Mono-amidinate complexes stabilized by a new sterically-hindered amidine†

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A novel amidinate ligand incorporating a bulky terphenyl group is used to prepare unusual, low-coordinate lithium and yttrium mono-amidinate complexes.

The search for ancillary ligands capable of facilitating a wide variety of catalytic processes is a challenging problem in inorganic chemistry. Metal complexes incorporating amidinate ligands have been actively studied over the past few years; a broad range of chemistry has appeared and important applications, for example, olefin polymerization, have been described.[1–7] A major goal of work in this area is to prepare ligands that can be easily tuned, sterically and electronically, in order to promote the formation of complexes displaying unusual structures and reactivities.

We now report the synthesis of a novel amidinate ligand incorporating a bulky terphenyl group that exerts steric control in its metal derivatives. The synthesis of an unusual Li salt and examples of Ln mono-amidinates are described. These are noteworthy since bis-amidinates are generally formed in Ln systems,[8,9] a situation that parallels, to some extent, the related cyclopentadienyl chemistry to which amidinates are frequently compared.[1,10]

Previous efforts to prepare bulky amidinates relied on adamantyl or $C_6H_3Pr^i{}_2$-2,6 substitutions at the N atoms,[11–13] giving rise to ligands that are essentially bulky only in the amidine plane [Fig. 1(a)]. In contrast, we envisaged use of a terphenyl substituent on the amidine carbon atom to provide steric hindrance not only in the plane of the ligand, but also above and below this plane, resulting in a more ‘bowl’-shaped environment [Fig. 1(b)]. Terphenyl groups are now well known to support unusual coordination environments,[14–17] the closest analogy to our work being the formation of hindered carboxylate complexes reported recently.[18,19]

The sterically demanding amidine *N,N′*-diisopropyl(2,6-dimesityl)benzamidine (Hdimb)[20] was isolated in 94% yield by addition of *N,N′*-diisopropylcarbodiimide to 2,6-dimesityl-(lithiobenzene)[21] followed by an aqueous work-up (Scheme 1).

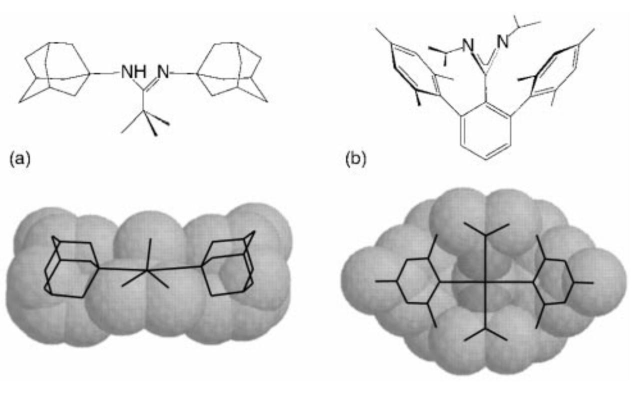
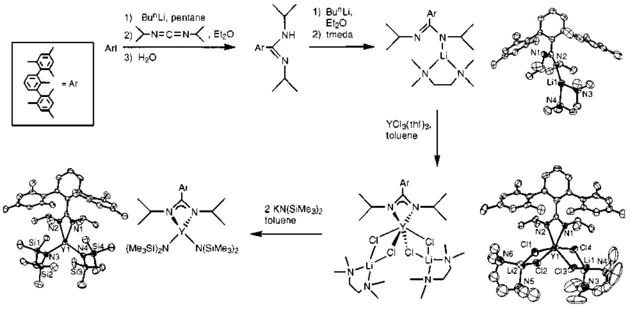


Fig. 1 Side (wire) and top (space-filling) views of (*a*) *N,N′*-bis(adamantyl)neopentamidine (ref. 12) and (*b*) *N,N′*-diisopropyl(2,6-bismesityl)benzamidine.



Scheme 1

In contrast to simple non-bulky amidines examined previously, the ^{1}H NMR spectrum of Hdimb is complex at room temp., showing two independent sets of amidine resonances. TOCSY data allowed deconvolution of the ^{1}H NMR resonances into two independent sets of peaks. As shown in Fig. 2, the four Pr^i resonances are differentiated into two pairs: one pair from the imine N and one pair from the amine N. A NOESY spectrum showed chemical exchange between the two Pr^i groups in each pair.[22] We attribute this exchange to interconversion between the *Z*- and *E-syn* isomers on the NMR timescale. Recently, Boeré *et al*. reported similar structural effects in bulky *N,N′*-bis(2,6-diisopropylphenyl)benzamidines.[13]

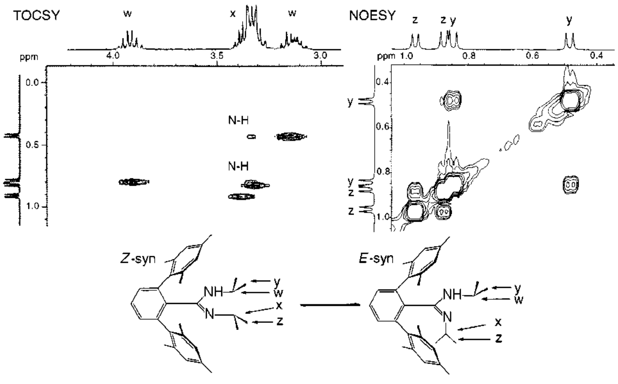


Fig. 2 2D ^{1}H NMR spectra and the indicated equilibrium.

Lithiation of the amidine with Bu^{n}Li in hexanes, followed by addition of *N,N,N′,N′*-tetramethylethylenediamine (tmeda) gave the Li derivative [(dimb)Li(tmeda)] [20] shown in Scheme 1, which was isolated in 64% yield as colorless crystals from Et$_2$O. The ^{1}H NMR spectrum shows two different Pr^i resonances, three inequivalent mesityl methyls, and two different mesityl aromatic signals, indicating an unsymmetrical product with C_s symmetry. For comparison, Li salts of simple amidines such as [PhC(PhN)$_2$]Li(tmeda) show spectra consistent with C_{2v} symmetry in solution.[23] The solid-state structure of [(dimb)Li(tmeda)][24] (Scheme 1) shows that the amidinate is coordinated in a monodentate fashion to the Li which resides in a distorted trigonal planar environment [sum of angles around Li = 358.4(3)°] made up of one amidinate N atom and both tmeda N atoms. Some localization is evident in the N–C–N core, with C(1)–N(1) 1.316(4) Å and C(1)–N(2) 1.337(4) Å. The amidi-

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† Electronic supplementary information (ESI) available: characterization data.

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nate N–Li bond [1.942(6) Å] is the shortest observed in a Li amidinate complex and the N–C–N angle is substantially more obtuse [126.5(3)°] than in related species.[25] In contrast, the N(tmeda)–Li bonds [2.115(6) and 2.126(6) Å] are typical.[26] To our knowledge, all reported complexes of the type (amidinate)-Li(tmeda) display four-coordinate Li in solution and in the solid state.[23] We attribute the unusual Li coordination in our compound to steric effects arising from the sterically bulky amidinate ligand.

The Li salt is a useful reagent for the synthesis of metal amidinates. For example, reaction of 1 equiv. of the Li amidinate with $YCl_3(thf)_3$ proceeds as shown in Scheme 1, with the colorless, crystalline product being isolated in moderate yield from Et_2O. The empirical formula, $[(dimb)YCl_4Li_2(tmeda)_2]$,[20] follows straightforwardly from ^1H NMR spectroscopy and elemental analysis, and confirmation of the solid-state structure is provided by X-ray diffraction.[27,28] The six-coordinate Y ion resides in a distorted octahedral coordination environment with a single amidinate ligand coordinated in the usual bidentate fashion. Examination of Y–Cl and Y–N bond lengths (av. 2.66 and 2.32 Å, respectively) show no anomalous values, although the N–C–N bond angle in the amidinate (*ca.* 111°) is nearly 5° less obtuse than in related Y compounds.[8,9,29–31] Although mixed amidinate/cyclopentadienyl and amidinate/cyclooctatetraenyl compounds have been previously characterized,[31,32] studies involving Y compounds having exclusively amidinate ligands as ancillary ligands have only resulted in the formation of bis-amidinate compounds,[8,9] making this the first example of a mono-amidinate yttrium halide species.

To test the robustness of the mono-amidinate moiety, (dimb)Y, towards substitution chemistry, $[(dimb)YCl_4Li_2(tmeda)_2]$ was treated with $KN(SiMe_3)_2$ as shown in Scheme 1. The metathesis proceeded smoothly to form $[(dimb)Y\{N(SiMe_3)_2\}_2]$[20] in excellent yield as colorless crystals from pentane. The compound shows a simple ^1H NMR spectrum and the solid state structure again features a mono-amidinate complex with the Y now four-coordinate in a distorted tetrahedron.[33] The Y–N(amidinate) bond lengths (av. 2.34 Å) are nearly the same as those observed in the parent compound and the N–C–N bond angle has opened slightly (113°), yet it remains narrower than previously reported related complexes.[8,9,31] The Y–N(amide) bond lengths (av. 2.24 Å) are well within the expected range.[34]

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20 *NMR data* (*J*/Hz): Hdimb (300 MHz) δ (*Z*-syn) 7.180 (t, 1H, *J* 5), 6.967 (d, 2H, *J* 5), 6.864 (s, 4H), 3.439 (s, 1H), 3.420 (spt, 1H, *J* 6), 3.257 (spt, 1H, *J* 6), 2.279 (s, 12H), 2.208 (s, 6H), 0.872 (d, 6H, *J* 6), 0.483 (d, 6H, *J* 6); (*E*-syn) 7.140 (t, 1H, *J* 5), 6.943 (d, 2H, *J* 5), 6.846 (s, 2H), 6.816 (s, 2H), 4.015 (spt, 1H, *J* 6), 3.484 (spt, 1H, *J* 6), 3.464 (s, 1H), 2.172 (s, 6H), 2.162 (s, 6H), 2.143 (s, 6H), 0.962 (d, 6H, *J* 6), 0.845 (d, 6H, *J* 6); [(dimb)Li(tmeda)] (500 MHz) δ 7.244 (t, 1H, *J* 7.5), 7.096 (d, 2H, *J* 7.5), 6.929 (s, 2H), 6.888 (s, 2H), 3.635 (spt, 1H, *J* 6), 2.978 (s, 6H), 2.798 (spt, 1H, *J* 6), 2.377 (s, 4H), 2.237 (s, 6H), 1.533 (s, 12H), 1.452 (s, 4H), 1.193 (d, 6H, *J* 6), 0.851 (d, 6H, *J* 6); $[(dimb)YCl_4Li_2(tmeda)_2]$ (500 MHz) δ 7.124 (d, 2H, *J* 9), 7.082 (t, 1H, *J* 9), 7.009 (s, 4H), 3.453 (spt d, 2H, J_{HH} 6, J_{YH} 2.5), 2.514 (s, 12H), 2.233 (s, 6H), 2.107 (s, 24H), 1.750 (s, 8H), 1.119 (d, 12H, *J* 6); $[(dimb)Y\{N(SiMe_3)_2\}_2]$ (500 MHz) δ 7.042 (t, 1H, *J* 7.5), 6.832 (d, 2H, *J* 7.5), 6.776 (s, 4H), 3.392 (spt d, 2H, J_{HH} 6, J_{YH} 2.5), 2.209 (s, 6H), 2.091 (s, 12H), 1.028 (d, 12H, *J* 6), 0.273 (s, 36H). Full characterization data are available in the supplementary information (http://www.rsc.org/suppdata/cc/1999/2149/).

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24 *Crystal data* for $C_{37}H_{55}N_4Li$: M = 562.81, orthorhombic, *Pbca* (no. 61), a = 17.7707(4), b = 19.7667(5), c = 20.3416(4) Å, V = 7145.4(2) Å^3, T = 160 K, Z = 8, μ(Mo-Kα) = 0.061 mm^{-1}, 34508 reflections measured, 7118 unique (R_{int} = 0.067), final R = 0.040, R_w = 0.043, R_{all} = 0.056. CCDC 182/1423.

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28 *Crystal data* for $C_{44}H_{73}Cl_4Li_2N_5OY$: M = 932.69, monoclinic, $P2_1/n$ (no. 14), a = 10.9930(4), b = 16.4195(5), c = 29.0041(9) Å, β = 93.891(1)° V = 5223.2(3) Å^3, T = 158 K, Z = 4, μ(Mo-Kα) = 1.356 mm^{-1}, 25212 reflections measured, 9579 unique (R_{int} = 0.077), final R = 0.054, R_w = 0.063, R_{all} = 0.137. CCDC 182/1423.

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33 *Crystal data* for $C_{43}H_{75}N_4Si_4Y$: M = 849.34, orthorhombic, *Pbca* (no. 61), a = 18.6326(6), b = 21.4487(5), c = 24.4451(7) Å, V = 9769.4(4) Å^3, T = 140 K, Z = 8, μ(Mo-Kα) = 1.325 mm^{-1}, 47309 reflections measured, 9772 unique (R_{int} = 0.085), final R = 0.030, R_w = 0.031, R_{all} = 0.105. CCDC 182/1423. For all structures see http://www.rsc.org/suppdata/cc/1999/2149/ for crystallographic files in .cif format.

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