

CpCo-moderated stereospecific dimerization of $(\text{Me}_3\text{SiC}_2)_2\text{S}$ to give $[\textit{trans}\text{-}\{(\text{Me}_3\text{Si})_2(\text{Me}_3\text{SiC}_2\text{S})_2\text{C}_4\}\text{CoCp}]$: synthesis and structure of $[\textit{trans}\text{-}\{(\text{Me}_3\text{Si})_2[(\text{Co}_2(\text{CO})_6)(\mu\text{-}\eta^2:\eta^2\text{-Me}_3\text{SiC}_2\text{S})]_2\text{C}_4\}\text{CoCp}]$

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Abstract

The cyclobutadiene complex $[\text{CpCo}\{\eta^4\text{-}\textit{trans}\text{-}(\text{Me}_3\text{Si})_2(\text{Me}_3\text{SiC}_2\text{S})_2\text{C}_4\}]$ (**4**) is formed with a high yield from a $[2 + 2]$ cycloaddition of $(\text{Me}_3\text{SiC}_2)_2\text{S}$ mediated by $[\text{CpCo}(\mu\text{-C}_5\text{H}_4)\text{Co}(\text{C}_2\text{H}_4)\text{Cp}]$ (**1**) or $[\text{CpCo}(\text{C}_2\text{H}_4)_2]$ (**6a**). On reaction with $[\text{Co}_2(\text{CO})_8]$, **4** is transformed into the pentanuclear complex $[\textit{trans}\text{-}\{(\text{Me}_3\text{Si})_2[(\text{Co}_2(\text{CO})_6)(\mu\text{-}\eta^2:\eta^2\text{-Me}_3\text{SiC}_2\text{S})]_2\text{C}_4\}\text{CoCp}]$ (**7**). Complex **7** crystallizes in the triclinic space group $P\bar{1}$ with $a = 13.624(7)$, $b = 17.940(9)$ and $c = 23.091(12)$ Å, $\alpha = 99.19(3)$; $\beta = 91.76(3)$ and $\gamma = 111.18(3)^\circ$ and $Z = 4$. The structure was refined using 18 228 unique diffractometer data to $wR_2 = 0.107$. The molecular structure of **7** consists of a substituted cyclobutadiene, which is η^4 coordinated to a CpCo fragment. The substituents are in the *trans* arrangement. Each of the two alkyne functionalities is coordinated to a $\text{Co}_2(\text{CO})_6$ moiety in the $\mu\text{-}\eta^2:\eta^2$ fashion.

Keywords: Cobalt; Coupling reaction; Alkyne

1. Introduction

Transition-metal-mediated coupling reactions of alkynes are of great synthetic importance. Recently we reported the unusual reactivity of the dicobalt μ -cyclopentadienylidene complexes **1** [1] and **2** [2] with certain alkynes [3]. Some silyl- and/or germyl-substituted alkynes $\text{R}_3\text{ECC}(\text{ER}_3)'$ ($\text{E} = \text{Si}$ or Ge) couple with **1** or **2** to give the novel cobaltapentalene complexes **3**. During this reaction a C–E bond is cleaved and an R_3E group is shifted to a cobalt atom. Within our efforts to broaden the scope of this reaction we also examined the reactivity of **1a** with a number of conjugated and non-conjugated silyl-substituted diynes. However, no reaction was observed up to 50°C with $(\text{Me}_3\text{SiC}_2)_2$, $(\text{Me}_3\text{SiC}_2)_2\text{CH}_2$ and $(\text{Me}_3\text{SiC}_2)_2\text{SiMe}_2$. Complete decomposition of the organometallic substrate took place when the reactions were carried out between 55 and 65°C . Only intractable products were obtained.

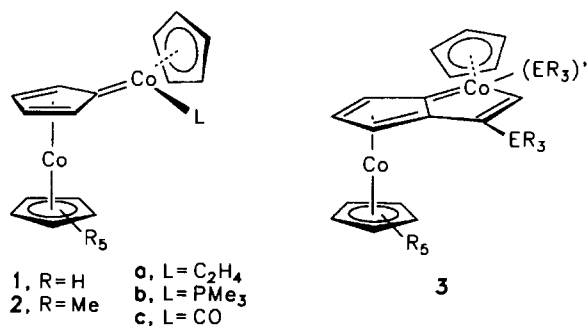
Upon heating of **1a** to 45°C with $(\text{Me}_3\text{SiC}_2)_2\text{S}$ in a $1:2$ molar ratio the mononuclear cyclobutadiene com-

plex **4** was formed with about 50% yield (based on Co). The reaction was essentially quantitative with respect to the alkyne substrate. Obviously, fragmentation of the dinuclear complex took place, accompanied by a CpCo-mediated $[2 + 2]$ cyclodimerization of the alkyne. There are two chemically different CpCo groups in **1**, and both could be involved in the formation of **4**. Therefore the cyclopentadienylidene complex **2a** with both a plane and a pentamethyl-labelled cyclopentadienyl cobalt group was reacted with a fourfold excess of $(\text{Me}_3\text{SiC}_2)_2\text{S}$. A mixture of the two cyclobutadiene complexes **4** and **5** was obtained (total yield, greater than 90% based on the alkyne), clearly indicating participation of both $(\text{C}_5\text{R}_5)\text{Co}$ groups. The fate of the carbene ligand in **1** and **2** is unknown.

Complex **4** was also obtained with a very high yield (greater than 90%) from the reaction of $[\text{CpCo}(\text{C}_2\text{H}_4)_2]$ (**6a**) with two molar equivalents of $(\text{Me}_3\text{SiC}_2)_2\text{S}$. No other organometallic product was formed in substantial amounts in this reaction.

Characterization of **4** and **5** is based on spectroscopic data, and on an X-ray crystal structure determination of the $[\text{Co}_2(\text{CO})_6]_2$ derivative of **4** (vide infra). The NMR spectra [4] of **4** are very simple; there are signals of two

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sets of two isochroneous SiMe₃ groups each in addition to the Cp resonance. Four quaternary carbon resonances were detected in the ¹³C NMR spectrum; those at a high field ($\delta = 76.21$ and 80.29) are attributed to the metal-coordinated cyclobutadiene ring. In the IR spectrum an absorption is observed at 2097 cm^{-1} , corresponding to the carbon–carbon stretch of a non-coordinated triple bond.

Although the spectra clearly indicate the formation of a cyclobutadiene complex, they do not allow a distinction between the *cis* (**4A**) and *trans* (**4B**) isomers. On steric grounds, structure **4B** appears more reasonable. However, several complexes with *cis*-bis(trimethylsilyl)

substituted cyclobutadienes are known [5,6]. Therefore the alternative structure **4A** cannot be ruled out a priori.

Complex **4** was always obtained as a red oil and did not show any tendency to crystallize. In order to obtain a solid derivative, **4** was treated with [Co₂(CO)₈] at room temperature. The red–brown pentanuclear complex **7** was obtained with a 71% yield after recrystallization. The ¹H NMR spectrum of **7** is only marginally different from that of **4**. Four bands are observed in the $\nu(\text{CO})$ region of the IR spectrum, typical of complexes of the type [Co₂(CO)₆(μ -alkyne)] [7]. This and the absence of an IR absorption in the $\nu(\text{C}\equiv\text{C})$ region indicate that both of the free carbon–carbon triple bonds of **4** are now bound each to a Co₂(CO)₆ moiety.

An X-ray crystal structure analysis was carried out on a single crystal of **7** which was obtained from a *n*-hexane solution at -20°C . The complex crystallizes with two independent molecules in the asymmetric unit. Crystal details are given in Section 2. Important bond lengths and angles are given in Tables 1 and 2.

The structure of one molecule is shown in Fig. 1. As can be seen from a superposition (Fig. 2), the two crystallographically independent molecules show only small differences, mainly concerning some of the bond and torsion angles. Evidently, the central cyclobutadiene is *trans* substituted. The C₄ rings have the form of a

Table 1

Selected bond lengths for **7** with estimated standard deviations in parentheses; equivalent bond lengths are given on the same line

Molecule 1		Molecule 2	
Atoms	Bond length (Å)	Atoms	Bond length (Å)
Co(1)–C(1)	1.995(4)	Co(6)–C(38)	1.988(4)
Co(1)–C(2)	1.967(3)	Co(6)–C(39)	1.970(4)
Co(1)–C(3)	1.988(4)	Co(6)–C(40)	1.978(4)
Co(1)–C(4)	1.964(4)	Co(6)–C(41)	1.970(4)
C(1)–C(2)	1.474(5)	C(38)–C(39)	1.469(5)
C(1)–C(4)	1.475(5)	C(38)–C(41)	1.477(5)
C(2)–C(3)	1.456(5)	C(39)–C(40)	1.471(5)
C(3)–C(4)	1.471(5)	C(40)–C(41)	1.472(5)
Si(1)–C(1)	1.865(4)	Si(5)–C(38)	1.869(4)
Si(2)–C(3)	1.872(4)	Si(6)–C(40)	1.885(4)
S(1)–C(2)	1.768(4)	S(3)–C(39)	1.755(4)
S(1)–C(16)	1.758(4)	S(3)–C(53)	1.755(4)
S(2)–C(4)	1.759(4)	S(4)–C(41)	1.750(4)
S(2)–C(27)	1.744(4)	S(4)–C(64)	1.744(4)
Si(3)–C(17)	1.847(4)	Si(7)–C(54)	1.850(5)
Si(4)–C(28)	1.844(4)	Si(8)–C(65)	1.854(4)
Co(2)–C(16)	1.962(4)	Co(7)–C(53)	1.964(4)
Co(2)–C(17)	1.977(4)	Co(7)–C(54)	1.970(4)
Co(2)–Co(3)	2.476(2)	Co(7)–Co(8)	2.4725(13)
Co(3)–C(16)	1.971(4)	Co(8)–C(53)	1.958(4)
Co(3)–C(17)	1.972(4)	Co(8)–C(54)	1.979(4)
C(16)–C(17)	1.359(5)	C(53)–C(54)	1.351(5)
Co(4)–C(27)	1.934(4)	Co(9)–C(64)	1.942(5)
Co(4)–C(28)	1.998(4)	Co(9)–C(65)	1.989(5)
Co(4)–Co(5)	2.460(2)	Co(9)–Co(10)	2.4669(14)
Co(5)–C(27)	2.018(4)	Co(10)–C(64)	2.003(4)
Co(5)–C(28)	1.967(4)	Co(10)–C(65)	1.976(4)
C(27)–C(28)	1.353(5)	C(64)–C(65)	1.345(5)

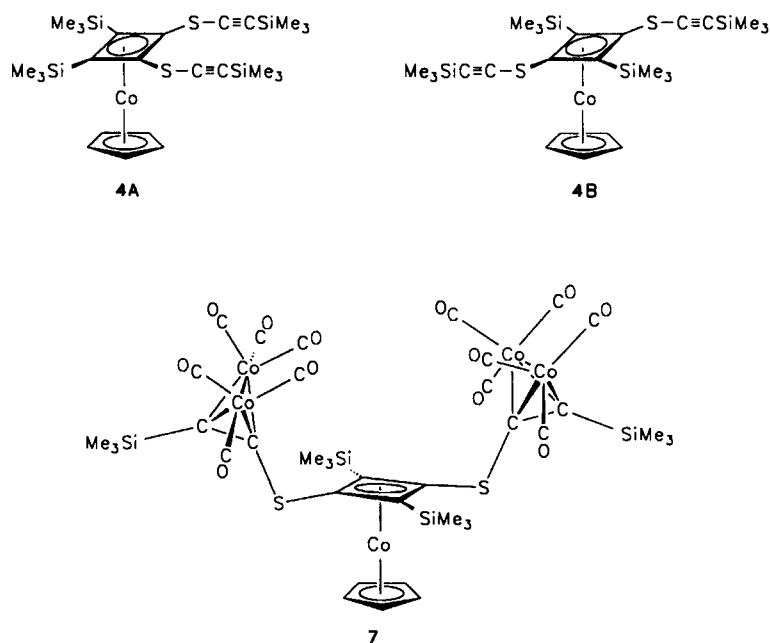
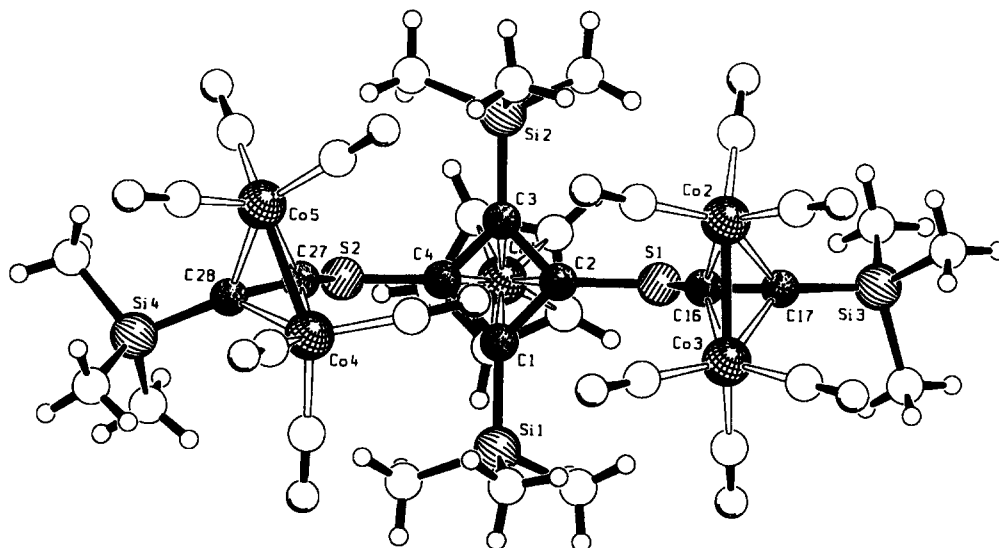


Table 2

Selected bond angles for 7 with estimated standard deviations in parentheses; equivalent bond angles are given on the same line

Molecule 1		Molecule 2	
Atoms	Bond angle (°)	Atoms	Bond angle (°)
C(2)–C(1)–C(4)	86.1(3)	C(39)–C(38)–C(41)	86.9(3)
C(3)–C(2)–C(1)	93.8(3)	C(38)–C(39)–C(40)	93.2(3)
C(2)–C(3)–C(4)	87.0(3)	C(39)–C(40)–C(41)	87.0(3)
C(3)–C(4)–C(1)	93.1(3)	C(40)–C(41)–C(38)	92.9(3)
C(2)–S(1)–C(16)	110.6(2)	C(39)–S(3)–C(53)	110.5(2)
C(4)–S(2)–C(27)	108.2(2)	C(41)–S(4)–C(64)	108.0(2)
S(1)–C(16)–C(17)	127.1(3)	S(3)–C(53)–C(54)	125.6(3)
S(2)–C(27)–C(28)	132.0(3)	S(4)–C(64)–C(65)	130.8(3)
Si(3)–C(17)–C(16)	146.1(3)	Si(7)–C(54)–C(53)	141.7(3)
Si(4)–C(28)–C(27)	146.0(3)	Si(8)–C(65)–C(64)	144.3(4)

Fig. 1. Molecular structure of 7. Only one of the two crystallographically independent molecules and only one of the two disordered C₃H₅ rings is shown.

planar diamond which has the more acute endocyclic bond angles at the silyl-substituted carbon atoms (averages of both molecules, $86.8(4)^\circ$ vs. $93.3(3)^\circ$). Within experimental error, the endocyclic carbon–carbon bond lengths are equal (average of both molecules, $1.471(6)$ Å). Both C–C and Co–C bond lengths in the CpCoC₄ units compare well with the values reported in the literature for related mononuclear cyclobutadiene complexes [8]. Of the substituents on the cyclobutadiene rings, the sulphur atoms are displaced by 0.16 – 0.22 Å from the ring plane towards the Co atom (Co(1) and Co(6) respectively). The silyl substituents lie more or less in the ring plane (deviations, between -0.03 and $+0.05$ Å).

The alkynyl groups are coordinated to Co₂(CO)₆ moieties via the carbon–carbon triple bonds. The coordination geometry within these units corresponds to the well-known dimetallatetrahedrane structure, with carbon–carbon (average of both molecules, $1.352(5)$ Å), cobalt–carbon (average, $1.969(7)$ Å) and cobalt–cobalt distances (average, $2.469(6)$ Å) well within the range reported for the numerous examples with this type of transversal coordination of an alkyne to a Co₂ unit [9].

Vollhardt and coworkers [5,6,10] have previously studied the coupling reactions of several trimethylsilyl substituted diynes using [CpCo(CO)₂] (**6b**) as a 'catalyst'. These reactions are very complicated indeed, and as many as 18 characterizable organometallic products were obtained for example with the 1,5-diyne (Me₃SiC₂)₂(CH₂)₂ [5]. The main reaction types of the alkyne functionalities are coupling with a carbon monoxide to give a cyclopentadienone ligand, [2 + 2] cycloaddition to give a CpCo-coordinated cyclobutadiene, carbon–carbon triple bond scission accompanied by (CpCo)₃ cluster formation and cyclotrimerization to

give the free substituted benzene derivatives. Discrimination between intramolecular and intermolecular cycloadditions was found to be based on steric factors.

The alkynes RCCR give a different range of products when treated with the more reactive [CpCo(C₂H₄)₂] (**6a**). For example, cyclotrimerization to give η⁶-coordinated arenes takes place with **6a** for R = Me [11] or C(O)OMe [12]. A dinuclear unsaturated complex [(CpCo)₂(μ-η²:η²-alkyne)] is formed with R = SiMe₃ [12,13]. In some cases (e.g. R = CF₃ or Ph), one of the ethylene ligands may take part in the cyclization reaction and the complexes [CpCo(η⁴-(CR)₄(CH₂)₂)] with 1,3-cyclohexadiene ligands are formed [12]. Normally, alkyne dimerization to give cyclobutadienes is not observed.

In the light of these results, it is not surprising that only intermolecular coupling of (Me₃SiC₂)₂S is observed with **1**, **2** and **6a**. We are, however, puzzled by the high selectivity of our reactions as far as both the exclusive formation of a single product and the stereospecificity are concerned. The reason for this unusual behaviour is unknown at present.

2. Experimental section

2.1. General procedures

All operations were carried out under an atmosphere of purified nitrogen (BASF R3-11 catalyst) using Schlenk techniques. Solvents were dried by conventional methods. The compounds [CpCo(C₂H₄)₂] (**6a**) [11], [CpCo(μ-C₅H₄)Co(η-L)Cp] (L = C₂H₄ (**1a**), CO (**1b**) or PMe₃ (**1c**)) [1] and [Cp*Co(μ-C₅H₄)Co(η-C₂H₄)Cp] (**2**) [2] were prepared as described in the

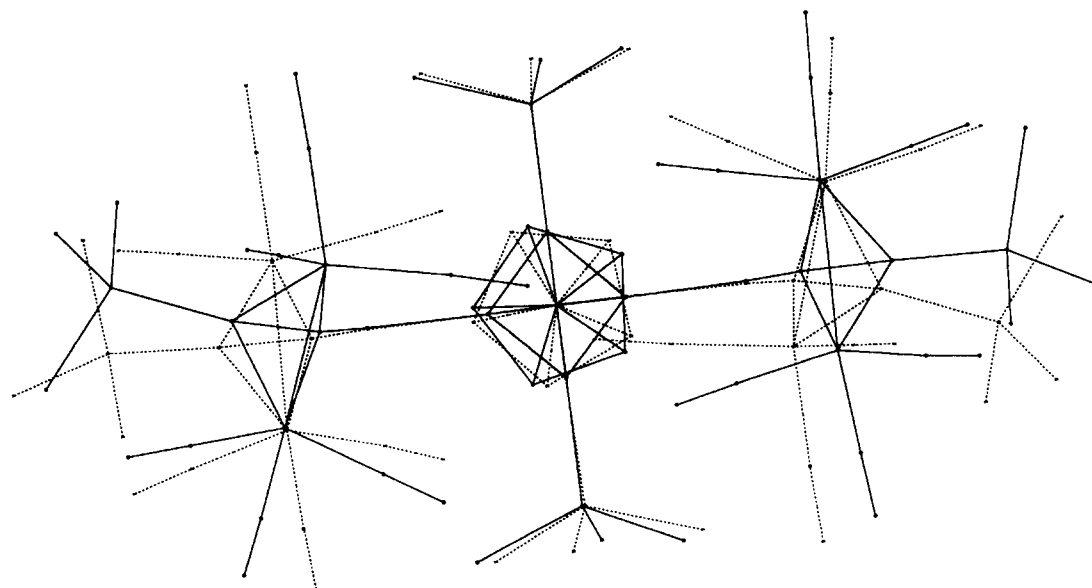


Fig. 2. Superposition of the two crystallographically independent molecules of **7**.

literature. NMR spectra were obtained on a Bruker AC 200 instrument (200.1 MHz for ^1H ; 50.3 MHz for ^{13}C). Mass spectra were measured in the electron impact ionization mode at 70 eV on a Finnigan MAT 8230.

2.2. $[\text{CpCo}\{\eta^4\text{-trans}-(\text{Me}_3\text{Si})_2(\text{Me}_3\text{SiC}_2\text{S})_2\text{C}_4\}]$ (4)

A mixture of 350 mg (1.03 mmol) of **1a** and 500 mg (2.20 mmol) of $(\text{Me}_3\text{SiC}_2)_2\text{S}$ in 50 ml of toluene is heated to 45°C for 5 h under slightly reduced pressure. After reduction of the volume under reduced pressure the mixture is chromatographed on silica (3 · 25 cm). With toluene as a mobile phase a single red fraction is obtained to give 600 mg (47%) of **4** as a deep-red oil after removal of solvent.

Using the above procedure, 536 mg (93%) of **4** are obtained from 180 mg (1.0 mmol) of **6a** and 455 mg (2.0 mmol) of $(\text{Me}_3\text{SiC}_2)_2\text{S}$ (4 h; 35°C). IR (in *n*-hexane): $\nu(\text{CC})$ 2097 cm^{-1} . Mass spectroscopy (MS); m/z 576 (92%, M^+), 350 (9, $[\text{CpCoC}_4\text{S}(\text{SiMe}_3)_2]^+$), 73 (100, $[\text{SiMe}_3]^+$).

2.3. $[\text{trans}\{-\{(\text{Me}_3\text{Si})_2[(\text{Co}_2(\text{CO})_6)(\mu\text{-}\eta^2 : \eta^2\text{-Me}_3\text{SiC}_2\text{S})_2\text{C}_4\}]\text{CoCp}\}]$ (7)

1.3 g (3.8 mmol) $[\text{Co}_2(\text{CO})_8]$ is added in small portions to a stirred solution of **4** (1.1 g, 1.9 mmol) in

80 ml of *n*-hexane. The solution is stirred for another 0.5 h after the evolution of gas has ceased. The volume of the mixture is then reduced to about 30 ml. After cooling to -20°C a batch of red-brown product is obtained, which is still contaminated with $[\text{Co}_2(\text{CO})_8]$. Recrystallization at -20°C from pentane gives pure crystalline **7** (1.1 g, 71%). The compound does not melt up to 260°C . ^1H NMR (C_6D_6); δ 0.32 (s, 18H, SiMe_3), 0.56 (s, 18H, SiMe_3), 4.69 (s, 5H, Cp). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , assignments by DEPT experiments): δ 0.09 (SiMe_3), 1.65 (SiMe_3), 82.98 (Cp), 86.05 (C), 89.92 (C); owing to the low solubility other quaternary carbon atoms were not observed. $^{29}\text{Si}\{^1\text{H}\}$ NMR: δ -6.69, -15.51. IR (*n*-pentane); $\nu(\text{CO})$ 2092 (m), 2055 (s), 2025 (s), 2018 (m) cm^{-1} .

2.4. X-ray crystal structure determination of $[\text{trans}\{-\{(\text{Me}_3\text{Si})_2[(\text{Co}_2(\text{CO})_6)(\mu\text{-}\eta^2 : \eta^2\text{-Me}_3\text{SiC}_2\text{S})_2\text{C}_4\}]\text{CoCp}\}]$ (7)

Crystals were mounted in Lindemann capillary tubes and transferred to a STOE Siemens four-circle diffractometer. Intensity data were collected at ambient temperature and corrected for Lorentz, polarization and absorption effects (Table 3). The structures were solved by the heavy-atom method and refined on F^2 with the full-matrix least-squares method using all measured

Table 3
Details of the crystal structure determination of **7**

Molecular formula	$\text{C}_{37}\text{H}_{41}\text{Co}_5\text{O}_{12}\text{S}_2\text{Si}_4$
Crystal size (mm)	$0.7 \times 0.3 \times 0.3$
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	13.624(7)
b (Å)	17.940(9)
c (Å)	23.091(12)
α (°)	99.19(3)
β (°)	91.76(3)
γ (°)	111.18(3)
V (Å ³)	5171(5)
Z	4
M_r	1148.83
d_c (g cm^{-3})	1.476
F_{000}	2328.0
μ (Mo $\text{K}\alpha$) (mm ⁻¹)	1.79
X-radiation; λ (Å)	Mo $\text{K}\alpha$, graphite monochromated; 0.71069
Data collection temperature	Ambient
2θ range (°)	3–50
hkl range	-16/16, -21/21, 0/27
Number of reflections, measured	18232
Number of reflections, unique	18232
Number of reflections, observed ($I \leq 2\sigma(I)$)	12744
Absorption correction	Empirical
Number of parameters refined	1167
R values R (observed reflections only)	0.041
wR_2 (all reflections)	0.107
$w = 1/[\sigma^2(F) + (AP)^2 + BP]$	
A ; B	0.0455; 2.73
P	$(\max(F_o^2, 0) + 2F_c^2)/3$
Goodness of fit	1.016

unique reflections [14]. All non-hydrogen atoms were given anisotropic displacement parameters.

All hydrogen atoms were input in calculated positions. Apparent disorder of the cyclopentadienyl rings in both molecules was accounted for by refinement of sets of two rigid regular pentagons (refined site occupation factors were 0.66/0.34 and 0.49/0.51 respectively).

The calculations were performed using the programs SHELXS-86 and SHELXL-93 [15]. Graphical representations were drawn with the SCHAKAL-92 program [16].

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