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Hypervalent selenium compounds containing N → Se intramolecular interactions: synthesis, characterization and X-ray structures of $[2\text{-}(Me_2NCH_2)C_6H_4]SeS(S)PR_2$ (R = Ph, O^iPr)

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$[2\text{-}(Me_2NCH_2)C_6H_4]Se-S(S)PR_2$ [R = Ph (1), O^iPr (2)] were prepared by reacting $[2\text{-}(Me_2NCH_2)C_6H_4]_2Se_2$ with the appropriate disulfanes, $[R_2P(S)S]_2$. The compounds were characterized by multinuclear magnetic resonance (^1H, ^{13}C, ^{31}P). The molecular structures of 1 and 2 were determined by single-crystal X-ray diffraction. Both compounds are monomeric and the nitrogen atom of the pendent CH_2NMe_2 arm is strongly coordinated to the selenium atom. The organophosphorus ligands are monodentate, thus resulting in a T-shaped coordination geometry around selenium. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: selenium; hypervalent compounds; X-ray; NMR

INTRODUCTION

Organochalcogen derivatives with intramolecular N → E interactions (E = Se, Te) have attracted considerable current interest.[1,2] These derivatives are remarkable, providing novel hypervalent, stable organo-selenium[3–8] or -tellurium[4,6,9–15] species with enhanced thermal and hydrolytic stability. Some derivatives containing *ortho*-selenurated benzylamino moieties have been reported, which generally display intramolecular coordination of the nitrogen atom of the pendent arm to the selenium atom.[5,6] Recently, we have reported on the molecular structures of $[2\text{-}(Me_2NCH_2)C_6H_4]TeS(S)PR_2$ (R = Me, Ph, O^iPr)[15] which were found to be monomeric, with the nitrogen atom of the pendent $-CH_2NMe_2$ arm strongly coordinated to the tellurium atom and the organophosphorus ligand acting as a monodentate unit, thus giving rise to a T-shaped coordination geometry around tellurium. Organoselenium compounds containing both (*C,N*) and dithio ligands have not been reported yet, and to examine the effect of a change of the chalcogen on the N → E interaction we decided to investigate the selenium analogues.

We report here on the synthesis and spectroscopic characterization, as well as the crystal and molecular structures, of $[2\text{-}(Me_2NCH_2)C_6H_4]SeS(S)PR_2$ (R = Ph, O^iPr).

RESULTS AND DISCUSSION

The diphenyldithiophosphinato (**1**) and diisopropyldithiophosphato (**2**) derivatives were obtained according to Eqn. (1), by reacting stoichiometric amounts of the diorganodiselenide, $[2\text{-}(Me_2NCH_2)C_6H_4]_2Se_2$, and the corresponding bis(diorganothiophosphinyl)disulfane, $[R_2P(S)S]_2$ (R = Ph, O^iPr), at room temperature, in methylene chloride:

$$[2\text{-}(Me_2NCH_2)C_6H_4]_2Se_2 + [R_2P(S)S]_2 \longrightarrow 2\ [2\text{-}(Me_2NCH_2)C_6H_4]SeS(S)PR_2 \quad (1)$$

$$R = Ph\ (\mathbf{1}), O^iPr\ (\mathbf{2})$$

The title compounds are yellow, crystalline solids, which can be recrystallized from chloroform or methylene dichlor-

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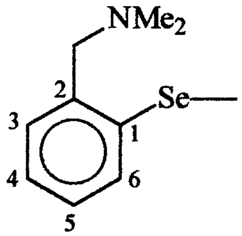

Scheme 1.

ide. Both compounds were characterized by IR and multinuclear (^{1}H, ^{13}C and ^{31}P) magnetic resonance spectroscopy, and the molecular structures were determined by single-crystal X-ray diffraction.

The IR spectra of **1** and **2** exhibit strong absorptions in the region 650–640 and around 530 cm^{-1}, which were assigned to asymmetric and symmetric $\nu(PS_2)$ stretching vibrations respectively, indicating the monodentate behaviour of the dithioligands.

The ^{1}H and ^{13}C chemical shifts for both selenium(II) compounds investigated in this work were assigned using 2D correlation spectra and exhibit a trend indicative of the *ortho*-selenurated benzylamino moiety (Scheme 1). At room temperature there is no clear evidence in the ^{1}H NMR spectra for significant N→Se interaction in solution, as the resonances for the pendent CH_2NMe_2 arm appear as singlets in the regions δ 2.2–2.4 and 3.4–3.7 ppm for the $N-CH_3$ and $-CH_2-N-$ protons respectively. Even at −60 °C the singlet pattern of these ^{1}H resonances is maintained. As expected, the proton and carbon resonances corresponding to the organic groups attached to the phosphorus atom exhibit doublet patterns, due to phosphorus–proton and phosphorus–carbon coupling respectively.

The NMR spectra of compound **2** exhibit in the alkyl region a pattern which is indicative of the diastereotopic nature of the CH_3 and CH groups in the isopropyl moieties attached to phosphorus atom.

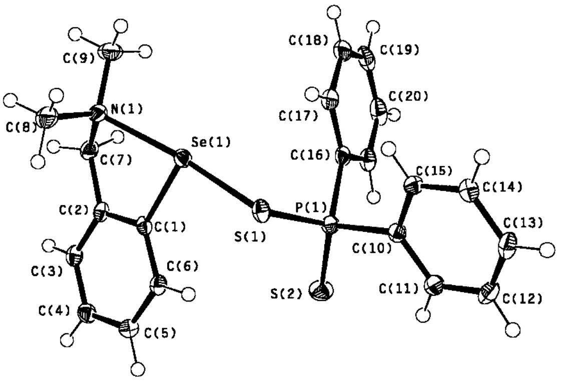

Figure 1. ORTEP diagram for [2-(Me_2NCH_2)C_6H_4]Se—S(S)PPh_2 (**1**). The atoms are drawn with 50% probability ellipsoids, except for the hydrogen atoms.

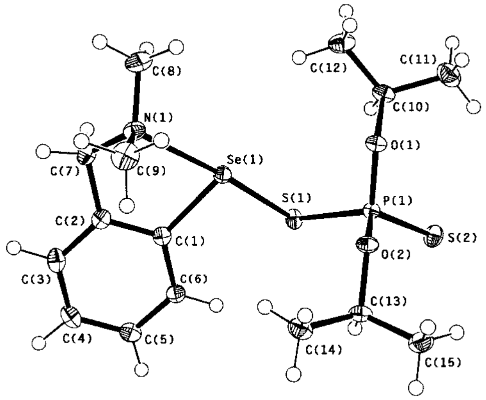

Figure 2. ORTEP diagram for [2-(Me_2NCH_2)C_6H_4]Se—S(S)P(O^iPr)$_2$ (**2**). The atoms are drawn with 50% probability ellipsoids, except for the hydrogen atoms.

The solid-state molecular structures of **1** and **2**, as established by single-crystal X-ray diffraction, are shown as ORTEP plots in Figures 1 and 2 respectively, and selected interatomic distances and angles are listed in Table 1. The crystals of both compounds contain discrete monomers, and no intermolecular interactions have been observed.

The compounds exhibit intramolecular N→Se inter-

Table 1. Important interatomic distances (Å) and angles (deg) for [2-(Me_2NCH_2)C_6H_4]SeS(S)PR_2 derivatives [R = Ph (**1**), O^iPr (**2**)]

	1	2
Se(1)−C(1)	1.9424(18)	1.935(2)
Se(1)−N(1)	2.3587(17)	2.397(2)
Se(1)−S(1)	2.3400(7)	2.3373(10)
S(1)−P(1)	2.0814(10)	2.0489(8)
S(2)−P(1)	1.9535(8)	1.9390(10)
N(1)−C(7)	1.467(3)	1.477(2)
N(1)−C(8)	1.469(3)	1.464(3)
N(1)−C(9)	1.471(3)	1.462(3)
C(1)−Se(1)−N(1)	78.95(7)	78.62(8)
C(1)−Se(1)−S(1)	98.78(6)	95.64(7)
N(1)−Se(1)−S(1)	171.72(4)	173.29(5)
P(1)−S(1)−Se(1)	110.08(3)	101.62(4)
S(2)−P(1)−S(1)	117.28(4)	107.07(4)
C(9)−N(1)−C(7)	112.75(16)	111.30(16)
C(9)−N(1)−C(8)	111.45(16)	111.87(17)
C(7)−N(1)−C(8)	111.88(17)	112.13(17)
C(9)−N(1)−Se(1)	110.81(13)	111.48(15)
C(7)−N(1)−Se(1)	102.33(11)	99.41(14)
C(8)−N(1)−Se(1)	107.12(13)	110.03(15)

Table 2. Crystal data and structure refinement for $[2\text{-}(Me_2NCH_2)C_6H_4]SeS(S)PPh_2$ (**1**) and $[2\text{-}(Me_2NCH_2)C_6H_4]SeS(S)P(O^iPr)_2$ (**2**)

	1	**2**
Empirical formula	$C_{21}H_{22}NPS_2Se$	$C_{15}H_{26}NO_2PS_2Se$
Formula weight	462.45	426.42
Temperature (K)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P1$
Unit cell dimensions		
a(Å)	11.838(2)	9.973(2)
b(Å)	9.3203(19)	10.431(2)
c(Å)	19.445(4)	11.527(2)
α(°)		63.15(3)
β(°)	104.66(3)	64.37(3)
γ(°)		80.12(3)
Volume (Å^3)	2075.5(7)	964.2(3)
Z	4	2
D_c (g cm^{-3})	1.480	1.469
Absorption coefficient (mm^{-1})	2.093	2.252
F(000)	944	440
Crystal size (mm^3)	0.22 × 0.22 × 0.18	0.24 × 0.24 × 0.23
θ range for data collections (°)	3.08–27.47	3.20–27.49
Reflections collected	16166	16976
Independent reflections	4728 ($R_{int} = 0.0436$)	4381 ($R_{int} = 0.0530$)
Max. and min. transmissions	0.7045 and 0.6560	0.6254 and 0.6140
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	4728/0/324	4381/0/304
Goodness-of-fit on F^2	1.045	1.093
Final R indices [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.0286$	$R_1 = 0.0273$
	$wR_2 = 0.0677$	$wR_2 = 0.0647$
R indices (all data)	$R_1 = 0.0369$	$R_1 = 0.0312$
	$wR_2 = 0.0714$	$wR_2 = 0.0665$
Extinction coefficient	0.0050(4)	0.0102(11)
Largest diff. peak and hole (e$^-$ Å^{-3})	0.523 and −0.535	0.520 and −0.610

actions [2.3587(17) Å in **1** and 2.397(2) Å in **2**] shorter than in $[2\text{-}(Me_2NCH_2)C_6H_4]_2Se_2$, (average N−Se 2.85 Å),[5] which is consistent with the higher electronegativity of the sulfur atom placed in the *trans* position relative to the N(1) atom in the X−Se−N fragment. The (*C,N*)SeS core is almost T-shaped, similar to that found in the tellurium(II) analogues, $[2\text{-}(Me_2NCH_2)C_6H_4]TeS(S)PR_2$ (R = Me, Ph, O^{i}Pr) and $[2\text{-}(Me_2NCH_2)C_6H_4]TeS{-}PPh_2{=}N{-}PPh_2{=}S$. The overall coordination geometry around the selenium atoms can be considered as essentially *pseudo*-trigonal bipyramidal, with C(1) and the two lone pairs occupying the equatorial positions and N(1) and S(1) atoms in axial positions [N(1)−Se(1)−S(1) 171.72(4)° in **1** and 173.29(3)° in **2**]. The distortion of the coordination geometry is mainly due to constraints arising from the five-membered chelate C_3NSe ring, particularly the N(1)−Se(1)−C(1) angle [78.95(7)° in **1** and 78.62(8)° in **2**]. These rings are not planar, but folded about the $Se\cdots C_{methylene}$ axis (dihedral angle $C_3Se/SeNC$ 38.2° for **1** and 42.6° for **2**).

In both compounds the dithio ligands act as monometallic monoconnective moieties, only one sulfur atom being bonded to the selenium atom. The Se(1)−S(1) bond distances [2.3400(7) Å in **1** and 2.3373(10) Å in **2**] are within the expected range for covalent selenium–sulfur single bonds. The second sulfur atom of the 1,1-dithiophosphorus ligand is not involved in any intra- or intermolecular interaction with selenium atoms. This behaviour is also reflected in the magnitude of the phosphorus–sulfur distances within the ligand moiety, which are consistent with single P−S and double P=S bonds [*e.g.* P(1)−S(1) 2.0814(10) Å, P(1)−S(2) 1.9535(8) Å in **1**, *vs.* P−S 2.077(1) Å and P=S 1.954(1) Å in $Ph_2P(S)SH$[16]]. However, the relative position of the sulfur atom double-bonded to phosphorus with respect to the selenium atom is different.

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[2\text{-}(Me_2NCH_2)C_6H_4]Se\text{-}S(S)PPh_2$ (**1**), where U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

	x	*y*	*z*	U_{eq}
Se(1)	5394(1)	4338(1)	1685(1)	18(1)
S(1)	4084(1)	5182(1)	2313(1)	20(1)
S(2)	1841(1)	6615(1)	1006(1)	28(1)
P(1)	2382(1)	5056(1)	1680(1)	18(1)
N(1)	6920(1)	3688(2)	1167(1)	20(1)
C(1)	5564(2)	6085(2)	1175(1)	16(1)
C(2)	6197(2)	5973(2)	655(1)	18(1)
C(3)	6350(2)	7179(2)	275(1)	20(1)
C(4)	5898(2)	8501(2)	404(1)	21(1)
C(5)	5269(2)	8598(2)	915(1)	21(1)
C(6)	5096(2)	7395(2)	1298(1)	19(1)
C(7)	6646(2)	4525(2)	506(1)	21(1)
C(8)	8018(2)	4155(2)	1657(1)	30(1)
C(9)	6916(2)	2132(2)	1040(1)	28(1)
C(10)	1585(2)	4938(2)	2367(1)	17(1)
C(11)	704(2)	5925(2)	2378(1)	20(1)
C(12)	99(2)	5836(2)	2906(1)	24(1)
C(13)	357(2)	4760(2)	3410(1)	24(1)
C(14)	1239(2)	3775(2)	3403(1)	21(1)
C(15)	1854(2)	3865(2)	2886(1)	19(1)
C(16)	2178(2)	3297(2)	1257(1)	19(1)
C(17)	2847(2)	2102(2)	1548(1)	23(1)
C(18)	2621(2)	772(2)	1214(1)	28(1)
C(19)	1743(2)	631(2)	590(1)	31(1)
C(20)	1072(2)	1801(3)	311(1)	30(1)
C(21)	1280(2)	3130(2)	638(1)	23(1)

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[2\text{-}(Me_2NCH_2)C_6H_4]Se\text{-}S(S)P(O^iPr)_2$ (**2**), where U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

	x	*y*	*z*	U_{eq}
Se(1)	2387(1)	1130(1)	4014(1)	16(1)
P(1)	278(1)	1902(1)	6847(1)	14(1)
S(1)	182(1)	2174(1)	5010(1)	17(1)
S(2)	−1606(1)	2503(1)	7933(1)	22(1)
N(1)	4602(2)	190(2)	2741(2)	20(1)
O(1)	746(1)	315(1)	7592(1)	16(1)
O(2)	1733(1)	2655(1)	6510(1)	17(1)
C(1)	2955(2)	2636(2)	2101(2)	15(1)
C(2)	3933(2)	2259(2)	1002(2)	17(1)
C(3)	4356(2)	3277(2)	−399(2)	22(1)
C(4)	3808(2)	4654(2)	−723(2)	24(1)
C(5)	2850(2)	5023(2)	370(2)	21(1)
C(6)	2431(2)	4030(2)	1782(2)	18(1)
C(7)	4455(2)	734(2)	1376(2)	21(1)
C(8)	4540(3)	−1383(2)	3455(3)	33(1)
C(9)	5938(2)	791(3)	2557(3)	29(1)
C(10)	−267(2)	−917(2)	8212(2)	19(1)
C(11)	−1016(3)	−1393(3)	9796(2)	31(1)
C(12)	674(2)	−2055(2)	7788(3)	26(1)
C(13)	1940(2)	4229(2)	5751(2)	19(1)
C(14)	3393(2)	4543(2)	4461(2)	25(1)
C(15)	1923(3)	4772(2)	6770(2)	26(1)

Thus, in **2**, the non-bonded sulfur atom is twisted as far as possible from the selenium atom [intramolecular non-bonding Se(1)···S(2) distance 5.161(1) Å]. By contrast, in **1**, the 1,1-dithio ligand moiety is twisted to bring the non-bonded S(2) atom much closer to the selenium atom [Se(1)···S(2) 4.596(1) Å].

EXPERIMENTAL

All manipulations were carried out under vacuum or argon by Schlenk techniques. Solvents were dried and distilled prior to use. The starting materials were prepared according to literature methods: $[2\text{-}(Me_2NCH_2)C_6H_4]_2Se_2$,[5] $[R_2P(S)S]_2$ (R = Ph,[17] O^iPr[18]). IR spectra were recorded in the range 4000–400 cm^{-1} as KBr pellets on a Jasco FT/IR-615 instrument. Solutions in dried $CDCl_3$ were used for NMR studies. The ^1H, ^{13}C and 2D NMR spectra were recorded on a Bruker DRX 400 instrument operating at 400.13 and 100.61 MHz, and ^{31}P NMR spectra were recorded on a Varian Gemini 300 instrument operating at 121.4 MHz. The chemical shifts are reported in parts per million relative to tetramethylsilane and 85% H_3PO_4 respectively. The ^1H and ^{13}C chemical shifts were assigned based on H,H-COSY45gs, H,C-HMQCgs and H,C-HMBCgs experiments using standard Bruker XWIN-NMR pulse sequencies.

Preparation of $[2\text{-}(Me_2NCH_2)C_6H_4]SeS(S)PPh_2$

Stoichiometric amounts of $[2\text{-}(Me_2NCH_2)C_6H_4]_2Se_2$ (0.23 g, 0.54 mmol) and $[Ph_2P(S)S]_2$ (0.26 g, 0.54 mmol) were stirred in methylene dichloride (50 ml) for 12 h at room temperature. The yellow solution was concentrated under reduced pressure to minimum volume and then kept at low temperature (−20 °C) for 24 h, when the title compound deposited as a solid. The compound was filtered off and recrystallized from CH_2Cl_2/n-hexane (1:5 by volume) to yield yellow crystals (0.44 g, 88%) (m.p. 125 °C). Analysis: Found: C 54.28, H 4.55, N 3.05, S 13.92; Calcd. For $C_{21}H_{22}NPS_2Se$: C 54.54, H 4.79, N 3.03, S 13.86%. IR: 652, 530 [asym, sym, $\nu(PS_2)$] cm^{-1}. ^1H NMR: δ, 2.28 (s, 6H, N-CH_3), 3.46 (s, 2H, $-CH_2-N-$), 6.95 [d, 1H, $-C_6H_4-$ (H-3), $^3J_{HH}$ 6.4 Hz], 7.03 [ddd, 1H, $-C_6H_4-$ (H-4), $^3J_{HH}$ 7.2, $^4J_{HH}$ 1.6 Hz], 7.06 [ddd, 1H, $-C_6H_4-$ (H-5), $^3J_{HH}$ 7.2, $^4J_{HH}$ 1.6 Hz], 7.35 (m, 6H, $P-C_6H_5$-*meta* + *para*), 7.80 [dd, 1H, $-C_6H_4-$ (H-6), $^3J_{HH}$ 7.2, $^4J_{HH}$ 2.0 Hz], 7.93 (ddd, 4H, $P-C_6H_5$-*ortho*,

$^3J_{PH}$ 13.6, $^3J_{HH}$ 8.4, $^4J_{HH}$ 1.6 Hz). ^{13}C NMR: δ, 43.86 (s, N−CH_3), 63.70 (s, −CH_2−N−), 125.84 (s, *C*-4); 126.52 (s, *C*-3), 127.94 (d, P−C_6H_5-*meta*, $^3J_{PC}$ 12.9 Hz), 128.01 (s, *C*-5), 130.55 (s, *C*-6), 131.13 (s, P−C_6H_5-*para*), 131.61 (d, P−C_6H_5-*ortho*, $^2J_{PC}$ 10.7 Hz), 135.49 (d, P−C_6H_5-*ipso*, $^1J_{PC}$ 80.9 Hz), 135.52 (s, *C*-1), 138.04 (s, *C*-2). ^{31}P NMR: δ, 65.1 (s).

Preparation of [2-(Me_2NCH_2)C_6H_4]SeS(S)P(O^iPr)$_2$

Stoichiometric amounts of [2-(Me_2NCH_2)C_6H_4]$_2$Se$_2$ (0.25 g, 0.58 mmol) and [(^{i}PrO)$_2$P(S)S]$_2$ (0.25 g, 0.58 mmol) were stirred in methylene dichloride (50 ml) for 12 h at room temperature. The yellow solution was concentrated under reduced pressure to minimum volume and then kept at low temperature (−20 °C) for 24 h, when the title compound deposited as a solid. The compound was filtered off and recrystallized from CH_2Cl_2/*n*-hexane (1:5 by volume) to yield yellow crystals (0.40 g, 80%) (m.p. 100–102 °C). Analysis: Found: C 42.24, H 6.08, N 3.34, S 14.98; Calcd. For $C_{15}H_{26}NO_2PS_2Se$: C 42.25, H 6.15, N 3.28, S 15.04%. IR: 962 [ν(PO)], 643, 531 [asym, sym, ν(PS$_2$)] cm^{-1}. ^{1}H NMR: δ, 1.21 [d, 6H$_A$, P−O−CH(CH_3)$_2$, $^3J_{HH}$ 6.4 Hz], 1.30 [d, 6H$_B$, P−O−CH(CH_3)$_2$, $^3J_{HH}$ 6.0 Hz], 2.39 (s, 6H, N−CH_3), 3.67 (s, 2H, −CH_2−N−), 4.80 [dh, 2H, P−O−*CH*(CH_3)$_2$, $^3J_{PH}$ 12.0, $^3J_{HH}$ 6.0 Hz], 7.10 [d, 1H, −C_6H_4− (H-3), $^3J_{HH}$ 6.8 Hz], 7.13 [dd, 1H, −C_6H_4− (H-4), $^3J_{HH}$ 7.2 Hz], 7.22 [ddd, 1H, −C_6H_4− (H-5), $^3J_{HH}$ 8.0, $^4J_{HH}$ 1.8 Hz], 8.02 [d, 1H, −C_6H_4− (H-6), $^3J_{HH}$ 8.0 Hz]. ^{13}C NMR: δ, 23.27 [d, C$_A$, P−O−CH(CH_3)$_2$, $^3J_{PC}$ 5.6 Hz], 23.61 [d, C$_B$, P−O−CH(CH_3)$_2$, $^3J_{PC}$ 4.0 Hz], 43.69 (s, N−CH_3), 63.67 (s, −CH_2−N−), 72.84 [d, P−O−CH(CH_3)$_2$, $^2J_{PC}$ 6.8 Hz], 125.87 (s, *C*-4); 126.74 (s, *C*-3), 128.03 (s, *C*-5), 130.33 (s, *C*-6), 135.58 (s, *C*-1), 137.82 (s, *C*-2). ^{31}P NMR: δ, 90.0 (s).

Crystallography

Pale yellow, block crystals of [2-(Me_2NCH_2)C_6H_4]SeS(S)PPh$_2$ (**1**) and [2-(Me_2NCH_2)C_6H_4]SeS(S)P(O^iPr)$_2$ (**2**) were mounted on glass fibres. Data were collected on an Enraf Nonius KappaCCD area detector with φ and ω scans and ω scans chosen to give a complete asymmetric unit. Data collection and cell refinement (Denzo)[19] gave cell constants corresponding to monoclinic (for **1**) and triclinic (for **2**) cells, whose dimensions are given in Table 2 along with other experimental parameters.

An absorption correction was applied (SORTAV),[20,21] which resulted in maximum and minimum transmissions ranging from 0.7045 to 0.6560 for **1**, and 0.6254 to 0.6140 for **2**. The structures were solved by direct methods[22] and the structure was refined using the WinGX version[23] of SHELXL-97.[24] All of the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The final cycle of full-matrix least-squares refinement[24] was based on 4728 (for **1**) and 4381 (for **2**) observed reflections and 324 (for **1**) and 304 (for **2**) variable parameters and converged (largest parameter shift was 0.001 times its ESD). Atomic coordinates and equivalent isotropic displacement parameters are given in Tables 3 and 4.

Crystallographic data for the structural analysis of compounds **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre (CCDC nos 182772, 182773). Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; or http://www.ccdc.cam.ac.uk).

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