ChemComm

A new and versatile diamide–diamine donor ligand set in early transition metal chemistry†

Michael E. G. Skinner, David A. Cowhig and Philip Mountford*

Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR.
E-mail: philip.mountford@chemistry.oxford.ac.uk

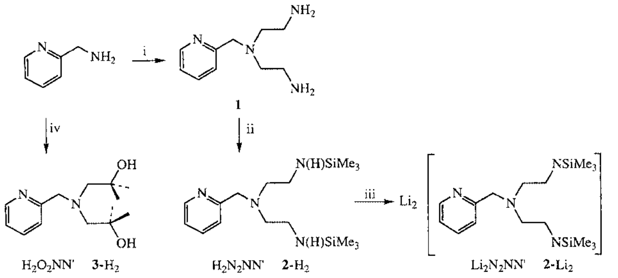
Received (in Cambridge, UK) 28th March 2000, Accepted 22nd May 2000

Straightforward, multigram synthesis of the new diamide–diamine proligand H_2N_2NN' [N_2NN' = (2-NC_5H_4)-$CH_2N(CH_2CH_2NSiMe_3)_2$] is described along with a preliminary survey of the five- and six-coordinate, neutral and cationic, single- and multiply-bonded complexes of groups 3, 4 and 5 that it can support; the related bis(alkoxide)–diamine proligand H_2O_2NN' is also described where H_2O_2NN' = (2-NC_5H_4)$CH_2N(CH_2CMe_2OH)_2$.

The bis(cyclopentadienyl) ligand set has been the dianionic environment *par excellence* for organotransition metal chemistry for *ca*. four decades.[1] Driven by the search for new fundamental and catalytic chemistry, the last ten years in particular have established the importance of polydentate di- and tri-anionic N-donor ligands as environments for early- to mid-transition metal coordination and organometallic complexes.[2]

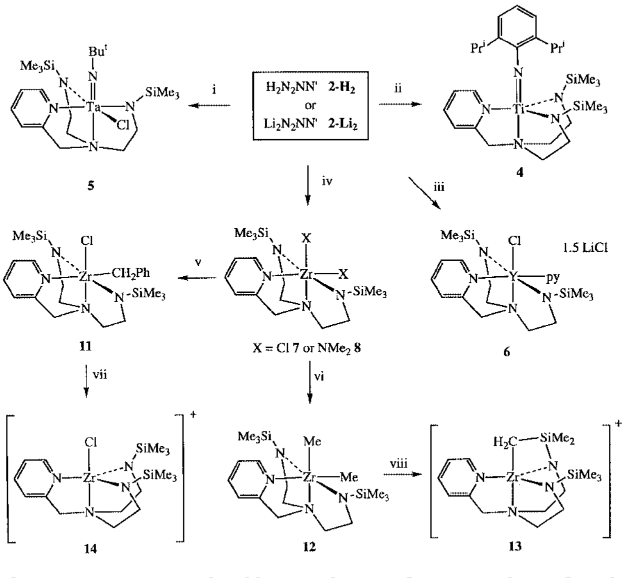
Among the tetradentate 'N_4' donor ligands, the porphyrins[2b] and tetraaza[14]annulenes[2c] are probably the best established *di*anionic ligands. They provide a really quite rigid, square-base donor environment. In contrast, the *tri*anionic triamidoamine 'tren' systems generally provide four vertices of a trigonal bipyramid or octahedron. Such ligands have been extremely successful in developing p-block, early-mid transition metal, lanthanide and actinide chemistry.[2d,3] Despite these successes, however, as a trianionic species the versatility of this ligand is hampered in certain regards for developing new lanthanide, and groups 3 and 4 chemistry in particular since there is only one (group 4) or no (lanthanide, group 3) metal electrons remaining for binding additional anionic ligands. Dianionic 'N_4' analogues of the tren systems will help advance early transition metal and lanthanide chemistry, and compliment the extensive studies of *tri*dentate diamido-donor systems.[2a] Indeed, it was recently reported that addition of an extra donor arm to bis(alkoxide)-donor systems can lead to enhanced ethylene polymerisation capability.[4]

The straightforward syntheses of the new proligands H_2N_2NN' **2**-H_2 and H_2O_2NN' **3**-H_2 are shown in Scheme 1.‡ The intermediate tetra-amine **1** has been previously described,[5] but we have found that the alternative synthesis shown from 2-aminomethylpyridine is more convenient on a large scale. The proligand **2**-H_2 is conveniently converted (Bu^nLi) to its lithiated derivative Li_2N_2NN' **2**-Li_2. The new proligands can all be prepared in multigram quantities: *e.g.* 5.4 g of **1** yields 7.1 g (75%) of **2**-H_2 and lithiation of this gives 4.2 g (57%) of Li_2N_2NN' **2**-Li_2.



Scheme 1 *Reagents and yields*: i, *N*-tosylaziridine (74% for this step) then conc. H_2SO_4 83% (61% overall); ii, 2 Me_3SiCl, 4 Et_3N, 75%; iii, 2.2 Bu^nLi, 57%; iv, 3-isobutylene oxide, 25%.

The ready availability of H_2N_2NN' **2**-H_2 and Li_2N_2NN' **2**-Li_2 has allowed us to develop a representative range of new five- and six-coordinate, neutral and cationic, single- and multiply-bonded complexes of groups 3, 4 and 5 (Scheme 2). They are formed by salt- (for **4**–**6**), and alkane- or amine- (for **7** and **8**) elimination reactions; the applicability of a range of such protocols will clearly permit these new ligands to be incorporated into a wide range of transition, lanthanide and main group metal derivatives. Thus reaction of Li_2N_2NN' **2**-Li_2 with [$Ti(NAr)Cl_2(py)_3$][6a] (Ar = $C_6H_3Pr^i_2$-2,6) or [$Ta(NBu^t)$-$Cl_3(py)_2$][6b] gives the five- and six-coordinate imides, [Ti-(NAr)(N_2NN')] **4** and [$Ta(NBu^t)Cl(N_2NN')$] **5**, respectively. Transition metal imides continue to attract considerable interest,[7] and those of group 4 with π-donor coligands can have a particularly rich reaction chemistry.[2a,7,8] Reaction of **2**-Li_2 with YCl_3 in pyridine affords the 'ate' complex **6**, formulated as '[$YCl(N_2NN')(py)$]·1.5LiCl' on the basis of elemental analyses and ^7Li NMR spectroscopy. Nonetheless, preliminary reactivity studies of **6** show that it behaves as though it were simply [$YCl(N_2NN')(py)$], and that it is a useful synthon with the Y-bound Cl ligand being readily substituted by bulky monoanionic donors.



Scheme 2 *Reagents and yields*: i, (with **2**-Li_2) [$Ta(NBu^t)Cl_3(py)_2$], 36 h, 29%; ii, (with **2**-Li_2) [$Ti(NC_6H_3Pr^i_2$-2,6)$Cl_2(py)_3$], 58%; iii, (with **2**-Li_2) YCl_3, 71%; iv, (with **2**-H_2) for **7**: [$ZrCl_2(CH_2SiMe_3)_2$·$2Et_2O$], 87%; for **8**: [$Zr(NMe_2)_4$], 55%; v, $PhCH_2MgCl$, 87%; vi, LiMe (2 equiv.), 88%; vii, $B(C_6F_5)_3$, 61% [counter ion = $B(CH_2Ph)(C_6F_5)_3^-$]; viii, $B(C_6F_5)_3$, 60% [counter ion = $BMe(C_6F_5)_3^-$].

---

† Electronic supplementary information (ESI) available: experimental details and characterisation. See http://www.rsc.org/suppdata/cc/b0/b002455o/

DOI: 10.1039/b002455o

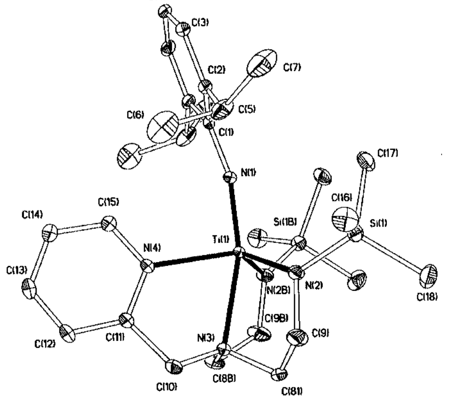


Fig. 1 Displacement ellipsoid plot of [Ti(N_2NN')($NC_6H_3Pr^i_2$-2,6)] **4**.

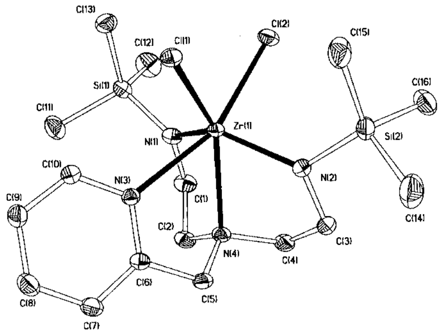
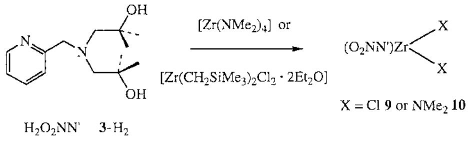


Fig. 2 Displacement ellipsoid plot of [Zr(N_2NN')Cl_2] **7**.

The group 4 compounds [Zr(X)$_2$(N_2NN')] (X = Cl **7** or NMe_2 **8**) are readily obtained from **2**-H_2 and [Zr(CH_2SiMe_3)$_2Cl_2$·$2Et_2O$][9] or [Zr(NMe_2)$_4$], respectively. Such *cis*-X_2 complexes are of great importance in the study of new stoichiometric and catalytic group 4 reaction chemistry.[10] The bis(alkoxide) analogues of **7** and **8**, namely [Zr(X)$_2$(O_2NN')] [X = Cl **9** or NMe_2 **10**, eqn. (1)] can be similarly prepared from H_2O_2NN' **3**-H_2. The compounds **9** and **10** will provide interesting comparisons with their more sterically-shielded tetraaza homologues **7** and **8**, and with very recent bis(phenoxide)–diamine ligands that are active ethylene polymerisation catalysts.[4]



(1)

We have structurally confirmed that the N_2NN' ligand can readily accommodate both five- and six-coordinate metal centres. Views of the X-ray structures of [Ti(NAr)(N_2NN')] **4** and [$ZrCl_2$(N_2NN')] **7** are shown in Fig. 1 and 2, respectively.§ The structure of **4** reveals an approximately trigonal bipyramidal geometry at the five-coordinate Ti centre. The structure of **7** reveals an approximately octahedral Zr centre; the chloride ligands are mutually *cis*. In both **4** and **7**, and indeed in all the derivatives to date of the N_2NN' ligand, including the crowded bis(dimethylamide) complex **8**, the pyridyl donor is firmly bound to the metal centre and establishes a well defined coordination environment.

One or both chloride ligands in [$ZrCl_2$(N_2NN')] **7** can be substituted using organo-magnesium or -lithium reagents forming the mono- and di-alkyl derivatives [Zr(CH_2Ph)Cl(N_2NN')] **11** and [$ZrMe_2$(N_2NN')] **12** in *ca.* 90% yield. There is no evidence in any of the reaction chemistry herein for metallation or other attack at the pyridyl donor group. *cis*-Dialkyl compounds such as **12** are potential precursors to Ziegler–Natta olefin polymerisation catalysts.[10] Treatment of **12** with $B(C_6F_5)_3$ or [CPh_3][$B(C_6F_5)_4$], however, affords the TMS-metallated cation **13** with counter anion [$MeB(C_6F_5)_3$]$^-$ or [$B(C_6F_5)_4$]$^-$; there is no evidence for interaction between **13** and the [$MeB(C_6F_5)_3$]$^-$ anion in solution. The [$MeB(C_6F_5)_3$]$^-$ salt of **13** is thermally stable at r.t. in both the solid state and CD_2Cl_2 solution, and has been fully characterised by NMR and elemental analysis. Cation **13** presumably forms *via* an intermediate cation [ZrMe(N_2NN')]$^+$ (not observed) followed by σ-bond metathesis with one of the $SiMe_3$ C–H bonds. Similar reactions have been seen in group 4 triamidoamine chemistry,[11] but can, in principle, be circumvented by use of alternative amide N-substituents: such protocols are well established.[2a,12] Indirect evidence for a five-coordinate cationic intermediate comes from the formation of the cation [ZrCl(N_2NN')]$^+$ **14** from the monobenzyl complex [Zr(CH_2Ph)Cl(N_2NN')] **11** and $B(C_6F_5)_3$. Salts of the cation **13** react sluggishly with ethylene (1 atm), but work is in progress to develop analogues of H_2N_2NN' with other, more robust amide N-substituents.

In summary, we have described the new diamido–diamine ligand H_2N_2NN' and a survey of its versatile complexation chemistry.

This work was supported by the EPSRC and Royal Society. We thank Dr G. A. Vaughan (Exxon Chemical Co.) for a gift of [Zr(NMe_2)$_4$] and Dr D. J. Watkin for help with the X-ray data collection.

Notes and references

‡ Full spectroscopic data and elemental analyses have been obtained as far as possible for all the new compounds.

§ *Crystal data* for **4**: $C_{28}H_{49}N_5Si_2Ti$, M = 559.80, orthorhombic, space group *Pbcm*, a = 9.8632(4), b = 18.413(1), c = 17.507(1) Å, U = 3179.4(8) Å^3, Z = 4, T = 170 K, μ = 0.36 mm^{-1}, 3688 independent reflections (R_{merge} = 0.035), 3240 with $I > 3\sigma(I)$ used in refinement, final R indices: R = 0.0574, R_w = 0.0434. For **7**·$0.5C_6H_6$: $C_{16}H_{32}Cl_2N_4Si_2Zr$·$0.5C_6H_6$, M = 537.81, monoclinic, space group $P2_1/n$, a = 8.4280(1), b = 14.3380(4), c = 21.5020(6) Å, β = 93.295(2)°, U = 2594.0 Å^3, T = 150 K, μ = 0.73 mm^{-1}, 5550 independent reflections (R_{merge} = 0.030), 4506 with $I > 3\sigma(I)$ used in refinement, final R indices: R = 0.0278, R_w = 0.0269. CCDC 182/1648. See http://www.rsc.org/suppdata/cc/b0/b002455o/ for crystallographic files in .cif format.

1 *Metallocenes: synthesis, reactivity, applications*, ed. A. Togni and R. L. Halterman, Wiley-VCH, New York, 1998, vol. 1 & 2.
2 Recent reviews: (*a*) diamide-donors in general; L. H. Gade, *Chem. Commun.*, 2000, 173 (Feature Article); (*b*) porphyrins: H. Brand and J. Arnold, *Coord. Chem. Rev.*, 1995, **140**, 137; (*c*) tetraaza[14]annulenes: P. Mountford, *Chem. Soc. Rev.*, 1998, **27**, 105; (*d*) triamidoamines: R. R. Schrock, *Acc. Chem. Res.*, 1997, **30**, 9; J. G. Verkade, *Acc. Chem. Res.*, 1993, **26**, 483.
3 P. Roussel, N. W. Alcock and P. Scott, *Chem. Commun.*, 1998, 801; P. Roussel, N. W. Alcock, R. Boaretto, A. Kingsley, I. J. Munslow, C. P. Sanders and P. Scott, *Inorg. Chem.*, 1999, **38**, 3651 and references therein.
4 E. Y. Tshuva, I. Goldberg, M. Kol, H. Weitman and Z. Goldschmidt, *Chem. Commun.*, 2000, 379.
5 H. Adams, N. A. Bailey, W. D. Carlisle, D. E. Fenton and G. Rossi, *J. Chem. Soc., Dalton Trans.*, 1990, 1271.
6 (*a*) A. J. Blake, P. E. Collier, S. C. Dunn, W.-S. Li, P. Mountford and O. V. Shishkin, *J. Chem. Soc., Dalton Trans.*, 1997, 1549; (*b*) J. Sundermeyer, J. Putterlik, M. Foth, J. S. Field and N. Ramesar, *Chem. Ber.*, 1994, **127**, 1201.
7 D. E. Wigley, *Prog. Inorg. Chem.*, 1994, **42**, 239; P. Mountford, *Chem. Commun.*, 1997, 2127 (Feature Article).
8 J. L. Bennett and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1997, **119**, 10 696 and references therein.
9 H. Brand, J. A. Capriotti and J. Arnold, *Organometallics*, 1994, **13**, 4469.
10 G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 429 and references therein.
11 C. Morton, N. W. Alcock and P. Scott, *Organometallics*, 1999, **18**, 4608; C. C. Cummins, R. R. Schrock and W. M. Davis, *Organometallics*, 1992, **11**, 1452.
12 G. E. Greco, A. I. Popa and R. R. Schrock, *Organometallics*, 1998, **17**, 5591.