23304	0.10182