Hypervalent Silicon *via* Thermolysis of a Cadmium Amide: Thermally Stable Magnesium and Zinc Amides [ML_2], L = N(8-Quinolyl)($SiMe_3$)

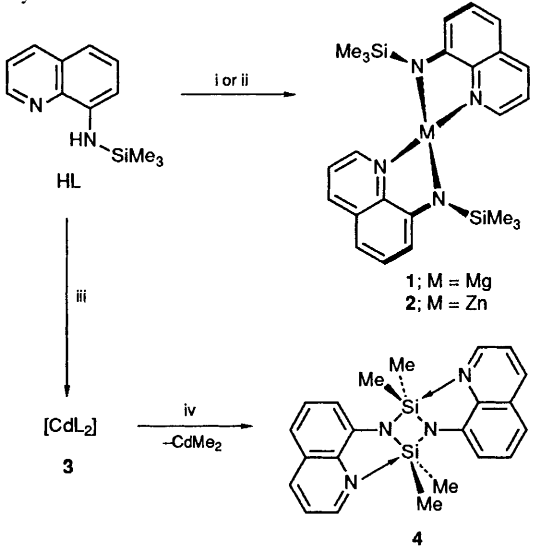
Lutz M. Englehardt,[b] **Peter C. Junk,**[a] **Wyona C. Patalinghug,**[b] **Rodney E. Sue,**[a] **Colin L. Raston,***[a] **Brian W. Skelton**[b] **and Allan H. White**[b]

[a] *Division of Science and Technology, Griffith University, Nathan, Brisbane, 4111, Australia*
[b] *Department of Physical and Inorganic Chemistry, The University of Western Australia, Nedlands, WA, 6009, Australia*

Structurally authenticated *N*-functionalized amides [ML_2], L = N(8-quinolyl)($SiMe_3$), derived from the reaction of 8-(trimethylsilylamino)quinoline with $MgBu^nBu^s$ or $ZnEt_2$ in hexane are sublimable *in vacuo* at 175 °C; the corresponding cadmium analogue, derived from $CdCl_2$ and LiL, decomposes at *ca.* 240 °C *in vacuo* yielding $CdMe_2$ and a novel dimeric five coordinate silicon species [$Me_2Si(\mu\text{-N–}C_9H_6N)(\mu\text{-N–}C_9H_6N)SiMe_2$] possessing an Si_2N_2 ring system, Si–$N_{bridging}$ (mean) 1.77 Å, Si–$N_{neutral}$ 2.33(1) Å.

There have been few studies on the structures of magnesium[1–3] and zinc[1,4,5] amides, and the amido chemistry of cadmium is poorly defined.[1] As part of a systematic study of amido chemistry based on the ligand N(8-quinolyl)($SiMe_3$), L, which to date has yielded unusual complexes of lithium,[6] boron and aluminium,[7] we report the synthesis and structure of bis-amides of magnesium and zinc and attempts to prepare the analogous cadmium and mercury complexes. For cadmium this yielded unexpected results; the formation of dimethylcadmium and a novel hypervalent silicon species, which has implications about the binding of the *N*-functional group with soft cadmium centres *vs.* complexation to silicon. Moreover, hypervalent species are of interest in that they are model compounds for nucleophilic substitutions at four coordinate silicon,[8] and as starting materials and reactive intermediates.[9]

Compounds [MgL_2], **1**, and [ZnL_2], **2**, were prepared by direct metallation using $\mathrm{MgBu^nBu^s}$ and $\mathrm{ZnEt_2}$, respectively (Scheme 1).† Both compounds are deep-red and are thermally stable, subliming without decomposition at *ca.* 175 °C. The reaction of $\mathrm{CdCl_2}$ and lithiated 8-trimethylsilylaminoquinoline yielded a red solid assumed to be $[\mathrm{CdL_2}]$, **3** (IR and ^{1}H, ^{13}C NMR spectroscopy), which proved difficult to separate from a white solid, assumed to be LiCl, and solutions of the products turned dark-grey over several hours. Heating a fresh reaction mixture *in vacuo* (0.1 mmHg) yielded a colourless liquid at 80 °C shown to be $[\mathrm{CdMe_2}]$ (NMR and IR spectroscopy)[10] then at 240 °C orange crystals of compound **4**. The same compound has also been prepared by treating the five coordinate silicon complex $\mathrm{SiMe_2Cl(NH\text{-}C_9H_6N)}$, **5**,[11] derived from 8-aminoquinoline and $\mathrm{SiMe_2Cl_2}$, with $\mathrm{LiN(SiMe_3)_2}$. The reaction of $\mathrm{HgCl_2}$ with the same lithium reagent under identical conditions resulted in rapid formation of mercury metal.



Scheme 1 *Reagents and conditions*: i, $\mathrm{MgBu^nBu^s}$, heptane, 0 °C; ii, $\mathrm{ZnEt_2}$, hexane, 0 °C; iii, $\mathrm{LiBu^n}$, hexane–thf then $\mathrm{CdCl_2}$; iv 80–240 °C

Scheme 2

High thermal stability of the zinc compound, but not of the analogous cadmium compound may be a consequence of the softer character of cadmium allowing competitive complexation with silicon for the neutral *N*-donor yielding five coordinate silicon centres, Scheme 2. This would activate the silicon centres towards loss of methyl, either yielding free 'L–Me' which then associates to $(\mathrm{L\text{–}Me})_2$, = **4**, or **4** directly from the metal coordination sphere of **3**. The mass spectrum of **4** shows a strong peak corresponding to $[\mathrm{L\text{–}Me}]^+$ suggesting that L–Me may be formed in the gas phase.

Results of the X-ray structure determinations‡ are presen-

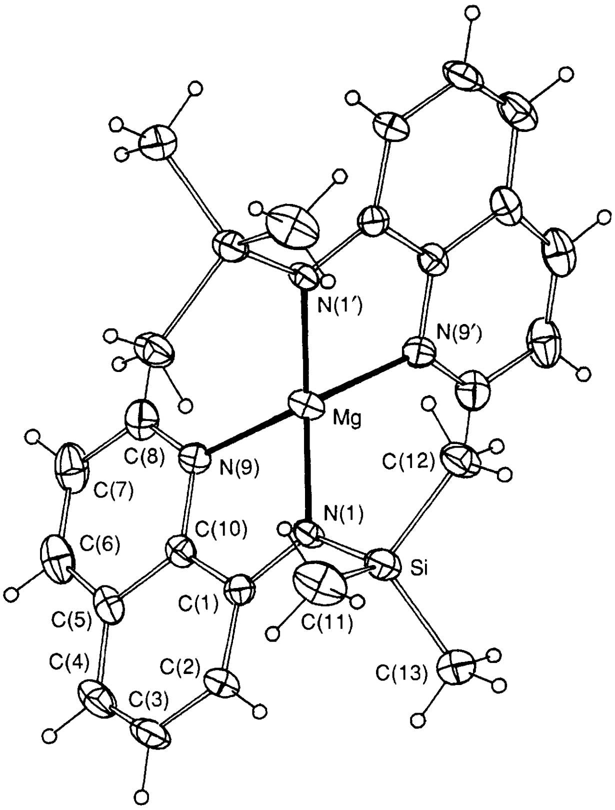


Fig. 1 Projection of one of the two independent molecules for $[\mathrm{MgL_2}]$, **1**, both possessing crystallographic C_2 symmetry, showing 20% thermal ellipsoids for the non-hydrogen atoms, and arbitrary radii for hydrogen atoms; molecules of $[\mathrm{ZnL_2}]$, **2**, are similar. Selected bond distances (Å) and angles (°) for molecules 1 and 2 respectively for **1**, and **2** in square brackets M–N(1) 1.992(4), 2.004(4) [1.940(4), 1.946(4)]; M–N(9) 2.103(4), 2.096(4) [2.070(4), 2.072(4)]; N(1)–M–N(1') 135.1(2), 138.7(2) [136.3(2), 137.8(2)]; N(9)–M–N(9') 116.8(2), 117.8(2) [115.0(2), 115.4(2)]; N(1)–M–N(9) 83.2(2), 82.1(2) [84.6(2), 84.5(2)]; N(1)–M–N(9') 121.3(1), 120.2(2) [119.7(2), 118.8(2)].

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† *Synthesis and characterization of* **1**–**4**: Compound **1**: To 8-(trimethylsilylamino)quinoline[6] (0.85 g, 3.94 mmol) in 30 ml of hexane at 0 °C was added $\mathrm{MgBu^nBu^s}$ in heptane (2.86 ml, 0.7 mol dm^{-3}, 2.0 mmol). Solvent was removed *in vacuo* and the orange solid recrystallized from hexane, m.p. 60–62 °C (1.66 g, 93%). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$), δ (rel. $\mathrm{SiMe_4}$) 0.41 (9H, s, $\mathrm{SiMe_3}$) 6.6–7.7 (6H, m, quinolyl); ^{13}C NMR ($\mathrm{C_6D_6}$) 1.3 ($\mathrm{SiMe_3}$) 109.6, 115.3, 120.5, 130.6, 139.4, 144.3 (CH) 131.0, 143.0, 156.1.

Compound **2**: Details similar to that for **1**, using neat $\mathrm{ZnEt_2}$, m.p. 152–154 °C (85%). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$), δ (rel. $\mathrm{SiMe_4}$) 0.42 (9H, s, $\mathrm{SiMe_3}$) 6.5–7.6 (6H, m, quinolyl); ^{13}C NMR ($\mathrm{C_6D_6}$) 1.5 ($\mathrm{SiMe_3}$) 109.5, 113.8, 120.9, 130.5, 139.1, 143.8 (CH) 130.8, 141.9, 155.1.

Compounds **3** and **4**: To 8-(trimethylsilylamino)quinoline[6] (1.0 g, 4.6 mmol) in 100 ml of tetrahydrofuran (thf) at 0 °C was added $\mathrm{LiBu^n}$ in hexane (3.1 ml, 1.6 mol dm^{-3}, 4.8 mmol) then 0.46 g of $\mathrm{CdCl_2}$ (2.5 mmol) yielding a red solution. After 1 h at *ca.* 20 °C the solvent was removed *in vacuo* and the complex extracted into $\mathrm{CH_2Cl_2}$ yielding a red solid when concentrated *in vacuo* [^{1}H NMR (250 MHz, $\mathrm{CD_2Cl_2}$), δ (rel. $\mathrm{SiMe_4}$) 1.30 (9H, s, $\mathrm{SiMe_3}$) 6.8–7.1 (5H, m, quinolyl) 8.25 (1H, d, *J* 3.5 Hz, quinolyl]. The solid was heated to 80 °C yielding a colourless liquid ($\mathrm{CdMe_2}$), then the product, **4**, was sublimed as orange needles at 240 °C (0.1 mmHg), m.p. 163 °C (0.15 g, 15% yield). ^{1}H NMR (250 MHz, $\mathrm{C_6D_6}$), δ (rel. $\mathrm{SiMe_4}$ 0.8 (6H, s, $\mathrm{SiMe_2}$) 6.7–7.6, 8.0 (10H, 2H m, quinolyl); mass spectrometry *m/z* 400 (36%, M$^+$) 385 (100%, M – Me$^+$), 200 (61.3%, M$_{/2}{}^+$), 185 (57%, M$_{/2}$ – Me$^+$).

Satisfactory elemental analyses were obtained for compounds **1**, **2** and **4**.

‡ *Crystal structure determinations* (T = 295 K; Syntex $P2_1$ diffractometer, crystals mounted in capillaries). Compound **1**: $\mathrm{C_{24}H_{30}N_4MgSi_2}$, M = 455.0, monoclinic, space group $C2/c$, a = 18.643(7), b = 15.213(4), c = 18.463(12) Å, β = 91.41(4)°, U = 5235(7) Å^3, $F(000)$ = 1936; Z = 8, D_c = 1.154 g cm^{-3}, μ(Mo-Kα) = 1.8 cm^{-1}, specimen 0.2 × 0.2 × 0.2 mm, 4306 unique reflections, 1944 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max}$ = 50°; R = 0.055, R_w = 0.049. Compound **2**: $\mathrm{C_{24}H_{30}N_4ZnSi_2}$, M = 496.1, monoclinic, space group $C_{2/c}$, a = 18.579(6), b = 15.262(6), c = 18.448(6) Å, β = 91.34(2)°, U = 5230(3) Å^3, $F(000)$ = 2080; Z = 8, D_c = 1.260 g cm^{-3}, μ(Mo-Kα) = 10.7 cm^{-1}, A* (A* = transmission coefficient) 1.10–1.21, specimen 0.34 × 0.10 × 0.44 mm, 4624 unique reflections, 2296 with $I > 2\sigma(I)$ used in the refinement, $2\theta_{max}$ = 50°; R = 0.058, R_w = 0.039. Compound **4**: $\mathrm{C_{22}H_{24}N_4Si_2}$, M = 400.6, monoclinic, space group $P2_1/c$, a = 9.748(4), b = 12.465(3), c = 9.593(4) Å, β = 116.49(3)°, U = 1043.3(6) Å^3, $F(000)$ = 424; Z = 2, D_c = 1.28 g cm^{-3}, μ(Mo-Kα) = 1.46 cm^{-1}, specimen 0.2 × 0.2 × 0.2 mm, 964 unique reflections, 596 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max}$ = 40°; R = 0.067, R_w = 0.064. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

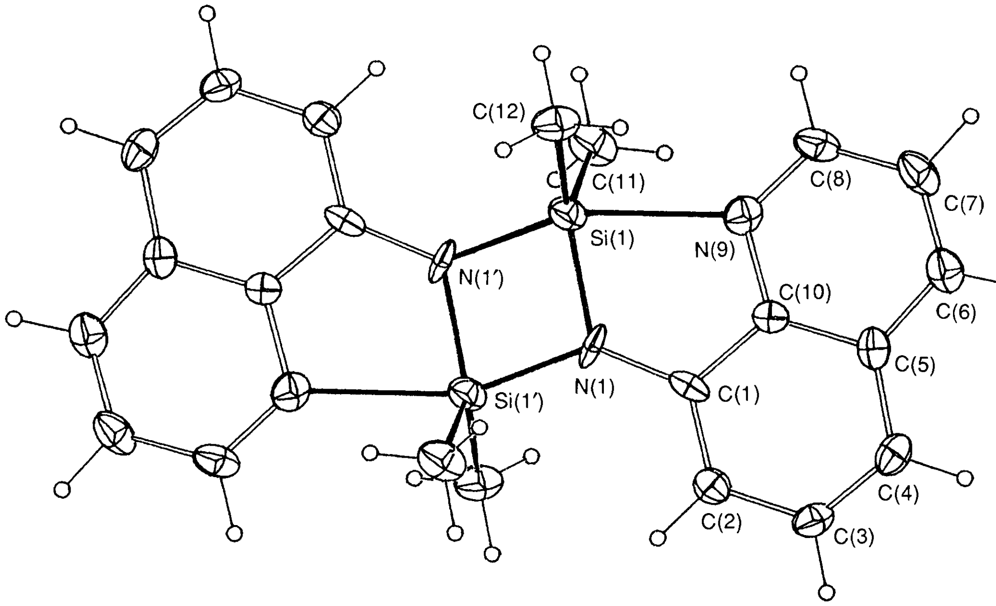

Fig. 2 Molecular projection of centrosymmetric **4**. Selected bond distances (Å) and angles (°): Si(1)–N(1) 1.770(7); Si(1)–N(1′) 1.77(1); Si(1)–C(11, 12) 1.88(1), 1.85(1); Si(1)–N(9) 2.33(1); Si(1) · · · Si(1) 2.696(5); Si(1)–N(1)–Si(1′) 99.4(4); N(1)–Si(1)–N(1′) 80.6(4); N(1)–Si(1)–C(11, 12) 121.6(5), 123.0(4); N(1)–Si(1)–N(9) 77.9(4); N(1′)–Si(1)–C(11, 12) 103.5(4), 103.6(5); N(1′)–Si(1)–N(9) 158.5(3); N(9)–Si(1)–C(11, 12) 88.8(5), 87.3(4); C(11)–Si(1)–C(12) 112.6(5).

ted in Figs. 1 and 2. Compounds **1** and **2** are isomorphous with two half molecules in the asymmetric unit, the other halves being generated by C_2 symmetry axes. Overall, the metals have a distorted tetrahedral geometry, the angle at the metal centres subtended by the chelating atoms being 82.7°, **1**, 84.6°, **2**. Mg–$N_{anionic}$ distances, mean 1.99(8) Å, are similar to non-bridging amides;[2] other magnesium amides are dimeric with bridging amides associated with three and four coordinate metal centres, the distances being significantly longer, 2.08–2.12 Å,[2,3] The corresponding distance in **2** is shorter, mean 1.94(3) Å. In general, zinc amides are bridging in the solid with Zn–N distances typically 2.08 Å.[4] A noteworthy exception is monomeric $[Zn\{N(SiMe_3)_2\}_2]$ (gas phase), Zn–N 1.824(14) Å.[5] The M–$N_{neutral}$ distances, mean 2.10, **1**, 2.07(1) Å, **2**, are shorter than in the closely related compounds $[M\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2]$, 2.13, 2.30 Å, respectively,[12] which reflects the chelate ring strain in these compounds relative to that in **1** and **2**, and the softer character of zinc.

Molecules of **4** lie on inversion centres with the quinolyl plane and Si_2N_2 ring almost coplanar, interplanar angle 2.4(3)°. Bond distances within this ring, mean 1.77 Å, are longer than in other Si_2N_2 ring systems, mean 1.73 Å in $[\{N(SiCl_3)SiCl_2\}_2]$[13] and $[\{N(SiMe_3)SiMe_2\}_2]$,[14] in accordance with an expanded coordination sphere in **4**. As in other five coordinate silicon structures,[15] the *N*-donor is in an axial position of a distorted trigonal bipyramidal stereochemistry, the Si–$N_{neutral}$ distance of 2.33(1) Å being shorter than in systems involving sp^3-*N*-donors [>2.44(1) Å],[15] but longer than in those involving sp^2-N-donors, 2.028(7)[15] and 2.066(9) Å.[16]

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