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Towards the formation of dimeric and trimeric lithium benzamidinates: characterization of intermediate structures

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p-Toluonitrile reacts with $\mathrm{LiN(TMS)_2}$ in diethyl ether (1 : 1) to yield a dimeric complex **1** containing a lithium benzamidinate unit, a molecule of *p*-toluonitrile attached to the lithium atom and a molecule of lithium bis(trimethylsilyl)amide coordinated to a lithium–nitrogen bond, of the benzamidinate unit, forming a four-membered ring. The crystal structure of **1** shows the molecularity, the stereochemistry and the manner of activation of nitriles by lithium amido salts in the formation of amidinates. When the same reaction is carried out in hexane, the trimeric complex **2** is formed, containing lithium atoms simultaneously π- and σ-bonded to amidine moieties. When the ratio of *p*-toluonitrile and $\mathrm{LiN(TMS)_2}$ in diethyl ether–hexane is 2 : 1, complex **1** is obtained, which can be treated with two equivalents of $\mathrm{LiN(TMS)_2}$ to produce **3**.

Introduction

During the last decade there has been increasing attention regarding the effect of added salts in miscellaneous chemical transformations.[1] The cases with the most substantial salt effects, which have been studied, are those corresponding to lithium salts (LiX).[2] This partly results from the properties of the lithium cation and its derivatives, particularly (i) higher charge density as compared to all other alkali-metal cations, (ii) fair solubility of the lithium salts and the corresponding organometallic complexes in organic solvents, and (iii) the ready availability of lithium reagents.[3]

The predominance of the lithium reagents in organic chemistry is well established and it is appraised that beyond 95% of the natural product syntheses employ at least one (among them, many lithium amides or other N-lithiated species).[4] Likewise, lithium salts are also obtained as intermediates and/or by-products in transfer reagents for anionic species,[5] metallation[6] and strong Brønsted bases and nucleophiles inducing deprotonation reactions.[7] For example, N-lithiated species constitute a very important class of organolithium reagents. They are the preferred bases for formation of ketone enolates,[8] generating low steady-state concentrations of some relatively unstable carbanions,[9] and for the preparation of heterocyclic thiazenes incorporating an RC(N–)N⟨ moiety using lithium amidinates.[10] Thus, a thorough understanding of the interactions between the LiX salts and other reactants in solution is of primary importance. However, the coordination chemistry of organolithium compounds and the mechanisms of organolithium–base reactions are uncommonly complex and poorly understood.[11] This complexity stems from a high tendency of organolithium compounds to self assemble into higher aggregates, an event that is considerably dependent on the choice of solvent and the precise preparation conditions. This complexity is enhanced also by the rapid solvent exchanges within the various aggregates as well as the extreme oxygen and moisture sensitivity of most organolithium derivatives. As an outcome, many of the organolithium reagents are prepared *in situ* without a thorough and accurate characterization.[4,6a,11d,12]

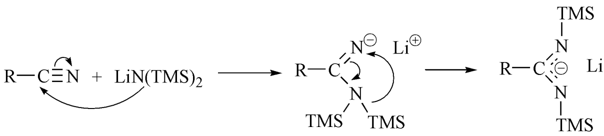
Among the diverse N-lithiated compounds, lithium amidinates and N-silylated lithium benzamidinates have been considered useful reagents for the bidentate chelation of main group, early- and late-transition metal centers.[13] Several methods have been utilized to synthesize amidine– or N-silylated benzamidine–transition metal complexes, but principal among these has been the *in situ* reaction of the corresponding lithium salt with the metal halide.[13] Using this type of procedure with early-transition metal halide salts, it is possible to produce homogeneous complexes that have been used as catalysts for the stereoregular polymerization of α-olefins.[14] Recently, we have shown that a new type of polymer (elastomeric polypropylene) was obtained using this type of complex.[15] Thus, the use of the amidine derivatives as novel types of ancillary spectator ligands in organometallic chemistry is spreading rapidly.[16]

However, despite the extensive use of lithium amidinate compounds, their structural characterization is rather incomplete because many are prepared *in situ* and used without direct spectroscopic evidence of their solution and/or solid state structure. It is noteworthy that published work on lithium amidinate compounds is restricted to a short metallation study *via* infrared spectroscopy,[17] and to the crystal structures of a series of arylbis(trimethylsilyl)amidinate complexes, $\mathrm{\{Li[4\text{-}MeC_6H_4C(NSiMe_3)_2]\cdot thf\}_2}$ (thf = tetrahydrofuran),[18] $\mathrm{\{Li[4\text{-}XC_6H_4C(NSiMe_3)_2]\cdot NCC_6H_4X\text{-}4\}_2}$ (X = H or Me),[19] $\mathrm{\{Li[PhC(NSiMe_3)_2]\}_3\cdot NCPh}$,[20] $\mathrm{Li[PhC(NPh)_2]\cdot pmdien}$ (pmdien = *N*,*N*,*N′*,*N″*,*N″*-pentamethyldiethylenetriamine),[21] $\mathrm{\{Li[PhNC(Ph)NPh]\cdot hmpa\}_2}$ (hmpa = $\mathrm{O{=}P(NMe_2)_3}$),[22] $\mathrm{Li[PhNC(Ph)NPh]\cdot tmen}$ (tmen = $\mathrm{Me_2N(CH_2)_2NMe_2}$),[21] $\mathrm{Li[PhNC(Ph)NPh]\cdot pmdien}$,[21] $\mathrm{\{Li[PhNC(Me)NPh]\cdot hmpa\}_2}$,[21] $\mathrm{Li_4Mg\{PhC(NSiMe_3)_2\}_4(O)}$,[23] and a series of $\mathrm{Li[{}^nBuC(N^tBu)_2]}$ compounds.[24]

Lithium N-silylated amidinates are frequently synthesized by the reaction of a nitrile with $\mathrm{LiN(TMS)_2}$ (TMS = $\mathrm{Si(CH_3)_3}$). This route is known to proceed by a mechanism in which the nitrile is attacked by the $\mathrm{LiN(TMS)_2}$ producing a lithium ketimide. The latter undergoes a rapid 1,3-sigmatropic shift rearrangement to the corresponding N-silylated benzamidinate (eqn. 1). Interestingly, a similar 1,3-sigmatropic hydrogen shift rearrangement has been observed recently for a sodium ketimide, bearing an *n*-butyl substituent to an imido carbon center, thus producing alkali-metal 1-azaallyl complexes.[25]

Another pathway for the preparation of lithium N-silylated benzamidinates is the reaction of carbodiimide with an organolithium compound (eqn. 2).

Conceptual questions regarding the activation of the nitrile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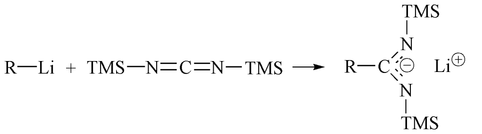

(2)

by the amido group preceding the rapid 1,3-sigmatropic shift rearrangement of N-silylated complexes, are: (i) is the nitrile activated by the LiN(TMS)$_2$, (ii) what is the molecularity for such a rearrangement process (monomeric *vs.* dimeric or polymeric), (iii) what is the approaching stereochemistry of the N-silylated amido group to the nitrile. To shed some light on them, we have studied the reaction of LiN(TMS)$_2$ with *p*-toluonitrile, used as a probe. Here we report the synthesis, characterization and solid state X-ray diffraction studies for a dimeric and a trimeric benzamidinate complex. The different compounds were obtained under similar conditions, when the syntheses were performed in different solvent media. The solid structure of the dimeric compound reveals the key intermediate for the formation of the amidinate salt, the mode of activation and the stereochemistry of the nitrile molecule together with the molecularity of the process.

Experimental

General procedure

All manipulations of air-sensitive materials were carried out with the vigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line, or interfaced to a high-vacuum (10^{-6} Torr) line, or in a nitrogen-filled Vacuum Atmospheres glove-box with a medium-capacity recirculator (1–2 ppm O_2). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Ether solvents were distilled under argon from sodium–benzophenone, hydrocarbon solvents (toluene, C_6D_6, hexane) under nitrogen from Na–K alloy. All solvents for vacuum line manipulations were stored *in vacuo* over Na–K alloy in resealable bulbs. *p*-Toluonitrile was degassed and freshly distilled under argon. The solid LiN(SiMe$_3$)$_2$ was prepared according to the literature method.[26] The ^{1}H NMR spectra were recorded on a Bruker AM-200 spectrometer. Chemical shifts are referenced to internal solvent resonances and reported relative to tetramethylsilane. The experiments were conducted in Teflon valve-sealed tubes (J. Young) after vacuum transfer of the solvent in a high-vacuum line.

Syntheses

Complex 1. To a Schlenk flask containing 20 mL dry diethyl ether, 2.651 g (15.87 mmol) of LiN(SiMe$_3$)$_2$ were added producing a white suspension. The mixture was stirred and, after cooling to 0 °C, 1.8573 g (1.89 mL, 15.87 mmol) of melted *p*-toluonitrile were introduced rapidly through a heated syringe (40 °C) under a flow of argon. After the addition was complete the mixture turned immediately into a yellow homogeneous solution. This was allowed to warm to room temperature and stirred for 16 h. The solvent was vacuum evaporated and the residue (viscous yellow oil) dissolved in 20 mL hexane and cooled to −45 °C for 70 hours. The precipitate was cold filtered and vacuum dried, producing 1.31 g (26%) of light yellow crystals of complex **1** (Found: C, 57.50; H, 8.73; N, 8.35. $C_{32}H_{60}Li_2N_4OSi_4$ requires C, 59.80; H, 9.35; N, 8.72%). ^{1}H NMR(200 MHz, C_6D_6): δ 7.30 (d, 2H, $^3J = 7.7$, *o*-H), 7.06 (d, 2H, $^3J = 8.0$, *o*-H), 6.95 (d, 2H, $^3J = 8.0$, *m*-H), 6.48 (d, 2H, $^3J = 7.7$, *m*-H), 3.40 (q, 4H, $^3J = 10$, OCH_2), 2.08 (s, 3H, CH$_3$), 1.74 (s, 3H, CH$_3$), 1.23 (t, 6H, $^3J = 10$ Hz, CH$_2$CH_3), 0.19 (s, 9H, Si(CH_3)$_3$), 0.03 (s, 9H, Si(CH_3)$_3$). MS (CI, isobutane): *m*/*z* 644 (M$^+$), 350 (M$^+$ − 4TMS).

Crystallography. Owing to the extreme sensitivity of the compound to moisture and oxygen, a suitable crystal for X-ray analysis was placed inside a glove-box in dry and degassed Parathon-N oil (Du-Pont). Then it was mounted on a Philips PW1100/20 four circle diffractometer where it met a cold stream of nitrogen at 220 K. It must be noted that the crystal has a weak diffraction power and, in addition, shows an anisotropic decay during more than a week the time required for full data collection. The anisotropic decay may be due to instability under X-ray irradiation. As a result, the observed reflections $[I > 2\sigma(I)]$ were only 23% of the total number of measured reflections. Intensities were corrected in the usual way except for absorption. The structure was solved by direct methods,[27a] and refined, based on F^2, by block-diagonal least-squares techniques.[27b] All non-hydrogen atoms were refined anisotropically. Owing to the above mentioned factors the refinement was halted at $R = 0.0866$. Hydrogen atoms were included at calculated positions and refined isotropically in one block. The *d*(C–H) used was 1.08 Å. Crystallographic experimental details, measurement conditions and structure refinement details are summarized in Table 1.

Complex 2. To a Schlenk flask containing 40 mL of dry hexane, 2.74 g (16.4 mmol) of LiN(SiMe$_3$)$_2$ were added producing a homogeneous solution. This was stirred and, after cooling to 0 °C, 1.962 g (2.0 mL, 16.4 mmol) of melted *p*-toluonitrile were introduced rapidly through a heated syringe (40 °C) under a flow of argon. After complete addition of the nitrile the mixture turned into a yellow solution. This was allowed to warm to room temperature and stirred for 16 h. The hexane was vacuum evaporated and the residue (viscous yellow oil) dissolved in 3 mL hexane and cooled to −78 °C for 3 weeks. The precipitate was cold filtered and vacuum dried, producing 1.25 g (24% based on the lithium complex) of light yellow crystals of complex **2** (Found: C, 59.72; H, 8.73; N, 10.32. $C_{50}H_{82}Li_3N_7Si_6$ requires C, 61.85; H, 8.45; N, 10.10%). ^{1}H NMR(200 MHz, C_6D_6): δ 7.25 (d, 2H, $^3J = 8.0$, *o*-H), 7.16 (d, 2H, $^3J = 8.0$, *o*-H), 7.09 (d, 2H, $^3J = 8.0$, *o*-H), 6.98 (d, 2H, $^3J = 8.0$, *o*-H), 6.90 (d, 2H, $^3J = 8.0$, *m*-H), 6.86 (d, 2H, $^3J = 8.0$, *m*-H), 6.41 (d, 2H, $^3J = 8.0$, *m*-H), 6.37 (d, 2H, $^3J = 8.0$ Hz, *m*-H), 2.04 (s, 3H, CH$_3$), 1.99 (s, 3H, CH$_3$), 1.70 (s, 3H, CH$_3$), 1.65 (s, 3H, CH$_3$), 0.59 (s, 9H, Si(CH_3)$_3$), 0.56 (s, 9H, Si(CH_3)$_3$), 0.17 (s, 18H, Si(CH_3)$_3$), 0.13 (s, 18H, Si(CH_3)$_3$).

Crystallography. X-Ray crystallographic experiments were carried out on a Nonius Kappa CCD diffractometer with graphite-monochromatized Mo-Kα radiation. Crystals were placed into Parathon-N oil in a glove-box. Single crystals were mounted on the diffractometer under a stream of cold N_2 at 220 K. Data collection and reduction and cell refinements were carried out with the Nonius software package.[28] The structure solution and refinement were carried out by the SHELXS 97[29] and SHELXL 97[30] software packages respectively. The ORTEP program incorporated in the TEXRAY Structure Analysis Package was used for molecular graphics.[31] Relevant crystallographic information is summarized in Table 1.

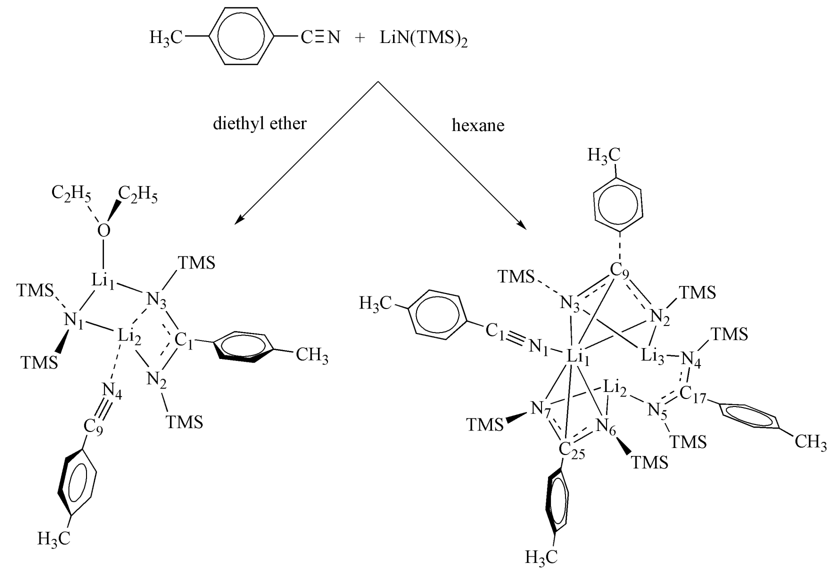
CCDC reference numbers 156013 and 156014.

See http://www.rsc.org/suppdata/dt/b1/b100251l/ for crystallographic data in CIF or other electronic format.

Complex 3. To a Schlenk flask containing 0.815 g (1.30 mmol) of the crystalline complex **1** dissolved in 35 mL dry diethyl ether, at 0 °C was introduced 0.296 g (0.3 mL, 2.60 mmol) of melted *p*-toluonitrile rapidly through a heated syringe (40 °C) under a flow of argon. After complete addition of the nitrile the mixture was stirred for 1 hour, and then at room

Table 1 Crystallographic experimental details for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{32}H_{60}Li_2N_4OSi_4$	$C_{50}H_{82}Li_3N_7Si_6$
Formula weight	643.08	970.59
T/K	220(2)	220(1)
Wavelength, λ/Å	0.71069	0.71069
Crystal system, space group	Monoclinic, $P2_1/n$	Orthorhombic, $P2_12_12_1$
a/Å	10.752(3)	13.506(2)
b/Å	10.695(3)	14.668(4)
c/Å	36.613(9)	30.918(9)
β/°	94.79(3)	
V/Å^3	4196(3)	6125(3)
Z	4	4
μ/mm^{-1}	0.168	0.172
Reflections collected/unique	7583/7279 [R(int) = 0.1611]	27733/5668 [R(int) = 0.0480]
Observed reflections [$I > 2\sigma(I)$]	1666	2679
Data/restraints/parameters	7279/0/404	5668/0/602
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0866, 0.1209	0.0383, 0.0658
(all data)	0.2635, 0.1573	0.1155, 0.0811



(3)

1 **2**

temperature for 16 h. The solvent was vacuum evaporated to obtain 1 g (99%) of complex **3** as compared with a spectroscopically pure sample. It was recrystallized from 5 mL hexane cooled to −20 °C for 24 hours, producing 0.31 g (30%) of light yellow crystals. The full characterization of complex **3** was obtained by comparing its ^{1}H NMR and crystal structure to those of an authentic sample.[19]

Results and discussion

Complex **1** was prepared by addition of bis(trimethylsilyl)-amidolithium to an equimolar solution of *p*-toluonitrile in diethyl ether. When the same reaction was carried out in the presence of hexane in the absence of polar solvents, complex **2** was obtained (eqn. 3). The light yellow crystals of both complexes were characterized by MS, NMR spectroscopy in addition to low-temperature X-ray diffraction studies.

The ^{1}H NMR spectrum of complex **1** exhibits the characteristic resonance for the N(SiMe$_3$) in accordance with the symmetric nature of the benzamidinate moiety (δ 0.03). An additional signal of equal intensity, which corresponds to a lithium N-silylated amide, was observed at δ 0.19. Likewise, two sets of singlets were observed for different methyl groups (δ 1.74 and 2.08) indicating two types of aromatic rings. That at δ 1.74 resembles the methyl signal of *p*-toluonitrile, and the signal at δ 2.08 coincides with the methyl signals obtained for *p*-methyl substituted benzamidinate complexes.[19] Furthermore, four sets of hydrogen resonances, each as a doublet, were found in the δ 6.48–7.30 downfield region, corroborating the formulation of two aromatic rings with different chemical environments. The spectrum also shows the presence of diethyl ether in equimolar amounts, as compared to either the amidinate or *p*-toluonitrile moiety.

The low temperature X-ray analysis of complex **1** (Fig. 1a) shows that the complex has an asymmetric structure having two lithium atoms bridged by the amidinate ligand and by an N-silylated amide ligand; each lithium is also coordinated by a monodentate molecule, Li1 by an ether molecule, Li2 by *p*-toluonitrile. The N(TMS)$_2$ ligand with Li1 may be considered as a molecule of LiN(TMS)$_2$ starting material coordinated in such a way that the electropositive lithium atom (Li1) is bonded to the electronegative nitrogen (N3) of the amidinate fragment, whereas the N-silylated nitrogen (N1) is bonded to Li2 of the amidinate moiety, thus forming a four-membered ring. Selected dimensions for complex **1** are given in Table 2 and a stereoscopic view **1** is presented in Fig. 1(b).

The Li1 atom exhibits an approximately symmetric planar trigonal environment displaying similar distances among the anion–lithium bonds [Li1–N1 1.958(5), Li1–N3 2.029(5) and Li1–O 1.998(5) Å], and bond angles that add to 359.6° [N1–Li1–O 127.9(3), N1–Li1–N3 115.1(2) and N3–Li1–O 116.6(2)]. The Li2 atom also has a planar trigonal coordination and bond angles that add to 357.1° [N2–Li2–N4 108.3(3), N2–Li2–N1 122.6(3) and N4–Li2–N1 126.3(3)], with three similar

Table 2 Selected bond distances (Å) and angles (°) for complex **1**

Li(1)–N(1)	1.958(5)	Li(2)–N(1)	2.063(6)
Li(1)–O(1)	1.998(5)	Li(2)–N(3)	2.397(6)
Li(1)–N(3)	2.029(5)	N(2)–C(1)	1.311(3)
Li(1)···Li(2)	2.450(7)	N(3)–C(1)	1.346(3)
Li(2)–N(2)	2.003(5)	N(4)–C(9)	1.156(4)
Li(2)–N(4)	2.029(6)		
N(1)–Li(1)–O(1)	127.9(3)	N(1)–Li(2)–N(3)	97.7(2)
N(1)–Li(1)–N(3)	115.1(2)	N(4)–Li(2)–Li(1)	159.7(3)
O(1)–Li(1)–N(3)	116.6(2)	Li(2)–N(4)–C(9)	165.4(3)
N(1)–Li(1)–Li(2)	54.4(2)	Li(2)–N(2)–C(1)	93.4(2)
O(1)–Li(1)–Li(2)	168.6(3)	N(2)–C(1)–N(3)	122.3(2)
N(3)–Li(1)–Li(2)	63.9(2)	Li(1)–N(3)–Li(2)	66.6(2)
N(2)–Li(2)–N(4)	108.3(3)	Li(1)–N(1)–Li(2)	75.0(2)
N(2)–Li(2)–N(1)	122.6(3)	Li(2)–N(2)–Si(3)	130.3(2)
N(4)–Li(2)–N(1)	126.3(3)	Si(3)–N(2)–C(1)	130.5(2)
N(2)–Li(2)–N(3)	63.1(2)	Li(1)–N(3)–Si(4)	117.2(2)
N(4)–Li(2)–N(3)	121.1(3)	Si(4)–N(3)–C(1)	130.0(2)

Table 3 Selected bond distances (Å) and angles (°) for complex **2**

Si(1)–N(2)	1.724(4)	N(3)–Li(2)	2.481(9)
Si(2)–N(3)	1.740(4)	N(4)–C(17)	1.327(5)
Si(3)–N(5)	1.705(4)	N(4)–Li(3)	1.950(9)
Si(4)–N(4)	1.707(4)	N(5)–C(17)	1.374(6)
Si(5)–N(7)	1.725(4)	N(5)–Li(2)	2.072(9)
Si(6)–N(6)	1.733(4)	N(6)–C(25)	1.332(5)
N(1)–C(1)	1.152(6)	N(6)–Li(1)	2.114(8)
N(1)–Li(1)	2.047(9)	N(6)–Li(2)	2.177(9)
N(2)–C(9)	1.331(5)	N(7)–C(25)	1.339(5)
N(2)–Li(3)	2.065(8)	N(7)–Li(2)	2.176(9)
N(2)–Li(1)	2.291(9)	N(7)–Li(1)	2.224(9)
N(3)–C(9)	1.352(5)	Li(1)···Li(2)	2.544(10)
N(3)–Li(3)	2.120(9)	Li(1)···Li(3)	2.734(12)
N(3)–Li(1)	2.185(9)	Li(2)···Li(3)	2.534(12)
C(1)–N(1)–Li(1)	164.7(5)	N(4)–C(17)–C(18)	119.7(5)
C(9)–N(2)–Li(3)	83.6(3)	N(5)–C(17)–C(18)	117.6(4)
C(9)–N(2)–Li(1)	75.4(3)	N(1)–Li(1)–N(6)	117.5(4)
Li(3)–N(2)–Li(1)	77.5(3)	N(1)–Li(1)–N(3)	131.7(4)
C(9)–N(3)–Li(3)	81.0(3)	N(6)–Li(1)–N(3)	110.7(4)
C(9)–N(3)–Li(1)	79.1(3)	N(1)–Li(1)–N(7)	96.9(4)
Li(3)–N(3)–Li(1)	78.9(3)	N(3)–Li(1)–N(7)	101.5(3)
C(17)–N(4)–Si(4)	130.1(3)	N(1)–Li(1)–N(2)	105.4(3)
C(17)–N(4)–Li(3)	109.1(4)	N(6)–Li(1)–N(2)	106.3(4)
Si(4)–N(4)–Li(3)	120.7(3)	N(7)–Li(1)–N(2)	157.7(4)
C(17)–N(5)–Si(3)	124.6(3)	N(1)–Li(1)–C(25)	97.3(4)
C(17)–N(5)–Li(2)	129.3(4)	N(3)–Li(1)–C(25)	122.1(4)
Si(3)–(5)–Li(2)	106.1(3)	N(2)–Li(1)–C(25)	140.7(4)
C(25)–N(6)–Li(1)	81.8(3)	N(1)–Li(1)–C(9)	109.5(4)
C(25)–N(6)–Li(2)	84.7(4)	N(6)–Li(1)–C(9)	126.2(4)
Si(6)–N(6)–Li(2)	134.3(3)	N(7)–Li(1)–C(9)	135.3(4)
Li(1)–N(6)–Li(2)	72.7(3)	C(25)–Li(1)–C(9)	153.1(4)
Si(5)–N(7)–Li(2)	140.2(3)	N(5)–Li(2)–N(7)	160.4(4)
C(25)–N(7)–Li(1)	77.4(3)	N(5)–Li(2)–N(6)	111.8(4)
Si(5)–N(7)–Li(1)	126.3(3)	N(7)–Li(2)–N(6)	63.5(3)
Li(2)–N(7)–Li(1)	70.6(3)	N(4)–Li(3)–N(2)	142.9(5)
N(1)–C(1)–C(2)	178.5(6)	N(4)–Li(3)–N(3)	114.7(4)
N(4)–C(17)–N(5)	122.7(4)	N(2)–Li(3)–N(3)	66.9(3)

(coordinative) and one longer (weak) lithium–nitrogen bond [Li2–N1 2.063(6), Li2–N2 2.003(5), Li2–N3 2.397(6), Li2–N4 2.029(6) Å]. Lithium–nitrogen coordinative bonds for amide and some benzamidinate salts have been reported to be in the range 2.06–2.08 Å,[11d] only for one similar dimeric benzamidinate containing a double diazaallyl lithium bridge, a longer coordinative Li–N bond [2.260(9) Å] has been reported.[19] The longer Li2–N3 bond derives from a weak η^1 interaction of the benzamidinate fragment with the lithium atom. Interestingly, a similar weak lithium–nitrogen interaction has recently been reported for a 1-amidoisoquinoline compound.[32] This is corroborated by the longer single bond C1–N3 [1.346(3) Å] as compared to the shorter double bond C1–N2 [1.311(3) Å], indicating that the bond Li2–N3 is relatively weak (the sum of ionic radii for Li and N is 2.31 Å), whereas the other three Li2–N bonds are mostly coordinative. The core units of complex **1** are one Li–N–C–N and one Li–N–Li–N four-membered ring. The latter is puckered along the Li1–Li2 vector with a dihedral angle of 158.5(5)°, whereas the former is slightly puckered along the Li2–C1 vector with a dihedral angle of 158.9(5)°. The two four-membered rings are fused through the weak bond Li2–N3.

The aromatic benzamidinate ring is perpendicular to the N2–C1–N3 plane (94.5(5)°) indicating that in the solid state no stabilizing electronic interactions are expected between the aromatic ring and the amidine moiety. The *p*-toluonitrile molecule is slightly distorted from linearity (vector passing from Li1 and Li2) of the Li–N–Li–N four-membered rings [Li1–Li2–N4 159.7(3)°], and dihedral angles of 84.6(7) and 74.9(8)° between the *p*-toluonitrile plane and the planes formed by Li2–N1–Li1 and Li2–N3–Li1, respectively.

Complex **2** was prepared in a similar procedure to that of **1**, but the reaction was carried out in hexane (eqn. 3). Its ^{1}H NMR spectrum is similar to that obtained for **1**, with each and every signal being doubled. The spectrum shows a pair of singlets at δ 0.13 and 0.17, and an additional pair of singlets at δ 0.56 and 0.59 with half the intensity as compared to the latter pair. Thus, there is a total of six TMS groups, two of which exhibit two signals arguing for different magnetic environments among them, and the further four TMS moieties display only two signals denoting similar magnetic environments for each two of the TMS groups. In addition, four benzylic methyl group signals with equal intensity are observed indicating that complex **2** is formed by three benzamidinate and one *p*-toluonitrile molecule. The aromatic region in the ^{1}H NMR spectrum corroborates this proposition, showing four different doublets of doublets as expected for four different *p*-toluonitrile aromatic rings.

The low temperature X-ray analysis of **2** (Fig. 2a) shows that the potentially symmetrical complex has an asymmetric structure having three amidinate moieties and one coordinatived *p*-toluonitrile molecule. Each benzamidinate is bonded to two different lithium atoms. In two benzamidinates, one of the lithium atoms is σ-bonded, whereas the second is π-bonded. Interestingly, the same lithium atom (Li1) is π-bonded to the two benzamidinates. Each of the other lithium atoms (Li2 and Li3) is in addition σ-bonded to one of the nitrogen atoms (N5 and N4) of the third benzamidinate, respectively. The stereoscopic view of complex **2** is presented in Fig. 2(b) and selected dimensions are given in Table 3.

Although Li1 is π-bonded to both amidine and *p*-toluonitrile groups, having a coordination number of seven (including the carbon atoms of the π-benzamidinate units), it is better represented as having a planar trigonal coordination taking the carbon atoms of the amidine moieties as the coordination point. Thus, the sum of the angles around Li1 [C9–Li1–N1 109.5(4), C9–Li1–C25 153.1(4), C25–Li1–N1 97.3(4)°] is 359.9°. The different Li1–N π-bond lengths show that the lithium is not symmetrically bonded to each of the amidines [Li1–N2 2.291(9), Li1–N3 2.185(9), Li1–N6 2.114(8), Li1–N7 2.224(9) Å]. Each Li2 and Li3 has a distorted trigonal symmetry [N5–Li2–N6 111.8(4), N6–Li2–N7 63.5(3), N5–Li2–N7 160.4(4)°; N2–Li3–N3 66.9(3), N2–Li3–N4 142.9(5), N3–Li3–N4 114.7(4)°] and both metals display similar Li–N σ-bond lengths [Li2–N5 2.072(9), Li2–N6 2.17(9), Li2–N7 2.176(9); Li3–N2 2.065(8), Li3–N3 2.120(9), Li3–N4 1.950(9) Å].

Interestingly, in both π-bonded benzamidinates the C–N bonds [N2–C9 1.331(5), N3–C9 1.352(5), N6–C25 1.332(5), N7–C25 1.339(5) Å] are in the range between C=N [1.302(7)] and C–N [1.360(8) Å] bond lengths reported for similar protonated uncomplexed N-phenyl-substituted ligands,[33] suggesting delocalization throughout each three-atom unit. The difference in bond length between the two lithium atoms, σ-bonded to the same benzamidinate unit [Li2–N5 2.072(9), Li3–N4 1.950(9) Å], is consistent with the slight difference

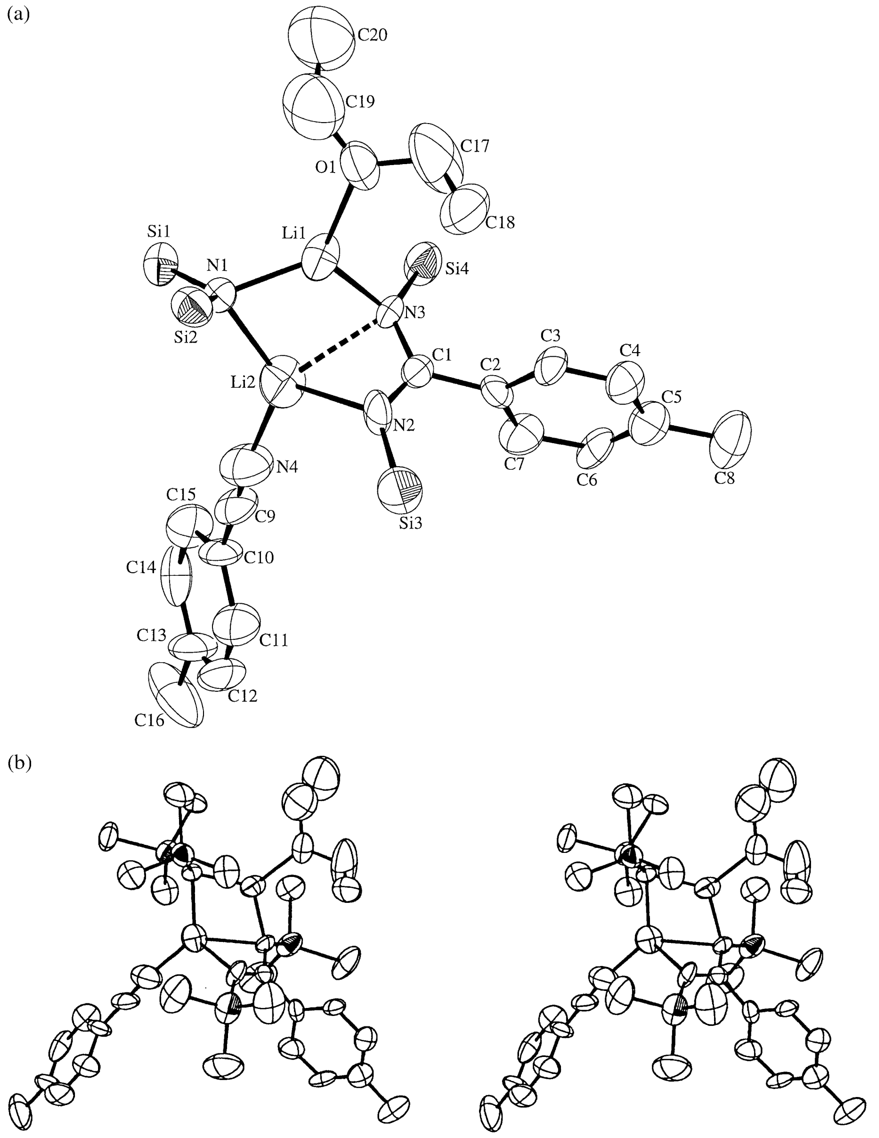
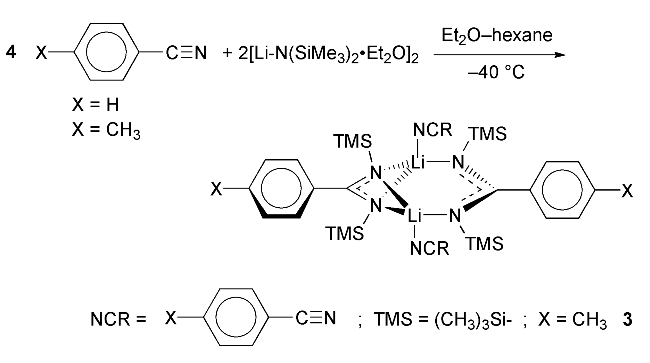


Fig. 1 (a) Molecular structure of complex **1**. Thermal ellipsoids are shown at 50% probability. The methyl groups bonded to the silyl atoms are omitted for clarity. (b) Stereoscopic view of **1**. The hydrogens are omitted for clarity.

observed for the C–N lengths at the amidinate fragment [C17–N4 1.327(5), C17–N5 1.374(6) Å]. The core units include two Li–N–C–N four-membered rings and one Li–N–C–N–Li five-membered ring. The two four-membered rings are equally puckered by 30°, whereas the five-membered ring is distorted from planarity exhibiting two torsional angles [Li3–N4–C17–N5 0.1(6), Li2–N5–C17–N4 19.6(8)°]. One of the aromatic benzamidinate rings is disposed almost perpendicular to the amidine unit [N3–C9–C10–C11 87.8(6)°], whereas the other two aromatic rings are tilted further from perpendicularity [N4–C17–C18–C19 79.9(7) and N6–C25–C26–C31 65.9(7)°]. Furthermore, Li1 is non-linear coordinatively bonded to the *p*-toluonitrile molecule [Li1–N1–C1 164.7(5)°].

Earlier, we have shown that the reaction of $LiN(TMS)_2$ with either an excess of benzonitrile or *p*-toluonitrile produces a dimeric complex of a double lithium η^3-diazaallyl bridge in the *N*,*N′*-bis(trimethylsilyl)benzamidinate compound $[4\text{-}XC_6H_4C(NSiMe_3)_2{\cdot}Li(NCC_6H_4X\text{-}4)]_2$ (X = H or Me (**3**) [Scheme 1)], and have demonstrated the rapid σ–π exchange of the lithium bonding in solution.[19]



Scheme 1 Stoichiometry in the synthesis of complex **3**.

Based on the results obtained earlier for the dynamic behavior of complex **3**, showing that both lithium atoms are labile, together with a structural comparison between **1** and **3**, it is possible to conceive that after the attack of the amido group the nitrile moiety with the subsequent sigmatropic shift rearrangement, complex **1** turns into **3** with an open coordination site that can be filled by either another nitrile or solvent molecule. To corroborate this, we have performed the reaction of complex **1** with two equivalents of *p*-toluonitrile in diethyl ether and obtained quantitatively **3**, as described in Scheme 2. Hence, complex **1** can formally be considered as an intermediate to **3**.

A close look at the structure of **1** reveals that the complex can be visualized as a lithium benzamidinate, coordinated to a *p*-toluonitrile molecule (either activation of the nitrile and/or

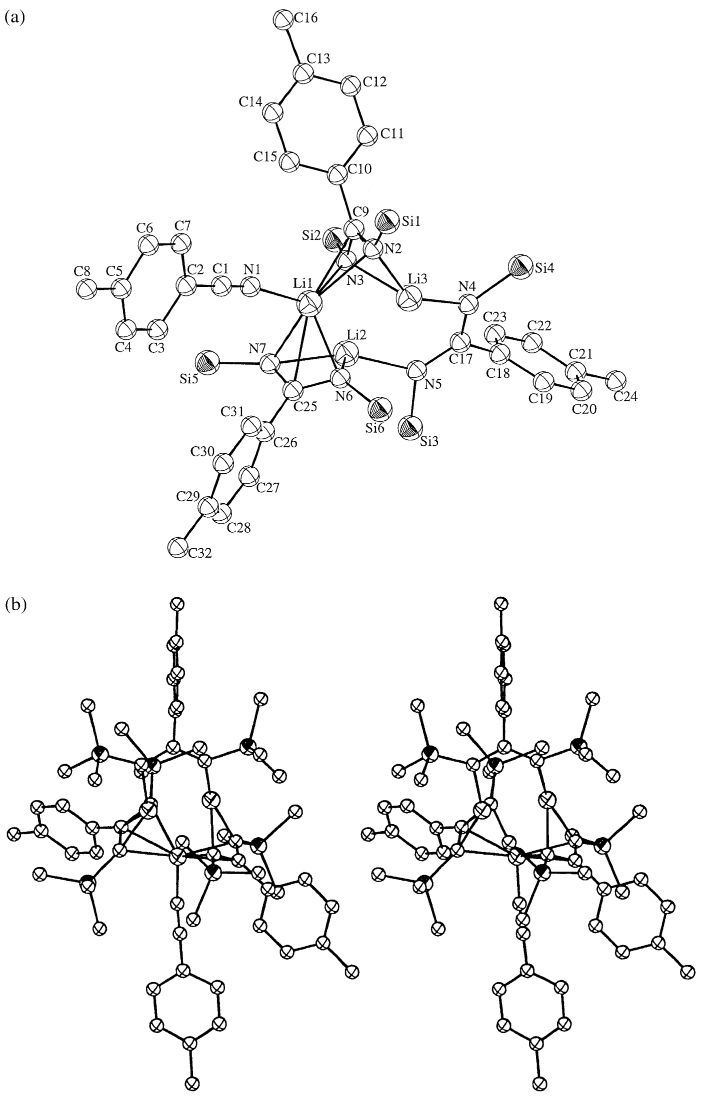
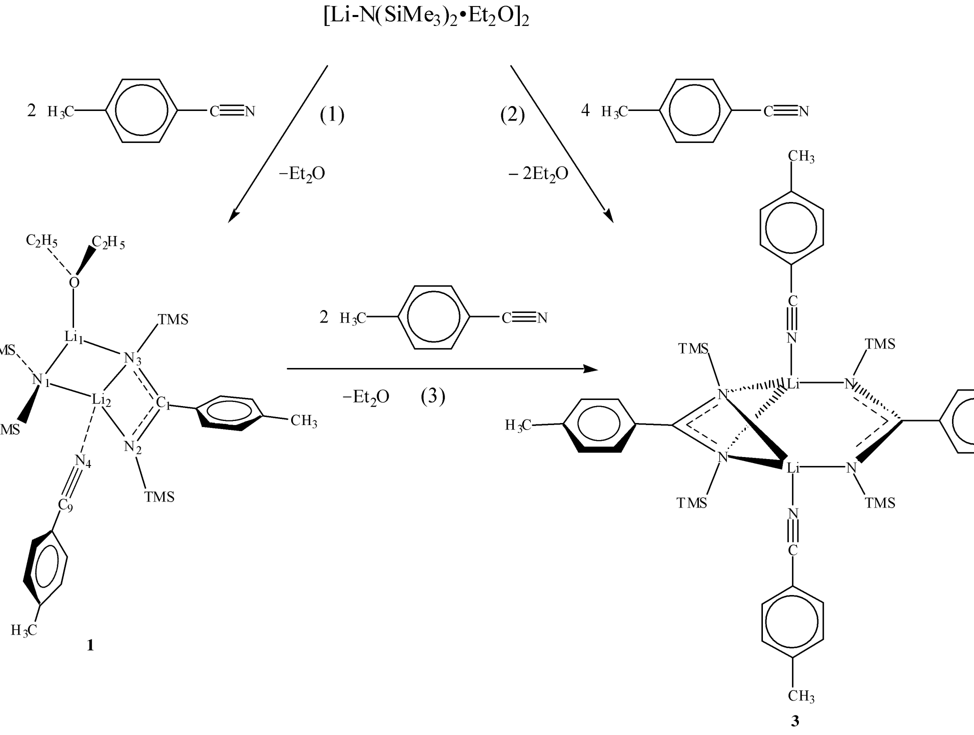


Fig. 2 (a) Molecular structure of complex **2**. Ideal spheres are shown for clarity. The methyl groups bonded to the silyl atoms are omitted for clarity. (b) Stereoscopic view of **2**. The hydrogens are omitted for clarity.



Scheme 2 Different synthetic routes for the preparation of complex **3**.

stabilization of the lithium atom) to which a monomeric Li[N(TMS)$_2$]·Et$_2$O approaches parallel to the corresponding Li2–N3 vector. In this structure each of the lithium atoms is facing a nitrogen atom, forming a slightly puckered four-membered ring, with both amido and nitrile groups at adjacent positions, spatially oriented toward the same side. Hence, the amido group approaches the carbon of the nitrile fragment from the opposite side to that of the benzamidinate ring, and its corresponding lithium atom (Li1) plausibly bonds the amidine nitrogen (N2) towards the formation of complex **3**.

Conclusion

We have shown that complex **1** is an intermediate to **3**. The formation of a ketimide is accomplished by activating a nitrile moiety with a lithium atom of another benzamidinate molecule. The lithium amido salt forms a four-membered puckered ring with one of the Li–N bonds of the amidinate, preceding the amido encounter with the nitrile molecule. The molecularity in the syntheses of complexes **1** and **3** is dimeric, with either a nitrile or a polar solvent, such as an ether molecule, coordinated to a lithium atom. When the reaction is totally carried out in hexane a trimer is formed, in which the lithium atoms gain stabilization by their coordination to other amidinate nitrogens (π bonding), thus forming a trimeric structure.

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References

1 A. Loupy and B. Tchoubar, *Salt Effect in Organic and Organometallic Chemistry*, VCH, Weinheim, 1992.

2 A. K. Beck, D. Seebach and A. Sturder, *Modern Synthetic Methods*, eds. B. Ernst and C. Leumann, VCH Acta, New York, 1995.

3 A. Streitwieser, S. M. Bacharach, A. Dorigo and P. v. R. Schleyer, *Lithium Chemistry: A Theoretical and Experimental Overview*, eds. A. M. Sapse and P. v. R. Schleyer, John Wiley, New York, 1995, ch. 1.

4 D. B. Collum and J. S. DePue, *J. Am. Chem. Soc.*, 1988, **110**, 5518; D. B. Collum, *Acc. Chem. Res.*, 1993, **5**, 227 and references therein; D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1624.

5 M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, *Metal and Metalloid Amides*, Horwood-Wiley, Chichester, 1980; Z. Duan, V. G. Young, Jr. and J. G. Verkade, *Inorg. Chem.*, 1995, **34**, 2179 and references therein.

6 (*a*) W. Clegg, A. J. Edwards, F. S. Mair and M. P. Nolan, *J. Chem. Soc., Chem. Commun.*, 1988, 23 and references therein; (*b*) P. R. Bernstein, A. E. Dorigo, K. W. Henderson and P. G. Williard, *Angew. Chem., Int. Ed. Engl.*, 1996, **108**, 1420; (*c*) F. Hampel, F. Newmann and P. v. R. Schleyer, *Inorg. Chem.*, 1995, **34**, 6553.

7 J. C. Stowell, *Carbanions in Organic Synthesis*, Wiley Interscience, New York, 1979; B. J. Wakefield, *Organolithium Methods*, Academic Press, San Diego, 1988; P. C. Andrews, R. E. Mulvey, W. Clegg and D. Reed, *J. Organomet. Chem.*, 1990, **386**, 287.

8 G. L. J. van Vliet, H. Luitjes, M. Schakel and G. W. Klumpp, *Angew. Chem., Int. Ed.*, 2000, **39**, 9, and references therein; C. H. Heatcock, *Comprehensive Carbanion Chemistry*, eds. E. Buncel and T. Durst, Elsevier, New York, 1980, vol. B, ch. 4.

9 V. Snieckus, *Chem. Rev.*, 1990, **90**, 879 and references therein.

10 R. T. Boeré, R. T. Oakley and R. W. Reed, *J. Organomet. Chem.*, 1987, **331**, 161.

11 (*a*) K. Gregory, P. v. R. Schleyer and R. Snaith, *Adv. Inorg. Chem.*, 1991, **37**, 47 and references therein; (*b*) R. E. Mulvey, *Chem. Soc. Rev.*, 1991, **20**, 167; (*c*) G. W. Klumpp, *Recl. Trav. Chim. Pays-Bas*, 1986, **105**, 1; (*d*) W. N. Setzer and P. v. R. Schleyer, *Adv. Organomet. Chem.*, 1985, **24**, 354.

12 D. B. Collum and J. S. DePue, *J. Am. Chem. Soc.*, 1988, **110**, 5524; A.-M. Sapse, D. C. Jain and K. Raghavachari, *Lithium Chemistry: A Theoretical and Experimental Overview*, eds. A. M. Sapse and P. v. R. Schleyer, John Wiley, New York, 1995, ch. 2; R. Snaith and D. S. Wright, *Lithium Chemistry: A Theoretical and Experimental Overview*, eds. A. M. Sapse and P. v. R. Schleyer, John Wiley, New York, 1995, ch. 8.

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

14 M. Shmulinson and M. S. Eisen, *J. Chem. Soc., Dalton Trans.*, 1997, 2483; J. Richter, F. T. Edelmann, M. Noltemeyer, H.-G. Schmidt, M. Schmulinson and M. S. Eisen, *J. Mol. Catal.*, 1998, **130**, 149.

15 V. Volkis, M. Shmulinson, C. Averbuj, A. Lisovskii, F. T. Edelmann and M. S. Eisen, *Organometallics*, 1998, **17**, 3155; C. Averbuj, E. Tish and M. S. Eisen, *J. Am. Chem. Soc.*, 1998, **120**, 8640.

16 D. S. Richeson and Y. Zhou, *Inorg. Chem.*, 1996, **35**, 1423; M. P. Coles and R. F. Jordan, *J. Am. Chem. Soc.*, 1997, **119**, 8125; W. W. Schoeller, A. Sundermann and M. Reiher, *Inorg. Chem.*, 1999, **38**, 29; G. R. Giesbrecht, A. Shafir and J. Arnold, *J. Chem. Soc., Dalton Trans.*, 1999, 3601.

17 A. I. Meyers, W. F. Rieker and L. M. Fuentes, *J. Am. Chem. Soc.*, 1982, **105**, 2082.

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

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

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

21 I. Cragg-Hine, M. G. Davidson, F. S. Mair, P. R. Raithby and R. Snaith, *J. Chem. Soc., Dalton Trans.*, 1993, 2423.

22 J. Baker, D. Barr, N. D. R. Barnett, W. Clegg, I. Cragg-Hine, M. G. Davidson, R. P. Davies, S. H. 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.

23 A. R. Kennedy, R. E. Mulvey and R. B. Rowlings, *J. Am. Chem. Soc.*, 1998, **120**, 7816.

24 T. Chivers, A. Downard and G. P. A. Yap, *J. Chem. Soc., Dalton Trans.*, 1998, 2603; T. Chivers, A. Downard and M. Parvez, *Inorg. Chem.*, 1999, **38**, 4347; A. R. Kennedy, R. E. Mulvey and R. B. Rowlings, *J. Am. Chem. Soc.*, 1998, **120**, 2716.

25 D. R. Amstrong, W. Clegg, L. Dunbar, S. T. Liddle, M. MacGregor, R. E. Mulvey, D. Reed and S. A. Quinn, *J. Chem. Soc., Dalton Trans.*, 1998, 3431.

26 F. C. Shaefer and L. A. Krapcho, *J. Org. Chem.*, 1962, **27**, 1255.

27 (*a*) G. M. Sheldrick, SHELXS 86, Program for the solution of crystal structures, University of Göttingen, 1986; (*b*) SHELX 76, Program for crystal structure refinement, Chemical Laboratory, Cambridge, 1976.

28 Kappa CCD Collect Program for data collection and HKL, Scalepack and Denzo (Otwinowski and Minor), software packages for data reduction and cell refinement, Nonius, Delft, 1997.

29 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

30 G. M. Sheldrick, SHELXL 97, Program for the refinement of crystal structures, University of Göttingen, 1997.

31 ORTEP, TEXRAY Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1999.

32 N. Feeder, R. Snaith and A. E. H. Wheatley, *Eur. J. Inorg. Chem.*, 1998, **7**, 879.

33 N. W. Alcock, J. Baker and M. Kilner, *Acta Crystallogr., Sect. C*, 1988, **44**, 712.