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

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Straightforward, multigram synthesis of the new diamidediamine proligand H_2N_2NN' [N_2NN' = (2- NC_5H_4)-C $H_2N(CH_2CH_2NSiMe_3)_2$] 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 diand tri-anionic N-donor ligands as environments for early- to mid-transition metal coordination and organometallic complexes.²

Among the tetradentate 'N₄' donor ligands, the porphyrins^{2b} and tetraaza[14]annulenes^{2c} are probably the best established dianionic ligands. They provide a really quite rigid, square-base donor environment. In contrast, the trianionic 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 'N4' analogues of the tren systems will help advance early transition metal and lanthanide chemistry, and compliment the extensive studies of tridentate 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 (BuⁿLi) to its lithiated derivative Li₂ N_2NN' **2**-Li₂. 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 Li₂ N_2NN' **2**-Li₂.

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 fiveand six-coordinate, neutral and cationic, single- and multiplybonded 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 incorpo-



Scheme 1 Reagents and yields: i, N-tosylaziridine (74% for this step) then conc. H₂SO₄ 83% (61% overall); ii, 2 Me₃SiCl, 4 Et₃N, 75%; iii, 2.2 BuⁿLi, 57%; iv, 3-isobutylene oxide, 25%.

rated 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 YCl₃ 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 Ybound Cl ligand being readily substituted by bulky monoanionic donors.



Scheme 2 *Reagents and yields*: i, (with **2**-Li₂) [Ta(NBu^t)Cl₃(py)₂], 36 h, 29%; ii, (with **2**-Li₂) [Ti(NC₆H₃Prⁱ₂-2,6)Cl₂(py)₃], 58%; iii, (with **2**-Li₂) YCl₃, 71%; iv, (with **2**-H₂) for **7**: [ZrCl₂(CH₂SiMe₃)₂·2Et₂O], 87%; for **8**: [Zr(NMe₂)₄], 55%; v, PhCH₂MgCl, 87%; vi, LiMe (2 equiv.), 88%; vii, B(C₆F₅)₃, 61% [counter ion = B(CH₂Ph)(C₆F₅)₃⁻]; viii, B(C₆F₅)₃, 60% [counter ion = BMe(C₆F₅)₃⁻].

[†] Electronic supplementary information (ESI) available: experimental details and characterisation. See http://www.rsc.org/suppdata/cc/b0/ b0024550/



Fig. 1 Displacement ellipsoid plot of [Ti(N2NN')(NC6H3Pri2-2,6)] 4.



Fig. 2 Displacement ellipsoid plot of [Zr(N₂NN')Cl₂] 7.

The group 4 compounds $[Zr(X)_2(N_2NN')]$ (X = Cl 7 or NMe₂ 8) are readily obtained from 2-H₂ and $[Zr(CH_2Si-Me_3)_2Cl_2\cdot 2Et_2O]^9$ or $[Zr(NMe_2)_4]$, respectively. Such *cis*-X₂ 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 NMe₂ 10, eqn. (1)] can be similarly prepared from

$$\bigcup_{\substack{O \in V_{1}, V_{2} \in V_{2}}} \bigcap_{\substack{O \in V_{2} \in V_{2} \in V_{2}}} \bigcap_{\substack{(Zr(CH_{2}SiMe_{3})_{2}Cl_{2} \cdot 2El_{2}O] \\ X = Cl 9 \text{ or } NMe_{2} 10}} (O_{2}NN)Zr \xrightarrow{X} (1)$$

 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

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 [ZrCl₂(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 $[MeB(C_6F_5)_3]^{-1}$ 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 CD₂Cl₂ 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 SiMe₃ 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 $[Zr(CH_2Ph)Cl(N_2NN^\prime)]\ 11$ 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.

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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: C₂₈H₄₉N₅Si₂Ti, M = 559.80, orthorhombic, space group *Pbcm*, a = 9.8632(4), b = 18.413(1), c = 17.507(1) Å, U = 3179.4(8) A³, Z = 4, T = 170 K, $\mu = 0.36$ 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**·0.5C₆H₆: C₁₆H₃₂Cl₂N₄Si₂Zr·0.5C₆H₆, M = 537.81, monoclinic, space group *P*2₁/*n*, a = 8.4280(1), b = 14.3380(4), c = 21.5020(6) Å, $\beta = 93.295(2)^\circ$, U = 2594.0 Å³, T = 150 K, $\mu = 0.73$ 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/b0024550/ for crystallographic files in .cif format.

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