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# Synthesis and characterization of novel chelated dimethylamino lithium alkoxides: molecular structures of [1-LiOC($C_6H_{11}$)$_2$-2-NMe$_2$C$_6$H$_4$]$_2$ and [1-LiOCPh$_2$CH$_2$-2-NMe$_2$C$_6$H$_4$]$_2$

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**From the reaction of 1-HOCPh$_2$-2-NMe$_2$C$_6$H$_4$ (1), 1-HOC(C$_6$H$_{11}$)$_2$-2-NMe$_2$C$_6$H$_4$ (2) and 1-HOCPh$_2$CH$_2$-2-NMe$_2$C$_6$H$_4$ (3) with *n*-BuLi in diethyl ether, the solvent-free chelated dimethylamino lithium alkoxides [1-LiOCPh$_2$-2-NMe$_2$C$_6$H$_4$]$_2$ (4), [1-LiOC(C$_6$H$_{11}$)$_2$-2-NMe$_2$C$_6$H$_4$]$_2$ (5) and [1-LiOCPh$_2$CH$_2$-2-NMe$_2$C$_6$H$_4$]$_2$ (6) were obtained. The lithium alkoxides 4–6 were characterized by $^1$H, $^7$Li, and $^{13}$C NMR spectroscopy. Crystal structure determinations of 5 and 6 were carried out. Compounds 5 and 6 are examples of structurally characterized solvent-free chelated dimethylamino lithium alkoxides and 6 is a rare example of this type containing a seven-membered ring. Copyright © 2002 John Wiley & Sons, Ltd.**

## INTRODUCTION

The first work on lithium alkoxides dates back to Chablay.[1] Knowledge about structures and reactivities of these compounds is limited, even though lithium alkoxides have been employed as catalysts in polymerization reactions since at least 1960[2] and in industrial processes.[2,3] Power and coworkers obtained the first detailed crystal structure of a lithium alkoxide in 1983, i.e. a THF-solvated dimer of lithium *tert*-butoxide.[4] Internal coordination by oxygen,[5] nitrogen,[6–13] phosphorus,[14,15] sulfur,[16] $\pi$-systems,[16–18] and cyclopropyl groups[19] have been identified in lithium alkoxides and show the diversity of the compounds. X-ray, NMR, and other techniques have confirmed a variety of different aggregate sizes of lithium alkoxides. The sizes of aggregates formed depend strongly on the solvent used.[20] Thus, monomers,[6,21] dimers[4,6,10,11,14,22] trimers,[6] tetramers,[5–9,12,13,20,23–25] hexamers,[8,9,15,16,18,20,23–29] heptamers,[28] nonamers,[28] undecamers,[4] tridecamers,[28] and sheet polymers[30–32] have been characterized.

In an extension of our studies on boron compounds,[33–35] we now report the successful high-yield synthesis and spectroscopic properties of the novel chelated dimethylamino lithium alkoxides [1-LiOCX-2-NMe$_2$C$_6$H$_4$]$_2$ [X = Ph$_2$ (**4**), (C$_6$H$_{11}$)$_2$ (**5**), Ph$_2$CH$_2$ (**6**)] and the structurally characterized solvent-free chelated dimethylamino lithium alkoxides **5** and **6**. Compounds **4**–**6** are of interest as starting materials for the synthesis of boron compounds in which a potentially intramolecularly coordinating tertiary amino group is present.

## SYNTHESIS AND SPECTROSCOPIC PROPERTIES

### Synthesis

We have found that the dimeric lithium derivatives **4**–**6** can be readily prepared [Eqns (1) and (2)] by addition of *n*-butyllithium in hexane to equimolar amounts of the organic ligands 1-HOCX-2-NMe$_2$C$_6$H$_4$ [X = Ph$_2$ (**1**),[36,37] (C$_6$H$_{11}$)$_2$ (**2**),[37] Ph$_2$CH$_2$ (**3**)[37,38] in diethyl ether at −15 °C. When the reaction was conducted in tetrahydrofuran, the reaction temperature had to be maintained at −15 °C in order to obtain the products **4**–**6**. When the solution temperature was allowed to rise to 20 °C, a brown solution was obtained; the nature of the by-products formed has not yet been elucidated. However, when diethyl ether was employed as the solvent, yields of the solvent-free chelated lithium alkoxides **4**–**6** of approximately 90–98% were obtained after complete addition of *n*-butyllithium at −15 °C. Even when the solution was allowed to warm to 20 °C, the yields were

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**Table 1.** Selected bond lengths (Å) and bond angles (deg) for **5** and **6**

| | **5** | | **6** |
|---|---|---|---|
| Li(1)—O(1) | 1.802 (3) | Li(1)—O(1) | 1.856 (5) |
| Li(1)—O(1a) | 1.817 (3) | Li(1)—O(2) | 1.855 (5) |
| Li(1)—N(1) | 2.014 (3) | Li(1)—N(1) | 2.075 (6) |
| Li(1)—O(1)—Li(1a) | 78.54 (16) | Li(1)—O(1)—Li(2) | 80.7 (2) |
| O(1)—Li(1)—O(1a) | 101.46 (16) | O(1)—Li(1)—O(2) | 98.1 (2) |
| N(1)—Li(1)—O(1)—Li(1a) | 150.7 (2) | N(1)—Li(1)—O(1)—Li(2) | 143.3 (3) |
| | | Li(1)—O(1)—Li(2)—O(2) | −1.6 (3) |

still as high as 80–93%.

$$\text{1-HOCR}_2\text{-2-NMe}_2\text{C}_6\text{H}_4 + n\text{-BuLi} \longrightarrow \frac{1}{2}[\text{1-LiOCR}_2\text{-2-NMe}_2\text{C}_6\text{H}_4]_2 \quad (1)$$

$$\text{R} = \text{Ph } (\mathbf{4}),\ \text{Cy } (\mathbf{5})$$

$$\text{1-HOCPh}_2\text{CH}_2\text{-2-NMe}_2\text{C}_6\text{H}_4 + n\text{-BuLi} \longrightarrow \frac{1}{2}[\text{1-LiOCPh}_2\text{CH}_2\text{-2-NMe}_2\text{C}_6\text{H}_4]_2 \quad (2)$$

$$(\mathbf{6})$$

## $^1$H and $^{13}$C NMR

In the $^1$H NMR spectrum, the most noticeable signal is that due to the $N(CH_3)_2$ protons, which gives rise to one (for **6**) or two singlets (for **4** and **5**) at about 1.92 and 2.02 (**4**), 2.30 and 2.66 (**5**) and 2.24 ppm (**6**). These signals are at higher field than those observed for the precursors **1** (2.83 ppm), **2** (2.70 ppm) and **3** (2.80 ppm). In **5**, the signals of the cyclohexyl protons are observed at 1.10–2.08 ppm. The $^1$H NMR signals of the aromatic rings of **4**–**6** are in the expected chemical shift range (6.53–7.92 ppm), as is also observed for **1, 2**[37] and **3**.[37,38] In **6**, the singlet at 3.65 ppm is assigned to the methylene protons.

The $^{13}$C NMR spectrum shows one (for **6**) or two signals (for **4** and **5**) for the $N(CH_3)_2$ carbon atoms at 46.2 and 46.8 (**4**), 48.2 and 49.1 (**5**) and at 46.1 ppm (**6**). The C—O carbon atom gives a singlet at 85.6 (**4**), 89.0 (**5**) or 79.3 ppm (**6**). The resonances of the aromatic (120–156 ppm) and the cyclohexyl (27–47 ppm) carbon atoms are in the expected ranges observed for **1, 2**[37] and **3**.[37,38] For **6**, the singlet at 45.7 ppm is assigned to the methylene carbon atom.

Both the $^1$H and $^{13}$C NMR spectra of **4** and **5** indicate that in these molecules the two equivalent $NMe_2$ substituents have inequivalent methyl groups. For **6**, both the $^1$H and $^{13}$C NMR spectrum show equivalent $NMe_2$ and methylene protons. The diastereotopicity of the $NMe_2$ groups in **4** and **5** and the equivalence of the $NMe_2$ and $CH_2$ protons in **6** indicates that Li—N coordination is present (within the NMR time scale), which results in puckered six-membered (for **4** and **5**) or seven-membered (for **6**) chelate rings and dimeric structures for **4**–**6** in solution.[39,40]

## $^7$Li NMR

The $^7$Li NMR spectra of the lithium alkoxides **4** and **5** in $C_6D_6$ consist of single signals at about 2.6 (**4**) and 2.5 ppm (**5**). As the $^1$H and $^{13}$C NMR spectra indicate that **4** and **5** do not dissociate into monomers but exist as dimers in solution, the two lithium atoms are isochronic.[39] In contrast, the $^7$Li NMR spectrum of the lithium alkoxide **6** in $C_6D_6$ consists of two signals at about 1.1 and 2.0 ppm (ratio 1:4), which suggests an Li—N dissociation–association process (within the $^7$Li NMR time scale).

## MOLECULAR STRUCTURE

Colorless crystals of **5** or **6** were obtained from toluene at 20 °C; compound **5** crystallizes in the monoclinic space group $P2_1/n$, and **6** in the monoclinic space group $P2_1/c$. Selected interatomic distances and angles are collected in Table 1. The molecular structures are depicted in Figs 1 and 2.

As in solution, **5** and **6** form centrosymmetric dimers in the

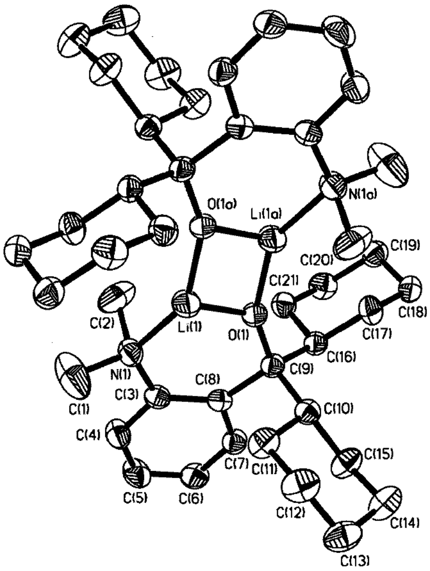


**Figure 1.** Molecular structure of **5** showing the atom numbering scheme employed (ORTEP plot, 50% probability, SHELXTL-PLUS; XP).[41] Hydrogen atoms are omitted for clarity.

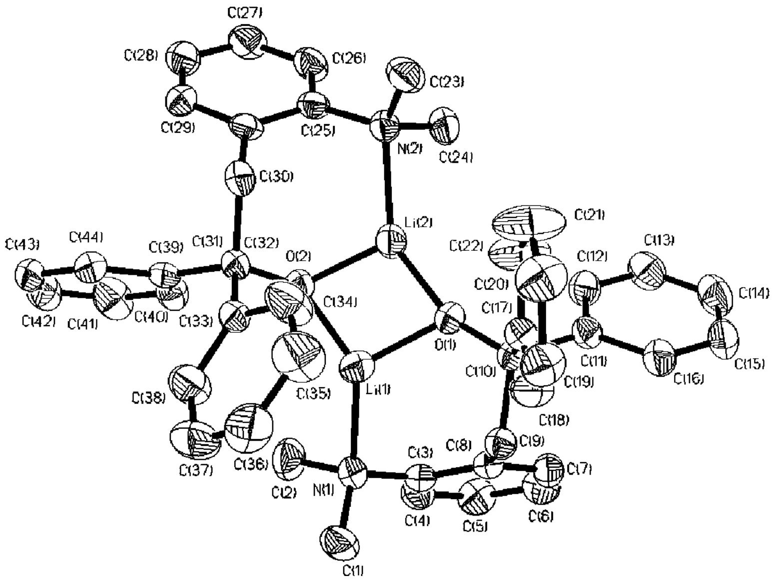


**Figure 2.** Molecular structure of **6** showing the atom numbering scheme employed (ORTEP plot, 50% probability, SHELXTL-PLUS; XP).[41] Hydrogen atoms omitted for clarity.

solid state (Table 1, Figs 1 and 2) in which the central four-membered $Li_2O_2$ ring is planar with smaller Li—O—Li and larger O—Li—O bond angles. The dimethylamino groups are coordinated to the lithium atoms [Li(1)—N(1) 2.014(3) Å (in **5**), 2.075(6) Å (in **6**)]. The Li—O bond lengths in **5** [Li(1)—O(1) 1.802(3) Å and Li(1)—O(1a) 1.817(3) Å] are comparable to those in $[Li(O\text{-}2,6\text{-}^tBu_2C_6H_2)(THF)]_2$ [av. Li—O 1.819(4) Å],[42] in which there is also a three-coordinate lithium atom, whereas related compounds with four-coordinate lithium atoms exhibit longer Li—O bonds, e.g. $[Li(O\text{-}2,6\text{-}^tBu_2C_6H_3)(THF)_2]_2$ [av. Li—O 1.848(7) Å],[43] $[Li(O\text{-}2,6\text{-}^tBu_2C_6H_3)(OEt_2)_2]_2$ [av. Li—O 1.875(7) Å],[44] $[Li(OPh)(OEt_2)_2]_2$ [av. Li—O 1.875(12) Å],[45] and $[Li(O\text{-}2,6\text{-}^tBu_2C_6H_2)(py)_2]_2$ [av. Li—O 1.851(2) Å].[42] In **6**, longer Li—O bonds [Li(1)—O(1) 1.856(5) Å and Li(1)—O(2) 1.855(5) Å] are also observed.

The bonding situation in lithium compounds is known to be dominated by electronic effects,[42] and a planar three-coordinated environment would be expected for the lithium atoms in **5** and **6**. However, the X-ray crystal structure determination shows a pyramidal environment of the three-coordinate lithium atoms: the sum of bond angles at lithium is 343 ° (in **5**) and 345 ° (in **6**), rather than the 360 ° expected for a trigonal-planar coordination. The pyramidal distortion of the environment of the lithium atoms in **5** and **6** and the out-of-plane bending of the nitrogen atoms can be attributed to repulsion between the dimethylamino and cyclohexyl (**5**) or phenyl (**6**) groups.[4]

The structure of the central core of **5** and **6** is similar to that of (1*R*,2*R*,4*S*)-*exo*-2-[*o*-(dimethylaminomethyl)phenyl]-1,3,3-trimethylbicyclo[2.2.1]heptan-*endo*-2-olate.[11] However, in the latter, the central $Li_2O_2$ ring is puckered [Li(1)—O(3)—Li(2)—O(4) dihedral angle 7 °], and the dihedral angle of the Li(1)—O(3)—O(4)—N(5) group (24 °) is larger (greater pyramidal distortion at lithium) than that observed for **5** and **6**. The Li—O and Li—N bonds are longer [Li(1)—O(3) 1.84 Å, Li(1)—O(4) 1.83 Å, Li(1)—N(5) 2.06 Å] than those of **5** but comparable to those of **6**. The sum of bond angles at lithium is smaller (341 °) than in **5** and **6**. The *syn* arrangement of the two $NMe_2$ methyl groups with respect to the $Li_2O_2$ core differs from the *anti* alignment of the two $NMe_2$ methyl groups with respect to the $Li_2O_2$ core in **5** and **6**. For dimeric methylzinc complexes of *exo*-3-(dimethylamino)isoborneol, Noyori and coworkers have also observed *syn* orientations for the homochiral and *anti* alignment for the heterochiral species.[46,47]

The bond lengths and angles of the organic fragments of **5** and **6** are similar to those observed for the corresponding organic compounds **2** and **3**.[37]

## EXPERIMENTAL DETAILS

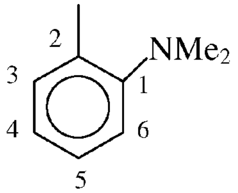
All experiments were carried out under purified dry nitrogen. Solvents were dried and freshly distilled under nitrogen. The NMR spectra (in $C_6D_6$, $\delta$/ppm) were recorded with an AVANCE DRX 400 spectrometer (Bruker); $^1H$ NMR (400 MHz): internal standard trace amount of protonated solvent, $C_6D_6$; $^{13}C$ NMR (100 MHz): internal standard solvent; $^7Li$ NMR (155 MHz): external standard 1 M LiCl; Elemental analyses were obtained with a VARIO EL (Heraeus). The melting points were determined in sealed capillaries under argon and are uncorrected; 1-HOCPh$_2$-

2-$NMe_2C_6H_4$ (**1**),[36] 1-$HOC(C_6H_{11})_2$-2-$NMe_2C_6H_4$ (**2**)[37] and 1-$HOCPh_2CH_2$-2-$NMe_2C_6H_4$ (**3**)[37,38] were prepared by literature procedures.

## Preparation of [1-$LiOCPh_2$-2-$NMe_2C_6H_4$]$_2$ (4)

A 150 ml Schlenk flask was charged with 1-$HOCPh_2$-2-$NMe_2C_6H_4$ (**1**) (0.48 g, 1.6 mmol) and diethyl ether (50 ml). Then *n*-butyllithium (one equivalent) was added dropwise at −15 °C. The solution was warmed to room temperature and left stirring for about 1 h. The solvent was then removed and the remaining solid was washed with pentane to give the product in 90% yield. M.p. 177–178 °C. Anal. Found: C, 81.52; H, 6.45; N, 4.52. Calc. for $C_{42}H_{40}Li_2N_2O_2$: C, 81.55; H, 6.47; N, 4.53%. $^1$H NMR: 1.92 (s, 6H, $N(CH_3)_2$), 2.02 (s, 6H, $N(CH_3)_2$), 6.77–7.61 (m, vbr, 28H, $C_6H_4$ and $C_6H_5$). $^{13}$C NMR: 46.2 (s, $N(CH_3)_2$), 46.8 (s, $N(CH_3)_2$), 85.6 (s, C—O), 123.5 (s, C4 in $C_6H_4$), 124.2 (s, C6 in $C_6H_4$), 125.0 (s, C3 in $C_6H_4$), 127.4 (s, C5 in $C_6H_4$), 128.0 (s, *p*-C in $C_6H_5$), 129.7 (s, *o*-C in $C_6H_5$), 129.9 (s, *m*-C in $C_6H_5$), 155.5 (s, C2 in $C_6H_4$), 155.6 (s, C1 in $C_6H_4$), 155.7 (s, *ipso*-C in $C_6H_5$). $^7$Li NMR: 2.6.

Phenyl ring numbering scheme:



## Preparation of [1-$LiOC(C_6H_{11})_2$-2-$NMe_2C_6H_4$]$_2$ (5)

A similar procedure to that described for **4** was used here, except that 1-$HOC(C_6H_{11})_2$-2-$NMe_2C_6H_4$ (**2**) (0.51 g, 1.6 mmol) was employed instead of **1** and colorless crystals were obtained from toluene at 20 °C in 80% yield. M.p. 170–172 °C. Anal. Found: C, 78.50; H, 9.95; N, 4.35. Calc. for $C_{42}H_{64}Li_2N_2O_2$: C, 78.51; H, 9.97; N, 4.36%. $^1$H NMR: 1.10–2.08 (vbr, 44H, $C_6H_{11}$), 2.30 (s, 6H, $N(CH_3)_2$), 2.66 (s, 6H, $N(CH_3)_2$), 6.97–7.16 (m, 8H, $C_6H_4$). $^{13}$C NMR: 27.0 (s, C4 in Cy), 28.1 (s, C3/C5 in Cy), 29.2 (s, C2/C6 in Cy), 30.4 (s, C2/C6 in Cy), 46.4 (s, C1 in Cy), 46.5 (s, C1 in Cy), 48.2 (s, $N(CH_3)_2$), 49.1 (s, $N(CH_3)_2$), 89.0 (s, C—O), 123.3 (s, C4 in $C_6H_4$), 124.9 (s, C6 in $C_6H_4$), 127.0 (s, C3 in $C_6H_4$), 129.8 (s, C5 in $C_6H_4$), 140.1 (s, C2 in $C_6H_4$), 154.6 (s, C1 in $C_6H_4$). $^7$Li NMR: 2.5.

## Preparation of [1-$LiOCPh_2CH_2$-2-$NMe_2C_6H_4$]$_2$ (6)

A similar procedure to that described for **4** was used here, except that 1-$HOCPh_2CH_2$-2-$NMe_2C_6H_4$ (**3**) (0.48 g, 1.5 mmol) was employed instead of **1** and colorless crystals were obtained from toluene at 20 °C in 93% yield. M.p. 140–145 °C. Anal. Found: C, 81.62; H, 6.76; N, 4.32. Calc. for $C_{44}H_{44}Li_2N_2O_2$: C, 81.65; H, 6.80; N, 4.33%. $^1$H NMR: 2.24 (s, 12H, $N(CH_3)_2$), 3.65 (s, 4H, $CH_2$), 6.53–7.92 (m, vbr, 28H, $C_6H_4$ and $C_6H_5$). $^{13}$C NMR: 45.7 (s, $CH_2$), 46.1 (s, $N(CH_3)_2$), 79.3 (s, C—O), 120.8 (s, C4 in $C_6H_4$), 125.7 (s, C6 in $C_6H_4$), 126.9 (s, C3 in $C_6H_4$), 127.1 (s, C5 in $C_6H_4$), 128.3 (s, *p*-C in $C_6H_5$), 128.5 (s, *o*-C in $C_6H_5$), 134.2 (s, *m*-C in $C_6H_5$), 148.6 (s, C2 in $C_6H_4$), 148.7 (s, C1 in $C_6H_4$), 152.5 (s, *ipso*-C in $C_6H_5$). $^7$Li NMR: 1.1, 2.0.

**Table 2.** Crystal data and structure refinement for **5** and **6**

| | 5 | 6 |
|---|---|---|
| Formula | $C_{42}H_{64}Li_2N_2O_2$ | $C_{44}H_{44}Li_2N_2O_2$ |
| Formula weight | 642.84 | 646.69 |
| Temperature (K) | 217(2) | 223(2) |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/c$ |
| $a$ (Å) | 9.569(2) | 14.138(1) |
| $b$ (Å) | 20.273(4) | 9.771(1) |
| $c$ (Å) | 10.292(2) | 26.546(3) |
| $\alpha$ (°) | 90 | 90 |
| $\beta$ (°) | 111.062(4) | 101.29(1) |
| $\gamma$ (°) | 90 | 90 |
| $V$ (Å$^3$) | 1863.2(6) | 3596.2(6) |
| $Z$ | 2 | 4 |
| $D_{calcd}$ (g cm$^{-1}$) | 1.146 | 1.194 |
| $F(000)$ | 704 | 1376 |
| Crystal size (mm$^3$) | 0.3 × 0.15 × 0.15 | 0.3 × 0.1 × 0.1 |
| Absorption coefficient (mm$^{-1}$) | 0.068 | 0.071 |
| No. of reflections collected | 7706 | 20 403 |
| No. of independent reflections | 3601 | 7066 |
| $R_{int}$ | 0.0315 | 0.0953 |
| No. of parameters | 345 | 628 |
| $R_1$ ($I > 2\sigma(I)$) | 0.0467 | 0.0467 |
| $wR_2$ (all data) | 0.1289 | 0.1448 |
| $(\Delta/\rho)_{min}$ (e$^-$ Å$^{-3}$) | 0.213 | 0.179 |
| $(\Delta/\rho)_{max}$ (e$^-$ Å$^{-3}$) | −0.160 | −0.187 |
| Deposition number | CCDC 184760 | CCDC 186419 |

## Data collection and structural refinement of 5 and 6

Crystallographic data are given in Table 2. Data [$\lambda$(Mo K$\alpha$) = 0.71073 Å] were collected with a Siemens CCD (SMART) diffractometer. All observed reflections were used for determination of the unit cell parameters. Empirical absorption correction with SADABS.[48] The structure was solved by direct methods (SHELXTL PLUS[41]). Restrictions for **5** and **6**: lithium, nitrogen, oxygen and carbon atoms anisotropic. Hydrogen atoms located by difference maps and refined isotropically.

## REFERENCES

1. Chablay ME. *Ann. Chim.* 1917; **8**: 145.
2. Bradley DC, Mehrotra RC, Rothwell IP and Singh A. *Alkoxo and Aryloxo Derivatives of Metals.* Academic Press, London, 2001.
3. Mehrotra RC, Singh A and Sogani S. *Chem. Soc. Rev.* 1994; **23**: 215.

4. Hvoslef J, Hope H, Murray BD and Power PP. *J. Chem. Soc., Chem. Commun.* 1983; 1438.
5. Goldfuss B, Khan SI and Houk KN. *Organometallics* 1999; **18**: 2927.
6. Armstrong DR, Davies JE, Davies RP, Raithby PR, Snaith R and Wheatley AEH. *New J. Chem.* 1999; **23**: 35.
7. Clegg W, Liddle ST, Snaith R and Wheatley AEH. *New J. Chem.* 1998; **22**: 1323.
8. Thompson A, Corley EG, Huntington MF, Grabowski EJJ, Remenar JF and Collum DB. *J. Am. Chem. Soc.* 1998; **120**: 2028.
9. Nichols MA, McPhail AT and Arnett EM. *J. Am. Chem. Soc.* 1991; **113**: 6222.
10. Armstrong DR, Davies RP, Raithby PR, Snaith R and Wheatley AEH. *New J. Chem.* 1999; **23**: 499.
11. Goldfuss B and Eisenträger F. *Aust. J. Chem.* 2000; **53**: 209.
12. Davies JE, Raithby PR, Snaith R and Wheatley AEH. *J. Chem. Soc., Chem. Commun.* 1997; 1721.
13. Arnett EM, Nichols MA and McPhail AT. *J. Am. Chem. Soc.* 1990; **112**: 7059.
14. Engelhardt LM, Harrowfield JM, Lappert MF, MacKinnon IA, Newton BH, Raston CL, Skelton BW and White AH. *J. Chem. Soc., Chem. Commun.* 1986; 846.
15. Feustel A and Müller G. *J. Chem. Soc., Chem. Commun.* 2001; 1024.
16. Goldfuss B, Schleyer PvR and Hampel F. *Organometallics* 1997; **16**: 5032.
17. Goldfuss B, Schleyer PvR and Hampel F. *J. Am. Chem. Soc.* 1997; **119**: 1072.
18. Nilsson Lill SO, Arvidsson PI and Ahlberg P. *Acta Chem. Scand.* 1998; **52**: 280.
19. Goldfuss B, Schleyer PvR and Hampel F. *J. Am. Chem. Soc.* 1996; **118**: 12 183.
20. Bains MS. *Can. J. Chem.* 1964; **42**: 945.
21. Beck G, Hitchcock PB, Lappert MF and MacKinnon IA. *J. Chem. Soc., Chem. Commun.* 1989; 1312.
22. Adler M, Marsch M, Nudelman NS and Boche G. *Angew. Chem., Int. Ed. Engl.* 1999; **38**: 1261.
23. Chisholm MH, Drake SR, Naiini AA and Streib WE. *Polyhedron* 1991; **10**: 805.
24. Halaska V, Lochmann L and Lim D. *Collect. Czech. Chem. Commun.* 1968; **33**: 3245.
25. Thomas RD, Bott SG, Gravelle PW and Nguyen HD. *Book of Abstracts, 215th ACS National Meeting, Dallas, 29 March–2 April* INOR: 1998.
26. Hartwell GE and Brown TL. *Inorg. Chem.* 1966; **5**: 1257.
27. Armstrong DR, Clegg W, Drummond AM, Liddle ST and Mulvey RE. *J. Am. Chem. Soc.* 2000; **122**: 11 117.
28. Kahn JD, Haag A and Schleyer PvR. *J. Phys. Chem.* 1988; **92**: 212.
29. Braun M, Waldmüller D and Mayer B. *Angew. Chem.* 1989; **101**: 953.
30. Wheatley PJ. *J. Chem. Soc.* 1960; 4270.
31. Wheatley PJ. *Nature* 1960; **185**: 681.
32. Dunken H and Krausse J. *Z. Chem.* 1960; **1**: 27.
33. Schlengermann R, Sieler J, Jelonek S and Hey-Hawkins E. *Chem. Commun.* 1997; 197.
34. Schlengermann R, Sieler J and Hey-Hawkins E. *Main Group Chem.* 1997; **2**: 141.
35. Papp R, Sieler J and Hey-Hawkins E. *Polyhedron* 2001; **20**: 1053.
36. Giumanini AG, Giumanini AB and Lepley AR. *Chim. Ind. (Milan)* 1969; **51**(2): 139.
37. Al-Masri HT, Sieler J, Lönnecke P, Blaurock S, Domasevitch K and Hey-Hawkins E. In preparation.
38. Ludt RE, Crowther GP and Hauser CR. *J. Org. Chem.* 1970; **35**: 1288.
39. Rietveld MHP, Wehman-Ooyevaar ICM, Kapteijn GM, Grove DM, Smeets WJJ, Kooijman H, Spek AL and van Koten G. *Organometallics* 1994; **13**: 3782.
40. Van der Schaff PA, Jastrzebski JTBH, Hogerheide MP, Smeets WJJ, Spek AL, Boersma J and van Koten G. *Inorg. Chem.* 1993; **32**: 4111.
41. SHELXTL PLUS, Siemens Analyt. X-ray Inst. Inc., 1990. XS: Program for Crystal Structure Solution, XL: Program for Crystal Structure Determination, XP: Interactiv Molecular Graphics.
42. Boyle TJ, Pedrotty DM, Alam TM, Vick SC and Rodriguez MA. *Inorg. Chem.* 2000; **39**: 5133.
43. Huffman JC, Geerts RL and Gaulton KG. *J. Crystallogr. Spectrosc. Res.* 1984; **14**: 541.
44. Kociok-Köhn G, Pickardt J and Schumann H. *Acta Crystallogr. Sect. C* 1991; **47**: 2649.
45. Watson KA, Fortier S, Murchie MP, Bovenkamp JW, Rodrigue A, Buchanan GW and Ratcliffe CI. *Can. J. Chem.* 1990; **68**: 1201.
46. Kitamura M, Yamakawa M, Oka H, Suga S and Noyori R. *Chem. Eur. J.* 1996; **2**: 1173.
47. Kitamura M, Okada S, Suga S and Noyori R. *J. Am. Chem. Soc.* 1989; **111**: 4028.
48. Sheldrick GM. *SADABS – a program for empirical absorption correction*, University of Göttingen, 1998.