CYCLOPENTADIENYL RUTHENIUM COMPLEXES WITH TRICARBOLLIDE LIGANDS

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Dedicated to Professor Bohumil Štíbr on the occasion of his 70th birthday.

Reaction of the tricarbollide anion $[7,8,9\text{-}C_3B_8H_{11}]^-$ (**1a**) with the naphthalene complex $[CpRu(C_{10}H_8)]^+$ under visible light irradiation in CH_2Cl_2 gives the 12-vertex *closo*-ruthenacarborane $1\text{-}Cp\text{-}1,2,3,5\text{-}RuC_3B_8H_{11}$ (**2**; 87% yield). This complex was also obtained by reaction of **1a** with CpRu(cod)Cl (97%). Upon heating at 80 °C in toluene **2** rearranges into isomer $1\text{-}Cp\text{-}1,2,4,10\text{-}RuC_3B_8H_{11}$ (**3**; 63%). Irradiation of **1a** with $[CpRu(C_{10}H_8)]^+$ in acetone gives the 11-vertex *closo*-$1\text{-}Cp\text{-}1,2,3,4\text{-}RuC_3B_7H_{10}$ (**4**; 32%). The latter was also prepared by reaction of **1a** with $[CpRu(MeCN)_3]^+$ (59%). Compound **2** slowly undergoes cage contraction in acetone giving **4**. Irradiation of **1a** with $[Cp^*Ru(C_{10}H_8)]^+$ affords the isomeric 12-vertex *closo*-ruthenacarboranes $1\text{-}Cp^*\text{-}1,2,3,5\text{-}RuC_3B_8H_{11}$ and $1\text{-}Cp^*\text{-}1,2,4,10\text{-}RuC_3B_8H_{11}$ (2.2:1 ratio; 56%). Reaction of the amino-substituted tricarbollide anion $[7\text{-}t\text{BuNH-}7,8,9\text{-}C_3B_8H_{10}]^-$ with $[(C_5R_5)Ru(C_{10}H_8)]^+$ (R = H, Me) selectively gives 12-vertex *closo*-ruthenacarboranes $1\text{-}(C_5R_5)\text{-}12\text{-}t\text{BuNH-}1,2,4,12\text{-}RuC_3B_8H_{10}$ (ca. 50%). The structures of **2** and **4** were confirmed by X-ray diffraction.

Keywords: Boron; Metallacarborane; Ruthenium; Tricarbollide; Polyhedral rearrangement.

In 1995 Štíbr, Teixidor et al.[1] have reported the preparation of the tricarbollide anions $[7\text{-}R\text{-}7,8,9\text{-}C_3B_8H_{10}]^-$ (R = H (**1a**), *t*BuNH (**1b**)). Due to the presence of the pentagonal open face and single negative charge, these species are analogous to Cp^- in coordinating ability towards transition metals[2]. A number of tricarbollide complexes were synthesized by reaction of anions **1a** and **1b** with metal halides or carbonyl halide complexes[3]. Unfortu-

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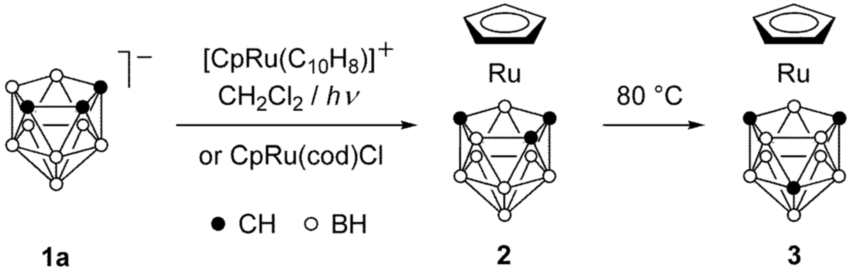
nately, this approach usually requires heating at high temperatures (>100 °C) which results in moderate yields of the products.

Iron and cobalt tricarbollide complexes have been prepared in high yields by visible light irradiation of anions **1a** and **1b** with $[CpFe(C_6H_6)]^+$, $[(C_6H_7)Fe(C_6H_6)]^+$ and $[(C_4Me_4)Co(C_6H_6)]^+$ (ref.[4]). Herein we describe the synthesis of ruthenium tricarbollides by analogous photochemical reactions of **1a** and **1b** with the naphthalene complexes $[(C_5R_5)Ru(C_{10}H_8)]^+$ (R = H, Me)[5].

RESULTS AND DISCUSSION

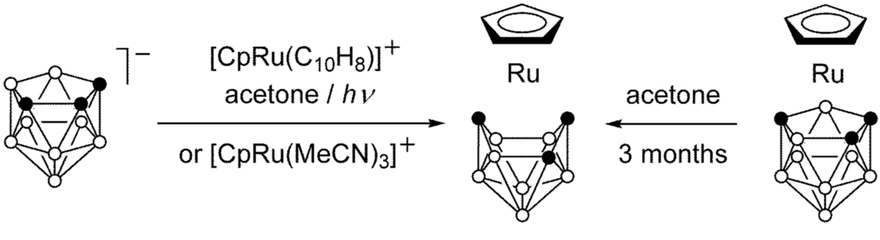
It was shown recently that the ruthenium complex $[CpRu(C_{10}H_8)]^+$ undergoes naphthalene replacement under both thermal and photochemical conditions[6]. We found that visible light irradiation of the tricarbollide anion **1a** with $[CpRu(C_{10}H_8)]^+$ in CH_2Cl_2 affords the 12-vertex *closo*-ruthenacarborane 1-Cp-1,2,3,5-$RuC_3B_8H_{11}$ (**2**) in 87% yield (Scheme 1). Compound **2** was also prepared by reaction of **1a** with CpRu(cod)Cl (97% yield; cod = 1,5-cyclooctadiene). Notably, the metal complexation is accompanied by room-temperature polyhedral rearrangement. Upon heating in toluene at 80 °C, compound **2** undergoes further rearrangement giving 1-Cp-1,2,4,10-$RuC_3B_8H_{11}$ (**3**) in 63% yield (50% conversion in 4 h, 100% in 12 h). The same isomerization sequence has been previously observed for CpFe, (C_4Me_4)Co and Cp*Ru tricarbollides[4b,4c]. Noteworthy, the first rearrangement step proceeds at room temperature only in the case of ruthenium.



SCHEME 1

Irradiation of **1a** with $[CpRu(C_{10}H_8)]^+$ in acetone unexpectedly gives 11-vertex *closo*-1-Cp-1,2,3,4-$RuC_3B_7H_{10}$ (**4**) (32%; Scheme 2). Compound **4** was also obtained in 59% yield by reaction of **1a** with $[CpRu(MeCN)_3]^+$. Interestingly, **4** is slowly formed via cage contraction of **2** in acetone at room temperature (50% conversion in 18 days, 100% in 3 months)[7].

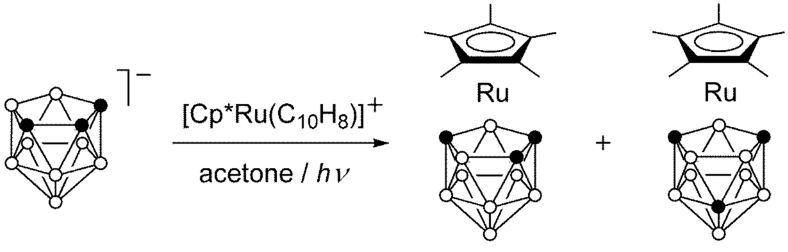
Similar contraction has been observed previously for the iron complexes 1-Cp-1,2,3,5-$FeC_3B_8H_{11}$ [4b] and 1-Cp-4-*t*BuNH-1,2,4-$FeSCB_9H_9$ [8].



1a **4** **2**

SCHEME 2

On the contrary, the irradiation of anion **1a** with the pentamethylated cyclopentadienyl complex $[Cp^*Ru(C_{10}H_8)]^+$ in acetone affords only the 12-vertex ruthenacarborane isomers 1-Cp*-1,2,3,5-$RuC_3B_8H_{11}$ (**5**) and 1-Cp*-1,2,4,10-$RuC_3B_8H_{11}$ (**6**) in 2.2:1 ratio and 56% total yield (Scheme 3). Presumably, higher donor ability and steric hindrance of the Cp* ligand prevents the cage contraction.

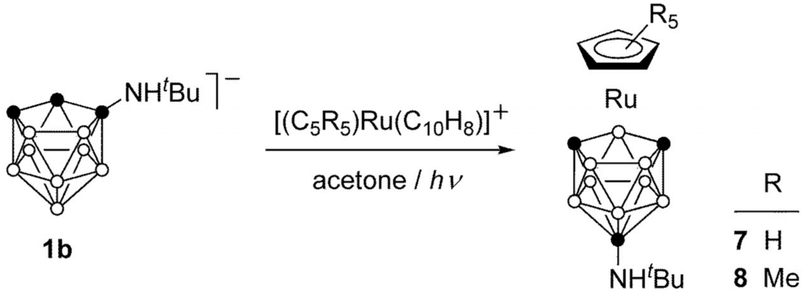


1a **5** **6**

SCHEME 3

Visible light irradiation of the amino-substituted tricarbollide anion $[7\text{-}t\text{BuNH-}7,8,9\text{-}C_3B_8H_{10}]^-$ (**1b**) with $[(C_5R_5)Ru(C_{10}H_8)]^+$ (R = H, Me) in acetone gives the 12-vertex *closo*-ruthenacarboranes 1-(C_5R_5)-12-*t*BuNH-1,2,4,12-$RuC_3B_8H_{10}$ (R = H (**7**), Me (**8**)) in ca. 50% yield (Scheme 4). This reaction is accompanied by room-temperature polyhedral rearrangement which is typical for complexation of anion **1b** [2].

Recently, we have shown that the phosphacarborane anions $[7,8,9\text{-}PC_2B_8H_{10}]^-$ and $[7,8,9\text{-}P_2CB_8H_9]^-$ react with $[CpFe(C_6H_6)]^+$ and $[(C_4Me_4)\text{-}Co(C_6H_6)]^+$ giving the corresponding iron and cobalt complexes[9]. Unfortunately, the reactions of these anions with $[(C_5R_5)Ru(C_{10}H_8)]^+$ (R = H, Me) do not give any isolable ruthenacarboranes. Presumably, strong coordination of ruthenium with the lone electron pair of the phosphorous atom prohibits the formation of desired products[9a,10].



SCHEME 4

New compounds **2**, **3**, **4** and **7** were characterized by ^{1}H and ^{11}B NMR spectroscopy and elemental analysis. The DFT-calculated ^{11}B NMR spectra for **2**, **3**, **4** and **7** show good correlation with the experimental data (mean deviation in chemical shifts is 1.6 ppm). Structures of **2** and **4** were determined by X-ray diffraction (Figs 1 and 2). The C_3B_2 face of the carborane

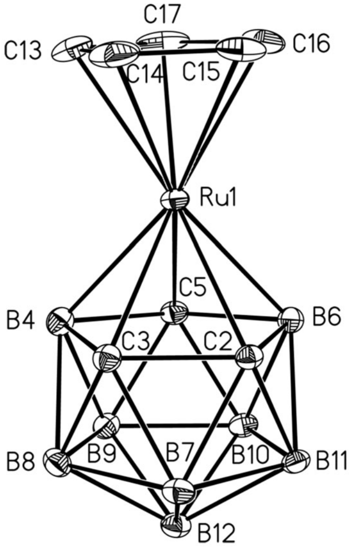


FIG. 1
Structure of **2**. Atoms are represented by 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected distances (in Å): Ru1–C2 2.1731(19), Ru1–C3 2.1630(19), Ru1–B4 2.178(2), Ru1–C5 2.2086(18), Ru1–B6 2.193(2), Ru1–C13 2.173(2), Ru1–C14 2.176(2), Ru1–C15 2.185(2), Ru1–C16 2.181(2), Ru1–C17 2.169(2), C2–C3 1.630(3)

ligand in **2** is folded by 9.0° along the B4···B6 line, which is close to 8.2° folding for the iron congener[4b] 1-Cp-1,2,3,5-$FeC_3B_8H_{11}$. The structure of **4** is generally similar to that of the substituted analogue[11] 1-Cp*-2-Ph-*closo*-1,2,3,4-$RuC_3B_7H_9$. The metal-to-ring distances Ru···Cp in **2** (1.813 Å) and **4** (1.817 Å) are close to that in ruthenocene (1.822 Å)[12].

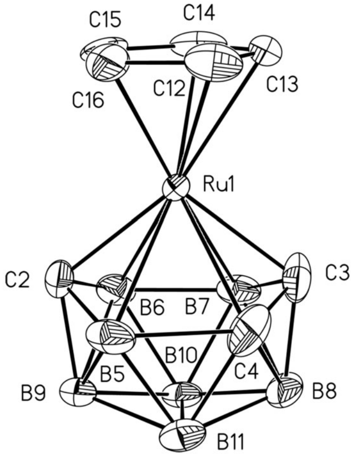


FIG. 2
Structure of **4**. Atoms are represented by 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected distances (in Å): Ru1–C2 2.058(4), Ru1–C3 2.091(5), Ru1–C4 2.289(5), Ru1–B5 2.342(5), Ru1–B6 2.366(5), Ru1–B7 2.358(5), Ru1–C12 2.165(5), Ru1–C13 2.204(5), Ru1–C14 2.192(5), Ru1–C15 2.159(4), Ru1–C16 2.135(5), C3–C4 1.505(7)

CONCLUSION

It was shown that 12-vertex *closo*-ruthenatricarbollides can be synthesized by reactions of tricarbollide anions with the naphthalene complexes $[(C_5R_5)Ru(C_{10}H_8)]^+$ under visible light irradiation. The complexation is accompanied by room-temperature polyhedral rearrangements. Ruthenium complexation of anion **1a** in polar solvents gives 11-vertex species **4** as a result of cage contraction.

EXPERIMENTAL

All reactions were carried out under argon in anhydrous solvents which were purified and dried according to the standard procedures. The isolation and purification of products was conducted in air. The starting materials CpRu(cod)Cl[13], $[CpRu(C_{10}H_8)]BF_4$[14], $[Cp*Ru(C_{10}H_8)]PF_6$[15], $[CpRu(MeCN)_3]BF_4$[14a], Cs[7,8,9-$C_3B_8H_{11}$] and $[NBu_4]$[7-*t*BuNH-7,8,9-$C_3B_8H_{10}$][1f]

were prepared according to the literature procedures. Visible light irradiation was performed by a high pressure mercury vapour lamp with a phosphor coated bulb DRL-400W (similar to Philips HPL-N 400W). The ^{1}H and ^{11}B{^{1}H} NMR spectra were recorded from $CDCl_3$ solution with a Bruker Avance-400 instrument. Chemical shifts are given in ppm (δ-scale) relative to internal $SiMe_4$ (^{1}H) or external $BF_3 \cdot OEt_2$ (^{11}B).

1-Cp-1,2,3,5-$RuC_3B_8H_{11}$ (**2**)

Method A: A suspension of [CpRu($C_{10}H_8$)]BF_4 (114 mg, 0.3 mmol) and Cs[7,8,9-$C_3B_8H_{11}$] (80 mg, 0.3 mmol) in CH_2Cl_2 (10 ml) was stirred for 2 h and then irradiated at room temperature for 20 h. The resulting mixture was evaporated, the residue was extracted with CH_2Cl_2–petroleum ether mixture (1:2) and filtered through a short layer (5 cm) of Al_2O_3. The solution was evaporated to give yellow crystals of **2** (78 mg; 87%).

Method B: A mixture of CpRu(cod)Cl (31 mg, 0.1 mmol) and Cs[7,8,9-$C_3B_8H_{11}$] (26 mg, 0.1 mmol) in CH_2Cl_2 (4 ml) was stirred at room temperature overnight and then evaporated. The residue was extracted with CH_2Cl_2–petroleum ether mixture (1:2) and filtered through a short layer (5 cm) of Al_2O_3. Yellow solution was evaporated and the resulting solid was washed with hexane (2 ml) to give **2** (29 mg; 97%).

^{1}H NMR: 5.09 (s, 5 H, C_5H_5), 3.54 (broad s, 2 H, CH), 2.78 (broad s, 1 H, CH). ^{11}B{^{1}H} NMR: –8.7 (1 B), –15.3 (2 B), –18.1 (2 B), –21.5 (1 B), –25.2 (2 B). Calculated ^{11}B NMR: –8.3 (1 B), –15.4 (2 B), –18.7 (2 B), –23.7 (1 B), –25.2 (2 B). For $C_8H_{16}B_8Ru$ (299.77) calculated: 32.05% C, 5.38% H, 28.85% B; found: 32.22% C, 5.47% H, 28.70% B.

1-Cp-1,2,4,10-$RuC_3B_8H_{11}$ (**3**)

A solution of **2** (24 mg, 0.08 mmol) in toluene (3 ml) was at 80 °C for 12 h. The resulting mixture was evaporated, the residue was extracted with CH_2Cl_2–petroleum ether mixture (1:4) and filtered through a short layer (5 cm) of Al_2O_3. The filtrate was evaporated to dryness and recrystallized from pentane at –78 °C to give yellow crystals of **3** (15 mg; 63%). ^{1}H NMR: 4.71 (s, 5 H, C_5H_5), 2.25 (broad s, 2 H, CH), 1.72 (broad s, 1 H, CH). ^{11}B{^{1}H} NMR: –8.7 (1 B), –9.1 (1 B), –10.4 (2 B), –19.8 (2 B), –25.0 (2 B). Calculated ^{11}B NMR: –9.5 (1 B), –9.5 (2 B), –10.4 (1 B), –22.4 (2 B), –25.4 (2 B). For $C_8H_{16}B_8Ru$ (299.77) calculated: 32.05% C, 5.38% H, 28.85% B; found: 32.46% C, 5.12% H, 28.59% B.

1-Cp-1,2,3,4-$RuC_3B_7H_{10}$ (**4**)

Method A: A solution of [CpRu($C_{10}H_8$)]BF_4 (114 mg, 0.3 mmol) and Cs[7,8,9-$C_3B_8H_{11}$] (80 mg, 0.3 mmol) in acetone (10 ml) was irradiated at room temperature for 20 h. The resulting orange mixture was evaporated, the residue was washed with hexane, extracted with CH_2Cl_2–petroleum ether mixture (2:1) and eluted through a short layer (5 cm) of Al_2O_3. Yellow band was collected and evaporated to give yellow-orange crystals of **4** (28 mg; 32%).

Method B: A solution of [CpRu(MeCN)$_3$]BF_4 (113 mg, 0.3 mmol) and Cs[7,8,9-$C_3B_8H_{11}$] (80 mg, 0.3 mmol) in THF (6 ml) was stirred overnight. The resulting orange mixture was evaporated, the residue was extracted with CH_2Cl_2–petroleum ether mixture (2:1) and eluted through a short layer (5 cm) of Al_2O_3. Yellow band was collected, evaporated to dryness and washed with hexane to give orange powder of **4** (53 mg; 59%).

^{1}H NMR: 5.90 (broad s, 1 H, CH), 5.20 (broad s, 1 H, CH), 5.06 (s, 5 H, C_5H_5), 1.94 (broad s, 1 H, CH). ^{11}B{^{1}H} NMR: 6.6 (1 B), –1.8 (1 B), –9.7 (2 B), –28.7 (1 B), –29.7 (2 B). Calculated

^{11}B NMR: 7.3 (1 B), –5.7 (1 B), –6.0 (1 B), –6.4 (1 B), –29.0 (1 B), –29.4 (1 B), –31.9 (1 B). For $C_8H_{15}B_7Ru$ (287.95) calculated: 33.37% C, 5.25% H, 26.28% B; found: 33.10% C, 5.36% H, 26.48% B.

1-Cp*-1,2,3,5-$RuC_3B_8H_{11}$ (**5**) and 1-Cp*-1,2,4,10-$RuC_3B_8H_{11}$ (**6**)

A solution of [Cp*Ru($C_{10}H_8$)]PF_6 (51 mg, 0.1 mmol) and Cs[7,8,9-$C_3B_8H_{11}$] (27 mg, 0.1 mmol) in acetone (5 ml) was irradiated at room temperature for 36 h. The resulting solution was evaporated, the brown residue was dissolved in CH_2Cl_2–petroleum ether mixture (1:1) and eluted through a short layer (5 cm) of Al_2O_3. The filtrate was evaporated to dryness and washed with a small amount of cold hexane to give a mixture of **5** and **6** in 2.2:1 ratio (20 mg; 56% total yield). The compounds were identified by their ^1H and ^{11}B NMR spectra[4b].

1-Cp-12-*t*BuNH-1,2,4,12-$RuC_3B_8H_{10}$ (**7**) and 1-Cp*-12-*t*BuNH-1,2,4,12-$RuC_3B_8H_{10}$ (**8**)

A solution of [CpRu($C_{10}H_8$)]BF_4 (38 mg, 0.1 mmol) and [NBu_4][7-*t*BuNH-7,8,9-$C_3B_8H_{10}$] (45 mg, 0.1 mmol) in acetone (5 ml) was irradiated at room temperature for 18 h. The resulting solution was evaporated, the residue was purified by silica gel column (10 cm) using hexane as an eluent. Pale yellow band was collected and evaporated to dryness to give crystals of **7** (20 mg; 54%). Analogous reaction of [Cp*Ru($C_{10}H_8$)]PF_6 (51 mg, 0.1 mmol) and [NBu_4][7-*t*BuNH-7,8,9-$C_3B_8H_{10}$] (45 mg, 0.1 mmol) gives **8** (24 mg; 55%) which was identified by its ^1H and ^{11}B NMR spectra[4a].

^1H NMR: 4.98 (s, 5 H, C_5H_5), 2.43 (broad s, 2 H, CH), 2.35 (broad s, 1 H, CH), 1.25 (s, 9 H, CH_3). $^{11}B\{^1H\}$ NMR: –10.1 (2 B), –13.7 (1 B), –17.9 (2 B), –20.1 (1 B), –24.4 (2 B). Calculated ^{11}B NMR: –7.3 (1 B), –10.6 (1 B), –17.8 (1 B), –18.1 (1 B), –22.2 (1 B), –23.2 (1 B), –25.0 (1 B), –27.6 (1 B). For $C_{12}H_{25}B_8NRu$ (370.89) calculated: 38.86% C, 6.79% H, 23.32% B; found: 38.95% C, 6.79% H, 22.78% B.

Computational Details

All DFT calculations were carried out using PRIRODA 6 software kindly provided by Dr. D. N. Laikov[16]. The geometries of **2**, **3**, **4** and **7** have been optimized without constraints using generalized gradient approximation (GGA) for the exchange-correlation function by Perdew, Burke and Ernzerhof (PBE)[17]. The 3z basis set (similar to TZP) of contracted Gaussian-type functions of the size (4s1p)/[2s1p] for H, (8s4p1d)/[4s2p1d] for B, C and N, (20s16p11d)/[8s7p5d] for Ru was used. Frequency calculations were performed to confirm the nature of the stationary points. For GIAO calculation of ^{11}B NMR shifts *ortho*-carborane was used as a standard instead of more commonly used B_2H_6 [18], because this provides a notable improvement for prediction of NMR spectra of the polyhedral compounds. Particularly, the isotropic shielding tensors were first calculated for *ortho*-carborane and summed with corresponding experimental chemical shifts giving average-weighted conversion value of 98.2 (vs 93.8 calculated from the data for B_2H_6 at the PBE/3z level). From this, the isotropic shielding tensors of **2**, **3**, **4** and **7** were subtracted to give chemical shift values. The visualization of calculation results was performed by ChemCraft (version 1.5) software (www.chemcraftprog.com).

X-ray Diffraction Study of 2 and 4

The crystal of **2** and **4** were grown by slow evaporation of their CH_2Cl_2 solutions. Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART APEX II CCD area detector diffractometer, using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å, ω-scans) at 100 K. Low temperature was maintained with a Cryostream open-flow N_2 gas cryostat (Oxford Cryosystems). Reflection intensities were integrated using SAINT software[19a,19b] and absorption correction was applied semi-empirically using SADABS program[19c]. The structures were solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. All carborane

TABLE I
Crystallographic data for **2** and **4**

Parameter	**2**	**4**
Formula	$C_8H_{16}B_8Ru$	$C_8H_{15}B_7Ru$
Color, habit	yellow, prism	orange, prism
Crystal size, mm	0.34 × 0.23 × 0.17	0.34 × 0.27 × 0.21
M, g mol^{-1}	299.76	287.94
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	6.5751(6)	8.428(3)
b, Å	10.4641(10)	10.610(3)
c, Å	17.7012(16)	13.010(4)
α, °	90.00	90.00
β, °	90.00	90.00
γ, °	90.00	90.00
V, Å^3	1217.89(19)	1163.3(6)
Z	4	4
D_c, g cm^{-3}	1.635	1.644
F	592	568
Data/restraints/parameters	8141/0/154	7156/0/146
GOF on F^2	1.003	1.009
Final R indices	$R1 = 0.0166$	$R1 = 0.0264$
$I > 2\sigma(I)$	$wR2 = 0.0389$	$wR2 = 0.0575$
R indices	$R1 = 0.0171$	$R1 = 0.0283$
All data	$wR2 = 0.0391$	$wR2 = 0.0588$

hydrogen atoms were located from difference Fourier syntheses, the H_C atoms were placed in geometrically calculated positions. All calculations were performed on an IBM PC/AT using the SHELXTL software[19d]. The details of crystal data collection and refinement are listed in Table I. CCDC 742640 (for **2**) and 742641 (for **4**) 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).

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