DALTON
FULL PAPER

Alkali-metal guanidinates: solid-state structural diversity in solvent-free derivatives

Garth R. Giesbrecht, Alex Shafir and John Arnold *

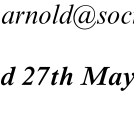
Department of Chemistry, University of California, Berkeley and the Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720-1460, USA.
E-mail: arnold@socrates.berkeley.edu

Received 27th May 1999, Accepted 12th August 1999

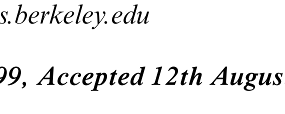
Reaction of 1,3-dicyclohexylcarbodiimide with alkali-metal amides, $MN(SiMe_3)_2$ (M = Li, Na or K), in non-co-ordinating solvents yielded the guanidinate salts $\{M[CyNC(N(SiMe_3)_2)NCy]\}_x$ (M = Li, $x = 2$; Na, $x = 3$; K, $x = 2$) in high yield. All three species were characterized by X-ray crystallography and found to be free from interaction with the solvent. These compounds represent the first base-free examples of alkali-metal guanidinate or amidinate species to be examined by X-ray crystallography. Although the structures of the lithium and potassium salts have precedent in amidinate and diazaallyl chemistry, the sodium salt represents a new mode of aggregation for species containing an anionic N–C–N linkage.

Introduction

Amidinates (**A**) are now well documented to be versatile ligands in organometallic chemistry, co-ordinating to a wide spectrum of metals from across the Periodic Table.[1] Recent work has shown that the related guanidinate anion (**B**)[2–4] can impart a similar co-ordination environment while offering increased stability due to the possibility of the additional resonance structure shown below.



A



B

While crystal structures of transition-,[2] lanthanide-[3] and main group-[4] metal guanidinate complexes have been reported, little is known about the structures and solid-state behavior of the corresponding alkali-metal salts of this class of ligands.[5] Our interest in alkali-metal guanidinates stems from some preliminary studies of lanthanide metals stabilized by N-donor ligands. A common problem encountered in lanthanide chemistry is the undesired incorporation of salt[6] and/or solvent molecules[7] into the lanthanide chloro precursors, LnL_2X (L = ancillary ligand, X = halide). To facilitate isolation of salt-free lanthanide complexes, the use of heavier alkali-metal salts is often favorable due to the ease of separation of the alkali-metal halide (*e.g.* NaCl or KCl).[8] Additionally, the avoidance of base-complexed starting materials would seem logical. Richeson and co-workers[3] recently described the isolation of $\{Li[CyNC(N(SiMe_3)_2)NCy]\}_x$ from diethyl ether, although the structure of this material has not yet been reported. Here we present the first solid-state structures of *base-free* lithium, sodium and potassium guanidinates, which are unique in that they represent new modes of co-ordination for the guanidinate ligand.

Experimental

General considerations

Standard Schlenk-line and glove box techniques were used.[9] Hexanes, toluene and benzene were purified by passage through a column of activated silica and degassed with argon prior to use,[10] C_6D_6 was vacuum transferred from sodium–benzophenone. 1,3-Dicyclohexylcarbodiimide was purchased from Sigma and distilled prior to use. Alkali-metal amides were prepared according to published procedures.[11] Melting points were determined in sealed capillary tubes under nitrogen and are uncorrected. The ^1H and $^{13}C-\{^1H\}$ NMR spectra were recorded at ambient temperature on a Bruker AM-300 spectrometer; ^1H chemical shifts are given relative to C_6D_5H (δ 7.15 ppm), $^{13}C-\{^1H\}$ to C_6D_6 (δ 128.3). The IR samples were prepared as Nujol mulls and taken between KBr plates. Elemental analyses were determined at the College of Chemistry, University of California, Berkeley. Single crystal X-ray determinations were performed at CHEXRAY, University of California, Berkeley.

General procedure for the syntheses of $\{M[CyNC(N(SiMe_3)_2)NCy]\}_x$ (M = Li, $x = 2$; Na, $x = 3$; K, $x = 2$)

1,3-Dicyclohexylcarbodiimide (1.23 g, 5.97 mmol) and $LiN(SiMe_3)_2$ (1.01 g, 6.00 mmol) were combined in a large Schlenk tube and toluene (15 mL) was added. The colorless solution was stirred overnight, the volume reduced and the solution cooled to −30 °C. The product was isolated as small colorless needles (2.05 g, 92% yield). Alternatively, the product may be crystallized from benzene. The sodium and potassium salts were prepared analogously in similar yields. $\{Li[CyNC(N(SiMe_3)_2)NCy]\}_2$, mp 160–163 °C (decomp.) (Found: C, 60.72; H, 10.79; N, 11.07%; *m*/*z* 367 (M^+, ligand only). $C_{19}H_{40}LiN_3Si_2$ requires C, 61.07; H, 10.79; N, 11.25%; *M* 747); $\tilde{\nu}_{max}/cm^{-1}$ 1496s, 1250s, 954s, 835s and 822s (Nujol); $\delta_H(C_6D_6)$ 3.38 (m, 2 H, unique Cy H), 1.95–1.15 (m, 20 H, C_6H_{10}) and 0.33 (s, 18 H, $SiMe_3$); $\delta_C(C_6D_6)$ 164.3 (NCN), 54.6, 39.0, 27.0 and 26.5 (C_6H_{11}), 3.0 ($SiMe_3$). $\{Na[CyNC(N(SiMe_3)_2)NCy]\}_3\cdot C_6H_5Me$, mp 154–156 °C (Found: C, 59.08; H, 11.02; N, 10.11%; *m*/*z* 367 (M^+, ligand only). $C_{19}H_{40}N_3NaSi_2$ requires C, 58.56; H, 10.35; N, 10.78%; *M* 1169); $\tilde{\nu}_{max}/cm^{-1}$ 1483s, 1340m, 1250s, 954s and 835s (Nujol); $\delta_H(C_6D_6)$ 3.37 (m, 2 H, unique Cy H), 1.95–1.20 (m, 20 H, C_6H_{10}) and 0.31 (s, 18 H, $SiMe_3$); $\delta_C(C_6D_6)$ 163.2 (NCN), 55.1, 39.0 and 26.2 (coincident) (C_6H_{11}) and 2.4 ($SiMe_3$). $\{K[CyNC(N(SiMe_3)_2)NCy]\}_2\cdot C_6H_6$, mp 164–167 °C (Found: C, 58.83; H, 10.23; N, 9.31%; *m*/*z* 367 (M^+, ligand only). $C_{22}H_{43}KN_3Si_2$ requires C, 59.40; H, 9.74; N, 9.45%;

M 890); $\tilde{\nu}_{max}$/cm^{-1} 1474s, 1335s, 1250s, 1110s, 961s, 935s and 834s (Nujol); δ_H(C_6D_6) 3.27 (m, 2 H, unique Cy H), 1.95–1.25 (m, 20 H, C_6H_{10}) and 0.32 (s, 18 H, $SiMe_3$); δ_C(C_6D_6) 157.5 (NCN), 55.6, 38.8, 26.8 and 26.5 (C_6H_{11}) and 2.8 ($SiMe_3$).

X-Ray crystallography

Table 4 lists a summary of crystallographic data for all structurally characterized compounds. Data for all three compounds were collected on a Siemens SMART diffractometer/CCD area detector[12] with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å); empirical absorption corrections were applied.[13] Structures were solved by direct methods[14] and refined by full matrix least squares procedures.[15] For the sodium and potassium salts all non-hydrogen atoms except for disordered solvent atoms were refined anisotropically. For the lithium salt, silicon atoms were refined anisotropically; all others were refined isotropically.

CCDC reference number 186/1624.

Results and discussion

The guanidinate salts $\{M[CyNC(N(SiMe_3)_2)NCy]\}_x$ (M = Li, $x = 2$; Na, $x = 3$; K, $x = 2$) were prepared from 1,3-dicyclohexylcarbodiimide and the corresponding alkali-metal amide following procedures established earlier, eqn. (1).[3] All three

$$CyN{=}C{=}NCy + MN(SiMe_3)_2 \xrightarrow[\text{hexanes or toluene}]{\text{RT}} \{M[CyNC(N(SiMe_3)_2)NCy]\}_x \quad (1)$$

M	x
Li	2
Na	3
K	2

complexes were obtained in high yields using hexanes or toluene as solvent. The ^{1}H NMR spectrum of each compound indicates the presence of a single, symmetric species in solution under ambient conditions. Formation of guanidinate complexes is further confirmed *via* IR spectroscopy by the absence of the N=C=N stretch of the parent carbodiimide (2117 cm^{-1}) and the appearance of a C=N stretch in the range 1496 to 1474 cm^{-1} for each of the alkali-metal derivatives. Attempts to elucidate the nuclearity of the compounds in the gas phase by EI-MS were unsuccessful; we therefore turned to X-ray crystallography in order to assess the nature of aggregation in the solid state.

Even though only a low resolution structure of the lithium guanidinate was available, it revealed all the major structural features of the compound in the solid state. The molecular structure of the lithium salt is illustrated in Fig. 1; bond lengths and angles are given in Table 1. The compound crystallizes as a dimer in which two guanidinate ligands are perpendicular to each other (the dihedral angle between the two N–C–N planes is 92.06°). The two lithium centers are approximately equidistant to three nitrogen atoms each [1.98(3) to 2.03(3) Å]. The vector passing through the two lithium atoms is roughly parallel to the N2–C1–N3 plane while orthogonal to the N–C–N plane of the second guanidinate. There is some disorder in the lithium sites although this does not affect the overall interpretation of the structure. Thus, lithium sites 1 and 2 were refined as being 63% occupied and a second pair of lithium atoms (Li3, Li4), orthogonal to the N2–C1–N3 plane and parallel to the N5–C20–N6 plane, were refined with 37% occupancy but are not shown in Fig. 1 for the sake of clarity. The structure is related to that of $\{[p\text{-}MeC_6H_4C(NSiMe_3)_2Li](NCC_6H_4Me\text{-}p)\}_2$,[17] which exhibits a similar core geometry, specifically in the dihedral twist of N–C–N planes.[18] Although the two guanidinate ligands are not chemically equivalent, solution ^{1}H NMR shows only one set of ligand resonances. This may be attributed to rapid equilibration of the ligands on the NMR timescale or a more highly symmetric solution structure.

Table 1 Selected bond distances (Å) and angles (°) for $\{Li[CyNC(N(SiMe_3)_2)NCy]\}_2$

C1–N2	1.33(1)	C1–N3	1.31(1)
C20–N5	1.31(2)	C20–N6	1.35(2)
N2–Li1	1.98(3)	N5–Li1	2.03(3)
N6–Li1	2.03(3)	N3–Li2	2.02(4)
N5–Li2	2.01(4)	N6–Li2	1.96(4)
N1–C1–N2	121(1)	N5–C20–N6	115(1)
N2–Li1–N5	126(2)	N2–Li1–N6	132(2)
N5–Li1–N6	67(1)	N3–Li2–N5	121(2)
N3–Li2–N6	125(2)	N5–Li2–N6	69(1)

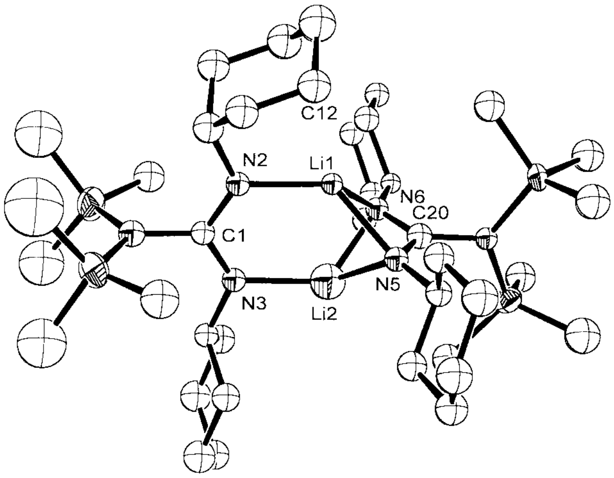


Fig. 1 An ORTEP[16] view of $\{Li[CyNC(N(SiMe_3)_2)NCy]\}_2$ drawn with 50% probability ellipsoids.

In addition to the unusual nature of the N_4Li_2 core, the dimer is free from interaction with the solvent. Although simple base-free lithium amides such as $[(Me_3Si)_2NLi]_3$[19] and $[(PhCH_2)_2NLi]_3$[20] have been crystallographically characterized, to our knowledge no such amidinate or guanidinate species have been reported.[21] An unusual feature of the solid-state structure is the bending of one of the cyclohexyl groups (C8–C13) towards the lithium atoms of the N_4Li_2 core. The closest Li2 ··· H distance (3.87 Å) is large enough to discount the possibility of an intramolecular interaction and is therefore more likely an effect of crystal packing.

An ORTEP view of the sodium salt is given in Fig. 2. Selected bond lengths and angles are presented in Table 2. The sodium salt crystallizes as trimeric aggregates composed of three sodium atoms bridged by three μ^2-guanidinate ligands. Two crystallographically independent trimers (A and B) possessing similar geometries exist in the asymmetric unit; for conciseness only A is shown. In each trimer the N–C–N planes of the guanidinate ligand are roughly orthogonal to the plane defined by the three sodium atoms, although one of the guanidinates in B is tilted significantly with respect to the Na_3 plane (114.1°). Each sodium atom is bound to four nitrogen atoms, with bond distances ranging from 2.335(7) to 2.726(7) Å, which are similar to those reported for the etherate, $[PhC(NSiMe_3)_2Na(Et_2O)]_2$ [2.397(5) to 2.725(5) Å].[22] The distances between sodium atoms within the trimer [3.156(5), 3.167(4) and 3.169(4) Å] are longer than that observed in $[PhC(NSiMe_3)_2Na(Et_2O)]_2$ [2.741(4) Å]. Although a number of sodium benzamidinates have been reported,[22,23] no base-free examples have been cited. We know of no previously reported sodium guanidinate species for comparison. Whereas planar M_3N_3 cores are known for base free amides,[19,20] this mode of aggre-

Table 2 Selected bond distances (Å) and angles (°) for $\{Na[CyNC(N(SiMe_3)_2)NCy]\}_3{\cdot}C_6H_5Me$ (trimer A only)

C1–N1	1.314(9)	C1–N2	1.342(9)
C2–N4	1.335(9)	C2–N5	1.34(1)
C3–N7	1.318(9)	C3–N8	1.311(9)
N1–Na1	2.726(7)	N1–Na2	2.370(7)
N2–Na1	2.347(7)	N2–Na2	2.532(7)
N4–Na2	2.403(7)	N4–Na3	2.678(7)
N5–Na2	2.585(7)	N5–Na3	2.335(7)
N7–Na1	2.361(7)	N7–Na3	2.598(7)
N8–Na1	2.557(7)	N8–Na3	2.345(7)
N1–C1–N2	116.4(7)	N4–C2–N5	116.3(7)
N7–C3–N8	116.5(7)	N1–Na1–N2	52.2(2)
N1–Na1–N7	119.1(2)	N1–Na1–N8	146.1(2)
N2–Na1–N7	157.0(3)	N2–Na1–N8	118.9(3)
N7–Na1–N8	53.9(2)	N1–Na2–N2	54.7(2)
N1–Na2–N4	163.9(3)	N1–Na2–N5	118.8(2)
N2–Na2–N4	120.9(3)	N2–Na2–N5	144.6(2)
N4–Na2–N5	54.1(2)	N4–Na3–N5	53.4(2)
N4–Na3–N7	147.1(2)	N4–Na3–N8	121.5(2)
N5–Na3–N7	116.6(3)	N5–Na3–N8	157.4(3)
N7–Na3–N8	53.5(2)		

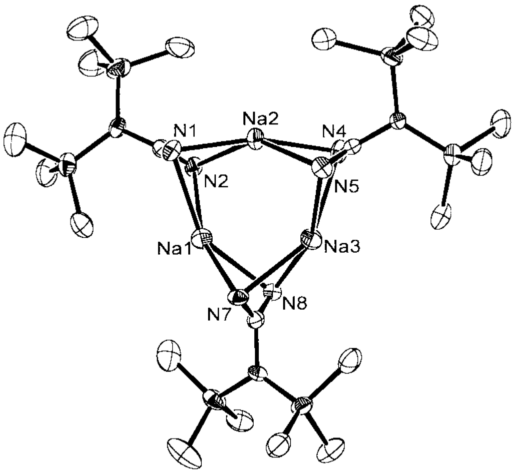


Fig. 2 An ORTEP view of $\{Na[CyNC(N(SiMe_3)_2)NCy]\}_3{\cdot}C_6H_5Me$ drawn with 50% probability ellipsoids. Only trimer A of the asymmetric unit is shown for clarity. The co-crystallized molecule of toluene is also omitted.

gation appears to be novel for alkali-metal salts of compounds incorporating anionic N–C–N units.

The molecular structure of the potassium derivative is presented in Fig. 3. A partial list of bond lengths and angles is available in Table 3. The molecule crystallizes as a dimer that lies on a crystallographic inversion center. In contrast to the dilithio species, the two guanidinate ligands in the potassium salt are parallel to each other. Each potassium is bound to all four nitrogen atoms of the N_4K_2 core [2.765(2) to 2.806(2) Å] with the K1 ··· K1* vector [3.2219(9) Å] orthogonal to the two guanidinate N–C–N planes. The N_4K_2 core is similar to that displayed in the 1,3-diazaallyl potassium salt $[\{N(SiMe_3)C(2,5\text{-}Me_2C_6H_3)NC(2,5\text{-}Me_2C_6H_3)CH(SiMe_3)\}(2,5\text{-}Me_2C_6H_3)K]_2$ [K ··· K′ 3.299(5), K–N 2.77(1) to 2.95(1) Å].[24] Each potassium center in the guanidinate shares a close intermolecular contact with a silylmethyl group [C(17)] of a neighboring dimer with a K ··· C distance of 3.244(2) Å and K ··· H distances ranging from 2.83 to 3.21 Å. The geometry of the core nitrogens is distorted tetrahedral, with bond angles ranging from 71.20(4) to 133.5(1)° for N1 and 70.32(4) to 136.7(1)° for N2. Although potassium, rubidium and cesium *N,N′*-bis(trimethylsilyl)benzamidinates are known,[22,23c] no structural data for these compounds have been reported.[25] As such, the potassium derivative represents the first base-free

Table 3 Selected bond distances (Å) and angles (°) for $\{K[CyNC(N(SiMe_3)_2)NCy]\}_2{\cdot}C_6H_6$

C1–N1	1.330(2)	C1–N2	1.324(2)
N1–K1	2.770(2)	N2–K1	2.789(2)
N1*–K1	2.765(2)	N2*–K1	2.806(2)
N1–C1–N2	117.3(2)	N1–K1–N2	48.11(5)
N1–K1–N1*	108.80(4)	N1–K1–N2*	89.67(5)

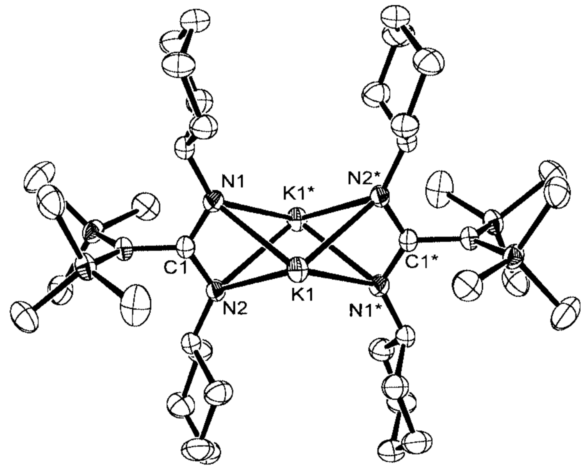


Fig. 3 An ORTEP view of $\{K[CyNC(N(SiMe_3)_2)NCy]\}_2{\cdot}C_6H_6$ drawn with 50% probability ellipsoids. The co-crystallized molecule of benzene is omitted for clarity.

potassium guanidinate or amidinate species to be structurally characterized.[26]

Conclusion

The species presented here fall into the general category of structures involving N–C–N anionic units bound to M^+ cations. Included in this group are amidinates,[1] guanidinates[2–5] and 2-aminopyridines.[27] Also of note are the related triazenides[26] in which the central carbon atom has been replaced by a nitrogen. Alkali-metal salts of these classes of compounds are well known, and the metal center is usually co-ordinated by either a basic solvent molecule (THF, Et_2O, MeCN) or an external base which has been added in order to promote isolation of the salt in a solid form (PhCN, TMEDA, PMDETA pentamethyldiethylenetriamine). Although simple solvent- or base-free alkali-metal amides are still quite unusual, it is well recognized that extra electronegative atoms or groups can compensate for the lack of Lewis basicity through aggregation. The general structural motif common to all three compounds is that in each two M^+ ions doubly bridge the two nitrogen centers of a given ligand. Although this bonding mode is common in alkali-metal chemistry, the metal centers are usually tetrahedral, with the last co-ordination site occupied by a Lewis base. Our goal in producing these metal salts is to be able to generate guanidinate lanthanide complexes whose reactivity will not be diminished by the presence of complexed solvents (THF or Et_2O) or salts (such as LiCl). The synthesis of lanthanide complexes utilizing these starting materials is currently underway and will be the subject of future reports.

Acknowledgements

We thank the Department of Energy for supporting this research.

References

1 J. Barker and M. Kilner, *Coord. Chem. Rev.*, 1994, **133**, 219; F. T. Edelmann, *Coord. Chem. Rev.*, 1994, **137**, 403.

Table 4 Crystallographic data for $\{M[CyNC(N(SiMe_3)_2NCy]\}_x$ (M = Li, $x = 2$; Na, $x = 3$; K, $x = 2$)

Formula	$C_{38}H_{80}Li_2N_6Si_4$	$C_{64}H_{128}N_9Na_3Si_6$	$C_{44}H_{86}K_2N_6Si_4$
M	747.32	1261.26	889.74
Color, habit	Colorless, needle	Colorless, plate	Colorless, block
Crystal size/mm	0.36 × 0.17 × 0.09	0.29 × 0.18 × 0.16	0.32 × 0.27 × 0.09
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)
a/Å	9.771(1)	56.127(1)	13.8550(2)
b/Å	29.892(4)	13.693(1)	13.8460(2)
c/Å	16.565(2)	42.392(1)	14.5240(1)
β/°	104.505(3)	93.930(1)	106.160(1)
V/Å^3	4684.30(1)	32503.6(7)	2676.14(5)
Z	4	16	2
D_c/g cm^{-3}	1.06	1.09	1.10
$2\theta_{max}$/°	41.5	52.1	52.1
T/°C	−103	−110	−113
Total reflections	14637	76799	12935
Independent reflections	4961	24305	4988
T_{max}	0.895	0.922	0.923
T_{min}	0.710	0.717	0.890
μ(Mo-Kα)/cm^{-1}	1.53	1.58	3.06
R_{int}	0.13	0.08	0.03
R	0.071	0.063	0.031
R'	0.078	0.081	0.039
Goodness of fit	1.66	2.10	1.28
Data	1639	10247	3426

2 K. T. Holman, S. D. Robinson, A. Sahajpal and J. W. Steed, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 15; J. R. S. da Maia, P. J. Gazard, M. Kilner, A. S. Batsanov and J. A. K. Howard, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 4625; S. D. Robinson and A. Sahajpal, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 3349; P. J. Bailey, S. F. Bone, L. A. Mitchell, S. Parsons, S. J. Taylor and L. J. Yellowlees, *Inorg. Chem.*, 1997, **36**, 867; P. J. Bailey, L. A. Mitchell and S. Parsons, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 2839; H. K. Yip, C. M. Che, Y. Zhou and T. C. W. Mak, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1369; E. M. A. Ratilla, B. K. Scott, M. S. Moxness and N. M. Kostic, *Inorg. Chem.*, 1990, **29**, 918.

3 Y. Zhou, G. P. A. Yap and D. S. Richeson, *Organometallics*, 1998, **17**, 4387.

4 S. J. Aeilts, M. P. Coles, D. C. Swenson, R. F. Jordan and V. G. Young, *Organometallics*, 1998, **17**, 3265; P. J. Bailey, R. O. Gould, C. N. Harmer, S. Pace, A. Steiner and D. S. Wright, *Chem. Commun.*, 1997, 1161.

5 For a related magnesium guanidinate salt see: B. Srinivas, C. C. Chang, C. H. Chen, M. Y. Chiang, I. T. Chen, Y. Wang and G. H. Lee, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 957.

6 D. L. Clark, R. V. Hollis, B. L. Scott and J. G. Watkins, *Inorg. Chem.*, 1996, **35**, 667 and refs. therein.

7 W. J. Evans, *Adv. Organomet. Chem.*, 1985, **24**, 131; C. J. Schaverien, *Adv. Organomet. Chem.*, 1994, **36**, 289.

8 D. L. Clark, A. P. Sattleberger, S. G. Bott and R. N. Vrtis, *Inorg. Chem.*, 1989, **28**, 1771; D. L. Clark, T. M. Frankcom, M. M. Miller and J. G. Watkin, *Inorg. Chem.*, 1992, **31**, 1628; D. L. Clark and J. G. Watkin, *Inorg. Chem.*, 1993, **32**, 1766.

9 E. F. Shriver and M. A. Bredzon, *The Manipulation of Air Sensitive Compounds*, Wiley, New York, 1986.

10 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.

11 C. R. Kruger and H. Niederprum, *Inorg. Synth.*, 1966, **8**, 15; E. H. Barash, *Inorg. Chem.*, 1993, **32**, 497.

12 SMART Area-Detector Software Package, Siemens, Madison, WI, 1993.

13 XPREP, Part of the SHELXTL Crystal Structure Determination Package, Siemens, Madison, WI, 1995.

14 SIR92, A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1993, **26**, 343.

15 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1992.

16 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

17 M. S. Eisen and M. Kapon, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 3507.

18 T. Gebauer, K. Dehnicke, H. Goesmann and D. Fenske, *Z. Naturforsch.*, *Teil B*, 1994, **49**, 1444.

19 (*a*) D. Mootz, A. Zinnius and B. Bottcher, *Angew. Chem.*, *Int. Ed. Engl.*, 1969, **8**, 378; (*b*) R. D. Rogers, J. L. Atwood and R. Gruning, *J. Organomet. Chem.*, 1978, **157**, 229.

20 D. R. Armstrong, R. E. Mulvey, G. T. Walker, D. Barr and R. Snaith, *J. Chem. Soc.*, *Dalton Trans.*, 1988, 617; D. Barr, W. Clegg, R. E. Mulvey and R. Snaith, *J. Chem. Soc.*, *Chem. Commun.*, 1984, 285.

21 J. Barker, D. Barr, N. D. R. Barnett, W. Clegg, I. Cragg-Hine, M. G. Davidson, R. P. Davies, S. M. Hodgson, J. A. K. Howard, M. Kilner, C. W. Lehmann, I. Lopez-Solera, R. E. Mulvey, P. R. Raithby and R. Snaith, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 951; T. Chivers, M. Parvez and G. Schatte, *J. Organomet. Chem.*, 1998, **550**, 213.

22 D. Stalke, M. Wedler and F. T. Edelmann, *J. Organomet. Chem.*, 1992, **431**, C1.

23 (*a*) M. Wedler, F. Knosel, M. Noltemeyer, F. T. Edelmann and U. Behrens, *J. Organomet. Chem.*, 1990, **388**, 21; (*b*) M. Wedler, F. Knosel, U. Pieper, D. Stalke, F. T. Edelmann and H. D. Amberger, *Chem. Ber.*, 1992, **125**, 2171; (*c*) K. Dehnicke, *Chem.-Ztg.*, 1990, **F114**, 295.

24 P. B. Hitchcock, M. F. Lappert and D. S. Liu, *J. Organomet. Chem.*, 1995, **488**, 241.

25 G. D. Whitener, J. R. Hagadorn and J. Arnold, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 1249.

26 P. Gantzel and P. J. Walsh, *Inorg. Chem.*, 1998, **37**, 3450.

27 L. M. Engelhardt, G. E. Jacobsen, P. C. Junk, C. L. Raston, B. W. Skelton and A. H. White, *J. Chem. Soc.*, *Dalton Trans.*, 1988, 1011 and refs. therein.

Paper 9/04295D