

Reactions of dodecacarbonyltriruthenium with unsaturated α, β -diketones¹

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Abstract

Reactions of $\text{Ru}_3(\text{CO})_{12}$ with endiones *trans*- $\text{ArCOCH}=\text{CHCOAr}$, $\text{Ar} = \text{Ph}$, *p*- MeC_6H_4 were studied. Three isomeric complexes were isolated from reactions with each of the ligands. All isomers involve one and the same central bicyclic fragment, as well as two peripheral oxaruthenacycles, concatenated with the central fragment via spiro metal atoms. The isomers differ from each other by the orientation of the peripheral metallacycles relative to the central bicyclic moiety. The structures of the two complexes have been established by means of single crystal X-ray diffraction studies. © 1997 Elsevier Science S.A.

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1. Introduction

Earlier we have shown that the reaction of $\text{Ru}_3(\text{CO})_{12}$ with unsaturated ketones involving the oxadiene $-\text{C}=\text{C}-\text{C}=\text{O}$ system yields bi- and polynuclear complexes with five-membered oxametallacycle as a main building block [1–4]. The present paper is focused on the reactions of $\text{Ru}_3(\text{CO})_{12}$ with unsaturated *trans*-1,4-diarylbut-2-en-1,4-diones, $\text{ArCOCH}=\text{CHCOAr}$, $\text{Ar} = \text{Ph}$ (**1a**), *p*- MeC_6H_4 (**1b**). Endiones contain a symmetrical 1,6-dioxahexatriene bond system $\text{O}=\text{C}-\text{C}=\text{C}-\text{C}=\text{O}$ and thus have a structure substantially different from that of the oxadienes studied earlier. Therefore, it seemed interesting to study the role of these structural differ-

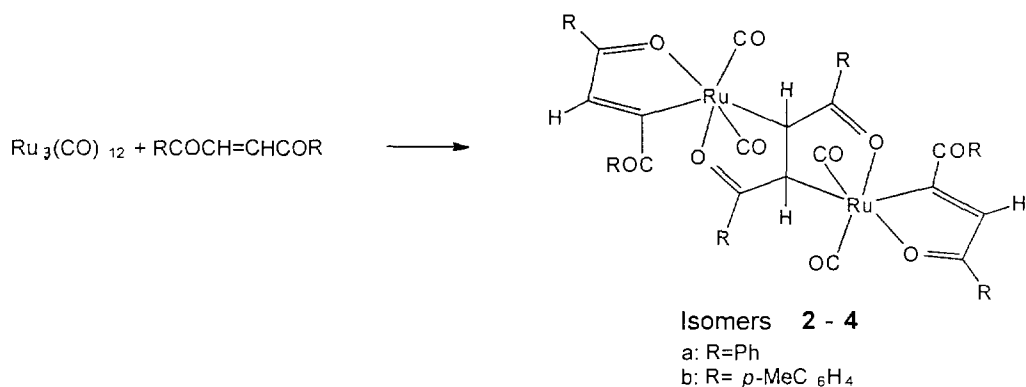
ences in the reactions of enone and endione derivatives with dodecacarbonyltriruthenium.

2. Results and discussion

Reactions of $\text{Ru}_3(\text{CO})_{12}$ with **1** were carried out in refluxing heptane; reagents were used in the molar ratio 1:5. The course of the reactions was monitored by IR spectroscopy. Heating was normally discontinued after $\text{Ru}_3(\text{CO})_{12}$ was completely consumed, and the products of reactions were recovered chromatographically. In many cases the isolation of individual compounds was achieved by repeated preparative TLC on silica gel. In each of the reactions (with **1a** and **1b** used as starting materials) three complexes (**2a**, **3a** and **4a**; **2b**, **3b** and **4b** respectively) were obtained in the form of yellow solids. [The complexes are labelled according to the values of R_f during chromatographic separation; complexes **2** have the largest R_f , whereas complexes **4** are those with the smallest R_f .]

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¹ Dedicated to the memory of Professor Yu.T. Struchkov.



The structures of complexes **2a** and **3b** were established by means of X-ray diffraction studies (Figs. 1 and 2). Selected bond lengths and angles for **2a** and **3b** are listed in Table 1. Taking into account the similarity of the IR and NMR spectra of **2b** and **3a** with those of **2a** and **3b** respectively, one may assume that compounds **2a** and **2b** as well as compounds **3a** and **3b** have analogous structures.

Both molecules **2a** and **3b** exhibit the same main structural motif, representing a bicyclic system, which involves two fused five-membered oxaruthenacycles. This system is formed as a result of chelating of two ruthenium atoms by one endone ligand. Such a motif naturally could not have occurred in the enone complexes, which we described in Refs. [1–4], and the reaction of $\text{Ru}_3(\text{CO})_{12}$ with dimethylfumarate [5] was in

fact the only case where this type of complexation was observed earlier.

Each of the two ruthenium atoms in **2a** and **3b** is also involved in a peripheral oxaruthenacycle formed as a result of chelating of the metal atom by one more endone ligand. Thus, the central bicyclic system appears to be concatenated with two peripheral five-membered rings via two spiro ruthenium atoms.

The molecular structures of **2a** and **3b** reveal an interesting case of geometrical isomerism, which is associated with a different arrangement of the peripheral chelate rings relative to the central bicyclic moiety. Indeed, the latter has a gabled roof shape (Fig. 3), and both peripheral chelate cycles in isomers **3** extend towards its exterior, whereas in **2** only one peripheral oxaruthenacycle (involving Ru(1)) is directed towards

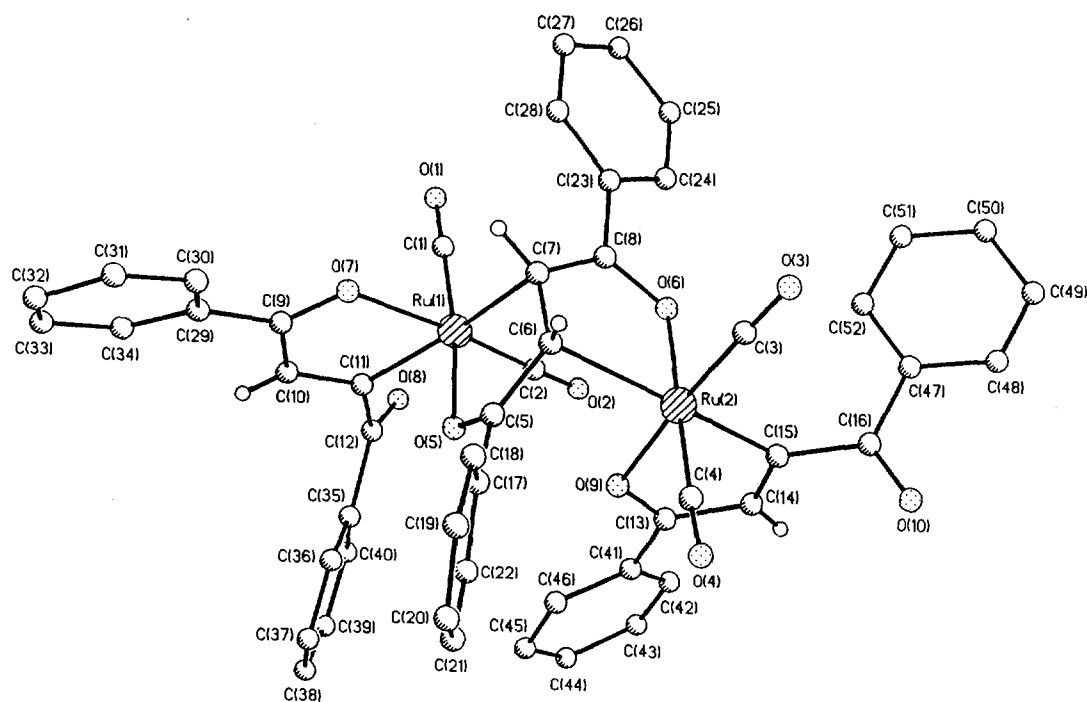


Fig. 1. Molecular structure of complex **2a**.

the exterior and the other peripheral cycle (involving Ru(2)) is directed towards the interior side of the bicyclic moiety. It is possible to assume that complexes **4**, which according to the elemental analysis also represent the isomers of complexes **2** and **3**, have both peripheral chelate rings directed towards the interior of the central bicyclic system. Unfortunately, we could not manage to grow the single crystals of isomers **4** suitable for X-ray experiment. It should be emphasized that complexes **2–4** exhaust all possibilities for the isomerism in the binuclear endione complexes, if we take into account that carbonyl ligands tend to occupy the coordination sites in *trans*-positions to the oxygen rather than to the carbon atoms. This regularity derived from the structures of all earlier studied carbonyl complexes with oxaruthenacycles may probably be correlated with the known strong *trans*-effect of the M–C σ -bonds, which usually causes considerable weakening of the coordination of the *trans*-positioned ligand.

Each ruthenium atom with five different ligands in the octahedral environment obviously represents a chiral centre, and its absolute configuration may be designated with the help of the Brown–Cook–Sloan extension of the Cahn–Ingold–Prelog rules [6,7]. This notation shows that the Ru(1) and Ru(2) atoms in complexes **2** have opposite configurations OC-6-33-A and OC-6-33-C (or vice versa for an alternative enantiomer which is also present in the racemic product), whereas their configura-

tions in complexes **3** and **4** appear to be the same. If we take into account that both C(6) and C(7) atoms in all isomers are also chiral, and introduce their chirality descriptors into the designation of each complex, we finally have the symbol OC-6-33-A[Ru(1)]-S[C(6)]-S[C(7)]-OC-6-33-A[Ru(2)] for the absolute configuration of one of the enantiomers of **3** (the alternative enantiomer will naturally have all A changed to C and all S changed to R) and symbols (using the same order of atoms) (OC-6-33-A)-(S)-(S)-(OC-6-33-C) and (OC-6-33-C)-(S)-(S)-(OC-6-33-C) for complexes **2** and **4** respectively. It is noteworthy that steric reasons would have made impossible the *trans*-fusion of two five-membered cycles, which excludes from consideration any isomers with different chiralities of the C(6) and C(7) atoms, i.e. RS and SR isomers. Furthermore, the overall symmetry of the system makes the isomers (OC-6-33-A)-(S)-(S)-(OC-6-33-C) and (OC-6-33-C)-(S)-(S)-(OC-6-33-A) identical, so that despite the fact that the complex contains four chiral centres, only three distinct pairs of diastereomers are possible.

It is noteworthy that the bridgehead C(6) and C(7) atoms undergo $sp^2 \rightarrow sp^3$ rehybridization in the course of complexation. The presence of the terminal hydrogens at these carbon atoms was unambiguously established in the X-ray structures of **2a** and **3b**, and confirmed by the ^1H NMR spectral data for these as well as for all other products **2–4**.

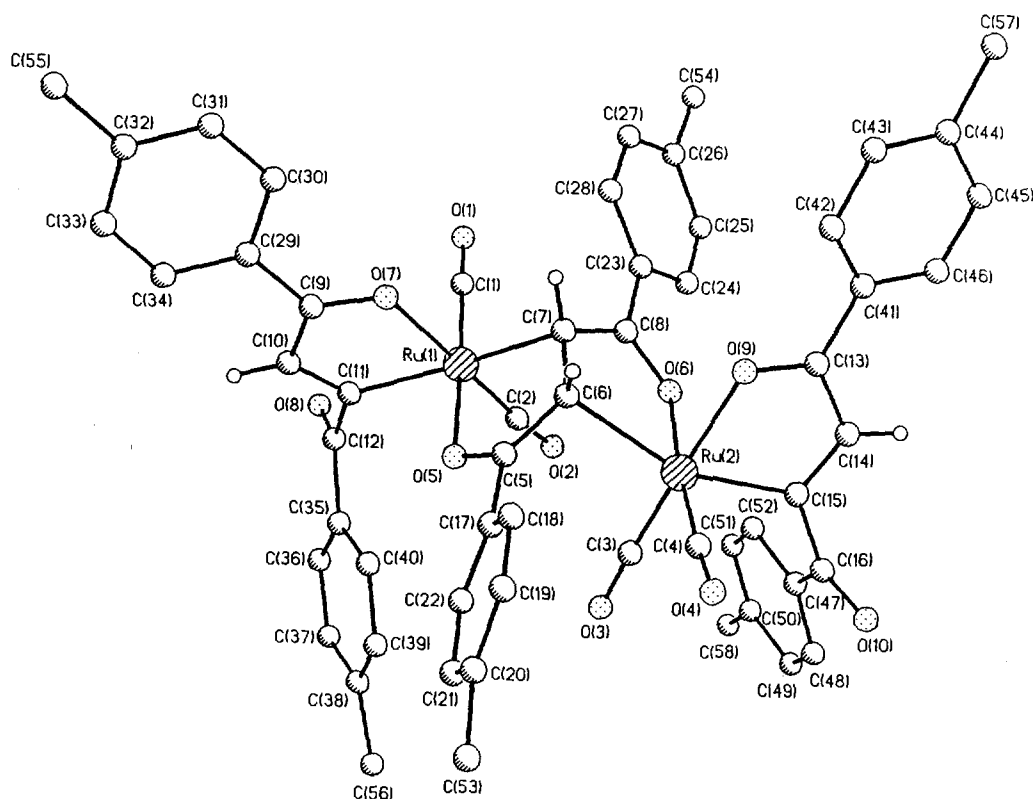


Fig. 2. Molecular structure of complex **3b**.

Table 1
Selected bond lengths (Å) and angles (°) for **2a** and **3b**

	2a		3b	
		A	B	
Ru(1)–C(2)	1.855(4)	1.82(2)	1.84(2)	
Ru(1)–C(1)	1.868(4)	1.87(2)	1.85(2)	
Ru(1)–C(11)	2.043(3)	2.08(1)	2.05(1)	
Ru(1)–O(5)	2.096(2)	2.085(8)	2.094(8)	
Ru(1)–O(7)	2.142(2)	2.116(9)	2.122(9)	
Ru(1)–C(7)	2.301(3)	2.26(1)	2.28(1)	
Ru(2)–C(3)	1.852(4)	1.80(2)	1.85(2)	
Ru(2)–C(4)	1.877(4)	1.85(2)	1.87(2)	
Ru(2)–C(15)	2.074(4)	2.07(1)	2.06(1)	
Ru(2)–O(6)	2.099(2)	2.078(8)	2.079(8)	
Ru(2)–O(9)	2.125(3)	2.105(9)	2.130(8)	
Ru(2)–C(6)	2.286(3)	2.28(1)	2.27(1)	
O(1)–C(1)	1.139(4)	1.16(2)	1.18(2)	
O(2)–C(2)	1.145(4)	1.16(2)	1.15(2)	
O(3)–C(3)	1.135(5)	1.19(2)	1.15(2)	
O(4)–C(4)	1.140(5)	1.16(2)	1.13(2)	
O(5)–C(5)	1.282(4)	1.29(1)	1.30(1)	
O(6)–C(8)	1.291(4)	1.27(2)	1.28(2)	
O(7)–C(9)	1.262(4)	1.26(1)	1.25(1)	
O(8)–C(12)	1.224(4)	1.22(2)	1.22(2)	
O(9)–C(13)	1.256(4)	1.28(2)	1.28(2)	
O(10)–C(16)	1.221(4)	1.23(2)	1.22(2)	
C(5)–C(6)	1.418(5)	1.39(2)	1.38(2)	
C(5)–C(17)	1.481(5)	1.52(2)	1.50(2)	
C(6)–C(7)	1.504(5)	1.52(2)	1.53(2)	
C(7)–C(8)	1.405(5)	1.42(2)	1.42(2)	
C(8)–C(23)	1.500(5)	1.51(2)	1.49(2)	
C(9)–C(10)	1.446(5)	1.46(2)	1.41(2)	
C(9)–C(29)	1.476(5)	1.49(2)	1.45(2)	
C(10)–C(11)	1.347(5)	1.35(2)	1.36(2)	
C(11)–C(12)	1.479(5)	1.49(2)	1.48(2)	
C(12)–C(35)	1.494(5)	1.49(2)	1.47(2)	
C(13)–C(14)	1.440(5)	1.46(2)	1.42(2)	
C(13)–C(41)	1.475(5)	1.49(2)	1.53(2)	
C(14)–C(15)	1.347(5)	1.33(2)	1.30(2)	
C(15)–C(16)	1.488(5)	1.48(2)	1.50(2)	
C(16)–C(47)	1.480(5)	1.48(2)	1.49(2)	
C(2)–Ru(1)–C(1)	86.8(2)	87.1(6)	87.7(6)	
C(2)–Ru(1)–C(11)	95.5(2)	99.8(6)	97.8(5)	
C(1)–Ru(1)–C(11)	88.02(14)	90.4(5)	90.0(5)	
C(2)–Ru(1)–O(5)	99.36(13)	95.9(5)	95.9(5)	
C(1)–Ru(1)–O(5)	173.49(12)	177.0(5)	176.2(5)	
C(11)–Ru(1)–O(5)	89.22(12)	88.6(4)	88.2(4)	
C(2)–Ru(1)–O(7)	173.82(12)	176.8(5)	175.5(5)	
C(1)–Ru(1)–O(7)	93.08(12)	90.8(5)	92.2(5)	
C(11)–Ru(1)–O(7)	78.32(12)	77.9(5)	77.6(4)	
O(5)–Ru(1)–O(7)	80.59(9)	86.3(3)	84.2(3)	
C(2)–Ru(1)–C(7)	99.85(14)	97.5(5)	99.3(5)	
C(1)–Ru(1)–C(7)	102.38(14)	101.4(5)	101.1(5)	
C(11)–Ru(1)–C(7)	161.85(13)	159.5(5)	159.9(5)	
O(5)–Ru(1)–C(7)	78.83(11)	78.8(4)	79.7(4)	
O(7)–Ru(1)–C(7)	86.22(11)	85.1(4)	85.2(4)	
C(3)–Ru(2)–C(4)	89.0(2)	88.6(6)	87.2(6)	
C(3)–Ru(2)–C(15)	97.5(2)	99.1(6)	97.0(6)	
C(4)–Ru(2)–C(15)	90.7(2)	90.2(6)	90.7(6)	
C(3)–Ru(2)–O(6)	89.18(13)	95.9(5)	96.0(5)	
C(4)–Ru(2)–O(6)	178.09(13)	175.0(5)	176.2(5)	
C(15)–Ru(2)–O(6)	90.21(11)	87.0(4)	86.8(4)	
C(3)–Ru(2)–O(9)	174.57(12)	175.6(5)	173.2(5)	
C(4)–Ru(2)–O(9)	92.78(14)	94.9(5)	97.7(5)	

Table 1 (continued)

	2a		3b	
		A	B	
C(15)–Ru(2)–O(9)	77.37(12)	78.3(5)	78.3(4)	
O(6)–Ru(2)–O(9)	89.05(10)	80.5(3)	79.0(3)	
C(3)–Ru(2)–C(6)	92.3(2)	99.8(6)	100.0(6)	
C(4)–Ru(2)–C(6)	100.34(14)	102.3(5)	101.6(5)	
C(15)–Ru(2)–C(6)	165.34(13)	157.5(5)	159.4(5)	
O(6)–Ru(2)–C(6)	79.02(11)	79.1(4)	79.9(4)	
O(9)–Ru(2)–C(6)	92.40(11)	82.0(4)	83.7(4)	
C(5)–O(5)–Ru(1)	116.5(2)	116.8(8)	115.4(8)	
C(8)–O(6)–Ru(2)	116.0(2)	116.2(8)	116.0(8)	
C(9)–O(7)–Ru(1)	112.8(2)	114.3(8)	114.9(9)	
C(13)–O(9)–Ru(2)	114.5(2)	113.2(9)	111.0(8)	
O(1)–C(1)–Ru(1)	178.8(3)	178.0(13)	178.9(12)	
O(2)–C(2)–Ru(1)	174.8(3)	175.0(13)	175.6(13)	
O(3)–C(3)–Ru(2)	177.0(3)	177.0(13)	176.9(13)	
O(4)–C(4)–Ru(2)	177.4(4)	177.2(13)	178.5(13)	
O(5)–C(5)–C(6)	121.0(3)	121.9(12)	122.4(12)	
O(5)–C(5)–C(17)	116.5(3)	114.0(11)	115.4(11)	
C(6)–C(5)–C(17)	122.4(3)	124.0(12)	122.1(12)	
C(5)–C(6)–C(7)	116.7(3)	115.9(11)	117.5(11)	
C(5)–C(6)–Ru(2)	101.3(2)	102.5(8)	101.5(9)	
C(7)–C(6)–Ru(2)	104.9(2)	104.2(8)	104.8(8)	
C(8)–C(7)–C(6)	117.2(3)	116.5(11)	115.6(12)	
C(8)–C(7)–Ru(1)	96.8(2)	101.1(9)	98.1(8)	
C(6)–C(7)–Ru(1)	104.4(2)	106.0(8)	103.9(8)	
O(6)–C(8)–C(7)	121.4(3)	120.4(13)	122.5(13)	
O(6)–C(8)–C(23)	115.6(3)	114.6(12)	116.6(12)	
C(7)–C(8)–C(23)	123.0(3)	124.9(13)	120.9(13)	
O(7)–C(9)–C(10)	118.4(3)	118.6(12)	117.0(13)	
O(7)–C(9)–C(29)	119.5(3)	119.6(12)	117.7(13)	
C(10)–C(9)–C(29)	122.0(3)	121.7(12)	125.3(13)	
C(11)–C(10)–C(9)	116.2(3)	115.0(12)	117.7(13)	
C(10)–C(11)–C(12)	120.7(3)	120.2(12)	124.3(12)	
C(10)–C(11)–Ru(1)	114.1(3)	113.9(10)	112.7(9)	
C(12)–C(11)–Ru(1)	125.1(2)	125.8(10)	122.6(9)	
O(8)–C(12)–C(11)	119.7(3)	117.9(13)	119.2(13)	
O(8)–C(12)–C(35)	121.8(3)	121.8(13)	122.4(13)	
C(11)–C(12)–C(35)	118.5(3)	120.3(12)	118.4(13)	
O(9)–C(13)–C(14)	118.1(3)	117.4(14)	117.8(13)	
O(9)–C(13)–C(41)	118.6(3)	116.5(13)	116.8(12)	
C(14)–C(13)–C(41)	123.3(3)	126.1(13)	125.4(13)	
C(15)–C(14)–C(13)	116.0(3)	116.3(14)	118.6(13)	
C(14)–C(15)–C(16)	120.7(3)	122.3(13)	121.4(12)	
C(14)–C(15)–Ru(2)	113.8(3)	113.2(11)	112.5(10)	
C(16)–C(15)–Ru(2)	125.4(2)	124.5(10)	126.1(9)	
O(10)–C(16)–C(47)	121.9(3)	122.5(13)	121.9(14)	
O(10)–C(16)–C(15)	118.6(3)	117.6(13)	118.1(13)	
C(47)–C(16)–C(15)	119.5(3)	119.9(13)	119.9(13)	

One may believe that formation of the central bicyclic systems proceeds in the same manner as the formation of monocyclic oxaruthenacomplexes, i.e. via insertion of the metal atom into the C(olefin)–H bond with coordination of the ruthenium atom by the ketone oxygen and subsequent hydrogenation of the C=C double bond. However, the bicyclic system is more likely to be produced by the alternative mechanism involving the addition of two carbonylruthenium groups to the olefinic carbon atoms of endiones and subsequent chelating of metal atoms by the ketone oxygen atoms.

All six crystallographically distinct five-membered rings of the central bicyclic systems (there are two independent molecules in the structure of **3b**) have flattened envelope conformations, in good agreement with the conformations of the central five-membered rings observed in the structure of the fumarate complex [5]. However, only in two such cycles (in **2a** and one of the molecules of **3b**), similarly to the complex observed in Ref. [5], is one of the bridgehead atoms in the flap of the envelope (atom C(6) is displaced from Ru(1)O(5)C(5)C(7) by 0.183 and 0.120 Å in **2a** and **3b** respectively). In four other cases the five-membered cycles are folded along the O(5) ··· C(6) and O(6) ··· C(7) lines, the displacements of the C(5) and C(8) atoms from the remaining four atoms in the cycle being in the range 0.085–0.223 Å. The dihedral angles formed by the mean planes of the five-membered rings in the bicyclic systems of each molecule are equal to 74.4 (**2a**) and 76.1 and 78.7° (**3b**).

The conformation and geometry of peripheral oxaruthenacycles in **2a** and **3b** closely resemble those found in the structure of the tetranuclear complex obtained by reaction of Ru₃(CO)₁₂ with enones [1]. These cycles also have the flattened envelope, or in some cases even planar, conformations, the Ru atoms being displaced from the remaining four atoms of the cycles by 0.01–0.31 Å.

As we have already mentioned, the peripheral oxaruthenacycles, in contrast to the metallacycles of the

bicyclic systems, retain the olefinic double bond, which is reflected in the differences between the corresponding bond lengths in the cycles of both types. Thus, the shortening of the single C–C bonds (average value in **2a** and **3b** 1.439 Å whereas the standard C_{sp²}–C_{sp²} bond as reported in Ref. [8] is equal to 1.478 Å) and the Ru–C σ-bonds (2.063 Å av. as compared with the standard 2.092 Å for Ru–C_{sp²} [9]) in the peripheral oxaruthenacycles may indicate a significant contribution of the π-conjugated ruthenafurane form in the bonding in these cycles [1]. At the same time the C(6)–C(7) (1.518 Å av.), C(5)–C(6) or C(7)–C(8) (1.405 Å av.) and C(5)–O(5) or C(8)–O(6) (1.286 Å av.) bond lengths in the central part of the endione ligands show the considerable role of the enolic type of coordination in the bicyclic fragments of the complexes. Such a representation is also corroborated by the shorter Ru–O bonds in the central bicyclic system as compared with the analogous bonds in the peripheral ruthenacycles (corresponding average values 2.089 and 2.123 Å), and somewhat longer Ru–C(carbonyl) bonds in *trans*-positions to the O atoms of the central moiety (1.864 Å av.) in comparison with the Ru–C(carbonyl) bonds in *trans*-positions to the peripheral Ru–O bonds (1.836 Å av.). It is also noteworthy that the Ru–C σ-bonds within the bicyclic system (2.280 Å av.) are much longer than the analogous bonds in the peripheral cycles and the standard Ru–C_{sp³} bonding distance (2.145 Å [9]).

An interesting conformational peculiarity is associ-

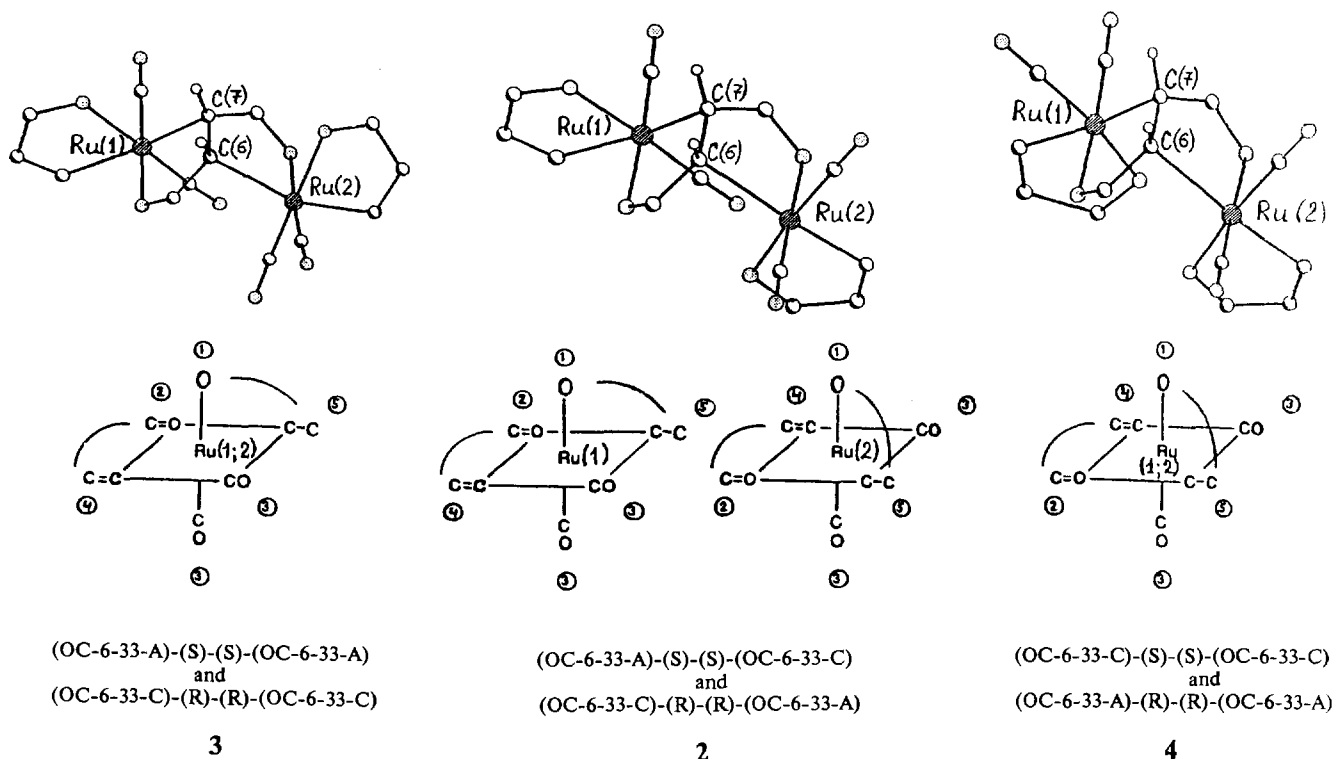


Fig. 3. Configuration descriptors of chiral centres in complexes **2–4**.

Table 2

¹H NMR data for complexes 2–4 in CDCl₃; chemical shifts are given in parts per million, *J* values are in hertz

Compound	–CH=	Aromatic	–CH–	–CH ₃
1a	s, 7.94	m, 7.35–8.05	—	—
1b	s, 7.95	d, 7.26 d, 7.93	—	s, 2.38
2a	s, 7.52 s, 7.69	m, 6.70–8.40	d, 5.64, <i>J</i> _{CH–CH} = 3.0 d, 5.69, <i>J</i> _{CH–CH} = 3.0	—
2b	s, 7.48 s, 7.61	m, 6.40–8.30	d, 5.58, <i>J</i> _{CH–CH} = 3.0 d, 5.62, <i>J</i> _{CH–CH} = 3.0	s, 2.25; s, 2.29; s, 2.32 s, 2.36; s, 2.39; s, 2.53
3a	s, 7.56	m, 7.20–8.50	s, 5.72	—
3b	s, 7.51	m, 7.10–8.15	s, 5.66	s, 2.29; s, 2.34; s, 2.36
4a	s, 7.64 s, 7.73	m, 6.70–8.40	d, 5.40, <i>J</i> _{CH–CH} = 2.6 d, 5.59, <i>J</i> _{CH–CH} = 2.6	—
4b	s, 7.12 s, 7.47	m, 6.90–8.10	d, 5.38, <i>J</i> _{CH–CH} = 2.5 d, 5.58, <i>J</i> _{CH–CH} = 2.5	s, 2.26; s, 2.29 s, 2.33; s, 2.35; s, 2.40

ated with the orientation of aryl and aroyl substituents relative to the metallacyclic fragments. In all cases in three independent molecules, each one containing four aryl and two aroyl substituents, the aryl planes are approximately coplanar with the corresponding metallacycles (the dihedral angles are in the range 12.0–38.6°), whereas the planes of aroyl substituents are almost perpendicular to the mean planes of the metallacycles (the range of the dihedral angles is 62.3–84.0°).

The ¹H NMR and IR data for complexes 2–4 are summarized in Tables 2 and 3. The spectral characteristics obtained are most exhaustive and clear for complexes **2b**, **3b** and **4b** with *p*-tolyl substituents in the ligands, as these complexes are more easily obtained in the individual form and their ¹H NMR spectra are much more informative than those of their phenyl analogues **2a**, **3a** and **4a**.

The spectra of complexes **2** and **3** are in good agreement with their structure. Thus, the equivalence of the coordination environments of both Ru atoms in **3** determines the simple character of the ¹H NMR spectra of these compounds. Thus, the hydrogens at the bridgehead carbon atoms in the bicyclic system give rise to singlets at $\delta = 5.66$ and 5.72 ppm in **3a** and **3b** respectively, and the H atoms at olefinic bonds in the peripheral oxaruthenacycles correspond to the singlets at $\delta = 7.56$ (**3a**) and 7.51 ppm (**3b**). Three pairs of equivalent methyl groups in **3b** correspond to three singlets of

equal intensity in its ¹H NMR spectrum. The differences in the chemical shifts between the chemically equivalent methyl hydrogens, H atoms of the central bicyclic system and peripheral oxaruthenacycles of **4** may probably be accounted for by the different orientations of the corresponding aromatic substituents relative to their respective metallacycles.

The results reported in the present paper show that the products of the reactions of Ru₃(CO)₁₂ with enediones are not so numerous and structurally diversified as the products of reactions of this cluster with enones.

Table 4
Crystal and structure refinement data for **2a** and **3b**

Compound	2a	3b
Formula	C ₅₂ H ₃₄ Ru ₂ O ₁₀	C ₅₈ H ₄₆ Ru ₂ O ₁₀
Formula weight	1020.93	1105.09
Temperature (K)	188(2)	153(2)
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	12.600(5)	14.047(5)
<i>b</i> (Å)	13.587(6)	31.439(10)
<i>c</i> (Å)	13.728(6)	24.050(8)
α (°)	88.97(3)	—
β (°)	89.80(3)	98.83(3)
γ (°)	70.95(3)	—
<i>V</i> (Å ³)	2221(2)	10495(6)
<i>Z</i>	2	8
<i>d</i> _{calc} (g cm ⁻³)	1.527	1.399
Radiation	Mo K α	Mo K α
μ (cm ⁻¹)	7.41	6.33
<i>F</i> (000)	1028	4496
Diffractionmeter	Syntex P2 ₁	Siemens P3/PC
Scan type	θ -2 θ	θ -2 θ
θ _{max} (°)	25.05	23.05
Independent reflections	7457	12112
Observed reflections (<i>I</i> > 2 σ (<i>I</i>))	5930	6809
Number of parameters	713	1286
Goodness-of-fit	1.050	1.130
<i>R</i> ₁ (observed reflections)	0.0339	0.0788
<i>wR</i> ₂ (all data)	0.0942	0.2256

Table 3

The CO bands in the IR spectra of complexes 2–4 in solution

Compound	ν (cm ⁻¹) (solvent)
2a	2036vs, 1976s, 1970s (CH ₂ Cl ₂)
2b	2042vs, 1986s, 1980s (heptane)
3a	2036vs, 1982s, 1966s (CH ₂ Cl ₂) 2045sh, 2040vs, 1990s, 1975s (heptane)
3b	2048sh, 2038vs, 1988s, 1974s (heptane)
4a	2035vs, 2024s, 1977s, 1952s (CH ₂ Cl ₂)
4b	2036vs, 2020s, 1976s, 1950s (CH ₂ Cl ₂)

Table 5

Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for **2a**

Atom	x	y	z	U_{eq}
Ru(1)	3395(1)	7873(1)	2812(1)	23(1)
Ru(2)	2987(1)	4928(1)	3413(1)	24(1)
O(1)	5079(2)	8356(2)	1493(2)	43(1)
O(2)	2619(2)	7099(2)	1007(2)	39(1)
O(3)	4810(3)	3065(2)	4179(2)	51(1)
O(4)	1441(3)	4486(3)	4915(2)	59(1)
O(5)	2248(2)	7670(2)	3841(2)	27(1)
O(6)	4127(2)	5182(2)	2402(2)	26(1)
O(7)	3852(2)	8616(2)	4028(2)	28(1)
O(8)	2003(2)	9716(2)	943(2)	44(1)
O(9)	1684(2)	6150(2)	2727(2)	30(1)
O(10)	2185(2)	2526(2)	2668(2)	47(1)
C(1)	4447(3)	8162(3)	1991(2)	29(1)
C(2)	2890(3)	7369(3)	1722(3)	28(1)
C(3)	4124(3)	3788(3)	3908(3)	33(1)
C(4)	2007(3)	4675(3)	4344(3)	37(1)
C(5)	2607(3)	6882(3)	4423(2)	26(1)
C(6)	3625(3)	6071(3)	4237(2)	25(1)
C(7)	4434(3)	6326(3)	3549(2)	24(1)
C(8)	4712(3)	5744(2)	2695(2)	24(1)
C(9)	3286(3)	9570(3)	4075(2)	27(1)
C(10)	2498(3)	10033(3)	3299(3)	31(1)
C(11)	2391(3)	9382(3)	2606(2)	27(1)
C(12)	1623(3)	9776(3)	1770(3)	30(1)
C(13)	1227(3)	5871(3)	2019(2)	27(1)
C(14)	1592(3)	4782(3)	1789(3)	30(1)
C(15)	2395(3)	4149(3)	2370(2)	27(1)
C(16)	2748(3)	2998(3)	2271(3)	30(1)
C(17)	1893(3)	6859(3)	5277(3)	31(1)
C(18)	2362(4)	6449(3)	6172(3)	40(1)
C(19)	1688(4)	6443(4)	6965(3)	50(1)
C(20)	536(4)	6822(4)	6864(4)	57(1)
C(21)	66(4)	7211(4)	5987(4)	60(1)
C(22)	738(4)	7252(4)	5191(3)	44(1)
C(23)	5703(3)	5715(3)	2074(2)	27(1)
C(24)	5806(3)	5281(3)	1161(3)	38(1)
C(25)	6710(4)	5238(4)	567(3)	48(1)
C(26)	7512(4)	5648(3)	890(3)	50(1)
C(27)	7442(4)	6062(3)	1795(4)	48(1)
C(28)	6543(3)	6092(3)	2396(3)	36(1)
C(29)	3390(3)	10161(3)	4940(3)	30(1)
C(30)	3871(4)	9631(3)	5784(3)	39(1)
C(31)	3883(4)	10174(4)	6620(3)	51(1)
C(32)	3427(4)	11240(4)	6620(3)	51(1)
C(33)	2997(5)	11777(4)	5775(4)	63(1)
C(34)	2975(4)	11237(3)	4937(3)	52(1)
C(35)	394(3)	10238(3)	1964(3)	31(1)
C(36)	-59(3)	10155(3)	2872(3)	41(1)
C(37)	-1197(4)	10615(4)	3039(4)	53(1)
C(38)	-1882(4)	11157(4)	2285(4)	54(1)
C(39)	-1439(4)	11236(4)	1380(4)	49(1)
C(40)	-313(3)	10773(3)	1217(3)	39(1)
C(41)	317(3)	6666(3)	1490(3)	31(1)
C(42)	25(4)	6528(3)	540(3)	41(1)
C(43)	-822(4)	7293(4)	57(4)	52(1)
C(44)	-1405(4)	8200(3)	536(4)	52(1)
C(45)	-1119(4)	8348(3)	1471(4)	50(1)
C(46)	-256(3)	7600(3)	1945(3)	40(1)
C(47)	3774(3)	2457(3)	1715(2)	27(1)
C(48)	4019(4)	1410(3)	1500(3)	36(1)
C(49)	4968(4)	893(3)	983(3)	40(1)

Table 5 (continued)

Atom	x	y	z	U_{eq}
C(50)	5694(3)	1400(3)	668(3)	40(1)
C(51)	5456(3)	2437(3)	870(3)	41(1)
C(52)	4507(3)	2967(3)	1390(3)	36(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

One may suggest that a such difference in chemical behaviour may be associated with the more symmetrical structure of endiones as compared with that of enones.

3. Experimental

All reactions were carried out in Ar atmosphere using absolute solvents. **1a** and **1b** were prepared according to Ref. [10].

3.1. Reaction of $\text{Ru}_3(\text{CO})_{12}$ with **1a**

A mixture of 130 mg (0.2 mmol) of $\text{Ru}_3(\text{CO})_{12}$ and 240 mg (1 mmol) of **1a** in 100 ml of heptane was refluxed for 5 h. After cooling, the reaction mixture was filtered and 160 mg of yellow precipitate was collected. This precipitate was chromatographed in a thin layer of silica gel, using a heptane/ CHCl_3 (3:1) mixture as eluent. The first yellow zone was collected and chromatographed again on silica gel, using a heptane/ CHCl_3 (8:1) mixture as eluent. Three yellow zones obtained yielded the complexes **2a**, **3a** and **4a**. ^1H NMR and IR spectral data for **2a**, **3a** and **4a** are given in Tables 2 and 3. The elemental analysis of the mixture of isomers was carried out before their chromatographic resolution. Anal. Found: C, 62.19; H, 3.45. $\text{C}_{52}\text{H}_{34}\text{O}_{10}\text{Ru}_2$ Calc.: C, 61.11; H, 3.55%. **2a** Anal. Found: C, 61.75; H, 3.78. $\text{C}_{52}\text{H}_{34}\text{O}_{10}\text{Ru}_2$ Calc.: C, 61.11; H, 3.55%.

3.2. Reaction of $\text{Ru}_3(\text{CO})_{12}$ with **1b**

A mixture of 260 mg (0.4 mmol) of $\text{Ru}_3(\text{CO})_{12}$ and 530 mg (2 mmol) of **1b** in 180 ml of heptane was refluxed for 4 h. After cooling, the reaction mixture was filtered and 230 mg of yellow precipitate was collected. This precipitate was chromatographed on a silica gel column, using a heptane/ CHCl_3 (8:1) mixture as eluent. The three yellow fractions were isolated and the solvent was evaporated. 50 mg (7.5%) of compound **2b**, 80 mg (12.1%) of **3b**, and 30 mg (4.5%) of **4b** were obtained. ^1H NMR and IR spectral data for **2b**, **3b** and **4b** are given in Tables 2 and 3. The elemental analysis of the mixture of isomers was carried out before their chromatographic resolution. Anal. Found: C, 61.25; H, 4.36. $\text{C}_{58}\text{H}_{46}\text{O}_{10}\text{Ru}_2$ Calc.: C, 63.03; H, 4.20%.

Table 6

Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for **3b**

Atom	x	y	z	U_{eq}
Ru(1A)	4029(1)	4461(1)	3223(1)	26(1)
Ru(2A)	5450(1)	3806(1)	4765(1)	25(1)
O(1A)	5064(7)	4833(3)	2321(4)	47(3)
O(2A)	4840(8)	3638(3)	2900(4)	49(3)
O(3A)	4093(7)	3151(3)	4193(4)	48(3)
O(4A)	4759(8)	3592(4)	5855(4)	59(3)
O(5A)	3279(6)	4227(3)	3842(3)	25(2)
O(6A)	6063(6)	3973(3)	4063(3)	23(2)
O(7A)	3463(6)	5064(3)	3389(3)	30(2)
O(8A)	2535(8)	4219(3)	1752(4)	56(3)
O(9A)	6491(6)	4243(3)	5140(4)	30(2)
O(10A)	6649(7)	2759(3)	5439(4)	40(3)
C(1A)	4668(11)	4698(4)	2671(6)	33(4)
C(2A)	4498(10)	3948(5)	3038(5)	32(4)
C(3A)	4623(10)	3419(5)	4410(6)	36(4)
C(4A)	5001(10)	3671(5)	5429(6)	37(4)
C(5A)	3685(9)	4271(4)	4357(6)	25(3)
C(6A)	4630(9)	4415(4)	4495(5)	23(3)
C(7A)	5100(9)	4580(4)	4008(5)	27(3)
C(8A)	5909(10)	4350(5)	3885(6)	31(4)
C(9A)	2647(10)	5142(4)	3110(5)	27(3)
C(10A)	2192(10)	4819(4)	2718(5)	29(4)
C(11A)	2735(9)	4471(5)	2669(5)	29(4)
C(12A)	2410(10)	4146(5)	2232(6)	34(4)
C(13A)	7343(11)	4089(5)	5225(5)	35(4)
C(14A)	7442(10)	3630(4)	5165(5)	28(3)
C(15A)	6635(10)	3415(5)	4992(5)	33(4)
C(16A)	6602(9)	2944(4)	4985(6)	31(4)
C(17A)	3057(9)	4135(4)	4787(5)	25(3)
C(18A)	3140(9)	4311(4)	5312(5)	27(3)
C(19A)	2595(11)	4167(5)	5709(6)	40(4)
C(20A)	1959(10)	3826(5)	5572(6)	34(4)
C(21A)	1859(10)	3655(4)	5040(5)	32(4)
C(22A)	2398(9)	3811(4)	4651(5)	28(3)
C(23A)	6603(9)	4508(5)	3511(5)	27(3)
C(24A)	7214(9)	4219(5)	3314(5)	32(4)
C(25A)	7861(10)	4359(4)	2984(5)	33(4)
C(26A)	7964(9)	4781(4)	2843(6)	29(4)
C(27A)	7351(10)	5066(4)	3060(6)	32(4)
C(28A)	6679(10)	4936(4)	3372(6)	30(4)
C(29A)	2204(10)	5571(4)	3154(6)	31(4)
C(30A)	2804(12)	5904(4)	3368(6)	38(4)
C(31A)	2413(14)	6313(5)	3412(6)	52(5)
C(32A)	1432(13)	6389(6)	3250(7)	53(5)
C(33A)	874(12)	6044(6)	3034(6)	53(5)
C(34A)	1227(11)	5651(5)	2991(6)	44(4)
C(35A)	1967(10)	3741(4)	2388(5)	30(4)
C(36A)	1596(11)	3461(5)	1970(6)	46(4)
C(37A)	1243(11)	3074(5)	2119(6)	46(4)
C(38A)	1238(10)	2944(5)	2666(6)	42(4)
C(39A)	1578(11)	3244(5)	3077(6)	46(4)
C(40A)	1962(11)	3640(5)	2946(6)	49(5)
C(41A)	8144(9)	4396(4)	5399(5)	27(3)
C(42A)	7945(11)	4802(5)	5516(6)	36(4)
C(43A)	8682(12)	5091(5)	5662(6)	49(5)
C(44A)	9627(11)	4982(5)	5715(6)	38(4)
C(45A)	9823(12)	4557(6)	5618(7)	58(5)
C(46A)	9089(11)	4263(5)	5452(6)	44(4)
C(47A)	6491(9)	2715(5)	4443(6)	30(4)
C(48A)	6366(11)	2279(5)	4448(7)	48(4)
C(49A)	6279(12)	2060(5)	3944(7)	57(5)

Table 6 (continued)

Atom	x	y	z	U_{eq}
C(50A)	6282(12)	2265(5)	3431(7)	53(5)
C(51A)	6385(11)	2698(5)	3440(6)	51(5)
C(52A)	6491(10)	2931(4)	3937(6)	33(4)
C(53A)	1377(9)	3644(5)	6010(5)	37(4)
C(54A)	8731(11)	4930(5)	2510(6)	48(4)
C(55A)	1021(14)	6832(5)	3324(7)	82(7)
C(56A)	910(11)	2516(5)	2810(6)	58(5)
C(57A)	10420(11)	5300(5)	5876(7)	62(5)
C(58A)	6156(14)	2012(6)	2880(7)	87(7)
Ru(1B)	-1386(1)	6004(1)	1001(1)	26(1)
Ru(2B)	-634(1)	6971(1)	-147(1)	25(1)
O(1B)	2(7)	5402(3)	1694(4)	45(3)
O(2B)	-273(7)	6701(3)	1646(4)	46(3)
O(3B)	-1538(7)	7417(3)	743(4)	47(3)
O(4B)	-1941(7)	7496(3)	-979(4)	46(3)
O(5B)	-2417(6)	6385(3)	514(4)	26(2)
O(6B)	352(6)	6611(3)	391(3)	24(2)
O(7B)	-2215(7)	5492(3)	607(4)	34(2)
O(8B)	-1842(8)	5954(3)	2504(4)	47(3)
O(9B)	150(7)	6672(3)	-731(3)	28(2)
O(10B)	372(7)	8140(3)	-218(4)	48(3)
C(1B)	-530(11)	5637(5)	1422(6)	34(4)
C(2B)	-725(11)	6445(5)	1388(6)	32(4)
C(3B)	-1175(11)	7240(5)	413(6)	38(4)
C(4B)	-1460(11)	7296(5)	-663(6)	32(4)
C(5B)	-2270(9)	6454(4)	3(5)	23(3)
C(6B)	-1428(9)	6339(4)	-184(5)	24(3)
C(7B)	-747(10)	6040(4)	189(5)	28(4)
C(8B)	166(10)	6214(5)	416(5)	29(3)
C(9B)	-2877(10)	5366(4)	861(6)	29(4)
C(10B)	-2997(10)	5583(4)	1361(6)	33(4)
C(11B)	-2366(9)	5901(4)	1538(5)	25(3)
C(12B)	-2306(10)	6117(5)	2091(6)	33(4)
C(13B)	967(11)	6853(5)	-730(5)	32(4)
C(14B)	1118(10)	7256(5)	-461(6)	33(4)
C(15B)	468(9)	7399(4)	-177(5)	21(3)
C(16B)	552(9)	7832(5)	87(6)	34(4)
C(17B)	-3063(9)	6687(4)	-366(5)	23(3)
C(18B)	-3334(10)	659-7(5)	-936(5)	34(4)
C(19B)	-4034(10)	6828(5)	-1258(5)	35(4)
C(20B)	-4479(10)	7183(5)	-1039(6)	35(4)
C(21B)	-4240(10)	7255(4)	-466(6)	37(4)
C(22B)	-3544(9)	7008(5)	-132(6)	32(4)
C(23B)	966(10)	5935(5)	681(5)	28(3)
C(24B)	1692(10)	6142(5)	1053(7)	49(4)
C(25B)	2455(12)	5906(6)	1333(7)	65(5)
C(26B)	2527(11)	5473(5)	1247(8)	47(5)
C(27B)	1822(14)	-5288(5)	877(7)	54(5)
C(28B)	1038(11)	5511(5)	589(6)	43(4)
C(29B)	-3444(10)	5005(4)	628(5)	29(4)
C(30B)	-3091(11)	4725(5)	278(6)	42(4)
C(31B)	-3594(12)	-4383(5)	49(6)	47(4)
C(32B)	-4491(14)	4288(5)	150(7)	56(5)
C(33B)	-4849(13)	4555(5)	520(8)	62(5)
C(34B)	-4352(11)	4914(5)	754(6)	45(4)
C(35B)	-2778(10)	6534(4)	2112(5)	31(4)
C(36B)	-2760(12)	6734(6)	2616(6)	52(5)
C(37B)	-3135(11)	7138(6)	2652(7)	56(5)
C(38B)	-3548(11)	7350(5)	2174(6)	47(4)
C(39B)	-3596(10)	7139(5)	1656(6)	40(4)
C(40B)	-3199(10)	6745(5)	1621(6)	39(4)
C(41B)	1710(10)	6611(5)	-1013(5)	34(4)
C(42B)	2610(10)	6774(5)	-1003(6)	40(4)

Table 6 (continued)

Atom	x	y	z	U_{eq}
C(43B)	3288(11)	6542(6)	1251(6)	52(5)
C(44B)	3057(11)	6160(6)	-1505(6)	44(4)
C(45B)	2157(11)	5992(4)	-1494(6)	38(4)
C(46B)	1464(11)	6223(5)	-1254(6)	42(4)
C(47B)	794(9)	7874(5)	709(6)	37(4)
C(48B)	737(13)	8267(5)	961(8)	62(5)
C(49B)	994(16)	8307(7)	1535(10)	92(8)
C(50B)	1245(16)	7964(8)	1864(8)	85(8)
C(51B)	1305(12)	7566(6)	1618(7)	66(6)
C(52B)	1083(10)	7510(5)	1034(6)	44(4)
C(53B)	-5182(11)	7453(5)	-1408(6)	52(5)
C(54B)	3389(12)	5220(6)	1536(8)	83(7)
C(55B)	-5046(13)	3897(5)	-87(8)	75(6)
C(56B)	-3930(12)	7797(5)	2206(6)	58(5)
C(57B)	3778(10)	5930(5)	-1786(7)	57(5)
C(58B)	1532(16)	8016(7)	2501(7)	116(9)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

3.3. Spectroscopic studies

^1H and ^{13}C NMR spectra were recorded on a Bruker WP-200SY spectrometer at 200.13 and 50.31 MHz (for ^1H and ^{13}C respectively). IR spectra were registered with a Specord 75IR in heptane solutions.

3.4. X-ray diffraction studies

Crystals of **2a** and **3b** were grown from their solutions in CH_2Cl_2 /heptane or CHCl_3 /heptane mixtures by slow evaporation of the solvents in a refrigerator at $+5^\circ\text{C}$. Details of crystal parameters, data collection and structure refinement for complexes **2a** and **3b** are given in Table 4. The structures were solved by direct methods and refined by the SHELXTL-PLUS 5 program (gamma version). H atoms in **2a** were located in the difference Fourier synthesis and included in the refinement in the isotropic approximation; H atoms in **3b** were placed in geometrically calculated positions and

refined in the riding model approximation. The coordinates of non-hydrogen atoms in the structures of **2a** and **3b** are given in Tables 5 and 6 respectively. Tables of hydrogen atoms coordinates, anisotropic thermal parameters, and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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