# Facile Synthesis of Sn$_4$N$_4$ Cubanes; Syntheses and Structures of [Sn(NC$_6$H$_{11}$)]$_4$ and [Sn(2-NCH$_2$C$_5$H$_4$N)]$_4$†

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The low-temperature reaction of Sn(NMe$_2$)$_2$ with primary amines (NH$_2$R) (1:1 equivalents) is a general route by which imido tin(II) cubanes [Sn(NR)]$_4$ can be prepared. It has been exemplified by the direct reactions of the relatively non-acidic primary amines NH$_2$(C$_6$H$_{11}$) and 2-H$_2$NCH$_2$C$_5$H$_4$N, producing the cubanes [Sn(NC$_6$H$_{11}$)]$_4$ **1** and [Sn(2-NCH$_2$C$_5$H$_4$N)]$_4$ **2**. The structures of both complexes have been established by X-ray crystallography.

Recently we have investigated the use of Group 15 metal dimethylamido-complexes ECl$_{3-x}$(NMe$_2$)$_x$ (E = Sb or Bi; $x$ = 2 or 3) as precursors in the syntheses of a variety of metallo-organic complexes.[1-4] We found that these species are particularly potent reagents and doubly deprotonate primary amines (NH$_2$R) at low temperatures, producing dimeric imido-complexes containing [E(μ-NR)]$_2$ cores.[1,2] Additionally, the reactions of dimethylamidometal complexes with metallated primary amines [*e.g.* (RNHLi)$_n$] results in a range of mixed-metal complexes containing early main-group metal cages.[3,4] With a view to extending this work to Group 14, we have initiated studies on the reactivity of Sn(NMe$_2$)$_x$ ($x$ = 2 or 4)[5] with primary and metallated primary amines. We present here the results of the metallation of the relatively non-acidic primary amines cyclohexylamine NH$_2$(C$_6$H$_{11}$) and 2-(aminomethyl)pyridine 2-(H$_2$NCH$_2$)C$_5$H$_4$N with Sn(NMe$_2$)$_2$ producing the imidotin(II) cubanes [Sn(NC$_6$H$_{11}$)]$_4$ **1** and [Sn(2-NCH$_2$C$_5$H$_4$N)]$_4$ **2**. Although several imidotin(II) cubanes have been prepared by a variety of routes,[6] the use of Sn(NMe$_2$)$_2$ allows the general synthesis of such complexes at low temperature and relatively non-acidic primary amines in which there is no conjugative stabilisation in the resulting imido-groups.

## Results and Discussion

Complexes **1** and **2** and the starting material Sn(NMe$_2$)$_2$ are air- and moisture-sensitive and were prepared under dry O$_2$-free argon using a vacuum-line and standard inert-atmosphere techniques.[7] The compound Sn(NMe$_2$)$_2$ was prepared in the manner described in the literature, as a light yellow powder in yields as high as 75%, by the reaction of LiNMe$_2$ with SnCl$_2$ in Et$_2$O.[5a] It is reasonably stable to storage under argon at room temperature (for *ca.* 2 weeks) and has high solubility in a range of polar and non-polar organic solvents.

Complexes **1** and **2** were prepared by the reactions of cyclohexylamine and 2-(aminomethyl)pyridine respectively with Sn(NMe$_2$)$_2$ (Scheme 1). Although the synthesis of **1** is particularly clean, a considerable amount of decomposition (giving metallic Sn) occurs in that of **2**. The thermal instability of **2**, which decomposes gradually above 30 °C, is reflected in the comparatively low isolated yield of the complex (38% for **2**, *cf.* 60% for **1**). Elemental analyses (C, H and N) and $^1$H NMR and IR spectroscopy initially confirmed the identities of the complexes prior to their characterisation by X-ray crystallography and the fact that double deprotonation of the amines had occurred.

$$4\mathrm{Sn(NMe_2)_2} + 4\mathrm{NH_2R} \longrightarrow [\mathrm{Sn(NR)}]_4 + 8\mathrm{NHMe_2}$$

**Scheme 1** R = C$_6$H$_{11}$ or NC$_5$H$_4$CH$_2$

The synthetic route applied for complexes **1** and **2** can be compared with those used previously in the syntheses of tin(II) imido cubanes. Veith and co-workers[6a-c] have shown that [Sn(NR)]$_4$ (E = Sn; R = Bu$^t$, Pr$^i$ or NMe$_2$) can be prepared at room temperature or above by the reactions of Sn[(Bu$^t$N)$_2$SiMe$_2$] with hydrazines or primary amines. This route allows the preparation of cubanes containing RN$^{2-}$ dianions which are not stabilised by conjugation within the organic group (R). The reactions of E(NSiMe$_3$)$_2$ (E = Sn or Pb) with suitable primary aromatic amines (in the melts at 50–60 °C) or borylamines (in hexane at reflux), yielding the cubanes [E(NR)]$_4$ [R = 2,6-Pr$^i_2$C$_6$H$_3$ or B(C$_6$H$_2$Me$_3$-2,4,6)$_2$], have also been investigated by Power and co-workers.[6d] However, it is noticeable that all the latter primary amines are inherently more acidic since charge dispersion from the imido nitrogen centre to the aromatic ring or to the vacant p orbital of the boron centre can occur. Although the previous study by Power and co-workers [6d] is closely related to the work presented here, the greater reactivity of Sn(NMe$_2$)$_2$ allows the low-temperature syntheses ($\leqslant$20 °C) in solution of complexes containing 'unstabilised' imido groups. This is particularly important in the preparation of **2** which is not stable to prolonged heating above 30 °C.

Low-temperature (153 K) X-ray crystallographic studies on complexes **1** and **2** were undertaken. Table 1 lists selected bond lengths and angles for both. Complexes **1** (Fig. 1) and **2** (Fig. 2) form similar cubane structures in the solid state. Within the Sn$_4$N$_4$ core of **1** all the Sn–N bonds are crystallographically identical [2.195(4)–2.205(4) Å]. Overall the angles at the tin (average 80.8°) and the nitrogen (average 98.5°) centres are uniform. The pattern of bond angles and lengths found is very similar to that observed in the solid-state structure of [Sn(NBu$^t$)]$_4$.[6b]

The pattern of bond lengths within the cubane core of complex **2** is far less regular than that of **1** [Sn–N 2.165(3)–2.235(3) Å]. Nonetheless, there are no marked angular distortions within the Sn$_4$N$_4$ unit and angles about the tin (average 80.3 °) and the nitrogen (average 98.8 °) centres are similar to those noted for **1**. Further examination of the structure of **2** sheds some light on the irregularity of the Sn–N bonds involved. The pyridyl nitrogen centres of three of the organic groups are bent towards the core and weakly interact

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

| | | | |
|---|---|---|---|
| Complex **1** * | | | |
| Sn(1)–N(1a) | 2.195(4) | Sn(2)–N(11a) | 2.195(4) |
| Sn(1)–N(1) | 2.203(4) | Sn(2)–N(1) | 2.199(4) |
| Sn(1)–N(11a) | 2.205(4) | Sn(2)–N(1a) | 2.205(4) |
| N–Sn–N | 80.8 (average) | Sn–N–Sn | 98.5 (average) |
| Complex **2** | | | |
| Sn(1)–N(1) | 2.165(3) | Sn(3)–N(4) | 2.198(3) |
| Sn(1)–N(3) | 2.201(4) | Sn(4)–N(4) | 2.197(3) |
| Sn(1)–N(2) | 2.212(3) | Sn(4)–N(3) | 2.199(3) |
| Sn(2)–N(4) | 2.179(3) | Sn(4)–N(1) | 2.235(3) |
| Sn(2)–N(2) | 2.206(3) | Sn(1,4,2)–N(3′,4′,2′) | 2.858–2.924 |
| Sn(2)–N(1) | 2.220(3) | | |
| Sn(3)–N(3) | 2.181(3) | Sn(3) ··· Sn(3a) | 3.40 |
| Sn(3)–N(2) | 2.195(4) | Sn(2) ··· Sn(2b) | 3.51 |
| N–Sn–N | 80.3 (average) | Sn–N–Sn | 98.8 (average) |

* Symmetry operation: a $-x + 1, y, -z + \frac{1}{2}$.

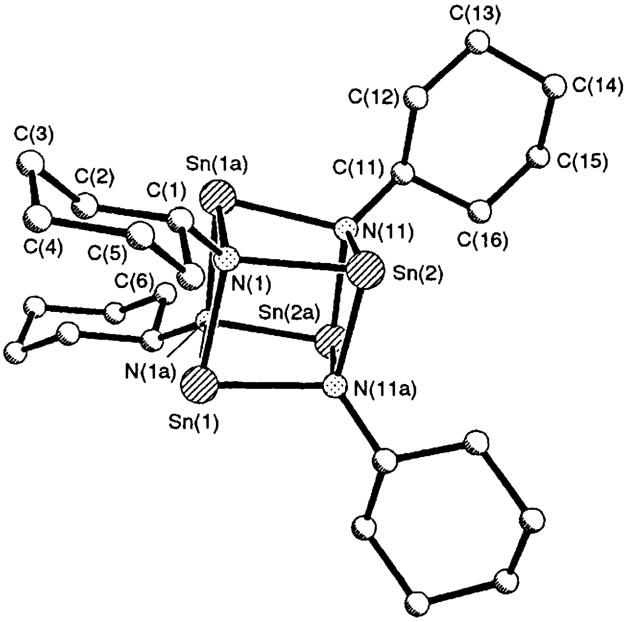

Fig. 1 Molecular structure of molecules of complex **1**. Hydrogen atoms have been omitted for clarity

with separate tin centres [Sn(1,4,2) ··· N(3′, 4′, 2′) 2.86–2.92 Å; *cf.* sum of van der Waals radii of Sn and N, 3.70 Å]. The result is that Sn(3) is the least sterically crowded tin centre of the core [closest Sn(3) ··· N(4′) 3.13 Å].

The pattern of intramolecular chelation in the core of complex **2** is subtly reflected in the packing of molecules in the lattice (Fig. 3). The cubane molecules are arranged in loose strands which are associated by weak intermolecular Sn ··· Sn interactions. The shortest metal–metal interaction occurs between the least-crowded tin centres of neighbouring molecules [Sn(3) ··· Sn(3a) 3.40 Å; *cf.* predicted van der Waals distance for Sn ··· Sn 4.40 Å]. Additionally, a slightly longer Sn ··· Sn link is made between one of the loosely chelated centres of two neighbouring molecules [Sn(2) ··· Sn(2b) 3.51 Å]. Such loose Sn ··· Sn interactions have been seen before in the solid-state structure of the cubane $[Sn(NNH_2)]_4$ (*ca.* 3.51 Å)[6a] where, as in the case of **2**, less sterically demanding organic groups are involved. However, in $[Sn(NNH_2)]_4$ two tin centres of each $Sn_4N_4$ unit interact symmetrically with one tin centre of a neighbouring cubane. The association of molecules of **2** in the solid state illustrates that such interactions can be modified by the effects of intramolecular donation within the $Sn_4N_4$ units.

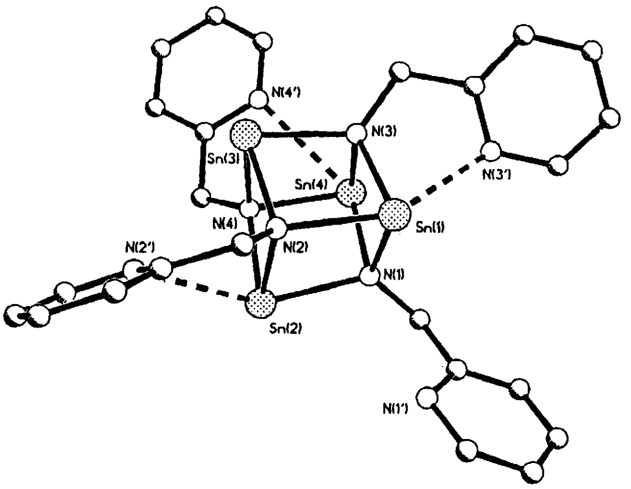

Fig. 2 Molecular structure of molecules of complex **2**. Hydrogen atoms have been omitted for clarity

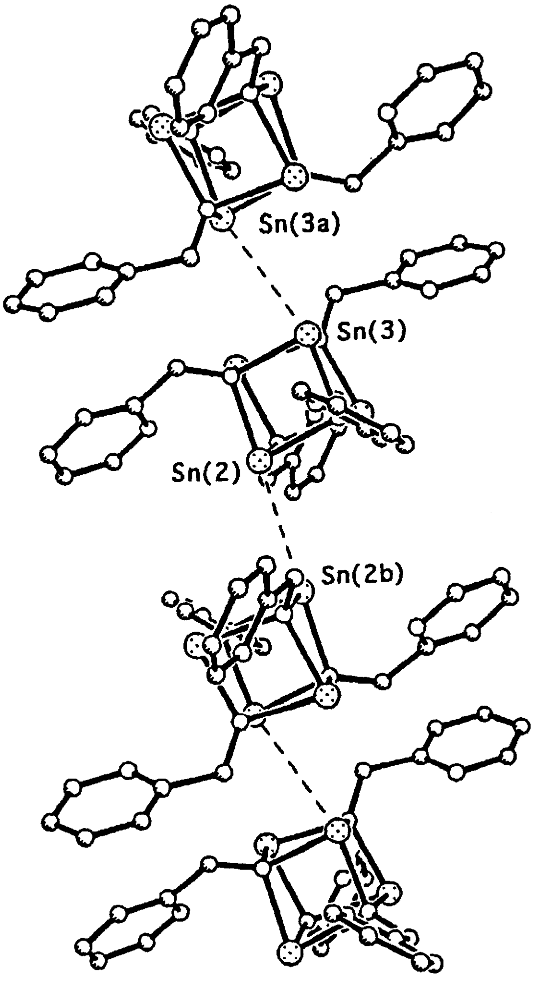

Fig. 3 Intermolecular packing of complex **2** *via* Sn ··· Sn interactions

The facile syntheses of $Sn_4N_4$ cubanes from relatively non-acidic primary amines and $Sn(NMe_2)_2$ potentially provides an easily accessible source of a broad range of imido dianions ($RN^{2-}$) for use in transmetallation reactions with metal salts. Such dianions are generally not readily prepared, *e.g.* from alkali-metal organometallics and primary amines. The synthesis of complex **2**, containing flexible pyridyl donor arms at the periphery of the cubane core, is also of interest. We are currently investigating its application and that of similar complexes as multidentate donor molecules to a range of metals.

## Experimental

*General Procedure.*—The products **1** and **2** and the starting materials $LiNMe_2$ and $Sn(NMe_2)_2$ are all air-sensitive. They were handled on a vacuum line using standard inert-atmosphere techniques[7] and under dry $O_2$-free Ar. The toluene and $Et_2O$ solvents were dried using sodium–benzophenone and degassed prior to the reactions, and the amines [cyclohexylamine and 2-(aminomethyl)pyridine] were dried using molecular sieves (13X). The compound $Sn(NMe_2)_2$ was prepared as described[5a] from $SnCl_2$ and $LiNMe_2$ (1:2 equivalents) in $Et_2O$, the product being obtained after filtration and removal of the solvent under vacuum as a light yellow powder (60–75%). All complexes were isolated and characterised with the aid of an argon-filled glove-box (Miller-Howe) fitted with an oxygen- and water-recirculation system. Melting points were determined by using a conventional apparatus and sealing samples in capillaries under Ar. Infrared spectra were recorded as Nujol mulls using NaCl windows on a Perkin-Elmer 2400 spectrophotometer. Elemental analyses were performed by sealing samples under Ar in air-tight aluminium boats (1–2 mg), using a Perkin-Elmer 240 Elemental Analyser. Proton NMR spectra were recorded on a Bruker WH 250 MHz spectrometer in dry $C_6D_6$ using the solvent resonances as the internal reference.

*Synthesis of* $[Sn(NC_6H_{11})]_4$ **1**.—To a solution of $Sn(NMe_2)_2$ (0.517 g, 2.5 mmol) in toluene (20 cm$^3$) was added $NH_2(C_6H_{11})$ (0.286 cm$^3$, 2.5 mmol) at 20 °C. An immediate change to yellow occurred. Filtration of a small amount of precipitate and reduction of the filtrate under vacuum to *ca.* 10 cm$^3$ resulted in the precipitation of a white solid. The solid was warmed back into solution and cubic crystals of complex **1** were grown at room temperature. Yield 0.32 g (60%); decomposes to black solid above 290 °C (Found: C, 33.5; H, 5.2; N, 6.4. Calc. for $C_{24}H_{44}N_4Sn_4$: C, 33.3; H, 5.1; N, 6.5%). $^1H$ NMR ($C_6D_6$, 250 MHz, +25 °C): δ 2.52 (1 H, m, α-H of $C_6H_{11}$) and 1.76–0.82 (10 H, br m, $CH_2$ of $C_6H_{11}$).

*Synthesis of* $[Sn(NCH_2C_5H_4N)]_4$ **2**.—To a solution of $Sn(NMe_2)_2$ (0.517 g, 2.5 mmol) in toluene (20 cm$^3$) and tetrahydrofuran (10 cm$^3$) at −78 °C was added 2-(aminomethyl)pyridine (0.258 g, 2.5 mmol). An immediate reaction occurred to give a red solution. Filtration of the reaction mixture at 20 °C (Celite, porosity 3 sinter) was necessary to remove black metallic tin. The clear red filtrate was reduced in volume under vacuum to *ca.* 10 cm$^3$ whereupon a yellow solid precipitated.

**Table 2** Crystal data and structure solutions of complexes **1** and **2***

| | | |
|---|---|---|
| Empirical formula | $C_{24}H_{44}N_4Sn_4$ | $C_{24}H_{24}N_8Sn_4$ |
| *M* | 433.70 | 899.27 |
| Crystal system | Monoclinic | Triclinic |
| Space group | *C*2/*c* | $P\bar{1}$ |
| Crystal size/mm | 0.34 × 0.33 × 0.29 | 0.26 × 0.22 × 0.19 |
| *a*/Å | 19.626(4) | 11.037(2) |
| *b*/Å | 9.550(2) | 11.659(2) |
| *c*/Å | 16.776(3) | 12.308(2) |
| α/° | — | 89.94(3) |
| β/° | 113.62(3) | 67.64(3) |
| γ/° | — | 72.17(3) |
| *U*/Å$^3$ | 2880.9(10) | 1382.3(4) |
| *Z* | 8 | 2 |
| $D_c$/Mg m$^{-3}$ | 1.991 | 2.161 |
| *F*(000) | 1664 | 848 |
| μ(Mo-Kα)/mm$^{-1}$ | 3.446 | 3.600 |
| θ range/° | 3.78–2.49 | 3.61–25.00 |
| Reflections collected | 1792 | 4968 |
| Independent reflections | 1792 | 4841 |
| Goodness of fit | 1.319 | 1.019 |
| *R* indices [$F > 4\sigma(F)$]: $R_1$, $wR_2$ | 0.0209, 0.0556 | 0.0220, 0.0590 |
| *R* indices (all data): $R_1$, $wR_2$ | 0.0250, 0.1014 | 0.0243, 0.0607 |
| Final difference peak and hole/e Å$^{-3}$ | 0.456, −0.5930 | 0.689, −0.601 |

* Details in common: λ(Mo-Kα) 0.710 73Å; *T* 153(2) K; $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2/3)$.[10]

**Table 3** Atomic coordinates ( × 10$^4$) for complex **1**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Sn(1) | 5484(1) | 1030(1) | 3587(1) |
| Sn(2) | 4202(1) | 3454(1) | 2645(1) |
| N(1) | 4329(2) | 1169(4) | 2616(3) |
| N(11) | 4594(2) | 3321(4) | 1586(3) |
| C(1) | 3741(3) | 276(5) | 2706(3) |
| C(2) | 3842(3) | −1264(5) | 2565(4) |
| C(3) | 3237(3) | −2179(6) | 2659(4) |
| C(4) | 3192(3) | −1945(6) | 3531(4) |
| C(5) | 3095(3) | −410(6) | 3690(4) |
| C(6) | 3704(3) | 478(6) | 3583(3) |
| C(11) | 4257(3) | 4265(5) | 818(3) |
| C(12) | 3411(3) | 4191(5) | 429(3) |
| C(13) | 3043(3) | 5222(6) | −320(3) |
| C(14) | 3317(3) | 6705(6) | −41(4) |
| C(15) | 4152(3) | 6787(5) | 291(4) |
| C(16) | 4513(3) | 5772(5) | 1047(4) |

**Table 4** Atomic coordinates ( × 10$^4$) for complex **2**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Sn(1) | −1276(1) | 2580(1) | 2450(1) |
| Sn(2) | −1029(1) | 340(1) | 4176(1) |
| Sn(3) | 342(1) | −325(1) | 1220(1) |
| Sn(4) | 1776(1) | 1037(1) | 2504(1) |
| N(1) | −422(3) | 1988(3) | 3753(3) |
| N(2) | −1595(3) | 796(3) | 2654(3) |
| N(3) | 784(3) | 1374(3) | 1234(3) |
| N(4) | 980(3) | −497(3) | 2716(3) |
| N(1′) | −3074(4) | 3673(4) | 5493(4) |
| N(2′) | −2131(4) | −1296(3) | 3334(3) |
| N(3′) | 876(4) | 3637(3) | 1565(3) |
| N(4′) | 3459(4) | −1126(3) | 857(3) |
| C(10) | −470(4) | 2885(3) | 4617(3) |
| C(11) | −1842(4) | 3870(3) | 5277(3) |
| C(12) | −1802(4) | 4942(4) | 5664(3) |
| C(13) | −3002(6) | 5840(5) | 6299(4) |
| C(14) | −4261(5) | 5690(4) | 6567(4) |
| C(15) | −4282(5) | 4627(5) | 6142(4) |
| C(20) | −2911(4) | 692(4) | 2711(4) |
| C(21) | −3131(4) | −489(4) | 3102(3) |
| C(22) | −4373(5) | −691(5) | 3247(5) |
| C(23) | −4562(6) | −1753(6) | 3645(5) |
| C(24) | −3524(6) | −2591(6) | 3887(5) |
| C(25) | −2326(6) | −2326(4) | 3721(5) |
| C(30) | 1508(5) | 1870(4) | 178(4) |
| C(31) | 1439(5) | 3156(4) | 423(4) |
| C(32) | 1895(6) | 3833(5) | −483(5) |
| C(33) | 1771(7) | 5015(6) | −201(7) |
| C(34) | 1203(6) | 5516(5) | 970(6) |
| C(35) | 784(6) | 4798(4) | 1815(5) |
| C(40) | 1966(4) | −1685(4) | 2653(3) |
| C(41) | 3223(4) | −2037(4) | 1483(3) |
| C(42) | 4071(5) | −3228(4) | 1078(4) |
| C(43) | 4546(5) | −1396(5) | −192(4) |
| C(44) | 5412(5) | −2553(5) | −654(4) |
| C(45) | 5178(5) | −3488(5) | −18(5) |

* See Fig. 2 for the notation N(1′), N(2′), N(3′) and N(4′).

This was heated gently back into solution and orange crystals of complex **2** were grown at room temperature. Yield 0.21 g (38%); decomposes gradually > 30 °C to a green solid (Found: C, 31.3; H, 3.0; N, 11.9. Calc. for $C_{24}H_{24}N_8Sn_4$: C, 32.0; H, 2.7; N, 12.4%). $^1H$ NMR (250 MHz, $C_6D_6$, +25 °C): δ 8.63 (1 H, d, $H^6$ of $C_5H_4N$), 7.91 (1 H, t, $H^5$ of $C_5H_4N$), 7.57 (1 H, d, $H^3$ of $C_5H_4N$), 7.43 (1 H, t, $H^4$ of $C_5H_4N$) and 4.50 (2 H, s, $CH_2$).

*X-Ray Crystallography.*—Crystals of complexes **1** and **2** were mounted directly from solution at room temperature under Ar using a perfluorocarbon oil which protects them from atmospheric moisture and oxygen (Riedel-de Haën). The oil 'freezes' at reduced temperatures and holds the crystal static in the X-ray beam.[8] Data were collected on a Stoe AED diffractometer, and a semiempirical absorption correction based on ψ scans was employed. The structures were solved by the direct method (SHELXTL PLUS)[9] and refined by full-matrix least squares on $F^2$ (SHELXL 93).[10] The H atoms were fixed geometrically in both structures. Details of the structure solutions and refinements for **1** and **2** are listed in Table 2, final atomic coordinates in Tables 3 and 4, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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