## Cobalt Complexes with 1,3-Bis(trimethylsilyl)cyclopentadienyl and Substituent-Free $P_n$ Ligands

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The thermal or photochemical reaction of  $[Cp''Co(CO)_2]$  (1)  $[Cp'' = C_5H_3(SiMe_3)_2-1,3]$  with white phosphorus  $(P_4)$  gives  $[\{Cp''Co\}_2(P_5-P_5)\{CoCp''\}_2]$  (2) and  $[\{Cp''Co\}_3P_4(\mu-CO)]$  (3)

as well as  $[\{Cp''Co\}_2(\mu-\eta^2:\eta^2-P_2)_2]$  (4). Cobalt complexes 2, 3, and 4 have been characterized by an X-ray crystal-structure determination.

#### Introduction

In the chemistry of transition-metal complexes with substituent-free ("naked")  $P_n$  ligands the choice of the additional  $Cp^R$  ligands plays an important role. [1] Illustrative examples are the reactions of  $[\{Cp^R(OC)_2Fe\}_2](Fe-Fe)$  with white phosphorus  $(P_4)$ .

Starting with  $Cp^R = C_5H_5$  the cothermolysis gives the tetranuclear cluster [{CpFe}\_4(P\_2)\_2] with a triangulated dodecahedral Fe<sub>4</sub>P<sub>4</sub> skeleton.<sup>[2]</sup> In the case of  $Cp^R = C_5H_2tBu_3$ -1,2,4 the complex [{Cp^R(OC)\_2Fe}\_2(\mu-\eta^1:\eta^1-P\_4)], a molecule with a P<sub>4</sub> butterfly framework was synthesized.<sup>[3]</sup> Finally, the use of  $Cp^R = C_5Me_5$  gave for the first time [Cp\*Fe( $\eta^5$ -P<sub>5</sub>)], a sandwich complex with a *cyclo*-P<sub>5</sub>-ligand, the all-phosphorus analogue of the cyclopentadienide ion  $C_5H_5^{-}$ .<sup>[4]</sup>

The photochemical route, realized for  $Cp^R = C_5H_4Me$  or  $C_5H_3tBu_2$ -1,3 (Cp''), affords [ $Cp^R_4Fe_4(CO)_6P_8$ ] with an open-edged  $P_8$  cuneane geometry<sup>[5]</sup> and all five members of the series [ $Cp''_2Fe_2P_4(CO)_{4-n}$ ] (n=0-4) with different  $P_4$  ligands.<sup>[6]</sup>

The experiences of the last decade have shown that especially highly alkylated  $\operatorname{Cp}^R$  ligands are very useful in the coordinative stabilization of different  $\operatorname{P}_n$  ligands. Interestingly, to the best of our knowledge, until now transitionmetal complexes with trimethylsilyl-substituted  $\operatorname{Cp}^R$  ligands are unknown as starting materials in  $\operatorname{P}_n$  chemistry.

# Thermal and Photochemical Reaction of $[Cp''Co(CO)_2]$ [1, $Cp'' = C_5H_3(SiMe_3)_2$ -1,3] with White Phosphorus $(P_4)$

According to Equation 1 the cothermolysis of  $[Cp''Co(CO)_2]$  (1) and  $P_4$  (Co/P  $\approx$  1:7) affords exclusively the tetranuclear cobalt complex 2 with a  $P_{10}$  ligand in the unusually high yield of 87%.

$$[Cp''Co(CO)_{2}] = \frac{P_{4}, \text{ xylene}}{72 \text{ h, ca. } 140 °C} \qquad [\{Cp''Co\}_{2}(P_{5}-P_{5})\{CoCp''\}_{2}] \qquad (1)$$

$$Cp'' = C_{5}H_{3}(SiMe_{3})_{2}-1,3$$

For a stoichiometry of Co/P  $\approx$  1:2 the photochemical alternative gives 30 % of 3 and 10 % of 4 (Equation 2) besides traces of 2.

The air-sensitive olive-green (2), dark-red (3), or black-purple (4) complexes are sparingly to well soluble in n-hexane and dissolve readily in toluene or dichloromethane.

#### NMR- and IR-Spectroscopic Investigations

The  $^{1}\text{H-}$ ,  $^{31}\text{P-NMR}$  data of the complexes **2**, **3**, and **4** as well as  $\tilde{v}(\text{CO})$  of **3** are compiled in Table 1.

The <sup>1</sup>H-NMR spectrum of **2** (measured at 340 K) affords 11 signals with relative integrals 2:2:2:2:2:1:1:18:18:18:18 in agreement with a local symmetric environment for each Cp'' ligand. In the <sup>31</sup>P-NMR spectrum of **2** (340 K) the P<sub>10</sub> skeleton (Figure 1) consists of an ABCC'DD'EE'FF' spin system. A comparison of the <sup>1</sup>J(P<sub>A</sub>P<sub>B</sub>) coupling constants of the P<sub>2</sub> bridge in **2** (-205 Hz) and **5** (-95 Hz)<sup>[7]</sup> suggests deviation of the lone pairs in the "bridge" P1-P1' from an antiperiplanar position for complex **2**.

The Schakal plot shows that each  $C_5H_3(SiMe_3)_2$ -1,3 ligand of **2** is locked between two adjacent ligands.

Comparing the spectroscopic data of 3 and  $7^{[8]}$  the following discrepancies were found: In contrast to the "remarkable high-field shift" discussed for  $7^{[8]}$  ( $\delta = -398.6$ ) for the P atom surrounded by three cobalt atoms, a value of  $\delta = 487.8$  (Table 1) was measured for 3. A redetermination of the <sup>31</sup>P-NMR spectrum of 7 gives instead of the

<sup>[\*]</sup> Crystal-structure analyses.

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Table 1. <sup>1</sup>H-, <sup>31</sup>P-NMR, and  $\tilde{v}(CO)$  data of the complexes 2, 3, and 4

$Cp'' = C_5H_3(SiMe_3)_2-1,3$	$[\{Cp''Co\}_4P_{10}]$ (2)	$[{Cp''Co}_3P_4(CO)]$ (3)	$[\{Cp''Co\}_2(P_2)_2]$ (4)
$^{1}$ H NMR $^{[a]}$ $\delta$ [ppm]	5.66 (s, 2 H) 5.52 (s, 2 H) 5.17 (s, 2 H) 5.02 (s, 2 H) 4.90 (s, 2 H) 4.68 (s, 1 H) 4.66 (s, 1 H) 0.70 (s, 18 H) 0.68 (s, 18 H) 0.36 (s, 18 H) 0.35 (s, 18 H)	5.89 (s, br, 2 H) 5.77 (s, br, 1 H) 5.05 (s, br, 6 H) 0.49 (s, 18 H) 0.45 (s, 18 H) 0.32 (s, 18 H)	4.54 (s, br, 4 H) 4.36 (s, br, 2 H) 0.47 (s, 36 H)
Spin system  31P NMR <sup>[b]</sup>	ABCC'DD'EE'FF' 269.6 (m, 1 P, P <sub>A</sub> ) 268.7 (m, 1 P, P <sub>B</sub> ) 74.4 (pdd, 2 P, P <sub>C</sub> )	AM <sub>2</sub> X 487.8 (t, 1 P, P <sub>A</sub> ) 239.7 (dd, 2 P, P <sub>M</sub> ) 22.0 (t, 1 P, P <sub>X</sub> )	A <sub>4</sub> -36.3 (s)
δ [ppm]  "J [Hz]	70.7 (pdd, 2 P, P <sub>D</sub> ) -137.2 (m, 2 P, P <sub>E</sub> ) -139.6 (m, 2 P, P <sub>F</sub> ) ${}^{1}J_{AB} = -205$ , ${}^{1}J_{AE} = -311$ ${}^{2}J_{AD} = 33$ ${}^{1}J_{BF} = -307$ , ${}^{2}J_{BC} = 6$ ${}^{1}J_{CE} = -359$ , ${}^{2}J_{CC'} = 79$ ${}^{1}J_{DF} = -358$ , ${}^{2}J_{DD'} = 75$ ${}^{2}J_{CE'} = 34$ , ${}^{2}J_{DF'} = 46$	$J_{\text{AM}} = 43$ ${}^{1}J_{\text{MX}} = -364$	
$\tilde{\nu}(CO) \; [cm^{-1}]^{[c]}$	- Di	1808 (s)	

<sup>[</sup>a] 400 MHz: 2: 340 K; 3/4: 298 K. - [b] 162 MHz: 2: 340 K; 3/4: 298 K ( $C_6D_6$ , 85%  $H_3PO_4$  ext.). - [c] 298 K, THF.

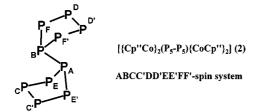


Figure 1. Spin system of complex 2

$$\begin{split} [\{Cp'''Co\}_2(P_5\text{-}P_3)\{CoCp'''\}] & \quad [\{Cp''Rh\}_2(P_5\text{-}P_5)\{RhCp''\}_2] \\ \\ 5 & \quad 6 \\ \\ Cp''' = C_5H_2Bu^t_3\text{-}1,2,4 & \quad Cp''' = C_5H_3Bu^t_2\text{-}1,3 \end{split}$$

reported<sup>[8]</sup>  $\delta = -398.6$  the expected low-field shift ( $\delta = 413.8$ ). The other <sup>31</sup>P-NMR signals (7:  $\delta = 227.5$ , 9.9) are in agreement with the published data.<sup>[8]</sup> Going from 7 to 3 all <sup>31</sup>P-NMR signals are shifted down-field in the bis(trimethylsilyl)cyclopentadienyl derivative 3 (cf. Table 1).

$$[\{Cp''Co\}_{3}P_{4}(\mu\text{-}CO)]$$

$$7$$

$$Cp'' = C_{5}H_{3}Bu_{2}^{t}-1,3$$

The redetermination of  $\tilde{v}(CO)$  in 7 gives 1793 cm<sup>-1</sup> instead of the published 1934 cm<sup>-1</sup>.<sup>[8]</sup> This value is in accordance with 1808 cm<sup>-1</sup> measured for 3. Both bands are in the region expected for a  $\mu$ -CO ligand (cf. Figure 5).

### X-ray Crystal-Structure Determinations of the Complexes 2, 3, and 4

#### Compound 2

The most interesting structural aspect of complex  $\bf 2$  is its  $Co_4P_{10}$  skeleton (Figure 2).

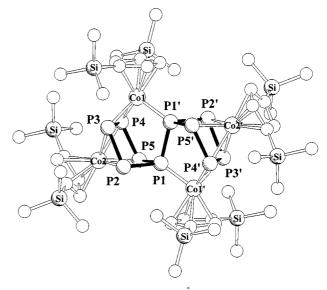


Figure 2. Selected bond lengths [Å] and angles [°]: P1-P1' 2.1793(18), P2-P1 2.1948(14), P2-P3 2.1573(14), P3-P4 2.4743(15), P4-P5 2.1573(14), P5-P1 2.1985(14), Co1-P1' 2.1311(11), Co1-P3 2.2405(11), Co1-P4 2.2446(11), Co2-P2 2.3108(12), Co2-P5 2.3196(12), Co2-P3 2.3355(11), Co2-P4 2.3753(11), Co1-Cp''(centr.) 1.72, Co2-Cp''(centr.) 1.72, P1'-Co1-P3 93.95(4), P1'-Co1-P4 93.44(4), P3-Co1-P4 66.96(4), Co1-P1'-P1 111.43(6), P2-P1-P1' 100.11(7), P2-P1-P5 90.82(5), P5-P1-P1' 101.18(6)

The  $P_{10}$  framework can be derived formally from the  $P_{10}$  dihydrofulvalene **A** (Figure 3) where the two  $4\pi$  systems bind to Co2(2') giving  $18e^-$  per cobalt atom. This electron count can also be obtained for Co1(1') taking into account the lone pair on P1(1') and the bond(s) P3(3')-P4(4') (2.47 Å, Figure 2) which is reasonably close to the longest known  $2c2e^--P-P$  bonds. For the side-on coordinated white phosphorus ( $P_4$ ) in  $[(Ph_3P)_2Rh(Cl)(\eta^2-P_4)]$  this edge is elongated from 2.21 Å ( $P_4$  itself) to 2.46 Å. [9] Interestingly, for the analogous  $Rh_4P_{10}$  compound **6** a distinctly longer  $P\cdots P$  bond (open edged) of 2.62 Å was found. [10] All the other P-P bond lengths of the  $P_{10}$  ligand in the complexes **2** and **6** are comparable [two shorter P2-P3, P4-P5: 2.16/2.15 Å (**2/6**); two longer: 2.20/2.19 Å (**2/6**)].



Figure 3. Hypothetic P<sub>10</sub> dihydrofulvalem

Alternatively, the  $\text{Co}_4\text{P}_{10}$  framework of **2** can also be derived from  $\text{Li}_3\text{P}_7$  (Figure 4, **B**), a well-known molecule in polyphosphide chemistry.<sup>[11]</sup>

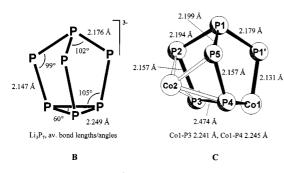


Figure 4. Comparison of P<sub>7</sub><sup>3-</sup> with the Co<sub>2</sub>P<sub>6</sub> cage of 2

Formally, C (Figure 4) can be derived from **B** by replacing one basal P atom by the Co1Cp'' fragment and capping the four-electron donor P2,3,4,5 unit by the Co2Cp'' unit. Electron count and d(P1'-Co1) are in favour of a multiple-bond character.

The connection of two  $\text{Co}_2\text{P}_6$  subunits  $\mathbf{C}$  with a common edge (P1-P1') formally gives the  $\text{Co}_4\text{P}_{10}$  skeleton of compound  $\mathbf{2}$  (Figure 2). The biggest difference in bond lengths between  $\mathbf{B}$  and  $\mathbf{C}$  occurs, as one would expect, in the basal triangle P3,P4,Co1 (P3-P4 2.47 Å).

A further interesting parallel is realized with complexes **8**,<sup>[12]</sup> synthesized by Eichhorn's group.

$$[(\eta^4 - P_7)\{M(CO)_3\}]^3$$
,  $M = Cr, Mo, W$ 

Its carbonylation affords  $[(\eta^2-P_7)W(CO)_4]^{3-}$  (9) where the norbornadiene-type geometry of the  $P_7$  ligand in 8 has changed to the nortricyclane-like structure of 9  $(\eta^4 \rightarrow \eta^2-P_7)$ . [12b]

The polycyclic  $P_{10}$  core of the paramagnetic complex  $[\{Cp(CO)_2Cr\}_5P_{10}]$  (10) consists of a  $P_7$  norbornane with a  $P_2$  bridge and a terminal P atom. [13]

#### **Compound 3**

Bond lengths and angles of the trinuclear cobalt complex 3 (Figure 5) differ only slightly from the values of the analogous complex 7 with  $C_5H_3tBu_2-1,3$  ligands.<sup>[8]</sup>

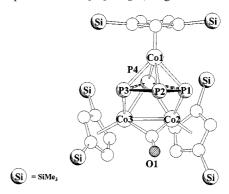


Figure 5. Selected bond lengths [Å] and angles [°]: P1-P2 2.1609(10), P2-P3 2.1585(9), P3···P4 2.5237(9), P4···P1 2.4879(8), Co2-Co3 2.4485(5), Co1-P1 2.3099(6), Co1-P2 2.2706(7), Co1-P3 2.3207(7), Co1-P4 2.2711(7), Co2-P1 2.2714(7), Co2-P4 2.2483(6), Co3-P3 2.2787(7), Co3-P4 2.2290(7), Co1-Cp''(centr.) 1.73, Co2-Cp''(centr.) 1.75, Co3-Cp''(centr.) 1.74, P1-P4-P3 78.93(3), P2-P1-P4 93.02(3), P2-P3-P4 92.09(3), P3-P2-P1 95.03(4), Co2-P4-Co3 66.30(2)

A small kite-like distortion of a *cyclo*-P<sub>4</sub> ligand was realized for the first time in  $[\{Cp^*(OC)_2Nb\}(\eta^4-P_4)]$  (11),  $Cp'' = C_5H_3tBu_2-1,3.^{[14]}$  Interestingly, a much stronger distortion was found for 3 and 7. For both complexes the P···P bonds to P4 coordinating to three  $CoCp^R$  fragments are distinctly longer [average of 3: 2.50; 7: 2.503(2) Å]. EHT calculations on 7 are in agreement with a weak P···P bonding<sup>[8]</sup> {c.f. the  $2c1e^-$  P···P bond length of 2.634(3) Å in the P<sub>4</sub> rectangle of the diradical  $[R_2N-CP_2]_2^{\bullet\bullet}$  ( $R=iPr)^{[15]}$ }.

In contrast to the planar  $P_4$  ligand of 7 the P4 atom in 3 lies 0.34 Å above the P1,P2,P3 plane (Figure 5). The missing mirror plane in compound 3 leads to small differences in bond lengths and angles relative to those in 7 (the mean values of both compounds are nearly identical).

According to the electron-counting rules [16] of Wade and Mingos complex 3 belongs to an *arachno* cluster with (n + 3) = 10 SEPs (skeleton electron pairs). Its framework can formally be derived from a *closo* tricapped trigonal prism by successive elimination of two vertices.

#### **Compound 4**

The bond lengths and angles of complex **4** (Figure 6) are very similar to those of the X-ray-crystallographically characterized derivatives [{Cp\*Co}<sub>2</sub>( $\mu$ - $\eta$ <sup>2</sup>: $\eta$ <sup>2</sup>-P<sub>2</sub>)] (**12**)<sup>[17]</sup> and [{Cp'''Co}<sub>2</sub>( $\mu$ - $\eta$ <sup>2</sup>: $\eta$ <sup>2</sup>-P<sub>2</sub>)] (**13**) (Cp''' = C<sub>5</sub>H<sub>2</sub>tBu<sub>3</sub>-1,2,4). <sup>[18]</sup>

For the side-on coordinated  $4e^-$  donor  $P_2$ , which is isoelectronic and isolobal with acetylene ( $|P \equiv P| \longrightarrow$ 

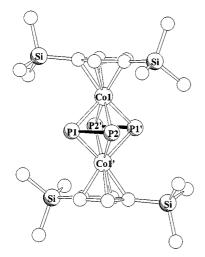


Figure 6. Selected bond lengths [Å] and angles [°]: P1-P2 2.0538(15),  $P1\cdots P2'$  2.7131(14), Co1-P1 2.3069(10), Co1-P1' 2.3162(10), Co1-P2 2.3050(10), Co1-P2' 2.3164(10), Co1-Cp''-(centr.) 1.70,  $Co1\cdots Co1'$  3.127; P1-P2-P1' 90.04(4), P2-P1-P2' 89.96(4)

HC=CH), d(P-P) lies in the range of 2.054 (4), 2.053 (12), and 2.052 Å (13) which is typical for P-P double bonds. [1] The long P···P edges of the rectangular (P<sub>2</sub>)<sub>2</sub> ligands have nonbonding distances of 2.713, 2.705 (mean value), and 2.663 Å, d(Co-P) ranges from 2.311 to 2.305 and 2.308 Å, respectively. Such small differences also exist for Co···Co (3.127, Figure 6) (12: 3.102; 13: 3.164 Å). For all three complexes the least-squares plane defined by the two μ- $\eta^2$ : $\eta^2$ -P<sub>2</sub> units and the planes of the two Cp<sup>R</sup> rings differ only slightly (2°, 1°, and 2°) from a parallel arrangement.

#### **Experimental Section**

All experiments were carried out under argon in anhydrous solvents. – NMR: Bruker AMX 400,  $^{1}$ H NMR (400.13 MHz),  $^{31}$ P NMR (161.98 MHz). – The  $^{31}$ P-NMR spectra of **2** was simulated with PERCH. $^{[20]}$  IR spectra were recorded with an FT-IR spectrometer Perkin–Elmer 16 PC. – UV irradiation: 150-W Hg highpressure lamp, TQ 150, Heraeus Quarzlampen GmbH, Hanau. –  $[Cp''Co(CO)_2]$  (1)  $[Cp'' = C_5H_3(SiMe_3)_2]$  was synthesized from  $[Co_2(CO)_8]$  and Cp''H in analogy to ref. [19]

Cothermolysis of [Cp''Co(CO)<sub>2</sub>] (1) and White Phosphorus (P<sub>4</sub>): 1.72 g (5.3 mmol) of 1 and 1.2 g (9.7 mmol) of P<sub>4</sub> were heated to reflux in 50 mL of xylene for 72 h. After evaporation of the solvent under oil-pump vacuum (0  $\rightarrow$  35°C), the residue was dissolved in ca. 20 mL of dichloromethane, and ca. 5 g of neutral Al<sub>2</sub>O<sub>3</sub> (activity grade II) was added. The solvent was evaporated under oil-pump vacuum from the mixture until the residue was free-flowing. It was placed on top of a column (2 × 15 cm) filled with neutral Al<sub>2</sub>O<sub>3</sub> and petroleum ether. A mixture of petroleum ether/diethyl ether (40:1) eluted [{Cp''Co}<sub>2</sub>(P<sub>5</sub>-P<sub>5</sub>){CoCp''}<sub>2</sub>] (2); yield 1.7 g (87 %) of olive-green crystals.  $-C_{50}H_{98}Co_4P_{10}Si_8$  (1469.4): calcd. C 40.86, H 6.72; found C 40.34; H 6.77.

Cophotolysis of 1 and  $P_4$ : 1.13 g (3.5 mmol) of 1 and 0.19 g (1.5 mmol) of  $P_4$  were irradiated (150-W Hg high-pressure lamp) for 14 h in 100 mL tetrahydrofuran until the  $\tilde{v}(CO)$  bands of 1 had disappeared and a new one at 1808 cm<sup>-1</sup> had emerged. Column chromatography as described for complex 2 gave with the same mixture of solvents as first fraction 115 mg (10%) of purple  $[Cp''Co]_2(P_2)_2$  (4) followed by 330 mg (30%) of red-brown  $[Cp''Co]_3P_4(CO)]$  (3). — 3:  $C_3H_{63}Co_3OP_4Si_6$  (957.1): calcd. C 42.66, H 6.63; found C 40.05, H 6.65. — 4:  $C_{22}H_{42}Co_2P_4Si_4$  (660.7): calcd. C 39.99, H 6.41; found C 27.19 (incomplete combustion), H 5.87

**Single-Crystal X-ray Structure Determination:** See also Table 2. Crystallographic data (excluding structure factors) for the struc-

Table 2. Crystallographic data for complexes 2, 3, and 4<sup>[a]</sup>

$Cp'' = C_5H_3(SiMe_3)_2-1,3$	$[\{Cp''Co\}_4P_{10}]$ (2)	$[\{Cp''Co\}_3P_4(CO)]$ (3)	$[\{Cp''Co\}_2(P_2)_2] \ \textbf{(4)}$
formula	C <sub>50</sub> H <sub>98</sub> Co <sub>4</sub> P <sub>10</sub> Si <sub>8</sub>	C <sub>34</sub> H <sub>63</sub> Co <sub>3</sub> OP <sub>4</sub> Si <sub>6</sub>	C <sub>22</sub> H <sub>42</sub> Co <sub>2</sub> P <sub>4</sub> Si <sub>4</sub>
$M_{ m r}$	1469.4	957.1	660.7
crystal size [mm]	$0.51 \times 0.30 \times 0.22$	$0.40 \times 0.20 \times 0.12$	$0.64 \times 0.29 \times 0.14$
crystal system	tr <u>i</u> clinic	monoclinic	tr <u>i</u> clinic
space group	$P\bar{1}$	$P2_1/n$	<i>P</i> 1
a [A] b [Å]	10.9820(10)	17.7233(15)	6.5930(10)
b [A]	14.117(2)	12.3106(6)	11.297(2)
c [A]	14.6760(10)	23.9381(18)	11.981(3)
α [°]	109.180(10)	90	79.42(2)
β [°]	102.050(10)	111.286(9)	79.08(2)
γ [°]	109.890(10)	90	78.95(2)
$V[A^3]$	1884.6(3)	4866.6(6)	849.9(3)
Z	1	4	1
T[K]	293	293	293
$d_{\text{calcd.}} [\text{g_cm}^{-3}]$	1.295	1.306	1.291
$\mu  [\text{mm}^{-1}]$	1.234	1.314	1.315
2Θ range [°]	2.05-25.00	2.43-27.50	2.74 - 27.50
measured refl.	7676	60076	4905
independent refl.	6341	11105	3897
refined parameters	339	451	152
$R1 \ (I \ge 2\sigma I)$	0.0410	0.0285	0.0409
wR2 (all data)	0.0997	0.0538	0.1144
residual electron	0.510/ 0.355	0.210/ 0.225	0.610/ 0.514
density [e·A <sup>-3</sup> ]	0.519/-0.255	0.318/-0.235	0.619/-0.514
diffractometer	Siemens P4	Stoe IPDS	Siemens P4

<sup>[</sup>a] Structure solution by Direct Methods SHELXL-97, SIR 92; refinement: full-matrix least-squares methods against F<sup>2</sup>.

tures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-115135 (2), -115137 (3), -115136 (4). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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