Unusual Orthometallation of a Tetraphenylcyclopentadienone Ligand†

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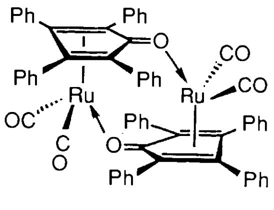
Controlled pyrolysis of the reaction between [Ru$_3$(CO)$_{12}$] and tetracyclone (tetraphenylcyclopentadienone) in refluxing heptane gives a new complex with the empirical formula [Ru$_3$(CO)$_5$(C$_4$Ph$_4$CO)$_2$] in moderate yield. The compound has been characterised by a single-crystal X-ray diffraction study [monoclinic, space group $P2_1/c$, $a = 12.130(8)$, $b = 20.972(9)$, $c = 20.861(12)$ Å, $\beta = 98.80(5)°$ and $Z = 4$], which reveals that the structure contains a diruthenium pentacarbonyl unit [Ru(1)–Ru(2) 2.810(2) Å], bridged by a tetracyclone ligand bonded in the planar 'hydroxycyclopentadienyl' mode. One of the phenyl groups of this ligand is cyclometallated in the *ortho* position, forming a Ru–C σ bond to Ru(1) [2.138(8) Å]. The same phenyl group is bonded in an η^6 manner to a third ruthenium atom, which in turn is ligated by the second tetracyclone (again bound as a planar η^5 ligand), forming a sandwich-type fragment. The hydrogen atom released by the metallation of C(30) is intramolecularly hydrogen bonded between the oxygen atoms of the two tetracyclone ligands [O(6) ··· H ··· O(7) 2.590(7) Å].

As part of our current study of complexes containing cyclopentadienone ligands, we have recently described the synthesis, X-ray crystal structure, and catalytic properties of the tetraphenylcyclopentadienone ruthenium dicarbonyl dimer **1**.[1] This complex is readily prepared in high yield by heating [Ru$_3$(CO)$_{12}$] with 3 equivalents of tetraphenylcyclopentadienone (tetracyclone) in dry heptane, whereupon it precipitates from the boiling solution and can be isolated by filtration. The more soluble mononuclear complex [Ru(CO)$_3$(C$_4$Ph$_4$CO)] **2**,[2,3] which is an intermediate in the formation of **1**, remains in solution. If water, alcohols or other protic compounds are present the related compound **3**, which contains a hydride ligand bridging the two ruthenium atoms and a further H hydrogen bonded between the two tetracyclone rings, is produced instead of **1**.[4,5] The reactivity and catalytic properties of **1** and **3** are similar because in solution both dissociate to the same catalytically active mononuclear fragments.[1]

Here we describe the isolation and structural characterisation of a novel triruthenium complex which is formed by pyrolysis of reaction mixtures leading to **1**, and which contains a cyclometallated cyclopentadienone ligand.



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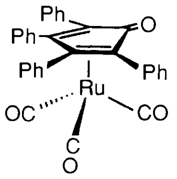

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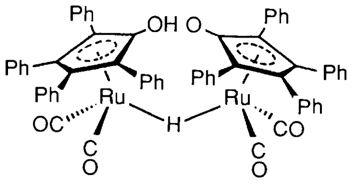

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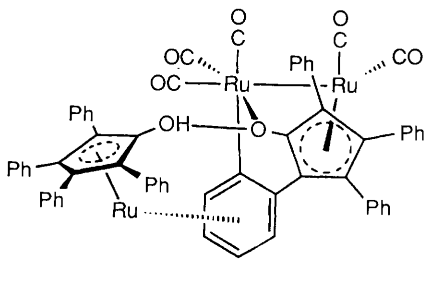

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Results and Discussion

During a recent synthesis of complex **1** the heptane solvent accidentally escaped from the reaction mixture overnight because of a leaking stopper. Instead of producing complete decomposition to Ru metal, however, the result was a brown residue which IR spectroscopy showed to consist mainly of a previously unobserved complex with five carbonyl absorptions (2068s, 2004s, 1980s, 1955m and 1906m cm^{-1} in CH$_2$Cl$_2$) together with a small amount of **1** (2020 and 1970 cm^{-1}). Suspending this material in more heptane and refluxing for 24 h did not produce any further change, and after passage through an alumina column to remove **1**, which is known to decompose on chromatography, the new complex **4** was isolated as an air-stable orange-yellow solid in 59% yield. A small amount of *cis/trans* 2,3,4,5-tetraphenylcyclopent-2-enone[6] was also isolated; this is a known product of the transition-metal-catalysed reduction of tetracyclone.[7]

Although first performed by accident, we find that deliberate slow distillation of the solvent from the reaction followed by pyrolysis of the residue for 20–30 min provides reproducible quantities of complex **4** in 20% yield. Pyrolysis of **1** or of mixtures of **1** and [Ru$_3$(CO)$_{12}$] gave only small amounts of **4**

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

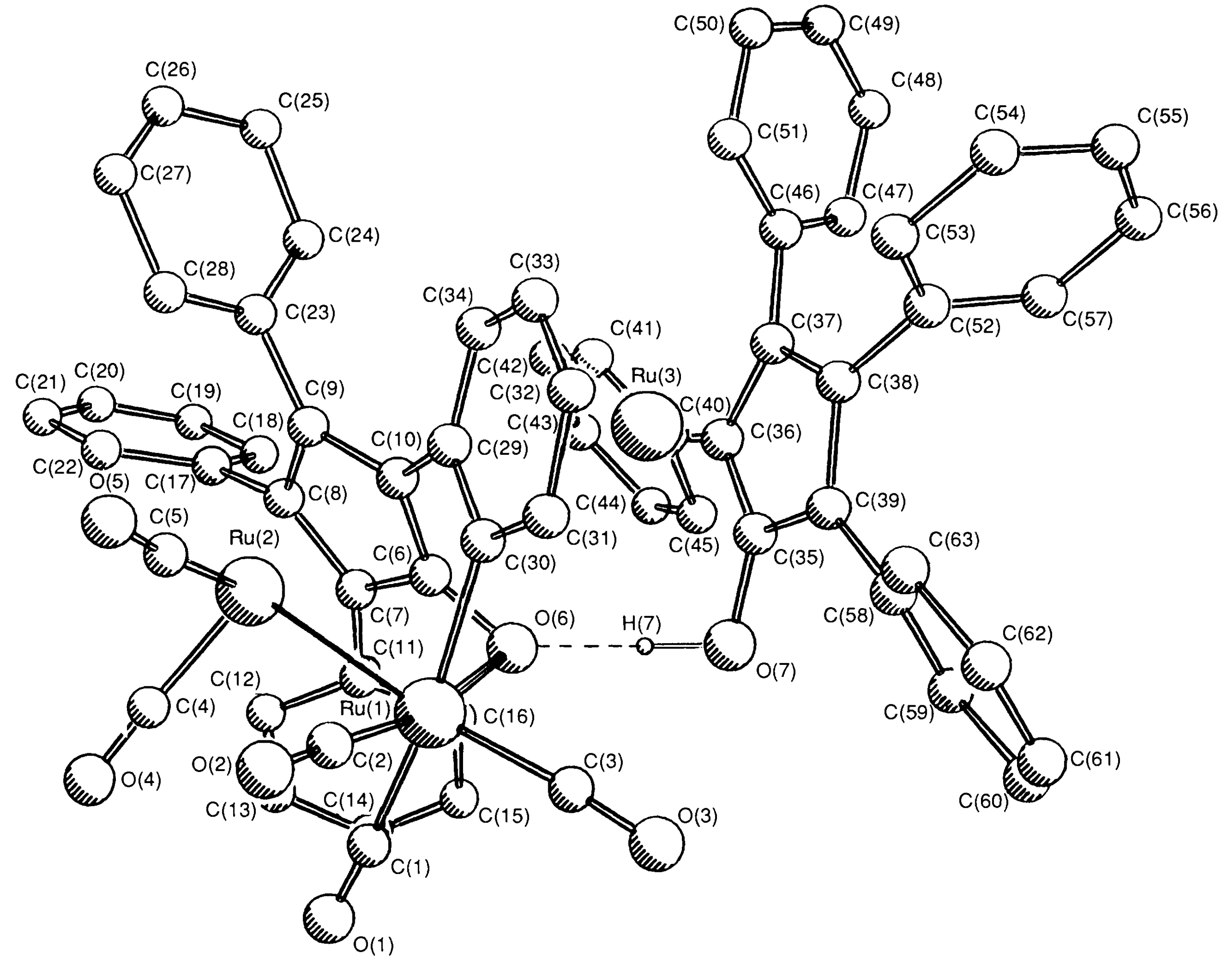

Fig. 1 Molecular structure of complex **4** showing the crystallographic numbering scheme

however. To an extent this synthetic method parallels the improved preparation of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$, in which evaporation of the solvent during the reaction also appears to play an important part.[8]

Elemental analysis of complex **4** was consistent with an empirical formula of $Ru_3(CO)_5(C_4Ph_4CO)_2$, but NMR spectra indicated that this was a deceptively simple view. Apart from aromatic protons, the ^1H NMR spectrum showed two triplets and two doublets, each integrating as one proton, in the region δ 4.7–6.0. The number and upfield shift of these signals indicated that one of the phenyl rings had become metallated, forming a C_6H_4 group which was also co-ordinated to ruthenium in an η^6 manner. In addition an unexpected singlet was observed at δ 11.0. In the ^{13}C NMR spectrum signals were observed for two co-ordinated tetracyclone ligands and again four peaks characteristic of the CH groups of an η^6-bound C_6H_4 unit.

Because these data were not sufficient to deduce the structure of the complex, an X-ray diffraction study was carried out on a suitable single crystal grown by diffusion of pentane into a dichloromethane solution. This revealed the structure depicted in Fig. 1, with the bond lengths and angles collected in Table 1. The molecule consists of a diruthenium unit linked by a metal–metal bond [Ru(1)–Ru(2) 2.810(2) Å]; Ru(2) bears two terminal carbonyl ligands and is also ligated in an η^5 manner by one tetracyclone ligand, the oxygen atom of which is also bonded to Ru(1), the ruthenium atom of a $Ru(CO)_3$ fragment. In contrast to **1** and to other η^4-cyclopentadienone complexes, where the ketonic carbonyl is bent back from the plane of the diene ligand,[3,9] the bridging tetracyclone in **4** is planar [root-mean-square (r.m.s.) deviation of the five-membered ring 0.017 Å; perpendicular distance of Ru(2) from the mean plane 1.899 Å; O(6) lies 0.003 Å out of this plane, away from the metal], rather like that in $[Mo_2(CO)_3(\mu\text{-}C_2Ph_2)(\eta\text{-}C_4Ph_4)(\mu\text{-}C_4Ph_4CO)]$.[10] Moreover, the C(6)–O(6) distance of 1.327(10) Å is significantly longer than in **1** [1.270(7) Å],[1] and, while not as long as the 1.38(2) Å found in the dimolybdenum complex above, it is similar to that observed for the bridging tetracyclone in $[Mo_2(CO)_3(\mu\text{-}PPh_2)(\mu\text{-}C_4Ph_4CO)(\eta^5\text{-}C_4Ph_4COH)]$.[11]

One of the phenyl substituents of the bridging tetracyclone has become metallated in the *ortho* position, and is attached to Ru(1) by a σ bond [Ru(1)–C(30) 2.138(8) Å]. This phenyl group is also bonded in an η^6 manner to Ru(3), as indicated by the NMR spectra, at a perpendicular distance from the mean plane of 1.720 Å. The second tetracyclone ligand is also bonded to Ru(3), again in a planar η^5 manner [r.m.s. deviation of the five-membered ring 0.004 Å; perpendicular distance of Ru(3) from the mean plane 1.832 Å; O(7) is situated 0.041 Å out of this plane away from the metal], thus forming the first example of an areneruthenium cyclopentadienone sandwich complex. The carbonyl bond length of this tetracyclone is even longer than that of the other [C(35)–O(7) 1.378(9) Å]. The oxygen of this carbonyl group, O(7), forms a short intramolecular hydrogen bond with the other ketonic oxygen [O(7) · · · H · · · O(6) 2.590(7) Å], thus explaining the ^1H NMR signal at δ 11.0. Precedent for such an interaction is provided by complex **2**; the O · · · H · · · O distance in the $C_4(C_6H_4Cl\text{-}p)_4CO$ analogue of **2**, which was structurally characterised, was 2.54 Å.[5] Although the hydrogen atom derived from the metallation of C(30) was not located directly in the crystallographic analysis, it is assumed to

Table 1 Selected bond lengths (Å) and angles (°) for complex **4**

Ru(1)–Ru(2)	2.810(2)	Ru(1)–O(6)	2.148(5)
Ru(1)–C(1)	1.969(10)	Ru(1)–C(2)	1.884(9)
Ru(1)–C(3)	1.950(10)	Ru(1)–C(30)	2.138(8)
Ru(2)–C(4)	1.875(9)	Ru(2)–C(5)	1.862(10)
Ru(2)–C(6)	2.278(8)	Ru(2)–C(7)	2.291(8)
Ru(2)–C(8)	2.280(8)	Ru(2)–C(9)	2.261(8)
Ru(2)–C(10)	2.210(8)	Ru(3)–C(29)	2.258(8)
Ru(3)–C(30)	2.301(8)	Ru(3)–C(31)	2.225(7)
Ru(3)–C(32)	2.214(8)	Ru(3)–C(33)	2.201(9)
Ru(3)–C(34)	2.197(9)	Ru(3)–C(35)	2.204(8)
Ru(3)–C(36)	2.206(7)	Ru(3)–C(37)	2.180(7)
Ru(3)–C(38)	2.200(8)	Ru(3)–C(39)	2.222(8)
O(1)–C(1)	1.141(12)	O(2)–C(2)	1.140(11)
O(3)–C(3)	1.124(12)	O(4)–C(4)	1.144(12)
O(5)–C(5)	1.157(13)	O(6)–C(6)	1.327(10)
O(7)–C(35)	1.378(9)	C(6)–C(7)	1.449(11)
C(6)–C(10)	1.436(11)	C(7)–C(8)	1.461(12)
C(7)–C(11)	1.489(11)	C(8)–C(9)	1.439(12)
C(8)–C(17)	1.496(13)	C(9)–C(10)	1.452(12)
C(9)–C(23)	1.497(13)	C(10)–C(29)	1.474(11)
C(29)–C(30)	1.449(11)	C(29)–C(34)	1.428(11)
C(30)–C(31)	1.421(12)	C(31)–C(32)	1.416(12)
C(32)–C(33)	1.405(12)	C(33)–C(34)	1.416(12)
C(35)–C(36)	1.420(11)	C(35)–C(39)	1.432(11)
C(36)–C(37)	1.450(11)	C(36)–C(40)	1.493(11)
C(37)–C(38)	1.441(11)	C(37)–C(46)	1.482(11)
C(38)–C(39)	1.441(11)	C(38)–C(52)	1.496(11)
C(39)–C(58)	1.492(12)	O(6) · · · O(7)	2.590(7)
O(6) · · · H(O7)	1.59		
Ru(2)–Ru(1)–O(6)	78.6(1)	Ru(2)–Ru(1)–C(1)	83.8(3)
O(6)–Ru(1)–C(1)	92.4(3)	Ru(2)–Ru(1)–C(2)	90.3(3)
O(6)–Ru(1)–C(2)	167.5(3)	C(1)–Ru(1)–C(2)	92.0(4)
Ru(2)–Ru(1)–C(3)	173.2(2)	O(6)–Ru(1)–C(3)	94.8(3)
C(1)–Ru(1)–C(3)	98.0(4)	C(2)–Ru(1)–C(3)	96.2(4)
Ru(2)–Ru(1)–C(30)	85.9(2)	O(6)–Ru(1)–C(30)	83.1(2)
C(1)–Ru(1)–C(30)	169.5(3)	C(2)–Ru(1)–C(30)	90.5(3)
C(3)–Ru(1)–C(30)	91.9(3)	Ru(1)–Ru(2)–C(4)	102.3(3)
Ru(1)–Ru(2)–C(5)	94.1(3)	C(4)–Ru(2)–C(5)	91.1(4)
Ru(1)–O(6)–C(6)	95.3(4)	Ru(1)–C(1)–O(1)	178.2(8)
Ru(1)–C(2)–O(2)	177.9(9)	Ru(1)–C(3)–O(3)	175.6(8)
Ru(2)–C(4)–O(4)	176.1(8)	Ru(2)–C(5)–O(5)	176.1(8)
O(6)–C(6)–C(7)	125.2(7)	O(6)–C(6)–C(10)	125.8(7)
C(7)–C(6)–C(10)	108.8(7)	C(6) – C(7)–C(8)	106.6(7)
C(7)–C(8)–C(9)	108.7(7)	C(8)–C(9)–C(10)	107.5(7)
C(6)–C(10)–C(9)	108.1(7)	C(6)–C(10)–C(29)	121.7(7)
C(9)–C(10)–C(29)	129.8(7)	C(10)–C(29)–C(30)	116.1(7)
C(10)–C(29)–C(34)	123.3(7)	C(30)–C(29)–C(34)	120.5(7)
Ru(1)–C(30)–C(29)	115.5(6)	Ru(1)–C(30)–C(31)	127.6(6)
C(29)–C(30)–C(31)	116.9(7)	C(30)–C(31)–C(32)	122.2(8)
C(31)–C(32)–C(33)	120.4(8)	C(32)–C(33)–C(34)	119.3(8)
C(29)–C(34)–C(34)	120.7(8)	O(7)–C(35)–C(36)	125.6(7)
O(7)–C(35)–C(39)	123.8(7)	C(36)–C(35)–C(39)	110.6(7)
C(35)–C(36)–C(37)	106.7(7)	C(35)–C(36)–C(40)	126.9(7)
C(37)–C(36)–C(40)	126.0(7)	C(36)–C(37)–C(38)	107.8(7)
C(37)–C(38)–C(39)	108.6(7)	C(35)–C(39)–C(38)	106.4(7)

lie somewhat closer to O(7) than O(6) based on the carbonyl bond lengths.

It is noticeable that the twist angles between the phenyl substituents and the five-membered ring are different for the two tetracyclone ligands. Those for that attached to Ru(3) (41, 70, 91 and 136°) are more normal, in that they form a cup arrangement for the fifth substituent, whereas for the bridging tetracyclone the corresponding angles are 35, 60, 82 and 37°; the σ-bonded phenyl group is twisted in the opposite direction to that expected as a consequence of its bridging character.

Although cyclometallation of the phenyl groups of phosphines and nitrogen-bound ligands is relatively common, the phenomenon is rarer for π-bound ligands. To our knowledge the only other example of a metallated cyclopentadienone-type ligand occurs in the complex [{$Ru_2(CO)_4$[μ-σ(C,O)-η^7-$C_4Ph_2Me(C_6H_4)CO$](μ-PPh_2)}$_2$], in which two non-bonded ruthenium atoms are bridged by an η^5-3-methyl-2,4,5-triphenylcyclopentadienone ligand formed by coupling of an allenyl fragment with a molecule of diphenylacetylene and a CO ligand during the reaction.[12]

The mechanism of formation of complex **4** is at present unknown. Since no evidence of orthometallation is seen during normal syntheses of **1**–**3** it is tempting to propose that the co-ordination of one ruthenium to the cyclopentadienone ring and a second to the phenyl ring in an η^6 manner is necessary before metallation of the phenyl ring can occur. Interestingly the co-ordination of $Cr(CO)_3$ units to the phenyl rings of tetracyclone rather than to the cyclopentadienone ring was suggested some years ago.[7]

The oxygen–ruthenium co-ordination in complex **1** is readily cleaved in solution, and in the presence of added ligands complexes of the type [$Ru(CO)_2L$(η^4-C_4Ph_4CO)] can be isolated.[1] The bridging tetracyclone in **4** is more robust however and no reaction is observed with CO or PPh_3.

Experimental

General techniques and instrumentation were as described in a recent paper from this laboratory.[13]

Synthesis of Complex **4**.—A solution of [$Ru_3(CO)_{12}$] (0.75 g, 1.17 mmol) and tetracyclone (1.36 g, 3.52 mmol) in heptane (170 cm^3) was placed in a two-necked round-bottomed flask. One neck was equipped with a condenser topped by an argon inlet, while the other was stoppered with a SubaSeal pierced by a wide-bore syringe needle. A 90° bend in the needle enabled the other end to pass through a SubaSeal into a second flask, this seal also being pierced by another syringe needle to allow egress of the argon. The solution was heated to reflux using a heating mantle and the heptane was allowed to distil slowly out into the second flask. After approximately 5 h the distillation was complete, but heating of the solid residue was continued for 20 min. Subsequent column chromatography on alumina eluting with hexane and dichloromethane (7:3) produced a mixture of tetracyclone and an unidentified ruthenium complex; further elution with a 1:1 mixture of the same solvents provided complex **4** as an orange-yellow powder after trituration with hexane. Yield 0.28 g (20%), m.p. 180 °C (decomp.). IR (CH_2Cl_2): 2068s, 2004s, 1980s, 1955m and 1906m cm^{-1}. NMR: ^1H ($CDCl_3$), δ 11.0 (s, 1 H), 7.55–6.82 (m, 36 H), 5.91 (t of d, *J* 5.5 and 0.8, 1 H), 5.58 (t of d, *J* 5.5 and 0.8, 1 H), 5.44 (d, *J* 6.0, 1 H) and 4.74 (d, *J* 6.0 Hz, 1 H); ^{13}C (CD_2Cl_2), δ 213.4, 208.6, 207.1, 195.5, 185.9 (all CO), 133.4–126.4 (m, Ph), 121.6, 106.6, 105.4, 102.6 (CH), 99.2, 96.6, 96.4, 93.6, 88.9, 85.0, 84.3 (CH), 84.2 (CH), 80.6 (CH) and 79.2 (only the CH carbons can be unambiguously identified in this region; the other ten peaks correspond to eight CPh ring carbons and the two remaining carbons of the η^6 phenyl ring) (Found: C, 62.40; H, 3.50. $C_{63}H_{40}O_7Ru_3$ requires C, 62.30; H, 3.30%).

X-Ray Crystallography.—Crystal data. $C_{63}H_{40}O_7Ru_3$ **4**, $M = 1212.21$, crystallised as yellow blocks, crystal dimensions 0.40 × 0.40 × 0.25 and 0.35 × 0.25 × 0.225 mm, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), $a = 12.130(8)$, $b = 20.972(9)$, $c = 20.861(12)$ Å, $\beta = 98.80(5)°$, $U = 5244(5)$ Å^3, $D_c = 1.535$ g cm^{-3}, $Z = 4$, Mo-Kα radiation ($\lambda = 0.710\ 69$ Å), μ(Mo-Kα) = 8.89 cm^{-1}, $F(000) = 2423.72$.

Three-dimensional room-temperature X-ray data were collected from two crystals in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 4-circle diffractometer by the ω-scan method. The 6267 independent reflections (of 10 493 measured) for which $|F|/\sigma|F| > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of six azimuthal scans from each crystal (minimum and maximum transmission coefficients 0.461 and 0.558, R_{merge} 0.020). The structure was solved by Patterson and Fourier techniques and refined by

Table 2 Atomic coordinates (× 10^4) for complex **4**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	5107(1)	2825(1)	4774(1)	C(28)	918(12)	3876(6)	5492(6)
Ru(2)	3183(1)	2682(1)	5358(1)	C(29)	3243(7)	3791(4)	4372(4)
Ru(3)	3811(1)	4179(1)	3467(1)	C(30)	4448(6)	3739(4)	4466(4)
O(1)	5615(6)	1450(3)	5296(4)	C(31)	5054(7)	4300(4)	4360(4)
O(2)	6359(7)	3406(4)	6000(3)	C(32)	4519(7)	4891(4)	4199(4)
O(3)	7073(6)	2969(4)	4016(4)	C(33)	3349(7)	4935(4)	4107(4)
O(4)	3849(7)	1631(4)	6328(4)	C(34)	2710(7)	4384(4)	4185(4)
O(5)	3800(7)	3732(4)	6336(4)	C(35)	4182(6)	3441(4)	2778(4)
O(6)	3921(4)	2494(2)	3972(2)	C(36)	3013(6)	3551(4)	2683(4)
O(7)	4697(5)	2865(3)	2944(3)	C(37)	2847(7)	4214(4)	2496(4)
C(1)	5438(7)	1952(5)	5096(4)	C(38)	3928(7)	4490(4)	2473(4)
C(2)	5870(8)	3186(4)	5543(4)	C(39)	4767(7)	4010(4)	2655(4)
C(3)	6326(7)	2913(4)	4270(4)	C(40)	2117(7)	3064(4)	2691(4)
C(4)	3611(8)	2045(5)	5977(4)	C(41)	1127(7)	3201(4)	2916(5)
C(5)	3591(8)	3316(5)	5974(5)	C(42)	289(8)	2748(5)	2888(5)
C(6)	3034(6)	2588(4)	4261(4)	C(43)	442(10)	2158(5)	2629(6)
C(7)	2367(6)	2089(4)	4491(4)	C(44)	1397(9)	2012(5)	2387(6)
C(8)	1496(7)	2406(4)	4786(4)	C(45)	2239(8)	2459(4)	2427(5)
C(9)	1643(7)	3085(4)	4744(4)	C(46)	1794(7)	4536(4)	2220(4)
C(10)	2627(6)	3195(4)	4441(4)	C(47)	1213(8)	4351(5)	1631(5)
C(11)	2522(6)	1390(4)	4418(4)	C(48)	312(9)	4687(6)	1320(7)
C(12)	2291(8)	949(4)	4887(5)	C(49)	−48(9)	5203(6)	1608(7)
C(13)	2455(8)	302(4)	4802(5)	C(50)	468(10)	5393(5)	2205(7)
C(14)	2858(9)	77(5)	4276(5)	C(51)	1407(9)	5062(5)	2514(7)
C(15)	3079(8)	498(4)	3807(5)	C(52)	4087(7)	5130(4)	2182(4)
C(16)	2900(7)	1149(4)	3872(4)	C(53)	4171(10)	5701(5)	2517(5)
C(17)	475(7)	2105(4)	4976(5)	C(54)	4258(11)	6271(5)	2191(6)
C(18)	−235(8)	1753(5)	4532(6)	C(55)	4255(8)	6293(5)	1551(5)
C(19)	−1208(10)	1490(6)	4692(9)	C(56)	4152(9)	5736(5)	1210(5)
C(20)	−1442(9)	1603(7)	5321(8)	C(57)	4076(8)	5158(5)	1524(4)
C(21)	−757(11)	1927(7)	5758(8)	C(58)	5991(7)	4073(4)	2652(4)
C(22)	219(10)	2186(5)	5605(6)	C(59)	6534(8)	3599(5)	2354(5)
C(23)	813(8)	3554(4)	4924(5)	C(60)	7668(10)	3678(8)	2320(7)
C(24)	−156(9)	3653(6)	4479(7)	C(61)	8245(10)	4189(8)	2556(7)
C(25)	−980(9)	4068(6)	4619(8)	C(62)	7715(9)	4656(6)	2845(6)
C(26)	−871(11)	4376(7)	5193(7)	C(63)	6580(8)	4613(5)	2901(5)
C(27)	53(14)	4285(7)	5625(7)				

blocked-cascade least-squares methods. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Refinement converged at a final *R* of 0.0673 (R' = 0.0582, 658 parameters, mean and maximum shift/e.s.d. 0.019 and 0.089 respectively, goodness of fit index 1.257), with allowance for the thermal anisotropy of all non-hydrogen atoms. A final difference electron-density synthesis showed peaks of −0.73 and +0.88 e Å^{-3}. Complex scattering factors were taken from the program package SHELXTL[14] as implemented on Data General Nova 3 and DG30 computers, which were used for structure solution and refinement. A weighting scheme $w^{-1} = [\sigma^2(F) + 0.000\,50(F)^2]$ was used in the latter stages of the refinement. Table 2 lists atomic positional parameters with estimated standard deviations.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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