NCO-CHELATED ORGANOANTIMONY(III) AND ORGANOBISMUTH(III) DICHLORIDES: SYNTHESES AND STRUCTURES

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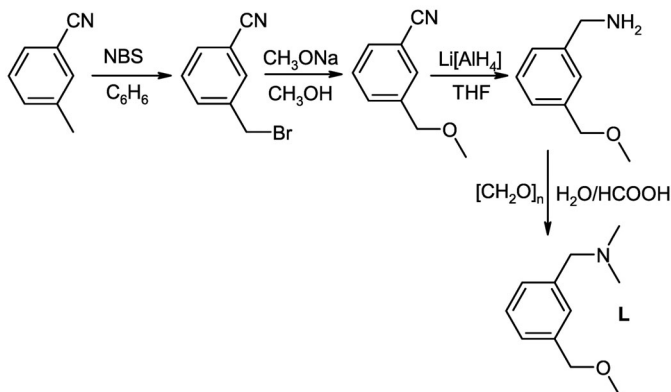
Dedicated to Dr. Bohumil Štíbr on the occasion of his 70th birthday in recognition of his outstanding contribution to inorganic and organometallic chemistry.
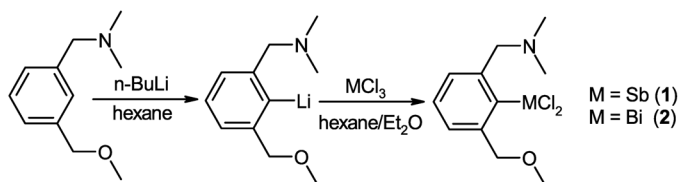
The novel NCO chelating ligand **L**, 1-$CH_2N(CH_3)_2$-3-CH_2OCH_3-C_6H_4, was prepared in four steps from commercially available *m*-tolunitrile in a good yield. Successful lithiation of this ligand was achieved by the reaction with *n*-BuLi in hexane. Using of this in situ prepared organolithium compound **LLi** in the reactions with MCl_3 (M = Sb, Bi) in 1:1 molar ratio led to isolation of the desired mono-organocompounds $MLCl_2$ (M = Sb (**1**), Bi (**2**)). Their structures were studied both in solution (NMR) and in the solid state (X-ray diffraction), and were compared with those of the NCN- and OCO-chelating analogues.
Keywords: Antimony; Bismuth; Chelating ligands; X-ray structure.

In 1978, van Koten et al. reported on the first utilization of potentially NCN terdentate ligand, $[2,6-(Me_2NCH_2)_2-C_6H_3]^-$ (Chart 1A), for stabilization of organotin(IV) cations[1]. Since that time, the chemistry of so-called pincer[2] ligands has developed to a well established branch of organometallic chemistry, with both main group[3] and transition metals[4]. Jurkschat et al. enriched the pincer chemistry of main groups by introduction of an OCO ligand (Chart 1B) in 1998 [5]; the chemistry of this ligand has been extended so far to Li, Si, Sn, Pb compounds[6]. We have reported on OCO pincer ligands based on etheral donor groups (Chart 1C) in 2002 [7] and developed their chemistry to Li, Al, Si, Sn, P, Sb, Bi as central atoms[8]. The utilization of the so-called hybrid pincer ligands containing a non-equivalent donor atom array, such as PCN, PCO or SCO, has been reported

recently as well, and they often exhibit special reactivity and physical properties[9].

As a part of our ongoing investigation of pincer type ligands bound to main group metals, we report here on the synthesis of a novel NCO chelating ligand $[2\text{-Me}_2\text{NCH}_2\text{-}6\text{-MeOCH}_2\text{-C}_6\text{H}_3]^-$ denoted as **L** hereinafter. This type of ligand enables us to compare the chemical properties of organometallic compounds based on this skeleton with compounds containing pure N- (Chart 1A) or O-donor (Chart 1B, C) ligands. The syntheses and structures of organoantimony(III) and organobismuth(III) dichlorides $MLCl_2$ (M = Sb (**1**) and Bi (**2**)) are described here as the first derivatives of this new ligand system.

A   **B**   **C**   **D**

R = Et, *i*-Pr

R = Me, Et, *i*-Pr, *t*-Bu
and mesityl

CHART 1

RESULTS AND DISCUSSION

The starting NCO chelating ligand **L** was prepared by a four step procedure according to Scheme 1. The ligand **L** was obtained as colorless, distillable liquid in a reasonable yield, see Experimental.

Successful lithiation of the ligand was achieved by using one molar equivalent of *n*-BuLi in hexane at room temperature. The organolithium compound was not isolated but used in an orange hexane solution for in situ reactions with metallic chlorides (Scheme 2).

Thus, the reaction of the organolithium compound **L**Li with $SbCl_3$ or $BiCl_3$ in 1:1 molar ratios gave, after workup, the corresponding dichlorides **1** and **2** (Scheme 2) as air-stable white solids. Both compounds melt with decomposition at 175 (**1**) and 180 °C (**2**). Their identity was established by satisfactory elemental analyses.

The molecular structures of **1** and **2** were unambiguously determined by single crystal X-ray diffraction (Figs 1 and 2). As a result of the rigid tridentate coordination of the NCO ligand **L** in both compounds, the coordination polyhedron around the central metal, Sb1 (**1**) and Bi1 (**2**), can be

SCHEME 1

SCHEME 2

best described as a distorted tetragonal pyramid with the apical position occupied by the *ipso*-carbon atom C1. The bond distances between donor and the central atoms, i.e., Sb1–O1 2.469(4), Sb1–N1 2.315(5) Å and Bi1–O1 2.515(12) , Bi1–N1 2.482(17) Å, indicate strong intramolecular interactions, all these values are close to those observed in organoantimony and bismuth cations containing OCO or NCN ligands[10]. The donor atoms O1 and N1 as well as both chlorido ligands Cl1 and Cl2 are placed in mutual *trans*-positions in the basal plane of the tetragonal pyramid, as demonstrated by the bond angles Cl1–Sb1–Cl2 174.44(5), O1–Sb1–N1 148.05(15)° for **1** and Cl1–Bi1–Cl2 178.92(13), O1–Bi1–N1 143.8(4)° for **2**. The significant deviation of the of O–M–N angles from the ideal value (180°) is a consequence of the chelating-ring strain.

The comparison of **1** and **2** with analogous compounds containing OCO or NCN ligands reveals some significant differences, especially in the case of the OCO ligand (Chart 2). Both oxygen atoms and chlorido ligands are placed in a *cis*-fashion (with the angles O–Sb–O 116.68°, Cl–Sb–Cl 84.54°)[8a] in the case of the OCO-chelated organoantimony dichloride (Chart 2A). Thus, the coordination of the OCO pincer type ligand may be described as

pseudofacial, and the resulting polyhedron around the antimony atom is a trigonal pyramid $SbCCl_2$ (the sum of angles describing the $SbCCl_2$ girdle reaching 279.7°), which is bicapped by two oxygen donor atoms. The donor (N, O) atoms as well as the chloride ligands are *trans*-arranged in compound **1** (Fig. 1) and the coordination of the NCO ligand is pseudo-meridional, leading to a distorted tetragonal pyramidal array around the antimony atom. This bonding situation in **1** is closely related to that in the NCN analogue[11a] (Chart 2**C**) where the ligand shows meridional coordination and the central antimony atom is located in a distorted tetragonal pyramidal environment with *trans*-positioned chlorido and nitrogen donor atoms (cf. the Cl–Sb–Cl angles of 174.0° and 174.08° (the mean value for the two independent molecules in **1**), and the N–Sb–N angle of 147.3° with the N–Sb–O angle of 148.4° (the mean value for the two independent molecules in **1**)).

The OCO-chelated bismuth compound (Chart 2**B**) forms a tightly bound dimer in the solid state via two chlorido bridges. The OCO ligand again pre-
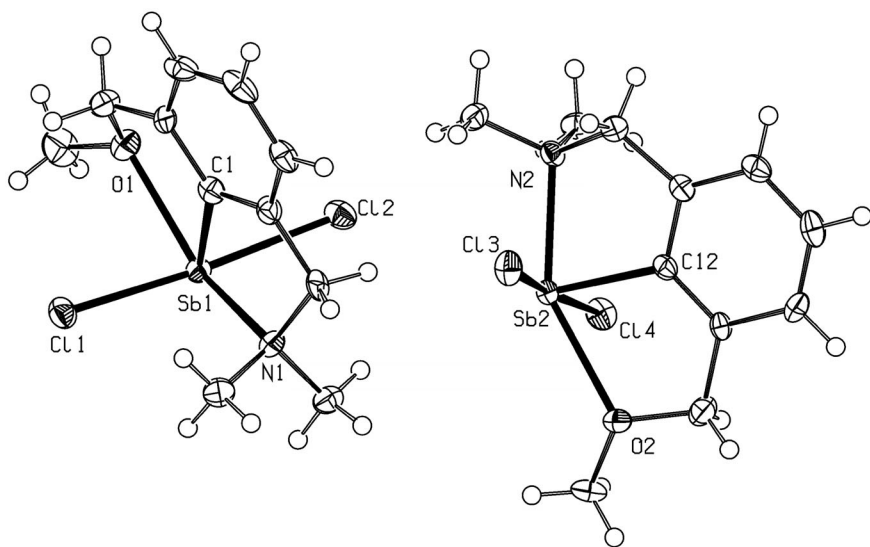
Fig. 1

The ORTEP plot of the molecular structure of compound **1** showing both independent molecules. Selected bond lengths (in Å) and angles (in °)]: Sb1–O1 2.469(4), Sb1–N1 2.315(5), Sb1–C1 2.118(8), Sb1–Cl1 2.5560(18), Sb1–Cl2 2.6569(16); Cl1–Sb1–Cl2 174.44(5), O1–Sb1–N1 148.05(15), C1–Sb1–Cl1 88.94(19), C1–Sb1–Cl2 85.54(19), C1–Sb1–O1 71.69(18), C1–Sb1–N1 76.5(2); Sb2–O2 2.481(4), Sb2–N2 2.312(4), Sb2–C12 2.099(7), Sb2–Cl3 2.6567(16), Sb2–Cl4 2.5612(16), Cl3–Sb2–Cl4 173.71(5), O2–Sb2–N2 148.73(14), C12–Sb2–Cl3 85.23(19), C12–Sb2–Cl4 88.50(19), C12–Sb2–O2 71.31(18), C12–Sb2–N2 77.46(19)

fers pseudofacial coordination, as demonstrated by the O–Bi–O bond angle of 127.50°. Compound **2** remains essentially mononuclear in the solid state and the meridional coordination of the NCO ligand (Fig. 2) resembles the situation in the NCN-chelated compound[11b] (Chart 2C; cf. the Cl–Bi–Cl
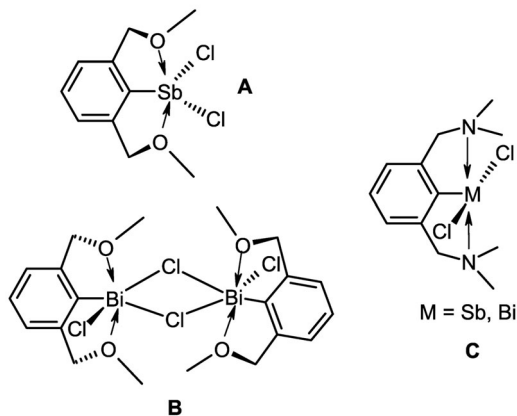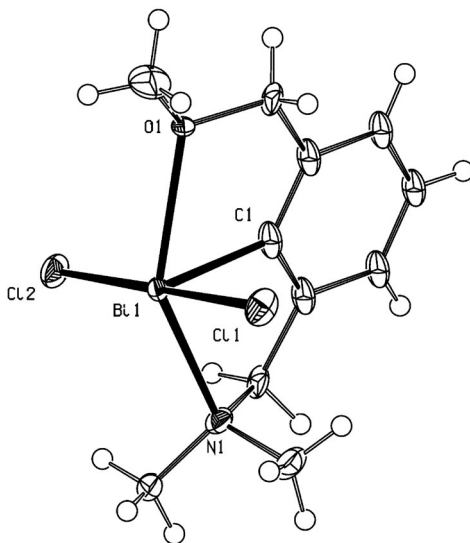

CHART 2

FIG. 2
The ORTEP plot of the molecular structure of compound **2**. Selected bond lengths (in Å) and angles (in °): Bi1–O1 2.521(12), Bi1–N1 2.483(17), Bi1–C1 2.189(14), Bi1–Cl1 2.643(4), Bi1–Cl2 2.704(4); Cl1–Bi1–Cl2 178.88(13), O1–Bi1–N1 143.5(4), C1–Bi1–Cl1 89.9(4), C1–Bi1–Cl2 89.1(4), C1–Bi1–O1 69.5(5), C1–Bi1–N1 74.2(5)

angles of 173.73 and 178.88° in **2**, and the N–Bi–N angle of 144.18° with the N–Bi–O angle of 143.5° in **2**). In summary, these data indicate that the NCO ligand **L**, in this limited series of compounds, prefers meridional coordination, thereby resembling analogous NCN-chelated compounds rather than the OCO derivatives. The preference of the NCO ligand to behave as an NCN analogue may be ascribed to the presence of the nitrogen donor atom in **1** and **2**, which is in general a better donor than the etheral oxygen, leading to a stronger donor atom–metal interaction. The latter may compel the ligand coordination geometry to change from pseudofacial (OCO type) to meridional (NCN and NCO types).

The ^{1}H and ^{13}C NMR spectra of **1** and **2** have revealed one set of sharp signals for both CH_2OMe and CH_2NMe_2 groups, indicating rigid tridenate (meridional) coordination of the ligand **L**, which is consistent with the molecular structures determined in the solid state (vide supra). The proton signals of CH_2O (δ 4.98 and 5.08 ppm for **1** and **2**, respectively) and CH_2N (δ 4.41 and 4.83 ppm for **1** and **2**, respectively) are shifted to a lower field in comparison with the non-substituted ligand (δ 4.46 ppm for CH_2O and 3.43 ppm for CH_2N), proving the metal–O(N) donor–acceptor interactions.

EXPERIMENTAL

All air sensitive operations were carried out under an argon atmosphere, using a standard Schlenk technique. Solvents were dried by standard procedures and distilled prior to use. ^{1}H and ^{13}C NMR spectra were measured on a Bruker 400 spectrometer. Chemical shifts (δ, ppm) have been referenced to residual signals of CDCl$_3$ (δ$_H$ 7.27, δ$_C$ 77.23). The starting compounds *m*-tolunitrile (98%), antimony chloride (99.99%) and bismuth chloride (99.999%) were obtained from commercial suppliers and used as received.

Synthesis of 1-CN-3-CH$_2$Br-C$_6$H$_4$

A mixture of *m*-tolunitrile (32 g, 0.27 mol) with *N*-bromosuccinimide (48.6 g, 0.27 mol) and benzoyl peroxide (1.1 g, 4.54 mmol) was heated in benzene (250 ml) to reflux for 3 h. The mixture was cooled to room temperature and the insoluble material was filtered off and discarded. The filtrate was evaporated, giving a cream solid that was washed twice with hexane (2 × 50 ml). The product was crystallized from ethanol and dried in vacuo to give 28.1 g (53%) of 1-CN-3-CH$_2$Br-C$_6$H$_4$, m.p. 97 °C. The sample was sufficiently pure for the next step. ^{1}H NMR (CDCl$_3$, 293 K): 4.47 s, 2 H (CH$_2$Br); 7.47 dd, 1 H (Ar-H5); 7.61 m, 2 H (Ar-H4,6); 7.69 s, 1 H (Ar-H2). ^{13}C NMR (CDCl$_3$, 293 K): 31.4 (CH$_2$Br); 113.1, 118.4, 129.9, 132.1, 132.6, 133.5 (Ar-C); 139.4 (CN). For C$_8$H$_6$BrN (196.1) calculated: 49.0% C, 3.1% H; found: 49.2% C, 3.3% H.

Synthesis of 1-CN-3-CH$_2$OCH$_3$-C$_6$H$_4$

1-CN-3-CH$_2$Br-C$_6$H$_4$ (13.5 g, 0.069 mol) was added as a THF solution (60 ml) to a solution of sodium methoxide (130 ml) prepared from the sodium metal (1.9 g, 0.083 mol). The reaction mixture was stirred for 5 h. The reaction mixture was evaporated to dryness and the residue was divided between diethyl ether (50 ml) and water (50 ml). The organic layer was separated and the water phase extracted with additional 50 ml of diethyl ether. Combined organic layers were dried over MgSO$_4$ and evaporated to give the product as a yellowish oil. The product was obtained after distillation at 90 °C (130 Pa) as colorless liquid 9.3 g (92%). It was used for next step without further purification. ^{1}H NMR (CDCl$_3$, 293 K): 3.42 s, 3 H (CH$_3$O); 4.48 s, 2 H (CH$_2$O); 7.46 dd, 1 H (Ar-H5); 7.57 m, 2 H (Ar-H4,6); 7.64 s, 1 H (Ar-H2). ^{13}C NMR (CDCl$_3$, 293 K): 58.6 (CH$_3$O); 73.5 (CH$_2$O); 112.6, 118.9, 129.3, 130.9, 131.3, 131.8 (Ar-C); 140.0 (CN). For C$_9$H$_9$NO (147.2) calculated: 73.5% C, 6.2% H; found: 73.4% C, 6.1% H.

Synthesis of 1-CH$_2$NH$_2$-3-CH$_2$OCH$_3$-C$_6$H$_4$

1-CN-3-CH$_2$OCH$_3$-C$_6$H$_4$ (9.1 g, 0.062 mol) was carefully added as a neat oil via syringe to a THF suspension (150 ml) of LiAlH$_4$ (2.5 g, 0.066 mol) under stirring at 0 °C. The reaction mixture was allowed to reach room temperature and remained stirred for additional 12 h. Subsequently, the reaction mixture was heated to reflux for 5 h. After cooling back to room temperature, the remaining LiAlH$_4$ was quenched with water (20 ml) and 2 M KOH (20 ml). The resulting mixture was extracted twice with diethyl ether (2 × 50 ml). The organic layer was dried over Na$_2$SO$_4$ and evaporated to yield 7.4 g (79%) of the product as a yellow oil that was used for next step without further purification. ^{1}H NMR (CDCl$_3$, 293 K): 1.88 s, 2 H (NH$_2$); 3.37 s, 3 H (CH$_3$O); 3.82 s, 2 H (CH$_2$N); 4.43 s, 2 H (CH$_2$O); 7.24 m, 4 H (Ar-H). ^{13}C NMR (CDCl$_3$, 293 K): 46.4 (CH$_2$N); 58.3 (CH$_3$O); 74.7 (CH$_2$O); 126.3, 126.5 overlap of two signals, 128.7, 131.5, 143.4 (Ar-C). For C$_9$H$_{13}$NO (151.2) calculated: 71.5% C, 8.7% H; found: 71.7% C, 8.4% H.

Synthesis of 1-CH$_2$N(CH$_3$)$_2$-3-CH$_2$OCH$_3$-C$_6$H$_4$ (L)

A mixture of 1-CH$_2$NH$_2$-3-CH$_2$OCH$_3$-C$_6$H$_4$ (7.4 g, 0.049 mol) was added to HCOOH (5 ml) in water (30 ml) at 0 °C, followed by paraformaldehyde (2.94 g, 0.098 mol) used as a water suspension (100 ml). The resulting mixture was heated to reflux for 5 h. After cooling to room temperature, an excess of solid KOH was added. The resulting mixture was extracted twice with diethyl ether (2 × 50 ml). The organic layer was dried over Na$_2$SO$_4$ and evaporated to give a yellow oil. The product was obtained after distillation at 65 °C (120 Pa) as a colorless oil, yield 7 g (80%). ^{1}H NMR (CDCl$_3$, 293 K): 2.25 s, 6 H (N(CH$_3$)$_2$); 3.40 s, 3 H (CH$_3$O); 3.43 s, 2 H (CH$_2$N); 4.46 s, 2 H (CH$_2$O); 7.27 m, 4 H (Ar-H). ^{13}C NMR (CDCl$_3$, 293 K): 45.4 ((CH$_3$)$_2$N); 58.2 (CH$_3$O); 64.5 (CH$_2$N); 74.8 (CH$_2$O); 126.6, 128.4, 128.5, 128.6, 138.3, 139.0 (Ar-C). For C$_{11}$H$_{17}$NO (179.3) calculated: 73.7% C, 9.6% H; found: 73.9% C, 9.5% H.

Synthesis of Sb(2-CH$_2$N(CH$_3$)$_2$-6-(CH$_2$OCH$_3$-C$_6$H$_3$)Cl$_2$ (1)

A hexane solution of 1.6 M n-BuLi (2.3 ml, 0.37 mmol) was added to a hexane solution (20 ml) of the ligand **L** (0.66 g, 0.37 mmol). The resulting yellow-orange solution was stirred

for 12 h. This solution of organolithium compound **L**Li was added to a pre-cooled (–70 °C) solution of SbCl$_3$ (0.84 g, 0.37 mmol) in diethyl ether (100 ml). The resulting cream suspension was stirred for 12 h at room temperature The insoluble material was filtered and washed with additional hexane (20 ml). The remaining solid was extracted with dichloromethane (50 ml). Evaporation of the filtrate gave compound **1** as a yellowish powder, yield 0.75 g (55%). Compound **1** was crystallized from a dichloromethane/hexane solution to give single crystals suitable for X-ray diffraction technique, m.p. 175 °C (decomp.). ^{1}H NMR (CDCl$_3$, 293 K): 3.03 s, 6 H (N(CH$_3$)$_2$); 3.87 s, 3 H (CH$_3$O); 4.41 s, 2 H (CH$_2$N); 4.98 s, 2 H (CH$_2$O); 7.24 m, 2 H (Ar-H3,5); 7.37 t, 1 H (Ar-H4). ^{13}C NMR (CDCl$_3$, 293 K): 48.9 ((CH$_3$)$_2$N); 59.9 (CH$_3$O); 67.0 (CH$_2$N); 74.8 (CH$_2$O); 124.3, 125.1, 130.2, 141.8, 143.1, 155.9 (Ar-C). For C$_{11}$H$_{17}$NO (370.9) calculated: 35.6% C, 4.4% H; found: 35.7% C, 4.5% H.

Synthesis of Bi(2-CH$_2$N(CH$_3$)$_2$-6-CH$_2$OCH$_3$-C$_6$H$_3$)Cl$_2$ (**2**)

A hexane solution of 1.6 M *n*-BuLi (2.9 ml, 0.47 mmol) was added to a hexane solution (20 ml) of the ligand **L** (0.83 g, 0.47 mmol). The resulting yellow-orange solution was stirred for 12 h. The dissolved organolithium product **L**Li was added to a pre-cooled (–70 °C) solution of BiCl$_3$ (1.48 g, 0.47 mol) in diethyl ether (100 ml). The resulting cream suspension was stirred at room temperature for 12 h. The insoluble material was filtered off and washed with additional hexane (20 ml). The remaining solid was extracted with dichloromethane (50 ml). Evaporation of the filtrate gave compound **2** as a yellowish powder, yield 1.3 g (61%). Compound **2** was crystallized by slow evaporation of a saturated dichloromethane solution to give single crystals suitable for X-ray diffraction analysis, m.p. 180 °C (decomp.). ^{1}H NMR (CDCl$_3$, 293 K): 3.15 s, 6 H (N(CH$_3$)$_2$); 3.86 s, 3 H (CH$_3$O); 4.83 s, 2 H (CH$_2$N); 5.08 s, 2 H (CH$_2$O); 7.49 dd, 1 H (Ar-H4); 7.73 d, 1 H (Ar-H); 7.85 d, 1 H (Ar-H). ^{13}C NMR (CDCl$_3$, 293 K): 48.9 ((CH$_3$)$_2$N); 60.8 (CH$_3$O); 71.6 (CH$_2$N); 78.8 (CH$_2$O); 127.0, 128.8, 129.5, 148.6, 152.6 (Ar-C); (Ar-C1) not observed. For C$_{11}$H$_{17}$NO (458.1) calculated: 28.8% C, 3.5% H; found: 28.7% C, 3.7% H.

X-ray Crystallography

The details of the crystal structure determination and refinement for studied compounds are given in Table I. The suitable single crystals were mounted on glass fibre with an oil and measured on four-circle diffractometer KappaCCD with CCD area detector by monochromatized MoKα radiation (λ = 0.71073 Å) at 150(1) K. The numerical[12] absorption corrections from crystal shape were applied for all crystals. The structures were solved by the direct method (SIR92)[13] and refined by a full matrix least squares procedure based on F^2 (SHELXL97)[14]. Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or 1.5 U_{eq} for the methyl moiety, with C–H = 0.96, 0.97 and 0.93 Å for methyl, methylene and hydrogen atoms in the aromatic ring, respectively. The final difference maps displayed no peaks of chemical significance, as the highest peaks and holes are in a close vicinity (~ 1 Å) of heavy atoms. The non-positive temperature factors of C1, C2 C3 and C7 in structure of **2** were treated by EADP instructions within the SHELXL97 program package[14]. CCDC 772343 (for **1**) and 772344 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk)

TABLE I
Crystallographic data for compounds **1** and **2**

Parameter	1	2
Crystal system	orthorhombic	monoclinic
Space group	$Pna2_1$	Cc
a, Å	13.3120(4)	9.7231(12)
b, Å	8.8241(16)	23.1532(14)
c, Å	22.9329(16)	6.9678(9)
β, °		119.40(2)
V, Å^3	2693.9(5)	1366.59(7)
Z	8	4
Density, g cm^{-3}	1.829	2.227
μ, mm^{-1}	2.425	13.272
T, K	150(1)	150(1)
No. of reflections measured	17672	5189
No. of unique reflections; R_{int}	5610; 0.035	2606; 0.069
No. of observed ref. [$I > 2\sigma(I)$]	4934	2556
No. of parameters	289	109
Final R indices [$I > 2\sigma(I)$]	0.029	0.052
wR2 indices (all data)	0.053	0.132

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