

Synthesis and spectroscopic characterisation of  
*closo*-Ru<sub>4</sub>(CO)<sub>12</sub>(μ<sub>4</sub>,η<sup>2</sup>-HC<sub>2</sub>Ph) and  
*closo*-Ru<sub>4</sub>(CO)<sub>9</sub>(μ-CO)<sub>2</sub>(μ<sub>4</sub>,η<sup>2</sup>-HC<sub>2</sub>Ph)(μ<sub>4</sub>-Se). Crystal structure of  
*closo*-Ru<sub>4</sub>(CO)<sub>12</sub>(μ<sub>4</sub>,η<sup>2</sup>-HC<sub>2</sub>Ph)

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### Abstract

Reaction of the chalcogen stabilised butterfly cluster Fe<sub>2</sub>(CO)<sub>6</sub>{μ-SeC(H)=C(Ph)Se} with Ru<sub>3</sub>(CO)<sub>12</sub> occurs under thermal conditions affording the clusters FeRu<sub>2</sub>(CO)<sub>9</sub>(μ-Se)<sub>2</sub> (**2**), *closo*-Ru<sub>4</sub>(CO)<sub>12</sub>(μ<sub>4</sub>,η<sup>2</sup>-HC<sub>2</sub>Ph) (**3**) and *closo*-Ru<sub>4</sub>(CO)<sub>9</sub>(μ-CO)<sub>2</sub>(μ<sub>4</sub>,η<sup>2</sup>-HC<sub>2</sub>Ph)(μ<sub>4</sub>-Se) (**4**) in 30%, 22% and 18% yield respectively. They were characterised by IR and <sup>1</sup>H, <sup>13</sup>C and <sup>77</sup>Se NMR spectroscopy. Compound **3** was further characterised by X-ray methods: space group *P*2<sub>1</sub>/*n*, *a* = 20.138(4), *b* = 9.333(2), *c* = 26.219(6) Å, β = 97.43(2)°, *Z* = 8, ρ<sub>calc</sub> = 2.291 g cm<sup>-3</sup>. The structure was solved using direct methods and was refined to the final values of the residuals *R* = 0.0377 and *R*<sub>w</sub> = 0.0455. The molecule consists of a butterfly arrangement of four ruthenium atoms with a quadruply bridged alkyne ligand. Compound **4** was characterised by comparison of its spectroscopic data with that of the analogous S-compound.

**Keywords:** Ruthenium; Selenium; Alkyne; Carbonyl; Cluster; X-ray diffraction

### 1. Introduction

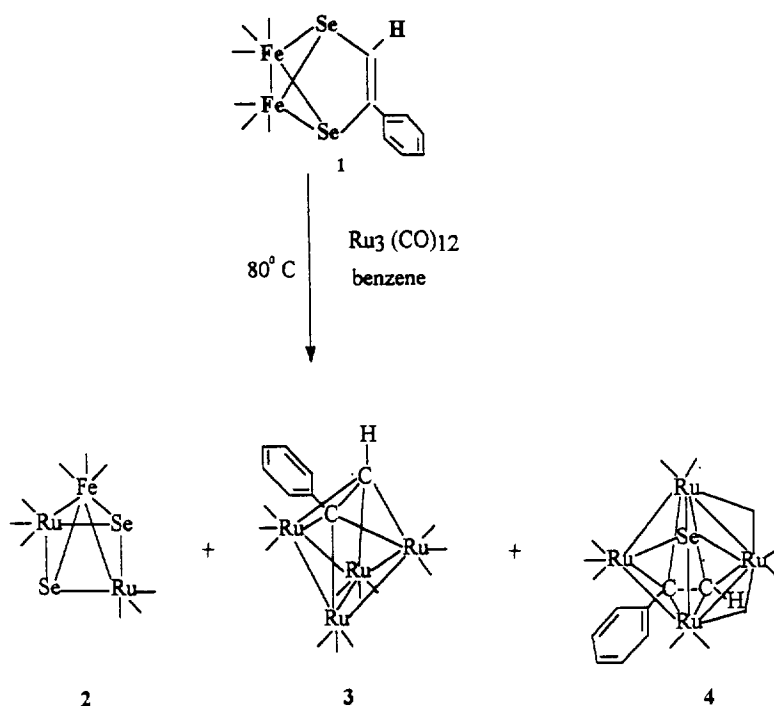
Interaction of alkynes with transition metals has been of considerable importance for a variety of chemical reactions, including several homogeneous and heterogeneous catalytic processes [1]. Metal alkyne chemistry continues to attract considerable interest, largely because of the variety of bonding modes observed between alkynes and metal atoms which facilitate a number of interesting transformations. Use of certain main group elements as bridging and stabilising ligands in designed cluster growth reactions has been extensively demonstrated in recent years [2]. Useful starting materials for various types of cluster growth reactions are the compounds Fe<sub>2</sub>(μ-E<sub>2</sub>)(CO)<sub>6</sub> (where E = S, Se, Te) [3–5]. In contrast to the relatively wide use of bridging S [6] and Te [7] ligands in cluster build-up reactions, the

use of Se as bridging ligand has been limited to fewer examples [8]. Acetylenes have been found to readily insert into the chalcogen–chalcogen bond of Fe<sub>2</sub>(μ-E<sub>2</sub>)(CO)<sub>6</sub> compounds to form Fe<sub>2</sub>(CO)<sub>6</sub>{μ-EC(R)=C(H)E} and [{Fe<sub>2</sub>(CO)<sub>6</sub>EE}<sub>2</sub>{μ-C(R)–C(H)}] [9]. The coordinated acetylene serves to block the reactive chalcogen sites, thus facilitating reaction at the Fe–Fe bond to form some unusual clusters [10]. In this paper we report the thermolytic reaction of Fe<sub>2</sub>(CO)<sub>6</sub>{μ-SeC(H)=C(Ph)Se} (**1**) [11] with Ru<sub>3</sub>(CO)<sub>12</sub> and the characterisation of the products obtained.

### 2. Results and discussion

Refluxing a benzene solution containing Fe<sub>2</sub>(CO)<sub>6</sub>{μ-SeC(H)=C(Ph)Se} (**1**) [11] and Ru<sub>3</sub>(CO)<sub>12</sub> led to the clean formation of FeRu<sub>2</sub>(CO)<sub>9</sub>(μ-Se)<sub>2</sub> (**2**) [12], *closo*-Ru<sub>4</sub>(CO)<sub>12</sub>(μ<sub>4</sub>,η<sup>2</sup>-HC<sub>2</sub>Ph) (**3**) and Ru<sub>4</sub>(CO)<sub>9</sub>(μ-CO)<sub>2</sub>(μ<sub>4</sub>,η<sup>2</sup>-HC<sub>2</sub>Ph)(μ-Se) (**4**) in moder-

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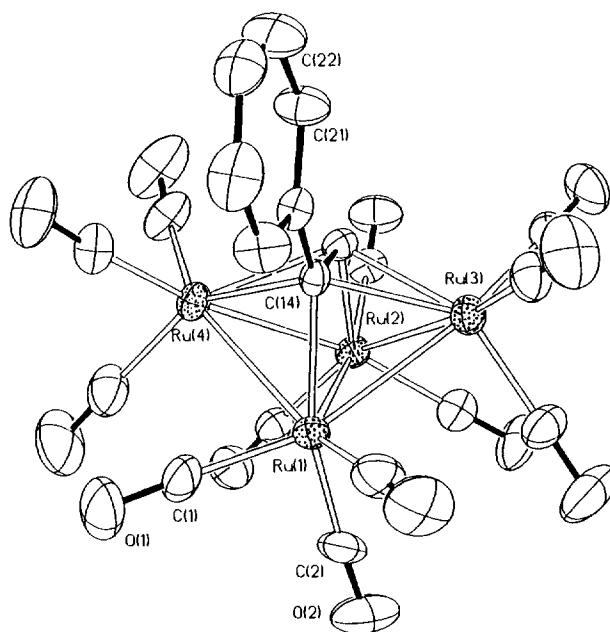


Scheme 1. Formation of compounds 2–4.

ate yields (Scheme 1). Compounds **3** and **4** were characterised by IR and NMR spectroscopy. The IR spectrum of **3** indicated the presence of only terminally bonded carbonyl groups, whereas **4** in the carbonyl region shows seven bands between 2092 and 1855  $\text{cm}^{-1}$ , indicating the presence of both terminal and bridging carbonyl groups. In the  $^1\text{H}$  NMR spectrum of **3** the farthest downfield signal at  $\delta = 10.2$  ppm is assigned to the  $-\text{CH}$  proton, whereas in **4** it is shifted to  $\delta = 4.66$  ppm. In the  $^{77}\text{Se}$  NMR spectrum of  $\text{Ru}_4(\text{CO})_9(\mu\text{-CO})_2(\mu_4, \eta^2\text{-HC}_2\text{Ph})(\mu_4\text{-Se})$  (**4**) the signal at  $\delta = -155$  ppm is consistent with the presence of a  $\mu_4\text{-Se}$  ligand ( $\text{Ru}_3\text{Fe}_2\text{SeTe}(\text{CO})_{17}$ ,  $\delta = -175$  ppm and  $\text{Ru}_3\text{Fe}_2\text{Se}_2(\text{CO})_{17}$ ,  $\delta = -148$  ppm) [13]. Compound **4** was characterised on the basis of comparison of its IR and NMR spectroscopic data with that of the reported analogous S-compound [14]. Structurally, compound **4** is very similar to  $\text{Ru}_4(\text{CO})_9(\mu\text{-CO})_2(\text{PhC}_2\text{Ph})(\mu_4\text{-PPh})$  [15] and  $\text{Os}_4(\text{CO})_{10}(\mu\text{-CO})(\mu_4\text{-HC}_2\text{CO}_2\text{Me})(\mu_4\text{-S})$  [16]. On one side of the cluster in **4** is a quadruply bridging selenido ligand, and on the other side a quadruply bridging  $\text{HC}_2\text{Ph}$  ligand.

Dark red air-stable crystals of **3** were obtained from a hexane/ $\text{CH}_2\text{Cl}_2$  solution at  $-4^\circ\text{C}$  and an X-ray diffraction analysis was undertaken. An ORTEP diagram of the molecular structure of *closo*- $\text{Ru}_4(\text{CO})_{12}(\mu_4, \eta^2\text{-HC}_2\text{Ph})$  (**3**) is shown in Fig. 1. There are two independent molecules in the asymmetric unit of **3** and the structure is best described as a butterfly arrangement of four ruthenium atoms and the olefinic fragment lies over the metal skeleton with the ethylenic C–C bond

parallel to the Ru–Ru hinge bond. Each acetylenic carbon atom forms one metal–carbon  $\sigma$  bond to the two hinge atoms [Ru(1) and Ru(2)] of average length 2.14 Å and two  $\pi$  bonds to the wing-tip atoms [Ru(3) and Ru(4)] of average length 2.24 Å and form a distorted octahedral core. The longest metal–metal bond within this cluster is that between the hinge metal atoms [Ru(1)–Ru(2) = 2.837(1) Å; Ru(1')–Ru(2') = 2.826(1) Å] with the remaining bonding distances falling

Fig. 1. Molecular structure of **3** with the atom labelling scheme.

in the range 2.710(1)–2.760(1) Å. Similar types of clusters with analogous  $M_4C_2$  frameworks have been structurally characterised [17–22]. The distorted octahedral structures of these butterfly clusters are fully consistent with Wade's skeleton electron counting rules [23], which predict a *closo*- $M_4C_2$  structure with six vertices. Each metal atom in **3** has three terminally bonded carbonyl ligands. The average M–C–O angles of 177.2° and C–O distances of 1.125 Å are typical for this formally two-electron donating ligand. The phenylacetylene ligand is coordinated to the four ruthenium atoms via a  $\sigma$  bond with the equatorial *cis* metal and a  $\pi$  bond with axial metals by overlap with the metal d orbital. Such an interaction has previously been described as bent  $\pi$ -type bonding [24].

### 3. Experimental section

All reactions and manipulations were carried out under an argon or nitrogen atmosphere, using standard Schlenk techniques. Solvents were deoxygenated immediately prior to use. Reactions were monitored by thin-layer chromatography (TLC). Infrared spectra were recorded on a Nicolet-Impact 400 FTIR spectrometer as an n-hexane solution in a sodium chloride cell at 0.1 mm path length. Elemental analyses were performed using a Carlo Erba automatic analyser. NMR spectra were recorded on a Varian VXR 300S spectrometer in  $CDCl_3$  at 25 °C. The operating frequency for  $^{77}Se$  NMR was 57.23 MHz with a pulse width of 15  $\mu s$  and a delay of 1.0 s.  $^{77}Se$  NMR spectra were referenced to  $Me_2Se$  ( $\delta = 0$  ppm). Dodecacarbonyl triruthenium and phenylacetylene ligand were purchased from Aldrich Chemical Co. and these were used without further purification.  $Fe_2(CO)_6(\mu-Se_2)$  [3] and  $Fe_2(CO)_6\{\mu-SeC(H)=C(Ph)Se\}$  (**1**) [11] were prepared as previously reported.

#### 3.1. Reaction of $Fe_2(CO)_6\{\mu-SeC(H)=C(Ph)Se\}$ (**1**) with $Ru_3(CO)_{12}$

To a solution of **1** (25 mg, 0.046 mmol) in dry benzene (30 ml) was added  $Ru_3(CO)_{12}$  (88 mg, 0.138 mmol). The reaction mixture was heated at 80 °C for 12 h under an atmosphere of argon. The solution was cooled to room temperature and the solvent was removed in vacuo. The residue was dissolved in a minimal amount of  $CH_2Cl_2$  and was chromatographed by TLC on silica gel with hexane as eluant to afford three bands. A reddish brown band eluted first and was characterised spectroscopically as  $FeRu_2(CO)_9(\mu-Se)_2$  (**2**) [12] (9.2 mg, 30%). The second band was identified as brown *closo*- $Ru_4(CO)_{12}(\mu_4,\eta^2-HC_2Ph)$  (**3**) (8.5 mg, 22%). The third band to elute gave, after concentration and cooling at

–4 °C, yellow crystals of  $Ru_4(CO)_9(\mu-CO)_2(\mu_4,\eta^2-HC_2Ph)(\mu_4-Se)$  (**4**) (7.4 mg, 18%).

**2**: IR ( $\nu(CO)$ ,  $cm^{-1}$ ): 2097(w), 2065(vs), 2057(w), 2050(w), 2037(vs), 2014(s), 2002(w), 1968(w, br).  $^{77}Se$  NMR:  $\delta$  571(s),  $\delta$  681(w).

**3**: IR ( $\nu(CO)$ ,  $cm^{-1}$ ): 2095(w), 2069(vs), 2045(s), 2037(vs), 2016(m), 1999(w), 1980(w), 1953(w).  $^1H$  NMR:  $\delta$  10.2 (s, –CH),  $\delta$  7.25–7.22 (m, 3H),  $\delta$  7.16–7.14 (m, 2H).  $^{13}C$  NMR:  $\delta$  198.3–190.2 (CO),  $\delta$  149.1 (–CPh),  $\delta$  128.2–126.1 (Ph),  $\delta$  109.4 (–CH). M.p. 114–116 °C. Anal. Found: C, 28.7; H, 0.75.  $C_{20}H_6O_{12}Ru_4$  Calc.: C, 28.5; H, 0.71%.

**4**: IR ( $\nu(CO)$ ,  $cm^{-1}$ ): 2092(w), 2058(s), 2040(s), 2034(s), 2004(m), 1990(w), 1855(w).  $^1H$  NMR:  $\delta$  7.08–7.09 (m, 3H),  $\delta$  6.50–6.46 (m, 2H),  $\delta$  4.66 (s, 1H).  $^{13}C$  NMR:  $\delta$  198 (CO),  $\delta$  151.2 (–CPh),  $\delta$  128–126 (Ph),  $\delta$  118.1(C–H).  $^{77}Se$  NMR:  $\delta$  –155

Table 1  
Summary of crystallographic data for **3**

Empirical formula	$C_{20}H_6O_{12}Ru_4$
Formula weight	1685.1
Space group	$P2_1/n$
Crystal system	Monoclinic
$a$ (Å)	20.138(4)
$b$ (Å)	09.333(2)
$c$ (Å)	26.219(6)
$\beta$ (°)	97.43(2)
$V$ (Å <sup>3</sup> )	4886.4(17)
$Z$	8
$D_{calc}$ (g cm <sup>–3</sup> )	2.291
$\mu$ (Mo K $\alpha$ ) (cm <sup>–1</sup> )	24.86
$F(000)$	3184
Temperature (K)	296
Radiation	Mo K $\alpha$ ( $\lambda = 0.71073$ Å)
$T_{max}/T_{min}$	0.2380/0.3074
Monochromator	Highly oriented graphite crystal
Crystal size (mm <sup>3</sup> )	0.22 × 0.26 × 0.31
$2\theta$ range (deg)	4.0 < $2\theta$ < 50.0
Scan type	Wyckoff
Scan speed	Variable; 7.32 to 19.53 Å min <sup>–1</sup> in $\omega$
$hkl$ ranges	–23 ≤ $h$ ≤ 23, 0 ≤ $k$ ≤ 11, 0 ≤ $l$ ≤ 31
Reflections collected	8795
Independent reflections	8594 ( $R_{int} = 3.33\%$ )
Observed reflections	6175 ( $F > 4.0\sigma(F)$ )
Final $R$ indices (observed data)	$R = 3.77\%$ , $wR = 4.55\%$
$R$ indices (all data)	$R = 6.06\%$ , $wR = 5.20\%$
Extinction correction	$\chi = 0.000044(6)$ where $F^* = F[1 + 0.002\chi F^2 / \sin(2\theta)]^{-1/4}$
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0008 F^2$
Number of parameters refined	650
Goodness-of-fit	1.03
Largest difference peak	0.72 e Å <sup>–3</sup>
Largest difference hole	–0.97 e Å <sup>3</sup>
Largest and mean $\Delta/\sigma$	0.014, 0.002

Table 2  
Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^3$ ) for **3**

Atom	x	y	z	$U_{\text{eq}}^a$
Ru(1)	3736.0(3)	4220.8(7)	1010.2(2)	37.6(2)
Ru(2)	3293.9(3)	3615.9(7)	1971.8(2)	34.9(2)
Ru(3)	4595.8(3)	4227.8(8)	1897(3)	43.0(2)
Ru(4)	3272.6(3)	1548.0(7)	1244.0(2)	38.1(2)
Ru(1')	1091.3(3)	2319.2(7)	1488.7(2)	34.6(2)
Ru(2')	-1864.9(3)	4815.9(7)	1569.6(3)	35.3(2)
Ru(3')	-2364.3(3)	2563.1(7)	975.6(2)	37.6(2)
Ru(4')	-727.7(3)	4847.9(7)	1085.8(3)	37.6(2)
O(1)	3069(6)	3274(10)	-35(3)	137(5)
O(2)	2890(4)	6913(9)	1063(3)	96(4)
O(3)	4821(4)	5842(9)	548(3)	91(4)
O(4)	1793(3)	3923(8)	1628(3)	69(3)
O(5)	3334(4)	6419(8)	2565(3)	81(3)
O(6)	3191(3)	1974(8)	2952(3)	70(3)
O(7)	4446(4)	7441(9)	1888(4)	102(4)
O(8)	6006(4)	4340(10)	1628(3)	92(4)
O(9)	4996(4)	3779(9)	3041(3)	77(3)
O(10)	2862(5)	-696(9)	1974(3)	106(4)
O(11)	1885(4)	2000(11)	666(4)	124(5)
O(12)	3632(4)	-717(9)	503(3)	85(3)
O(1')	352(3)	1467(9)	1405(4)	101(4)
O(2')	-927(5)	2520(12)	2646(3)	127(5)
O(3')	-1548	-760(8)	1541(3)	91(4)
O(4')	-1020(3)	6691(8)	2353(3)	69(3)
O(5')	-2920(4)	3789(10)	2437(3)	102(4)
O(6')	-2853(4)	7214(9)	1262(3)	91(3)
O(7')	-3052(4)	1142(8)	1800(3)	77(3)
O(8')	-2486(4)	-138(9)	318(3)	93(4)
O(9')	-3632	3950(9)	452(3)	94(4)
O(10')	308(3)	5351(9)	2009(3)	88(3)
O(11')	-790(5)	7873(9)	662(4)	109(4)
O(12')	350(3)	3972(9)	455(3)	78(3)
C(1)	3302(6)	3606(11)	366(4)	78(5)
C(2)	3190(5)	5873(11)	1037(4)	61(4)
C(3)	4426(5)	5242(12)	728(4)	63(4)
C(4)	2347(4)	3799(9)	1754(3)	45(3)
C(5)	3335(4)	5390(11)	2326(4)	53(3)
C(6)	3215(4)	2614(9)	2588(3)	43(3)
C(7)	4504(5)	6251(11)	1892(4)	61(4)
C(8)	5493(5)	4310(11)	1725(4)	56(3)
C(9)	4876(4)	3955(10)	2627(4)	51(3)
C(10)	3001(5)	119(10)	1682(4)	60(4)
C(11)	2404(5)	1819(12)	878(5)	76(5)
C(12)	3495(4)	134(10)	764(3)	50(3)
C(13)	4081(3)	2198(8)	1841(3)	36(3)
C(14)	4314(3)	2431(8)	1345(3)	32(2)
C(21)	5160(5)	426(11)	1430(3)	56(3)
C(22)	5603(5)	-434(12)	1225(4)	73(4)
C(23)	5770(5)	-193(12)	747(4)	62(4)
C(24)	5492(5)	914(13)	468(4)	69(4)
C(25)	5016(5)	1787(11)	660(3)	58(4)
C(26)	4842(4)	1544(9)	1151(3)	37(3)
C(1')	-179(5)	1792(11)	1436(4)	64(4)
C(2')	-988(6)	2455(12)	2214(4)	74(4)
C(3')	-1399(5)	408(10)	1507(3)	52(3)
C(4')	-1315(4)	5986(10)	2049(3)	44(3)
C(5')	-2343(5)	4147(12)	2106(4)	60(4)
C(6')	-2480(5)	6313(10)	1383(3)	53(3)
C(7')	-2804(4)	1686(10)	1491(3)	52(3)
C(8')	-2453(5)	864(12)	556(4)	60(4)
C(9')	-3166(5)	3397(11)	643(4)	58(4)

Table 2 (continued)

Atom	x	y	z	$U_{\text{eq}}^a$
C(10')	-85(5)	5178(10)	1663(4)	57(4)
C(11')	-759(5)	6776(10)	820(4)	57(4)
C(12')	-38(4)	4281(10)	698(3)	50(3)
C(13')	-1764(4)	4413(8)	790(3)	35(2)
C(14')	-1387(3)	3116(8)	716(3)	31(2)
C(21')	-1382(5)	3425(11)	-236(3)	56(3)
C(22')	-1243(5)	2919(13)	-714(4)	68(4)
C(23')	-984(5)	1567(13)	-742(4)	68(4)
C(24')	-832(5)	757(11)	-315(4)	62(4)
C(25')	-963(5)	1252(10)	155(4)	55(3)
C(26')	-1250(4)	2598(9)	199(3)	35(2)

<sup>a</sup> Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

( $\mu_4$ -Se). M.p. 148–150 °C (decomp.). Anal. Found: C, 25.6; H, 0.64.  $\text{C}_{19}\text{O}_{11}\text{H}_6\text{SeRu}_4$  Calc.: C, 25.5; H, 0.67%.

### 3.2. Crystal structure determination of *closo-Ru<sub>4</sub>(CO)<sub>12</sub>( $\mu_4$ , $\eta^2$ -HC<sub>2</sub>Ph)*

Crystals of **3** were grown from a hexane/ $\text{CH}_2\text{Cl}_2$  solvent mixture at -4 °C and a crystal of dimensions  $0.22 \times 0.26 \times 0.31 \text{ mm}^3$  was used for data collection. Single crystal X-ray data were collected on a Siemens  $P_4$  diffractometer by using Mo  $K\alpha$  radiation. Suitable crystals were selected and mounted with epoxy cement to glass fibres. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ( $20^\circ \leq 2\theta \leq 25^\circ$ ). Compound **3** crystallised in the monoclinic crystal system. The space group  $P2_1/n$  was determined from systematic absences observed in the diffraction data for **3**. The structure was solved using direct methods, completed by the subsequent difference Fourier synthesis and refined by full-matrix least-squares procedures. Semi-empirical absorp-

Table 3  
Selected bond lengths ( $\text{\AA}$ ) for **3**<sup>a</sup>

Molecule 1		Molecule 2	
Ru(1)–Ru(2)	2.837(1)	Ru(1')–Ru(2')	2.826(1)
Ru(1)–Ru(3)	2.715(1)	Ru(1')–Ru(3')	2.746(1)
Ru(1)–Ru(4)	2.760(1)	Ru(1')–Ru(4')	2.724(1)
Ru(2)–Ru(3)	2.715(1)	Ru(2')–Ru(3')	2.730(1)
Ru(2)–Ru(4)	2.710(1)	Ru(2')–Ru(4')	2.758(1)
Ru(1)–C(1)	1.887(10)	Ru(1')–C(1')	1.924(10)
Ru(1)–C(2)	1.900(10)	Ru(1')–C(2')	1.889(10)
Ru(1)–C(14)	2.157(7)	Ru(1')–C(14')	2.169(7)
Ru(2)–C(13)	2.126(8)	Ru(2')–C(13')	2.113(7)
Ru(3)–C(13)	2.156(8)	Ru(3')–C(13')	2.197(8)
Ru(4)–C(13)	2.192(7)	Ru(4')–C(13')	2.169(7)
Ru(3)–C(14)	2.241(7)	Ru(1')–C(14')	2.225(7)
Ru(4)–C(14)	2.236(7)	Ru(4')–C(14')	2.232(7)
C(13)–C(14)	1.455(11)	C(13')–C(14')	1.455(11)
O(1)–C(1)	1.140(13)	O(1')–C(1')	1.125(13)

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digit.

Table 4  
Selected bond angles (°) for **3**<sup>a</sup>

Molecule 1	Molecule 2		
Ru(2)–Ru(1)–Ru(3)	58.5(1)	Ru(2')–Ru(1')–Ru(3')	58.6(1)
Ru(2)–Ru(1)–Ru(4)	57.9(1)	Ru(2')–Ru(1')–Ru(4')	59.5(1)
Ru(3)–Ru(1)–Ru(4)	90.5(1)	Ru(3')–Ru(1')–Ru(4')	91.1(1)
Ru(1)–Ru(2)–Ru(4)	58.5(1)	Ru(1')–Ru(2')–Ru(3')	59.2(1)
Ru(1)–Ru(2)–Ru(3)	59.6(1)	Ru(1')–Ru(2')–Ru(4')	58.4(1)
Ru(3)–Ru(2)–Ru(4)	91.5(1)	Ru(3')–Ru(2')–Ru(4')	90.7(1)
Ru(1)–Ru(3)–Ru(2)	63.0(1)	Ru(1')–Ru(3')–Ru(2')	62.1(1)
Ru(1)–Ru(4)–Ru(2)	62.5(1)	Ru(1')–Ru(4')–Ru(2')	62.1(1)
Ru(2)–Ru(1)–C(1)	124.9(4)	Ru(2')–Ru(1')–C(1')	139.2(3)
Ru(3)–Ru(1)–C(1)	159.7(3)	Ru(3')–Ru(1')–C(1')	145.7(3)
Ru(4)–Ru(1)–C(1)	78.1(3)	Ru(4')–Ru(1')–C(1')	83.5(3)
Ru(2)–Ru(1)–C(14)	72.5(2)	Ru(2')–Ru(1')–C(14')	72.5(2)
Ru(3)–Ru(1)–C(14)	53.3(2)	Ru(3')–Ru(1')–C(14')	52.2(2)
Ru(4)–Ru(1)–C(14)	52.4(2)	Ru(4')–Ru(1')–C(14')	52.8(2)
C(1)–Ru(1)–C(14)	106.9(4)	C(1')–Ru(1')–C(14')	99.8(4)
Ru(1)–Ru(2)–C(13)	69.8(2)	Ru(1')–Ru(2')–C(13')	70.0(2)
Ru(3)–Ru(2)–C(13)	51.1(2)	Ru(3')–Ru(2')–C(13')	52.1(2)
Ru(4)–Ru(2)–C(13)	52.2(2)	Ru(4')–Ru(2')–C(13')	50.8(2)
Ru(1)–Ru(3)–C(13)	72.0(2)	Ru(1')–Ru(3')–C(13')	70.6(2)
Ru(2)–Ru(3)–C(13)	50.2(2)	Ru(2')–Ru(3')–C(13')	49.3(2)
Ru(1)–Ru(3)–C(14)	50.5(2)	Ru(1')–Ru(3')–C(14')	50.4(2)
Ru(2)–Ru(3)–C(14)	73.9(2)	Ru(2')–Ru(3')–C(14')	73.8(2)
C(13)–Ru(3)–C(14)	38.6(3)	C(13')–Ru(3')–C(14')	38.4(3)
Ru(1)–Ru(4)–C(13)	70.6(2)	Ru(1')–Ru(4')–C(13')	71.5(2)
Ru(2)–Ru(4)–C(13)	50.0(2)	Ru(2')–Ru(4')–C(13')	49.0(2)
Ru(1)–Ru(4)–C(14)	49.8(2)	Ru(1')–Ru(4')–C(14')	50.7(2)
Ru(2)–Ru(4)–C(14)	74.0(2)	Ru(2')–Ru(4')–C(14')	73.1(2)
Ru(1)–C(1)–O(1)	176.0(12)	Ru(1')–C(1')–O(1')	179.1(9)
Ru(2)–C(13)–Ru(3)	78.7(3)	Ru(2')–C(13')–Ru(3')	78.6(3)
Ru(3)–C(13)–Ru(4)	126.8(4)	Ru(3')–C(13')–Ru(4')	126.8(3)
Ru(2)–C(13)–C(14)	73.9(4)	Ru(2')–C(13')–C(14')	71.8(4)
Ru(3)–C(14)–Ru(4)	120.5(3)	Ru(3')–C(14')–Ru(4')	122.3(3)
Ru(2)–C(13)–Ru(4)	77.7(2)	Ru(2')–C(13')–Ru(4')	80.2(2)
Ru(1)–C(14)–Ru(4)	77.8(2)	Ru(1')–C(14')–Ru(4')	76.5(2)

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digit.

tion correction was applied to the data set. Two independent but chemically equivalent compound molecules were located in the asymmetric unit. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealised contributions.

All software and sources of the scattering factors are contained in either the SHELXTL (5.1) or SHELXTL PLUS (4.2) program libraries (G.M. Sheldrick, Siemens XRD, Madison, WI). Crystallographic data for **3** are summarised in Table 1. Final fractional atomic coordinates, selected bond distances and bond angles are given in Tables 2–4. Fractional atomic coordinates for the hydrogen atoms, anisotropic thermal parameters, bond distances and bond angles and the structure factor tables are available from the authors.

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