**1926** *Inorg. Chem.* **2011**, *50*, 1926–1930
DOI: 10.1021/ic102401w

Inorganic Chemistry
Article

# Magnesium(II) Complexes of 2,4-*N,N′*-Disubstituted 1,3,5-Triazapentadienyl Ligands: Synthesis and Characterization of $[N(Dipp)C(NMe_2)NC(NMe_2)N(SiMe_3)MgBr]_2$ and $[N(R)C(R')NC(R')N(SiMe_3)]_2Mg$ (Dipp = 2,6-$^iPr_2-C_6H_3$, R = Ph, $SiMe_3$; R′ = $NMe_2$, 1-piperidino)

**Meisu Zhou,* Tao Gong, Xiaoli Qiao, Hongbo Tong, Jianping Guo, and Diansheng Liu**

*Institute of Applied Chemistry, Shanxi University, Taiyuan 030006, People's Republic of China,*

Received December 1, 2010

Treatment of the appropriate lithium or sodium 2,4-*N,N′*-disubstituted 1,3,5-triazapentadienate $[RNC(R')NC(R')N(SiMe_3)M]_2$ (R = Ph, 2,6-$^iPr_2-C_6H_3$(Dipp) or $SiMe_3$; R′ = $NMe_2$ or 1-piperidino; M = Li or Na) with one or half equivalent portion of $MgBr_2(THF)_2$ in $Et_2O$ under mild conditions furnishes in good yield the first structurally characterized molecular magnesium 2,4-*N,N′*-disubstituted 1,3,5-triazapentadienates $[DippNC(NMe_2)NC(NMe_2)N(SiMe_3)MgBr]_2$ (**1**), $[\{RNC(R')NC(R')N(SiMe_3)\}_2Mg]$ (R = Ph, R′ = $NMe_2$ **2**; R = Ph, R′ = 1-piperidino **3**; R = $SiMe_3$, R′ = 1-piperidino **4**). The solid-state structure of **1** is dimeric and those of **2**, **3**, and **4** are monomeric. The ligand backbone NCNCN in **1** adopts a W-shaped configuration, while in **2**, **3** and **4** adopts a U-shaped configuration.

## Introduction

1,3,5-triazapentadienyl ligand frameworks containing donor nitrogen atoms have turned out to be the most promising ligands since the powerful ligands not only coordinate to a remarkably wide range of metal ions, but also show a rich variety of coordination modes.[1−4] On the basis of their structural characters, the easy tuning of their steric and electronic properties by variation of the substituents at the nitrogen atoms makes these ligands very attractive for the synthesis of main group and transition metal complexes of this system.[5−7] Recently, the utilities of some fluorinated 1,3,5-triazapentadienato or 2,4-alkoxy-1,3,5-triazapentadienato metal complexes as catalysts were investigated.[8−10] The structurally characterized magnesium(II) adducts of 1,3,5-triazapentadienyl ligands are rare. The perfluoraoalkyl-substituted chelating 1,3,5-triazapentadienyl $[C_3F_7-C(NPh)-N-C(NPh)-C_3F_7]_2Mg$ was the only such example in the literature, which was prepared from the corresponding ligand $C_3F_7-C(=NPh)-N=C(PhNH)-C_3F_7$ and $(C_5H_5)_2Mg$ in toluene.[11] Other monoanionic nitrogen-chelating magnesium(II) complexes such as $\beta$-diketiminates,[12,13] symmetric and asymmetric amidinates,[14,15] and guanidinates[16] are well-known. The magnesium(II) boratahetero-amidinates including bis(organomagnesium) complexes $\{[PhB(\mu_3\text{-}N^tBu)_2](Mg^tBu)_2(\mu_3\text{-}Cl)Li(OEt_2)_3\}$, $\{[PhB(\mu_3\text{-}N^tBu)_2](MgR)_2(THF)_2\}$ (R = $^i$Pr or Ph) and mononuclear $\{[PhB(\mu\text{-}NDipp)_2]Mg(OEt_2)_2\}$ were reported.[17] Several chelating magnesium(I) derivatives $[\{N(Dipp)C(Me)\}_2CH]_2Mg_2$ and $[N(Dipp)C(N(^iPr)_2)N(Dipp)]_2Mg_2$ (Dipp = 2,6-$(^iPr)_2C_6H_3$) were also described.[13,18] We have recently synthesized some main-group and transition metal complexes bearing 2,4-*N,N′*-disubstituted 1,3,5-triazapentadienyl ligands $[(N(R)C(R'))_2N]^{-}{}_2$ (R = $SiMe_3$;

---

*To whom correspondence should be addressed. Tel: +86-351-7010722. Fax: +86-351-7016048. E-mail: mszhou@sxu.edu.cn.

(1) Dias, H. A. R.; Singh, S. *Dalton Trans.* **2006**, 1995–2000.

(2) Dias, H. A. R.; Singh, S.; Flores, J. A. *Inorg. Chem.* **2006**, *45*, 8859–8861.

(3) Dias, H. A. R.; Singh, S. *Inorg. Chem.* **2004**, *43*, 7396–7402.

(4) Dias, H. A. R.; Singh, S. *Inorg. Chem.* **2004**, *43*, 5786–5788.

(5) Siedle, A. R.; Webb, R. J.; Brostrom, M.; Chou, S.-H.; Weil, D. A.; Newmark, R. A.; Behr, F. E.; Young, V. G. *Inorg. Chem.* **2003**, *42*, 2596–2601.

(6) Siedle, A. R.; Webb, R. J.; Newmark, R. A.; Brostrom, M.; Weil, D. A.; Erickson, K.; Behr, F. E.; Young, V. G. *J. Fluorine Chem.* **2003**, *122*, 175–182.

(7) Siedle, A. R.; Webb, R. J.; Brostrom, M.; Newmark, R. A.; Behr, F. E.; Young, V. G. *Organometallics* **2004**, *23*, 2281–2286.

(8) Flores, J. A.; Badarinarayana, V.; Singh, S.; Lovely, C. J.; Dias, H. V. R. *Dalton Trans.* **2009**, 7648–7652.

(9) Flores, J. A.; Dias, H. V. R. *Inorg. Chem.* **2008**, *47*, 4448–4450.

(10) Figiel, P. J.; Kopylovich, M. N.; Lasri, J.; Silva, M. F. C. G.; Silva, J. J. R. F.; Pombeiro, A. J. L. *Chem. Commun.* **2010**, *46*, 2766–2768.

(11) Siedle, A. R.; Webb, R. J.; Behr, F. E.; Newmark, R. A.; Weil, D. A.; Erickson, K.; Naujok, R.; Brostrom, M.; Mueller, M.; Chou, S.-H.; Young, V. G. *Inorg. Chem.* **2003**, *42*, 932–934.

(12) Caro, C. F.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1999**, 1433–1434.

(13) Green, S. P.; Jones, C.; Stasch, A. *Science* **2007**, *318*, 1754–1757.

(14) Lee, H.-K.; Lam, T. S.; Lam, C.-K.; Li, H.-W.; Fung, S.-M. *New. J. Chem.* **2003**, *27*, 1310–1318.

(15) Boeré, R. T.; Cole, M. L.; Junk, P. C. *New. J. Chem.* **2005**, *29*, 128–134.

(16) Srinivas, B.; Chang, C.-C.; Chen, C.-H.; Chiang, M. Y.; Chen, I.-T.; Wang, Y.; Lee, G.-H. *J. Chem. Soc., Dalton Trans.* **1997**, 957–963.

(17) Chivers, T.; Eisler, D. J.; Fedorchuk, C.; Schatte, G.; TuononenRené T. Boeré, H. M. *Inorg. Chem.* **2006**, *45*, 2119–2131.

(18) Westerhausen, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 2185–2187.

R′ = $NMe_2$) and $[N(Ar)C(NMe_2)NC(NMe_2)N(R)]^{-}{}_2$ (Ar = Ph, 2,6-$^{i}Pr_2-C_6H_3$; R = H, $SiMe_3$),[19,20] closely related analogues of the popular 1,5-diazapentadienyl systems, which have been widely investigated.[21−25] As part of a broader study of the coordination chemistry of triazapentadienyl ligands, we report here on the 2,4-*N*,*N*′-disubstituted 1,3,5-triazapentadienyl ligands in magnesium(II) chemistry: the synthesis and molecular structures of dimeric $[DippNC(NMe_2)NC(NMe_2)N(SiMe_3)MgBr]_2$ **1**, and monomeric $[\{RNC(R')NC(R')N(SiMe_3)\}_2Mg]$ (R = Ph, R′ = $NMe_2$ **2**; R =Ph, R′ = 1-piperidino **3**; R = $SiMe_3$, R′ = 1-piperidino **4**). The NCNCN ligands backbone in dimeric **1** adopted W-shaped configuration, bridging two metal centers with three *N*-centers of each coordinated to two Mg atoms, while in homoleptic complexes **2**−**4** NCNCN backbone adopted U-shaped configuration, chelating the Mg center via the terminal nitrogen atoms. Five-coordinate Mg(II) atom in complex **1** featured a much distorted trigonal bipyramidal environment, while in **2**−**4** tetrahedral or distorted tetrahedral structures were found.

## Experimental Section

**General Procedures.** All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were purchased from commercial sources. Deuterated solvents $C_5D_5N$, $CDCl_3$ were dried over activated molecular sieves (4 Å) and vacuum transferred before use. Diethyl ether was dried and distilled from sodium/benzophenone and stored over a sodium mirror under argon. Dichloromethane was distilled from activated molecular sieves (4 Å) or $CaH_2$. The compounds (Dipp)N(Li)$SiMe_3$ and PhN(Li)$SiMe_3$ were obtained according to published procedures.[14,26−28] PhN(Na)$SiMe_3$ was prepared in situ by direct transmatallation in hexane of PhN(Li)$SiMe_3$ with Na($OBu^t$). The lithium amide $LiN(SiMe_3)_2$ was easily accessible via the lithiation of 1,1,1,3,3,3-hexamethyldisilazane with $LiBu^n$ in hexane. Glassware was oven-dried at 150 °C overnight. The NMR spectra were recorded on a Bruker DRX-300 instrument, and solvent resonances were used as the internal references for $^1H$ spectra and $^{13}C$ spectra. Melting points were measured in sealed capillaries and are uncorrected. Elemental analyses were carried out using a Vario EL-III analyzer (Germany).

**Preparations.** $[DippNC(NMe_2)NC(NMe_2)N(SiMe_3)MgBr]_2$ **(1).** *N*,*N*-dimethylcyanamide (0.36 mL, 4.4 mmol) was added slowly to a solution of compound (Dipp)N(Li)$SiMe_3$ (0.56 g, 2.2 mmol) in $Et_2O$ (30 mL) at −78 °C. The resultant pale-yellow solution was allowed to warm to room temperature (rt) and was stirred overnight. Then $MgBr_2(THF)_2$ (0.61 g, 1.85 mmol) was added slowly to the above solution at −78 °C. The resultant mixture was allowed to warm to rt and stirred for overnight. The volatiles were removed in vacuo, and the residue was extracted with dichloromethane and filtered. The filtrate was concentrated in vacuo to ca. 15 $cm^3$, yielding colorless crystals of **1** (0.85 g, 36%). Mp 240−242 °C. (Found: C, 48.44; H, 7.31, N, 12.88%. $C_{43}H_{78}Br_2Cl_2Mg_2N_{10}Si_2$ requires C, 48.24; H, 7.34, N, 13.08%. $^1H$ NMR ($C_5D_5N$): $\delta$ 0.72 (s, 18 H, Si(C*H*$_3$)$_3$), 1.16−1.18 (d, 24 H, CH(C*H*$_3$)$_2$), 2.62−2.91 (m, 24 H, N(C*H*$_3$)$_2$), 3.02−3.16 (m, 4 H, PhC*H*(CH$_3$)$_2$), 7.38−7.59 (m, 6 H, Ph), 4.20 (s, 2 H, C*H*$_2$Cl$_2$). $^{13}C$ NMR ($C_5D_5N$): $\delta$ 3.06 Si(*C*H$_3$)$_3$, 24.86, 25.86 (CH(*C*H$_3$)$_2$), 29.55 *C*H(CH$_3$)$_2$), 38.00, 38.61, 39.91, 40.79 (N(*C*H$_3$)$_2$), 121.99 (*p*-*C*Ar), 129.58 (*m*-*C*Ar), 140.45 (*o*-*C*Ar), 156.34 (*C*ipso),161.61 (Me$_3$SiN*C*N), 184.00 (ArN*C*N), 56.13 (*C*H$_2$Cl$_2$).

$[\{RNC(R')NC(R')N(SiMe_3)\}_2Mg]$ **(R = Ph, R′ = $NMe_2$) (2).** *N*,*N*-dimethylcyanamide (0.58 mL, 7.18 mmol) was added slowly to a solution of compound PhN(Li)$SiMe_3$ (0.67 g, 3.59 mmol) in $Et_2O$ (30 mL) at −78 °C. The resultant pale-yellow solution was allowed to warm to rt and was stirred overnight. Then $MgBr_2(THF)_2$ (1.18 g, 3.59 mmol) was added slowly to the above solution at −78 °C. The resultant white solution was also allowed to warm to rt and was stirred overnight. The solvent was removed in vacuo. The residue was dissolved in $CH_2Cl_2$ and filtered. The filtrate was concentrated and crystallized at rt to give colorless crystals of **2** (0.35 g, 30%). Mp 227−229 °C. (Found: C, 56.74; H, 8.18, N, 22.28%. $C_{30}H_{52}MgN_{10}Si_2$ requires: C, 56.90; H, 8.28 N, 22.12%). $^1H$ NMR ($C_5D_5N$): $\delta$ 0.20−0.37 (m, 18 H, Si(C*H*$_3$)$_3$), 2.78, 2.94 (d, 24 H, N(C*H*$_3$)$_2$), 6.78−7.21 (m, 10 H, Ph). $^{13}C$ NMR ($C_5D_5N$): $\delta$ 0.96 (Si(*C*H$_3$)$_3$), 37.88, 38.39, 40.08, 40.34 (N(*C*H$_3$)$_2$), 122.05 (*p*-*C*Ph), 123.62 (*m*-*C*Ph), 128.14 (*o*-*C*Ph), 150.2 (*C*ipso), 158.57, 160.65 (N*C*N).

$[\{RNC(R')NC(R')N(SiMe_3)\}_2Mg]$ **(R = Ph, R′ = 1-piperidino) (3).** 1-Piperidinecarbonitrile (0.57 mL, 4.88 mmol) was added to a solution of PhN(Na)$SiMe_3$ (0.46 g, 2.44 mmol) in $Et_2O$ (30 $cm^3$) at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred for overnight. $MgBr_2(THF)_2$ (0.40 g, 1.22 mmol) was added at −78 °C. The resulting white mixture was warmed to ca. 25 °C, stirred overnight, and then filtered. The filtrate was concentrated in vacuo to ca. 15 $cm^3$ and cooled at −25 °C for several days, yielding colorless crystals of **3** (0.37 g, 38%). Mp 200−202 °C. (Found: C, 64.10; H, 8.96, N, 17.28%. $C_{42}H_{68}MgN_{10}Si_2$ requires: C, 63.57; H, 8.64 N, 17.65%). $^1H$ NMR ($CDCl_3$): $\delta$ 0.12 (s, 18 H, Si(C*H*$_3$)$_3$, 1.32−1.55 (m, 24 H, (C*H*$_2$)$_3$), 3.04−3.12 (m, 16 H, N(C*H*$_2$)), 6.68−7.26 (m, 10 H, Ph). $^{13}C$ NMR ($CDCl_3$): $\delta$ 2.12 (Si(*C*H$_3$)$_3$), 24.67, 24.92, 25.85 ((*C*H$_2$)$_3$), 48.09, 51.15 (N(*C*H$_2$)$_2$), 119.12 (*p*-*C*Ph), 121.64 (*m*-*C*Ph), 128.65 (*o*-*C*Ph), 151.40 (*C*ipso), 161.12, 169.67 (N*C*N).

$[\{RNC(R')NC(R')N(SiMe_3)\}_2Mg]$ **(R = $SiMe_3$, R′ = 1-piperidino) (4).** 1-Piperidinecarbonitrile (0.45 mL, 3.88 mmol) was added to a solution of $LiN(SiMe_3)_2$ (0.32 g, 1.94 mmol) in $Et_2O$ (30 $cm^3$) at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred for overnight. $MgBr_2(THF)_2$ (0.414 g, 1.26 mmol) was added at −78 °C. The resulting white mixture was warmed to ca. 25 °C, stirred overnight, and then filtered. The filtrate was concentrated in vacuo to ca. 10 $cm^3$ and left at room temperature for 3 d to to give colorless crystals of **4** (0.48 g, 58%). Mp 125−127 °C. (Found: C, 55.24; H, 9.52, N, 16.57%. $C_{40}H_{86}MgN_{10}OSi_4$ requires: C, 55.88; H, 10.08 N, 16.29%). $^1H$ NMR ($CDCl_3$): $\delta$ 0.04−0.08 (m, 36 H, Si(C*H*$_3$)$_3$, 1.49 (s, 24 H, (C*H*$_2$)$_3$), 3.04 (s, 16 H, CN(C*H*$_2$)), 1.16−1.20 (t, 6 H, OCH$_2$C*H*$_3$), 3.44−3.46 (q, 4 H, OC*H*$_2$CH$_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 2.59 (Si(*C*H$_3$)$_3$), 24.24, 25.44 ((*C*H$_2$)$_3$), 45.14−48.01 (N(*C*H$_2$)$_2$), 14.60 (OCH$_2$*C*H$_3$), 65.20 (O*C*H$_2$CH$_3$), 166.01 (N*C*N).

**X-ray Crystallography.** X-ray diffraction data for each of **1**, **2**, and **4** were collected on an Bruker SMART APEX diffractometer/CCD area detector using monochromated Mo−Kα radiation, $\lambda$ = 0.71073 Å. Crystals were coated in oil and then

---

(19) Zhou, M.-S.; Li, P.; Tong, H.-B.; Song, Y.-P.; Gong, T.; Guo, J.-P.; Weng, L.-H.; Liu, D.-S. *Inorg. Chem.* **2008**, *47*, 1886–1888.

(20) Zhou, M.-S.; Song, Y.-P.; Gong, T.; Tong, H.-B.; Guo, J.-P.; Weng, L.-H.; Liu, D.-S. *Inorg. Chem.* **2008**, *47*, 6692–6700.

(21) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031–3066.

(22) Hitchcock, P. B.; Lappert, M. F.; Linnolahti, M.; Sablong, R.; Severn, J. R. *J. Organomet. Chem.* **2009**, *694*, 667–676.

(23) (a) Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S. *J. Chem. Soc., Chem. Commun.* **1994**, 1699–1700. (b) Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S. *J. Chem. Soc., Chem. Commun.* **1994**, 2637–2638. (c) Lappert, M. F.; Liu, D.-S. *J. Organomet. Chem.* **1995**, *500*, 203–217.

(24) (a) Annibale, V. T.; Lund, L. M.; Song, D. -T. *Chem. Commun.* **2010**, *46*, 8261–8263. (b) Hadzovic, A.; Song, D.-T. *Inorg. Chem.* **2008**, *47*, 12010–12017.

(25) (a) Panda, A; Stender, M; Wright, R. J; Olmstead, M. M.; Klavins, P.; Power, P. P. *Inorg. Chem.* **2002**, *41*, 3909–3916. (b) Wright, R. J; Power, P. P; Scott, B. L; Kiplinger, J. L. *Organometallics* **2004**, *23*, 4801–4803.

(26) Bezombes, J.-P.; Hitchcock, P. B.; Lappert, M. F.; Merle, P. G. *J. Chem. Soc., Dalton Trans.* **2001**, 816–821.

(27) Hitchcock, P. B.; Lappert, M. F.; Merle, P. G. *Dalton Trans.* **2007**, 585–594.

(28) Antolini, F.; Hitchcock, P. B.; Lappert, M. F.; Merle, P. G. *Chem. Commun.* **2000**, 1301–1302.

**Table 1.** Crystal and Refinement Data for **1**, **2**, and **4**

| compound | **1** | **2** | **4** |
|---|---|---|---|
| formula | $C_{43}H_{78}Br_2Cl_2Mg_2N_{10}Si_2$ | $C_{30}H_{52}MgN_{10}Si_2$ | $C_{40}H_{86}MgN_{10}OSi_4$ |
| $M$ | 1070.67 | 633.31 | 859.86 |
| crystal system | triclinic | triclinic | monoclinic |
| space group | $P\bar{1}$ (No.2) | $P\bar{1}$ (No.2) | $P2_1/c$ (No.14) |
| $a$/Å | 12.3170(8) | 11.175(3) | 15.188(4) |
| $b$/Å | 13.8217(9) | 11.979(4) | 28.697(7) |
| $c$/Å | 17.1073(11) | 16.136(5) | 11.888(3) |
| α° | 73.8230(10) | 90.077(4) | 90.00 |
| $\beta$ ° | 82.7830(10) | 107.705(4) | 100.801(3) |
| $\gamma$ ° | 76.2170(10) | 115.707(4) | 90.00 |
| $U$/Å$^3$ | 2711.0(3) | 1831.6(10) | 5090(2) |
| $Z$ | 2 | 2 | 4 |
| absorption coeff (mm$^{-1}$) | 1.700 | 0.148 | 0.168 |
| unique reflections, $R_{\text{int}}$ | 9387, 0.0126 | 6227, 0.0279 | 8707, 0.0395 |
| reflections with $I > 2\sigma(I)$ | 7904 | 5064 | 6367 |
| final $R$ indices [ $I > 2\sigma(I)$ ] $R_1$, w$R_2$ | 0.0337, 0.0893 | 0.0723, 0.1916 | 0.0558, 0.1534 |
| $R$ indices (all data) $R_1$, w$R_2$ | 0.0419, 0.0940 | 0.0946, 0.2350 | 0.0787, 0.1833 |

**Table 2.** Selected Bond Lengths (Å) and Angles (°) for **1**

| | | | |
|---|---|---|---|
| Mg1−Br1 | 2.4622(7) | Mg1−N3 | 2.1757(18) |
| Mg1−N5 | 2.1429(19) | N1−C13 | 1.308(3) |
| N2−C13 | 1.361(3) | N3−C13 | 1.388(3) |
| N3−C16 | 1.406(3) | N4−C16 | 1.349(3) |
| N5−C16 | 1.311(3) | | |
| N3−Mg1−N5 | 63.69(7) | N1−C13−N2 | 127.4(2) |
| N1−C13−N3 | 113.16(19) | N2−C13−N3 | 119.41(19) |
| N3−C16−N4 | 118.59(19) | N3−C16−N5 | 113.92(18) |
| N4−C16−N5 | 127.35(19) | C13−N3−C16 | 122.49(17) |

**Table 3.** Selected Bond Lengths (Å) and Angles (°) for **2**

| | | | |
|---|---|---|---|
| Mg−N1 | 2.040(3) | C1−N2 | 1.330(4) |
| Mg−N5 | 2.049(3) | C1−N3 | 1.330(4) |
| Mg−N6 | 2.052(3) | C2−N3 | 1.331(4) |
| Mg−N10 | 2.039(3) | C2−N4 | 1.376(5) |
| C1−N1 | 1.365(4) | C2−N5 | 1.329(4) |
| N1−Mg−N5 | 94.20(12) | N6−Mg−N10 | 94.19(12) |
| Mg−N1−C1 | 119.3(2) | Mg−N5−C2 | 113.0(2) |
| N1−C1−N3 | 122.8(3) | N3−C2−N5 | 126.8(3) |
| C1−N3−C2 | 127.9(3) | | |

directly mounted on the diffractometer under a stream of cold nitrogen gas. A total of $N$ reflections were collected by using $\omega$ scan mode. Corrections were applied for Lorentz and polarization effects as well as absorption using multiscans (SADABS).[29] The structure was solved by direct method (SHELXS-97).[30] Then the remaining non-hydrogen atoms were obtained from the successive difference Fourier map. All non-H atoms were refined with anisotropic displacement parameters, while the H atoms were constrained to parent sites, using riding modes (SHELXTL).[31] Crystal data and details of data collection and refinements for **1**, **2** and **4** are summarized in Table 1. Selected bond distances and bond angles are listed in Tables 2−4.

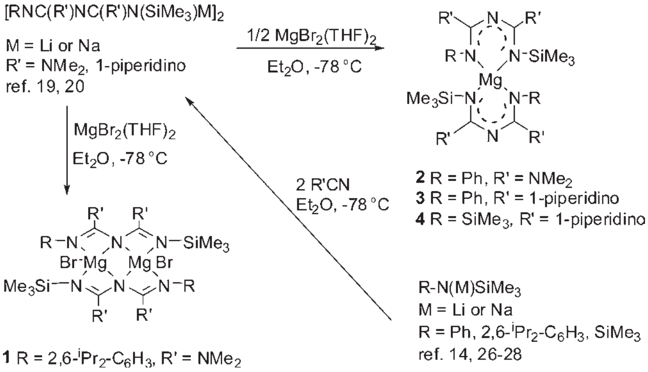
## Results and Discussion

**Synthesis and Characterization.** The starting materials for the synthesis of **1**−**4** were [RNC(R′)NC(R′)N(SiMe$_3$)-M]$_2$ (R = Ph, 2,6-$^i$Pr$_2$−C$_6$H$_3$(Dipp) or SiMe$_3$; R′ = NMe$_2$ or 1-piperidino; M = Li or Na).[19,20] Complexes **1** was obtained in 36% yield by treatment of corresponding lithium 1,3,5-triazapentadienate with magnesium bromide at the ratio of 1:1 in Et$_2$O and crystallization from CH$_2$Cl$_2$.

**Table 4.** Selected Bond Lengths (Å) and Angles (°) for **4**

| | | | |
|---|---|---|---|
| Mg−N1 | 2.082(2) | Mg−N5 | 2.062(2) |
| Mg−N6 | 2.073(2) | Mg−N10 | 2.058(3) |
| C1−N1 | 1.320(4) | C1−N2 | 1.403(4) |
| C1−N3 | 1.338(4) | C2−N3 | 1.327(4) |
| C2−N4 | 1.443(4) | C2−N5 | 1.311(4) |
| C19−N6 | 1.330(3) | C19−N7 | 1.390(4) |
| C19−N8 | 1.346(4) | C20−N8 | 1.321(4) |
| C20−N9 | 1.435(4) | C20−N10 | 1.326(4) |
| N1−Mg−N5 | 95.08(10) | N6−Mg−N10 | 94.84(10) |
| Mg−N1−C1 | 116.02(18) | N1−C1−N3 | 127.5(2) |
| C1−N3−C2 | 128.3(2) | N3−C2−N5 | 129.1(2) |
| Mg−N5−C2 | 116.84(18) | N6−C19−N8 | 126.7(2) |
| C19−N8−C20 | 128.4(2) | N8−C20−N10 | 128.8(3) |
| Mg−N6−C19 | 117.35(18) | Mg−N10−C20 | 116.47(19) |

**Scheme 1.** Synthetic Routes to Complexes **1**−**4**



Compounds **2**, **3**, and **4** were obtained similarly to the procesure of complex **1** at the ratio of 2:1 by treatment of lithium or sodium (for 3) 1,3,5-triazapentadienate, and crystallization from dichloromethane for **2**, and from Et$_2$O for **3** and **4** (Scheme 1). The colorless, sharp melting, crystalline 2,4-$N$,$N'$-disubstituted 1,3,5-triazapentadienyl compounds **1**−**4** gave satisfactory $^1$H NMR, $^{13}$C NMR, microanalyses as well as single crystal X-ray (**1**, **2**, and **4**) data.

**Crystal Structures. Structure of 1.** The X-ray structurally characterized crystalline **1** (Figure 1) shows that there are two independent molecules in one unit cell. For each molecule, it is a head-to-tail dimer built around a planar MgNMgN ring; the angles at the magnesium atoms [87.69(7), 87.69(7)°] are narrower than those at the nitrogen atoms [92.31(7), 92.31(7)°]. Each magnesium

---

[29] Sheldrick, G. M. *Correction Software*; University of Göttinggen: Germany, 1996.

[30] Sheldrick, G. M. *Program for the Solution of Crystal Structures*; University of Göttinggen: Germany, 1997.

[31] *Program for Crystal Structure Refinement*; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1998.

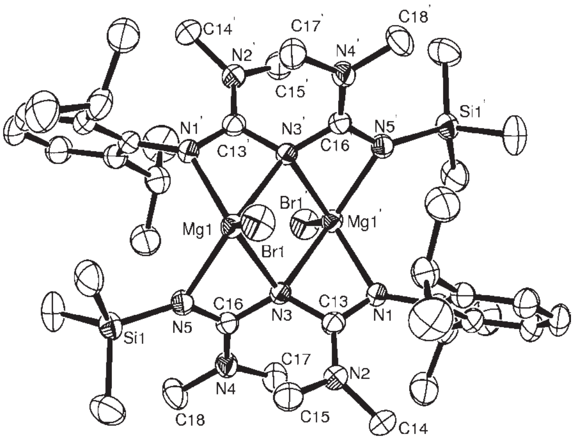


**Figure 1.** Molecular structure of **1**.

atom is coordinated with four nitrogen atoms from two ligands and one bromide atom in a much distorted trigonal bipyramidal environment with the fifth position being occupied by the bromide. Each ligand NCNCN backbone adopts a twisted W-shaped conformation. The dihedral angles between the two MgNCN moieties linked by N3 and Mg1 are 61.9 and 119.1°, respectively. The molecule has two fused tricyclic ladder motifs comprising a central plane Mg1N3Mg1′N3′ ring flanked by parallel planes Mg1N3C16N5 and Mg1′N3′C16′N5′, Mg1′N1-C13N3, and Mg1N1′C13′N3′, respectively. The dihedral angle between the core Mg1N3Mg1′N3′ and the adjacent four-membered rings Mg1N1′C13′N3′ and Mg1N3C-16N5 are 46.7 and 40.0°. The bond distances N1−C13, C13−N3, N3−C16, and C16−N5 are 1.308(3), 1.388(3), 1.406(3), and 1.311(3) Å, respectively, indicating an obvious short−long−long−short pattern of C−N bond lengths in the NCNCN backbone. The *C*=N and C−N bonding is consistent with previously reported dimeric W-shaped triazapentadienyl lithium complexes $[(SiMe_3)NC(NMe_2)NC(NMe_2)N(SiMe_3)]^{-}_{2}$[19] and $[N(Dipp)C(NMe_2)NC(NMe_2)N(SiMe_3)]^{-}_{2}$.[20] The coordination mode that the ligands to bridge two metal centers with three N-centers of each coordinated to two Mg atoms in complex **1** is quite similar to that in the corresponding triazapentadienyl lithium complexes[19,20] because $Li^+$ and $Mg^{2+}$ have closer sizes, and there is a well-known diagonal periodicity between these two ions (ionic radii for $Li^+$ = 0.60 Å, $Mg^{2+}$ = 0.65 Å).

For the $CN_3$ ($C13N_3$ and $C16N_3$) frameworks in **1**, the C−N bond distances are in the range of 1.308(3) ~1.406(3) Å, and the dihedral angles between N1C13N3 and C14N2C15, N3C16N5 and C17N4C18 are 21.7 and 9.9°, respectively, indicating the presence of delocalized $CN_3$ fragments to some extent. This is related to the structural nature of guanidinate complexes and $sp^2$ hybridization necessary for conjugation.

**Structures of 2, 3 and 4.** The monomeric structures of complexes **2**−**4** with tetrahedral Mg(II) centers are very similar. Although crystals of **3** have not yet proved suitable for X-ray crystallographic studies, the X-ray data is enough to confirm the outline of the molecule. Crystals of **2** and **4** yielded a good data set that upon refinement gave the structures presented in Figures 2 and 3, respectively.

The low-temperature X-ray diffraction analysis reveals that in molecule **2** (Figure 2) the magnesium atom is in a nearly rigorously tetrahedral environment defined by the four nitrogen atoms from the two bidentate 1,3,5-triazapentadienato ligands with dihedral angle of 90.4° between planes N1MgN5 and N6MgN10. Each of the bidentate 1,3,5-triazapentadieno ligand forms a planar six-membered metallacycle MgNCNCN with a mean deviation of 0.13 Å. The Mg−N bond distances are 2.040(3) [Mg−N1], 2.049(3) [Mg−N5], 2.052(3) [Mg−N6], and 2.039(3) Å [Mg−N10], respectively. The bond angles N1−Mg−N5 and N6−Mg−N10 are 94.20(12) and 94.19(12)°, respectively. Within the 1,3,5-triazapentadieno ligand, the bond distances N1−C1[1.365(4) Å], C1−N3 [1.330(4) Å], N3−C2 [1.331(4)] Å], and C2−N5 [1.329(4) Å] are almost identical, suggesting delocalization in the ligand backbone. Bond angles N1−C1−N3, C1−N3−C2, and N3−C2−N5 are 122.8(3), 127.9(3) and 126.8(3)°, respectively.

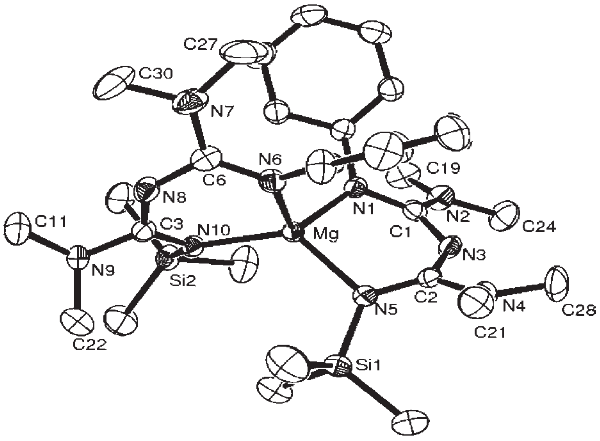


**Figure 2.** Molecular structure of **2**.

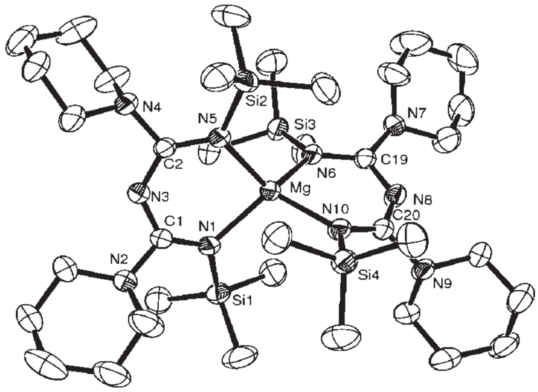
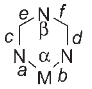
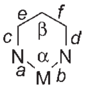


**Figure 3.** Molecular structure of **4**.

Complex **4** (Figure 3) crystallizes in the monoclinic space $P2_1/c$. The coordination mode of central metal magnesium in complex **4** is similar to that in magnesium complex **2**. Complex **4** contains two $\eta^2$-chelating 1,3,5-triazapentadieno ligands around the magnesium center, adopting a highly distorted tetrahedral coordination geometry, with a dihedral angle of 73.3° between planes N1MgN5 and N6MgN10. Very similar structures to complexes **2** and **4** were found in the previously reported transition metal Mn(II), Fe(II), and Co(II) 2,4-*N*,*N*′-disubstituted 1,3,5-triazapentadienyl complexes[20] and the related magnesium $\beta$-diketiminate complex $[Mg(\{N(R)C(Ph)\}_2CH)_2]$.[12] All of the analogues featured

**Table 5.** Selected Bond Lengths [Å] and Angles [°] of **2**, **4** and Their Four-Coordinate Analogues





**I**

| parameters | 2 | 4 | I | II | III |
|---|---|---|---|---|---|
| *a*/Å | 2.040(3) | 2.082(2) | 2.096(8) | 1.996(5) | 2.014(2) |
| *b*/Å | 2.049(3) | 2.063(2) | 2.068(8) | 2.027(4) | 2.038(2) |
| *c*/Å | 1.365(4) | 1.320(4) | 1.299(11) | 1.296(3) | 1.330(4) |
| *d*/Å | 1.329(4) | 1.311(4) | 1.318(11) | 1.305(3) | 1.358(4) |
| *e*/Å | 1.330(4) | 1.338(4) | 1.432(13) | 1.356(3) | 1.338(4) |
| *f*/Å | 1.331(4) | 1.327(4) | 1.403(13) | 1.342(3) | 1.346(3) |
| α/° | 94.20(12) | 95.08(10) | 99.7(3) | 92.58(18) | 94.57(8) |
| *β*/° | 127.9(3) | 128.3(2) | 131.5(9) | 123.4(2) | 127.3(2) |

$\eta^2$-bonded ligands with a U-shaped ligand backbone and gave planar six-membered MNCCCN metallacycles. A comparison of some of the relevant bond lengths and angles for complexes **2** and **4** with those of several other known *N*,*N'* chelating four-coordinate monoanionic complexes such as magnesium *β*-diketiminate $[\{N(SiMe_3)C(Ph)\}_2CH]_2Mg$ (**I**),[12] lithium fluorinated 1,3,5-triazapentadienate $N\{(C_3F_7)C(Mes)N\}_2Li(THF)_2$ (Mes = 2,4,6-trimethylphenyl) (**II**)[9] and transition metal 2, 4-*N*,*N'*-disubstituted 1,3,5-triazapentadienate $[N(Ph)C(NMe_2)NC(NMe_2)N(SiMe_3)]_2Fe$ (**III**)[20] is presented in Table 5.

The bond distances of Mg−N in **4** are in the range of 2.058(3)∼2.082(2) Å, slightly longer than those in **2** [2.039(3)∼2.052(3) Å], Li−N in **II** and Fe−N in **III**, comparable to the Mg−N bond distances in **I**. Both the bite angles N−Mg−N in **4** [95.08(10) and 94.84(10) °] and in **2** [94.19(12) and 94.20(12) °] are comparable to those in other 1,3,5- triazapentadienyl metal systems such as **II** and **III**, narrower than that in the 1,5-diazapentadienyl system **I**. Although there are minor differences among the N−C bond lengths in those complexes, all of them are falling in the normal range for π-delocalization in each ligand NCNCN backbone.[22] In **4**, the metallacycle MgNCNCN is almost planar with a mean deviation of 0.09 Å. The bond angle at central nitrogen atom of NCNCN backbone in **4** is similar to that in other 2,4-*N*,*N'*-disubstituted 1,3,5-triazapentadienyl systems **2** and **III**, wider than that in four-coordinate fluorinated 1,3,5-triazapentadienato lithium complex **II**, but narrower than that at the central carbon atom of NCCCN of its 1,5-diazapentadienyl analogue **I**.

The dihedral angles formed by the planar $NR_2$ (2-, 4- positions) functions and their adjacent NCN planes [between N1C1N3 and C3N2C7; N3C2N5 and C8N4-C12] are 16.0 and 26.4° in **2**, 48.8 and 69.7° in **4**, respectively. They are much smaller than those nearly perpendicular orientation moieties found in guanidinato complexes $^{i}PrNC[N(SiMe_3)_2]N^{i}Pr\}_2ZrCl_2]$ [88.2°], $[\{CyNC[N(SiMe_3)_2]NCy\}_2ZrCl_2]$ [86.3°], or $[\{CyNC[N(SiMe_3)_2]NCy\}_2HfCl_2]$ [85.8°],[32] again indicating stronger or a little π-bonding interactions between NCN and $NR_2$ moieties in **2** or **4**.

The dimeric and monomeric structures of complexes **1**−**4** seem to be the result of the two modes of coordination exhibited by the ligand. A comparison of the structural features of complexes **1**−**4** suggests that the dimeric structure for complex **1** will be sterically favored due to the presence of the bulky diisopropylphenyl substitution at the nitrogen atom. And the W- form should be the preferred conformer that is free of steric strain and the electron density is distributed over a maximum distance. Whereas in less bulky complexes **2**−**4**, the magnesium atomic radii allowed the NCNCN backbone to span from one terminus of the 1,3,5-triazapentadienyl moiety to the other provided the latter coils up to adopt the U shape. This was also found in pentadienyl species and substituted 1,3-diphenylallyllithium species.[33,34]

In conclusion, 1,3,5-triazapentadienyl ligands have proven to be useful in the preparation of a family of 2,4-*N*,*N'*-disubstituted 1,3,5-triazapentadienyl magnesium complexes $[DippNC(NMe_2)NC(NMe_2)N(SiMe_3)MgBr]_2$ **1**, $[\{RNC(R')NC(R')N(SiMe_3)\}_2Mg]$ (R = Ph, R′ = $NMe_2$ **2**; R = Ph, R′ = 1-piperidino **3**; R = $SiMe_3$, R′ = 1-piperidino **4**). From these results, it is clear that the ligands bridge two metal centers with three *N*-centers of each coordinated to two Mg atoms in complex **1**, whereas in homoleptic compounds **2**−**4**, the ligands chelate the Mg center via the terminal nitrogen atoms of NCNCN. Conjugation occurs in the ligand backbone NCNCN of **2**−**4**, and a partial delocalization is observed in **1**. The orientation of the $NR_2$ substituents at 2- and 4-positions to its adjacent NCN planes in **1**, **2**, and **4** result in guanidinate structural features for the ligand system. The first structurally characterized 2,4-*N*,*N'*-disubstituted 1,3,5-triazapentadienyl magnesium(II) complexes **1**−**4** represent a novel class of lighter alkaline-earth metal complexes having NCNCN ligand system. Our continuing investigations are focus on the use of the reported magnesium(II) complexes and the steric and electronic features that influence the coordination chemistry and the properties of alkaline-earth metal 2,4-*N*,*N'*-disubstituted 1,3,5-triazapentadienyl complexes.

**Acknowledgment.** The authors acknowledge the financial support of the Natural Science Foundation of China (No.20672070, 20772074), and Shanxi Scholarship Council of China (No. 201012, M.S.Z.).

**Supporting Information Available:** X-ray crystallographic data for **1**, **2**, and **4** (CCDC reference numbers 710048, 710049, and 716179). This material is available free of charge via the Internet at http://pubs.acs.org.

---

(32) Wood, D.; Yap, G. P. A.; Richeson, D. S. *Inorg. Chem.* **1999**, *38*, 5788–5794.

(33) Boche, G.; Buckl, K.; Martens, D.; Schneider, D. R. *Liebigs Ann. Chem.* **1980**, 1135–1171.

(34) Schlusser, M.; Desponds, O.; Lehman, R.; Muret, E.; Rauchschwsdbe, G. *Tetrahedron* **1993**, *49*, 10175–10203.