Formation and structure of diruthenium complexes $Ru_2(CO)_{6-n}(PPh_3)_n\{\mu\text{-}C(CH{=}CHPh)C(Ph)C(CH{=}CHPh)C(Ph)\}$ (n = 1, 2)

V. I. Zdanovich, V. Yu. Lagunova, F. M. Dolgushin, A. I. Yanovsky, M. G. Ezernitskaya, P. V. Petrovskii, and A. A. Koridze**

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: +7 (095) 135 5085. E-mail: koridz@ineos.ac.ru

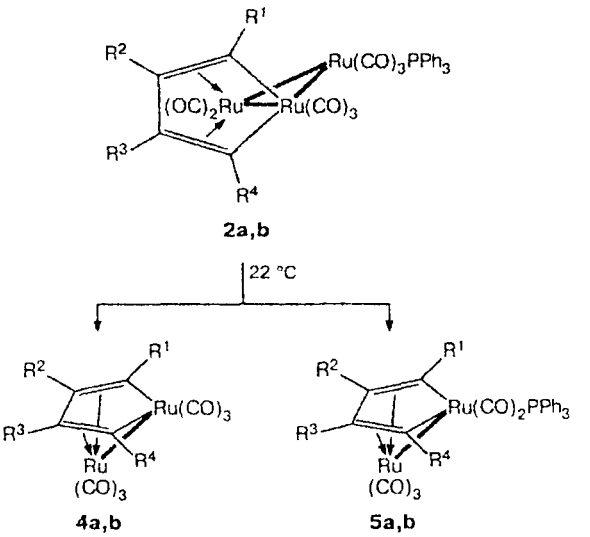
Ruthenium carbonyl triphenylphosphine complexes $Ru_2(CO)_{6-n}(PPh_3)_n\{\mu\text{-}C(CH{=}CHPh)C(Ph)C(CH{=}CHPh)C(Ph)\}$ (n = 1, 2) were obtained by the reaction of complex $Ru_2(CO)_6\{\mu\text{-}C(CH{=}CHPh)C(Ph)C(CH{=}CHPh)C(Ph)\}$ containing the ruthenacyclopentadiene moiety with PPh_3 in refluxing toluene. The complexes were characterized by IR and by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, and by X-ray analysis. The monophosphine derivative is identical to the complex formed by fragmentation of the $Ru_3(CO)_8(PPh_3)\{\mu\text{-}C(CH{=}CHPh)C(Ph)C(CH{=}CHPh)C(Ph)\}$ cluster and contains the PPh_3 ligand at the ruthenium atom of the ruthenacyclopentadiene moiety.

Key words: ruthenium clusters, ruthenium complexes, ruthenacyclopentadienes, ruthenium carbonyl phosphines; IR spectra, ^1H, ^{13}C, and ^{31}P NMR spectra; X-ray analysis.

Recently,[1] we have shown that in the reaction between the triruthenium cluster $Ru_3(CO)_8\{\mu_3\text{-}C(CH{=}CHPh)C(Ph)C(CPh)C(CH{=}CHPh)\}$ (**1a**), containing the ruthenacyclopentadiene moiety, and PPh_3 the phosphine ligand replaces the π-coordinated alkenyl group in the coordination sphere of the Ru atom to give the labile cluster $Ru_3(CO)_8(PPh_3)\{\mu\text{-}C(CH{=}CHPh)C(Ph)C(Ph)C(CH{=}CHPh)\}$ (**2a**). This cluster loses a PPh_3 or CO group even at room temperature in benzene to form triruthenium cluster **1a** or its phosphine derivative $Ru_3(CO)_7(PPh_3)\{\mu_3\text{-}C(CH{=}CHPh)C(Ph)C(Ph)C(CH{=}CHPh)\}$ (**3a**), respectively. Fragmentation of the trinuclear cluster also occurs under the same conditions, and the reaction mixture contains diruthenium complexes $Ru_2(CO)_5L\{\mu\text{-}C(CH{=}CHPh)C(Ph)C(Ph)C(CH{=}CHPh)\}$ (L = CO (**4a**),[2] PPh_3 (**5a**),[1] Scheme 1), whose fraction increases as the duration of the reaction increases, along with clusters **1a**, **2a**, and **3a**.

The reaction between cluster $Ru_3(CO)_8\{\mu_3\text{-}C(CH{=}CHPh)C(Ph)C(CH{=}CHPh)C(Ph)\}$ (**1b**) (in contrast to cluster **1a**, the dienediyl ligand in complex **1b** is formed by coupling of two 1,4-diphenylbut-1-en-3-yne molecules according to the "head-to-tail" type) and triphenylphosphine occurs analogously to give diruthenium complexes $Ru_2(CO)_5L\{\mu\text{-}C(CH{=}CHPh)C(Ph)C(CH{=}CHPh)C(Ph)\}$ (L = CO (**4b**), PPh_3 (**5b**), see Scheme 1). Complexes **5a** and **5b** exhibit rather similar spectroscopic (IR and ^{31}P NMR) characteristics, which suggests their analogous structure.

Scheme 1



a: $R^1 = R^4$ = CH=CHPh, $R^2 = R^3$ = Ph
b: $R^1 = R^3$ = CH=CHPh, $R^2 = R^4$ = Ph

Since in the initial triruthenium clusters the PPh_3 ligand is coordinated to neither of the two Ru atoms bound to dienediyl, it was unclear to which site it is coordinated in diruthenium complexes **5a** and **5b**.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 1836—1843, September, 1998.

1066-5285/98/4709-1789 $20.00

The known monophosphine derivatives of iron[3,4] and ruthenium[5,6] complexes of the ferrole type were obtained by replacing the CO group by a phosphine ligand, and, as was shown in the X-ray diffraction studies of complexes $Fe_2(CO)_5(PPh_3)(\mu\text{-}C_4Ph_4)$ [4] and $Ru_2(CO)_5(PMe_3)\{\mu\text{-}C_{21}H_{17}N\}$,[5] the phosphine ligand in these compounds is coordinated to the metal atom of the metallacycle.

It made sense to compare the structures of triphenylphosphine derivatives of complexes **4a** or **4b** obtained by thermal reactions with triphenylphosphine and those of complexes **5a** and **5b** formed by fragmentation of triruthenium clusters. In this work, we synthesized complexes **5b** and $Ru_2(CO)_4(PPh_3)_2\{\mu\text{-}C(CH{=}CHPh)C(Ph)C(CH{=}CHPh)C(Ph)\}$ (**6**) by the reaction of compound **4b** with PPh_3 and showed that monophosphine derivatives of diruthenium complexes obtained both by substitution of the CO group by PPh_3 in isomeric complexes $Ru_2(CO)_6\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ and by fragmentation of corresponding triruthenium clusters $Ru_3(CO)_8(PPh_3)\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ contain the PPh_3 ligand coordinated to the Ru atom of the ruthenacycle.

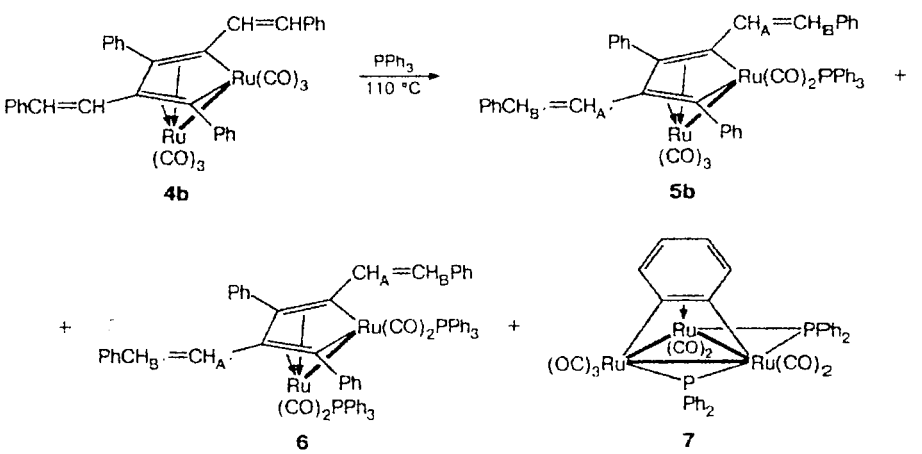
Results and Discussion

The reaction between equimolecular amounts of complex **4b** and PPh_3 was carried out in refluxing toluene. The products of the reaction are the yellow complexes **5b** (the main product) and **6**, and the known red cluster $Ru_3(CO)_7(\mu\text{-}PPh_2)_2(\mu_3\text{-}C_6H_4)$ (**7**) (Scheme 2). The last compound was obtained previously by pyrolysis of complex $Ru_3(CO)_9(PPh_3)_3$ in refluxing decane and characterized by X-ray analysis.[7,8] The reaction of complex **4b** with PPh_3 is accompanied by its partial fragmentation with the formation of $Ru_3(CO)_{12}$ which reacts with PPh_3 to give complex $Ru_3(CO)_9(PPh_3)_3$, which is a precursor of cluster **7**.

The IR spectrum of complex **5b** in hexane contains the νCO absorption bands at 2056 (sh), 2044 (s), 2008 (s), 1988 (s), and 1957 (sh) cm^{-1}. Its ^1H NMR spectrum (C_6D_6, 22 °C) contains signals of ethylene protons at δ 5.87 (d, J = 16.7 Hz), 6.36 (d, J = 15.6 Hz), and 6.59 (d, J = 16.7 Hz) and a broad multiplet of seven Ph groups at δ 6.8—7.8 superimposed on the signal of the ethylene hydrogen atom. A singlet at δ 47.98 is observed in the ^{31}P NMR spectrum of complex **5b**. The asymmetric binuclear complex with the PPh_3 ligand, which is formed by fragmentation of the corresponding triruthenium cluster, has the same spectral characteristics. Therefore, the complexes of composition $Ru_2(CO)_5(PPh_3)\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ obtained using two different methods are identical.

The ^{13}C NMR data (C_6D_6, 22 °C) indicate the coordination site of the PPh_3 ligand in complex **5b**. Three doublets at δ 202.84 (J_{CP} = 8.0 Hz), 200.65 (J_{CP} = 8.4 Hz), and 199.66 (J_{CP} = 11.6 Hz) with the ratio of relative integrated intensities 3 : 1 : 1 are observed in the carbonyl region of the ^{13}C NMR spectrum. As is known,[4,9] the carbonyl groups in the ^{13}C NMR spectra of complexes of the ferrole type $M_2(CO)_6(C_4R_4)$ (M = Fe, Ru, Os) manifest themselves as three signals with the intensity ratio 3 : 1 : 2, and the signal with intensity 3 is due to the CO groups at the metal atom π-coordinated to the hydrocarbon ligand. Averaging of the signals of the three CO groups mentioned above is due to a permutation process. Hence, the presence of the signal with intensity 3 at δ 202.84 in the ^{13}C NMR spectrum of complex **5b** indicates the presence of the $Ru(CO)_3$ group π-coordinated to the diene system in this compound. In such a situation, the PPh_3 ligand should be coordinated to the Ru atom of the ruthenacycle; most likely, it is in the sterically less hindered axial position. The magnetic nonequivalence of two CO ligands at the same Ru atom is a consequence of the asymmetric structure of the dienediyl ligand.

Scheme 2



4b **5b** **6** **7**

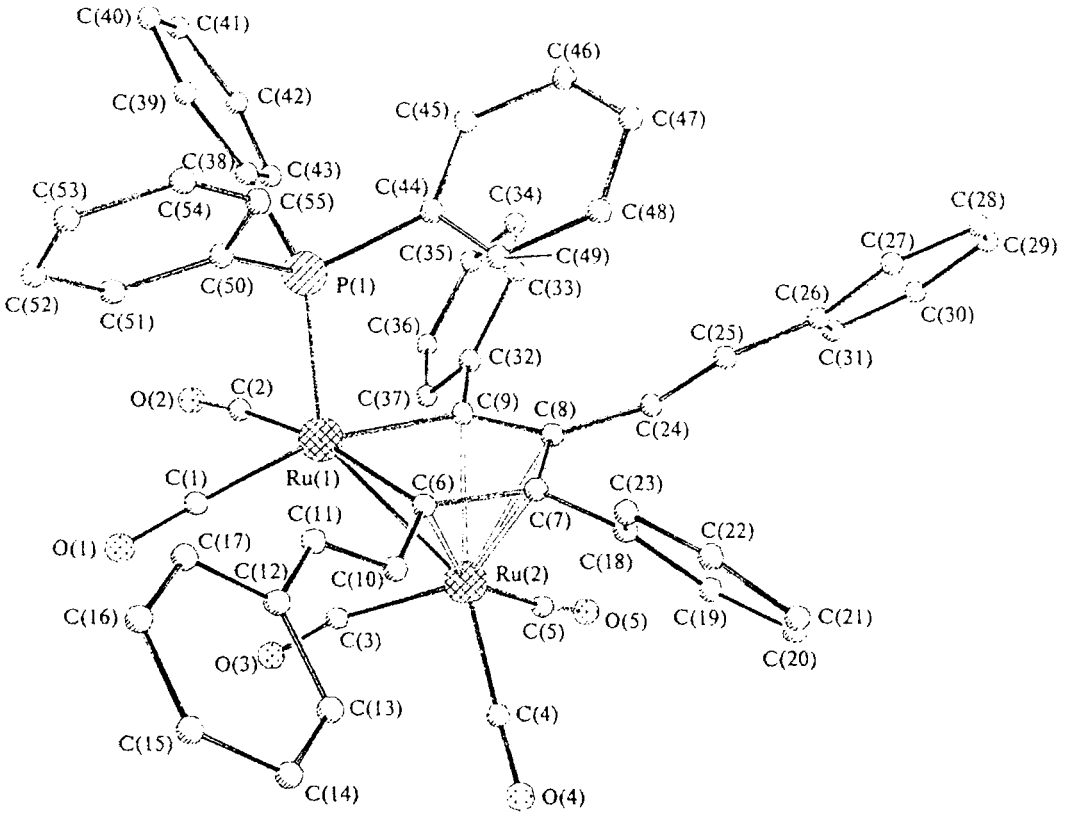


Fig. 1. Molecular structure of complex $Ru_2(CO)_5(PPh_3)\{\mu$-C(CH=CHPh)C(Ph)C(CH=CHPh)C(Ph)$\}$ (**5b**).

Table 1. Selected bond lengths (d) and bond angles (ω) in complex **5b**

Bond	d/Å	Bond	d/Å	Bond	d/Å	Bond	d/Å
Ru(1)—C(1)	1.929(7)	Ru(2)—C(3)	1.914(7)	O(1)—C(1)	1.144(7)	C(7)—C(18)	1.499(8)
Ru(1)—C(2)	1.930(7)	Ru(2)—C(9)	2.233(6)	O(2)—C(2)	1.147(8)	C(8)—C(9)	1.428(8)
Ru(1)—C(6)	2.074(6)	Ru(2)—C(8)	2.275(6)	O(3)—C(3)	1.157(8)	C(8)—C(24)	1.476(8)
Ru(1)—C(9)	2.112(6)	Ru(2)—C(7)	2.279(5)	O(4)—C(4)	1.145(8)	C(9)—C(32)	1.485(8)
Ru(1)—P(1)	2.306(2)	Ru(2)—C(6)	2.283(6)	O(5)—C(5)	1.144(8)	C(10)—C(11)	1.334(8)
Ru(1)—Ru(2)	2.7340(8)	P(1)—C(38)	1.833(6)	C(6)—C(7)	1.459(8)	C(11)—C(12)	1.466(8)
Ru(2)—C(5)	1.907(7)	P(1)—C(50)	1.833(6)	C(6)—C(10)	1.491(8)	C(24)—C(25)	1.309(9)
Ru(2)—C(4)	1.911(8)	P(1)—C(44)	1.841(6)	C(7)—C(8)	1.454(8)	C(25)—C(26)	1.486(9)
Angle	**ω/deg**	**Angle**	**ω/deg**	**Angle**	**ω/deg**	**Angle**	**ω/deg**
C(1)—Ru(1)—C(2)	87.5(3)	C(5)—Ru(2)—C(9)	95.8(3)	C(38)—P(1)—C(44)	101.6(3)	C(8)—C(7)—C(6)	112.6(5)
C(1)—Ru(1)—C(6)	94.5(2)	C(4)—Ru(2)—C(9)	160.0(2)	C(50)—P(1)—C(44)	102.8(3)	C(8)—C(7)—C(18)	123.7(5)
C(2)—Ru(1)—C(6)	165.8(3)	C(3)—Ru(2)—C(9)	101.3(3)	C(38)—P(1)—Ru(1)	118.3(2)	C(6)—C(7)—C(18)	123.7(5)
C(1)—Ru(1)—C(9)	164.7(2)	C(5)—Ru(2)—C(8)	93.0(2)	C(50)—P(1)—Ru(1)	117.0(2)	C(9)—C(8)—C(7)	114.4(5)
C(2)—Ru(1)—C(9)	97.6(3)	C(4)—Ru(2)—C(8)	124.2(2)	C(44)—P(1)—Ru(1)	114.2(2)	C(9)—C(8)—C(24)	120.9(5)
C(6)—Ru(1)—C(9)	77.0(2)	C(3)—Ru(2)—C(8)	137.7(3)	O(1)—C(1)—Ru(1)	174.9(6)	C(7)—C(8)—C(24)	124.6(6)
C(1)—Ru(1)—P(1)	98.2(2)	C(5)—Ru(2)—C(7)	119.5(3)	O(2)—C(2)—Ru(1)	174.7(6)	C(8)—C(9)—C(32)	119.7(5)
C(2)—Ru(1)—P(1)	95.5(2)	C(4)—Ru(2)—C(7)	95.3(2)	O(3)—C(3)—Ru(2)	165.4(6)	C(8)—C(9)—Ru(1)	116.9(4)
C(6)—Ru(1)—P(1)	98.1(2)	C(3)—Ru(2)—C(7)	138.4(2)	O(4)—C(4)—Ru(2)	177.3(6)	C(32)—C(9)—Ru(1)	122.4(4)
C(9)—Ru(1)—P(1)	95.7(2)	C(5)—Ru(2)—C(6)	156.1(3)	O(5)—C(5)—Ru(2)	174.2(7)	C(11)—C(10)—C(6)	124.7(6)
C(5)—Ru(2)—C(4)	91.1(3)	C(4)—Ru(2)—C(6)	96.2(3)	C(7)—C(6)—C(10)	116.1(5)	C(10)—C(11)—C(12)	127.5(6)
C(5)—Ru(2)—C(3)	100.2(3)	C(3)—Ru(2)—C(6)	101.6(2)	C(7)—C(6)—Ru(1)	118.2(4)	C(25)—C(24)—C(8)	126.8(7)
C(4)—Ru(2)—C(3)	95.8(3)	C(38)—P(1)—C(50)	100.5(3)	C(10)—C(6)—Ru(1)	125.7(4)	C(24)—C(25)—C(26)	126.1(6)

The X-ray study of complex **5b** confirmed its structure, suggested on the basis of spectral data. In molecule **5b** (Fig. 1, Table 1) the PPh_3 ligand is bonded to the Ru atom of the ruthenacycle and is in the axial position.

Two types of complexes differing in the relative conformation of metallocarbonyl fragments are characteristic of the molecules of ferrole type in the crystal. The first is characterized by an almost linearly arranged OC—M—M—CO fragment with eclipsed substituents at both metal atoms. In the chemistry of ruthenium, $Ru_2(CO)_6(\mu\text{-}C_4H_2Fc_2)$[10] (Fc is ferrocenyl) belongs to such type of complexes. More typical are other complexes in which carbonyl ligands at the metal atoms are in staggered conformation and one of the CO groups is a semibridging one. Among these are compounds $Ru_2(CO)_6(\mu\text{-}C_4R_2R_2')$, where R = R′ = COOMe (**8**);[11] R = R′ = CH_2OH;[12] R = CH_2CH_2OH, R′ = Et;[12] and R = Ph, R′ = C≡CPh.[13] As can be seen in Fig. 1, complex **5b** belongs to the second type; therein the semibridging CO group deviates from linearity, the Ru(2)—C(3)—O(3) angle is equal to 165.4°, and the Ru(1)—C(3) distance is equal to 2.701(7) Å. Noteworthy is that the presence of the phosphine ligand in molecule **5b** has no pronounced effect on the Ru—Ru distance whose value (2.7340(8) Å) is comparable to that in hexacarbonyl complexes (*e.g.*, 2.734(2) and 2.753(2) Å for two independent molecules of complex **8**).[11] The ruthenacyclopentadiene moiety has conventional structure, *viz.*, the C—C bond lengths become equalized, the metallacycle adopts the conformation of a flattened envelope, the Ru atom deviates from the plane of the diene carbon atoms in the opposite direction from the second metal atom, and the angle of folding along the C(6)...C(9) axis is equal to 7.5°.

Two doublets at δ 49.65 and 40.13 (J_{PP} = 4.8 Hz) are observed in the ^{31}P NMR spectrum of complex **6**. Comparison with the spectrum of complex **5b** makes it possible to assign the signal at δ 49.65 to the phosphine ligand at the Ru atom of the ruthenacycle. Complex **6** has also been characterized by X-ray analysis (Fig. 2, Tables 2 and 3). As was expected, the PPh_3 ligands are coordinated to two different Ru atoms. In contrast to

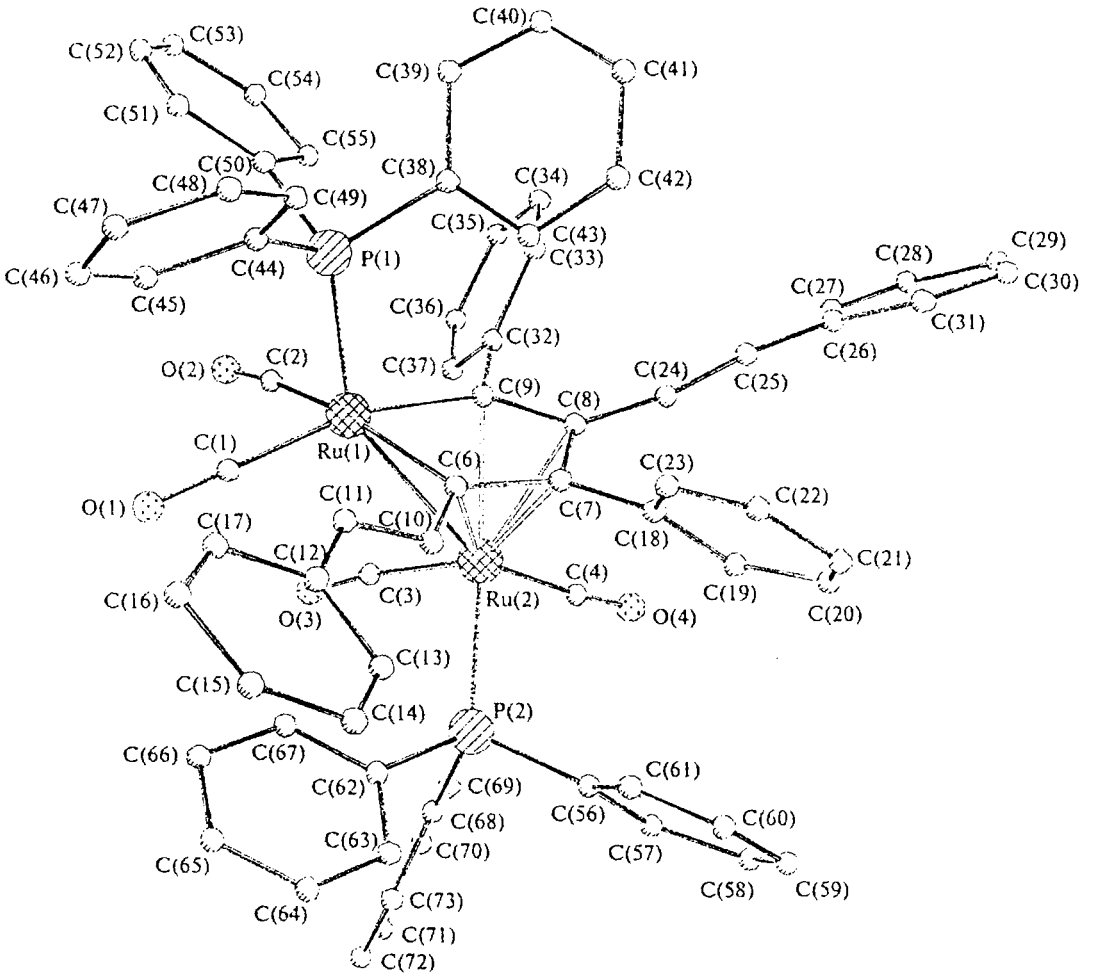


Fig. 2. Molecular structure of complex $Ru_2(CO)_4(PPh_3)_2\{\mu\text{-}C(CH{=}CHPh)C(Ph)C(CH{=}CHPh)C(Ph)\}$ (**6**).

Table 2. Selected bond lengths (d) and bond angles (ω) in complex **6**

Bond	d/Å	Bond	d/Å	Bond	d/Å	Bond	d/Å
Ru(1)—C(1)	1.887(11)	Ru(2)—C(7)	2.288(11)	P(2)—C(68)	1.840(12)	C(7)—C(18)	1.46(2)
Ru(1)—C(2)	1.925(13)	Ru(2)—C(8)	2.299(11)	O(1)—C(1)	1.150(13)	C(8)—C(9)	1.42(2)
Ru(1)—C(9)	2.080(9)	Ru(2)—C(6)	2.350(11)	O(2)—C(2)	1.135(14)	C(8)—C(24)	1.50(2)
Ru(1)—C(6)	2.104(11)	Ru(2)—P(2)	2.371(3)	O(3)—C(3)	1.15(2)	C(9)—C(32)	1.55(2)
Ru(1)—P(1)	2.320(3)	P(1)—C(50)	1.829(11)	O(4)—C(4)	1.135(14)	C(10)—C(11)	1.35(2)
Ru(1)—Ru(2)	2.761(1)	P(1)—C(38)	1.838(12)	C(6)—C(10)	1.45(2)	C(11)—C(12)	1.50(2)
Ru(2)—C(4)	1.869(12)	P(1)—C(44)	1.853(12)	C(6)—C(7)	1.45(2)	C(24)—C(25)	1.29(2)
Ru(2)—C(3)	1.90(2)	P(2)—C(56)	1.80(2)	C(7)—C(8)	1.45(2)	C(25)—C(26)	1.50(2)
Ru(2)—C(9)	2.254(9)	P(2)—C(62)	1.829(13)				
Angle	**ω/deg**	**Angle**	**ω/deg**	**Angle**	**ω/deg**	**Angle**	**ω/deg**
C(1)—Ru(1)—C(2)	85.9(5)	C(4)—Ru(2)—C(8)	88.1(5)	C(38)—P(1)—Ru(1)	118.1(4)	C(7)—C(6)—Ru(1)	117.8(8)
C(1)—Ru(1)—C(9)	163.9(4)	C(3)—Ru(2)—C(8)	131.5(5)	C(44)—P(1)—Ru(1)	117.2(4)	C(6)—C(7)—C(8)	111.9(10)
C(2)—Ru(1)—C(9)	95.7(6)	C(4)—Ru(2)—C(6)	142.9(5)	C(56)—P(2)—C(62)	104.9(7)	C(6)—C(7)—C(18)	127.4(10)
C(1)—Ru(1)—C(6)	97.6(5)	C(3)—Ru(2)—C(6)	116.2(5)	C(56)—P(2)—C(68)	103.4(6)	C(8)—C(7)—C(18)	119.7(10)
C(2)—Ru(1)—C(6)	164.5(5)	C(4)—Ru(2)—P(2)	89.0(4)	C(62)—P(2)—C(68)	99.7(5)	C(9)—C(8)—C(7)	115.0(10)
C(9)—Ru(1)—C(6)	76.9(5)	C(3)—Ru(2)—P(2)	90.5(4)	C(56)—P(2)—Ru(2)	114.2(5)	C(9)—C(8)—C(24)	117.9(10)
C(1)—Ru(1)—P(1)	96.3(3)	C(9)—Ru(2)—P(2)	167.1(3)	C(62)—P(2)—Ru(2)	118.2(4)	C(7)—C(8)—C(24)	127.1(10)
C(2)—Ru(1)—P(1)	92.6(3)	C(7)—Ru(2)—P(2)	105.1(3)	C(68)—P(2)—Ru(2)	114.5(4)	C(8)—C(9)—C(32)	118.2(9)
C(9)—Ru(1)—P(1)	99.6(3)	C(8)—Ru(2)—P(2)	137.7(3)	O(1)—C(1)—Ru(1)	175.8(12)	C(8)—C(9)—Ru(1)	117.5(9)
C(6)—Ru(1)—P(1)	101.9(3)	C(6)—Ru(2)—P(2)	98.4(3)	O(2)—C(2)—Ru(1)	175.2(11)	C(32)—C(9)—Ru(1)	123.5(9)
C(4)—Ru(2)—C(3)	99.9(6)	C(50)—P(1)—C(38)	102.7(5)	O(3)—C(3)—Ru(2)	173.1(12)	C(11)—C(10)—C(6)	124.9(10)
C(4)—Ru(2)—C(9)	101.2(4)	C(50)—P(1)—C(44)	101.8(6)	O(4)—C(4)—Ru(2)	175.5(12)	C(10)—C(11)—C(12)	125.9(11)
C(3)—Ru(2)—C(9)	95.5(5)	C(38)—P(1)—C(44)	99.0(6)	C(10)—C(6)—C(7)	115.7(10)	C(25)—C(24)—C(8)	125.2(12)
C(4)—Ru(2)—C(7)	106.6(5)	C(50)—P(1)—Ru(1)	115.4(4)	C(10)—C(6)—Ru(1)	126.4(8)	C(24)—C(25)—C(26)	125.2(12)
C(3)—Ru(2)—C(7)	149.2(5)						

molecule **5b**, the conformation of complex **6** is intermediate between an eclipsed and staggered one, and the P(1)—Ru(1)—Ru(2)—C(3) torsion angle is equal to 155°, *i.e.*, a deviation of 25° from staggered conformation is observed. In spite of this, in molecule **6** the C(3)O(3) group is semibridging and the Ru(1)...C(3) distance is equal to 2.93(1) Å. It is of interest that a similar situation with an "asymmetric" CO group is also observed in the hexacarbonyl complex **8**,[11] where the deviation from the staggered conformation is equal to 15° and the Ru...C distance is equal to 2.91 Å (the average value for two independent molecules). The Ru—Ru distance (2.761(1) Å) in molecule **6** is somewhat longer than that in molecule **5b**. The ruthenacyclopentadiene moiety of complex **6** also has conventional structure, *viz.*, the Ru atom deviates from the plane of the diene carbon atoms, and the angle of folding along the C(6)...C(9) axis is equal to 5.7°.

Thus, in monophosphine derivatives of the ferrole type complexes the phosphorus ligand is always coordinated to

Table 3. Crystallographic data and parameters of refinement for compounds **5b** and **6**

Parameter	Complex **5b**	Complex **6**
Empirical formula	$C_{55}H_{39}O_5PRu_2$	$C_{72}H_{54}O_4P_2Ru_2 \cdot 2CH_2Cl_2$
M	1012.97	1417.08
Space group	$P\bar{1}$	$Pna2_1$
a/Å	12.613(2)	25.922(10)
b/Å	13.863(2)	13.063(4)
c/Å	14.264(2)	19.297(7)
α/deg	88.69(1)	—
β/deg	68.04(1)	—
γ/deg	88.72(1)	—
V/Å^3	2312.4(6)	6534(4)
Z	2	4
d_{calc}/g cm^{-3}	1.455	1.440
Diffractometer	Syntex $P2_1$	Siemens P3/PC
Radiation (λ/Å)	Mo-Kα (0.71073)	
μ/cm^{-1}	7.36	7.24
Temperature/K	193(2)	293(2)
Scan type	$\theta/2\theta$	$\theta/2\theta$
$2\theta_{max}$/deg	52	50
Number of independent reflections	8199	5978
R_1 (F-refinement for reflections with $I > 2\sigma(I)$)	0.0594 (5549 reflections)	0.0582 (4303 reflections)
wR_2 (F-refinement for all reflections)	0.1613 (8146 reflections)	0.1792 (5915 reflections)
Number of refined parameters	724	775
Weight scheme	$W^{-1} = \sigma^2(F_0^2) + (aP)^2 + bP$, where $P = 1/3\,(F^0 + 2F_c^2)$	
a	0.0841	0.0897
b	0.0894	4.1016

Table 4. Atomic coordinates ($\times 10^4$, for H atoms $\times 10^3$) and their equivalent isotropic thermal parameters ($U_{eq} \times 10^3$) in structure **5b**

Atom	*x*	*y*	*z*	U_{eq}/Å^2
Ru(1)	−2249(1)	−2759(1)	−1476(1)	26(1)
Ru(2)	−4380(1)	−3148(1)	−1439(1)	29(1)
P(1)	−394(1)	−2623(1)	−2619(1)	26(1)
O(1)	−1822(4)	−3841(4)	255(3)	46(1)
O(2)	−2286(5)	−932(4)	−283(4)	62(2)
O(3)	−4709(4)	−2584(4)	705(4)	60(2)
O(4)	−5863(5)	−4934(4)	−726(4)	59(2)
O(5)	−6322(5)	−1904(5)	−1614(5)	84(2)
C(1)	−1932(5)	−3451(5)	−419(5)	32(1)
C(2)	−2247(6)	−1588(5)	−770(5)	38(2)
C(3)	−4431(5)	−2784(5)	−137(5)	39(2)
C(4)	−5324(6)	−4253(5)	−973(5)	39(2)
C(5)	−5636(6)	−2402(6)	−1513(5)	47(2)
C(6)	−2684(5)	−3981(4)	−2056(4)	28(1)
C(7)	−3127(5)	−3855(4)	−2861(4)	25(1)
C(8)	−3276(5)	−2845(4)	−3088(4)	28(1)
C(9)	−3021(5)	−2181(4)	−2453(4)	28(1)
C(10)	−2542(5)	−4997(4)	−1751(4)	26(1)
C(11)	−1632(5)	−5340(5)	−1582(4)	29(1)
C(12)	−1425(5)	−6332(4)	−1306(4)	29(1)
C(13)	−2246(7)	−7064(5)	−1128(6)	44(2)
C(14)	−2024(8)	−7989(6)	−840(7)	53(2)
C(15)	−995(8)	−8201(6)	−726(6)	57(2)
C(16)	−199(7)	−7495(5)	−912(6)	46(2)
C(17)	−403(6)	−6567(5)	−1201(5)	40(2)
C(18)	−3433(5)	−4676(4)	−3373(4)	27(1)
C(19)	−4469(6)	−4736(5)	−3504(5)	35(2)
C(20)	−4712(6)	−5524(5)	−3961(6)	43(2)
C(21)	−3960(6)	−6271(5)	−4271(5)	43(2)
C(22)	−2920(6)	−6244(5)	−4163(5)	37(2)
C(23)	−2657(5)	−5452(5)	−3735(5)	31(1)
C(24)	−3653(6)	−2498(5)	−3901(5)	33(2)
C(25)	−3258(6)	−2780(5)	−4841(5)	35(2)
C(26)	−3536(6)	−2338(5)	−5682(5)	35(2)
C(27)	−2995(7)	−2700(6)	−6641(5)	42(2)
C(28)	−3239(8)	−2308(7)	−7455(6)	53(2)
C(29)	−3970(8)	−1552(7)	−7319(6)	57(2)
C(30)	−4501(7)	−1155(6)	−6379(7)	52(2)
C(31)	−4290(7)	−1560(6)	−5555(6)	46(2)
C(32)	−3105(5)	−1127(5)	−2627(5)	36(2)
C(33)	−2514(6)	−706(5)	−3568(6)	42(2)
C(34)	−2518(8)	290(6)	−3719(8)	62(2)
C(35)	−3104(9)	879(7)	−2930(9)	67(3)
C(36)	−3701(8)	500(6)	−1995(9)	63(2)
C(37)	−3711(7)	−502(6)	−1849(7)	46(2)
C(38)	350(6)	−1490(4)	−2673(5)	34(2)
C(39)	1495(7)	−1470(6)	−2867(8)	64(3)
C(40)	2053(8)	−599(7)	−2956(10)	91(4)
C(41)	1442(9)	251(7)	−2862(9)	75(3)
C(42)	307(8)	254(5)	−2678(6)	49(2)
C(43)	−243(7)	−614(5)	−2568(5)	39(2)
C(44)	−231(5)	−2753(5)	−3948(4)	31(1)
C(45)	170(6)	−2005(5)	−4651(5)	43(2)
C(46)	246(7)	−2130(7)	−5645(6)	51(2)
C(47)	−27(6)	−2979(6)	−5947(5)	49(2)
C(48)	−429(6)	−3729(6)	−5246(5)	43(2)
C(49)	−529(5)	−3608(5)	−4256(5)	32(1)
C(50)	658(5)	−3497(4)	−2489(4)	28(1)
C(51)	793(5)	−3559(5)	−1565(5)	34(2)
C(52)	1620(6)	−4164(5)	−1440(5)	38(2)
C(53)	2318(6)	−4722(5)	−2224(5)	42(2)
C(54)	2188(6)	−4675(6)	−3140(5)	40(2)
C(55)	1351(5)	−4058(5)	−3269(5)	33(1)
H(10)	−312(6)	−539(5)	−170(5)	32(18)
H(11)	−108(4)	−488(3)	−166(3)	2(11)
H(13)	−292(6)	−686(5)	−121(5)	42(19)
H(14)	−249(7)	−845(6)	−80(6)	54(24)
H(15)	−78(7)	−888(6)	−59(6)	69(25)
H(16)	53(6)	−772(5)	−86(5)	34(17)
H(17)	18(6)	−607(5)	−137(6)	54(22)
H(19)	−497(6)	−423(5)	−317(5)	39(19)
H(20)	−550(8)	−549(6)	−401(7)	85(29)
H(21)	−412(5)	−684(4)	−453(4)	17(14)
H(22)	−242(5)	−668(4)	−437(4)	20(16)
H(23)	−200(4)	−544(4)	−367(4)	5(12)
H(24)	−408(5)	−199(4)	−379(4)	13(14)
H(25)	−280(6)	−334(5)	−498(5)	45(20)
H(27)	−256(6)	−324(5)	−672(5)	33(18)
H(28)	−282(7)	−261(6)	−801(6)	61(26)
H(29)	−412(8)	−130(7)	−787(7)	85(30)
H(30)	−500(7)	−63(6)	−616(6)	64(26)
H(31)	−470(5)	−128(5)	−498(5)	32(18)
H(33)	−215(4)	−111(4)	−408(4)	3(12)
H(34)	−211(6)	54(5)	−452(6)	57(22)
H(35)	−308(8)	152(7)	−310(8)	91(33)
H(36)	−424(6)	93(5)	−138(6)	46(20)
H(37)	−410(7)	−74(6)	−138(6)	51(29)
H(39)	195(6)	−205(5)	−284(5)	51(21)
H(40)	295(8)	−51(6)	−297(7)	88(29)
H(41)	167(6)	74(5)	−294(5)	26(18)
H(42)	−16(5)	78(5)	−253(5)	27(17)
H(43)	−102(5)	−65(4)	−252(4)	12(13)
H(45)	33(5)	−132(5)	−443(5)	38(18)
H(46)	53(5)	−174(4)	−617(5)	26(16)
H(47)	5(6)	−306(5)	−663(6)	42(19)
H(48)	−56(5)	−428(5)	−542(5)	32(19)
H(49)	−73(6)	−415(5)	−381(5)	43(20)
H(51)	42(6)	−313(5)	−100(6)	44(20)
H(52)	166(6)	−418(6)	−86(6)	57(24)
H(53)	285(5)	−504(5)	−213(5)	28(17)
H(54)	255(5)	−500(4)	−360(5)	20(16)
H(55)	125(5)	−414(5)	−398(5)	39(18)

the metal atom of the metallacycle. It is likely that such an isomer is thermodynamically more stable than that where the same ligand is coordinated to the metal atom π-coordinated to the diene system. Such a coordination of the phosphorus ligand is observed only in the diphosphine derivatives formed by successive substitution of two CO groups in hexacarbonyl binuclear complexes. As to the formation of compounds **5a** and **5b** from the corresponding triruthenium clusters, they can be obtained as a result of the following transformations. Fragmentation of clusters $Ru_3(CO)_8(PPh_3)\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**2a,b**) occurs with the formation of unstable 16ē-species $[Ru(CO)_3PPh_3]$ and "unsaturated" pentacarbonyl complex $[Ru_2(CO)_5\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}]$ containing

Table 5. Atomic coordinates ($\times 10^4$) and their equivalent isotropic thermal parameters ($U_{eq} \times 10^3$) in structure **6**

Atom	x	y	z	U_{eq}/Å^2
Ru(1)	850(1)	21826(1)	2659(1)	35(1)
Ru(2)	−186(1)	21347(1)	2603(1)	35(1)
P(1)	1504(1)	22857(2)	2226(2)	37(1)
P(2)	−507(1)	19679(2)	2382(2)	40(1)
O(1)	1496(4)	19913(7)	2868(6)	84(4)
O(2)	1128(5)	22231(8)	4175(5)	82(3)
O(3)	102(4)	20691(7)	4068(5)	59(2)
O(4)	−1255(4)	22092(8)	2925(6)	77(3)
C(1)	1256(4)	20636(9)	2762(7)	46(3)
C(2)	1033(5)	22122(9)	3605(7)	45(3)
C(3)	26(5)	20940(10)	3505(8)	52(3)
C(4)	−859(4)	21774(10)	2794(8)	53(4)
C(6)	461(4)	21390(8)	1750(6)	36(2)
C(7)	21(4)	21996(8)	1537(6)	39(3)
C(8)	−71(4)	22850(9)	2003(6)	41(3)
C(9)	238(3)	22853(7)	2613(8)	36(2)
C(10)	593(4)	20546(8)	1300(5)	35(2)
C(11)	1074(5)	20165(8)	1216(6)	41(3)
C(12)	1223(5)	19310(9)	741(6)	44(3)
C(13)	889(5)	18798(10)	299(6)	54(3)
C(14)	1046(8)	18048(12)	−150(8)	68(5)
C(15)	1571(7)	17803(11)	−145(8)	70(4)
C(16)	1910(6)	18265(12)	295(9)	76(4)
C(17)	1749(5)	19037(11)	740(7)	58(4)
C(18)	−258(4)	21938(8)	880(6)	38(3)
C(19)	−791(5)	21995(9)	845(7)	50(3)
C(20)	−1038(7)	22020(12)	199(8)	66(5)
C(21)	−771(7)	21922(12)	−400(8)	74(5)
C(22)	−238(6)	21851(12)	−377(8)	64(4)
C(23)	4(5)	21866(9)	252(6)	49(3)
C(24)	−461(5)	23690(9)	1916(7)	46(3)
C(25)	−524(5)	24230(9)	1362(7)	47(3)
C(26)	−887(5)	25121(10)	1293(7)	49(3)
C(27)	−1083(5)	25632(10)	1866(7)	56(3)
C(28)	−1413(6)	26428(11)	1802(9)	69(4)
C(29)	−1552(6)	26785(11)	1147(10)	73(5)
C(30)	−1352(7)	26300(13)	576(10)	85(5)
C(31)	−1007(6)	25470(12)	644(8)	72(4)
C(32)	158(4)	23730(8)	3142(7)	42(3)
C(33)	258(5)	24752(9)	2934(7)	49(3)
C(34)	209(6)	25525(10)	3383(8)	63(4)
C(35)	113(7)	25338(11)	4066(8)	74(4)
C(36)	19(6)	24371(10)	4288(7)	60(4)
C(37)	55(5)	23576(9)	3825(6)	49(3)
C(38)	1332(5)	23837(9)	1582(6)	40(3)
C(39)	1587(6)	24794(11)	1554(8)	61(4)
C(40)	1490(7)	25428(10)	1006(8)	70(4)
C(41)	1157(6)	25204(11)	508(8)	65(4)
C(42)	884(6)	24267(12)	536(8)	70(4)
C(43)	977(5)	23598(12)	1066(7)	61(4)
C(44)	2032(4)	22216(9)	1746(7)	47(3)
C(45)	2308(5)	21447(12)	2100(9)	67(4)
C(46)	2705(6)	20954(14)	1750(13)	93(6)
C(47)	2827(7)	21170(17)	1071(14)	104(7)
C(48)	2531(7)	21853(16)	719(10)	91(6)
C(49)	2141(6)	22413(13)	1061(8)	68(4)
C(50)	1861(5)	23593(9)	2873(6)	46(3)
C(51)	2383(5)	23571(11)	2981(7)	61(4)
C(52)	2598(7)	24129(15)	3499(10)	87(5)
C(53)	2338(7)	24714(14)	3921(8)	82(5)
C(54)	1802(7)	24751(13)	3835(8)	68(5)
C(55)	1556(6)	24208(11)	3310(8)	65(4)
C(56)	−1003(6)	19627(12)	1727(7)	50(4)
C(57)	−1521(6)	19753(13)	1914(8)	72(4)
C(58)	−1904(8)	19772(17)	1424(12)	104(7)
C(59)	−1804(10)	19664(15)	741(13)	105(7)
C(60)	−1302(10)	19544(14)	550(9)	96(6)
C(61)	−898(8)	19541(11)	1028(8)	75(5)
C(62)	−46(5)	18683(9)	2136(7)	47(3)
C(63)	−135(6)	17902(10)	1682(8)	63(4)
C(64)	223(8)	17122(13)	1581(12)	89(6)
C(65)	675(10)	17151(12)	1929(11)	96(7)
C(66)	790(7)	17935(11)	2408(9)	80(5)
C(67)	413(6)	18700(9)	2510(10)	68(5)
C(68)	−810(4)	19055(9)	3134(6)	43(3)
C(69)	−1037(6)	19581(11)	3662(7)	48(4)
C(70)	−1271(5)	19079(12)	4206(7)	60(3)
C(71)	−1303(6)	18054(12)	4225(8)	69(4)
C(72)	−1065(7)	17495(12)	3713(8)	75(5)
C(73)	−850(5)	18002(9)	3156(7)	56(3)
Cl(1S)*	2163(6)	17550(10)	3701(7)	247(6)
Cl(2S)*	2253(4)	17441(11)	2260(7)	225(5)
C(1S)*	2421(19)	16990(30)	2990(26)	249(24)
Cl(3S)*	2580(7)	16031(18)	−927(8)	336(11)
Cl(4S)*	1600(10)	15428(12)	−1389(7)	357(13)
C(2S)*	2165(21)	14709(46)	−807(46)	392(43)

* For solvated molecules.

the multiple Ru=Ru bond or the 4ē-carbonyl ligand. The addition of CO or PPh_3 (the $[Ru(CO)_3PPh_3]$ species present in solution acts as their source) to the pentacarbonyl complex should result in complexes $Ru_2(CO)_6\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**4a,b**) or $Ru_2(CO)_5(PPh_3)\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**5a,b**), respectively.

Experimental

NMR spectra were recorded on a Bruker AMX-400 spectrometer in C_6D_6 relative to Me_4Si (for ^1H and ^{13}C) and to 85% H_3PO_4 (for ^{31}P). IR spectra were recorded on a Bruker-IFS-113v instrument. Chemapol L 40/100 μ silica gel was used for chromatographic separation of the reaction products.

Reaction of complex $Ru_2(CO)_6\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (4b) with triphenylphosphine. A mixture of complex **4b** (230 mg, 0.3 mmol) and PPh_3 (80 mg, 0.3 mmol) in 30 mL of toluene was refluxed for 11 h in an argon atmosphere. The reaction mixture was concentrated to dryness, and the residue was dissolved in a minimum amount of benzene and chromatographed on a column with silica gel. First, a yellow and a red fraction were eluted with a petroleum ether (b.p. 40—70 °C)—benzene (5 : 1) mixture. The starting complex **4b** (10 mg) and 6 mg of complex $Ru_3(CO)_7(\mu\text{-}PPh_2)_2(\mu_3\text{-}C_6H_4)$ (**7**) were isolated from the yellow and red fractions, respectively. Then, an orange-yellow fraction containing 220 mg (72%) of complex $Ru_2(CO)_5(PPh_3)\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**5b**) was eluted with a petroleum ether—benzene (2 : 1) mixture. Further elution

of a narrow orange fraction with benzene gave 10 mg (3%) of complex $Ru_2(CO)_4(PPh_3)_2\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (**6**).

Complex $Ru_2(CO)_5(PPh_3)\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (5b) is a yellow crystalline substance. Found (%): C, 65.48; H, 4.41. $C_{55}H_{39}O_5PRu_2$. Calculated (%): C, 65.21; H, 3.88. IR (hexane), $\nu CO/cm^{-1}$: 2056 (sh), 2044 s, 2008 s, 1988 s, 1957 (sh). ^1H NMR, δ: 5.87 (d, 1 H, $H_{B'}$, J = 16.7 Hz); 6.36 (d, 1 H, H_B, J = 15.6 Hz); 6.59 (d, 1 H, $H_{A'}$, J = 16.7 Hz); 6.8—7.8 (m, 36 H, 5 Ph + H_A). ^{31}P NMR, δ: 47.98. ^{13}C NMR, δ (the carbonyl region): 202.84 (d, 3 C, J = 8.0 Hz); 200.65 (d, 1 C, J = 8.4 Hz); 199.66 (d, 1 C, J = 11.6 Hz).

Complex $Ru_2(CO)_4(PPh_3)_2\{\mu\text{-}C_4Ph_2(CH{=}CHPh)_2\}$ (6) is a yellow-orange crystalline substance. Found (%): P, 4.82. $C_{72}H_{54}O_4P_2Ru_2$. Calculated (%): P, 4.97. IR (CH_2Cl_2), $\nu CO/cm^{-1}$: 2055 w, 1999 s, 1968 s, 1936 m, 1920 (sh). ^1H NMR, δ: 5.82 (d, 1 H, $H_{B'}$, J = 16.9 Hz); 6.36 (d, 1 H, H_B, J = 15.6 Hz); 6.52 (d, 1 H, H_A, J = 16.9 Hz); 6.8—7.9 (m, 51 H, 10 Ph + H_A). ^{31}P NMR, δ: 40.13 (d, 1 P, J = 4.8 Hz); 49.65 (d, 1 P, J = 4.8 Hz).

Reaction of cluster $Ru_3(CO)_8\{\mu_3\text{-}C(CH{=}CHPh)C(Ph)C(CH{=}CHPh)C(Ph)\}$ (1b) with triphenylphosphine. A mixture of complexes **4b** and **5b** in the ratio ~4 : 1 was obtained by the reaction of brown cluster **1b** (IR (hexane), $\nu CO/cm^{-1}$: 2072 m, 2045 s, 2028 s, 2009 s, 1990 s; ^1H NMR, δ: 5.14 (d, 1 H, J = 12.5 Hz); 5.35 (br.d, 1 H, J = 12.5 Hz); 6.27 (d, 1 H, J = 16.5 Hz); 6.72 (d, 1 H, J = 16.5 Hz); 6.9—7.3 (m, 20 H)), which was isolated in the reaction of $Ru_3(CO)_{12}$ with $PhC{\equiv}CCH{=}CHPh$,[2] with equimolar amount of PPh_3 under conditions analogous to those described for isomer **1a** [1] (benzene, 22 °C, 168 h).

X-ray study. Single crystals of complexes **5b** and **6** suitable for X-ray study were obtained by crystallization from hexane and from a hexane—CH_2Cl_2 (5 : 1) mixture, respectively. Crystallographic data and selected parameters of the refinement for compounds **5b** and **6** are listed in Table 3. Both structures were solved by direct methods. The positions and thermal parameters of non-hydrogen atoms were refined isotropically and then anisotropically by the full-matrix least-squares method. Hydrogen atoms in structure **5b** were located unequivocally and included in the isotropic refinement, and the calculated positions of the hydrogen atoms in structure **6** were included in the refinement using the riding model. In both cases, no absorption correction was introduced. The absolute structure of compound **6** was established by refining the value of the Flack parameter,[14] which was equal to −0.04(6). All calculations were carried out on a personal computer using the SHELXTL PLUS 5 [15] program package. The coordinates of non-hydrogen atoms in structures **5b** and **6** are listed in Tables 4 and 5, respectively.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 97-03-32929 and 97-03-33783).

References

1. A. A. Koridze, V. I. Zdanovich, V. Yu. Lagunova, M. G. Ezernitskaya, P. V. Petrovskii, F. M. Dolgushin, and A. I. Yanovsky, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1017 [*Russ. Chem. Bull.*, 1998, **47**, 988 (Engl. Transl.)].
2. A. A. Koridze, V. I. Zdanovich, N. V. Andrievskaya, Yu. Siromakhova, P. V. Petrovskii, M. G. Ezernitskaya, F. M. Dolgushin, A. I. Yanovsky, and Yu. T. Struchkov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1261 [*Russ. Chem. Bull.*, 1996, **45**, 1200 (Engl. Transl.)].
3. E. Weiss, W. Hübel, and R. Merenyl, *Chem. Ber.*, 1962, **95**, 1155.
4. L. J. Todd, J. P. Hickey, J. R. Wilkinson, J. C. Huffman, and K. Folting, *J. Organomet. Chem.*, 1976, **112**, 167.
5. G. Cetini, O. Gambino, E. Sappa, and M. Valle, *J. Organomet. Chem.*, 1969, **17**, 437.
6. W. Zigler and H. Behrens, *J. Organomet. Chem.*, 1992, **427**, 379.
7. M. I. Bruce, G. Shaw, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1972, 2094.
8. M. I. Bruce, J. M. Guss, R. Mason, B. W. Skelton, and A. H. White, *J. Organomet. Chem.*, 1983, **251**, 261.
9. S. Aime and E. Occhiello, *J. Chem. Soc., Dalton Trans.*, 1986, 1863.
10. A. A. Koridze, A. I. Yanovsky, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1992, **441**, 277.
11. M. I. Bruce, J. G. Matisons, B. W. Skelton, and A. H. White, *J. Organomet. Chem.*, 1983, **251**, 249.
12. A. Astier, J-C. Daran, Y. Jeannin, and C. Rigault, *J. Organomet. Chem.*, 1983, **241**, 53.
13. S. P. Tunik, E. V. Grachova, V. R. Denisov, G. L. Starova, A. B. Nikol'skii, F. M. Dolgushin, A. I. Yanovsky, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1997, **536—537**, 339.
14. H. D. Flack, *Acta Crystallogr., A*, 1983, **39**, 876.
15. G. M. Sheldrick, *SHELXTL Version 5, Software Reference Manual*, Siemens Industrial Automation, Inc., Madison, 1994.

Received March 11, 1998;
in revised form April 17, 1998