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Note

Bis[bis(trimethylsilyl)cyclopentadienyl]selane as a ligand: selena-2,2′,4,4′-tetrakis(trimethylsilyl)-[1]ferrocenophane and 1,2,3-triselena-2,2′,4,4′-tetrakis(trimethylsilyl)-[3]ferrocenophane

Georg Thaler, Barbara Klotz, Klaus Wurst, Fritz Sladky *

Institut für Allgemeine, Anorganische und Theoretische Chemie der Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

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Abstract

Bis[bis(trimethylsilyl)cyclopentadienyl]selane (**1**) was prepared from lithium 5,5-bis(trimethylsilyl)cyclopentadienide and selenium bis(diethyldithio)carbamate, $Se(S_2CNEt_2)_2$. Reaction of the dianion of **1** with $FeCl_2$ gave selena-2,2′,4,4′-tetrakis(trimethylsilyl)-[1]ferrocenophane (**2**) and 1,2,3-triselena-2,2′,4,4′-tetrakis(trimethylsilyl)-[3]ferrocenophane (**3**). Compounds **1**–**3** have been characterized by ^1H-NMR, ^{13}C-NMR and single-crystal X-ray analyses. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Selenium; Cyclopentadienyl; [1]Ferrocenophane; [3]Ferrocenophane; Crystal structures

1. Introduction

We are currently developing a multifunctional ligand system that consists of chalcogens bound to appropriately substituted cyclopentadienes (Fig. 1). Recently we reported the synthesis of $[(Me_3Si)_3Cp]_2Te{\cdot}W(CO)_5$ [1]. In this context we prepared bis[bis(trimethylsilyl)cyclopentadienyl]selane, $[(Me_3Si)_2C_5H_3]Se$ (**1**), which in contrast to $(Me_5C_5)_2Se$ [2], the only other known bis(cyclopentadienyl)selane, is the first selane which still possesses acidic hydrogen atoms and thus can be functionalized. Ferrocenophanes have received much attention because of their interesting strained structures, their potential for the synthesis of materials with novel electrochemical and magnetic properties [3] and as precursors for ring-opening polymerisation reactions (ROP) [4]. Since the first [1]ferrocenophane containing a Ph_2Si-bridge was synthesized in 1975 [5], this class of complex has been extended to species bridged with the elements from group 13 (B) [6], 14 (Si, Ge, Sn) [7], 15 (P, As) [7a,b, 8], 16 (S, Se) [9], 4 (Ti, Zr, Hf) [10] and most recently uranium [11].

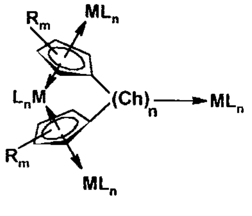

Fig. 1. Multifunctional ligand system.

In this paper we describe the use of **1** as a bifunctional ligand for iron with the synthesis of selena-2,2′,4,4′-tetrakis(trimethylsilyl)-[1]ferrocenophane (**2**) and of 1,2,3-triselena-2,2′,4,4′-tetrakis(trimethylsilyl)-[3]ferrocenophane (**3**). Compounds **2** and **3** are also one of the few examples of ferrocenophanes with substituents on the Cp rings [12]. This also demonstrates an alternative to the usually used preparative route to [1]ferrocenophanes by reacting dilithioferrocene with element halides [5–8] or one-atom synthons like $S(O_2SPh)_2$ [9a] or $Se(S_2CNEt_2)_2$ [9b].

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* Corresponding author. Tel.: +43-512-507-5121; fax: +43-512-507-2934.

E-mail address: fritz.sladky@uibk.ac.at (F. Sladky).

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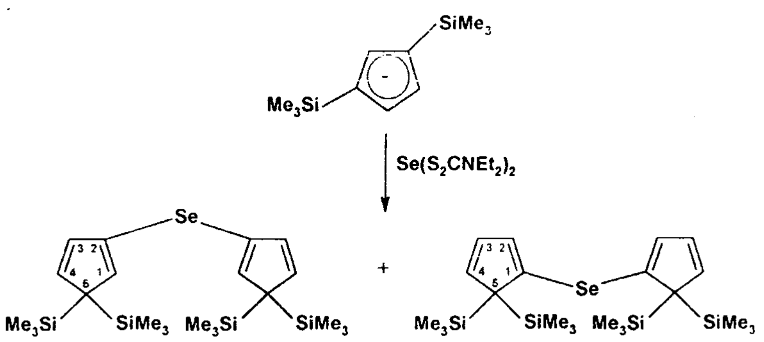
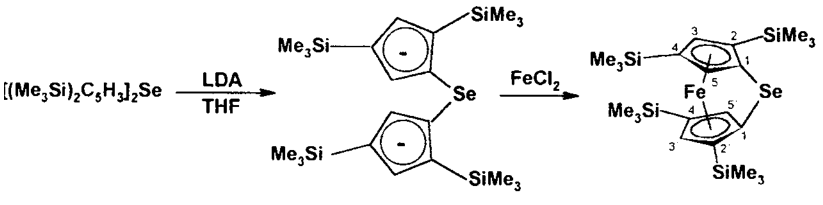


Scheme 1.



Scheme 2.

2. Results and discussion

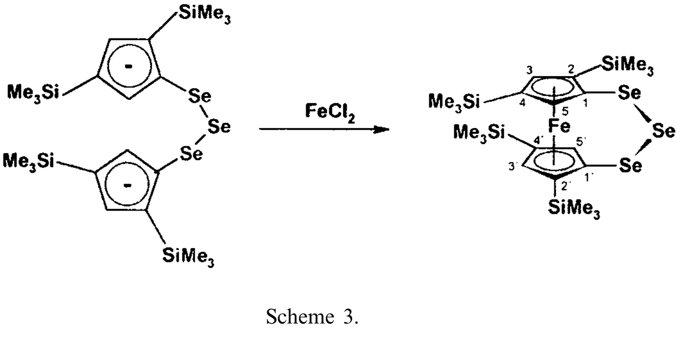
Complex **1** is obtained from the reaction of selenium bis(diethyldithio)carbamate with lithium bis(trimethylsilyl)cyclopentadienide (Scheme 1). The selenium atom is fluxonial and prefers the vinylic positions in contrast to the Me_3Si groups which occupy the allylic positions. This allows in solution the existence of two isomers **1a** and **1b** in a ratio of 9:1 with the selenium in the vinylic 2- or 1-position. Out of such a solution the sterically less strained isomer **1a** crystallizes exclusively.

Selane **1** can be deprotonated to the respective dianion which complexes iron with formation of the corresponding selena[1]ferrocenophane (**2**) (Scheme 2). Some NMR spectroscopic evidence for the related dicyclopentadienylsulfide dianion has been given previously [13]. Because of some nucleophilic carbon–selenium bond breaking in the dianion and subsequent selenium atom rearrangement followed by disproportionation, the respective di- and triselane are also present in the reaction mixture. Using bis[bis(trimethylsilyl)cyclopentadienyl]triselane, isolation of 1,2,3-triselane-2,2′,4,4′-tetrakis(trimethylsilyl-[3]ferrocenophane (**3**) was also achieved (Scheme 3).

Characterization of **1**, **2** and **3** by NMR spectroscopy confirmed the assigned structures. Besides the two $SiMe_3$ singlet resonances, the ^1H-NMR spectrum (in $CDCl_3$) of **2** consists only of a pair of widely separated singlets at 3.96 and 5.02 ppm, assigned to the α and γ Cp protons. The ^{13}C-NMR spectrum of **2** shows the resonance of the Cp-Se *ipso*-carbon at 11.5 ppm. This remarkably large upfield shift is in accordance with other highly strained [1]ferrocenophanes [9]. The ^1H-NMR spectrum (in $CDCl_3$) of the less strained molecule **3** shows the α and the γ Cp protons less widely separated at 3.95 and 4.11 ppm and the ^{13}C-NMR shift of the Cp-Se *ipso*-carbon at 24.0 ppm.

The molecular structure of **1** is dominated by the optimal staggering of the allylic Me_3Si groups which leads to an interplanar angle of the Cp-rings of 48.61(0.10)° (Fig. 2). The Se–C bond lengths of 1.910(3) Å are shorter than the sum of covalent radii (1.94 Å), in contrast to the Se–C bond lengths in Cp_2 *Se (2.000 Å) [2] with selenium in allylic position. This may indicate a strengthening interaction of chalcogen orbitals in vinylic position with the π-system of the Cp-rings further enhanced by the $-I$ effect of the Me_3Si groups. The C–Se–C angle of 97.8(2)° in **1** is similar to other diorganylselanes (Me_2Se: 96.3° [14], PhSeMe: 99.6° [15]).

The structure of **1** changes drastically with the formation of the respective dianion which then functions as a ligand in the corresponding selena[1]ferrocenophane (**2**)



Scheme 3.

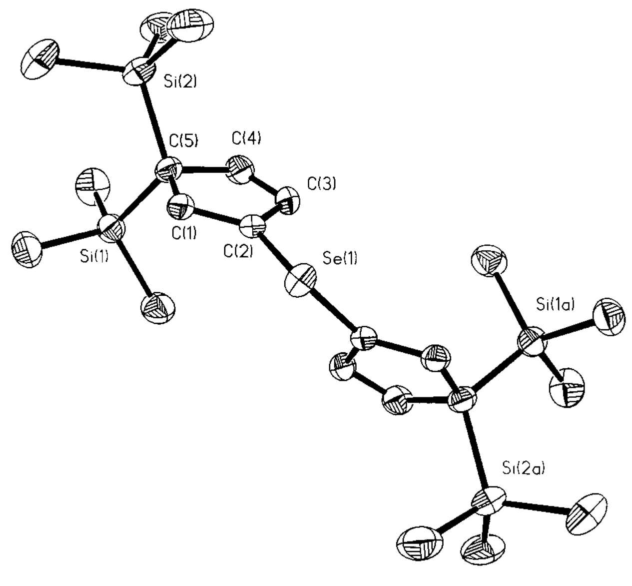


Fig. 2. Molecular structure of **1a**; anisotropic displacement parameters depicting 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Se(1)–C(2) 1.910(3); C(2)–Se(1)–C(2a) 97.8(2), interplane angle 48.61(0.10).

(Fig. 3). The previously allylic Me_3Si groups adopt in-plane positions at the 2,2′- and 4,4′-carbon atoms whereas the previously in-plane bonds to selenium are bent out of the Cp ring planes by 29.7(2)°. The less effective orbital overlap results in a drastic Se–C bond lengthening to 1.961(4) Å. Also striking is the reduction of the C–Se–C angle to 86.3(2)° in **2** which is 11.5° smaller than in uncomplexed **1**. The ferrocenophane moiety is primarily characterized by a tilt-angle of 26.9(2)° between the planes of the Cp rings which is 0.5° larger than in the unsubstituted selena[1]ferrocenophane [9] but 4.1° smaller than in thia[1]ferrocenophane [9]. The Cp ring-tilting is accompanied by a Cp–Fe–Cp angle of 160.3° compared to 180° which results in only a 0.096 Å displacement of the iron atom away from selenium. The tilted Cp rings, related to each other by a twofold axis running through iron and selenium, maintain an eclipsed conformation which allows an optimal staggering of the Me_3Si groups and the selenium atom. The distance between Fe and the bridging Se of 2.8920(10) Å is somewhat shorter than in the unsubstituted selena[1]ferrocenophane [2.9058(6) Å] and might indicate a weak interaction (sum of covalent radii = 2.42 Å).

With respect to structural data, 1,2,3-triselena-[3]ferrocenophane **3** is the last missing member of the 1,2,3-trichalcogena-[3]ferrocenophane series $Fe(C_5H_4E)_2E$ (E = S [16], Te [17]). Like the other two members the Cp rings of **2** are eclipsed and almost coplanar (tilt angle = 1.01°) (Fig. 4) with an optimal staggering of the substituents on the Cp rings. In contrast to **2,** the Se–C distances [190.8(6) Å and 190.1(6) Å] and the central selenium angle [100.76(4)°] are now almost identical to uncomplexed **1,** which indicates a largely unstrained molecule.

In contrast to 1,2,3-triselena[3]ruthenophane [18] and 1,2,3-tritellura[3]ferrocenophane [17] which exhibit an unusual molecular packing with alternating chalcogen and metallocene layers with short intermolecular chalcogen-chalcogen contacts, this is not the case in **3** probably because of the bulky Me_3Si groups.

3. Experimental

All reactions were performed under argon using standard Schlenk techniques. THF was purified and dried according to standard methods. $(Me_3Si)_2C_5H_4$ [19a] and $Se(S_2CNEt_2)_2$ [19b] were prepared as previously de-

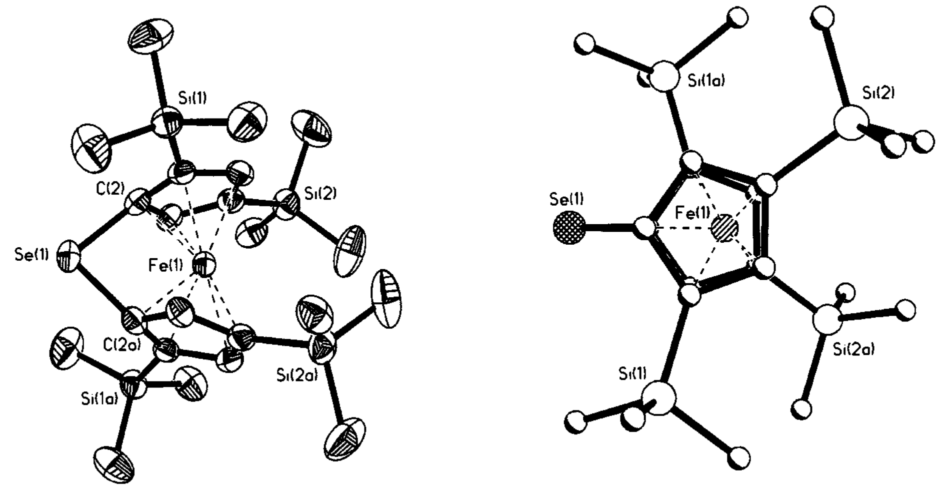


Fig. 3. Molecular structure of **2**; anisotropic displacement parameters depicting 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Se(1)–C(2) 1.961(4), Fe(1)–C(1) 2.015(4), Fe(1)–C(2) 1.984(4), Fe(1)–C(3) 2.052(4), Fe(1)–C(4) 2.083(4), Fe(1)–C(5) 2.108(4), Fe(1)–Se(1) 2.8920(10); C(2)–Se(1)–C(2′) 86.4(2), tilt angle 26.9(0.2).

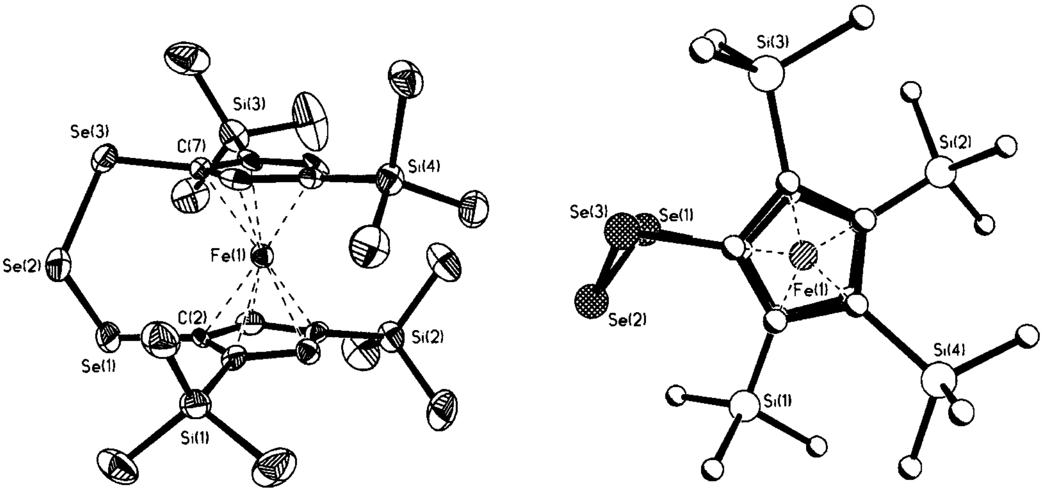


Fig. 4. Molecular structure of **3**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Se(1)–C(2) 1.908(6), Se(1)–Se(2) 2.321(12), Se(2)–Se(3) 2.316(1), Se(3)–C(7) 1.901(6); Se(1)–Se(2)–Se(3) 100.6(4), C(7)–Se(3)–Se(2) 101.1(2), C(2)–Se(1)–Se(2) 100.0(2).

scribed. Selenium powder, and $FeCl_2$ were purchased from Aldrich. Flash chromatography was performed with Merck silica gel (Type 60, 230–400 mesh) and petroleum ether as eluent. ^{1}H-, ^{13}C-, and ^{77}Se-NMR spectra were recorded on Bruker AC 200 and Bruker WP 80 spectrometers. ^{1}H and ^{13}C chemical shifts are referred to solvent signals ($CDCl_3$: $\delta_H = 7.26$, $\delta_C = 77.7$) and ^{77}Se chemical shifts to external Me_2Se. Mass spectra were recorded on a Varian CH-7 instrument.

*3.1. Bis[bis(trimethylsilyl)cyclopentadienyl]selenium (**1**)*

Butyllithium (6.00 ml, 2.0 M, 12.0 mmol) was added to a toluene solution (200 ml) of 2.52 g $(Me_3Si)_2C_5H_4$ (12.0 mmol) at − 40 °C. After stirring for 3 h at 25 °C the suspension formed was cooled to − 15 °C and a solution of 2.25 g $(Et_2NCS_2)_2Se$ (6.00 mmol) in toluene (100 ml) was added within 15 min. The suspension was stirred for 1 h at ambient temperature, filtered over silica gel and the solvent removed in vacuo. Purification by chromatography followed by recrystallization from hexanes gave 1.87 g of **1** (62.6%) as pale yellow, stable crystals. M.p. 17–20 °C. ^{1}H-NMR (200 MHz, $CDCl_3$): **1a**: $\delta = -0.06$ (s, 18 H, 5,5-$SiMe_3$), 6.46 (dd, ^3J(H,H) = 4.33 Hz, ^4J(H,H) = 2.66 Hz, 1 H, H4), 6.52 (dd, ^4J(H,H) = 2.66 Hz, ^4J(H,H) = 1.33 Hz, 1 H, H1), 6.61 (dd, ^3J(H,H) = 4.33 Hz, ^4J(H,H) = 1.33 Hz, 1 H, H3); **1b**: $\delta = -0.045$ (s, 1 H, 5,5-$SiMe_3$), 6.65 (dd, 1 H, H3), 6.77 (dd, 1 H, H2), (H4 not observed); ^{13}C-NMR (50 MHz, $CDCl_3$): **1a**: $\delta = 0.40$ (5,5-$SiMe_3$), 60.0 (C5), 130 (C2), 135 (C3), 137 (C4), 139.5 (C1); **1b**: $\delta = 0.42$ (5,5′-$SiMe_3$), 135.2 (C3), 137.3 (C4), 142 (C2), (C1 and C5 not observed); ^{77}Se-NMR (15.28 MHz, THF): **1a**: $\delta = 230$; **1b**: $\delta = 374$; EI-MS (70 eV): *m/z* (%): 498 (100) [M^+], 483 (20) [$M^+ - Me$], 425 (35) [$M^+ - SiMe_3$], 289 (50) [$M^+ - Cp(SiMe_3)$]; $C_{22}H_{42}SeSi_4$ (497.88): Anal. Found: C, 53.38; H, 8.46. Calc.: C, 53.07; H, 8.50%.

*3.2. Selena-2,2′,4,4′-tetrakis(trimethylsilyl)[1]ferrocenophane (**2**) and 1,2,3-triselena-2,2′,4,4′-tetrakis-(trimethylsilyl)[3]ferrocenophane (**3**)*

LDA solution in THF (2.68 ml, 1.5 M, 4.02 mmol) was added to a solution of 1.00 g of **1** (2.01 mmol) in 200 ml THF. The solution was stirred for 2 h at − 30 °C and for 1 h at 25 °C. After addition of 0.25 g $FeCl_2$ (2.01 mmol) at − 55 °C, the solution was allowed to warm, and stirring was continued for 12 h at 25 °C. Removal of the solvent in vacuo, chromatography and recrystallization from hexanes afforded 0.12 g of **2** (10.8%) as orange prisms, and 0.09 g of **3** (6.4%) as red platelets.

2: M.p. 95–99 °C. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 0.14$ (s, 9 H; 2-$SiMe_3$), 0.33 (s, 9 H; 4-$SiMe_3$), 3.96 (s, 1 H; H5), 5.02 (s, 1 H; H3); ^{13}C-NMR (50 MHz, $CDCl_3$): $\delta = 0.49$ (2-$SiMe_3$), 1.30 (4-$SiMe_3$), 11.5 (*ipso*-C), 83.6 (C2), 88.2 (C4), 88.7 (C2), 89.2 (C5); EI-MS (40 eV): *m/z* (%): 552 (100) [M^+], 496 (9) [$M^+ - Fe$]; $C_{22}H_{40}FeSeSi_4$ (551.71): Anal. Found: C, 47.98; H, 7.27. Calc.: C, 47.89; H, 7.31%.

3: M.p. 88–91 °C. ^{1}H-NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 0.11$ (s, 9 H; 2-$SiMe_3$), 0.18 (s, 9 H; 4-$SiMe_3$), 3.95 (s, 1 H; H5), 4.11 (s, 1 H; H3); ^{13}C-NMR (50 MHz, $CDCl_3$): $\delta = 0.15$ (2-$SiMe_3$), 1.15 (4-$SiMe_3$), 24.0 (*ipso*-C), 75.5 (C2), 79.0 (C4), 86.1 (C3), 88.7 (C5); EI-MS (40 eV): *m/z* (%): 710 (100) [M^+], 632 (28) [$M^+ - Se$], 552 (10) [M^+-2Se]; $C_{22}H_{40}Fe_3SeSi_4$ (709.63): Anal. Found: C, 37.12; H, 5.69. Calc.: C, 37.24; H, 5.68%.

*3.3. Solution and refinement of structures **1a**, **2** and **3***

Crystal data for all structures are presented in Table 1. Data were collected on a Siemens P4 diffractometer

Table 1
Crystal structure data for **1a**, **2** and **3**

	1a	**2**	**3**
Formula	$C_{22}H_{42}SeSi_4$	$C_{22}H_{40}FeSeSi_4$	$C_{22}H_{40}FeSe_3Si_4$
M_r	497.88	551.71	709.63
Crystal size (mm)	0.44 × 0.34 × 0.19	0.45 × 0.35 × 0.25	0.6 × 0.46 × 0.24
Temperature (K)	208(2)	213(2)	213(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$C2/c$ (no. 15)	$C2/c$ (no. 15)	$P1$ (no. 2)
a (Å)	14.631(5)	12.356(1)	11.064(2)
b (Å)	6.768(1)	18.277(3)	11.278(2)
c (Å)	28.461(6)	12.539(1)	14.231(2)
α (°)	90	90	79.18(1)
β (°)	92.53(2)	93.86(1)	80.66(1)
γ (°)	90	90	61.12(1)
V (Å^3)	2815.5(12)	2825.3(6)	1521.9(4)
Z	4	4	2
ρ_{calc} (g cm^{-1})	1.175	1.297	1.548
μ (mm^{-1}]	1.510	1.999	4.250
F(000)	1056	1152	712
$2\theta_{max}$ (°)	44.00	45.98	42.98
Reflections collected	1822	2133	3680
Independent reflections	1612	1921	3455
Absorption correction	ψ-scan	ψ-scan	ψ-scan
T_{min}, T_{max}	0.831, 0.954	0.800, 0.930	0.546, 1.000
Parameters	123	128	271
R_1 ($I > 2\sigma(I)$) [a]	0.0337,	0.0345	0.0442
wR_2 (all data) [b]	0.0852	0.0838	0.1255
Largest difference peak and hole (e Å^{-3})	0.221, −0.270	0.269, −0.326	1.287, −0.728

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

with Mo–K$_\alpha$ ($\lambda = 0.71073$ Å) radiation (graphite monochromator) and ω-scans. All structures were solved by direct methods using SHELXS-86 [20a] and refined by a full-matrix least-squares procedure on F^2 using SHELXL-93 [20b]. The positions of the hydrogen atoms were calculated and included in the refinement with isotropic temperature parameters $U_{eq} = 1.5U_{eq}$ of parent carbon atom.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC no. 406441 for **1**, CCDC no. 192744 for **2** and CCDC no. 162743 for **3**. Copies of this 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).

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