Homoleptic lanthanide(II)–bis(guanidinate) complexes, $[Ln(Giso)_2]$ (Giso = $[(ArN)_2CN(C_6H_{11})_2]^-$, Ar = $C_6H_3Pr^i{}_2$-2,6): planar 4-coordinate (Ln = Sm or Eu) *vs* distorted tetrahedral (Ln = Yb) geometries†

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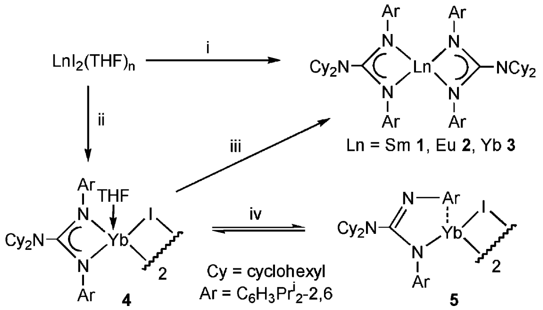
The first homoleptic lanthanide(II)–guanidinate complexes have been prepared and shown to have differing coordination geometries (including unprecedented examples of planar 4-coordination) that depend on the size of the lanthanide metal.

The chemistry of amidinato- and guanidinato-lanthanide(III) complexes has been extensively developed and such compounds have found a number of applications, mainly as polymerisation catalysts.[1] Considering the significant potential that related lanthanide(II) complexes have as soluble one-electron reductants in organic and organometallic synthesis (*e.g.* SmI_2[2] and $SmCp^*{}_2$[3]), it is surprising that to date only two bis(amidinato)lanthanide(II) complexes have been structurally characterised, *viz.* *trans*-octahedral $[Sm\{(ArN)_2CH\}_2(THF)_2]$ (Ar = $C_6H_3Pr^i{}_2$-2,6)[4] and $[Yb\{(Me_3SiN)_2CPh\}_2(THF)_2]$.[5] If homoleptic examples could be prepared, the accessibility of their metal centres to substrates, and thus their usefulness as reductants, may be significantly enhanced. We have recently developed synthetic routes to very bulky guanidinate ligands, *e.g.* $[(ArN)_2CN(C_6H_{11})_2]^-$ (Giso$^-$), and have utilised these in the stabilisation of novel low oxidation state main group complexes, *e.g.* $[\{M(Giso)\}_n]$ (n = 1, M = Ga, In or Tl;[6] n = 2, M = Ge[7]). It seemed reasonable that bulky ligands of this type could also stabilise low coordinate lanthanide(II) complexes. In this respect, it is noteworthy that the stabilising properties of Giso$^-$ appear to be similar to those of bulky, N,N′-chelating β-diketiminates $[\{(R^1)NC(R^2)\}_2CR^3]^-$ (nacnac$^-$), which have recently been utilised in the formation of tetrahedral Yb(II) complexes, $[Yb(nacnac)_2]$.[8] Here, we report the first examples of structurally characterised homoleptic Ln(II)–guanidinates, two of which contain the first examples of planar 4-coordinate lanthanide centres.

The 2 : 1 reactions of K[Giso] with LnI_2 (Ln = Sm, Eu or Yb) in THF afforded the deeply coloured homoleptic complexes, **1–3**, in moderate yields (Scheme 1). When the reactions were carried out in 1 : 1 stoichiometries **1–3** were also the major products. This is not surprising given the known propensity of (amido)lanthanide(II) halides to undergo redistribution reactions.[9] However, from the 1 : 1 or 2 : 1 reactions that gave deep green **3**, was also isolated a small amount (6%) of yellow **4**. When this was re-dissolved in THF it redistributed over several hours at 25 °C to give **3** and $YbI_2(THF)_n$. It seems likely that the Sm and Eu analogues of **4** are too short-lived to be isolated as their respective redistributions to **1** and **2** are more facile due to the larger ionic radii of the metals involved (values for 7-coordinate Ln: Sm^{2+} 1.22 Å, Eu^{2+} 1.20 Å and Yb^{2+} 1.08 Å).[10]



Scheme 1 Reagents and conditions: i, 2 K[Giso], THF, −KI; ii, Ln = Yb, K[Giso], THF, −KI; iii, $-YbI_2(THF)_n$; iv, ±THF.

An interesting property of yellow **4** was observed when it was subject to reduced pressure (*ca.* 10^{-2} mmHg) at 25 °C in the solid state for several minutes, whereupon it took on a deep red coloration. Recrystallisation of this solid from toluene afforded red crystals of **5** (Scheme 1). Therefore, it appears that, not only are the coordinating THF molecules of **4** readily removed *in vacuo*, but that this process also involves a change in the coordination mode of the Giso$^-$ ligand from κ^2-*N*,*N*′-chelating in **4** to η^1-*N*,η^6-*arene*-chelating in **5**. This rearrangement is quantitatively reversed by dissolving **5** in THF.[11]

Due to the paramagnetic nature of **1** and **2**, no useful information could be obtained from their NMR spectra. Those for **3** and **4**‡ are consistent with their proposed structures, whereas the solution state NMR spectra of **5** are more symmetrical than its solid state structure would suggest. This observation is compatible with a fluxional process occurring in solution, though an examination of this by variable temperature NMR studies was thwarted by the low solubility of **5** in D_8-toluene below ambient temperature. It is noteworthy, however, that the NMR spectra of the related complex, $[Tl(\eta^1\text{-}N,\eta^3\text{-}Ar\text{-}Giso)]$,[6] are similarly symmetrical and unchanging at temperatures down to −90 °C. In that case, this was said to be indicative of a low energy fluxional process. No signals were observed in the $^{171}Yb\{^1H\}$ NMR spectrum of a strong sample of **3** at 25 °C, despite closely related $[Yb(nacnac)_2]$ complexes displaying signals at δ 2650 ±200 ppm in their spectra.[8b] However, in those cases, the signals are usually very broad and sometimes not observable.

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† Electronic supplementary information (ESI) available: Full synthetic details for **1–5** and ORTEP diagrams for **2** and **3**. See DOI: 10.1039/b614028a

The X-ray crystal structures§ of homoleptic **1** (Fig. 1, relevant geometrical parameters for **2** and **3** included in caption) and **2** are isomorphous and both possess planar 4-coordinate metal centres, as evidenced by the small twist angles between their $CN_2LnC_{(adjacent\ backbone)}$ least squares planes (**1**: 1.4°, **2**: 1.7°)†. In contrast, the coordination geometry of **3** can be considered as distorted tetrahedral (*cf.* [Yb(nacnac)$_2$][8]), as the same angle is 57.9° for that compound. There is no crystallographic or spectroscopic evidence to suggest the presence of hydride ligands in either **1** or **2**. The guanidinate ligands in all three complexes appear to be largely delocalised and their Ln–N distances are in the normal ranges[12] and decreasing from Ln = Sm > Eu > Yb. The differences in the coordination geometry of **3** presumably arise from the considerably smaller Ln^{2+} ionic radius of Yb relative to the other two metals. To the best of our knowledge, there are no previously reported examples of complexes containing planar 4-coordinate Ln^{2+} centres, and it seems that in **1** and **2** this geometry is not enforced by the steric bulk of the ligands when the tendency towards tetrahedral coordination of the smaller metal in **3** is considered.[13] If the $Giso^-$ ligands of **1–3** are regarded as single point donors, then they are notionally related to the formally 2-coordinate Ln(II)–bis(alkyls), [Ln{C(SiMe$_3$)$_3$}$_2$] (Ln = Sm, Eu or Yb).[14] However, the latter complexes are bent (C–Ln–C angle: Sm 143.4°, Eu 136.0°, Yb 137.0°) whereas the C(1)–Ln–C(38) angles in **1** (171.4°) and **2** (170.1°) are close to linear. It might be expected that in these planar complexes, $Ln\cdots Me$ agostic interactions might occupy sites on either side of the coordination plane. Although such interactions are well known for Ln^{3+} complexes, they have been rarely reported for Ln^{2+} species.[15] However, in both complexes there is only one $Ln\cdots C$ interaction less than 3.7 Å (**1**: 3.64 Å, **2**: 3.61 Å), which can, at best, be considered as at the upper end of the $Sm^{2+}\cdots Me$ or $Eu^{2+}\cdots Me$ agostic interaction ranges.[12,15] Indeed, these interactions are considerably longer than in other Ln(II)–amides, *e.g.* closest $Ln\cdots C$ interaction: 3.32 Å in [Sm{N(SiMe$_3$)$_2$}$_2$(THF)$_2$][16] and 2.971 Å in Na[Eu{N(SiMe$_3$)$_2$}$_3$].[17] It is an appealing possibility that the planar geometries of **1** and **2** could lend them to use as soluble 1-electron reductants of small organic substrates that may be able to access their metal centres in solution, despite the unsolvated nature of these centres in the solid state.

The molecular structure of heteroleptic **4** (Fig. 2) reveals it to form dimeric units through effectively symmetrically bridging iodide ligands. Each metal centre is chelated by a largely delocalised $Giso^-$ ligand and additionally coordinated by a THF molecule to give them heavily distorted trigonal bipyramidal geometries. In line with this proposal are the longer Yb–N bonds from the apical nitrogens, N(1), than those from the equatorial N-centres, N(2). Considering the lability of the coordinated THF molecules, it is surprising that the Yb–O distances lie close to the mean for those in all previously reported Yb–THF interactions (3.88 Å).[12] It is of note that the structure of a related monomeric Yb–nacnac complex has been reported, *viz.* [YbCl{κ^2N,N'-(ArNCMe)$_2$CH}(η^6-C_7H_8)],[18] and this has been used as an effective pre-catalyst for the polymerisation of methyl methacrylate.

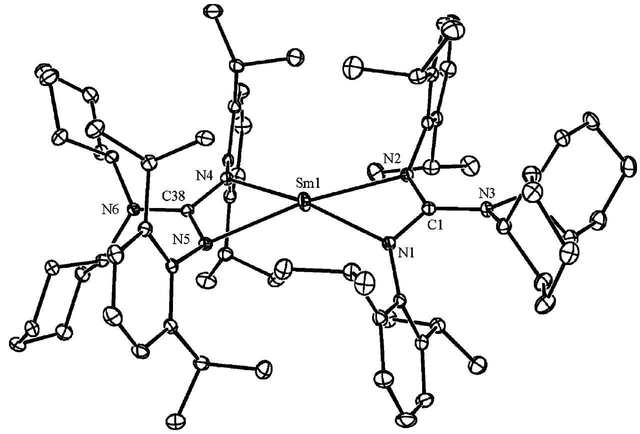

Fig. 1 Molecular structure of **1** (hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Sm(1)–N(1) 2.529(2), Sm(1)–N(4) 2.530(2), Sm(1)–N(2) 2.554(2), Sm(1)–N(5) 2.570(2), N(1)–C(1) 1.355(3), N(2)–C(1) 1.344(3), N(3)–C(1) 1.399(3), N(4)–C(38) 1.348(3), N(5)–C(38) 1.342(3), N(6)–C(38) 1.401(3), N(1)–Sm(1)–N(2) 52.55(7), N(4)–Sm(1)–N(5) 52.18(7); N(2)–C(1)–N(1) 113.0(2), N(5)–C(38)–N(4) 113.0(2). Selected bond lengths (Å) and angles (°) for **2**: Eu(1)–N(4) 2.525(2), Eu(1)–N(1) 2.527(2), Eu(1)–N(2) 2.544(2), Eu(1)–N(5) 2.563(2), N(1)–C(1) 1.351(3), N(2)–C(1) 1.349(3), N(3)–C(1) 1.400(3), N(4)–C(38) 1.345(3), N(5)–C(38) 1.345(3), N(6)–C(38) 1.403(3); N(1)–Eu(1)–N(2) 52.81(6), N(4)–Eu(1)–N(5) 52.41(6), N(2)–C(1)–N(1) 113.2(2), N(5)–C(38)–N(4) 113.2(2). Selected bond lengths (Å) and angles (°) for **3**: Yb(1)–N(2) 2.378(2), Yb(1)–N(5) 2.385(2), Yb(1)–N(4) 2.397(2), Yb(1)–N(1) 2.430(2), N(1)–C(1) 1.345(4), N(2)–C(1) 1.356(3), N(3)–C(1) 1.400(3), N(4)–C(38) 1.366(4), N(5)–C(38) 1.345(3), N(6)–C(38) 1.391(3); N(2)–Yb(1)–N(1) 55.79(8), N(5)–Yb(1)–N(4) 56.48(8), N(5)–Yb(1)–N(1) 132.92(8), N(2)–Yb(1)–N(4) 127.82(8), N(1)–C(1)–N(2) 112.8(2), N(5)–C(38)–N(4) 113.1(2).

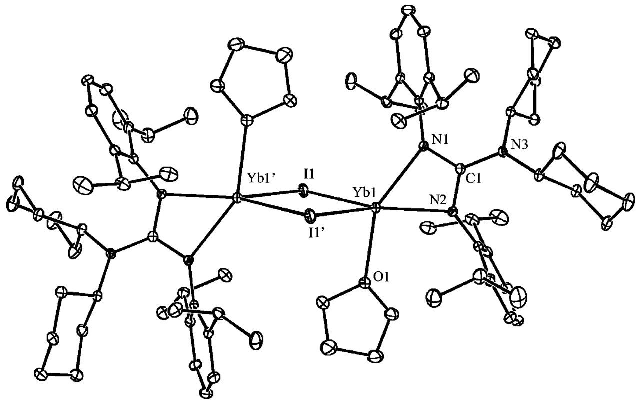

Fig. 2 Molecular structure of **4** (hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Yb(1)–N(2) 2.373(3), Yb(1)–N(1) 2.426(3), Yb(1)–O(1) 2.441(3), Yb(1)–I(1)′ 3.1129(8), Yb(1)–I(1) 3.1424(9), N(1)–C(1) 1.343(5), C(1)–N(2) 1.351(5), C(1)–N(3) 1.405(5); N(2)–Yb(1)–N(1) 55.55(11), Yb(1)′–I(1)–Yb(1) 86.58(3), N(1)–C(1)–N(2) 112.3(3). Symmetry operation ′: $-x + 1, -y + 1, -z + 1$.

Complex **5** is also an iodide bridged dimer (Fig. 3), though its $Giso^-$ ligands have rearranged upon THF desolvation to "chelate" its ytterbium centres *via* η^1-amide and η^6-arene interactions.[19] The former is shorter than the Yb–N interactions of **3** and **4**, and the N_3C fragment of the ligand appears to be significantly more localised than in those complexes. There is a close relationship between the Giso–M interaction in **5** and that in monomeric [Tl(η^1-N,η^3-Ar-Giso)].[6]

In conclusion, the first examples of homoleptic bis(guanidinato)lanthanide(II) complexes have been reported,

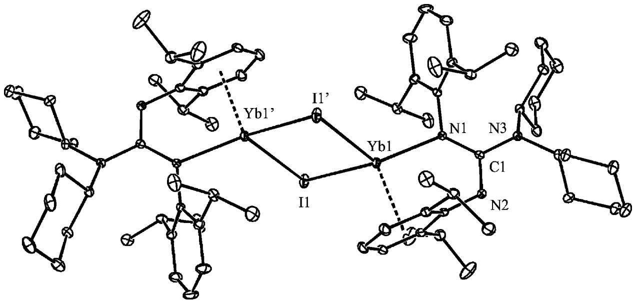

Fig. 3 Molecular structure of **5** (hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Yb(1)–N(1) 2.360(3), Yb(1)–I(1)′ 3.0478(7), Yb(1)–I(1) 3.0992(10), Yb(1)–Ar centroid 2.424(4), N(1)–C(1) 1.361(4), C(1)–N(2) 1.325(4), C(1)–N(3) 1.405(4); N(1)–Yb(1)–I(1)′ 119.56(7), N(1)–Yb(1)–I(1) 130.93(7), N(1)–Yb(1)–Ar centroid 93.49(2), I(1)′–Yb(1)–I(1) 90.69(3), Yb(1)′–I(1)–Yb(1) 89.31(3), N(2)–C(1)–N(1) 120.6(3). Symmetry operation ′: $-x + 1, -y, -z$.

two of which contain the first structurally characterised planar 4-coordinate lanthanide centres. The use of these as 1-electron reductants in organic and organometallic synthesis is currently being examined.

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Notes and references

‡ Selected data for **1**: Yield: 64% (deep violet crystals); mp 205–206 °C. IR ν/cm^{-1} (Nujol): 1612(m), 1583(m), 1387(m), 1319(m), 1022(m), 931(m); MS (EI 70 eV), *m/z* (%): 544 [GisoH$^+$, 32], 501 [GisoH$^+$ − Pr^i, 68]. **2**: Yield: 48% (red-orange crystals); mp 205–207 °C. IR ν/cm^{-1} (Nujol): 1612(m), 1583(m), 1377(m), 1318(m), 1023(m), 931(m); MS (EI 70 eV), *m/z* (%): 544 [GisoH$^+$, 36], 501 [GisoH$^+$ − Pr^i, 82]. **3**: Yield: 50% (deep green crystals); mp 222–224 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.82–1.40 (m, 40 H, CH_2), 1.32 (br. overlapping m, 48 H, $CH(CH_3)_2$), 3.35 (br. m, 8 H, $CH(CH_3)_2$), 3.59 (br. m, 4 H, NC*H*), 6.85–7.16 (m, 12 H, Ar*H*); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 20.8 (CH_2), 24.7 (CH_2), 26.4 ($CH(CH_3)_3$), 25.9 ($CH(CH_3)_3$), 27.2 ($CH(CH_3)_3$), 34.9 (CH_2), 57.7 (N*C*H), 120.6, 122.0, 139.4, 145.2 (Ar*C*), 164.7 (N_3C); IR ν/cm^{-1} (Nujol): 1612(m), 1583(m), 1109(m), 1023(m), 931(m); MS (EI 70 eV), *m/z* (%): 1259 [MH$^+$, 3%], 544 [GisoH$^+$, 15], 501 [GisoH$^+$ − Pr^i, 26]. **4**: Yield: 6%; mp 158–160 °C (decomp.). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.88–1.86 (m, 40 H, CH_2), 1.44 (br. overlapping m, 48 H, $CH(CH_3)_2$), 1.58 (br., 8 H, THF), 3.31 (br., 8 H, OCH_2), 3.42 (br. m, 4 H, NC*H*), 3.79 (br. m, 8 H, $CH(CH_3)_2$), 7.03–7.38 (m, 12 H, Ar*H*); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 22.0 (CH_2), 22.8 (CH_2), 24.9 (THF), 26.0 ($CH(CH_3)_3$), 27.1 ($CH(CH_3)_3$), 28.4 ($CH(CH_3)_3$), 35.2 (CH_2), 58.4 (*C*HN), 69.4 (THF), 121.3, 123.1, 141.2, 145.2 (Ar*C*), CN_3 not observed.; IR ν/cm^{-1} (Nujol): 1611(m), 1583(m), 1108(m), 1020(m), 933(m); MS (EI 70 eV), *m/z* (%): 544 [GisoH$^+$, 21], 501 [GisoH$^+$ − Pr^i, 52]. **5**: Yield: 5%; mp 218–220 °C (decomp.). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 1.11–1.75 (m, 40 H, CH_2), 1.22 (br. overlapping m, 48 H, $CH(CH_3)_2$), 2.94 (br. m, 4 H, NC*H*), 3.26 (br. m, 8 H, $CH(CH_3)_2$), 6.73–7.18 (m, 12 H, Ar*H*); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 21.5 (CH_2), 22.0 (CH_2), 25.9 ($CH(CH_3)_3$), 27.0 ($CH(CH_3)_3$), 28.9 ($CH(CH_3)_3$), 32.6 (CH_2), 58.0 (*C*HN), 123.1, 125.5, 137.6, 145.2 (Ar*C*), CN_3 not observed.; IR ν/cm^{-1} (Nujol): 1611(m), 1583(m), 1108(m), 1023(m), 893(m); MS (EI 70 eV), *m/z* (%): 844 [(Giso)YbI, 1], 544 [GisoH$^+$, 36], 501 [GisoH$^+$ − Pr^i, 56].

§ Crystal data for **1**·(C_6H_6): $C_{80}H_{118}N_6Sm$, $M = 1314.15$, monoclinic, space group $P2_1/n$, $a = 12.620(3)$ Å, $b = 31.033(6)$ Å, $c = 18.640(4)$ Å, $\beta = 99.11(3)°$, $V = 7208(2)$ Å^3, $Z = 4$, $D_c = 1.211$ g cm^{-3}, $F(000) = 2808$, μ(Mo-Kα) = 0.861 mm^{-1}, 150(2) K, 13347 unique reflections [*R*(int) 0.0330], *R* (on *F*) 0.0392, *wR* (on F^2) 0.0810 ($I > 2\sigma I$). **2**·(C_6H_6): $C_{80}H_{118}N_6Eu$, $M = 1315.76$, monoclinic, space group $P2_1/n$, $a = 12.631(3)$ Å, $b = 30.988(6)$ Å, $c = 18.627(4)$ Å, $\beta = 99.16(3)°$, $V = 7198(2)$ Å^3, $Z = 4$, $D_c = 1.214$ g cm^{-3}, $F(000) = 2812$, μ(Mo-Kα) = 0.918 mm^{-1}, 150(2) K, 13989 unique reflections [*R*(int) 0.0232], *R* (on *F*) 0.0387, *wR* (on F^2) 0.0843 ($I > 2\sigma I$). **3**·$(C_7H_8)_2$: $C_{88}H_{128}N_6Yb$, $M = 3904.7(14)$, triclinic, space group $P\bar{1}$, $a = 13.822(3)$ Å, $b = 16.195(3)$ Å, $c = 17.916(4)$ Å, $\alpha = 89.75(3)°$, $\beta = 78.04(3)°$, $\gamma = 84.48(3)°$, $V = 3904.7(14)$ Å^3, $Z = 2$, $D_c = 1.227$ g cm^{-3}, $F(000) = 1536$, μ(Mo-Kα) = 1.245 mm^{-1}, 150(2) K, 15245 unique reflections [*R*(int) 0.0387], *R* (on *F*) 0.0426, *wR* (on F^2) 0.0930 ($I > 2\sigma I$). **4**·$(C_6H_6)_{0.5}$: $C_{44}H_{67}IN_3OYb$, $M = 953.95$, triclinic, space group $P\bar{1}$, $a = 11.277(2)$ Å, $b = 11.998(2)$ Å, $c = 17.583(4)$ Å, $\alpha = 76.56(3)°$, $\beta = 88.31(3)°$, $\gamma = 71.46(3)°$, $V = 2191.2(8)$ Å^3, $Z = 2$, $D_c = 1.446$ g cm^{-3}, $F(000) = 966$, μ(Mo-Kα) = 2.872 mm^{-1}, 150(2) K, 9509 unique reflections [*R*(int) 0.0327], *R* (on *F*) 0.0367, *wR* (on F^2) 0.0792 ($I > 2\sigma I$). **5**·(C_7H_8): $C_{44}H_{64}IN_3Yb$, $M = 934.92$, triclinic, space group $P\bar{1}$, $a = 10.530(2)$ Å, $b = 13.562(3)$ Å, $c = 15.958(3)$ Å, $\alpha = 80.99(3)°$, $\beta = 71.19(3)°$, $\gamma = 80.40(3)°$, $V = 2114.2(7)$ Å^3, $Z = 2$, $D_c = 1.469$ g cm^{-3}, $F(000) = 944$, μ(Mo-Kα) = 2.974 mm^{-1}, 150(2) K, 9217 unique reflections [*R*(int) 0.0263], *R* (on *F*) 0.0320, *wR* (on F_2) 0.0713 ($I > 2\sigma I$). CCDC reference numbers 619010–619014. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b614028a

1 See, for example: (*a*) F. T. Edelmann, D. M. M. Freckmann and H. Schumann, *Chem. Rev.*, 2002, **102**, 1851; (*b*) F. T. Edelmann, *Coord. Chem. Rev.*, 1994, **137**, 403; (*c*) C. Villiers, P. Thuery and M. Ephritikhine, *Eur. J. Inorg. Chem.*, 2004, 4624; (*d*) A. A. Trifonov, G. G. Skvortsov, D. M. Lyubov, N. A. Skorodumova, G. K. Fukin, E. V. Baranov and V. N. Glushakova, *Chem.–Eur. J.*, 2006, **12**, 5320 and references therein.
2 G. A. Molander and C. R. Harris, *Chem. Rev.*, 1996, **96**, 307 and references therein.
3 See, for exapmle: W. J. Evans, R. A. Keyer and J. W. Ziller, *J. Organomet. Chem.*, 1990, **394**, 87.
4 M. L. Cole and P. C. Junk, *Chem. Commun.*, 2005, 2695.
5 M. Wedler, M. Noltemeyer, U. Pieper, H.-G. Schmidt, D. Stalke and F. T. Edelmann, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 894. NB: A solvent free Yb(II)–bis(amidinate) complex was also reported, though not structurally characterised.
6 C. Jones, P. C. Junk, J. A. Platts and A. Stasch, *J. Am. Chem. Soc.*, 2006, **128**, 2206.
7 S. P. Green, C. Jones, P. C. Junk, K.-A. Lippert and A. Stasch, *Chem. Commun.*, 2006, 3978.
8 (*a*) S. Harder, *Angew. Chem., Int. Ed.*, 2004, **43**, 2714; (*b*) A. G. Avent, P. B. Hitchcock, A. V. Khostov, M. F. Lappert and A. V. Protchenko, *Dalton Trans.*, 2003, 1070.
9 N. M. Scott and R. Kempe, *Eur. J. Inorg. Chem.*, 2005, 1319 and references therein.
10 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
11 The reversible removal of THF from Ln(II) centres has been previously observed. See, for example: J. Wang, R. I. J. Amos, A. S. P. Frey, M. G. Gardiner, P. C. Junk and M. L. Cole, *Organometallics*, 2005, **24**, 2259.
12 As determined from a survey of the Cambridge Crystallographic Database, August, 2006.
13 In contrast, homoleptic, Ar-substituted bis(amidinato)–first row transition metal complexes appear to have a steric preference for planar 4-coordinate over tetrahedral geometries: C. A. Nijhuis, E. Jellema, T. J. J. Sciarone, A. Meetsma, P. H. M. Budzelaar and B. Hessen, *Chem.–Eur. J.*, 2005, 2089.
14 (*a*) G. Qi, Y. Nitto, A. Saiki, T. Tomohiro, Y. Nakayama and H. Yasuda, *Tetrahedron*, 2003, **59**, 10409; (*b*) C. Eaborn, P. B. Hitchcock, K. Izod, Z.-R. Lu and J. D. Smith, *Organometallics*, 1996, **15**, 4783; (*c*) C. Eaborn, P. B. Hitchcock, K. Izod and J. D. Smith, *J. Am. Chem. Soc.*, 1994, **116**, 12071.
15 X. Chen, S. Lim, C. E. Plecnik, S. Liu, B. Du, E. A. Meyers and S. G. Shore, *Inorg. Chem.*, 2005, **44**, 6052 and references therein.
16 W. J. Evans, D. K. Drummond, H. Zhang and J. L. Atwood, *Inorg. Chem.*, 1988, **27**, 575.
17 T. D. Tilley, R. A. Andersen and A. Zalkin, *Inorg. Chem.*, 1984, **23**, 2271.
18 Y. Yao, Y. Zhang, Z. Zhang, Q. Shen and K. Yu, *Organometallics*, 2003, **22**, 2876.
19 Ln(II)–η^6-arene interactions are well known. See, for example: G. B. Deacon and Q. Shen, *J. Organomet. Chem.*, 1996, **511**, 1.