Electronic Supplementary Information

Unsolvated $Al(C_6F_5)_3$: Structural Features and Electronic Interaction with Ferrocene

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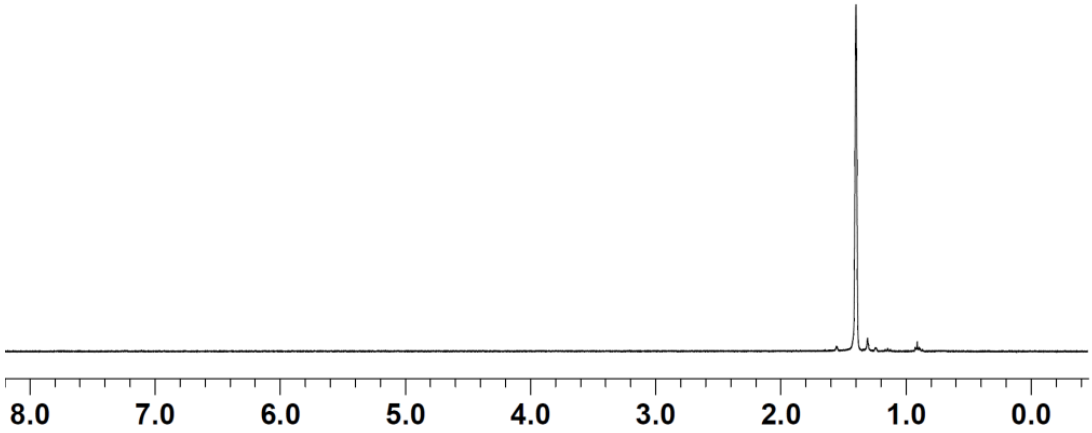

Figure S1. ^1H NMR (C_6D_{12}, 25 °C) spectrum of $[Al(C_6F_5)_3]_2$.

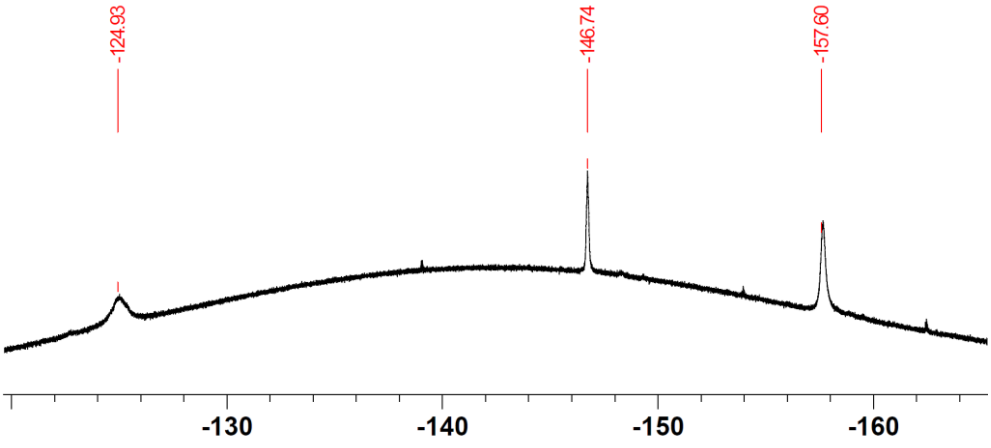

Figure S2. ^{19}F NMR (C_6D_{12}, 25 °C) spectrum of $[Al(C_6F_5)_3]_2$. A trace amount of C_6F_5H (–139.2, –154.2, –162.50) was also present.

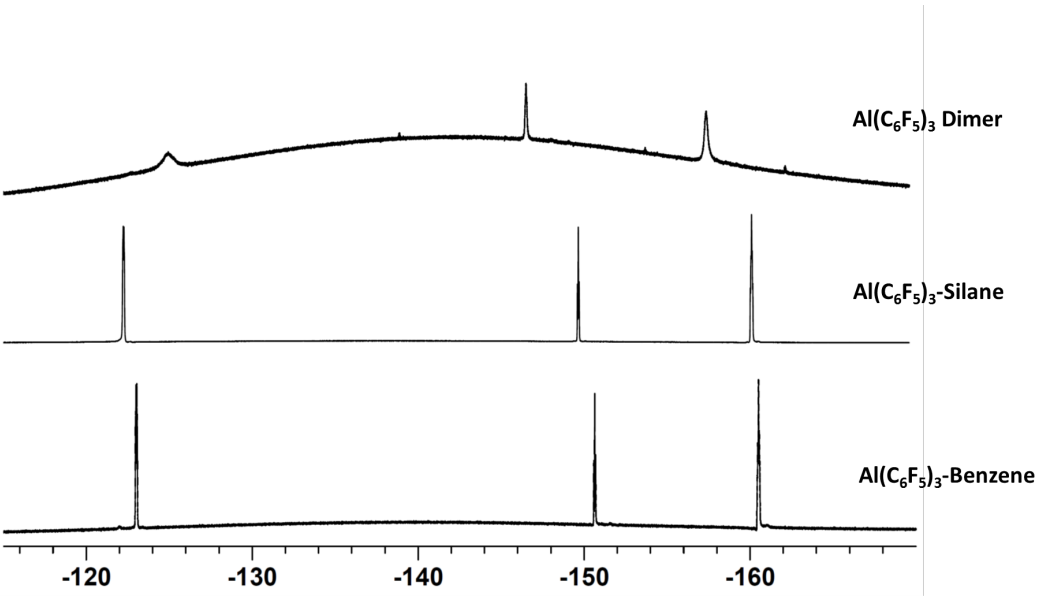

Figure S3. ^{19}F NMR (25 °C) spectra of $[Al(C_6F_5)_3]_2$ and $Et_3SiH{\cdot}Al(C_6F_5)_3$ in C_6D_{12}, and $C_6D_6{\cdot}Al(C_6F_5)_3$ in C_6D_6.

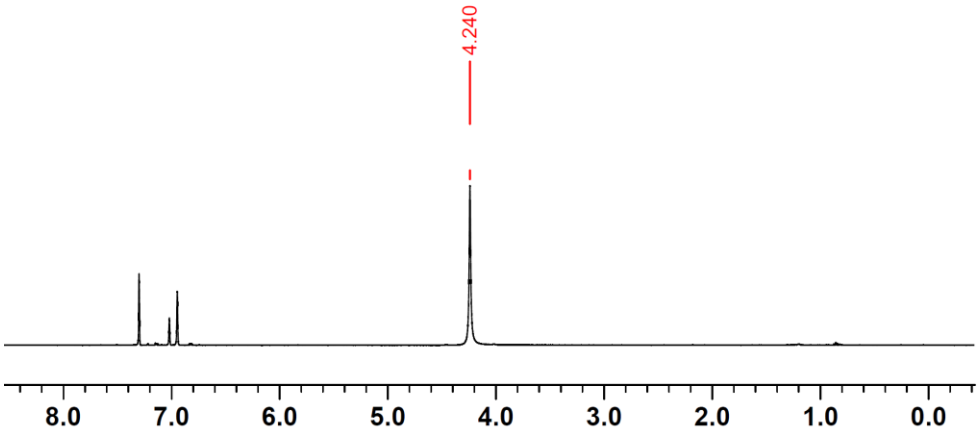

Figure S4. ^{1}H NMR (C_6D_5Br, 25 °C) spectrum of $Cp_2Fe{\cdot}Al(C_6F_5)_3$.

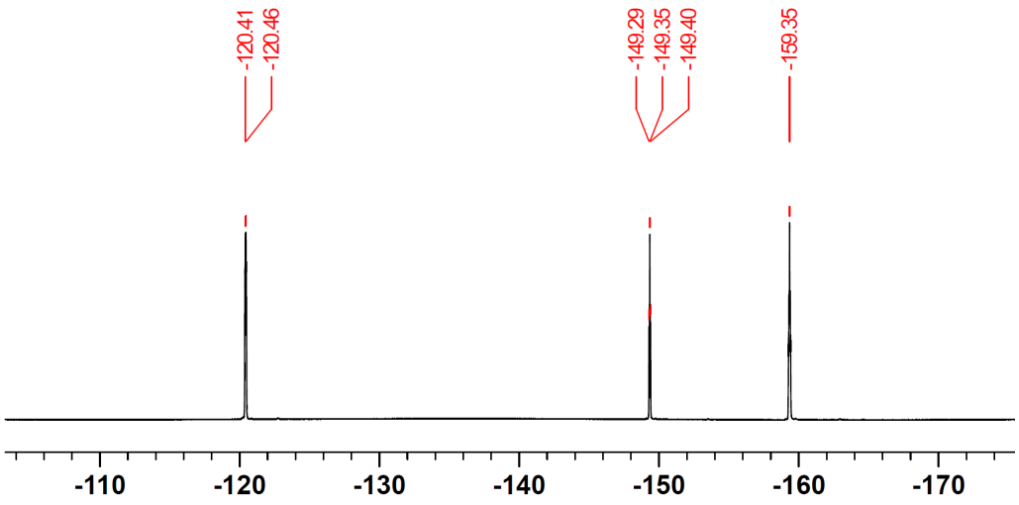

Figure S5. ^{19}F NMR (C_6D_5Br, 25 °C) spectrum of $Cp_2Fe{\cdot}Al(C_6F_5)_3$.

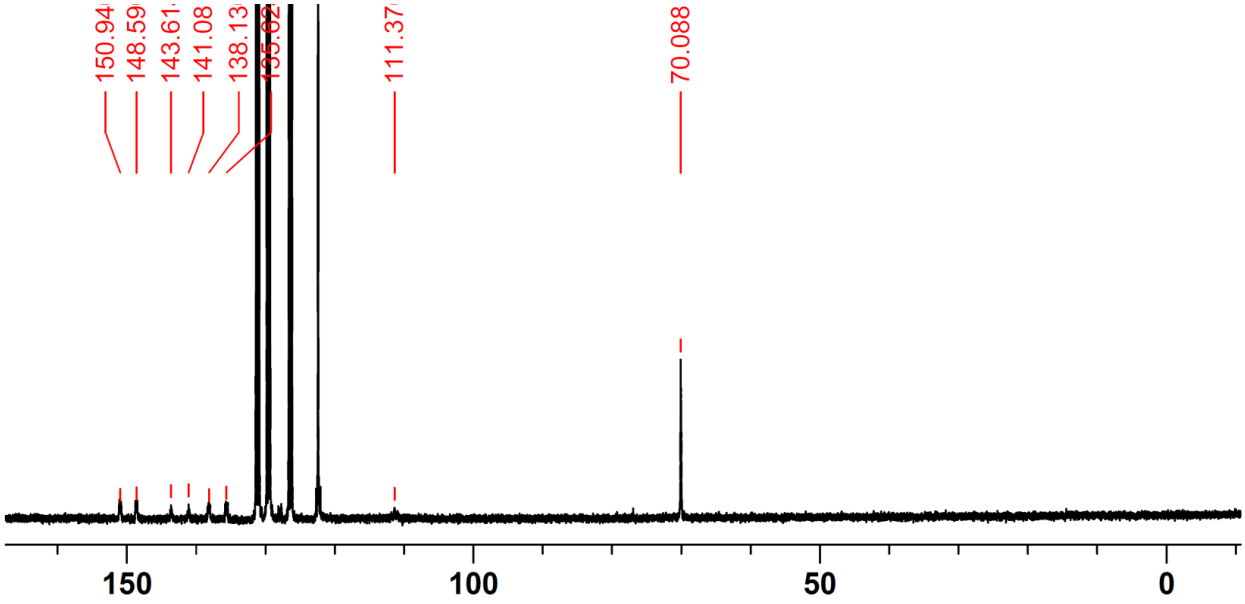

Figure S6. ^{13}C NMR (C_6D_5Br, 25 °C) spectrum of $Cp_2Fe{\cdot}Al(C_6F_5)_3$.

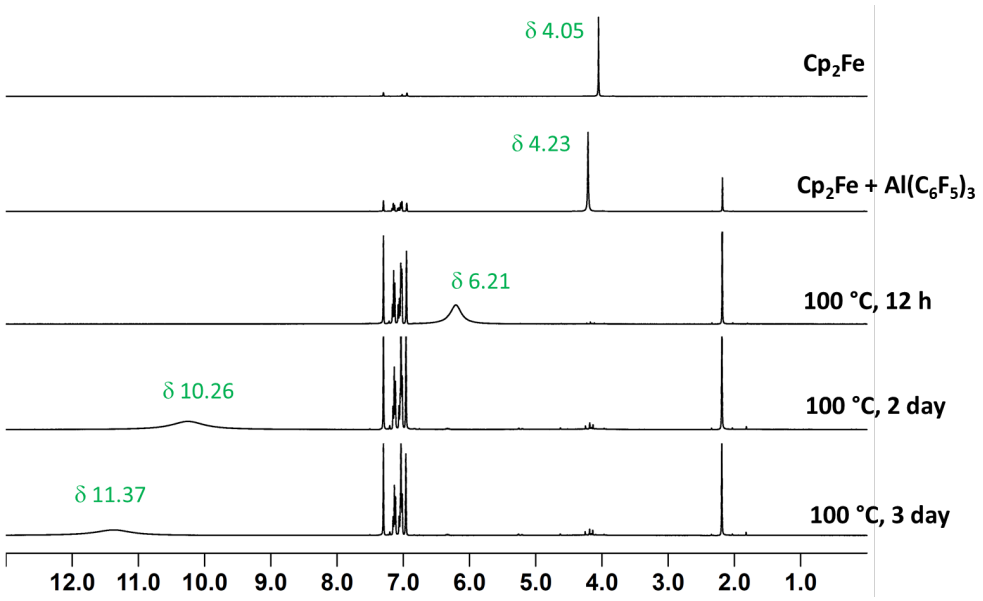

Figure S7. ^{1}H NMR (C_6D_5Br, 25 °C) investigation of coordination and electronic interaction between ferrocene and $Al(C_6F_5)_3$.

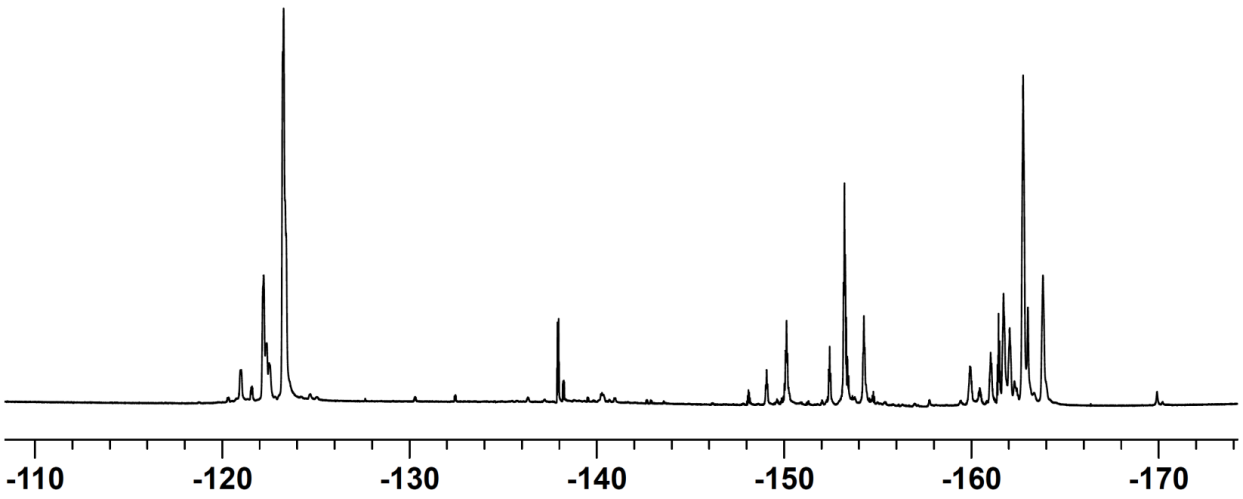

Figure S8. ^{19}F NMR (C_6D_5Br, 25 °C) of a mixture of ferrocene and $Al(C_6F_5)_3$ heated at 100 °C for 3 days, showing the decomposition of $Al(C_6F_5)_3$.

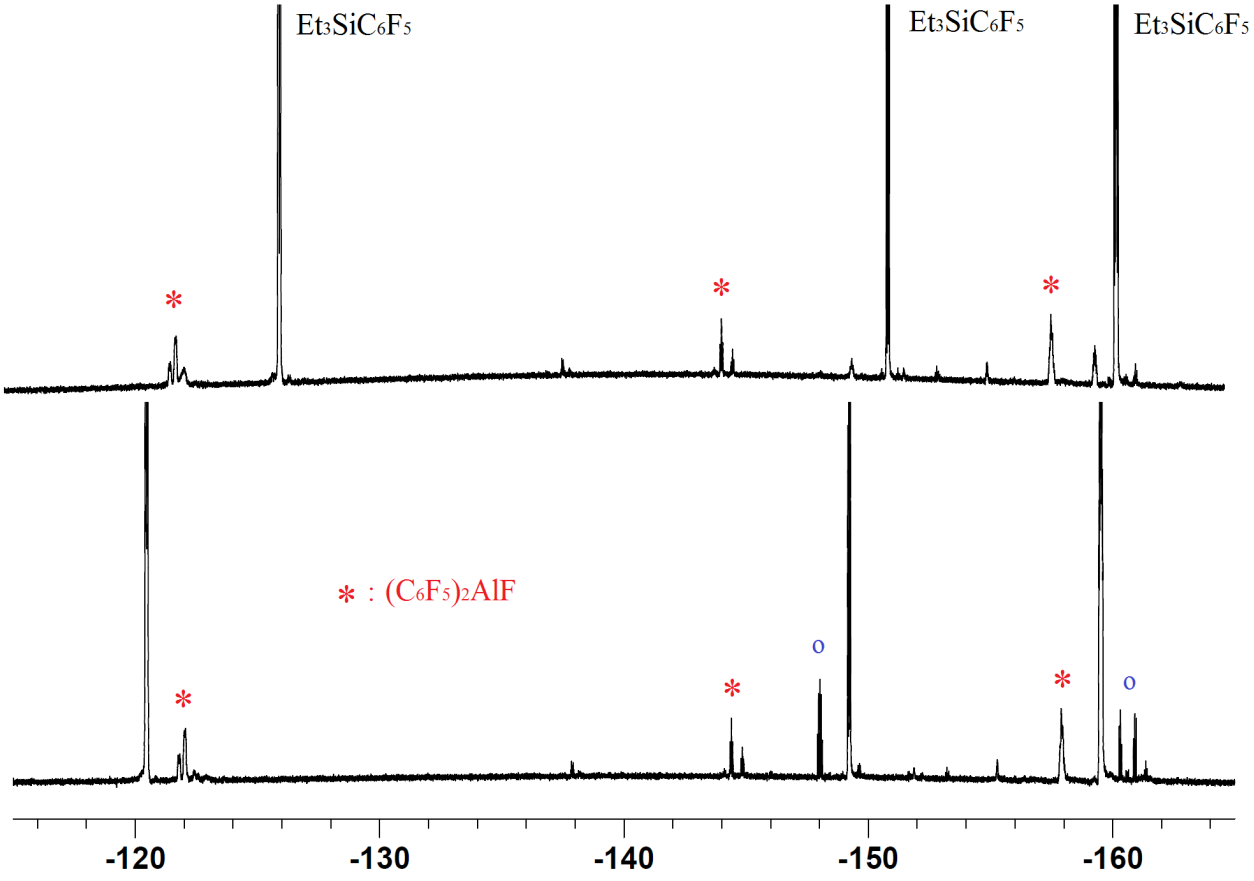

Figure S9. ^{19}F NMR (C_6D_5Br, 25 °C) spectra of metathesis between Et_3SiF and $Al(C_6F_5)_3$ (top spectrum, the resulting $(C_6F_5)_2AlF$ has limited solubility hence the stoichiometry in the spectrum was off), and the decomposition (about 10%) of $Al(C_6F_5)_3$ in C_6D_5Br at 100 °C for 3 days (bottom spectrum). Peaks marked as "*" were assigned to $(C_6F_5)_2AlF$, while those with "o" were assigned to species (such as dimer or trimer) presumably derived from the transient tetrafluorobenzyne.

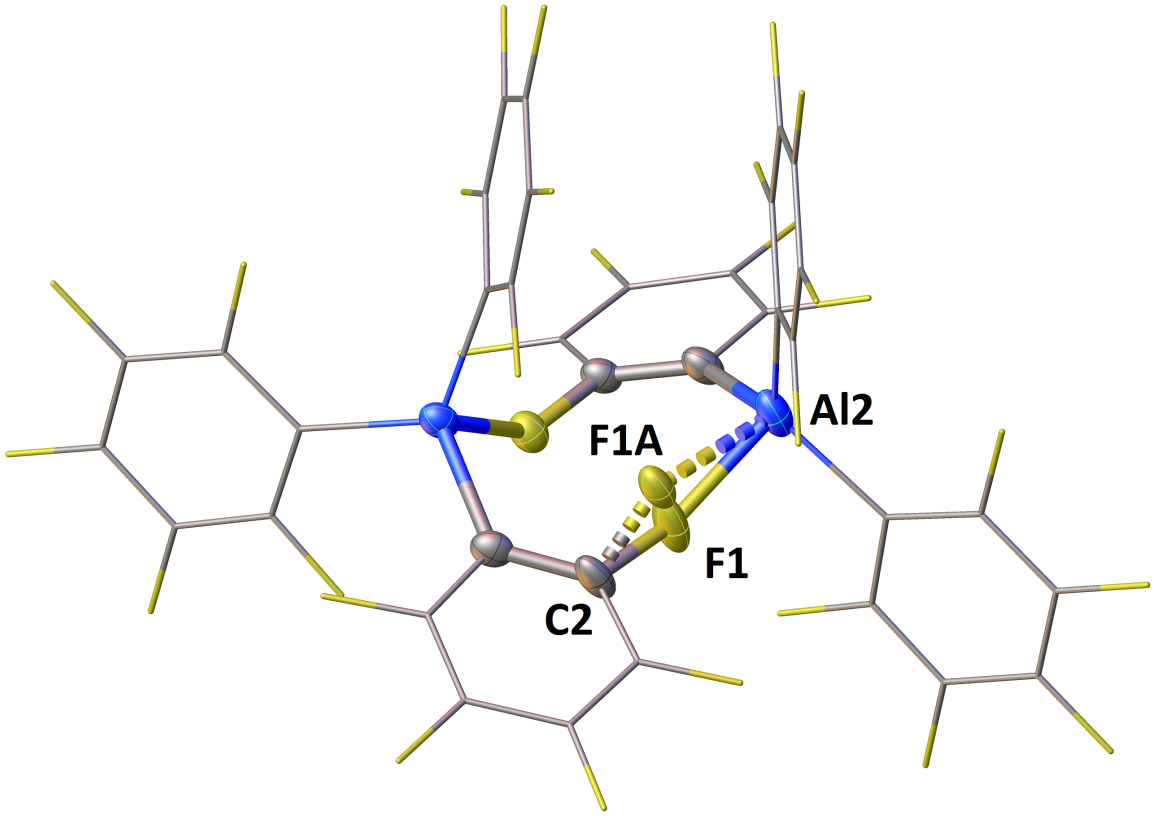

Figure S10. Modeling of the disorder issue for one of the bridging fluorines. The Site Occupancy Factors for F1 and F1A are 0.690 and 0.310, respectively. Other fluorines with high ADP max/min ratio are difficult to model and left as is.

Table S1. Crystal data and structure refinement details

Compound	$[Al(C_6F_5)_3]_2$	$Cp_2Fe{\cdot}Al(C_6F_5)_3$
empirical formula	$C_{36}Al2F_{30}$	$C_{28}H_{10}AlF_{15}Fe$
MW	1056.32	714.19
T, K	120(2)	100(2)
wavelength, Å	MoKa, 0.71073	CuKa, 1.54178
crystal system	Triclinic	Monoclinic
space group	P-1	$P2_1/n$
a, Å	11.2560(4)	10.5849(5)
b, Å	12.5872(5)	19.2778(9)
c, Å	13.6116(5)	12.6011(6)
α, deg	91.372(2)	90
β, deg	92.041(2)	97.400(3)
γ, deg	109.371(2)	90
V, Å^3	1816.88(12)	2549.9(2)
Z	2	4
ρ_{calc}, g cm^{-3}	1.931	1.651
μ , mm^{-1}	0.27	0.25
crystal size, mm	0.56×0.54×0.50	0.67×0.64×0.56
θ range, deg	1.9-35.9	4.2-70.4
limiting indices	$-18\le h\le 12$	$-12\le h\le 12$
	$-20\le k\le 20$	$-22\le k\le 22$
	$-22\le l\le 22$	$-14\le l\le 15$
reflns collected	85247	24676
independent reflns	16955 [R(int) = 0.046]	4601 [R(int) = 0.022]
absorption correction	Multi-scan	Numerical
data/restraints/para's	16955 / 13 / 623	4603 / 0 / 411
goodness-of-fit on F^2	1.01	1.01
final R indices	$R1$ = 0.057	$R1$ = 0.023
[I >2σ(I)] [a]	w$R2$ = 0.139	w$R2$ = 0.060
R indices (all data) [a]	$R1$ = 0.113; w$R2$ = 0.174	$R1$ = 0.025; w$R2$ = 0.061
peak$_{max}$/hole$_{min}$ (e Å^{-3})	0.69 / –0.54	0.33 / –0.33
Flack parameter	--	--

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S2. Bond lengths [Å] and angles [º] for $[Al(C_6F_5)_3]_2$

Geometric parameters (Å, º)

Al1—F16	1.9621 (12)	C22—F18	1.334 (2)
Al1—C7	1.9648 (17)	C22—C23	1.378 (3)
Al1—C13	1.9724 (18)	C23—F19	1.341 (2)
Al1—C1	1.9839 (18)	C6—F5	1.350 (2)
Al2—C25	1.960 (2)	C6—C5	1.385 (3)
Al2—C31	1.966 (2)	C5—F4	1.338 (2)
Al2—C19	1.9824 (18)	C27—F22	1.347 (2)
Al2—F1A	2.021 (7)	C27—C26	1.377 (3)
C7—C12	1.384 (3)	C27—C28	1.379 (3)
C7—C8	1.391 (2)	C28—F23	1.343 (3)
C12—F10	1.354 (2)	C28—C29	1.385 (4)
C12—C11	1.389 (2)	C30—F25	1.353 (3)
C21—F17	1.334 (2)	C30—C29	1.366 (4)
C21—C20	1.379 (2)	C29—F24	1.339 (3)
C20—C19	1.371 (2)	C14—F11	1.3504 (19)
C20—F16	1.4233 (19)	C14—C15	1.386 (2)
C8—F6	1.357 (2)	C14—C13	1.386 (2)
C8—C9	1.381 (3)	C13—C18	1.396 (2)
C11—F9	1.341 (2)	C18—F15	1.355 (2)
C11—C10	1.385 (3)	C18—C17	1.376 (3)
C1—C2	1.366 (3)	C17—F14	1.343 (2)
C1—C6	1.381 (2)	C17—C16	1.383 (3)
C4—F3	1.328 (2)	C15—F12	1.340 (2)
C4—C5	1.376 (3)	C15—C16	1.384 (3)
C4—C3	1.379 (2)	C16—F13	1.340 (2)
C25—C26	1.383 (3)	C31—C32	1.388 (3)
C25—C30	1.385 (3)	C31—C36	1.396 (3)
C2—C3	1.378 (3)	C32—F26	1.350 (2)
C2—F1A	1.425 (5)	C32—C33	1.386 (3)
C19—C24	1.393 (3)	C36—F30	1.357 (3)
C10—F8	1.339 (2)	C36—C35	1.372 (4)
C10—C9	1.384 (3)	C33—F27	1.341 (3)
C3—F2	1.333 (2)	C33—C34	1.385 (3)
C9—F7	1.343 (2)	C35—F29	1.349 (3)
C24—F20	1.351 (2)	C35—C34	1.379 (4)
C24—C23	1.382 (3)	C34—F28	1.344 (3)
F16—Al1—C7	100.19 (6)	F19—C23—C24	121.07 (19)
F16—Al1—C13	103.68 (6)	C22—C23—C24	119.31 (17)
C7—Al1—C13	120.74 (8)	F5—C6—C1	118.60 (17)
F16—Al1—C1	96.22 (6)	F5—C6—C5	118.04 (17)
C7—Al1—C1	117.06 (7)	C1—C6—C5	123.35 (18)

C13—Al1—C1	113.15 (7)	F4—C5—C4	118.62 (17)
C25—Al2—C31	120.71 (8)	F4—C5—C6	120.97 (18)
C25—Al2—C19	117.26 (9)	C4—C5—C6	120.42 (16)
C31—Al2—C19	115.03 (9)	F22—C27—C26	121.28 (19)
C25—Al2—F1A	105.8 (3)	F22—C27—C28	119.7 (2)
C31—Al2—F1A	88.3 (4)	C26—C27—C28	119.0 (2)
C19—Al2—F1A	102.10 (18)	F23—C28—C27	119.8 (2)
C12—C7—C8	115.07 (15)	F23—C28—C29	120.6 (2)
C12—C7—Al1	124.14 (12)	C27—C28—C29	119.6 (2)
C8—C7—Al1	120.79 (13)	F25—C30—C29	117.8 (2)
F10—C12—C7	119.57 (15)	F25—C30—C25	118.8 (2)
F10—C12—C11	116.86 (16)	C29—C30—C25	123.3 (2)
C7—C12—C11	123.57 (16)	F24—C29—C30	121.1 (3)
F17—C21—C20	121.62 (16)	F24—C29—C28	119.6 (3)
F17—C21—C22	120.81 (16)	C30—C29—C28	119.3 (2)
C20—C21—C22	117.57 (17)	F21—C26—C27	117.36 (17)
C19—C20—C21	126.24 (16)	F21—C26—C25	119.39 (19)
C19—C20—F16	118.82 (14)	C27—C26—C25	123.25 (19)
C21—C20—F16	114.91 (14)	F11—C14—C15	117.48 (15)
F6—C8—C9	117.26 (15)	F11—C14—C13	118.81 (15)
F6—C8—C7	119.00 (15)	C15—C14—C13	123.71 (15)
C9—C8—C7	123.74 (17)	C14—C13—C18	114.97 (16)
F9—C11—C10	119.97 (16)	C14—C13—Al1	122.21 (12)
F9—C11—C12	121.32 (16)	C18—C13—Al1	122.25 (13)
C10—C11—C12	118.71 (17)	F15—C18—C17	116.90 (15)
C2—C1—Al1	124.55 (12)	C17—C18—C13	123.49 (17)
C6—C1—Al1	122.65 (14)	F14—C17—C18	121.32 (18)
F3—C4—C5	120.10 (15)	F14—C17—C16	119.67 (18)
F3—C4—C3	120.96 (16)	C18—C17—C16	119.00 (16)
C5—C4—C3	118.94 (16)	F12—C15—C16	119.53 (17)
C26—C25—C30	115.5 (2)	F12—C15—C14	121.87 (16)
C26—C25—Al2	124.55 (15)	C16—C15—C14	118.60 (16)
C30—C25—Al2	119.91 (16)	F13—C16—C17	120.15 (18)
C1—C2—C3	127.67 (16)	F13—C16—C15	119.62 (18)
C1—C2—F1A	108.1 (4)	C17—C16—C15	120.21 (17)
C3—C2—F1A	120.9 (3)	C32—C31—C36	115.2 (2)
C20—C19—C24	113.27 (16)	C32—C31—Al2	123.30 (14)
C20—C19—Al2	131.76 (13)	C36—C31—Al2	121.43 (19)
C24—C19—Al2	114.97 (13)	F26—C32—C33	116.3 (2)
F8—C10—C9	120.27 (17)	F26—C32—C31	119.88 (19)
F8—C10—C11	119.61 (18)	C33—C32—C31	123.8 (2)
C9—C10—C11	120.12 (16)	F30—C36—C35	118.4 (2)
F2—C3—C2	122.50 (16)	F30—C36—C31	118.5 (2)

F2—C3—C4	120.53 (16)	C35—C36—C31	123.1 (2)
C2—C3—C4	116.97 (16)	F27—C33—C34	120.3 (2)
F7—C9—C8	122.02 (18)	F27—C33—C32	121.7 (2)
F7—C9—C10	119.21 (16)	C34—C33—C32	118.0 (3)
C8—C9—C10	118.77 (16)	F29—C35—C36	121.5 (3)
F20—C24—C23	118.32 (17)	F29—C35—C34	119.1 (3)
F20—C24—C19	117.75 (17)	C36—C35—C34	119.4 (2)
C23—C24—C19	123.92 (18)	F28—C34—C35	120.1 (2)
F18—C22—C23	120.53 (18)	F28—C34—C33	119.4 (3)
F18—C22—C21	119.78 (18)	C35—C34—C33	120.5 (2)
C23—C22—C21	119.68 (16)	C20—F16—Al1	143.40 (10)
F19—C23—C22	119.61 (18)	C2—F1A—Al2	152.6 (10)

Table S3. Bond lengths [Å] and angles [º] for $Cp_2Fe{\cdot}Al(C_6F_5)_3$

Geometric parameters (Å, º)

Fe1—C2	2.0102 (16)	C10—H10	1.0000
Fe1—C5	2.0230 (15)	C9—C8	1.417 (2)
Fe1—C9	2.0378 (16)	C9—H9	1.0000
Fe1—C8	2.0421 (16)	C8—H8	1.0000
Fe1—C3	2.0479 (16)	C3—C2	1.414 (2)
Fe1—C10	2.0542 (17)	C3—C4	1.426 (2)
Fe1—C1	2.0543 (15)	C3—H3	1.0000
Fe1—C4	2.0538 (16)	C2—C1	1.464 (2)
Fe1—C7	2.0554 (17)	C2—H2	1.0000
Fe1—C6	2.0599 (17)	C1—C5	1.465 (2)
F15—C28	1.3600 (18)	C1—H1	0.90 (2)
F12—C25	1.3446 (18)	C5—C4	1.418 (2)
F14—C27	1.3434 (19)	C5—H5	1.0000
F13—C26	1.3397 (18)	C4—H4	1.0000
F11—C24	1.3541 (18)	C28—C27	1.380 (2)
F10—C22	1.3562 (18)	C28—C23	1.383 (2)
F7—C19	1.3465 (19)	C27—C26	1.378 (2)
F6—C18	1.3532 (19)	C26—C25	1.380 (2)
F8—C20	1.3405 (18)	C25—C24	1.378 (2)
F9—C21	1.3447 (19)	C24—C23	1.388 (2)
F2—C13	1.3424 (17)	C22—C17	1.380 (2)
F5—C16	1.3556 (18)	C22—C21	1.381 (2)
F1—C12	1.3576 (18)	C17—C18	1.388 (2)
F4—C15	1.3442 (18)	C18—C19	1.378 (2)
Al1—C11	1.9847 (16)	C19—C20	1.376 (3)
Al1—C23	1.9942 (16)	C20—C21	1.382 (2)
Al1—C17	1.9977 (16)	C13—C14	1.379 (2)
Al1—C1	2.2137 (15)	C13—C12	1.378 (2)
C7—C6	1.412 (3)	C12—C11	1.385 (2)

C7—C8	1.416 (3)	C11—C16	1.386 (2)
C7—H7	1.0000	C16—C15	1.378 (2)
C6—C10	1.420 (3)	C15—C14	1.381 (2)
C6—H6	1.0000	C14—F3	1.3380 (18)
C10—C9	1.418 (3)		

C2—Fe1—C5	71.08 (6)	C4—C3—H3	125.5
C2—Fe1—C9	159.51 (7)	Fe1—C3—H3	125.5
C5—Fe1—C9	119.15 (7)	C3—C2—C1	107.88 (14)
C2—Fe1—C8	122.84 (7)	C3—C2—Fe1	71.04 (9)
C5—Fe1—C8	153.73 (7)	C1—C2—Fe1	70.50 (9)
C9—Fe1—C8	40.64 (7)	C3—C2—H2	126.0
C2—Fe1—C3	40.78 (7)	C1—C2—H2	126.0
C5—Fe1—C3	69.27 (6)	Fe1—C2—H2	126.0
C9—Fe1—C3	122.97 (7)	C5—C1—C2	106.32 (14)
C8—Fe1—C3	105.69 (7)	C5—C1—Fe1	67.80 (8)
C5—Fe1—C10	107.53 (7)	C5—C1—Al1	98.17 (10)
C9—Fe1—C10	40.55 (7)	C2—C1—Al1	97.17 (10)
C8—Fe1—C10	68.22 (7)	Fe1—C1—Al1	153.27 (9)
C3—Fe1—C10	160.53 (7)	C5—C1—H1	125.7 (13)
C2—Fe1—C1	42.21 (6)	C2—C1—H1	125.0 (12)
C5—Fe1—C1	42.12 (6)	Fe1—C1—H1	114.3 (12)
C9—Fe1—C1	156.47 (7)	Al1—C1—H1	92.4 (12)
C8—Fe1—C1	162.13 (7)	C4—C5—C1	107.71 (14)
C3—Fe1—C1	69.12 (6)	C4—C5—Fe1	70.82 (9)
C10—Fe1—C1	122.20 (7)	C1—C5—Fe1	70.08 (8)
C2—Fe1—C4	69.32 (7)	C4—C5—H5	126.1
C5—Fe1—C4	40.69 (6)	C1—C5—H5	126.1
C9—Fe1—C4	106.00 (7)	Fe1—C5—H5	126.1
C8—Fe1—C4	118.88 (7)	C5—C4—C3	108.91 (14)
C3—Fe1—C4	40.69 (7)	C5—C4—Fe1	68.48 (9)
C10—Fe1—C4	124.62 (7)	C3—C4—Fe1	69.43 (9)
C1—Fe1—C4	69.05 (6)	C5—C4—H4	125.5
C2—Fe1—C7	107.11 (7)	C3—C4—H4	125.5
C5—Fe1—C7	164.16 (8)	Fe1—C4—H4	125.5
C9—Fe1—C7	68.05 (7)	F15—C28—C27	116.64 (14)
C8—Fe1—C7	40.42 (7)	F15—C28—C23	119.01 (13)
C3—Fe1—C7	120.19 (7)	C27—C28—C23	124.34 (14)
C10—Fe1—C7	67.96 (7)	F14—C27—C28	121.70 (14)
C1—Fe1—C7	126.25 (7)	F14—C27—C26	119.61 (14)
C4—Fe1—C7	154.44 (8)	C28—C27—C26	118.69 (15)
C2—Fe1—C6	122.15 (7)	F13—C26—C25	120.04 (15)
C5—Fe1—C6	126.78 (8)	F13—C26—C27	120.25 (15)
C9—Fe1—C6	67.86 (7)	C25—C26—C27	119.69 (14)
C8—Fe1—C6	67.77 (7)	F12—C25—C26	119.32 (14)
C3—Fe1—C6	156.28 (8)	F12—C25—C24	121.48 (14)

C10—Fe1—C6	40.37 (8)	C26—C25—C24	119.19 (14)
C1—Fe1—C6	109.72 (7)	F11—C24—C25	116.30 (13)
C4—Fe1—C6	162.70 (8)	F11—C24—C23	119.98 (13)
C7—Fe1—C6	40.13 (8)	C25—C24—C23	123.71 (15)
C11—Al1—C23	115.55 (6)	C28—C23—C24	114.25 (14)
C11—Al1—C17	114.13 (6)	C28—C23—Al1	122.70 (11)
C23—Al1—C17	108.95 (6)	C24—C23—Al1	122.95 (11)
C11—Al1—C1	105.34 (6)	F10—C22—C17	119.95 (14)
C23—Al1—C1	107.12 (6)	F10—C22—C21	115.94 (14)
C17—Al1—C1	104.89 (6)	C17—C22—C21	124.11 (15)
C6—C7—C8	107.96 (16)	C22—C17—C18	113.96 (14)
C6—C7—Fe1	70.10 (10)	C22—C17—Al1	128.73 (12)
C8—C7—Fe1	69.28 (9)	C18—C17—Al1	117.27 (11)
C6—C7—H7	126.0	F6—C18—C19	116.66 (14)
C8—C7—H7	126.0	F6—C18—C17	118.94 (14)
Fe1—C7—H7	126.0	C19—C18—C17	124.40 (15)
C7—C6—C10	108.43 (16)	F7—C19—C20	120.02 (15)
C7—C6—Fe1	69.77 (10)	F7—C19—C18	121.00 (15)
C10—C6—Fe1	69.60 (10)	C20—C19—C18	118.98 (15)
C7—C6—H6	125.8	F8—C20—C19	120.42 (15)
C10—C6—H6	125.8	F8—C20—C21	120.23 (16)
Fe1—C6—H6	125.8	C19—C20—C21	119.34 (15)
C6—C10—C9	107.42 (16)	F9—C21—C20	119.78 (15)
C9—C10—Fe1	69.10 (9)	C20—C21—C22	119.19 (15)
C6—C10—H10	126.3	F2—C13—C14	120.06 (14)
C9—C10—H10	126.3	F2—C13—C12	121.02 (14)
Fe1—C10—H10	126.3	C14—C13—C12	118.92 (14)
C8—C9—C10	108.26 (15)	F1—C12—C13	116.25 (14)
C8—C9—Fe1	69.84 (9)	F1—C12—C11	119.24 (14)
C10—C9—Fe1	70.35 (9)	C13—C12—C11	124.49 (15)
C8—C9—H9	125.9	C16—C11—C12	113.93 (14)
C10—C9—H9	125.9	C16—C11—Al1	125.18 (12)
Fe1—C9—H9	125.9	C12—C11—Al1	120.76 (11)
C7—C8—C9	107.93 (16)	F5—C16—C15	116.29 (14)
C7—C8—Fe1	70.30 (10)	F5—C16—C11	119.74 (14)
C9—C8—Fe1	69.52 (9)	C15—C16—C11	123.94 (15)
C7—C8—H8	126.0	F4—C15—C16	120.92 (14)
C9—C8—H8	126.0	F4—C15—C14	119.71 (14)
Fe1—C8—H8	126.0	C16—C15—C14	119.36 (14)
C2—C3—C4	108.94 (14)	F3—C14—C13	120.37 (14)
C2—C3—Fe1	68.18 (9)	F3—C14—C15	120.35 (14)
C4—C3—Fe1	69.88 (9)	C13—C14—C15	119.27 (14)
C2—C3—H3	125.5		