Control of metal/ligand stoichiometry and structure in aminopyridinato complexes of zirconium: *N*-alkyl is better than trimethylsilyl†

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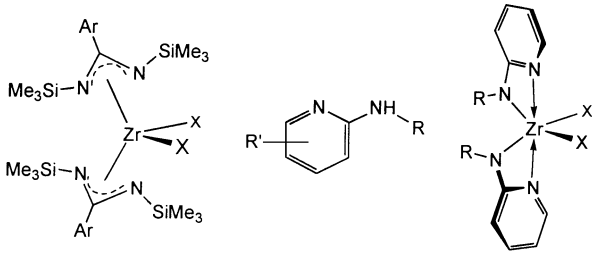
Received (in Cambridge, UK) 11th August 2000, Accepted 21st September 2000
First published as an Advance Article on the web 12th October 2000

_N_-Adamantyl-2-aminopyridines (HL) readily form C_2-symmetric aminopyridinato complexes with zirconium [ZrL_2X_2] (X = Cl, NMe_2, CH_2Ph, CH_2Bu^t) which are stable with respect to ligand redistribution and lead to catalysts for ethylene polymerisation with similar productivity to the related [Zr(benzamidinate)$_2X_2$] system.

Of the many ligand sets that may provide an alternative to cyclopentadienyl,[1] the amidinates have been among the most productive in terms of both new stoichiometric chemistry and catalytic activity.[2] Of particular note recently are reports that complexes such as **I** support an impressive range of ancillary



I **II** **III**

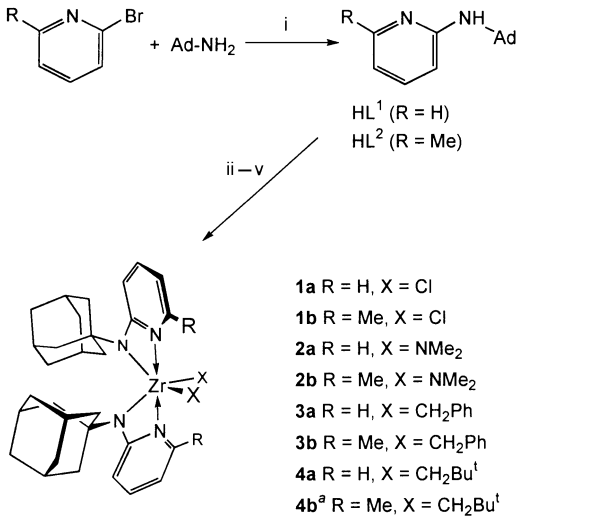
ligand- and metal-centred reactivity,[3] and are catalysts for alkene oligomerisation[4] and the synthesis of isotactic poly(propylene).[5] For the closely related aminopyridinato complexes of zirconium,[6] most commonly based on **II** (R = $SiMe_3$),[7] control of the number of such ligands about each metal centre is challenging. For example, treatment of [$Zr(NEt_2)_2Cl_2$] with aminopyridines **II** (R = $SiMe_3$) gave complexes with one or three (but not two) aminopyridinato ligands, depending on substitution at pyridine R′. Complexes of the type **III** analogous to **I** have thus never been isolated, although for the lighter congener titanium unsymmetric complexes [Ti(2-PyNR)$_2$(N-Me_2)Cl] (Py = 2-C_5H_3N; R = Me, Ph) have been crystallographically characterised.[8]

Inspired by the success of alkylanilide ligands in early transition and actinide chemistry,[9] we began to investigate the coordination chemistry of aminopyridines with sterically demanding alkyl (as opposed to trialkylsilyl) substituents R. We report here our initial findings, and in particular that control of metal/ligand stoichiometry and synthesis of catalytically competent species can be achieved.

The Buchwald arylation of amines[10] is particularly successful in the case where arene = pyridine, and we were able to synthesise the 1-adamantyl-2-pyridyl amines HL^1 and HL^2 in good yield from commercially available bromopyridines and 1-adamantylamine using this methodology (Scheme 1).‡

The lithium amide LiL^1 generated *in situ* from HL^1 and lithium butyl§ gave the complex [$L^1{}_2ZrCl_2$] **1a** on reaction with $ZrCl_4$ in diethyl ether. The free amine HL^1 reacted smoothly with [$Zr(NMe_2)_4$], [$Zr(CH_2Ph)_4$] and [$Zr(CH_2Bu^t)_4$] in toluene to give the target complexes [$L^1{}_2Zr(NMe_2)_2$] **2a**,

† Electronic supplementary information (ESI) available: characterisation data. See http://www.rsc.org/suppdata/cc/b0/b006603f/



Scheme 1 Synthesis of proligands and complexes **1**–**4**. *Reagents and isolated yields*: i, [$Pd_2(dba)_3$], dppp, $NaOBu^t$, toluene, 60% (L^1), 52% (L^2); ii, Bu^nLi, $ZrCl_4$, diethyl ether, 56% (**1a**), 49% (**1b**); iii, [$Zr(NMe_2)_4$], toluene, 70% (**2a**), pentane, 78% (**2b**); iv, [$Zr(CH_2Ph)_4$], toluene, 86% (**3a**), pentane, 59% (**3b**); v, [$Zr(CH_2Bu^t)_4$], toluene, 63% (**4a**). [a] **4b** not isolated (see text).

[$L^1{}_2Zr(CH_2Ph)_2$] **3a** and [$L^1{}_2Zr(CH_2Bu^t)_2$] **4a**, respectively. NMR tube scale experiments showed that these reactions are essentially quantitative. The analogous complexes **1b**–**3b** of L^2 were prepared similarly. In no instance was a complex of the type [L_3ZrX][6a] detected, although an intermediate [$\{L^1Zr(CH_2Bu^t)_3\}_n$] was observed by NMR spectroscopy when the synthesis of **4a** was conducted in d^8-toluene. The reaction of HL^2 with [$Zr(CH_2Bu^t)_4$] gives a similar monosubstituted intermediate which is converted slowly to **4b**. 2-Methyl substitution on the pyridine ring in L^2 thus appears to have a profound steric effect in the complex, as further evidenced by the broadness of the ^1H NMR spectrum of **4b** in the aliphatic (adamantyl) region. Steric compression in the auxiliary ligand sphere is probably also responsible for the slow thermal decomposition of this compound with elimination of neopentane. In contrast, **4a** and the other alkyls did not decompose in solution over a period of several days at room temperature.

The molecular structure of the six-coordinate neopentyl complex **4a** is shown in Fig. 1.¶ The neopentyl methylene groups and amido N atoms occupy mutually *cis* positions with C(31)–Zr(1)–C(36) and N(2)–Zr(1)–N(4) angles of 98.18(15) and 99.82(11)°, respectively. The two pyridine N atoms are mutually *trans* [N(3)–Zr–N(1) 174.85(11)°]. The overall structure is thus closely related to the bis(benzamidinate)dichlorozirconium complex[3b,5c] but is very different from the *ansa*-bis(aminopyridonato) complexes of titanium in which the quadridentate ligand adopts a planar disposition.[11]

The C_2-symmetry of **4a** is apparent from Fig. 2. The angle between the planes formed by C(36), Zr(1), C(31) and N(2), Zr(1), N(4) is *ca.* 61.85°. It is clear from space-filling models that the conformation of the neopentyl ligands serves to minimise steric interactions between their *tert*-butyl groups and

DOI: 10.1039/b006603f

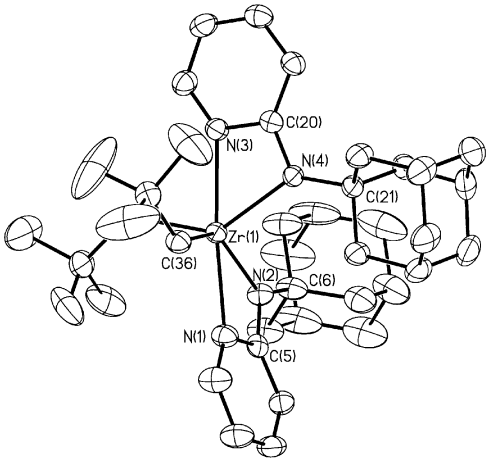


Fig. 1 Thermal ellipsoid plot of the molecular structure of **4a**; hydrogen atoms omitted. Selected bond lengths (Å) and angles(°) Zr(1)–N(4) 2.201(3), Zr(1)–N(2) 2.208(3), Zr(1)–C(36) 2.279(4), Zr(1)–C(31) 2.279(4), Zr(1)–N(3) 2.346(3), Zr(1)–N(1) 2.356(3); N(4)–Zr(1)–N(2) 99.82(11), C(36)–Zr(1)–C(31) 98.18(15).

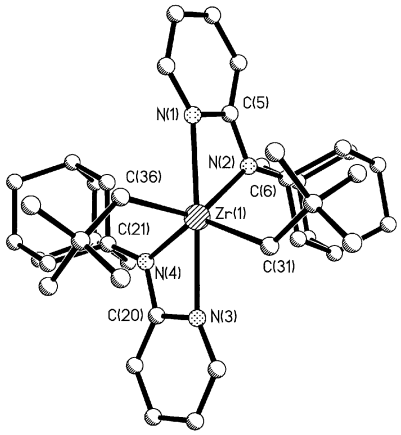


Fig. 2 Molecular structure of **4a** viewed along the approximate C_2 axis.

the pyridine rings. As we suggested above, a methyl group in the 1-position of the ring (as in L[2]) would lead to excessive steric compression in these positions, at least for a ligand as large as neopentyl.

The structures of the complexes in solution are similar to that observed in the solid state for **4a** as judged from NMR spectra. In all instances only one set of resonances for the aminopyridinato ligands is observed at accessible temperatures, and the metal-bound methylene groups in both sets of complexes **3** and **4** appear as pairs of AB doublets in the ^{1}H spectra at room temperature. At elevated temperatures these latter signals coalesce indicating that the complexes racemise, presumably through rotation of the aminopyridinato ligands. From lineshape analysis of the spectra of **3a** a value $\Delta G^{\ddagger}_{298}$ = 60(1) kJ mol^{-1} was extracted. The related amidinate complexes have much lower barriers to inversion, and for example [Zr{CyNC(Me)NCy}$_2$Cl$_2$] has spectroscopically equivalent cyclohexyl groups.[12]

The new complexes are moderately active[1] procatalysts for the polymerisation of ethene. For example, **1a**/MAO in toluene at 25 °C exposed to *ca.* 1 atm. of ethylene gave a reproducible productivity of 20 kg mol^{-1} h^{-1} bar^{-1} for a 1 h run. This exceeds significantly that obtained with previously reported aminopyridinates,[11] and compares favourably with that for the comprehensively studied benzamidinates.[5c] Although the nature of the catalytic system for ethene polymerisation produced from **1a** is as yet unknown it is likely to be of similar nature to the 'alkyl cation' [ZrCp$_2$R]$^+$ implicated in metallocene based catalysis.[13] The reactions of **3a** and **3b** with B(C$_6$F$_5$)$_3$ give species which ^{1}H NMR spectra indicate are the cations [ZrL$_2$(CH$_2$Ph)][B(C$_6$F$_5$)$_3$(CH$_2$Ph)] or ionisation isomers thereof.

We have thus shown that control of ligand stoichiometry and structure can be achieved in aminopyridinato chemistry of zirconium by careful choice of amido *N*-substituent; in this respect alkyl is better than trialkylsilyl. Given that the adamantyl group is close in steric demand to the commonly used SiMe$_3$ the dramatic disparity in the properties of the two systems is likely to arise from the electronic influence of the Si atom on the amido N–Zr bonds in the latter.[14] We note Jordan's comments to the effect that control of ligand stoichiometry in pyridine(alkoxide) complexes of zirconium depends on the proton acidity of the ligand as much as its steric demand.[15] The bis(alkylaminopyridinato) unit is thus established as a robust ligand set for the stabilisation of zirconium complexes with halide, amide and alkyl ligands. We will report further chemistry of these versatile ligands and more detailed catalysis studies in due course.

P.S. wishes to thank EPSRC for postdoctoral fellowships (to C.M. and P.O.'S.).

Notes and references

‡ We have synthesised several related ligands from sterically demanding alkyl and aryl amines and we will report their chemistry in due course.

§ The aminopyridines are also rapidly deprotonated with sodium and potassium hydrides.

¶ *Crystal data* for **4a**: M = 760.29, triclinic, a = 11.456(2), b = 13.352(3), c = 14.019(3) Å, α = 89.456(4), β = 79.991(5), γ = 87.587(4)°, U = 2109.9(7) A^3, T = 180(2) K, space group $P\bar{1}$, Z = 2, μ(Mo-Kα) = 0.295 mm^{-1}, 20512 reflections measued, 10117 unique (R_{int} = 0.0711), R_1 [for 10117 reflections with $I > 2\sigma(I)$] = 0.0674, $wR2$ = 0.1495. Data were collected on a Siemens SMART CCD. The structure was solved by direct methods with additional light atoms found by Fourier methods.

CCDC 182/1787. See http://www.rsc.org/suppdata/cc/b0/b006603f/ for crystallographic files in .cif format.

1 G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428.
2 F. T. Edelmann, *Coord. Chem. Rev.*, 1994, **137**, 403.
3 (*a*) J. R. Hagdahorn and J. Arnold, *Organometallics*, 1998, **17**, 1355; (*b*) J. R. Hagdahorn and J. Arnold, *J. Chem. Soc., Dalton Trans.*, 1997, 3087.
4 E. A. C. Brussee, A. Meetsma, B. Hessen and J. H. Teuben, *Chem. Commun.*, 2000, 497.
5 (*a*) V. Volkis, M. Schmulinson, C. Averbuj, A. Livovskii, F. T. Edelmann and M. S. Eisen, *Organometallics*, 1998, **17**, 3155; (*b*) C. Averbuj, E. Tish and M. S. Eisen, *J. Am. Chem. Soc.*, 1998, **120**, 8640; (*c*) D. Herskovics-Korine and M.S. Eisen, *J. Organomet. Chem.*, 1998, **503**, 307.
6 (*a*) R. Kempe, S. Brenner and P. Arndt, *Organometallics*, 1996, **15**, 1071; (*b*) M. Oberthür, G. Hillebrand, P. Arndt and R. Kempe, *Chem. Ber.*, 1997, **130**, 789; (*c*) H. Fuhrmann, S. Brenner, P. Arndt and R. Kempe, *Inorg. Chem.*, 1996, **35**, 6742.
7 C. L. Raston, B. W. Skelton, V. A. Tolhurst and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2000, 1279; H. K. Lee, Y.-L. Wong, Z.-Y. Zhou, Z.-Y. Zhang, D. K. P. Ng and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 2000 539 and references 10–15 therein.
8 R. Kempe and P. Arndt, *Inorg. Chem.*, 1996, **35**, 2644.
9 C. C. Cummins, *Chem. Commun.*, 1998, 1777.
10 J. P. Wolfe, H. Tomori, J. P. Sadighi, J. Yin and S. L. Buchwald, *J. Org. Chem.*, 2000, **65**, 1158.
11 M. Oberthür, P. Arndt and R. Kempe, *Chem. Ber.*, 1996, **129**, 1087.
12 A. Littke, N. Sleiman, C. Bensimon, D. S. Richeson, G. P. A. Yap and S. J. Brown, *Organometallics*, 1998, **14**, 446.
13 H. H. Brintzinger, D. Fischer, R. Mulhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143.
14 M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, *Metal and Metalloid Amides*, Ellis Horwood, Chichester, 1980, p. 244.
15 T. Tsukahara, D. C. Swenson and R. F. Jordan, *Organometallics*, 1997, **16**, 3303.