Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

for

Oxidative Addition or Werner Coordination Complex? Reactivity of β-diketiminate Supported Main Group and First-row Transition Metal Complexes towards Ammonia

by

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Table S1. Comparison of selected bond parameters of reported nacnacM compounds.

		QAMXOR (M = Al)	XEDHOD (M = Ga)	BICXAN (M = In)	CEPHAH (M = Si)	GEMDAE (M = Ge)	XUGQOG (M = Si)	HOVGOP (M = Ge)
M-N BOND LENGTH (Å)	**Experimental**	1.9931	2.0793	2.3077	1.735	1.865	1.727	2.0297
		1.9882	2.0793	2.3072	1.734	1.866	1.724	2.0296
							1.653	1.8448
	Calculated	1.9576	2.0528	2.2756	1.736	1.852	1.737	2.0297
		1.9570	2.0560	2.2682	1.750	1.869	1.728	2.0296
							1.699	1.8449
N-M-N ANGLE (°)	**Experimental**	88.5	86.6	80.7	99.3	95.8	103.1	88.6
	Calculated	89.9	87.5	81.1	98.6	95.8	103.1	88.6
M-N-C-C ANGLE (°)	**Experimental**	-5.3	0.0	-2.3	-0.8	2.4	7.8	-95.4
		3.8	-0.0	2.3	-1.2	0.1	-11.0	
	Calculated	1.9	2.1	2.3	0.0	0.0	-3.9	-95.4
		1.53695	1.7	0.9	0.0	0.0	-5.5	
REFERENCE		1	2	3	4	5	6	7

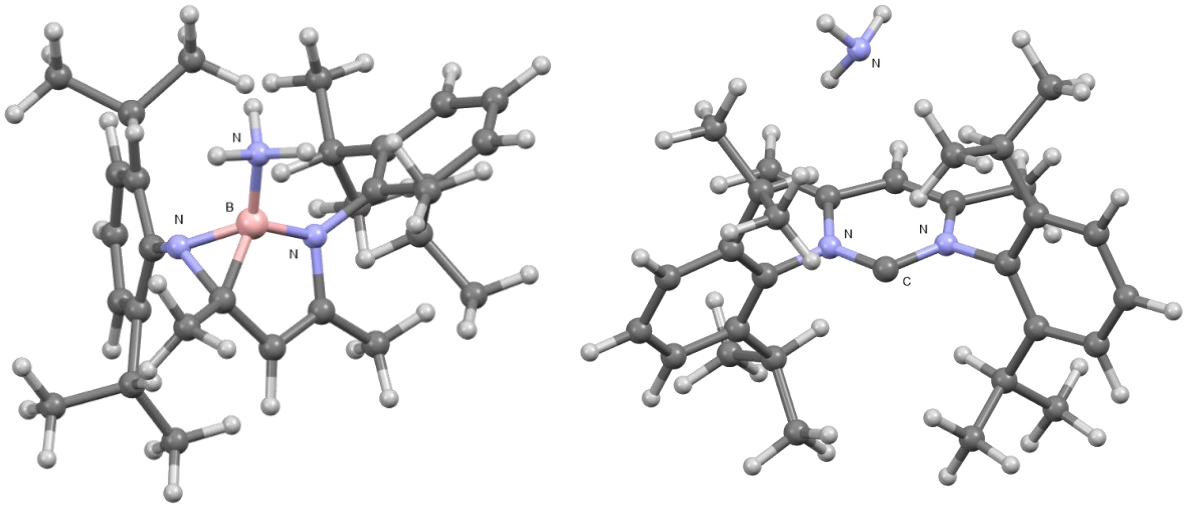

Figure S1. Optimised structure of NacNacB·NH_3 (left) and NacNacC·NH_3 (right).

Table S2. Comparison of group 14 NacnacM relative stabilities of 1,1- and 1,4-oxidative addition reaction products. The differences to free starting materials NacnacM and NH_3 are given in Gibbs free energies (kJ/mol).

Compound	1,1-oxidative addition (kJ/mol)	1,4-oxidative addition (kJ/mol)
NacnacC	-67.3	42.5
NacnacSi	-126.6	-48.1
NacnacGe	10.1	-46.8
NacnacSn	95.5	-70.1
NacnacPb	242.2	-66.2

Table S3. EDA-NOCV derived most important deformation densities for the interaction between NacnacM and NH_3 fragments in NacnacM·NH_3 complexes.

Compound	Orbital interaction (kJ/mol)	Percentage of all orbital interactions (%)
NacnacFe	-50.1	38
NacnacCo	-55.8	46
NacnacNi	-94.0	62
NacnacCu	-64.1	58
NacnacAl	-98.1	72
NacnacGa	-47.6	71
NacnacIn	-41.1	68
NacnacSi	-180.9	77
NacnacGe	-134.8	77
NacnacSn	-99.2	74
NacnacPb	-78.1	72

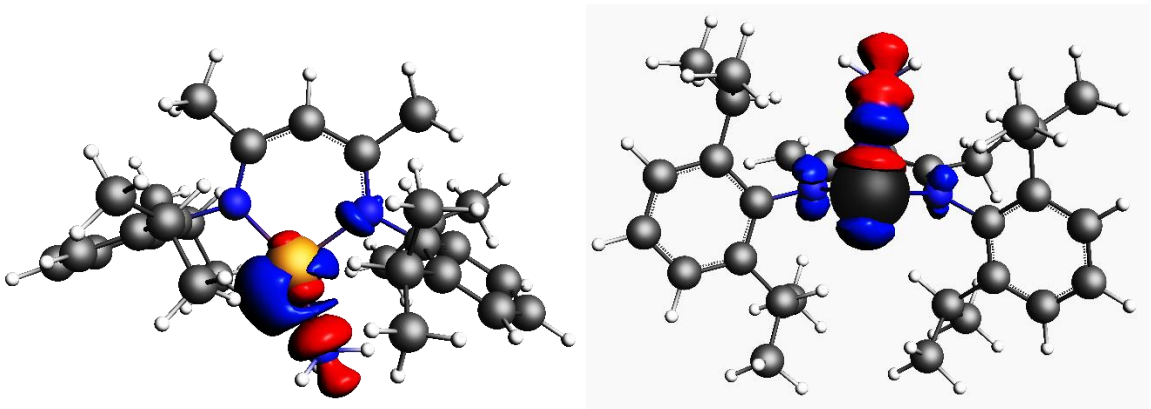

Figure S2. The most important EDA-NOCV deformation density of NacnacCu·NH_3 (left) and NacnacPb·NH_3 (right). Isovalue set at ±0.002 a.u. and red contour corresponds to the depletion of electron density and blue contour the accumulation of electron density.

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