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Carbonyl insertion into zirconium–nitrogen bonds; synthesis and X-ray structure of a carbene complex composed of $[Zr(NMe_2)_4]_2$ and three $Fe(CO)_5$ units containing Fe → Zr donor–acceptor interactions

Wolfgang Petz *, Frank Weller, Evgeni V. Avtomonov

Fachbereich Chemie der Universität Marburg, Hans-Meerweinstrasse, D-35032 Marburg, Germany

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Abstract

The reaction of $[Zr(NMe_2)_4]_2$ with $Fe(CO)_5$ leads to the multicarbene complex (**1**) containing two zirconium and three iron atoms. The crystal structure revealed that **1** results from the insertion of five CO groups into Zr–N bonds generating chelating biscarbene ligands at two iron atoms and one terminal carbene ligand at the third iron atom. Thus, a planar and a boat-configured ring are formed (**A** and **B**) with relatively short Fe–Zr distances of 284 and 282 pm, respectively, indicating early–late transition-metal interactions. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Zirconium; Ironpentacarbonyl; Crystal structure; Zirconium–iron interaction; Carbene complexes; Metal amides

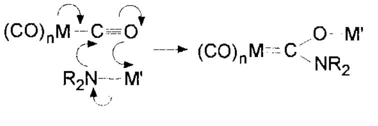
1. Introduction

Carbene complexes of the Fischer type with one or two 'heteroatoms' can be synthesized by successive addition of a hard nucleophile and a hard electrophile at a carbonyl group coordinated to a transition metal in a terminal manner [1]. We have demonstrated that reactions between carbonyl complexes and special main-group or transition-metal amides generate O,N-heteroatom stabilized carbene complexes in one step. Addition of M′–N bonds to CO easily takes place if M′ is Lewis acidic and backbonding of the lone nitrogen electron pair to M′ plays no significant role [2–4]. Binary carbonyl compounds from Groups 6 to 8 and Group 10 elements have been found to be suitable as acceptors. This type of addition can also be considered as an insertion of a carbonyl group into the M′–N bond (Scheme 1).

Thus, 'elementoxycarbene' complexes have been obtained with amides of aluminum [2,5], tin [4,6], and titanium [3,7]. Recently, also $CpZr(NMe_2)_3$ was found to react similarly [8]; further zirconoxycarbenes have been obtained by addition of Zr–H bonds to carbonyl groups [9]. Scandoxycarbene derivatives have also been reported by addition of Sc–H, Sc–C, and Sc–N bonds to carbonyl groups of $Cp_2M(CO)$ (M = Mo, W) or $CpM(CO)_2$ (M = Co, Rh) compounds [10]. A different reaction was found with $Fe(CO)_5$ and $N(SnMe_3)_3$ leading to $(CO)_4Fe(SnMe_3)_2$ and $OCNSnMe_3$ [11].

In some cases addition of two $R_2N–M'$ bonds to neighboring CO groups also occurs, leading to six-membered ring systems realized with some amides of Sn [4] and Ti [7].

In an earlier report by Bradley et al., 1:2 addition products are mentioned to be obtained with Group 4 amides and $Fe(CO)_5$, but no properties of the resulting compounds have been reported [12]. In this paper we describe our first results of the reaction between $Fe(CO)_5$ and $[Zr(NMe_2)_4]_2$.



Scheme 1.

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* Corresponding author.

E-mail address: petz@mailer.uni-marburg.de (W. Petz)

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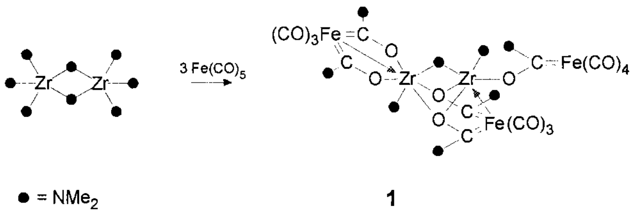
2. Results and discussion

Reactions of the amides of Sn, Al, and Ti with $Fe(CO)_5$ under mild conditions first generate the 1:1 insertion product as depicted in Scheme 1. However, this is not the case with $[Zr(NMe_2)_4]_2$. The components react even at low temperature in toluene to give orange–yellow solutions which on warming to room temperature darken smoothly to yield brown oily materials. The NMR spectra are consistent with mixtures of products. From one run, however, we could isolate yellow crystals of the unusual dinuclear compound **1** along with an oily material from which the crystals were separated mechanically. The crystals were found to be the result of a 1:3 insertion product as shown in Scheme 2.

The complex **1** is the result of the addition of five Zr–N bonds to carbonyl groups of three $Fe(CO)_5$ molecules. The IR spectrum of **1** exhibits six bands all assigned to terminal CO groups; a relatively strong broad band at 1506 cm^{-1} can be assigned to the ν(C=N) vibrations indicating some double bond character.



Scheme 2.

The ^{13}C-NMR and ^{1}H-NMR spectra were recorded at −50°C in toluene-d_8. In the carbonyl region the ^{13}C-NMR spectrum shows 11 signals according to CO and $FeC_{carbene}$ carbon atoms reflecting the low symmetry of **1**. The strongest signal at 217 ppm can be attributed to the chemically equivalent carbonyl groups of the $Fe(CO)_4$ fragment. The 16 methyl groups of the dimethylamino ligands produce 15 signals between 34.5 and 44.8 ppm, indicating hindered rotation of the NMe_2 groups about the C–N bond with the exception of one group for which either free rotation at this temperature or an accidental signal coincidence is operative. The low-field shifts are probably due to the NMe_2 groups that have remained at the Zr atoms; the signals for terminal and bridging groups of $[Zr(NMe_2)_4]_2$ are located at 43.6 and 43.5 ppm, respectively [13].

In order to get more detail about the properties of the compound, the molecular structure of **1** has been determined by single-crystal X-ray diffraction measurements. The molecular structure indicates that the dimeric nature of the starting $(NMe_2)_3Zr(\mu\text{-}NMe_2)_2Zr(NMe_2)_3$ [13] has been maintained. Three of the eight NMe_2 groups of the amide have been left intact (two terminal and one bridging) while five have moved from zirconium to carbonyl carbon atoms under formation of seven Zr–O bonds. The molecular structure of the complex is shown in Fig. 1.

The insertion reaction has generated three types of iron atoms. The iron atom Fe(3) is part of the zir-

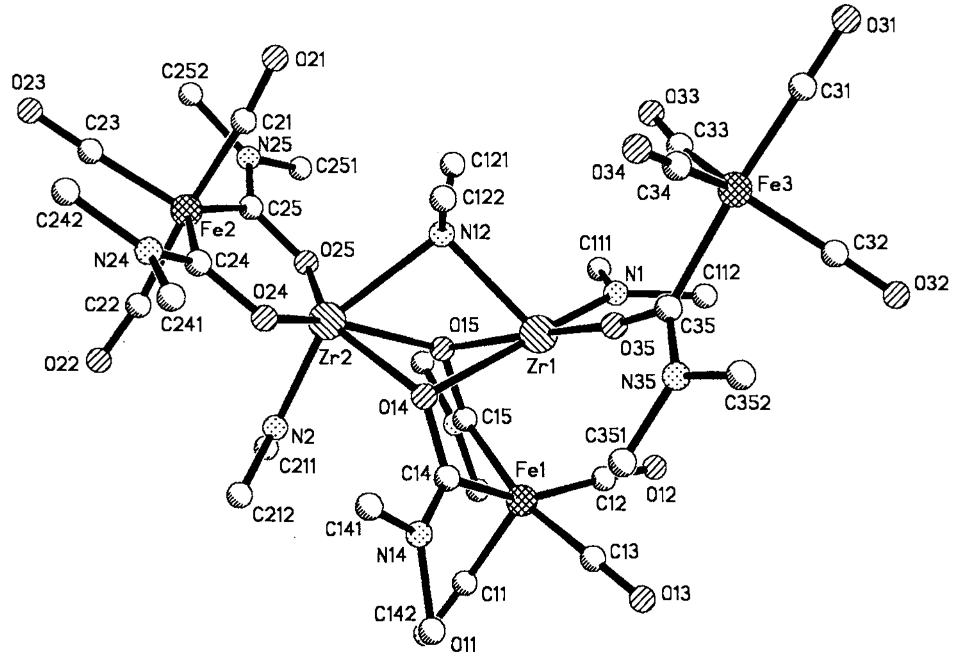


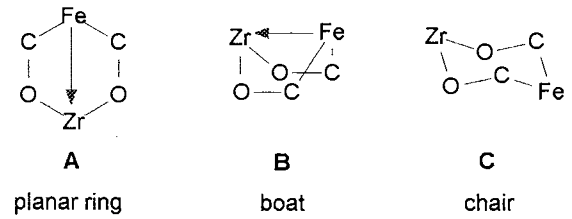
Fig. 1. The molecular structure of **1** showing the atomic numbering scheme.

conoxycarbene complex $(CO)_4Fe{=}C(NMe_2)O\{Zr\}$ resulting from the insertion of one CO group into a Zr–N bond. The other two iron atoms belong to biscarbene complexes formed through the insertion of two CO groups into Zr–N bonds and are chemically different. The pairwise insertion generates three types of six-membered ring systems as depicted in Scheme 3. Ring **A** containing Zr(2) and Fe(2) is planar while a boat conformation is realized in the ring **B** with participation of Zr(1) and Fe(1); the bridging function of the oxygen atoms forms an additional chair conformation (**C**) containing Zr(2) and Fe(1).

The Fe–$C_{Carbene}$ distances in **1** range from 197 pm in ring **A** over 200 pm at Fe(3) to 201 pm in ring **B**, and are 5–8 pm shorter than in the related carbamoyl complex $[(CO)_4FeC(O)NMe_2]^-$ (205.3 pm), indicating some Fe–C double-bond character. The distances correspond to those found in typical electron-rich heteroatom stabilized carbene complexes of the type $(CO)_4Fe{=}C(O,N)$ [5,14] and $(CO)_4Fe{=}C(N,N)$ [15]; shorter distances of about 190 pm were recorded in carbene compounds of the type $(CO)_4Fe{=}C(O,O)$ [16].

Ring **A** is approximately planar and compressed in such a manner to allow the atoms Zr(2) and Fe(2) coming closer together to establish a Dewar-benzene like arrangement. The distribution of the inner angles of the ring along with the deviation of the atoms from the best plane are shown in Fig. 2; the sum of the angles amounts to 718° and is close to that in a six-membered aromatic ring like benzene.

The Zr···Fe distance in the planar ring **A** is only 2.5 pm longer than the corresponding distance in the boat-configured ring **B**. It is remarkable that the short one is only 7 pm longer than that in $Cp(CO)_2FeZr\{(Me_3SiNCH_2)_2CH_2\}Cp$ (274.5 pm) containing an Fe–Zr σ bond [17]; two further compounds with $Cp(CO)_2Fe$ groups bonded to zirconium are described with distances of 260.5 and 266.5 pm [18]. The short contacts in the rings **A** and **B** justify discussion of an iron–zirconium donor interaction, which allows enhancement of the number of electrons from 12 to 14 for Zr(2) and from 10 to 12 for Zr(1). The contacts are appreciably shorter than the sum of the van der Waals radii of 450 pm. The Zr(2)···Fe(1) distance in the chair conformation **C** with 427.7 pm is too long for a binding interaction (Table 1).



Scheme 3.

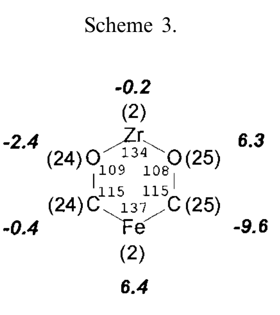


Fig. 2. Angles and deviation from the best plan (bold numbers, pm) in the planar ring **A** (number of atoms in brackets see Fig. 1).

The sum of bond distances in ring **B** is 38 pm longer than that in ring **A** accompanied by much smaller O–Zr–O and C–Fe–C angles (75.2° and 94.0° in **B** versus 133.8° and 137.1° in **A**). Assuming a donor–acceptor interaction between Fe(1) and Zr(1) (ring **B**) both atoms attain coordination number 6 as for Zr(2). The large deviation of the angles in **A** at Fe(2) and Zr(2) from the ideal 120° and 90° to 134° and 137°, respectively, brings the transition metals close together, and may also be discussed in terms of a metal–metal interaction as we do in ring **B**.

A nearly linear sp-hybridized oxygen atom with a C(35)–O(35)–Zr(1) angle of 172° is indicative of some O–C and O–Zr double-bond character; the corresponding angles in titanoxy- (165°) [8] and in aluminoxycarbene complexes (150° and 155°) [5] are smaller. Zr(1) lies in the basal plane of a distorted tetragonal pyramid formed by the atoms O(15), O(14), O(35), and N(1) and is located 2.4 pm above the best plane of these atoms; the sum of the angles in the basal plane is 360°. A similar coordination is realized for Fe(1), which lies 32 pm above the basal plane ($\Sigma = 355°$).

The coordination at Fe(2) is exactly trigonal bipyramidal with the chelating carbene ligand and one carbonyl group in the equatorial plane; the sum of the equatorial angles is 360°.

The Zr···Zr distance has decreased from 370 pm in the starting amide [13] to 338 pm in **1**. In the related compound, $(Me_2N)_3Zr(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)_2(THF)$, a distance of 358 pm has been recorded [19]. Shorter distances (323 pm) are found in a trinuclear linear complex with μ-NMe_2 and μ-H ligands [20]. However, much shorter Zr···Zr distances (299 pm) are recorded in the anion $[Zr_2Cl_6(\mu\text{-}NPMe_3)_3]^-$ containing three μ-phosphaniminato ligands [21].

1 contains seven Zr–O distances differing by more than 30 pm. The shortest distance is that in the zirconoxycarbene fragment $(CO)_4Fe{=}C(NMe_2)O\{Zr\}$ with 201 pm and increases from ring **A** (209 and 211 pm) over ring **B** (223 and 226 pm) finally to the longest ones in the chair ring **C** (229 and 232 pm). Zirconoxycarbenes with less donating ligands at the carbene carbon atom (e.g. H instead of NMe_2) exhibit Zr–O distances below 200 pm [9].

The iron atoms in **1** are in the formal oxidation state zero and act in the rings **A** and **B** as Lewis bases toward

Table 1
Selected bond lengths (pm) and angles (°) for compound **1**

Bond lengths			
Zr(1)–O(35)	201.25(19)	Fe(2)–C(21)	176.6(4)
Zr(1)–N(1)	202.8(2)	Fe(2)–C(23)	177.4(4)
Zr(1)–O(15)	222.46(18)	Fe(2)–C(22)	179.4(3)
Zr(1)–N(12)	223.0(2)	Fe(2)–C(25)	196.8(3)
Zr(1)–O(14)	225.46(17)	Fe(2)–C(24)	197.1(3)
Zr(1)–Fe(1)	281.55(6)	Fe(3)–C(31)	177.7(3)
Zr(1)–Zr(2)	338.28(5)	Fe(3)–C(34)	178.1(3)
Zr(2)–N(2)	204.9(2)	Fe(3)–C(32)	178.8(3)
Zr(2)–O(25)	209.32(19)	Fe(3)–C(33)	180.2(4)
Zr(2)–O(24)	211.32(19)	Fe(3)–C(35)	199.6(3)
Zr(2)–O(14)	229.03(17)	C(14)–O(14)	132.9(3)
Zr(2)–O(15)	232.32(18)	C(14)–N(14)	132.9(3)
Zr(2)–N(12)	236.0(2)	C(15)–O(15)	132.4(3)
Zr(2)–Fe(2)	284.16(6)	C(15)–N(15)	132.7(4)
Fe(1)–C(12)	176.1(3)	C(24)–O(24)	131.1(3)
Fe(1)–C(11)	178.7(3)	C(24)–N(24)	131.9(4)
Fe(1)–C(13)	178.7(3)	C(25)–O(25)	131.6(4)
Fe(1)–C(15)	200.8(3)	C(25)–N(25)	133.0(4)
Fe(1)–C(14)	200.9(3)	C(35)–O(35)	131.0(3)
Bond angles			
O(35)–Zr(1)–N(1)	101.16(9)	O(25)–Zr(2)–O(15)	76.40(7)
O(35)–Zr(1)–O(15)	168.47(7)	O(24)–Zr(2)–O(15)	148.34(7)
N(1)–Zr(1)–O(15)	90.29(9)	O(14)–Zr(2)–O(15)	70.21(6)
O(35)–Zr(1)–N(12)	102.51(8)	N(2)–Zr(2)–N(12)	154.40(9)
N(1)–Zr(1)–N(12)	107.11(9)	O(25)–Zr(2)–N(12)	94.44(8)
O(15)–Zr(1)–N(12)	72.41(7)	O(24)–Zr(2)–N(12)	95.78(8)
O(35)–Zr(1)–O(14)	96.05(7)	O(14)–Zr(2)–N(12)	69.78(7)
N(1)–Zr(1)–O(14)	162.29(9)	O(15)–Zr(2)–N(12)	68.37(7)
O(15)–Zr(1)–O(14)	72.64(6)	C(13)–Fe(1)–C(15)	166.96(12)
N(12)–Zr(1)–O(14)	72.77(7)	C(14)–Fe(1)–C(15)	93.98(11)
O(35)–Zr(1)–Fe(1)	110.04(6)	C(12)–Fe(1)–C(14)	152.55(14)
N(1)–Zr(1)–Fe(1)	101.09(7)	C(11)–Fe(1)–Zr(1)	153.17(13)
O(15)–Zr(1)–Fe(1)	68.50(5)	C(21)–Fe(2)–C(22)	172.45(15)
N(12)–Zr(1)–Fe(1)	131.28(6)	C(23)–Fe(2)–C(25)	110.02(16)
O(14)–Zr(1)–Fe(1)	68.71(4)	C(23)–Fe(2)–C(24)	112.88(16)
N(2)–Zr(2)–O(25)	92.98(9)	C(25)–Fe(2)–C(24)	137.10(12)
N(2)–Zr(2)–O(24)	96.64(9)	C(34)–Fe(3)–C(32)	131.45(16)
O(25)–Zr(2)–O(24)	133.79(8)	C(34)–Fe(3)–C(33)	115.30(16)
N(2)–Zr(2)–O(14)	90.88(8)	C(32)–Fe(3)–C(33)	113.16(16)
O(25)–Zr(2)–O(14)	146.35(7)	O(14)–C(14)–Fe(1)	119.11(17)
O(24)–Zr(2)–O(14)	78.69(7)	O(15)–C(15)–Fe(1)	118.05(18)
N(2)–Zr(2)–O(15)	89.74(8)	C(24)–O(24)–Zr(2)	108.95(17)
Zr(1)–O(14)–Zr–(2)	96.20(6)	O(25)–C(25)–Fe(2)	115.3(2)
Zr(1)–O(15)–Zr–(2)	96.09(6)	C(25)–O(25)–Zr(2)	107.97(17)
C(14)–O(14)–Zr(1)	97.88(14)	O(35)–C(35)–N(35)	114.1(2)
C(15)–O(15)–Zr(1)	98.78(16)	C(35)–O(35)–Zr(1)	172.41(18)

the zirconium atoms. It is not unusual that trigonal pyramidal configured iron(0) compounds donate electrons in the equatorial plane to other metals brought into close proximity to the iron atom. This weak bonding interaction can be stabilized by bidentate ligands in the axial positions (**I**) [22] and is also found in the complex $[(CO)_4FeC(O)NMe_2]_2Ni$ with a carbamoyl bridge (**II**) [23] (Scheme 4). The electron donation is accompanied by opening of the OC–Fe–CO angle from 120° to values ranging from 130° up to 150° depending on the nature of the accepting metal M.

Closely related to the structural motif **B** are the carbenoid compounds of the type **III** $(CO)_3Fe(=C(R)O)_2Fe(CO)_3$ with a similar boat conformation [24].

Further studies on the reaction of metal amides with transition metal carbonyl complexes are in progress.

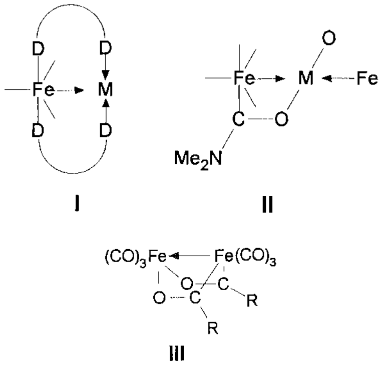
3. Experimental

3.1. General

All operations were carried out under an argon atmosphere in dried and degassed solvents using Schlenk techniques. The solvents were thoroughly dried and freshly distilled prior to use. The IR spectra were run on a Nicolet 510 spectrometer. The NMR spectra were recorded on a Bruker DRX 400 instrument. Elemental analyses were performed by the analytical service of the Fachbereich Chemie der Universität Marburg, Germany. $\{Zr(NMe_2)_4\}_2$ was prepared by a published method [25]; commercially available $Fe(CO)_5$ was used without further purification.

3.2. Preparation of $(CO)_3Fe(\mu\text{-}C(NMe_2)O)_2Zr(NMe_2)(\mu\text{-}NMe_2)Zr(NMe_2)(OC(NMe_2){=}Fe(CO)_4)(\mu_3\text{-}OC(NMe_2))_2Fe(CO)_3$ (**1**)

A 100 ml Schlenk tube containing a solution of $Zr(NMe_2)_4$ (1.40 g, 5.24 mmol) in 50 ml of a mixture of toluene–pentane (3:1) and maintained under a positive flow of argon was cooled to −80°C. To this solution was added dropwise under magnetic stirring a solution of $Fe(CO)_5$ (1.03 g, 5.24 mmol) in 5 ml of toluene. The resulting yellow solution was slowly allowed to come to room temperature (r.t.). When the temperature reached about 10°C an orange oil separated. The mixture was kept at −20°C for 3 days. The solvent was decanted and the oily residue was dried under vacuum. The resulting yellow–orange oily product was extracted with about 10 ml of toluene and the filtered solution



Scheme 4.

Table 2
Crystallographic data for compound **1**

Formula	$C_{38}H_{56}Fe_3N_8O_{15}Zr_2$
M	1214.90
Temperature (K)	203
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (pm)	1228.79(12)
b (pm)	1467.4(2)
c (pm)	1475.53(15)
α (°)	94.691(10)
β (°)	94.903(8)
γ (°)	109.094(10)
U (pm^3)	$2597.2(5) \times 10^6$
Z, D_{calc} (g cm^{-3})	2, 1.554
Absorption coefficient (mm^{-1})	1.273
Crystal size (mm)	$0.25 \times 0.29 \times 0.43$
Reflections collected	10 935
Unique data	10 506 ($R_{int} = 0.0172$)
Data/restraints/parameters	10 506/0/624
Goodness-of-fit on F^2	1.034
R, wR_2 [$I > 2\sigma(I)$ data]	0.0334, 0.0845
R, wR_2 (all data)	0.0418, 0.0890

layered with pentane. After a few days yellow crystals along with an orange–yellow oil had separated. The solvent was removed by decantation and the crystals dried under vacuum. ^{1}H-NMR (toluene-d_8, 223 K): δ 3.05–2.07 (m, CH_3). ^{13}C-NMR (toluene-d_8, 223 K): δ 231.99, 231.80, 228.81, 227.75, 226.98, 226.90, 221.31, 221.19, 217.07, 213.80, 210.46 (CFe + CO), 44.84, 44.28, 43.96, 43.30, 42.14, 42.02, 41.31, 40.64, 40.57, 40.48, 40.42, 38.28, 38.05, 35.69, 34.48 (Me). IR (Nujol): 2035, 2000, 1975, 1940 (sh), 1929 (br), 1890 (sh) (CO), 1506, 1380, 1340, 1281, 1233, 1208, 1105, 1045, 952, 941, 891, 873, 733, 704, 679, 667, 646, 631, 608, 598, 585, 550, 498, 465, 438 cm^{-1}. Anal. Found: C, 31.41; H, 4.25; N, 7.77. Calc. for (**1**·C_7H_8) $C_{38}H_{56}Fe_3N_8O_{15}Zr_2$: C, 37.56; H, 4.65; N, 9.23%.

3.3. X-ray data collection and crystal-structure determination

Essential crystal and refinement data can be found in Table 2. Suitable crystals of **1** with one molecule toluene were grown as described above from toluene by layering with pentane. A crystal measuring $0.25 \times 0.29 \times 0.43$ mm^3 was selected, mounted on a glass thread and brought into the cold nitrogen stream (203 K) of a CAD4 four-circle diffractometer (Enraf-Nonius). From a set of 25 reflections $12.32 < \theta < 20.18°$ the exact unit cell dimensions were derived. Data collection was carried out using ω-scans. After data reduction [26] and space group determination [27] the starting model was obtained by direct methods [28]. Subsequent and repeated least-squares refinements and difference Fourier syntheses [29] gave the final R values R_1 ($I > 2\sigma(I)) = 0.0334$ and wR_2 (all data) = 0.0890.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 135505. 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 or www: http://www.ccdc.cam.ac.uk).

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