

## Electronic Supplementary Information

Mechanistic Investigation of Ligand Exchange in Guanidinate Ligand Systems

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### Single-point energy calculations using G3(MP2)

For the purpose of modeling the reaction pathway of [1], single-point G3(MP2) calculations were performed on reduced models of frozen structures previously optimized by B971<sup>1</sup>, where CH<sub>3</sub> and CH(CH<sub>3</sub>)<sub>2</sub> substituents are replaced by hydrogen atoms. This is used in order to calculate energy values that correct the G3(MP2) electronic energy with the B971 vibrational data for enthalpies and free-energies. This is accomplished using equation [2]. By correcting the G3(MP2) calculations in this ONIOM-type scheme we are able to account for the steric effects associated with the guanidinate ligand.

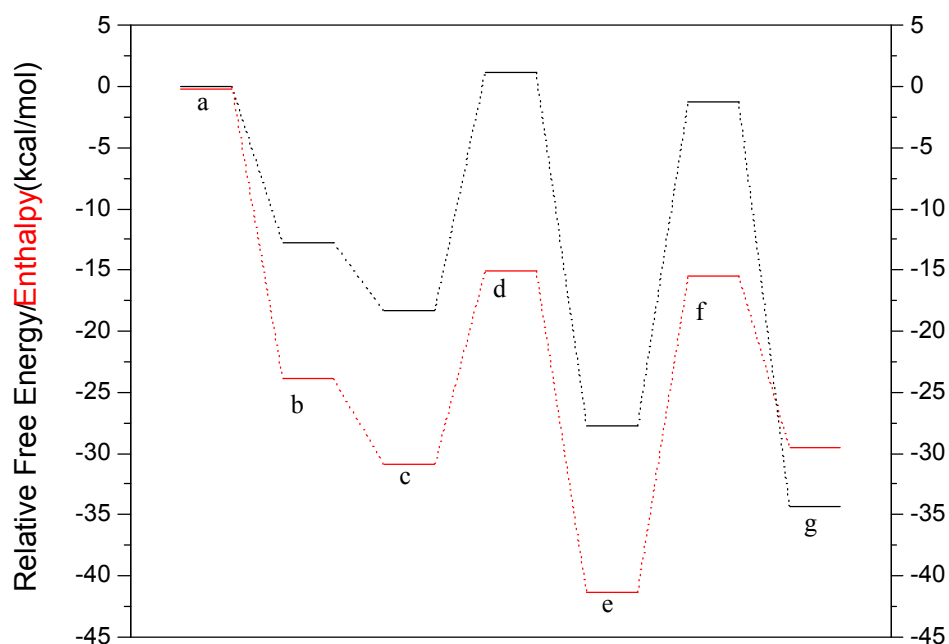


$$\Delta H = (E_{\text{G3MP2}(0\text{ K})} - E_{\text{ZPE}}) + E_{\text{B971}} - E_{\text{B971}(\text{reduced})} + E_{\text{B971}(\text{enthalpy/free-energy})} \quad [2]$$

where  $E_{\text{ZPE}}$  is the zero-point energy from the HF component of (G3MP2),  $E_{\text{B971}}$  is the electronic energy,  $E_{\text{B971}(\text{reduced})}$  is the electronic energies from the hydrogen terminated geometries and  $E_{\text{B971}(\text{enthalpy/free-energy})}$  is the thermal correction to enthalpy or free-energy obtained from the B971 vibration calculations.

### Calculated Enthalpies and Free Energies for the Stationary Points

The calculated enthalpies and free energies for the stationary points for the exchange reaction [1] are shown in Fig. S1. Studying the enthalpies for the reaction mechanism suggests that the most stable stationary point is the dimer bridged by two guanidinate ligands. This calculated structure is stabilized by 41.36 kcal/mol compared to the original reactants and 10.48 kcal/mol lower in enthalpy than the chlorine bridged structure. The formation of the monomeric species from the dimeric structure is an uphill process, with a barrier of 25.86 kcal/mol and a stable calculated structure that is 11.82 kcal/mol higher in energy than the doubly guanidinate-bridged dimer. While experimentally the reaction does proceed rapidly to **1**, within minutes of mixing the reactants, and the species is long-lived, the reaction does proceed to the monomeric product over a few days. The calculated relative free energies of the exchange reaction shows that the monomeric species allows for a stabilization of 6.64 kcal/mol from the dimer and 34.36 kcal/mol from the original reactants. Therefore, by comparing the enthalpy and the free energy of the reaction coordinate of [1] it can be seen that the process is driven by entropy to some extent.



**Fig. S1** Calculated free energies and enthalpies of stationary points along the ligand exchange reaction. The labeled structures of each stationary point correspond to Fig. 4 in the article.

### Comparison of Crystal and Calculated Structural Parameters of **1**

**Table S1:** Bond lengths for crystal structure and calculated structure of  $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2\text{AlCl}_2]_2$

	Bond Lengths (Å)				
	XRD	DFT	XRD	DFT	
Al1-N1	1.855(4)	1.908	N4-C13	1.353(7)	1.352
Al1-N6	1.880(4)	1.900	N4-C10	1.543(9)	1.510
Al1-C12	2.153(2)	2.178	N5-C13	1.350(6)	1.371
Al1-C11	2.155(2)	2.184	N5-C14	1.458(7)	1.461
Al2-N4	1.875(5)	1.914	N5-C15	1.461(8)	1.461
Al2-N3	1.886(4)	1.911	N6-C13	1.351(6)	1.350
Al2-C14	2.153(2)	2.183	N6-C16	1.487(6)	1.513
Al2-C13	2.164(19)	2.180	C1-C3	1.502(15)	1.530
N1-C4	1.360(7)	1.351	C1-C2	1.519(16)	1.536
N1-C1	1.550(19)	1.512	C7-C8	1.520(8)	1.536
N2-C4	1.351(6)	1.373	C7-C9	1.530(6)	1.531
N2-C6	1.452(8)	1.462	C10-C12	1.529(9)	1.530
N2-C5	1.456(7)	1.462	C10-C11	1.539(11)	1.535
N3-C4	1.349(6)	1.354	C16-C17	1.518(8)	1.533
N3-C7	1.498(6)	1.511	C16-C18	1.527(7)	1.538

**Table S2:** Bond angles for crystal structure and calculated structure of  $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2\text{AlCl}_2]_2$ 

	Bond Angles (°)				
	XRD	DFT	XRD	DFT	
N1-Al1-N6	122.25(18)	122.75	C13-N5-C14	122.4(5)	122.46
N1-Al1-Cl2	109.00(16)	111.45	C13-N5-C15	122.0(5)	122.11
N6-Al1-Cl2	103.17(14)	102.42	C14-N5-C15	115.5(5)	115.24
N1-Al1-Cl1	104.52(14)	101.50	C13-N6-C16	122.7(4)	122.77
N6-Al1-Cl1	107.18(15)	107.26	C13-N6-Al1	116.7(3)	117.68
Cl2-Al1-Cl1	110.58(9)	111.46	C16-N6-Al1	120.0(3)	118.79
N4-Al2-N3	124.23(18)	123.20	C3-C1-C2	116(2)	111.00
N4-Al2-Cl4	101.77(14)	100.18	C3-C1-N1	103.8(11)	110.80
N3-Al2-Cl4	110.43(14)	110.35	C2-C1-N1	107(2)	113.89
N4-Al2-Cl3	109.98(14)	111.01	N3-C4-N2	122.2(5)	120.15
N3-Al2-Cl3	101.78(13)	101.22	N3-C4-N1	116.3(4)	119.41
Cl4-Al2-Cl3	108.05(8)	110.99	N2-C4-N1	121.5(5)	120.44
C4-N1-C1	103.0(8)	117.99	N3-C7-C8	113.5(4)	114.70
C4-N1-Al1	114.8(3)	116.57	N3-C7-C9	109.6(4)	110.36
C1-N1-Al1	139.8(8)	123.05	C8-C7-C9	110.0(5)	111.12
C4-N2-C6	122.6(5)	122.05	C12-C10-C11	108.8(9)	110.99
C4-N2-C5	122.6(5)	122.29	C12-C10-N4	108.1(6)	110.76
C6-N2-C5	114.8(5)	115.64	C11-C10-N4	110.0(7)	114.06
C4-N3-C7	118.2(4)	117.25	N5-C13-N6	121.9(5)	120.85
C4-N3-Al2	115.0(3)	116.75	N5-C13-N4	121.7(4)	120.89
C7-N3-Al2	125.7(3)	124.56	N6-C13-N4	116.3(4)	118.26
C13-N4-C10	110.1(5)	118.00	N6-C16-C17	114.1(4)	114.33
C13-N4-Al2	116.2(3)	116.35	N6-C16-C18	115.2(5)	115.13
C10-N4-Al2	132.4(5)	123.41	C17-C16-C18	111.3(4)	111.32

The bond angles of C1-N1-Al1, C4-N1-C1 and C10-N4-Al2 are significantly different between the XRD and DFT structures. This is a consequence of the two isopropyl groups (C10 and C1) being disordered each in two positions with refined site occupancies of roughly 60/40 for complex **1** in the XRD structure.

**Table S3:** Torsion angles for crystal structure and calculated structure of  $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2\text{AlCl}_2]_2$ 

	Torsion Angles (°)				
	XRD	DFT	XRD	DFT	
N6-Al1-N1-C4	-63.2(4)	-50.7	C6-N2-C4-N3	40.2(7)	46.3
C12-Al1-N1-C4	176.6(3)	-172.5	C5-N2-C4-N3	-139.3(5)	-132.4
C11-Al1-N1-C4	58.4(3)	68.7	C6-N2-C4-N1	-141.2(5)	-133.9
N6-Al1-N1-C1	138.0(9)	147.3	C5-N2-C4-N1	39.3(7)	47.4
C12-Al1-N1-C1	17.9(9)	25.4	C1-N1-C4-N3	-144.2(7)	-152.6
C11-Al1-N1-C1	-100.4(9)	-93.3	Al1-N1-C4-N3	49.7(4)	44.4
N4-Al2-N3-C4	-60.3(4)	-64.3	C1-N1-C4-N2	37.1(8)	27.6
C14-Al2-N3-C4	178.6(3)	177.8	Al1-N1-C4-N2	-129.0(4)	-135.4
C13-Al2-N3-C4	64.0(3)	60.2	C4-N3-C7-C8	-118.8(5)	-119.0
N4-Al2-N3-C7	131.8(3)	129.8	Al2-N3-C7-C8	48.7(5)	46.8
C14-Al2-N3-C7	10.7(4)	11.9	C4-N3-C7-C9	117.7(5)	114.5
C13-Al2-N3-C7	-103.8(3)	-105.7	Al2-N3-C7-C9	-74.8(5)	-79.6
N3-Al2-N4-C13	-57.0(4)	-51.2	C13-N4-C10-C12	115.1(7)	113.6
C14-Al2-N4-C13	68.0(3)	71.5	Al2-N4-C10-C12	-78.3(8)	-84.1
C13-Al2-N4-C13	-177.7(3)	-171.2	C13-N4-C10-C11	-126.2(9)	-120.3
N3-Al2-N4-C10	137.0(5)	146.2	Al2-N4-C10-C11	40.4(10)	42.0
C14-Al2-N4-C10	-98.0(5)	-91.1	C14-N5-C13-N6	-138.1(5)	-135.4
C13-Al2-N4-C10	16.4(5)	26.2	C15-N5-C13-N6	44.5(7)	49.7
N1-Al1-N6-C13	-59.0(4)	-65.7	C14-N5-C13-N4	43.2(7)	44.7
C12-Al1-N6-C13	63.9(4)	60.2	C15-N5-C13-N4	-134.2(6)	-130.2
C11-Al1-N6-C13	-179.3(3)	177.6	C16-N6-C13-N5	36.7(7)	35.1
N1-Al1-N6-C16	130.7(3)	123.9	Al1-N6-C13-N5	-133.4(4)	-134.9
C12-Al1-N6-C16	-106.4(3)	-110.1	C16-N6-C13-N4	-144.5(4)	-145.0
C11-Al1-N6-C16	10.3(4)	7.3	Al1-N6-C13-N4	45.4(5)	45.1
C4-N1-C1-C3	117.3(11)	114.6	C10-N4-C13-N5	32.0(6)	28.3
Al1-N1-C1-C3	-82.4(14)	-83.6	Al2-N4-C13-N5	-137.0(4)	-135.3
C4-N1-C1-C2	-120.0(15)	-119.4	C10-N4-C13-N6	-146.8(5)	-151.6
Al1-N1-C1-C2	40.2(18)	42.4	Al2-N4-C13-N6	44.2(5)	44.8
C7-N3-C4-N2	29.6(6)	31.1	C13-N6-C16-C17	27.1(6)	28.7
Al2-N3-C4-N2	-139.3(4)	-135.8	Al1-N6-C16-C17	-163.1(3)	-161.4
C7-N3-C4-N1	-149.1(4)	-148.7	C13-N6-C16-C18	-103.5(5)	-102.0
Al2-N3-C4-N1	42.1(4)	44.3	Al1-N6-C16-C18	66.3(5)	67.8

<sup>1</sup> The G3(MP2) method incorporates MP2/6-31G(d) geometry optimizations as part of the general procedure. In our calculations, however, the B971 optimized structures are used instead. This necessitates freezing the coordinates of the B971-optimized structures during the G3(MP2) calculations.