Synthetic, Structural and Computational Studies on Heavier Tetragen and Chalcogen Triazenide Complexes.

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Experimental Section

General procedures: Elemental analyses were performed externally by London Metropolitan University Elemental Analysis Service using an Exeter Analytical CE 440 analyser.

^{1}H, $^{13}C\{^{1}H\}$, $^{119}Sn\{^{1}H\}$ and $^{207}Pb\{^{1}H\}$ NMR spectra were recorded on Bruker Advance 300 or 500 MHz FT–NMR spectrometers, as appropriate, as saturated solutions at room temperature. Chemical shifts are in ppm with respect to Me_4Si (^{1}H, ^{13}C).

All reactions were carried out under an inert atmosphere using standard Schlenk techniques. Solvents were dried and degassed under an argon atmosphere over activated alumina columns using an Innovative Technology solvent purification system (SPS).

The metal amides, $[Ge\{N(SiMe_3)_2\}_2]$,[S1] $[Sn\{N(SiMe_3)_2\}_2]$, [S2] $[Pb\{N(SiMe_3)_2\}_2]$, [S2] $[Se\{N(SiMe_3)_2\}_2]$ and $[Te\{N(SiMe_3)_2\}_2]$,[S3] were prepared according to literature methods. The pro-ligand, $H\{L^{(Dipp)}\}$ ($L^{(Dipp)}$ = $N(NDipp)_2$, Dipp = 2,6-*di-iso*propylphenyl), was also synthesized following literature methods. [S4]

Synthesis of $[\{L^{(Dipp)}\}_2Ge]$ (1).

A solution of $[\{L^{(Dipp)}\}H]$ (2 mmol) dissolved in toluene (10 mL) was added to a stirred solution of $[\{(Me_3Si)N\}_2Ge]$ (1 mmol) in toluene (10 mL) at 0°C. After 2 h. the yellow solution was filtered and reduced to afford yellow crystals at -28 °C. (0.43 mmol, 43%)

^{1}H NMR (500 MHz, C_6D_6): δ 7.13-7.06 (m, 6H, C-*H*), 3.41 (m, 4H, $\{CH(CH_3)_2\}$, 1.12 (d, *J* = 6.9Hz, 12H, $\{CH(CH_3)_2\}$), 1.10 (d, *J* = 6.9Hz, 12H, $\{CH(CH_3)_2\}$)

$^{13}C\{^{1}H\}$ NMR (125.8 MHz, C_6D_6): δ 144.8 (*p*-C_6H_3), 141.6 (*o*-C_6H_3), 128.3 (*i*-C_6H_3), 123.9 (*m*-C_6H_3), 29.3 ($CH(CH_3)_2$), 25.3, 23.9 ($CH(CH_3)_2$)

Elemental analysis (expected): C – 71.94% (71.91%), H – 8.58% (8.55%), N – 10.50% (10.48%)

Synthesis of [{L$^{(Dipp)}$}$_2$Sn] (2).

A solution of [{L$^{(Dipp)}$}H] (12.66 mmol) in toluene (25 mL) was added to a solution of [{(Me$_3$Si)N}$_2$Sn] (6.33 mmol) in toluene (25 mL) at 0°C and allowed to stir for 3 h. After removal of volatiles *in vacuo*, solids were dissolved in hexane (30 mL) and filtered. Crystallisation at -28 °C yielded orange crystals. (1.86 mmol, 30%)

^{1}H NMR (500MHz, C_6D_6): δ 7.11-7.05 (m, 6H, $C_6\underline{H}_3$), 3.42 (m, 4H, {C*H*(CH$_3$)$_2$}), 1.13 (d, *J* = 6.9 Hz, 12H, {CH(*C*H$_3$)$_2$}), 1.11 (d, *J* = 6.9 Hz, 12H, {CH(*C*H$_3$)$_2$})

^{13}C NMR (125.8MHz, C_6D_6): δ 144.2 (*p*-$\underline{C}_6H_3$), 142.6 (*o*-$\underline{C}_6H_3$), 127.3 (*i*-$\underline{C}_6H_3$), 123.9 (*m*-$\underline{C}_6H_3$), 29.3 ({*C*H(CH$_3$)$_2$}), 25.3, 23.9 ({CH(*C*H$_3$)$_2$})

^{119}Sn NMR (186.5MHz, C_6D_6): δ -198.9

Elemental analysis (expected): C – 67.90% (68.00%), H – 8.21% (8.08%), N – 4.90% (4.94%)

Synthesis of [{L$^{(Dipp)}$}$_2$Pb] (3).

[{(Me$_3$Si)N}$_2$Pb] (1 mmol) was dissolved in toluene (10 mL) and added to a stirred solution of [{L$^{(Dipp)}$}H] (2 mmol) in toluene (10 mL) at 0°C. After 2 h. the orange solution was reduced and yellow crystals were obtained at -28°C. (0.75 mmol, 75%)

^{1}H NMR (500MHz, C_6D_6): δ 7.11 (d, *J* = 7.5 Hz, 4H, *meta*-$C_6\underline{H}_3$), 7.05 (t, *J* = 7.7 Hz, 2H, *para*-$C_6\underline{H}_3$), 3.40 (sept, *J*=6.6 Hz, 4H, {C*H*(CH$_3$)$_2$}), 1.12 (d, *J* = 6.4 Hz, 24H, {CH(C*H*$_3$)$_2$})

^{13}C NMR (75.5MHz, C_6D_6): δ 146.53 (*p*-$\underline{C}_6H_3$), 144.3 (*o*-$\underline{C}_6H_3$), 123.3 (*i*-$\underline{C}_6H_3$), 123.9 (*m*-$\underline{C}_6H_3$), 29.2 ({*C*H(CH$_3$)$_2$}), 24.9 ({CH(*C*H$_3$)$_2$})

^{207}Pb NMR (104.6MHz, C_6D_6): δ 2520.

Elemental analysis (expected): C – 61.43% (61.57%), H – 7.41% (7.32%), N – 8.94% (8.98%)

Synthesis of [{L$^{(Dipp)}$}$_2$Te] (5).

[{(Me$_3$Si)N}$_2$Te] (1.81 mmol) was dissolved in THF (30 mL) and mixed with [{L$^{(Dipp)}$}H}] (3.62 mmol) affording a dark red solution after stirring for 12 h. After removal of the THF *in vacuo* the viscous red oil was dissolved in hexane and filtered through celite. Orange crystals were obtained from solution at -28°C. (0.50 mmol, 28%)

^{1}H NMR (300 MHz, C_6D_6): δ 7.30-7.20 (m, 4H, $C_6\underline{H}_3$), 7.15-7.10 (m, 2H, $C_6\underline{H}_3$) 3.53 (sept, *J*=9 Hz, 4H, {C$\underline{H}$(CH$_3$)$_2$}), 1.26 (d, *J*=12 Hz, 24H, {CH(C$\underline{H}_3$)$_2$})

^{13}C NMR (75.5MHz, C_6D_6): δ 145.4 (*p*-$\underline{C}_6H_3$), 141.3 (*o*-$\underline{C}_6H_3$), 129.3 (*i*-$\underline{C}_6H_3$), 123.9 (*m*-$\underline{C}_6H_3$), 28.8 ({$\underline{C}$H(CH$_3$)$_2$}), 24.3 ({$\underline{C}$H($\underline{C}$H$_3$)$_2$})

Elemental analysis (expected): C – 67.41% (67.30%), H – 8.12% (8.00%), N – 9.85% (9.81%)

Single Crystal X-ray Diffraction:

Experimental details relating to the single-crystal X-ray crystallographic studies for compounds **1**-**3** and **5** are summarized in Table S1. Single Crystal X-ray crystallography data were collected at 150 K on RIGAKU SuperNova Dual wavelength diffractometer equipped with an Oxford Cryostream, featuring a micro source with MoK$_\alpha$ radiation (λ= 0.71073 Å) and CuK$_\alpha$ radiation (λ= 1.5418 Å). Crystals were isolated from an argon filled Schlenk flask and immersed under oil before being mounted onto the diffractometer. All structures were solved by direct methods followed by full-matrix least squares refinement on F^2 using the WINGX-2014[S5] suite of programs or OLEX2.[S6] All hydrogen atoms were included in idealized positions and refined using the riding model.

The asymmetric unit cell of complexes **1**, **2**, **3** and **5** comprises of one molecule of the complex. In the case of complexes **1** and **5**, there is rotational disorder of one of the ^{i}Pr groups on a singular {L$^{(Dipp)}$} ligand. The disorder was modeled such that the affected ^{i}Pr unit i.e. C34/35/36 and C34/C35A/C36A in **1**; C10/C11/C12 and C10/C11/C12 in **5**, were modeled over two positions, using a freely refined occupancy variable.

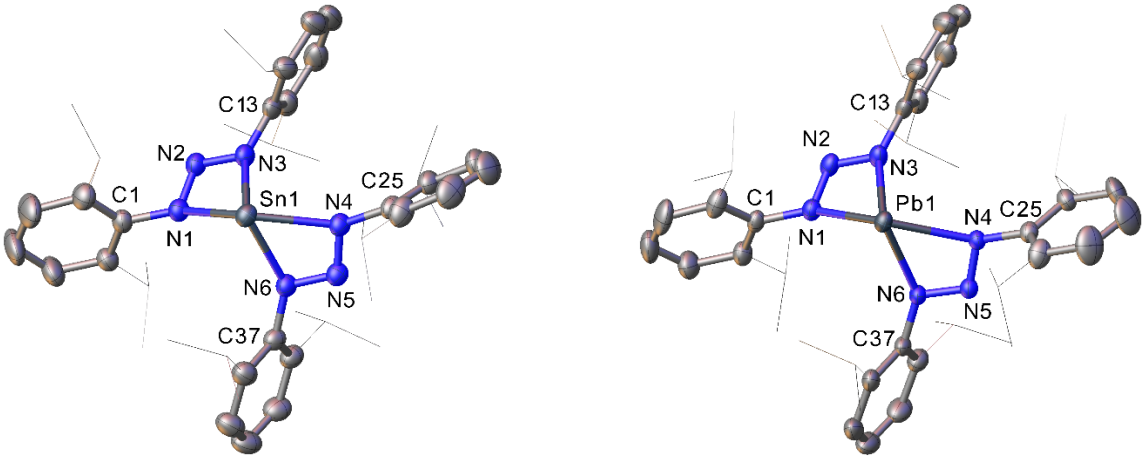


Figure S1. Molecular structure of the complexes [{L$^{(Dipp)}$}$_2$M] (M = Sn (**2**) left, Pb (**3**)) with thermal ellipsoids drawn at the 50% probability level. {^{i}Pr} groups are shown as wire frames and hydrogen atoms are omitted for clarity.

Table S1 X-ray Crystallographic Data for Compounds **1-3** and **5**

Compound reference	**1**	**2**	**3**	**5**
Chemical formula	$C_{48}H_{68}GeN_6$	$C_{48}H_{68}N_6Sn$	$C_{48}H_{68}N_6Pb$	$C_{48}H_{68}N_6Te$
Formula Mass	801.67	847.77	936.27	856.68
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
a/Å	14.71565(19)	14.61420(10)	14.73370(10)	11.33000(10)
b/Å	15.90663(18)	16.3702(2)	16.5950(2)	12.70800(10)
c/Å	20.9036(3)	20.8531(2)	20.5127(2)	17.7500(2)
α/°	90	90	90	75.9280(10)
β/°	110.2538(15)	110.1230(10)	110.1012(5)	76.6520(10)
γ/°	90	90	90	70.9240(10)
Unit cell volume/Å^3	4590.49(11)	4684.30(8)	4709.96(8)	2310.68(4)
Temperature/K	150(2)	150(2)	150(2)	150(2)
Space group	*P*21/*n*	*P*21/*c*	*P*21/*c*	$P\bar{1}$
No. of formula units per unit cell, *Z*	4	4	4	2
Radiation type	Cu Kα	MoKα	MoKα	MoKα
Absorption coefficient, *μ*/mm^{-1}	1.184	0.583	3.619	0.681
No. of reflections measured	25826	74700	69057	42916
No. of independent reflections	8469	10732	10738	10513
R_{int}	0.0214	0.0375	0.0423	0.0304
Final R_1 values ($I > 2\sigma(I)$)	0.0461	0.0309	0.0281	0.0223
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1325	0.0736	0.0612	0.0535
Final R_1 values (all data)	0.0524	0.0459	0.0386	0.0252
Final $wR(F^2)$ values (all data)	0.1379	0.0844	0.0664	0.0552
Goodness of fit on F^2	1.048	1.084	1.126	1.058
CCDC number	1953499	1953500	1953501	1953502

Table S2. Angles between the {M1-N1-N2-N3} plane and the phenyl rings {C1-C6}, {C13-C18} and also for {M1-N4-N5-N6} vs {C25-C30} and {C37-C42}.

	M = Ge	M = Sn	M = Pb
$\{MN_3\}$-{C1-C6}	84.68(3)°	85.07(4)°	79.55(3)°
$\{MN_3\}$-{C13-C18}	59.01(5)°	53.43(4)°	55.62(3)°
$\{MN_3\}$-{C25-C30}	74.29(3)°	75.01(4)°	87.91(3)°
$\{MN_3\}$-{C37-C42}	59.66(3)°	57.70(3)°	55.29(3)°

Computations

The molecular geometries of **1**, **2**, **4** and **5** were fully optimized without symmetry constraints using the hybrid-DFT B3LYP functional[S7] and 3-21G* basis set[S8] for all atoms with the Gaussian 09 package.[S9] B3LYP/3-21G* is shown to be an appropriate model chemistry for metal complexes elsewhere.[S10] Compound **3** was not looked at computationally here due to **3** being so similar to **2** and computed results from **3** would not be expected to be highly significant to this study. The very good agreement in the geometric parameters between optimized and experimental geometries of **1**, **2** and **5** is shown in Table S3. Frequency calculations confirmed all geometries to be true minima. Transition state (TS) geometries for **1**, **2**, **4** and **5** were optimized with a D_2 symmetry constraint so the central atom lies on the N_4 plane (N1..N3..N4..N6). Different TS geometries for **1** and **2** were also located where all four N atoms in N-Dipp groups were constrained on a plane to show the low energy barriers of these TS geometries in the expected fluxional processes in solutions for **1** and **2**. Each TS geometry was confirmed to have one imaginary frequency from frequency calculations. The figures of the optimized geometries were generated using Mercury[S11] or GaussView[S12] software. The orbital figures - obtained from electronic structure calculations – were made using the GabEdit[S13] software. Natural bond analysis (NBO) calculations (Gaussian NBO[S14] version 3.1 within the Gaussian 09 package) were carried out on the optimized geometries.

Table S3. Comparison of selected experimental (X-ray) and optimized (Opt) geometrical parameters for **1**, **2** and **5**. The Opt data in parentheses are with the mixed basis set LANL2DZ/6-31G(d) with the pseudopotential LANL2DZ for Ge, Sn and Te and 6-31G(d) for other atoms instead of the 3-21G* basis set for all atoms.

Compound	Bond (Å)	X-ray	Opt	Angle (°)	X-ray	Opt
1	Ge-N1	2.186	2.195 (2.232)	N1-Ge-N4	137.4	140.3 (138.0)
	Ge-N4	2.206	2.195 (2.232)	N3-Ge-N6	104.2	108.8 (111.9)
	Ge-N3	2.014	2.022 (2.073)	N1-Ge-N3	59.5	61.1 (58.6)
	Ge-N6	2.002	2.022 (2.073)	N4-Ge-N6	59.8	61.1 (58.6)
2	Sn-N1	2.340	2.327 (2.355)	N1-Sn-N4	129.2	130.6 (131.1)
	Sn-N4	2.338	2.327 (2.355)	N3-Sn-N6	101.4	109.5 (111.3)
	Sn-N3	2.229	2.260 (2.266)	N1-Sn-N3	55.2	56.6 (54.9)
	Sn-N6	2.216	2.260 (2.266)	N4-Sn-N6	55.4	56.6 (54.9)
5	Te-N1	2.400	2.421 (2.513)	N1-Te-N4	165.5	159.5 (163.4)
	Te-N4	2.624	2.456 (2.526)	N3-Te-N6	88.6	91.0 (92.6)
	Te-N3	2.170	2.209 (2.236)	N1-Te-N3	54.9	55.5 (52.9)
	Te-N6	2.161	2.202 (2.246)	N4-Te-N6	52.4	55.0 (53.0)

Table S4. Total electronic and Gibbs (at 298.15 K, 1 atm) energies of optimized 'gas-phase' geometries for computed reaction energies.

	Total Energy (a.u.)	Total Gibbs Energy (a.u.)
[(Dipp)N=N-N(H)(Dipp)] = {L^{Dipp}}H	-1093.851756	-1093.360968
$(Me_3Si)_2NH$	-869.520079	-869.321474
$[Ge\{N(SiMe_3)_2\}]$	-3805.090058	-3804.688079
$[\{L^{Dipp}\}Ge\{N(SiMe_3)\}]$	-4029.455966	-4028.762884
$[Ge\{L^{Dipp}\}_2]$	-4253.807510	-4252.821242
$[Sn\{N(SiMe_3)_2\}]$	-7737.234519	-7736.835537
$[\{L^{Dipp}\}Sn\{N(SiMe_3)\}]$	-7961.605595	-7960.915248
$[Sn\{L^{Dipp}\}_2]$	-8185.970398	-8184.984461
$[Se\{N(SiMe_3)_2\}]$	-4128.279895	-4127.874283
$[\{L^{Dipp}\}Se\{N(SiMe_3)\}]$	-4352.620769	-4351.926864
$[Se\{L^{Dipp}\}_2]$	-4576.951901	-4575.965929
$[Te\{N(SiMe_3)_2\}]$	-8323.788344	-8323.385225
$[\{L^{Dipp}\}Te\{N(SiMe_3)\}]$	-8548.129398	-8547.438719
$[Te\{L^{Dipp}\}_2]$	-8772.482949	-8771.501161

Calculated reaction energies

$$\{L^{Dipp}\}H + [Ge\{N(SiMe_3)_2\}] \rightarrow [\{L^{Dipp}\}Ge\{N(SiMe_3)\}] + (Me_3Si)_2NH$$

-21.5 kcal mol^{-1} (Gibbs -22.2 kcal mol^{-1})

$$\{L^{Dipp}\}H + [\{L^{Dipp}\}Ge\{N(SiMe_3)\}] \rightarrow [Ge\{L^{Dipp}\}_2] + (Me_3Si)_2NH$$

-12.5 kcal mol^{-1} (Gibbs -11.8 kcal mol^{-1})

$$2\ \{L^{Dipp}\}H + [Ge\{N(SiMe_3)_2\}] \rightarrow [Ge\{L^{Dipp}\}_2] + 2\ (Me_3Si)_2NH$$

-34.0 kcal mol^{-1} (Gibbs -34.0 kcal mol^{-1})

$$\{L^{Dipp}\}H + [Sn\{N(SiMe_3)_2\}] \rightarrow [\{L^{Dipp}\}Sn\{N(SiMe_3)\}] + (Me_3Si)_2NH$$

-24.7 kcal mol^{-1} (Gibbs -25.2 kcal mol^{-1})

$$\{L^{Dipp}\}H + [\{L^{Dipp}\}Sn\{N(SiMe_3)\}] \rightarrow [Sn\{L^{Dipp}\}_2] + (Me_3Si)_2NH$$

-20.8 kcal mol^{-1} (Gibbs -18.6 kcal mol^{-1})

$$2\ \{L^{Dipp}\}H + [Sn\{N(SiMe_3)_2\}] \rightarrow [Sn\{L^{Dipp}\}_2] + 2\ (Me_3Si)_2NH$$

-45.5 kcal mol^{-1} (Gibbs -43.6 kcal mol^{-1})

$$\{L^{Dipp}\}H + [Se\{N(SiMe_3)_2\}] \rightarrow [\{L^{Dipp}\}Se\{N(SiMe_3)\}] + (Me_3Si)_2NH$$

-5.8 kcal mol^{-1} (Gibbs -8.2 kcal mol^{-1})

$$\{L^{Dipp}\}H + [\{L^{Dipp}\}Se\{N(SiMe_3)\}] \rightarrow [Se\{L^{Dipp}\}_2] + (Me_3Si)_2NH$$

+0.3 kcal mol^{-1} (Gibbs +0.3 kcal mol^{-1})

$$2\ \{L^{Dipp}\}H + [Se\{N(SiMe_3)_2\}] \rightarrow [Se\{L^{Dipp}\}_2] + 2\ (Me_3Si)_2NH$$

-5.5 kcal mol^{-1} (Gibbs -7.9 kcal mol^{-1})

$$\{L^{Dipp}\}H + [Te\{N(SiMe_3)_2\}] \rightarrow [\{L^{Dipp}\}Te\{N(SiMe_3)\}] + (Me_3Si)_2NH$$

-5.9 kcal mol^{-1} (Gibbs -8.8 kcal mol^{-1})

$$\{L^{Dipp}\}H + [\{L^{Dipp}\}Te\{N(SiMe_3)\}] \rightarrow [Te\{L^{Dipp}\}_2] + (Me_3Si)_2NH$$

-13.7 kcal mol^{-1} (Gibbs -14.4 kcal mol^{-1})

$$2\ \{L^{Dipp}\}H + [Te\{N(SiMe_3)_2\}] \rightarrow [Te\{L^{Dipp}\}_2] + 2\ (Me_3Si)_2NH$$

-19.6 kcal mol^{-1} (Gibbs -23.2 kcal mol^{-1})

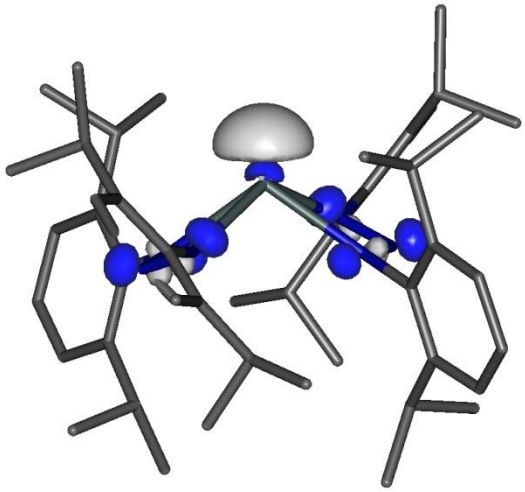


Figure S2. HOMO of **2** showing the lone pair on the metal.

Transition state geometries

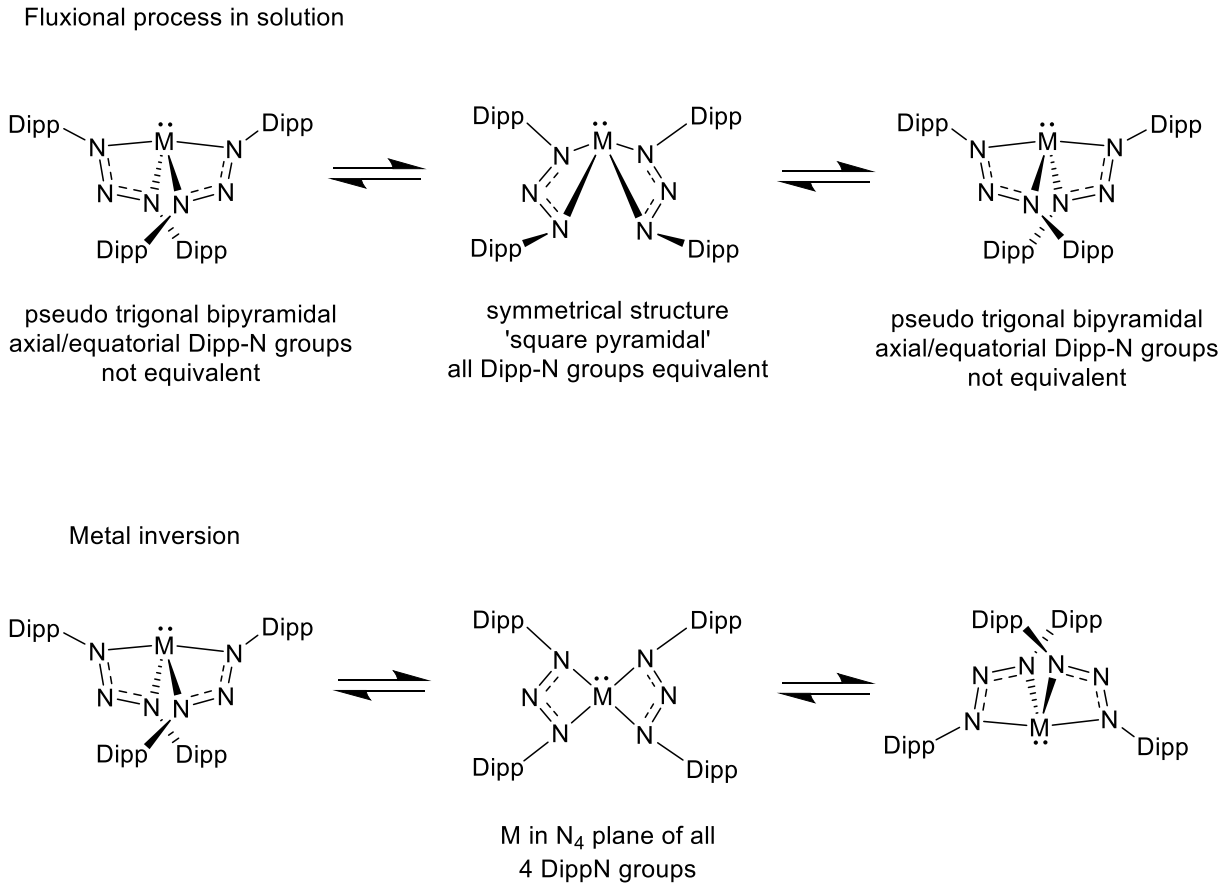
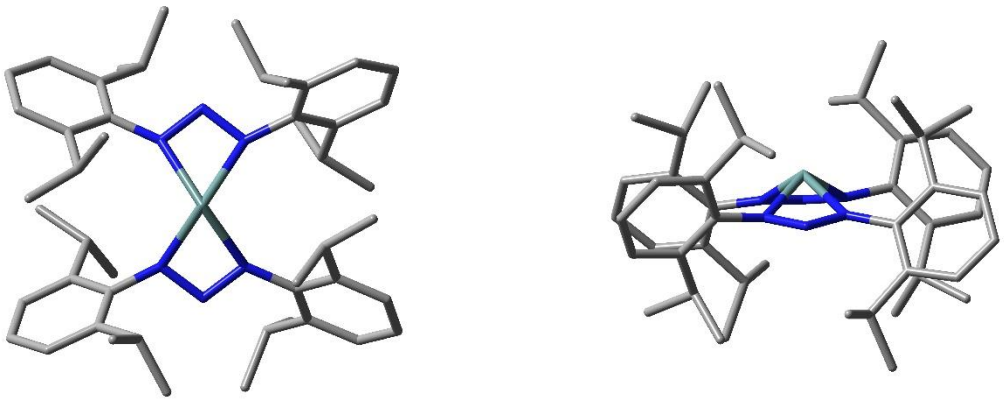
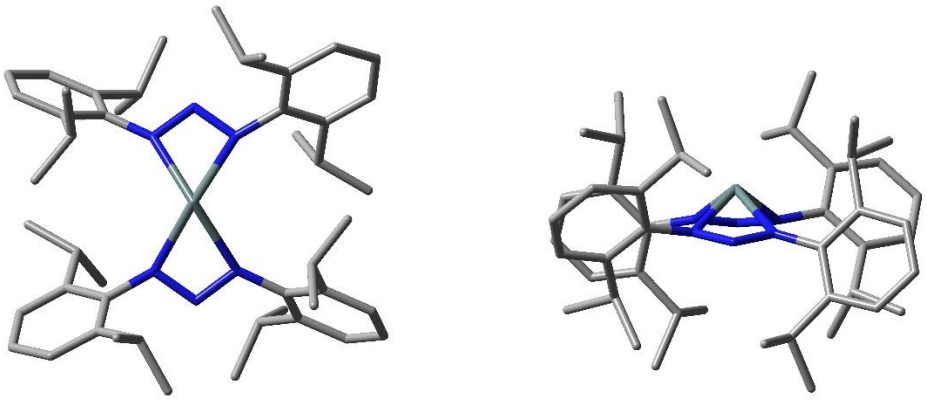


Figure S3. Fluxional processes explored for **1** (M = Ge) and **2** (M = Sn).

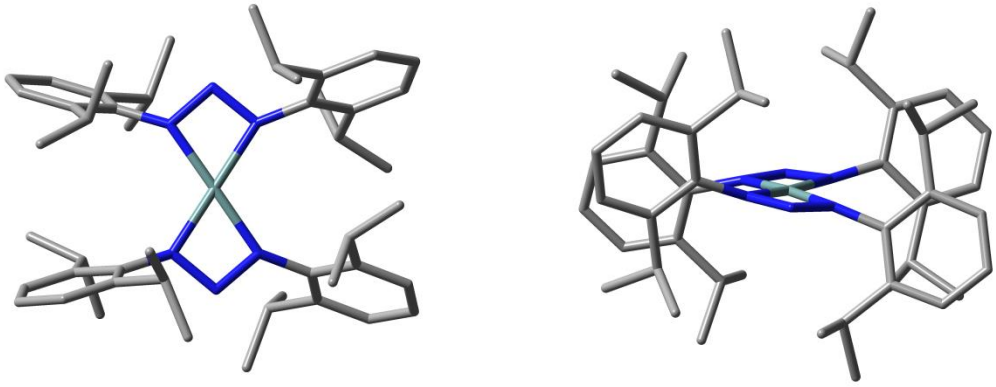


0.6 kcal mol^{-1} (2.6 kcal mol^{-1} Gibbs) vs lowest energy minimum of **1**

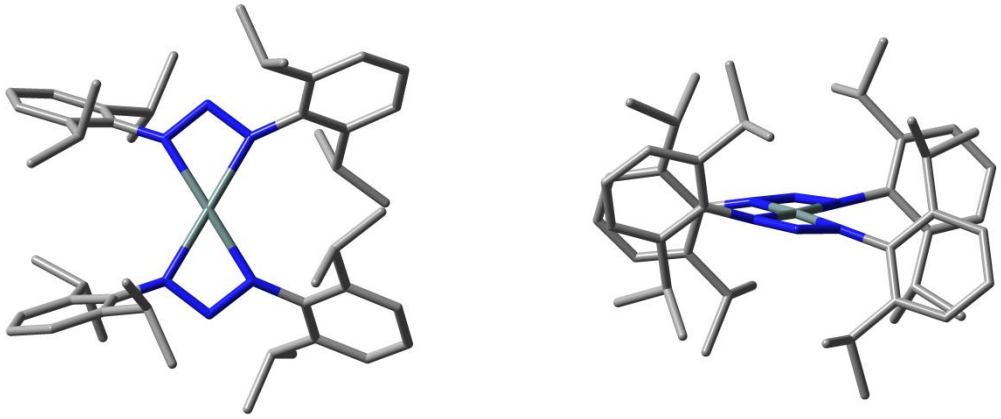


2.3 kcal mol^{-1} (1.4 kcal mol^{-1} Gibbs) vs lowest energy minimum of **2**

Figure S4. Transition state geometries located via the fluxional processes observed in solutions for **1** and **2**. Gibbs energies calculated at 298.15 K and 1 atm in the gas phase.



32.9 kcal mol^{-1} (34.1 kcal mol^{-1} Gibbs) vs lowest energy minimum of **1**



47.7 kcal mol^{-1} (43.9 kcal mol^{-1} Gibbs) vs lowest energy minimum of **2**

Figure S5. Transition state geometries located via the inversion process at the metal centre for **1** and **2**. Gibbs energies calculated at 298.15 K and 1 atm in the gas phase.

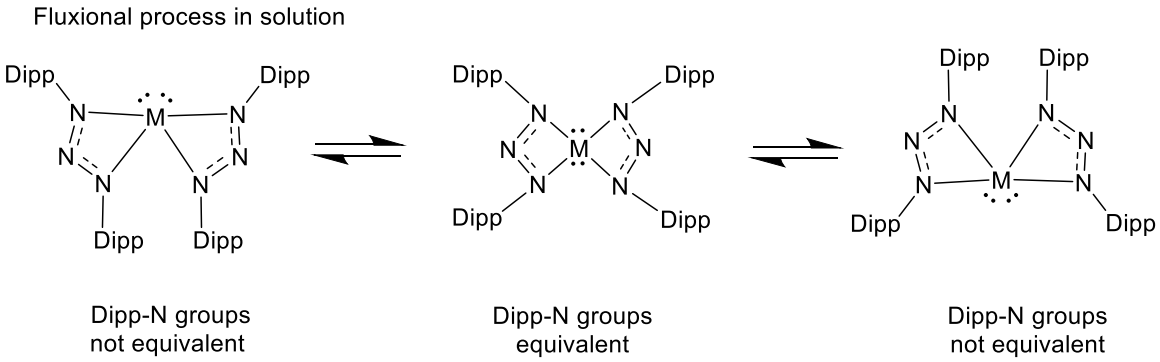
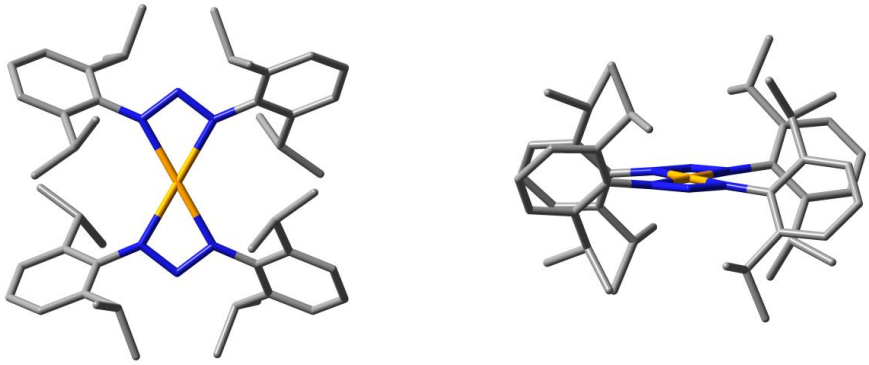
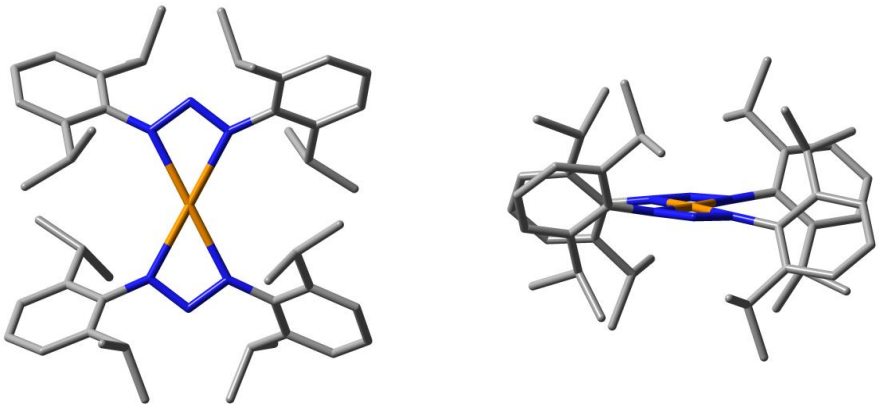


Figure S6. Fluxional processes explored for **4** (M = Se) and **5** (M = Te). Metal inversion fluxionality is non-existent as metal is in N_4 plane of all 4 Dipp-N groups in minimum.



13.1 kcal mol^{-1} (14.1 kcal mol^{-1} Gibbs) vs lowest energy minimum of **4**



12.0 kcal mol^{-1} (13.4 kcal mol^{-1} Gibbs) vs lowest energy minimum of **5**

Figure S7. Transition state geometries located via the fluxional process for **4** and **5**. Gibbs energies calculated at 298.15 K and 1 atm in the gas phase.

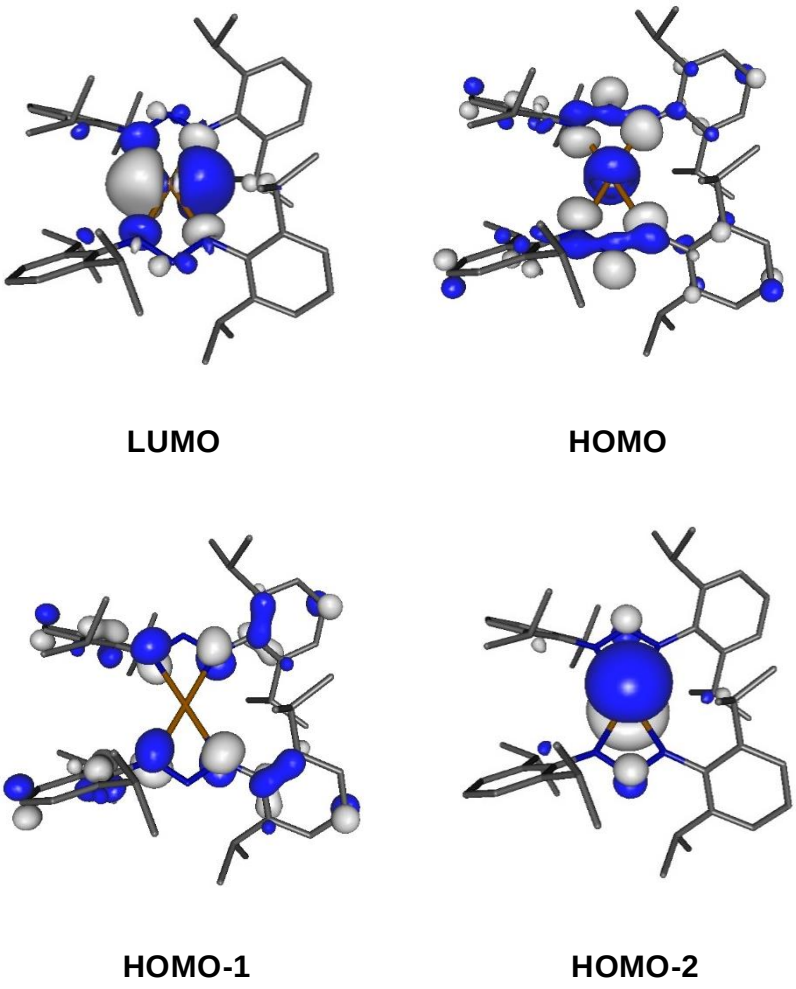


Figure S8. Selected orbitals from electronic structure calculations on the transition state geometry for **5**. The expected lone pair orbitals at HOMO and HOMO-1 were not observed – the lone pair orbitals would be expected to be located at Te like LUMO and HOMO-2. From NBO calculations, one lone pair has 100% s character and the other lone pair has 100% p character.

Cartesian coordinates of fully optimized geometries

1

Ge	-0.000114	0.000132	-0.958713
N	0.329779	-1.610629	0.218548
N	-0.932050	-2.132123	0.219121
N	-1.721403	-1.139432	-0.213297
N	1.721403	1.139496	-0.212924
N	0.932032	2.132063	0.219642
N	-0.329804	1.610531	0.219005
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C	-3.623544	2.584474	1.980833
H	-4.143921	3.536061	1.822719
H	-3.939054	2.169244	2.945858
H	-3.903484	1.891481	1.183245
C	4.255841	-0.691106	-2.317110
H	3.956944	0.105101	-1.634479
C	2.206121	3.031901	0.822225
C	4.276605	-2.002500	-1.530099
C	2.375677	4.098223	1.712789
H	2.726119	5.052362	1.340516
C	-1.172768	2.901171	-1.768236
C	-1.672015	4.709751	0.323384
H	-1.879392	5.413435	1.118774
C	1.710947	2.705340	3.567472
H	1.547779	2.582992	4.630908
C	-2.087394	2.822014	1.975943
H	-1.586895	1.860564	2.129289
C	1.198922	0.236076	3.287207
H	0.747668	-0.361559	2.492024
C	2.193427	-3.771344	1.199261
H	1.807290	-2.807923	1.541960
C	0.198694	0.276680	4.463743
H	0.625673	0.780399	5.337798
H	-0.056616	-0.747136	4.760852
H	-0.722186	0.794546	4.175865
C	-4.938448	-3.417255	0.891622
H	-5.118910	-4.046617	1.754206
C	-1.700230	3.768533	3.132978

H	-0.633135	4.000766	3.110616
H	-1.930620	3.283166	4.088704
H	-2.275828	4.700267	3.089759
C	5.127548	-4.257578	-1.209844
H	5.830813	-5.037093	-1.479930
C	-4.496320	-1.781640	-1.353262
C	-2.654160	-3.770485	2.805203
H	-3.564979	-4.206682	3.229776
H	-1.942815	-3.620990	3.625774
H	-2.222550	-4.484629	2.095449
C	-3.100970	-1.670397	-3.432113
H	-2.197063	-1.804515	-2.829685
H	-2.845647	-1.081974	-4.321352
H	-3.459615	-2.655196	-3.751647
C	4.175827	-4.489042	-0.221176
H	4.142752	-5.450285	0.276847
C	5.172113	-3.024297	-1.858593
H	5.909557	-2.857276	-2.633000
C	-4.200250	-0.952998	-2.603632
H	-3.812188	0.013565	-2.275021
C	-1.006140	1.949195	-2.953220
H	-0.993343	0.927128	-2.569184
C	-3.570088	-1.417116	3.125237
H	-3.731479	-0.446101	2.646711
H	-2.908308	-1.277930	3.988741
H	-4.536177	-1.795001	3.478760
C	1.521313	1.614478	2.711412
C	2.661166	3.157268	-0.627363
H	2.133218	2.393727	-1.204380
C	2.122034	3.941138	3.072580
H	2.265145	4.775154	3.750805
C	-5.569468	-2.677054	-1.316468
H	-6.236857	-2.742334	-2.165772
C	-1.175353	4.283204	-1.998394
H	-1.003850	4.654060	-3.002350
C	2.524504	-0.451034	3.712304
H	3.206075	-0.510658	2.858400
H	2.327095	-1.464295	4.082717
H	3.008369	0.126317	4.508151
C	4.182207	2.845785	-0.681583
H	4.734569	3.600840	-0.110802
H	4.539303	2.859511	-1.718506
H	4.383246	1.863260	-0.245431
C	-2.210294	2.091980	-3.918859
H	-3.151079	1.903137	-3.392827
H	-2.117244	1.374160	-4.742298
H	-2.246974	3.101713	-4.342353
C	0.321420	2.188006	-3.710312
H	0.358542	3.200762	-4.126301
H	0.414661	1.473193	-4.536028
H	1.174801	2.056771	-3.039496
C	3.188276	-0.795871	-3.439057
H	3.447584	-1.609302	-4.125749
H	3.134785	0.141662	-4.005448
H	2.202924	-0.999476	-3.008091
C	5.626609	-0.304560	-2.913189
H	6.404589	-0.297236	-2.142448
H	5.561733	0.698250	-3.350208
H	5.925804	-0.995472	-3.709420
C	2.372878	4.537749	-1.254149
H	1.311211	4.784184	-1.180591

H	2.655752	4.521656	-2.313352
H	2.960815	5.323997	-0.767276
C	-5.442809	-0.688839	-3.481384
H	-5.805677	-1.612325	-3.946751
H	-5.177511	0.007113	-4.285150
H	-6.255289	-0.247659	-2.894204
C	-5.794692	-3.486069	-0.203622
H	-6.635392	-4.170489	-0.193601
C	2.745514	-4.529592	2.428192
H	1.957964	-4.629179	3.184222
H	3.589554	-3.990916	2.871107
H	3.078103	-5.537866	2.158066
C	1.020595	-4.555964	0.556174
H	0.594703	-3.992895	-0.281903
H	0.228650	-4.735640	1.293095
H	1.374717	-5.520683	0.175887

References:

S1. Chorley, R. W.; Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P.; Power, P. P.; Olmstead, M. M. Subvalent Group 14 metal compounds. XIV. The X-ray crystal structures of two monomeric Group 14 metal bisamides, $Ge[N(SiMe_3)_2]_2$ and $Sn[NMe_2]_2$. *Inorg. Chim. Acta*, **1992,** 198-200, 203-209.

S2. Fjeldberg, T.; Hope, H.; Lappert, M. F.; Power, P. P.; Thorne, A. J. Molecular structures of the main group 4 metal(II) bis(trimethylsilyl)-amides $M[N(SiMe_3)_2]_2$ in the crystal (X-ray) and vapour (gas-phase electron diffraction). *J. Chem. Soc., Chem. Commun.*, **1983,** (11), 639-641.

S3. Bjoergvinsson, M.; Roesky, H. W.; Pauer, F.; Stalke, D.; Sheldrick, G. M. Preparation and structural characterization of the bis[bis(trimethylsilyl)amido]chalcogenides of selenium and tellurium. *Inorg. Chem.*, **1990,** 29 (26), 5140-5143.

S4. Barrett, A. G. M.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B.; Kociok-Köhn, G.; Procopiou, P. A. Triazenide Complexes of the Heavier Alkaline Earths: Synthesis, Characterization, And Suitability for Hydroamination Catalysis. *Inorg. Chem.*, **2008,** 47 (16), 7366-7376.

S5. Farrugia, L. J. WinGXsuite for small-molecule single-crystal crystallography. *J. Appl. Crystallog.*, **1999,** 32 (4), 837-838.

S6. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. $OLEX^2$: a complete structure solution, refinement and analysis program. *J. Appl. Crystallog.*, **2009,** 42 (2), 339-341.

S7. (a) Becke, A. D. Density-Functional Thermochemistry. 3. The role of exact exchange. *J. Chem. Phys.*, 1993, 98 (7), 5648-5652; (b) Lee, C.; Yang W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron-density. *Phys. Rev. B*, **1988**, 37 (2), 785-789.

S8. (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. Self-consistent molecular-orbital methods. 21. Small split-valence basis-sets for 1^{st}-row elements. *J. Am. Chem. Soc.*, 1980, **102**, 939-947; (b) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro W. J.; Hehre, W. J. Self-consistent molecular-orbital methods. 22. Small split-valence basis-sets for 2^{nd}-row elements. *J. Am. Chem. Soc.*, 1982, **104**, 2797-2803; (c) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; Defrees, D. J.; Pople J. A.; Binkley, J. S. Self-consistent molecular-orbital methods. 24. Supplemented small split-valence basis-sets for 2^{nd}-row elements. *J. Am. Chem. Soc.*, **1982**, 104, 5039-5048; (d) Dobbs, K. D.; Hehre, W. J. Molecular-orbital theory of the properties of inorganic and organometallic compounds. 4. – Extended basis-sets for 3^{rd}-row and 4^{th}-row, main-group elements. *J. Comp. Chem.*, **1986**, 7 (3), 359-378.

S9. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; ; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.;

Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision A.02. *Gaussian, Inc Wallingford CT* **2009**.

S10. (a) Neil, E.R.; Fox, M.A.; Pal, R.; Pålsson, L.-O.; O'Sullivan B.A.; Parker, D. Chiral probe development for circularly polarised luminescence: comparative study of structural factors determining the degree of induced CPL with four heptacoordinate europium(III) complexes. *Dalton Trans.*, **2015**, 44 (33), 14937-14951; (b) Merhi, A.; Zhang, X.; Yao, D.; Drouet, S.; Mongin, O.; Paul, F.; Williams, J.A.G.; Fox, M.A.; Paul-Roth, C.O. New donor-acceptor conjugates based on a trifluorenylporphyrin linked to a redox-switchable ruthenium unit. *Dalton Trans.*, 2015, 44 (20), 9470-9485; (c) Oerthel, M.C.; Yufit, D.S.; Fox, M. A.; Bryce, M. R.; Low, P.J. Syntheses and Structures of Buta-1,3-Diynyl Complexes from "on Complex" Cross-Coupling Reactions. *Organometallics,* **2015**, 34 (11), 2395-2405; (d) Zhang, X.; Abid, S.; Shi, L.; Williams, J. A. G.; Fox, M. A.; Miomandre, F.; Tourbillon, C.; Audibert, J.-F.; Mongin, O.; Paul, F.; Paul-Roth, C. O. Fluorenylporphyrins functionalized by electrochromic ruthenium units as redox-triggered fluorescence switches. *Dalton Trans.*, **2019**, 48 (31), 11897-11911.

S11. Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. Mercury CSD 2.0 - new features for the visualization and investigation of crystal structures. *J. Appl. Cryst.*, **2008**, 41 (2), 466–470.

S12. GaussView 6.0.16, Dennington II, R. D.; Keith, T. A.; Millam, J. M. *Semichem, Inc.*, Shawnee Mission KS, **2016**.

S13. Allouche, A.R. Gabedit-A Graphical User Interface for Computational Chemistry Softwares. *J. Comp. Chem.*, **2011**, 32 (1), 174-182.

S14. Weinhold F.; Carpenter, J. E. in *The Structure of Small Molecules and Ions*, Ed. R. Naaman and Z. Vager (Plenum, 1988) 227-236.