Electronic Supplementary Material (ESI) for Dalton Transactions

Influences of the substituents on the M-M bonding in Cp_4Al_4 and $Cp_2M_2X_2$ (M=B, Al, Ga; $Cp=C_5H_5$, X=halogen)

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Table S1 Calculated geometry parameters of $Cp_4^*Al_4$ at different levels

Methods	B3LYP	M06-2X	*w*B97XD	BLYP-D3
$BL_{Al1\text{-}Al2}$	2.866	2.771	2.742	2.758
$BL_{Al1\text{-}C5}$	2.389	2.341	2.309	2.383
$BL_{H11\text{-}H12}$	2.466	2.520	2.434	2.456
$BL_{H11\text{-}H13}$	2.642	2.620	2.519	2.552
$BL_{H15\text{-}H16}$	2.223	2.179	2.173	2.206
$BL_{H15\text{-}H17}$	2.285	2.351	2.320	2.245
$A_{Al1\text{-}Al2\text{-}Al3}$	60.0	60.0	60.0	60.0
$D_{Al1\text{-}Al2\text{-}Al3\text{-}Al4}$	70.8	70.8	70.9	70.7
$D_{Al1\text{-}C5\text{-}C9\text{-}C7}$	64.7	63.3	63.5	63.9

Table S2 Cartesian coordinates for the optimized structures of Cp_4Al_4

Al	-0.36213700	1.31431200	0.96015200
Al	-1.31431200	-0.36213700	-0.96015200
Al	1.31431200	0.36213700	-0.96015200
Al	0.36213700	-1.31431200	0.96015200
C	-0.52888200	2.28866800	3.09054300
C	-1.80663400	2.36355200	2.48691600
C	-1.70494700	3.20314400	1.35221200
C	-0.36518400	3.64688000	1.25469800
H	0.03721200	4.28467500	0.48206900
C	0.36213700	3.08156700	2.32915800
H	-0.27339700	1.71127900	3.96649000
H	-2.69648300	1.85076400	2.81972300
H	-2.50377900	3.44204400	0.66632000
H	1.41641200	3.21270900	2.52125400
C	-0.36213700	-3.08156700	2.32915800
C	0.52888200	-2.28866800	3.09054300
C	1.80663400	-2.36355200	2.48691600
C	1.70494700	-3.20314400	1.35221200
H	2.50377900	-3.44204400	0.66632000
C	0.36518400	-3.64688000	1.25469800
H	-1.41641200	-3.21270900	2.52125400
H	0.27339700	-1.71127900	3.96649000
H	2.69648300	-1.85076400	2.81972300
H	-0.03721200	-4.28467500	0.48206900
C	3.64688000	0.36518400	-1.25469800
C	3.20314400	1.70494700	-1.35221200
C	2.36355200	1.80663400	-2.48691600
C	2.28866800	0.52888200	-3.09054300
H	1.71127900	0.27339700	-3.96649000
C	3.08156700	-0.36213700	-2.32915800
H	4.28467500	-0.03721200	-0.48206900
H	3.44204400	2.50377900	-0.66632000
H	1.85076400	2.69648300	-2.81972300
H	3.21270900	-1.41641200	-2.52125400
C	-3.64688000	-0.36518400	-1.25469800
C	-3.08156700	0.36213700	-2.32915800
C	-2.28866800	-0.52888200	-3.09054300
C	-2.36355200	-1.80663400	-2.48691600
H	-1.85076400	-2.69648300	-2.81972300
C	-3.20314400	-1.70494700	-1.35221200
H	-4.28467500	0.03721200	-0.48206900
H	-3.21270900	1.41641200	-2.52125400
H	-1.71127900	-0.27339700	-3.96649000

H	-3.44204400	-2.50377900	-0.66632000

Table S3 Cartesian coordinates for the optimized structures of $Cp^*_4Al_4$

Al	0.13985800	1.37218900	0.98436400
Al	-0.13985800	-1.37218900	0.98436400
Al	-1.37218900	0.13985800	-0.98436400
Al	1.37218900	-0.13985800	-0.98436400
C	-2.26147500	1.46452900	-2.66316100
C	-0.60354400	3.19147200	2.26419300
C	-0.29054000	-3.67680300	1.27031400
C	-1.56405200	-3.09125600	1.51261100
C	2.26147500	-1.46452900	-2.66316100
C	3.67680300	-0.29054000	-1.27031400
C	1.46452900	2.26147500	2.66316100
C	-3.67680300	0.29054000	-1.27031400
C	-2.32138000	0.12261600	-3.12439700
C	-3.19147200	-0.60354400	-2.26419300
C	0.29054000	3.67680300	1.27031400
C	3.19147200	0.60354400	-2.26419300
C	3.09125600	-1.56405200	-1.51261100
C	0.12261600	2.32138000	3.12439700
C	2.32138000	-0.12261600	-3.12439700
C	-3.09125600	1.56405200	-1.51261100
C	-1.46452900	-2.26147500	2.66316100
C	-0.12261600	-2.32138000	3.12439700
C	-3.55126200	-2.04467300	-2.47645900
H	-4.04354100	-2.17608700	-3.44479900
H	-2.66347300	-2.68541200	-2.46974200
H	-4.23067000	-2.41200500	-1.70792500
C	1.56405200	3.09125600	1.51261100
C	1.65274500	0.46562900	-4.33106200
H	2.36118200	1.07320300	-4.90035800
H	1.27451900	-0.31325700	-4.99415100
H	0.80933400	1.10757300	-4.05947400
C	4.65382900	0.00565300	-0.16886300
H	5.49081800	-0.69647000	-0.19871200
H	5.06779700	1.01007700	-0.26454400
H	4.19092200	-0.07193000	0.82084100
C	0.60354400	-3.19147200	2.26419300
C	-3.32979100	2.81674900	-0.72552400
H	-3.96309400	3.51618200	-1.28082200
H	-3.82359300	2.59764300	0.22263800
H	-2.38756100	3.32263900	-0.49901400
C	-4.65382900	-0.00565300	-0.16886300

H	-5.49081800	0.69647000	-0.19871200
H	-5.06779700	-1.01007700	-0.26454400
H	-4.19092200	0.07193000	0.82084100
C	3.55126200	2.04467300	-2.47645900
H	4.04354100	2.17608700	-3.44479900
H	2.66347300	2.68541200	-2.46974200
H	4.23067000	2.41200500	-1.70792500
C	1.46452900	-2.59580600	-3.24384700
H	1.98746800	-3.54491300	-3.10590600
H	0.48064300	-2.68836000	-2.76726300
H	1.30276900	-2.45816100	-4.31486900
C	-2.81674900	-3.32979100	0.72552400
H	-3.51618200	-3.96309400	1.28082200
H	-3.32263900	-2.38756100	0.49901400
H	-2.59764300	-3.82359300	-0.22263800
C	-1.46452900	2.59580600	-3.24384700
H	-1.98746800	3.54491300	-3.10590600
H	-0.48064300	2.68836000	-2.76726300
H	-1.30276900	2.45816100	-4.31486900
C	-0.00565300	4.65382900	0.16886300
H	0.69647000	5.49081800	0.19871200
H	0.07193000	4.19092200	-0.82084100
H	-1.01007700	5.06779700	0.26454400
C	0.00565300	-4.65382900	0.16886300
H	-0.69647000	-5.49081800	0.19871200
H	-0.07193000	-4.19092200	-0.82084100
H	1.01007700	-5.06779700	0.26454400
C	2.04467300	-3.55126200	2.47645900
H	2.17608700	-4.04354100	3.44479900
H	2.41200500	-4.23067000	1.70792500
H	2.68541200	-2.66347300	2.46974200
C	-0.46562900	1.65274500	4.33106200
H	-1.07320300	2.36118200	4.90035800
H	-1.10757300	0.80933400	4.05947400
H	0.31325700	1.27451900	4.99415100
C	2.59580600	1.46452900	3.24384700
H	3.54491300	1.98746800	3.10590600
H	2.45816100	1.30276900	4.31486900
H	2.68836000	0.48064300	2.76726300
C	-2.59580600	-1.46452900	3.24384700
H	-3.54491300	-1.98746800	3.10590600
H	-2.45816100	-1.30276900	4.31486900
H	-2.68836000	-0.48064300	2.76726300
C	-2.04467300	3.55126200	2.47645900

H	-2.17608700	4.04354100	3.44479900
H	-2.41200500	4.23067000	1.70792500
H	-2.68541200	2.66347300	2.46974200
C	3.32979100	-2.81674900	-0.72552400
H	3.82359300	-2.59764300	0.22263800
H	2.38756100	-3.32263900	-0.49901400
H	3.96309400	-3.51618200	-1.28082200
C	-1.65274500	-0.46562900	-4.33106200
H	-1.27451900	0.31325700	-4.99415100
H	-0.80933400	-1.10757300	-4.05947400
H	-2.36118200	-1.07320300	-4.90035800
C	0.46562900	-1.65274500	4.33106200
H	1.10757300	-0.80933400	4.05947400
H	-0.31325700	-1.27451900	4.99415100
H	1.07320300	-2.36118200	4.90035800
C	2.81674900	3.32979100	0.72552400
H	3.32263900	2.38756100	0.49901400
H	2.59764300	3.82359300	-0.22263800
H	3.51618200	3.96309400	1.28082200

Table S4 Cartesian coordinates for the optimized structures of $Cp_2M_2X_2$(M=B, Al, and Ga)

$Cp_2B_2F_2$

C	0.80137300	2.55804600	0.92682300
C	0.44569200	2.93535700	-0.41755500
C	-0.78832500	2.43471800	-0.71387300
C	-1.24031500	1.60503800	0.43225900
C	-0.20739200	1.81415400	1.45738100
C	0.20739200	-1.81415400	1.45738100
C	-0.80137300	-2.55804600	0.92682300
C	-0.44569200	-2.93535700	-0.41755500
C	0.78832500	-2.43471800	-0.71387300
C	1.24031500	-1.60503800	0.43225900
H	1.73650200	2.80188900	1.41125700
H	1.07135700	3.51012400	-1.08633400
H	-1.33452100	2.55264200	-1.63882600
H	-2.29560800	1.57055300	0.68909700
H	-0.22929300	1.36393900	2.44006200
H	0.22929300	-1.36393900	2.44006200
H	-1.73650200	-2.80188900	1.41125700
H	-1.07135700	-3.51012400	-1.08633400
H	1.33452100	-2.55264200	-1.63882600
H	2.29560800	-1.57055300	0.68909700
B	-0.80137300	0.30088000	-0.40957400
B	0.80137300	-0.30088000	-0.40957400

F	-1.79097900	-0.28697300	-1.09751000
F	1.79097900	0.28697300	-1.09751000

$Cp_2B_2Cl_2$

C	0.42618300	2.71663100	1.33278200
C	0.04925000	3.17133400	0.00873400
C	-1.03374200	2.47481900	-0.41564400
C	-1.37360900	1.44446400	0.61792800
C	-0.42618300	1.73867700	1.72166900
C	0.42618300	-1.73867700	1.72166900
C	-0.42618300	-2.71663100	1.33278200
C	-0.04925000	-3.17133400	0.00873400
C	1.03374200	-2.47481900	-0.41564400
C	1.37360900	-1.44446400	0.61792800
H	1.26693500	3.09333500	1.89896700
H	0.56274900	3.94241800	-0.54948100
H	-1.55075900	2.58255100	-1.35839300
H	-2.42889600	1.31783900	0.85722000
H	-0.40411600	1.19560000	2.65592400
H	0.40411600	-1.19560000	2.65592400
H	-1.26693500	-3.09333500	1.89896700
H	-0.56274900	-3.94241800	-0.54948100
H	1.55075900	-2.58255100	-1.35839300
H	2.42889600	-1.31783900	0.85722000
B	-0.81294800	0.23665400	-0.24894500
B	0.81294800	-0.23665400	-0.24894500
Cl	-1.98928600	-0.60356200	-1.28543100
Cl	1.98928600	0.60356200	-1.28543100

$Cp_2B_2Br_2$

Br	1.56829300	1.46850100	-1.09470600
Br	-1.56829300	-1.46850100	-1.09470600
C	-0.83458600	2.59943300	1.80630200
C	-1.35087400	2.91471900	0.48686600
C	-2.00213800	1.83715400	-0.01133200
C	-1.87221600	0.70404700	0.96437100
C	-1.17014300	1.32623000	2.11780200
C	1.17014300	-1.32623000	2.11780200
C	0.83458600	-2.59943300	1.80630200
C	1.35087400	-2.91471900	0.48686600
C	2.00213800	-1.83715400	-0.01133200
C	1.87221600	-0.70404700	0.96437100
H	-0.26339400	3.27857900	2.42438900
H	-1.22535300	3.86452000	-0.01506500

H	-2.49327800	1.75595200	-0.97050400
H	-2.78141900	0.13854800	1.16786600
H	-0.92994600	0.79711500	3.02898200
H	0.92994600	-0.79711500	3.02898200
H	0.26339400	-3.27857900	2.42438900
H	1.22535300	-3.86452000	-0.01506500
H	2.49327800	-1.75595200	-0.97050400
H	2.78141900	-0.13854800	1.16786600
B	-0.83458600	-0.12420900	0.09900000
B	0.83458600	0.12420900	0.09900000

$Cp_2B_2I_2$

C	1.23426100	2.48312700	2.13097300
C	1.08468500	3.09256500	0.82092600
C	-0.11871400	2.75701500	0.30233000
C	-0.81334300	1.82643600	1.25677400
C	0.11871400	1.77532800	2.41763500
C	-0.11871400	-1.77532800	2.41763500
C	-1.23426100	-2.48312700	2.13097300
C	-1.08468500	-3.09256500	0.82092600
C	0.11871400	-2.75701500	0.30233000
C	0.81334300	-1.82643600	1.25677400
H	2.10809100	2.57923000	2.76082100
H	1.82787300	3.71367200	0.33971600
H	-0.52307700	3.04949500	-0.65600700
H	-1.85544100	2.06779800	1.46904800
H	-0.07823300	1.21188600	3.31856600
H	0.07823300	-1.21188600	3.31856600
H	-2.10809100	-2.57923000	2.76082100
H	-1.82787300	-3.71367200	0.33971600
H	0.52307700	-3.04949500	-0.65600700
H	1.85544100	-2.06779800	1.46904800
B	-0.66556400	0.50992100	0.39240200
B	0.66556400	-0.50992100	0.39240200
I	-2.29301900	0.03812100	-0.95784900
I	2.29301900	-0.03812100	-0.95784900

$Cp_2Al_2F_2$

Al	-0.03979800	1.24843500	-0.01137500
Al	0.03979800	-1.24843500	-0.01137500
C	-2.35873600	-1.41348800	-0.27395000
C	-1.64950400	-2.24910300	-1.17175500
C	-0.88995000	-3.17696200	-0.40709500
C	-1.08799300	-2.86707400	0.96470600
C	-2.00849800	-1.77972100	1.03299200

C	2.00849800	1.77972100	1.03299200
C	2.35873600	1.41348800	-0.27395000
C	1.64950400	2.24910300	-1.17175500
C	0.88995000	3.17696200	-0.40709500
C	1.08799300	2.86707400	0.96470600
H	-2.96359500	-0.56149100	-0.54476300
H	-1.69573900	-2.21365900	-2.25001900
H	-0.23932400	-3.94574600	-0.79474900
H	-0.64305200	-3.38804300	1.79919100
H	-2.34252200	-1.29451600	1.93780300
H	2.34252200	1.29451600	1.93780300
H	2.96359500	0.56149100	-0.54476300
H	1.69573900	2.21365900	-2.25001900
H	0.23932400	3.94574600	-0.79474900
H	0.64305200	3.38804300	1.79919100
F	-1.64950400	1.77703100	-0.09655300
F	1.64950400	-1.77703100	-0.09655300

$Cp_2Al_2Cl_2$

Al	0.05658200	-1.26096800	-0.01764100
Al	-0.05658200	1.26096800	-0.01764100
C	2.19375800	1.60120500	0.68923500
C	2.15735100	1.71350600	-0.70547900
C	1.22940100	2.74122900	-1.04806600
C	0.72240000	3.28796800	0.16140600
C	1.28468000	2.54931300	1.23732400
C	-1.28468000	-2.54931300	1.23732400
C	-2.19375800	-1.60120500	0.68923500
C	-2.15735100	-1.71350600	-0.70547900
C	-1.22940100	-2.74122900	-1.04806600
C	-0.72240000	-3.28796800	0.16140600
H	2.74702200	0.85764600	1.24261000
H	2.68691700	1.07929800	-1.40042800
H	0.98446400	3.08044400	-2.04354100
H	-0.01047100	4.07545000	0.24455700
H	1.08729100	2.71739900	2.28567100
H	-1.08729100	-2.71739900	2.28567100
H	-2.74702200	-0.85764600	1.24261000
H	-2.68691700	-1.07929800	-1.40042800
H	-0.98446400	-3.08044400	-2.04354100
H	0.01047100	-4.07545000	0.24455700
Cl	2.15735100	-1.85666300	-0.12388600
Cl	-2.15735100	1.85666300	-0.12388600

$Cp_2Al_2Br_2$

Al	0.54660500	1.11235200	-0.04533100
Br	-0.54660500	2.95944600	-0.92261000
Al	-0.54660500	-1.11235200	-0.04533100
Br	0.54660500	-2.95944600	-0.92261000
C	-2.43446700	0.39245400	1.31468100
C	-2.88281500	-0.07757800	0.07313200
C	-2.66098200	-1.47753500	0.01006600
C	-2.05234800	-1.86919000	1.25844900
C	-1.90599300	-0.69245300	2.03656600
C	1.90599300	0.69245300	2.03656600
C	2.43446700	-0.39245400	1.31468100
C	2.88281500	0.07757800	0.07313200
C	2.66098200	1.47753500	0.01006600
C	2.05234800	1.86919000	1.25844900
H	-2.42943300	1.42649900	1.62803800
H	-3.29375600	0.52728500	-0.72200000
H	-2.98565000	-2.15159400	-0.76974600
H	-1.83812400	-2.88234400	1.56628300
H	-1.46160800	-0.65071200	3.02069600
H	1.46160800	0.65071200	3.02069600
H	2.42943300	-1.42649900	1.62803800
H	3.29375600	-0.52728500	-0.72200000
H	2.98565000	2.15159400	-0.76974600
H	1.83812400	2.88234400	1.56628300

$Cp_2Al_2I_2$

Al	0.07576100	1.26902300	0.14433100
Al	-0.07576100	-1.26902300	0.14433100
C	-2.28381700	-1.36020300	1.01587500
C	-2.31777800	-1.63541700	-0.35919100
C	-1.48861200	-2.77025300	-0.60796700
C	-0.96063000	-3.20222000	0.63859900
C	-1.42188000	-2.30269000	1.63785900
C	1.42188000	2.30269000	1.63785900
C	2.28381700	1.36020300	1.01587500
C	2.31777800	1.63541700	-0.35919100
C	1.48861200	2.77025300	-0.60796700
C	0.96063000	3.20222000	0.63859900
H	-2.76212000	-0.52053900	1.49692700
H	-2.83823900	-1.05253800	-1.10428900
H	-1.31150300	-3.23923400	-1.56444200
H	-0.28018500	-4.02557900	0.78751800
H	-1.18432400	-2.35620700	2.68997900

H	1.18432400	2.35620700	2.68997900
H	2.76212000	0.52053900	1.49692700
H	2.83823900	1.05253800	-1.10428900
H	1.31150300	3.23923400	-1.56444200
H	0.28018500	4.02557900	0.78751800
I	-2.31777800	2.21358400	-0.34213300
I	2.31777800	-2.21358400	-0.34213300

$Cp_2Ga_2F_2$

C	1.64854500	1.96692400	0.78696500
C	1.17457500	2.63034200	-0.35939900
C	-0.19823400	2.89779400	-0.19033500
C	-0.58381600	2.36605000	1.10658100
C	0.58381600	1.80895800	1.68455800
C	-0.58381600	-1.80895800	1.68455800
C	-1.64854500	-1.96692400	0.78696500
C	-1.17457500	-2.63034200	-0.35939900
C	0.19823400	-2.89779400	-0.19033500
C	0.58381600	-2.36605000	1.10658100
H	2.66231600	1.62216000	0.93565200
H	1.75763500	2.88193400	-1.23359700
H	-0.82545100	3.50793500	-0.82627800
H	-1.52699300	2.55175300	1.60234800
H	0.63081900	1.33083500	2.65271300
H	-0.63081900	-1.33083500	2.65271300
H	-2.66231600	-1.62216000	0.93565200
H	-1.75763500	-2.88193400	-1.23359700
H	0.82545100	-3.50793500	-0.82627800
H	1.52699300	-2.55175300	1.60234800
Ga	0.90834300	-0.80111800	-0.39726300
Ga	-0.90834300	0.80111800	-0.39726300
F	2.58239000	-0.82931400	-0.99843400
F	-2.58239000	0.82931400	-0.99843400

$Cp_2Ga_2Cl_2$

C	1.67381500	1.92487300	1.03047000
C	1.28747500	2.59386700	-0.14489500
C	-0.08228000	2.91185900	-0.05328100
C	-0.55745500	2.40369100	1.22423400
C	0.55745500	1.80972300	1.86798800
C	-0.55745500	-1.80972300	1.86798800
C	-1.67381500	-1.92487300	1.03047000
C	-1.28747500	-2.59386700	-0.14489500
C	0.08228000	-2.91185900	-0.05328100

C	0.55745500	-2.40369100	1.22423400
H	2.66389400	1.54251900	1.23581200
H	1.92590000	2.81512100	-0.98821200
H	-0.64978800	3.54456800	-0.72220500
H	-1.51484700	2.63542000	1.67077400
H	0.53283300	1.33778100	2.83974900
H	-0.53283300	-1.33778100	2.83974900
H	-2.66389400	-1.54251900	1.23581200
H	-1.92590000	-2.81512100	-0.98821200
H	0.64978800	-3.54456800	-0.72220500
H	1.51484700	-2.63542000	1.67077400
Ga	0.87180600	-0.85206500	-0.28149400
Ga	-0.87180600	0.85206500	-0.28149400
Cl	-2.90506400	0.93629000	-1.10921700
Cl	2.90506400	-0.93629000	-1.10921700

$Cp_2Ga_2Br_2$

C	-2.43785900	0.68354700	1.33271200
C	-2.89812200	0.09816400	0.13920600
C	-2.62344400	-1.28302900	0.17883000
C	-1.95401100	-1.55231000	1.44262900
C	-1.86675100	-0.31512400	2.13037200
C	1.86675100	0.31512400	2.13037200
C	2.43785900	-0.68354700	1.33271200
C	2.89812200	-0.09816400	0.13920600
C	2.62344400	1.28302900	0.17883000
C	1.95401100	1.55231000	1.44262900
H	-2.49503700	1.73537900	1.57572700
H	-3.36808100	0.61897000	-0.68281200
H	-2.97280400	-2.03492200	-0.51560600
H	-1.77058300	-2.53555600	1.85419900
H	-1.41679000	-0.17773400	3.10341500
H	1.41679000	0.17773400	3.10341500
H	2.49503700	-1.73537900	1.57572700
H	3.36808100	-0.61897000	-0.68281200
H	2.97280400	2.03492200	-0.51560600
H	1.77058300	2.53555600	1.85419900
Ga	0.41823700	1.14937400	-0.05435500
Ga	-0.41823700	-1.14937400	-0.05435500
Br	-0.41823700	3.12991800	-0.99978300
Br	0.41823700	-3.12991800	-0.99978300

$Cp_2Ga_2I_2$

Ga	-0.01899900	1.22631000	0.14065700

I	-1.64352300	2.91128400	-0.91206500
Ga	0.01899900	-1.22631000	0.14065700
I	1.64352300	-2.91128400	-0.91206500
C	-2.54161200	-0.24364400	1.50454300
C	-2.73507200	-0.99458000	0.33068900
C	-1.96172900	-2.17012600	0.41528300
C	-1.25057700	-2.12671800	1.68414300
C	-1.64352300	-0.92834500	2.33167000
C	1.64352300	0.92834500	2.33167000
C	2.54161200	0.24364400	1.50454300
C	2.73507200	0.99458000	0.33068900
C	1.96172900	2.17012600	0.41528300
C	1.25057700	2.12671800	1.68414300
H	-2.99097200	0.71724700	1.71295200
H	-3.35794300	-0.71481100	-0.50695600
H	-1.99884200	-3.02176300	-0.25012500
H	-0.71307700	-2.95417800	2.12679200
H	-1.28891000	-0.60059800	3.29845000
H	1.28891000	0.60059800	3.29845000
H	2.99097200	-0.71724700	1.71295200
H	3.35794300	0.71481100	-0.50695600
H	1.99884200	3.02176300	-0.25012500
H	0.71307700	2.95417800	2.12679200

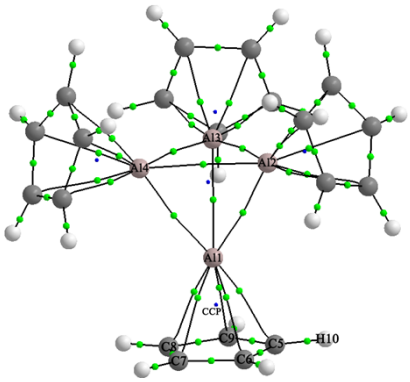
Table *S*5 Topological properties of M-M bonding in $Cp^*_2M_2X_2$

complexes	BCP	ρ_b	$\nabla^2\rho_b$	G_b	V_b	$-G_b/V_b$	H_b	*DI*
$B_2Cp^*_2F_2$	B1 - B2	0.1606	-0.3898	0.0116	-0.1207	0.0965	-0.1091	0.7798
$B_2Cp^*_2Cl_2$	B1 - B2	0.1622	-0.3890	0.0136	-0.1245	0.1095	-0.1109	0.7997
$B_2Cp^*_2Br_2$	B1 - B2	0.1637	-0.3959	0.0147	-0.1284	0.1145	-0.1137	0.8219
$B_2Cp^*_2I_2$	B1 - B2	0.1628	-0.3898	0.0158	-0.1291	0.1225	-0.1133	0.8616
$Al_2Cp^*_2F_2$	Al1 - NNA	0.0620	-0.0497	0.0192	-0.0509	0.3778	-0.0316	0.3658
$Al_2Cp^*_2Cl_2$	Al1 - NNA	0.0608	-0.0588	0.0161	-0.0468	0.3431	-0.0308	0.3628
$Al_2Cp^*_2Br_2$	Al1 - NNA	0.0600	-0.0636	0.0143	-0.0444	0.3211	-0.0302	0.3533
$Al_2Cp^*_2I_2$	Al1 - NNA	0.0594	-0.0687	0.0124	-0.0420	0.2957	-0.0296	0.3373
$Ga_2Cp^*_2F_2$	Ga1 - Ga2	0.0689	-0.0159	0.0221	-0.0482	0.4588	-0.0261	0.7369
$Ga_2Cp^*_2Cl_2$	Ga1 - Ga2	0.0663	-0.0145	0.0202	-0.0441	0.4589	-0.0239	0.7229
$Ga_2Cp^*_2Br_2$	Ga1 - Ga2	0.0648	-0.0131	0.0195	-0.0423	0.4613	-0.0228	0.7122
$Ga_2Cp^*_2I_2$	Ga1 - Ga2	0.0635	-0.0117	0.0189	-0.0407	0.4644	-0.0218	0.7021

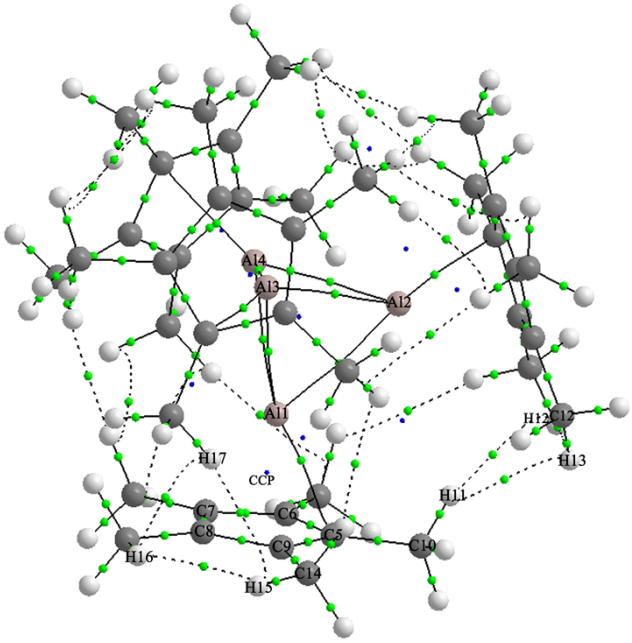
Table S6. Electrostatic (E^{ele}), exchange (E^{ex}), repulsion (E^{rep}), polarization (E^{pol}), and dispersion (E^{disp}) terms as well as the interaction energy (E^{int}) at the MP2/6-311G(d, p) level[a]

	E^{ele}	E^{ex}	E^{rep}	E^{pol}	E^{disp}	E^{int}
$Cp_2B_2F_2$	-157.64(0.39)	-140.33(0.34)	305.65	-85.66(0.21)	-22.64(0.06)	-100.61
$Cp_2B_2Cl_2$	-155.70(0.37)	-149.18(0.35)	318.43	-90.19(0.21)	-26.51(0.06)	-103.15
$Cp_2B_2Br_2$	-155.37(0.36)	-152.45(0.36)	323.73	-92.36(0.22)	-27.47(0.06)	-103.92
$Cp_2B_2I_2$	-38.38(0.14)	-79.28(0.28)	172.61	-126.99(0.46)	-34.35(0.12)	-106.38
$Cp_2Al_2F_2$	-101.95(0.45)	-70.56(0.31)	165.12	-39.08(0.17)	-15.70(0.07)	-62.17
$Cp_2Al_2Cl_2$	-102.05(0.42)	-84.76(0.35)	184.83	-39.67(0.16)	-18.75(0.07)	-60.39
$Cp_2Al_2Br_2$	-101.88(0.41)	-88.48(0.35)	190.81	-43.95(0.17)	-21.26(0.08)	-64.76
$Cp_2Al_2I_2$	-30.97(0.40)	-38.98(0.26)	80.48	-56.44(0.38)	-21.18(0.14)	-67.09
$Cp_2Ga_2F_2$	-116.92(0.39)	-106.29(0.35)	228.47	-54.76(0.18)	-22.48(0.07)	-71.98
$Cp_2Ga_2Cl_2$	-114.58(0.39)	-105.32(0.36)	226.12	-53.91(0.18)	-23.83(0.08)	-71.52
$Cp_2Ga_2Br_2$	-112.09(0.38)	-104.37(0.36)	223.50	-53.78(0.18)	-23.91(0.08)	-70.65
$Cp_2Ga_2I_2$	-30.92(0.16)	-64.36(0.33)	128.12	-70.71(0.37)	-25.87(0.13)	-63.75

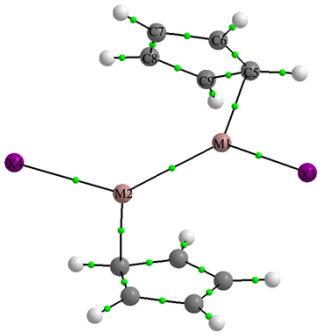
[a]All energies are in kcal/mol and the data in parentheses are the ratio of the component to the sum of ($E_{ele} + E_{ex} + E_{pol} + E_{disp}$)



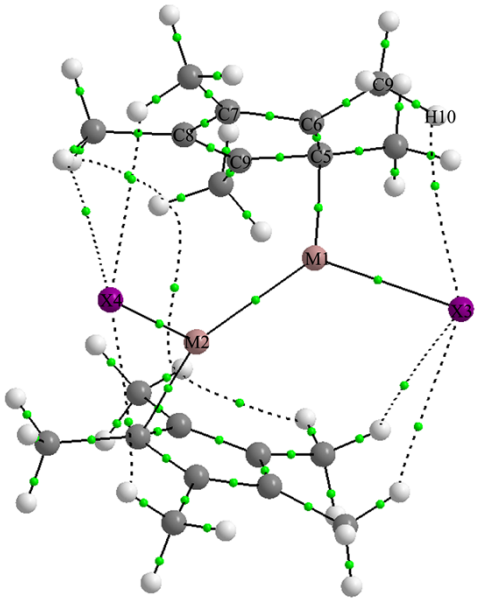
Cp_4Al_4



$Cp^*_4Al_4$



$Cp_2M_2X_2$



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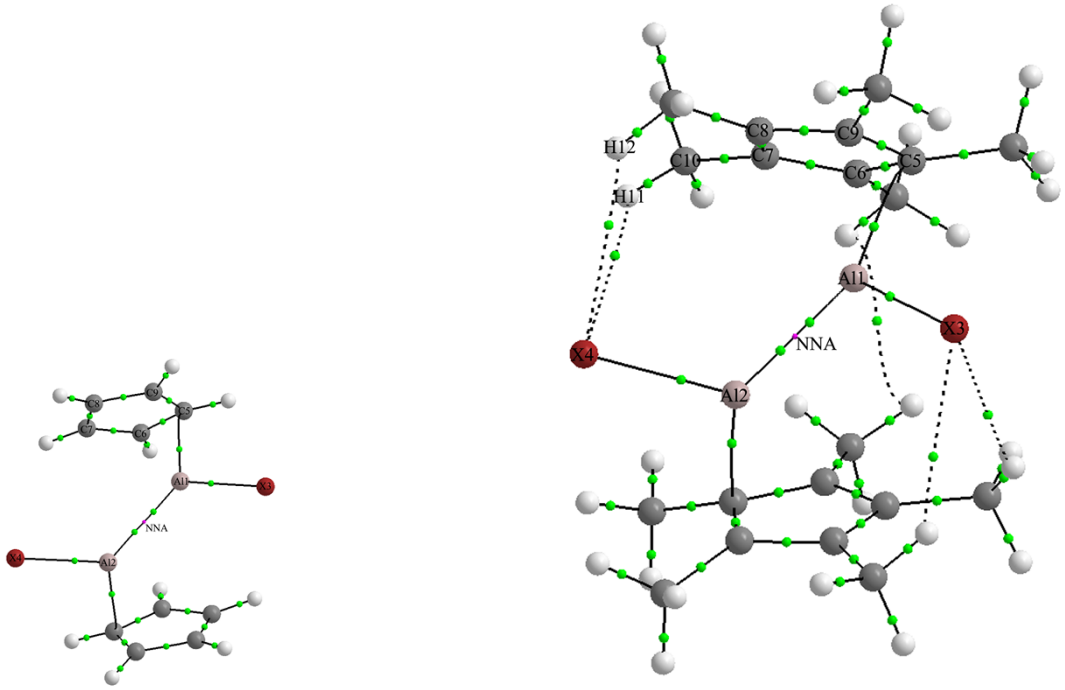

$Cp_2Al_2X_2$ $Cp^*_2Al_2X_2$

Figure S1 Large version of Figure 2 Molecular graphs of the studied compounds (BCPs in green)