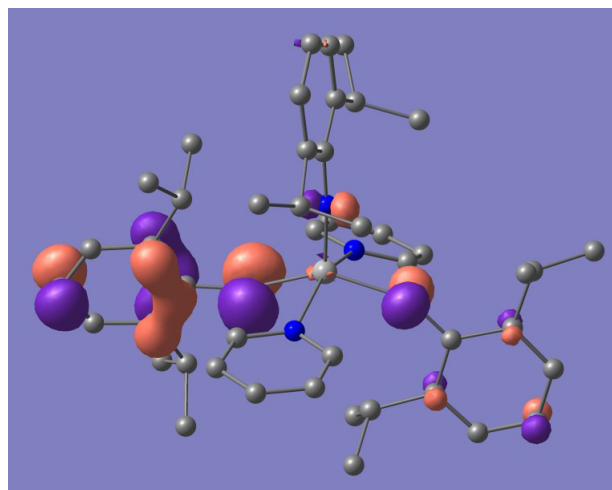


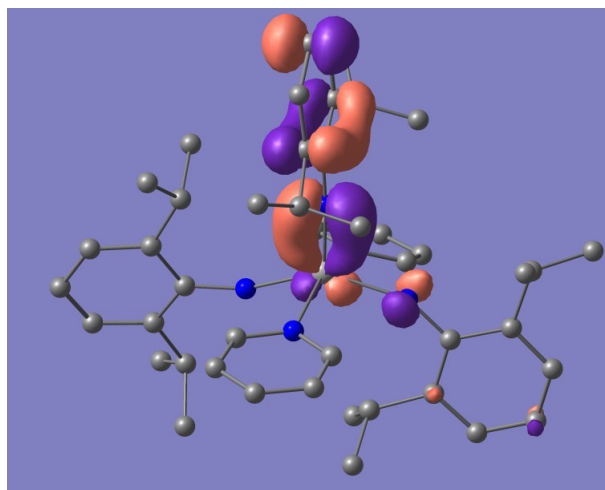
The First Group 4 Metal Bis(imido) and Tris(imido) Complexes

Andrew D. Schwarz, Alastair J. Nielson and Philip Mountford

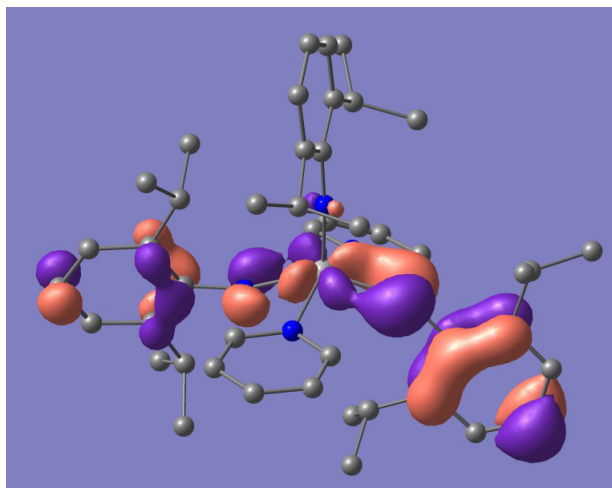
SUPPORTING INFORMATION



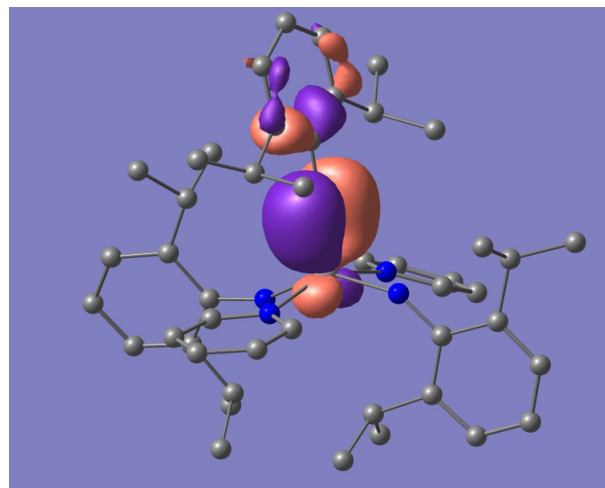
HOMO (-4.49 eV)



HOMO-1 (-4.81 eV)



HOMO-2 (-4.92 eV)



HOMO-5 (-5.99 eV)

Figure S1. Isosurfaces of selected orbitals and their energies for $[\text{Ti}(\text{NAr})(\text{NHAr})_2(\text{py})_2]$ (**1**). The value for the isosurfaces is 0.06 au. All H atoms are omitted. C atoms are shown in dark grey, Ti atom in light grey, N atoms in blue and Li atoms in magenta.

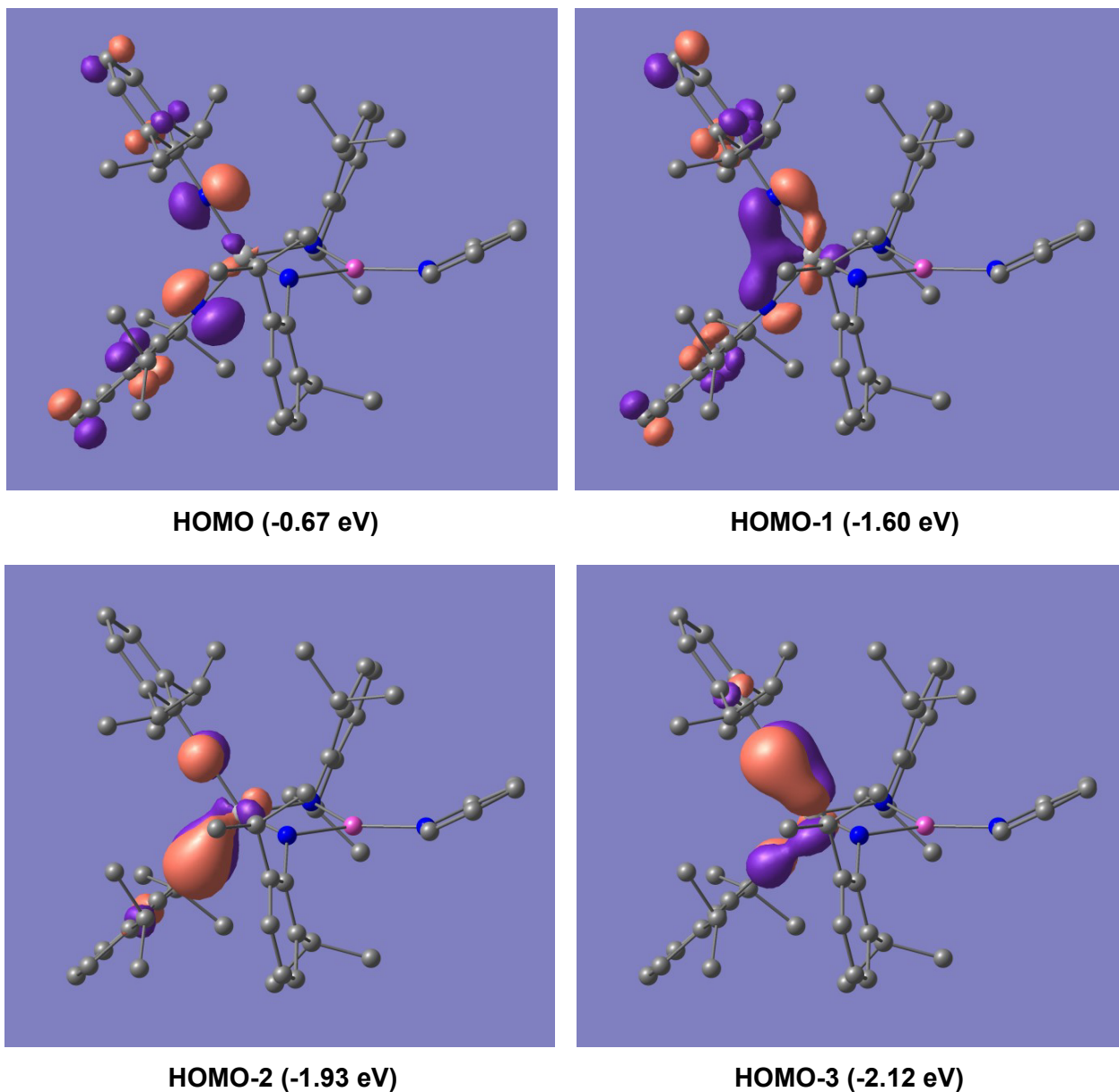
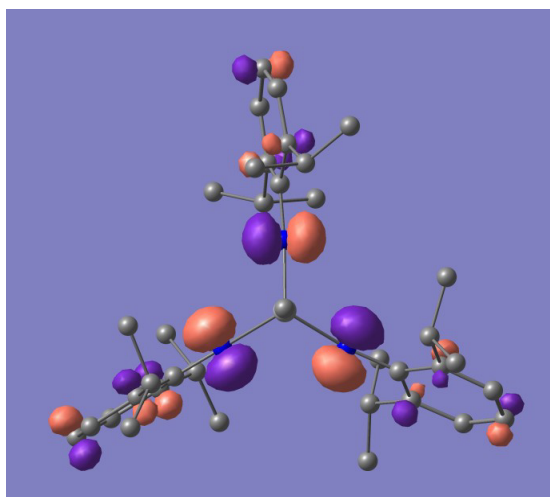
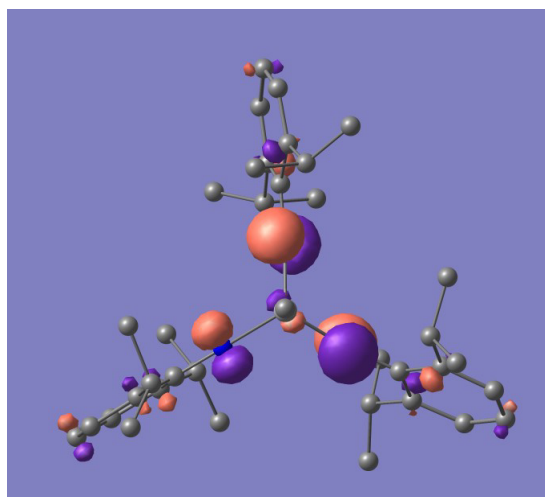


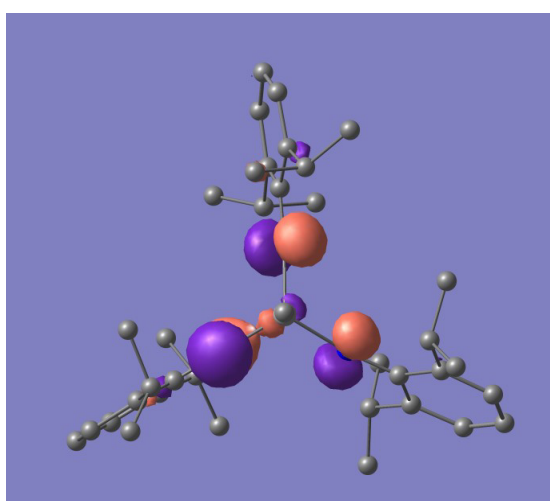
Figure S2. Isosurfaces of selected orbitals and their energies for $[\text{Ti}(\text{NAr})_2(\text{NHAr})_2\{\text{Li}(\text{py})\}]^-$ (**3a**). The value for the isosurfaces is 0.06 au. All H atoms are omitted. C atoms are shown in dark grey, Ti atom in light grey, N atoms in blue and Li atoms in magenta.



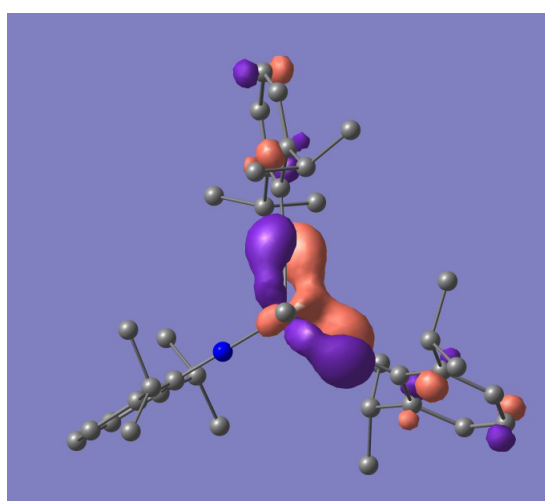
HOMO (5.49 eV)



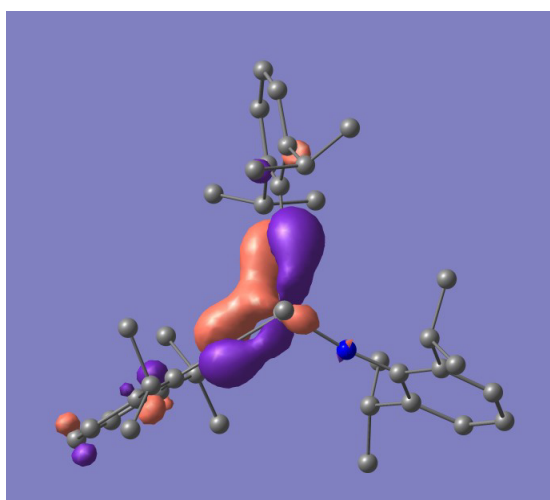
HOMO-1 (5.13 eV)



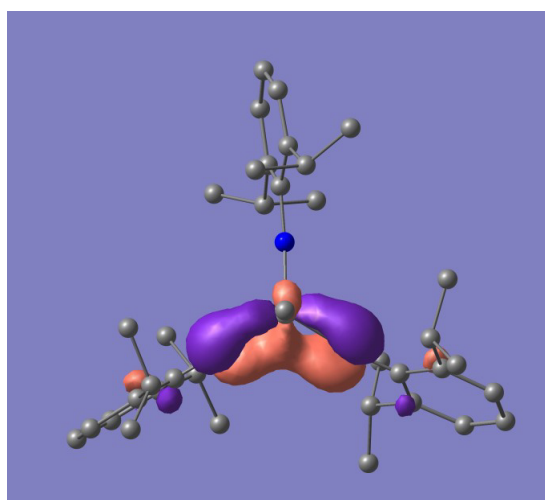
HOMO-2 (5.06 eV)



HOMO-3 (4.32 eV)



HOMO-4 (4.14 eV)



HOMO-5 (4.10 eV)

Figure S3. Isosurfaces of selected orbitals and their energies for $[\text{Ti}(\text{Me})(\text{NAr})_3]^{3-}$ (**2a**). The value for the isosurfaces is 0.06 au. All H atoms are omitted. C atoms are shown in dark grey, Ti atom in light grey, N atoms in blue.

General methods and instrumentation. All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent. Toluene was refluxed over sodium and distilled. Deuterated solvents were dried over sodium (toluene- d_8), potassium (C_6D_6) or P_2O_5 (CD_2Cl_2), distilled under reduced pressure and stored under dinitrogen in Teflon valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. 1H , 2H , 7Li and ^{13}C - $\{^1H\}$ NMR spectra were recorded on Varian Mercury-VX 300 and Varian Unity Plus 500 spectrometers at ambient temperature unless stated otherwise and referenced internally to residual protio-solvent (1H) or solvent (^{13}C) resonances, and are reported relative to tetramethylsilane ($\delta = 0$ ppm). 7Li spectra were referenced externally to LiCl and the 2H NMR spectrum was referenced to the natural abundance deuterium resonance of the protio solvent (C_6H_6). 1H and ^{13}C assignments were confirmed using two dimensional 1H - 1H and ^{13}C - 1H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. IR spectra were recorded on a Nicolet Magna 560 E.S.P. FTIR spectrometer. Samples were prepared in a dry-box as Nujol mulls between NaCl plates, and the data are quoted in wavenumbers (cm^{-1}). Elemental analyses were carried out by the Elemental Analysis Service at the London Metropolitan University or Elemental Microanalysis Ltd., Devon.

Starting materials. $Ti(NMe_2)_4$ and CD_3Li were synthesised according to literature procedures.¹ Other reagents were purchased from Sigma-Aldrich and used without further purification.

X-ray structure determinations. Crystals were mounted on MiTeGen MicroMounts using perfluoropolyether oil and cooled rapidly in a stream of cold N_2 using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer. As appropriate, absorption and decay corrections were applied to the data and equivalent reflections merged.² The structures were solved with SIR92³ and further refinements and all other crystallographic calculations were performed using either the CRYSTALS program suite.⁴ Other details of the structure solution and refinements are given in the CIF Supporting Information which has been deposited at the Cambridge Crystallographic Data Centre (CCDC codes 813857, 813858 and 813859).

Computational procedures. Single point density functional theory calculations were carried out at the experimentally determined geometries of **1**, **2** and **3** using the hybrid B3PW91 functional, as implemented in the Gaussian 09 Rev. A.02 code.⁵ The 6-31G** basis set was applied to all atoms, and the default integration grid and SCF convergence parameters were employed. In order to calculate the Mayer bond orders, analogous calculations were performed in the Amsterdam Density Functional 2010.02 code⁶ using the B3LYP hybrid functional (B3PW91 is not available in the

Amsterdam Density Functional code). All-electron Slater Type Orbital basis sets of DZP quality were used for all atoms bar Ti, for which a TZP basis set was employed. The default SCF convergence criteria were used, together with an integration grid of 4.5. In order to verify that the different functionals employed in the Gaussian and ADF calculations do not significantly affect the results, B3LYP calculations on compounds **1** – **3** were also performed. Corresponding methods were used for the models **2a** and **3a** which were calculated at the experimental geometries of **2** and **3** but with the appropriate number of $[\text{Li}(\text{py})]^+$ cations removed.

References

1. (a) D. C. Bradley and I. M. Thomas, *J. Chem. Soc.*, 1960, 3857; (b) K. A. Reynolds, D. O'Hagan, D. Gani and J. A. Robinson, *J. Chem. Soc., Perkin Trans. 1*, 1988, 3195.
2. Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode*, Academic press, New York, 1997.
3. A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.
4. P. W. Betteridge, J. R. Cooper, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Cryst.*, 2003, **36**, 1487.
5. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision A.2*, (2009) Gaussian 09, Revision A.2, Gaussian, Inc., Wallingford CT.
6. (a) C. Fonseca Guerra, J. G. Snijders, G. te Velde and E. J. Baerends, *Theo. Chem. Acc.*, 1998, **99**, 391; (b) G. te Velde, F. M. Bickelhaupt, S. Van Gisbergen, C. Fonseca Guerra, E. J. Baerends, J. G. Snijders and T. Ziegler, *J. Comput. Chem.*, 2001, **22**, 931.