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Bis{[diphenyl(piperidinomethyl)silyl]methyl}cadmium and -magnesium

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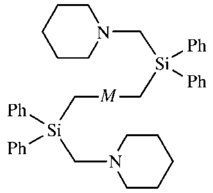
The homoleptic and monomeric metal alkyls bis{[diphenyl(piperidinomethyl)silyl]methyl}cadmium, $[Cd(C_{19}H_{24}NSi)_2]$ or $[Cd\{CH_2SiPh_2(CH_2NC_5H_{10})\}_2]$, (I), and bis{[diphenyl(piperidinomethyl)silyl]methyl}magnesium, $[Mg(C_{19}H_{24}NSi)_2]$ or $[Mg\{CH_2SiPh_2(CH_2NC_5H_{10})\}_2]$, (II), ($CH_2NC_5H_{10}$ is piperidinomethyl) are isostructural, and the molecules exhibit crystallographically imposed C_2 symmetry. The metal centres are located on special positions and, for each structure, half of the molecule is located in the asymmetric unit. The metal centres are intramolecularly coordinated and stabilized by two piperidinomethyl groups (side-arm donation). The Si—C and *M*—C bonds (*M* is Cd or Mg) are shortened compared with the corresponding non-metallated compounds, indicating stabilization by the diffuse polarizable Si centres (α effect). The C—*M*—C angle is 140.53 (12)° in (I) and 123.39 (11)° in (II).

Comment

We are interested in the synthesis of enantiomerically enriched [(aminomethyl)silylmethyl]metal compounds bearing metals which are essential for preparative organic and inorganic chemistry. By the principle of side-arm donation, a chiral amine can introduce stereochemical information into the system and fix (stabilize) the metal at the stereogenic metallated carbon centre by intramolecular coordination. The synthesis of compounds of this type starts from the corresponding [(aminomethyl)silylmethyl]lithium compounds by reaction with metal halides.

In a pre-study, we synthesized non-chiral bis{[diphenyl(piperidinomethyl)silyl]methyl}metal compounds to study them in the solid state. We obtained two interesting molecules of this type for the metals cadmium, (I), and magnesium, (II), the metal centres being intramolecularly coordinated by two piperidinomethyl groups. Compounds (I) and (II) are isostructural and isomorphous. Through two *M*—C and two *M*—N contacts (*M* is Cd or Mg), a spirocyclic system is obtained, with Mg or Cd in the centre, exhibiting distorted tetrahedral geometry at *M*.

When compared with similar intramolecularly stabilized structures, both (I) and (II) show rather small C—*M*—C angles. In comparable structures (Henderson *et al.*, 1986; Khan *et al.*, 1987; Schumann *et al.*, 1998), these angles range from 174 (3) to 166.2 (2)°, whereas in (I), the angle is found to be more than 20° smaller (Table 1). In related Mg compounds, the C—Mg—C angle ranges from 147.68 (8) to 157.0 (7)° (Seidel *et al.*, 2001; Henderson *et al.*, 1986); again, this angle is more than 20° smaller in (II) (Table 2).



(I) *M* = Cd
(II) *M* = Mg

Another feature of these two compounds, as for other polar [(aminomethyl)silylmethyl]metal compounds, is the length of

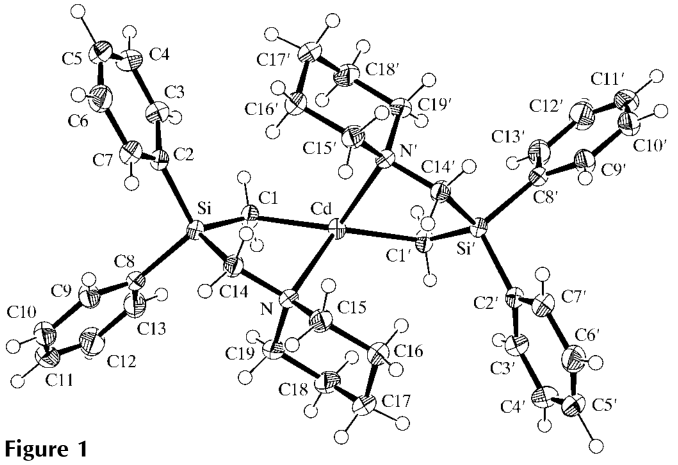


Figure 1
A view of the molecule of (I), shown with 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii. Primes indicate atoms in the symmetry-related part of the molecule, at $(-x, y, \frac{1}{2} - z)$.

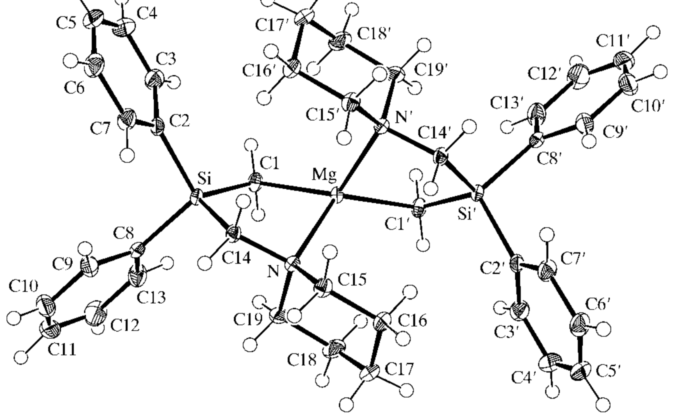


Figure 2
A view of the molecule of (II), shown with 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii. Primes indicate atoms in the symmetry-related part of the molecule, at $(-x, y, \frac{1}{2} - z)$.

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the Si—C bond between Si and the metallated carbon centre. Since it is well known that Si centres have a stabilizing effect on α-carbanionic centres (α effect), the Si—C bond length depends on the polarity of the M—C bond. In a related non-metallated (silylmethyl)amine (crystallized as an ammonium salt), the Si—C bond length is 1.914 (9) Å (Strohmann *et al.*, 2002). The values in (I) and (II) (Tables 1 and 2) indicate a much more polar M—C bond in (II).

By the formal replacement of CH_2 by $SiPh_2$, the C—Cd—C angle decreases (accompanied by a shorter M—N distance), when (I) is compared with a similar structure reported by Schumann *et al.* (1998). The same observation is made for the C—Mg—C angle of (II), considering related structures reported by Seidel *et al.* (2001). Whether these interesting angles are the result of electronic or steric effects emerging from the presence of Si in the present structures still remains to be established (*e.g.* by computational methods).

Experimental

A 1.7 M solution of *t*-BuLi in *n*-pentane (1.09 ml, 1.86 mmol) was added to a solution of [(methyldiphenylsilyl)methyl]piperidine (550 mg, 1.86 mmol) in *n*-pentane (4 ml) at 183 K. After warming to room temperature, yellow crystals of {[(lithiomethyl)diphenylsilyl]-methyl}piperidine (504 mg, 1.67 mmol, 90%) were isolated. These crystals were dissolved in tetrahydrofuran (THF; 6 ml), and a suspension of $CdCl_2$ or $[Mg(THF)_4Br_2]$ (0.835 mmol) in THF (2 ml) was added at 183 K. The mixture was allowed to warm to room temperature, the solvent was removed and toluene (5 ml) was added. After removal of the lithium halide, compound (II) was crystallized from toluene and compound (I) from toluene–*n*-pentane. The crystals of both compounds were mounted at 173 K (N_2 stream), using an X-TEMP device (Kottke & Stalke, 1993).

Spectroscopic data for (I): ^{1}H NMR (400.1 MHz, toluene-d_8, δ, p.p.m.): −0.06 (*s*, $^2J_{H,Cd}$ = 61.3 Hz, 4H, $CdCH_2Si$), 1.13 (*br*, 4H, $NCCCH_2C$), 1.42–1.47 (*m*, 8H, $NCCH_2C$), 2.28 (*br*, 12H, $SiCH_2N$, NCH_2C), 7.14–7.27 (*m*, 12H, aromatic H), 7.71–7.73 (*m*, 8H, aromatic H); {^{1}H}^{13}C NMR (100.6 MHz, toluene-d_8, δ, p.p.m.): −11.7 ($^1J_{C,Cd}$ = 503.1 Hz, $CdCH_2Si$), 23.8 ($NCCCH_2C$), 25.8 ($NCCH_2C$), 51.6 ($SiCH_2N$), 59.0 (NCH_2C), 128.0 (C-*meta*), 128.8 (C-*para*), 134.7 (C-*ortho*), 141.4 (C-*ipso*); {^{1}H}^{29}Si NMR (59.6 MHz, toluene-d_8, δ, p.p.m.): −5.4 ($^2J_{Si,Cd}$ = 35.0 Hz).

Spectroscopic data for (II): ^{1}H NMR (300.1 MHz, THF-d_8, δ, p.p.m.): −1.05 (*s*, 4H, $MgCH_2Si$), 1.33–1.37 (*m*, 4H, $NCCCH_2C$), 1.44–1.49 (*m*, 8H, $NCCH_2C$), 2.41–2.49 (*m*, 12H, $SiCH_2N$, NCH_2C), 7.54–7.61 (*m*, 12H, aromatic H), 7.62–7.68 (*m*, 8H, aromatic H); {^{1}H}^{13}C NMR (75.5 MHz, THF-d_8, δ, p.p.m.): −16.5 ($MgCH_2Si$), 24.9 ($NCCCH_2C$), 27.4 ($NCCH_2C$), 50.2 ($SiCH_2N$), 59.6 (NCH_2C), 128.0 (C-*meta*), 128.6 (C-*para*), 135.4 (C-*ortho*), 144.1 (C-*ipso*); {^{1}H}^{29}Si NMR (59.6 MHz, THF-d_8, δ, p.p.m.): −9.0.

Compound (I)

Crystal data

$[Cd(C_{19}H_{24}NSi)_2]$
M_r = 701.36
Monoclinic, $C2/c$
a = 27.277 (5) Å
b = 6.4390 (10) Å
c = 19.675 (4) Å
β = 94.06 (3)°
V = 3447.0 (11) Å^3
Z = 4

D_x = 1.351 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7500 reflections
θ = 2.5–27.0°
μ = 0.73 mm^{-1}
T = 173 (2) K
Needle, pale yellow
0.5 × 0.2 × 0.2 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: numerical (*FACEIT* in *IPDS*; Stoe & Cie, 1997)
T_{min} = 0.810, T_{max} = 0.868
17 317 measured reflections

3736 independent reflections
3346 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
θ_{max} = 27°
$h = -34 \rightarrow 34$
$k = -8 \rightarrow 8$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.103
S = 1.04
3736 reflections
291 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0597P)^2 + 1.3741P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.71 e Å^{-3}
$\Delta\rho_{min}$ = −1.37 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Cd—C1	2.202 (2)	Si—C2	1.880 (2)
Cd—N	2.5409 (17)	Si—C8	1.892 (2)
Si—C1	1.832 (2)	Si—C14	1.912 (2)
C1^i—Cd—C1	140.53 (12)	C1—Cd—N	84.56 (7)
C1^i—Cd—N	122.80 (8)	N^i—Cd—N	97.15 (8)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

Compound (II)

Crystal data

$[Mg(C_{19}H_{24}NSi)_2]$
M_r = 613.27
Monoclinic, $C2/c$
a = 27.215 (5) Å
b = 6.4100 (10) Å
c = 19.576 (4) Å
β = 93.38 (3)°
V = 3409.1 (11) Å^3
Z = 4

D_x = 1.195 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6000 reflections
θ = 2.5–26.0°
μ = 0.15 mm^{-1}
T = 173 (2) K
Needle, colourless
0.6 × 0.2 × 0.1 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: numerical (*FACEIT* in *IPDS*; Stoe & Cie, 1997)
T_{min} = 0.905, T_{max} = 0.975
13 184 measured reflections

3223 independent reflections
2453 reflections with $I > 2\sigma(I)$
R_{int} = 0.059
θ_{max} = 26°
$h = -33 \rightarrow 33$
$k = -7 \rightarrow 7$
$l = -22 \rightarrow 21$

Table 2
Selected geometric parameters (Å, °) for (II).

Mg—C1	2.1816 (18)	Si—C2	1.886 (2)
Mg—N	2.2545 (17)	Si—C8	1.895 (2)
Si—C1	1.818 (2)	Si—C14	1.9200 (19)
C1^i—Mg—C1	123.39 (11)	C1^i—Mg—N	124.81 (7)
C1—Mg—N^i	89.60 (7)	N^i—Mg—N	107.02 (9)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.044$	$w = 1/[\sigma^2(F_o^2) + (0.0760P)^2]$
$wR(F^2) = 0.115$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{\max} < 0.001$
3223 reflections	$\Delta\rho_{\max} = 0.34$ e Å^{-3}
291 parameters	$\Delta\rho_{\min} = -0.38$ e Å^{-3}

For both compounds, data collection: *EXPOSE* in *IPDS* (Stoe & Cie, 1997); cell refinement: *CELL* in *IPDS*; data reduction: *INTEGRATE* in *IPDS*; program(s) used to solve structure: *SHELXS*90 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1214). Services for accessing these data are described at the back of the journal.

References

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Henderson, M. J., Papasergio, R. I., Raston, C. L., White, A. H. & Lappert, M. F. (1986). *J. Chem. Soc. Chem. Commun.* pp. 672–674.

Khan, O. F. Z., Frigo, D. M., O'Brien, P., Howes, A. & Hursthouse, M. B. (1987). *J. Organomet. Chem.* **334**, C27–30.

Kottke, T. & Stalke, D. (1993). *J. Appl. Cryst.* **26**, 615–619.

Schumann, H., Freitag, S., Girgsdies, F., Hemling, H. & Kociok-Köhn, G. (1998). *Eur. J. Inorg. Chem.* pp. 245–252.

Seidel, N., Jacob, K., Fischer, A. K., Pietzsch, C., Zanello, P. & Fontani, M. (2001). *Eur. J. Inorg. Chem.* pp. 145–151.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Stoe & Cie (1997). *IPDS*. Version 2.87. Stoe & Cie, Darmstadt, Germany.

Strohmann, C., Lehmen, K., Wild, K. & Schildbach, D. (2002). *Organometallics*, **21**, 3079–3081.