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Reactions of the $Ru_3(CO)_{10}(\mu\text{-}Ph_2PCH_2PPh_2)$ cluster with enynes RCH=CHC≡CR (R is phenyl or ferrocenyl). Formation of indenone derivatives of triruthenium clusters

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The thermal reaction of $Ru_3(CO)_{10}(\mu\text{-}Ph_2PCH_2PPh_2)$ (**1**) with enyne PhCH=CHC≡CPh afforded the trinuclear ruthenium clusters $Ru_3(CO)_6\{\mu_3\text{-}P(Ph)CH_2PPh_2\}\{\mu_3\text{-}C(Ph)=CHC\overbracket{C(Ph)(1,2\text{-}C_6H_4)C}(=O)\}$ (**2**), $Ru_3(\mu\text{-}H)(CO)_5\{\mu_3\text{-}P(Ph)CH_2PPh_2\}\{\mu_3\text{-}CH(Ph)=CHC\overbracket{C(Ph)(1,2\text{-}C_6H_4)C}(—O)\}$ (**3**), and $Ru_3(CO)_6(\mu\text{-}CO)\{\mu_3\text{-}P(Ph)CH_2PPh_2\}\{\mu_3\text{-}C(C=CPh_2)CH=C(H)Ph\}$ (**4**) and also two isomers of $Ru_3(CO)_5(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)\{\mu_3\text{-}C_4Ph_2(CH=CHPh)_2\}$ (**5a** and **5b**). Clusters **2**, **3**, and **4** were characterized by IR spectroscopy, ^1H and ^{31}P NMR spectroscopy, and X-ray diffraction analysis. The reaction of complex **1** with enyne FcCH=CHC≡CFc gave rise to the $Ru_3(CO)_6\{\mu_3\text{-}P(Ph)CH_2PPh_2\}\{\mu_3\text{-}C(Fc)=CHC\overbracket{C(Fc)(1,2\text{-}C_6H_4)C}(=O)\}$ (**6**) and $Ru_3(\mu\text{-}H)(CO)_5\{\mu_3\text{-}P(Ph)CH_2PPh_2\}\{\mu_3\text{-}CH(Fc)=CHC\overbracket{C(Fc)(1,2\text{-}C_6H_4)C}(—O)\}$ (**7**) clusters. According to the spectral data, the latter compounds are isostructural to complexes **2** and **3**, respectively.

Key words: ruthenium clusters, carbonyl phosphines, indenone derivatives, enynes, ferrocenylacetylenes, coupling of enyne, CO, and dehydrobenzene, X-ray diffraction analysis.

It is known that the reactions of metal carbonyl clusters with tertiary arylphosphines as well as thermolysis of carbonyl phosphine clusters are often accompanied by activation of the C—H and C—P bonds in phosphines. The reactions, which proceed with the cleavage of the C—P bond, were described.[1—4] These reactions either result in the loss of the benzene (arene) molecule or lead to the formation of dehydrobenzene complexes. Examples of the coupling of the dehydrobenzene or phenyl (aryl) group with other ligands at a metal cluster are also known.[5,6]

Recently, we have reported[6] an interesting example of such a coupling in the reaction of carbonyl phosphine $Ru_3(CO)_{10}(\mu\text{-dppm})$ (**1**, dppm = $Ph_2PCH_2PPh_2$) with enyne PhCH=CHC≡CPh giving rise to the indenone complex $Ru_3(CO)_6\{\mu_3\text{-}P(Ph)CH_2PPh_2\}\{\mu_3\text{-}C(Ph)=CHC\overbracket{C(Ph)(1,2\text{-}C_6H_4)C}(=O)\}$ (**2**). The latter was characterized by X-ray diffraction analysis. Earlier, indenone derivatives have been obtained in the reactions of the iron complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ (R = $SnAr_3$, Ar) or nickel carbonyl $Ni(CO)_4$ and *o*-diiodobenzene with various alkynes.[7—9] A palladium-catalyzed (the $Pd(PPh_3)_4/Zn$ system) procedure was developed for the preparation of indenones from *o*-diiodobenzene, CO, and alkynes.[9] More recently, the synthesis of indenones from benzene, CO, and alkynes catalyzed by the rhodium cluster $Rh_4(CO)_{12}$ was carried out.[10]

The reactions of cluster **1** with PhCH=CHC≡CPh and its diferrocenyl analog FcCH=CHC≡CFc (Fc = $C_5H_4FeC_5H_5$) were studied in detail, which made it possible to obtain a series of new unusual complexes, including those with the dimerized enyne ligand.[11]

Results and Discussion

In the present study, we examined the reactions of cluster **1** with enynes PhCH=CHC≡CPh and FcCH=CHC≡CFc, the former reaction being investigated more comprehensively. These reactions were found to follow two paths. One path, which prevailed under the conditions used, involves elimination of the phenyl group from the diphosphine ligand dppm followed by coupling of the six-membered ring with the enyne. Another path involves dimerization of the enyne, while the diphosphine ligand remains intact.[11]

Previously, the reaction of cluster **1** with PhCH=CHC≡CPh has been carried out in boiling THF.[6] Heating of the reaction mixture for 3 h afforded com-

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plex **2** as the only product in 20% yield, while cluster **1** remained largely unconsumed. When the reaction (THF, 60 °C) was conducted for 22 h, ~50% of the starting complex **1** remained intact and several new complexes were isolated in low yields along with complex **2**. These complexes were purified by repeated thin layer chromatography on silica gel. Since the spectroscopic (IR, ^1H and ^{31}P NMR) data were insufficient for establishing the structures of these unusual complexes, the latter were studied by X-ray diffraction analysis. The complexes $Ru_3(CO)_6\{\mu_3\text{-}P(Ph)CH_2PPh_2\}\{\mu_3\text{-}C(Ph){=}CH\overline{CC(Ph)(1,2\text{-}C_6H_4)C}(=O)\}$ (**2**), $Ru_3(\mu\text{-}H)(CO)_5\{\mu_3\text{-}P(Ph)CH_2PPh_2\}\{\mu_3\text{-}CH(Ph){=}CH\overline{CC(Ph)(1,2\text{-}C_6H_4)C}(—O)\}$ (**3**), and $Ru_3(CO)_6(\mu\text{-}CO)\{\mu_3\text{-}P(Ph)CH_2PPh_2\}\{\mu_3\text{-}C(C{=}CPh_2)CH{=}C(H)Ph\}$ (**4**), which were characterized by X-ray diffraction analysis, and the isomeric complexes with the dimerized enyne ligand described in our previous study,[11] *viz.*, $Ru_3(CO)_5(\mu\text{-dppm})\{\mu_3\text{-}C(CHCHPh)C(Ph)C(Ph)C(CH{=}CHPh)\}$ (**5a**) and $Ru_3(CO)_5(\mu\text{-dppm})\{\mu_3\text{-}C(CHCHPh)C(Ph)\text{-}C(CH{=}CHPh)C(Ph)\}$ (**5b**), are shown in Scheme 1.

The ^{31}P NMR spectra of the resulting complexes indicated that either the starting diphosphine ligand in these compounds was transformed into the phosphinophosphide ligand (compounds **2**—**4**) or this ligand remained intact (compounds **5a** and **5b**). In the former case, this is manifested in a substantial downfield shift of one of the ^{31}P signals. Thus, the ^{31}P NMR spectra of complexes **2**, **3**, and **4** each have two doublets at δ 210.3 and 16.5 (both being splitted with $J_{P,P}$ = 24.8 Hz), 198.3 and 40.6 ($J_{P,P}$ = 69.2 Hz), and 123.4 and 10.3 ($J_{P,P}$ = 72.0 Hz), respectively. At the same time, the difference in the chemical shifts of the ^{31}P nuclei in complex **5a** is less significant (δ 53.8 and 23.3, both being splitted with $J_{P,P}$ = 64.5 Hz).

Scheme 1

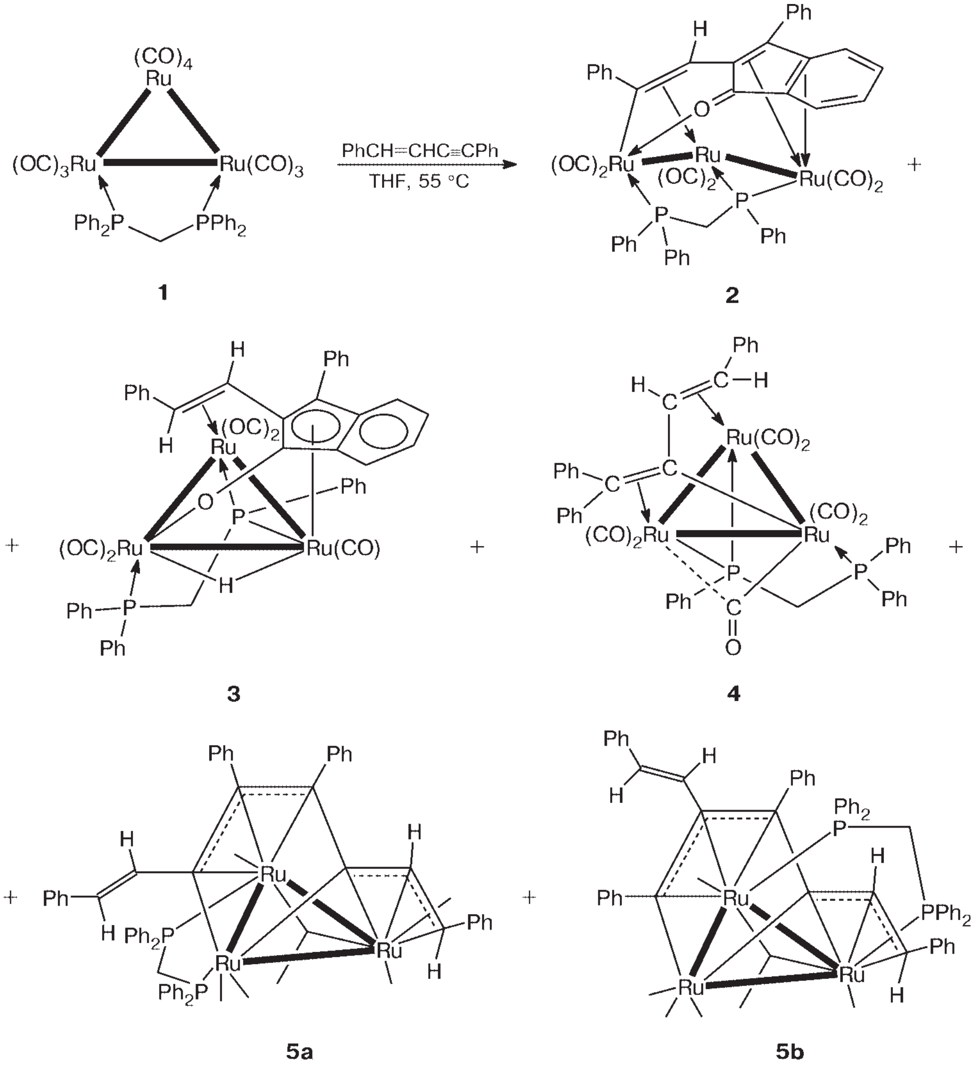


Table 1. Selected bond lengths (*d*) and bond angles (ω) in complex **2**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Ru(1)—Ru(2)	2.7776(13)	Ru(3)—C(9)	2.426(4)	O(7)—C(10)	1.263(5)
Ru(2)—Ru(3)	3.0278(11)	Ru(3)—C(10)	2.472(4)	C(7)—C(8)	1.402(6)
Ru(1)—P(1)	2.4100(14)	Ru(3)—C(11)	2.342(5)	C(7)—C(18)	1.496(6)
Ru(1)—O(7)	2.133(3)	Ru(3)—C(12)	2.285(5)	C(8)—C(9)	1.450(6)
Ru(1)—C(1)	1.900(5)	Ru(3)—C(13)	2.263(5)	C(9)—C(13)	1.472(6)
Ru(1)—C(2)	1.838(5)	P(1)—C(30)	1.828(5)	C(9)—C(10)	1.478(6)
Ru(1)—C(7)	2.070(5)	P(1)—C(31)	1.836(5)	C(10)—C(11)	1.434(6)
Ru(2)—P(2)	2.2679(13)	P(1)—C(37)	1.835(5)	C(11)—C(14)	1.431(7)
Ru(2)—C(3)	1.856(6)	P(2)—C(30)	1.848(5)	C(11)—C(12)	1.434(7)
Ru(2)—C(4)	1.936(6)	P(2)—C(43)	1.824(5)	C(12)—C(17)	1.431(6)
Ru(2)—C(7)	2.275(4)	O(1)—C(1)	1.132(6)	C(12)—C(13)	1.449(6)
Ru(2)—C(8)	2.209(4)	O(2)—C(2)	1.156(6)	C(13)—C(24)	1.476(6)
Ru(2)—C(9)	2.446(4)	O(3)—C(3)	1.134(6)	C(14)—C(15)	1.340(8)
Ru(3)—P(2)	2.3248(13)	O(4)—C(4)	1.131(7)	C(15)—C(16)	1.419(9)
Ru(3)—C(5)	1.891(6)	O(5)—C(5)	1.143(7)	C(16)—C(17)	1.360(8)
Ru(3)—C(6)	1.865(6)	O(6)—C(6)	1.133(7)		
Angle	**ω/deg**	**Angle**	**ω/deg**	**Angle**	**ω/deg**
Ru(1)—Ru(2)—Ru(3)	102.09(3)	C(30)—P(2)—Ru(2)	119.2(2)	O(7)—C(10)—C(11)	125.2(4)
C(7)—Ru(1)—O(7)	90.1(2)	C(43)—P(2)—Ru(3)	119.9(2)	O(7)—C(10)—C(9)	128.1(4)
C(7)—Ru(1)—P(1)	147.10(13)	C(30)—P(2)—Ru(3)	108.3(2)	C(11)—C(10)—C(9)	106.7(4)
O(7)—Ru(1)—P(1)	86.79(9)	Ru(2)—P(2)—Ru(3)	82.47(5)	C(14)—C(11)—C(12)	119.8(4)
C(7)—Ru(1)—Ru(2)	53.60(13)	C(10)—O(7)—Ru(1)	120.6(3)	C(14)—C(11)—C(10)	129.2(5)
O(7)—Ru(1)—Ru(2)	84.63(9)	O(1)—C(1)—Ru(1)	175.0(5)	C(12)—C(11)—C(10)	110.0(4)
P(1)—Ru(1)—Ru(2)	93.50(3)	O(2)—C(2)—Ru(1)	176.9(5)	C(17)—C(12)—C(11)	119.8(5)
P(2)—Ru(2)—Ru(1)	89.62(4)	O(3)—C(3)—Ru(2)	176.4(6)	C(17)—C(12)—C(13)	131.6(5)
P(2)—Ru(2)—Ru(3)	49.57(3)	O(4)—C(4)—Ru(2)	175.9(6)	C(11)—C(12)—C(13)	108.3(4)
P(2)—Ru(3)—Ru(2)	47.95(3)	O(5)—C(5)—Ru(3)	176.7(6)	C(12)—C(13)—C(9)	107.1(4)
C(30)—P(1)—C(37)	98.5(2)	O(6)—C(6)—Ru(3)	177.8(6)	C(12)—C(13)—C(24)	123.1(4)
C(30)—P(1)—C(31)	105.3(2)	C(8)—C(7)—C(18)	114.6(4)	C(9)—C(13)—C(24)	126.9(4)
C(37)—P(1)—C(31)	102.0(2)	C(8)—C(7)—Ru(1)	123.5(3)	C(15)—C(14)—C(11)	118.4(5)
C(30)—P(1)—Ru(1)	104.1(2)	C(18)—C(7)—Ru(1)	121.9(3)	C(14)—C(15)—C(16)	122.1(5)
C(37)—P(1)—Ru(1)	123.7(2)	C(7)—C(8)—C(9)	122.1(4)	C(17)—C(16)—C(15)	122.1(5)
C(31)—P(1)—Ru(1)	119.9(2)	C(8)—C(9)—C(13)	126.0(4)	C(16)—C(17)—C(12)	117.7(5)
C(43)—P(2)—C(30)	102.9(2)	C(8)—C(9)—C(10)	124.4(4)	P(1)—C(30)—P(2)	112.1(2)
C(43)—P(2)—Ru(2)	123.3(2)	C(13)—C(9)—C(10)	107.7(4)		

The ^{1}H NMR spectra of the compounds obtained have multiplets for the aromatic protons belonging to products of transformation of enynes and the diphosphine ligand and multiplets for the methylene protons of the P—CH_2—P fragment of the phosphorus-containing ligand. In addition, these spectra made it possible to readily identify the protons of the coordinated and "free" CH=CHPh groups. For example, the spectrum of complex **3** shows resonances at δ 5.31 (dd, 1 H, $^3J_{H,H}$ = 11.6 Hz, $^3J_{H,P}$ = 2.0 Hz) and 5.39 (dd, 1 H, $^3J_{H,H}$ = 11.6 Hz, $^3J_{H,P}$ = 1.0 Hz) corresponding to the CH=CHPh group coordinated to the ruthenium atom. The presence of the resonance for the hydride ligand at δ –16.50 (ddd, 1 H, $^2J_{H,P}$ = 16.0 and 8.8 Hz; $^4J_{H,H}$ = 4.0 Hz) was observed only for complex **3**.

The spectroscopic data for compounds **2—4** in solutions are in complete agreement with their structures in the crystalline state established by X-ray diffraction analysis (Figs. 1—3). The principal geometric characteristics of complexes **2—4** are given in Tables 1—3, respectively. The results of X-ray diffraction study of isomers **5a** and **5b** have been reported previously.[11]

Crystal structure of $Ru_3(CO)_6\{\mu_3\text{-}P(Ph)CH_2PPh_2\}\{\mu_3\text{-}C(Ph){=}CH\overbrace{CC(Ph)(1,2\text{-}C_6H_4)C}({=}O)\}$ (2). As can be seen from Fig. 1, three ruthenium atoms in cluster **2** are arranged in an "open" fashion. The nonbonded Ru(1)...Ru(3) distance is 4.517(1) Å and the Ru(1)—Ru(2)—Ru(3) angle is 102.09(3)°. Each ruthenium atom is coordinated by two terminal CO groups.

Table 2. Selected bond lengths (*d*) and bond angles (ω) in complex **3**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Ru(1)—Ru(2)	2.9042(3)	Ru(3)—C(5)	1.869(3)	O(6)—C(10)	1.296(3)
Ru(1)—Ru(3)	2.8962(3)	Ru(3)—C(9)	2.329(3)	C(7)—C(8)	1.408(4)
Ru(2)—Ru(3)	2.9091(3)	Ru(3)—C(10)	2.266(3)	C(7)—C(18)	1.472(4)
Ru(1)—H(1)	1.79(3)	Ru(3)—C(11)	2.267(3)	C(8)—C(9)	1.436(4)
Ru(3)—H(1)	1.73(3)	Ru(3)—C(12)	2.280(3)	C(9)—C(10)	1.483(4)
Ru(1)—P(1)	2.2999(8)	Ru(3)—C(13)	2.235(3)	C(9)—C(13)	1.483(3)
Ru(1)—O(6)	2.1939(19)	P(1)—C(30)	1.834(3)	C(10)—C(11)	1.448(4)
Ru(1)—C(1)	1.901(3)	P(1)—C(31)	1.822(3)	C(11)—C(12)	1.437(4)
Ru(1)—C(2)	1.879(3)	P(1)—C(37)	1.832(3)	C(11)—C(14)	1.422(4)
Ru(2)—P(2)	2.2814(7)	P(2)—C(30)	1.835(3)	C(12)—C(13)	1.433(4)
Ru(2)—C(3)	1.869(3)	P(2)—C(43)	1.827(3)	C(12)—C(17)	1.439(4)
Ru(2)—C(4)	1.888(3)	O(1)—C(1)	1.148(4)	C(13)—C(24)	1.492(4)
Ru(2)—C(7)	2.348(3)	O(2)—C(2)	1.148(3)	C(14)—C(15)	1.358(4)
Ru(2)—C(8)	2.206(3)	O(3)—C(3)	1.150(3)	C(15)—C(16)	1.433(5)
Ru(2)—C(9)	2.517(3)	O(4)—C(4)	1.143(4)	C(16)—C(17)	1.349(5)
Ru(3)—P(2)	2.2906(7)	O(5)—C(5)	1.145(3)		

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Ru(3)—Ru(1)—Ru(2)	60.204(7)	C(5)—Ru(3)—P(2)	89.87(9)	C(7)—C(8)—C(9)	121.5(3)
Ru(1)—Ru(2)—Ru(3)	59.763(7)	P(2)—Ru(3)—Ru(1)	78.756(17)	C(8)—C(9)—C(10)	126.3(2)
Ru(1)—Ru(3)—Ru(2)	60.033(7)	P(2)—Ru(3)—Ru(2)	50.344(18)	C(8)—C(9)—C(13)	126.2(2)
O(6)—Ru(1)—P(1)	169.76(5)	C(31)—P(1)—C(37)	103.67(14)	C(10)—C(9)—C(13)	107.2(2)
C(1)—Ru(1)—Ru(2)	172.89(9)	C(31)—P(1)—C(30)	105.62(13)	O(6)—C(10)—C(11)	126.9(2)
C(1)—Ru(1)—Ru(3)	113.36(8)	C(37)—P(1)—C(30)	101.34(13)	O(6)—C(10)—C(9)	126.4(2)
C(2)—Ru(1)—Ru(2)	91.73(8)	C(31)—P(1)—Ru(1)	117.80(9)	C(11)—C(10)—C(9)	106.7(2)
C(2)—Ru(1)—Ru(3)	149.56(8)	C(37)—P(1)—Ru(1)	117.05(11)	C(14)—C(11)—C(12)	120.7(3)
O(6)—Ru(1)—Ru(2)	85.62(5)	C(30)—P(1)—Ru(1)	109.60(10)	C(14)—C(11)—C(10)	130.3(3)
O(6)—Ru(1)—Ru(3)	74.46(5)	C(43)—P(2)—C(30)	99.94(12)	C(12)—C(11)—C(10)	108.9(2)
P(1)—Ru(1)—Ru(2)	87.338(18)	C(43)—P(2)—Ru(2)	123.93(9)	C(13)—C(12)—C(11)	109.6(2)
P(1)—Ru(1)—Ru(3)	95.568(18)	C(30)—P(2)—Ru(2)	119.40(9)	C(13)—C(12)—C(17)	131.4(3)
C(3)—Ru(2)—Ru(1)	87.22(9)	C(43)—P(2)—Ru(3)	123.56(9)	C(11)—C(12)—C(17)	119.0(3)
C(3)—Ru(2)—Ru(3)	143.22(9)	C(30)—P(2)—Ru(3)	111.48(10)	C(12)—C(13)—C(9)	106.9(2)
C(3)—Ru(2)—P(2)	111.22(9)	Ru(2)—P(2)—Ru(3)	79.03(2)	C(12)—C(13)—C(24)	125.3(2)
C(4)—Ru(2)—Ru(1)	172.68(9)	C(10)—O(6)—Ru(1)	101.01(16)	C(9)—C(13)—C(24)	125.0(2)
C(4)—Ru(2)—Ru(3)	116.89(9)	O(1)—C(1)—Ru(1)	177.8(3)	C(15)—C(14)—C(11)	118.1(3)
C(4)—Ru(2)—P(2)	94.16(9)	O(2)—C(2)—Ru(1)	176.7(3)	C(14)—C(15)—C(16)	121.6(3)
P(2)—Ru(2)—Ru(1)	78.724(18)	O(3)—C(3)—Ru(2)	170.9(3)	C(17)—C(16)—C(15)	122.0(3)
P(2)—Ru(2)—Ru(3)	50.623(19)	O(4)—C(4)—Ru(2)	174.2(3)	C(16)—C(17)—C(12)	118.5(3)
C(5)—Ru(3)—Ru(1)	120.79(8)	O(5)—C(5)—Ru(3)	177.2(3)	P(1)—C(30)—P(2)	108.13(15)
C(5)—Ru(3)—Ru(2)	140.19(9)	C(8)—C(7)—C(18)	123.6(3)		

The formation of cluster **2** was accompanied by the transformation of the diphosphine ligand dppm into the phosphinophosphide ligand due to the loss of the phenyl group. The complex organic ligand coordinated to three ruthenium atoms is formally formed through the coupling of dehydrobenzene (dppm as a source), CO, and enyne and can be considered as an indenone derivative.

The indenone fragment in complex **2** is nonplanar (the folding angle along the C(11)—C(12) bond is 9.7°). The five-membered ring consisting of the C(9), C(10), C(11), C(12), and C(13) atoms is planar to within 0.02 Å.

In complex **2**, the ethylene fragment of the enyne is metallated by the Ru(1) atom (the Ru(1)—C(7) σ-bond length is 2.070(5) Å) and the same metal atom is coordinated by the oxygen atom of the ketone group (Ru(1)—O(7), 2.133(3) Å). As a result, the six-membered Ru(1)C(7)C(8)C(9)C(10)O(7) heterocycle is formed. This ring adopts a boat conformation with the C(7), C(8), C(10), and O(7) atoms lying in a single plane ($\Delta = 0.03$ Å) and the Ru(1) and C(9) atoms deviating from this plane toward the Ru(2) atom by 0.617 and 0.175 Å, respectively.

The Ru(1) atom is bound to the phosphine P(1) atom of the phosphinophosphide ligand. The phosphide P(2) atom is bridging between the Ru(2) and Ru(3) atoms, which are coordinated by the organic ligand through the

Table 3. Selected bond lengths (*d*) and bond angles (ω) in complex **4**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Ru(1)—Ru(2)	2.821(3)	Ru(2)—C(4)	1.92(3)	P(1)—C(37)	1.81(2)
Ru(1)—Ru(3)	2.812(3)	Ru(3)—C(5)	1.85(3)	P(2)—C(12)	1.82(2)
Ru(2)—Ru(3)	2.735(3)	Ru(2)—C(7)	1.98(2)	P(2)—C(43)	1.78(2)
Ru(1)—P(2)	2.279(7)	Ru(2)—C(10)	2.12(2)	C(8)—C(9)	1.43(3)
Ru(1)—C(1)	1.89(3)	Ru(3)—P(2)	2.285(7)	C(8)—C(13)	1.48(3)
Ru(1)—C(2)	1.90(3)	Ru(3)—C(6)	1.89(3)	C(9)—C(10)	1.44(3)
Ru(1)—C(3)	2.73(3)	Ru(3)—C(7)	2.39(2)	C(10)—C(11)	1.43(3)
Ru(1)—C(8)	2.35(2)	Ru(3)—C(10)	2.26(2)	C(11)—C(19)	1.56(3)
Ru(1)—C(9)	2.27(2)	Ru(3)—C(11)	2.32(2)	C(11)—C(25)	1.51(3)
Ru(2)—P(1)	2.393(7)	P(1)—C(12)	1.81(2)		
Ru(2)—C(3)	1.98(3)	P(1)—C(31)	1.83(2)		

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Ru(3)—Ru(1)—Ru(2)	58.09(7)	C(43)—P(2)—Ru(3)	122.5(8)	O(7)—C(7)—Ru(3)	128(2)
Ru(3)—Ru(2)—Ru(1)	60.79(8)	C(12)—P(2)—Ru(3)	118.6(7)	Ru(2)—C(7)—Ru(3)	76.7(8)
Ru(2)—Ru(3)—Ru(1)	61.13(7)	Ru(1)—P(2)—Ru(3)	76.1(2)	C(9)—C(8)—C(13)	128(2)
C(37)—P(1)—C(12)	105(1)	O(1)—C(1)—Ru(1)	176(2)	C(8)—C(9)—C(10)	128(2)
C(37)—P(1)—C(31)	103(1)	O(2)—C(2)—Ru(1)	174(2)	C(11)—C(10)—C(9)	113(2)
C(12)—P(1)—C(31)	107(1)	O(3)—C(3)—Ru(2)	165(2)	C(11)—C(10)—Ru(2)	126(2)
C(37)—P(1)—Ru(2)	121.2(9)	O(3)—C(3)—Ru(1)	123(2)	C(9)—C(10)—Ru(2)	118(2)
C(12)—P(1)—Ru(2)	103.4(7)	Ru(1)—C(3)—Ru(2)	72(1)	C(10)—C(11)—C(25)	127(2)
C(31)—P(1)—Ru(2)	116.2(7)	O(4)—C(4)—Ru(2)	174(2)	C(10)—C(11)—C(19)	111(2)
C(43)—P(2)—C(12)	100(1)	O(5)—C(5)—Ru(3)	177(3)	C(25)—C(11)—C(19)	109(2)
C(43)—P(2)—Ru(1)	122.0(8)	O(6)—C(6)—Ru(3)	175(3)	P(1)—C(12)—P(2)	113(1)
C(12)—P(2)—Ru(1)	118.4(7)	O(7)—C(7)—Ru(2)	154(2)		

η^2-ethylene (Ru(2)—C(7), 2.275(4) Å; Ru(2)—C(8), 2.209(4) Å) and η^4-diene (Ru(3)—C(9), 2.426(4) Å; Ru(3)—C(13), 2.263(5) Å; Ru(3)—C(12), 2.285(5) Å; and Ru(3)—C(11), 2.342(5) Å) bonds, respectively. When assuming this coordination of the organic ligand to the "open" Ru_3 core taking into account the additional ligand environment, each ruthenium atom in cluster **2** has the 18-electron shell.

In the structure of complex **2**, there are also short contacts between the C(9) and Ru(2) atoms (2.446(4) Å) and between the carbonyl C(10) atom and the Ru(3) atom (2.472(4) Å). This provides evidence for a contribution of the structure in which the allyl C(7)—C(8)—C(9) fragment is η^3-coordinated to the Ru(2) atom. The occurrence of this contribution is also supported by the larger distance between the Ru(3) and C(9) atoms (Ru(3)—C(9), 2.426 Å) compared to the distances between the Ru atoms and other carbon atoms of the diene fragment (2.263—2.342 Å).

In the five-membered ring of the indenone fragment, the bond lengths are nonequivalent. Thus, the bonds at the C(9) atom (C(9)—C(10) and C(9)—C(13)) are substantially longer than the remaining three bonds in the ring. In the six-membered ring of the indenone fragment, the alternation of the bond lengths is even more pronounced (the C(14)—C(15) and C(16)—C(17) bonds are essentially shorter than the remaining bonds).

The C(10)—O(7) distance in the ketone group of complex **2** (1.263(5) Å) is somewhat longer than that found in the cyclopentadienone complex $Ru(CO)_3(C_4Ph_4CO)$**[12]** (1.224(4) Å) and is close to that observed in the $[Ru(CO)_2(C_4Ph_4CO)]_2$ dimeric complex**[13]** (1.270(7) Å) with the bridging cyclopentadienone ligands containing the >C=O→Ru fragment. To the contrary, the >C=O bond length in another complex with the bridging C_4Ph_4CO ligand, *viz.*, $Mo_2(CO)_3(\mu\text{-}C_2Ph_2)(\mu\text{-}C_4Ph_4CO)(\eta\text{-}C_4Ph_4)$,**[14]** in which the η^5-coordination of the C_4Ph_4CO ligand is assumed, is substantially larger (1.38(2) Å) and is virtually identical to the exocyclic C—O bond length (1.362(3) Å) in the ruthenium hydroxycyclopentadienyl complex $Ru(CO)_2(\eta^1\text{-}COMe)\{\eta^5\text{-}C_5H_2(SiMe_3)_2OH\}$.**[15]**

Crystal structure of the trinuclear complex $Ru_3(\mu\text{-}H)(CO)_5\{\mu_3\text{-}P(Ph)CH_2PPh_2\}\{\mu_3\text{-}CH(Ph){=}CH\overline{CC(Ph)(1,2\text{-}C_6H_4)C}(\text{—}O)\}$ (3). Although the organic ligand in complexes **2** is structurally similar to that in **3** (see Fig. 2), the latter has the following distinguishing features. Three ruthenium atoms in complex **3** form a virtually regular triangle, *i.e.*, the ruthenium atoms are located at bonded distances. The Ru(1)—Ru(3) distance (2.8962(3) Å) between the atoms bound to the bridging hydride ligand is somewhat shorter than the Ru(1)—Ru(2) and Ru(2)—Ru(3) distances (2.9042(3) and

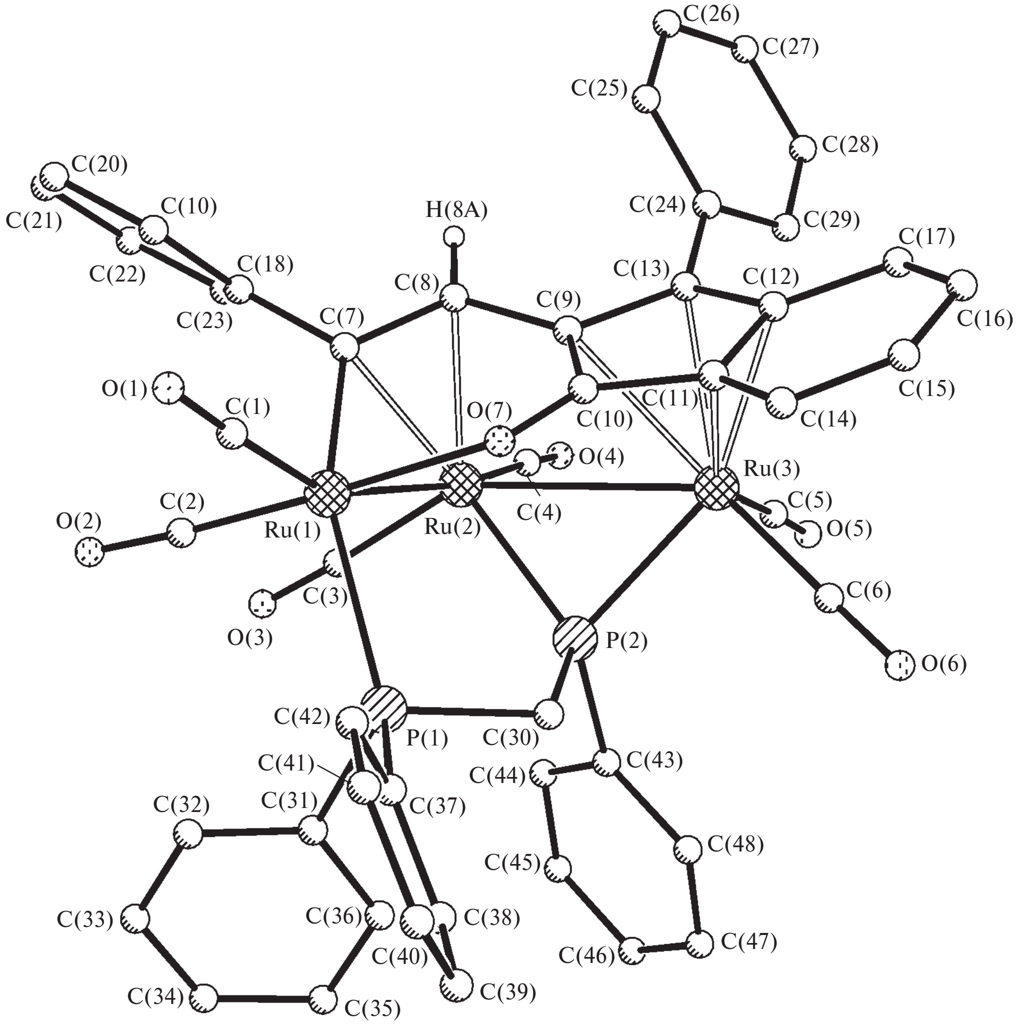


Fig. 1. Structure of complex **2**.

2.9091(3) Å, respectively). The Ru(1) and Ru(2) atoms are coordinated by two CO groups each, whereas the Ru(3) atom is coordinated by one terminal CO group. As in complex **2**, the organic ligand in cluster **3** can be considered as that formed through the coupling of dehydrobenzene, CO, and enyne. However, the vinyl fragment in cluster **3** is not metallated by the Ru(1) atom. There are also some other differences in binding of the organic ligand with the Ru_3 core.

In cluster **3**, the Ru(2) atom is η^2-coordinated by the vinyl group, whereas the Ru(3) atom is coordinated by all five atoms of the five-membered carbocycle; the ruthenium—carbon distances are in the range of 2.235—2.280(3) Å, except for the Ru(3)—C(9) distance (2.329(3) Å) involving the carbon atom bound to the vinyl group. It is remarkable that the same C(9) atom is at a distance of 2.517(3) Å from the Ru(2) atom.

Hence, the five-membered carbocycle in cluster **3** forms the η^5-dienyl bond with the Ru(3) atom. This is consistent also with the C(10)—O(6) distance (1.296(3) Å), which is somewhat larger than the C(10)—O(7) distance in the corresponding fragment in complex **2** although, strictly speaking, one cannot judge whether the C(10)—O(6) bond is single or double from its length as such.

The five-membered C(9)C(10)C(11)C(12)C(13) ring is nonplanar. The C(9) and C(13) atoms deviate from the C(10)C(11)C(12) plane by 0.07 Å toward the metal core and in the opposite direction, respectively. The C(10)—C(9)—C(13)—C(12) torsion angle is 9°. There is the noticeable alternation of the bond lengths in the five-membered ring. Thus, the C(9)—C(10) and C(9)—C(13) bonds are essentially longer (1.483 Å) than the remaining three bonds in the ring (1.43—1.44 Å). In the six-membered ring, the C(14)—C(15) and C(16)—C(17) bonds are short (1.35 Å). The C(8)—C(9) bond (1.436 Å) is shorter than the C_{sp^2}—C_{sp^2} single bond but is substantially longer than the C(7)—C(8) bond (1.408 Å). The planar configuration of the C(9) atom is only slightly distorted with the deviation of this atom from

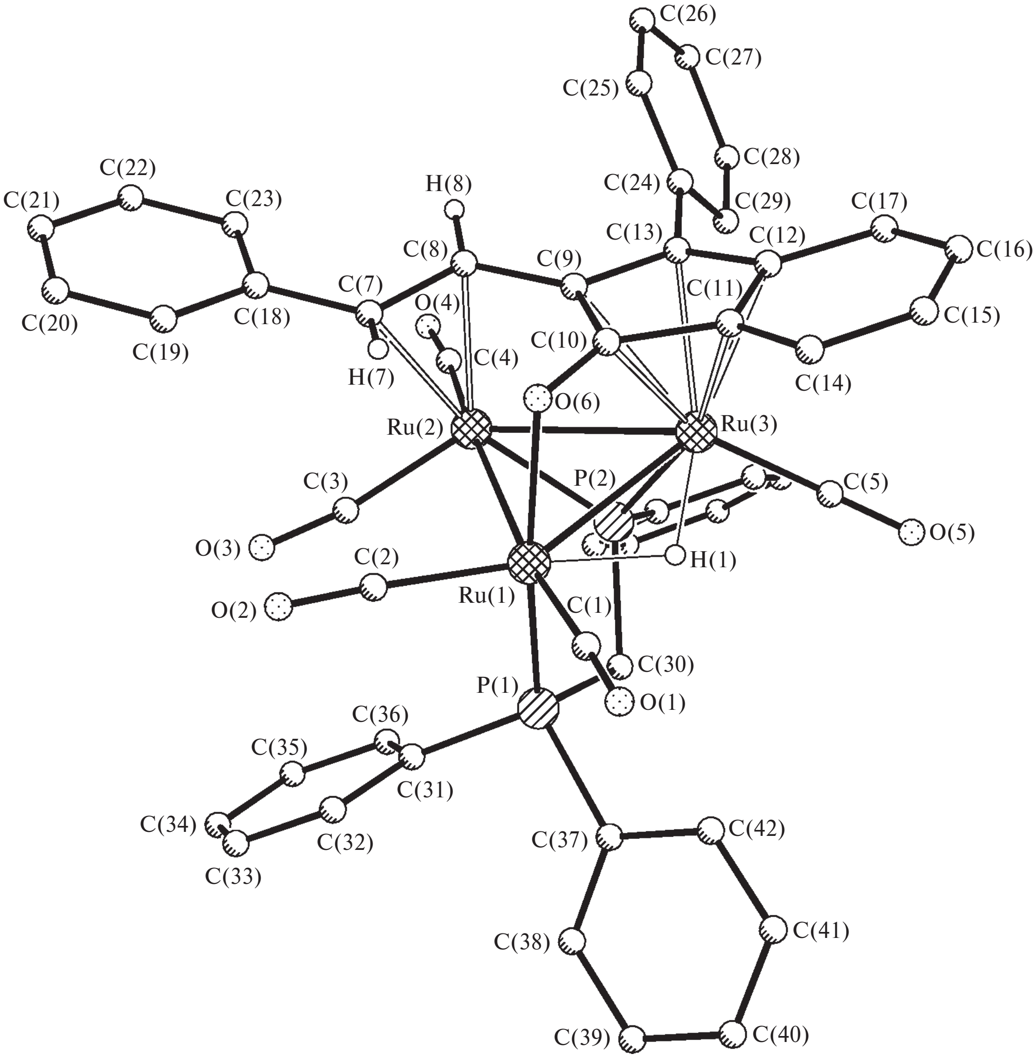


Fig. 2. Structure of complex **3**.

the C(8)C(10)C(13) plane toward the Ru(2) atom by 0.05 Å.

The organic ligand as a whole (without considering the phenyl substituent at the C(13) atom) is nearly planar; the C(9)—C(8)—C(7)—C(8) and C(8)—C(7)—C(18)—C(19) torsion angles are 174.6 and 164.1°, respectively. The angle between the average plane of the C(7)—C(17) organic ligand and the plane of the Ru_3 triangle is 8.5°.

Crystal structure of $Ru_3(CO)_6(\mu\text{-}CO)\{\mu_3\text{-}P(Ph)CH_2PPh_2\}\{\mu_3\text{-}C(C{=}CPh_2)CH{=}C(H)Ph\}$ (4). As can be seen from Fig. 3, molecule **4** contains the Ru_3 triangle coordinated by the μ_3-phosphinophosphide ligand. Each ruthenium atom is coordinated by two carbonyl groups, one of the CO groups at the Ru(2) atom being semibridging (the Ru(2)—C(3)—O(3) angle is 165(2)°). In addition, another group, *viz.*, C(7)O(7), serves as an unsymmetrical bridging ligand coordinated to the Ru(2) and Ru(3) atoms (the Ru(2)—C(7)—O(7) angle is 154(2)°, the Ru(3)—C(7) distance is 2.39(2) Å).

The structure of the organic ligand is worthy of notice. This ligand is the 1,1,4-triphenylbuta-1,3-dien-2-yl group. The ethylene fragments of this group are η^2-coordinated to the Ru(1) and Ru(3) atoms. The C(10) atom forms also a σ bond with the Ru(2) atom with the length of 2.12(2) Å. The C(13)C(8)C(9)C(10) and C(8)C(9)C(10)C(11) torsion angles are 173.3 and 158.9°, respectively. The dienone skeleton has a transoid configuration.

In attempting to elucidate the mechanism of formation of products **2—4** by isolation of intermediates, we conducted the reaction of cluster **1** with sterically more hindered enyne FcCH=CHC≡CFc. However, we succeeded in isolating only compounds isostructural to clusters **2** and **3**. The reaction of enyne FcCH=CHC≡CFc with cluster **1** proceeded slower than the reaction with diphenyl-substituted enyne, apparently, for steric reasons. Because of this, we carried out the reaction of FcCH=CHC≡CFc with compound **1** in benzene at 70 °C.

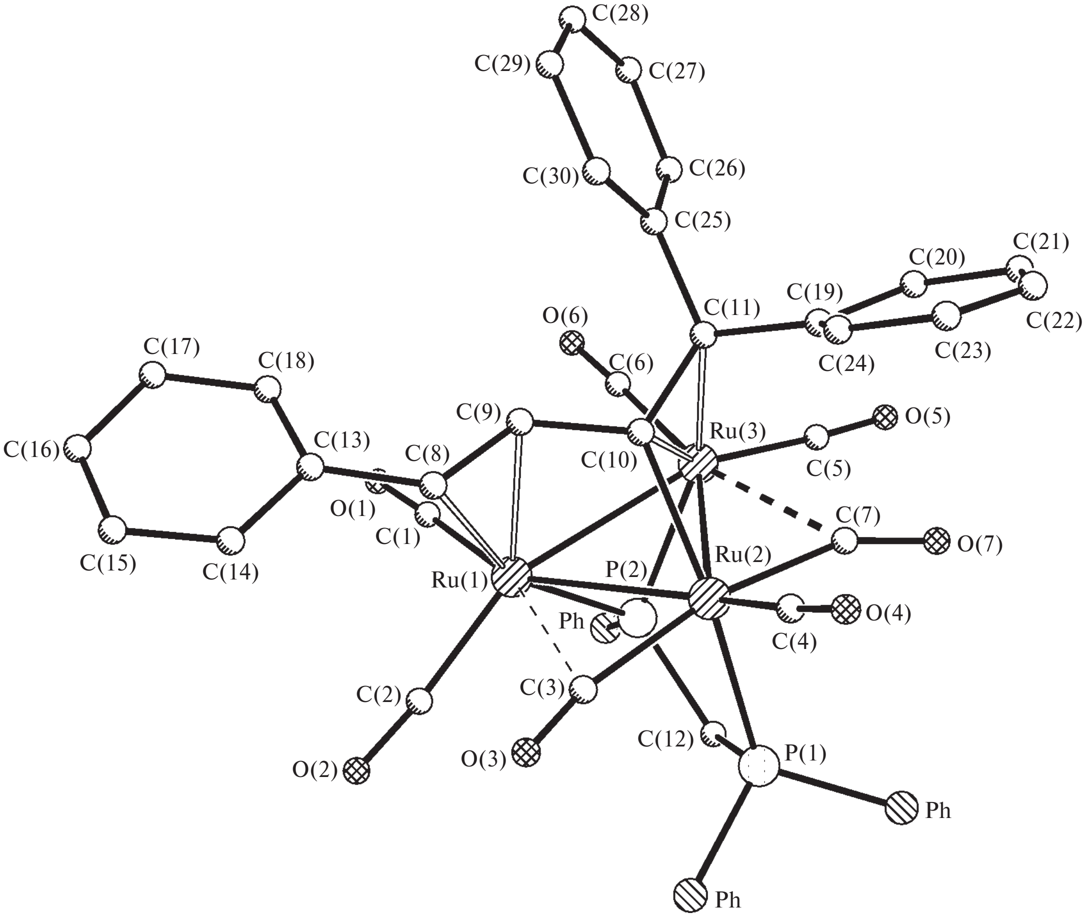


Fig. 3. Structure of complex **4**.

As a result, we isolated three individual compounds two of which were identified based on the spectroscopic data.

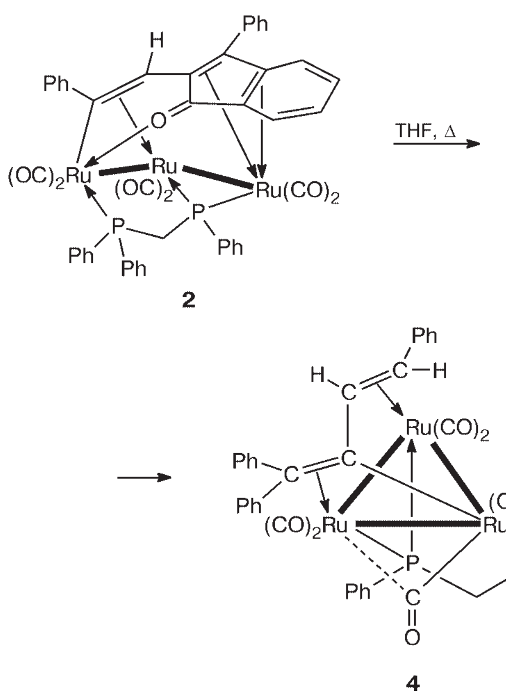
Thus, judging from the spectroscopic data, the red $Ru_3(CO)_6\{\mu_3\text{-}P(Ph)CH_2PPh_2\}\{\mu_3\text{-}C(Fc){=}CH\overline{CC(Fc)(1,2\text{-}C_6H_4)C}({=}O)\}$ complex (**6**) is a structural analog of cluster **2**. The ^1H NMR spectrum of complex **6** has resonances for the protons of the unsubstituted cyclopentadienyl rings of two ferrocenyl groups at δ 4.10 and 4.29 and resonances of the substituted C_5H_4 rings in the region of δ 4.11—5.25. The carbonyl region of the IR spectrum of complex **6** is similar to that of complex **2**. The ^{31}P NMR spectrum of cluster **6** shows two doublets at δ 203.2 and 17.5 with the splitting $J_{P,P} = 24.9$ Hz.

We believe that the red-brown hydride complex $Ru_3(\mu\text{-}H)(CO)_5\{\mu_3\text{-}P(Ph)CH_2PPh_2\}\{\mu_3\text{-}CH(Fc){=}CH\overline{CC(Fc)(1,2\text{-}C_6H_4)C}({-}O)\}$ (**7**) is a structural analog of hydride complex **3**. In the hydride region of the ^1H NMR spectrum of complex **7**, a complex multiplet is observed at δ −16.69 (ddd, 1 H); the multiplet nature of the signal results from spin-spin coupling with two nonequivalent phosphorus nuclei ($J_{H,P} = 16.0$ and 8.8 Hz) and one of the ethylene hydrogen atoms ($J_{H,H} = 4.0$ Hz). The ^{31}P NMR spectrum of complex **7** shows two doublets at δ 196.2 and 40.5 with the splitting $J_{P,P} = 70.9$ Hz.

Although the details of the formation of complexes **2—4** remain unclear, a special experiment performed in the present study demonstrated that complex **2** is a precursor of cluster **4**. Thus, thermolysis of complex **2** in boiling THF for 6 h afforded cluster **4** in 30% yield (Scheme 2). The generation of cluster **4** from complex **2** must involve the cleavage of the C(10)—C(11) bond in the latter compound and decarbonylation of the hydrocarbon ligand. Formally, the generation of complex **4** involves a series of successive transformations accompanied by phenylation of the starting enyne with the dppm ligand of the starting cluster **1**.

Therefore, in the course of formation of complexes **2**, **3**, and **4**, the terminal CO group of the starting complex **1** was successively transformed into the organic ketone group, the alkoxide group, and again the CO group. All these transformations were accompanied by a series of reactions of the formation and cleavage of the car-

Scheme 2



bon—carbon bonds, which proceeded under mild conditions due, apparently, to the presence of the triruthenium cluster.

Experimental

The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.13 and 161.98 MHz, respectively). The IR spectra were measured on a Bruker IFS-113v instrument. The reactions were carried out under argon. The chromatographic separation of the products was performed in air with the use of silica gel (40/100 μm) and Sorbfil plates. Tetrahydrofuran was distilled over sodium benzophenone ketyl under argon.

Reaction of PhCH=CHC≡CPh with $\mathbf{Ru_3(CO)_{10}}$(μ-dppm). A solution of PhCH=CHC≡CPh (160 mg, 0.8 mmol) and $Ru_3(CO)_{10}$(μ-dppm) (400 mg, 0.4 mmol) in THF (50 mL) was heated at 60 °C for 22 h. After evaporation of the solvent, the residue was chromatographed on a column with SiO_2 and the following five fractions were isolated: a red fraction containing the starting $Ru_3(CO)_{10}$(μ-dppm) complex (190 mg, 47%) (1 : 1 hexane—benzene mixture as the eluent); an orange fraction (1 : 1 hexane—benzene mixture as the eluent) from which complex **4** was isolated (10 mg, 2.3%) after additional chromatography on plates; a red fraction (1 : 1 hexane—benzene mixture as the eluent) from which complex **2** was isolated (40 mg, 9%) after additional purification; a dark-red fraction (benzene as the eluent) containing complexes **5a** and **5b**[11] (10 mg, 2%); and a brown fraction (benzene as the eluent) from which complex **3** was isolated (10 mg, 2.3%).

1,1,2,2,3,3-Hexacarbonyl-μ-[(diphenylphosphinomethyl)phenylphosphido-P(Ru^1),P´(Ru^2,Ru^3)]-μ$_3$-[(*trans*-2-(1´-oxo-3´-phenylinden-2´-yl)-1-phenylethen-1-yl)-C^1(Ru^1),O(Ru^1),C^{1,2}(Ru^2),C$^{2´,3´,3a´,7a´}$(Ru^3)]triruthenium (2), red crystals. Found (%): P, 5.47. $C_{48}P_{32}O_7P_2Ru_3$. Calculated (%): P, 5.70. IR (CH_2Cl_2), ν(CO)/cm^{-1}: 2030 m, 2005 s, 1983 s, 1973 sh, 1941 m, 1921 m, 1533 w. ^{1}H NMR ($CDCl_3$, 25 °C), δ: 4.38 (m, 1 H, $C\underline{H}_AH_B$); 4.68 (m, 1 H, $CH_A\underline{H}_B$); 5.60 (dd, 1 H, CH=, $^3J_{H,P}$ = 7.3 and 2.5 Hz); 6.6—8.2 (m, 29 H, $C_6H_5 + C_6H_4$). ^{31}P NMR ($CDCl_3$, 25 °C), δ: 16.5 (d, $^2J_{P,P}$ = 24.8 Hz); 210.3 (d, $^2J_{P,P}$ = 24.8 Hz).

1,1,2,2,3-Pentacarbonyl-μ-hydrido(Ru^1,Ru^2)-μ$_3$-[(diphenylphosphinomethyl)phenylphosphido-P(Ru^1),P´(Ru^2,Ru^3)]-μ$_3$-[(*trans*-2-phenylethen-1´-yl)-3-phenyl-1-indenyloxy-C$^{1´,2´}$(Ru^2),O(Ru^2),C^{1,2,3,3a,7a}(Ru^3)]-*triangulo*-triruthenium (3), red-brown crystals. IR (CH_2Cl_2), ν(CO)/cm^{-1}: 2015 m, 1983 s, 1960 s, 1941 w. ^{1}H NMR (C_6D_6, 25 °C), δ: –16.5 (ddd, 1 H, Ru—H, $^2J_{H,P}$ = 16.0 and 8.8 Hz; $^2J_{H,H}$ = 4.0 Hz); 3.81 (m, 1 H, $C\underline{H}_AH_B$); 4.44 (m, 1 H, $CH_A\underline{H}_B$); 5.31 (dd, 1 H, CH=, $^3J_{H,H}$ = 11.6 Hz, $^3J_{H,P}$ = 2.0 Hz); 5.39 (dd, 1 H, CH=, $^3J_{H,H}$ = 11.6 Hz, $^3J_{H,P}$ = 1.0 Hz). ^{31}P NMR (C_6D_6, 25 °C), δ: 40.6 (d, $^2J_{P,P}$ = 69.2 Hz); 198.3 (d, $^2J_{P,P}$ = 69.2 Hz).

1,3-μ-Carbonyl-1,1,2,2,3,3-hexacarbonyl-μ$_3$-[(diphenylphosphinomethyl)phenylphosphido-P(Ru^1),P´(Ru^2,Ru^3)]-μ$_3$-[(1,1,4-triphenylbuta-1,3-dien-2-yl)-C^{1,2}(Ru^1),C^2(Ru^3),C^{3,4}(Ru^2)]-*triangulo*-triruthenium (4), yellow-orange crystals. IR (CH_2Cl_2), ν(CO)/cm^{-1}: 2028 w, 1999 s, 1971 m, 1952 m, 1867 w. ^{1}H NMR ($CDCl_3$, 25 °C), δ: 3.55 (m, 1 H, $C\underline{H}_AH_B$); 4.02 (m, 1 H, $CH_A\underline{H}_B$); 4.47 (dd, 1 H, CH=, $^3J_{H,H}$ = 11.6 Hz, $^3J_{H,P}$ = 6.0 Hz); 4.90 (d, 1 H, CH=, $^3J_{H,H}$ = 11.6 Hz); 7.0—8.0 (m, C_6H_5). ^{31}P NMR ($CDCl_3$, 25 °C), δ: 10.3 (d, $^2J_{P,P}$ = 72.0 Hz); 123.4 (d, $^2J_{P,P}$ = 72.0 Hz).

Thermolysis of complex 2. Complex **2** whose purity was checked by ^{31}P NMR spectroscopy was heated in boiling THF for 6 h after which the color of the solution changed from red to yellow. The solvent was distilled off *in vacuo*. The ^{31}P NMR spectrum of the residue in $CDCl_3$ has doublets at δ 10.1 and 123.4 ($^2J_{P,P}$ = 72.0 Hz) characteristic of yellow-orange complex **4** along with doublets at δ 16.4 and 210.4 ($^2J_{P,P}$ = 24.8 Hz) belonging to red complex **2**. A comparison of the intensities of the ^{31}P signals of complexes **2** and **4** indicated that the conversion of complex **2** into complex **4** was 30%.

Reaction of FcCH=CHC≡CFc with $\mathbf{Ru_3(CO)_{10}}$(μ-dppm). A solution of FcCH=CHC≡CFc (0.09 g, 0.2 mmol) and $Ru_3(CO)_{10}$(μ-dppm) (0.2 g, 0.2 mmol) in dry benzene (60 mL) was heated at 70 °C for 33 h. After evaporation of the solvent, the residue was chromatographed on plates with Al_2O_3 (rough separation). The subsequent separation of the compounds was carried out on Sorbfil. A yellow layer was eluted with a 1 : 1 light petroleum—benzene mixture. This layer contained a mixture of complex **1** and the enyne. The $Ru_3(CO)_6\{\mu_3\text{-}P(Ph)PCH_2PPh_2\}\{\mu_3\text{-}C(Fc)\text{=}CH\overline{CC(Fc)(1,2\text{-}C_6H_4)C}(\text{=}O)\}$ compound (**6**) was obtained from the next red layer in a yield of 0.02 g (7.4%). A nonidentified compound was isolated from the cranberry-colored layer in a yield of 0.01 g. The $Ru_3(\mu\text{-}H)(CO)_5\{\mu_3\text{-}P(Ph)CH_2PPh_2\}\{\mu_3\text{-}CH(Fc)\text{=}CH\overline{CC(Fc)(1,2\text{-}C_6H_4)C}(\text{—}O)\}$ complex (**7**) was isolated from the red-brown layer in a yield of 0.02 g (7.4%).

1,1,2,2,3,3-Hexacarbonyl-μ$_3$-[(diphenylphosphinomethyl)phenylphosphido-P(Ru^1),P´(Ru^2,Ru^3)]-μ$_3$-[(*trans*-2-(1´-oxo-3´-ferrocenylinden-2´-yl)-1-ferrocenylethen-1´-yl)-C^1(Ru^1),O(Ru^1),C^{1,2}(Ru^2),C$^{2´,3´,3a´,7a´}$(Ru^3)]triruthenium (6).

IR (cyclohexane), ν(CO)/cm^{-1}: 2026 s, 2007 v.s, 1980 v.s, 1973 m, 1944 w, 1928 s. ^1H NMR (C_6D_6), δ: 4.07 (s, 5 H, C_5H_5); 4.29 (s, 5 H, C_5H_5); 4.12—4.35 (m, 9 H, C_5H_4 + $C\underline{H}_AH_B$); 4.64 (m, 1 H, $CH_A\underline{H}_B$), 6.50—8.32 (m, 20 H, $C_6H_5+C_6H_4$+CH=). ^{31}P NMR (C_6D_6), δ: 17.5 (d, 1 P, $^2J_{P,P}$ = 24.9 Hz); 203.2 (d, 1 P, $^2J_{P,P}$ = 24.9 Hz).

1,1,2,2,3-Pentacarbonyl-μ-hydrido(Ru^1,Ru^2)]-$μ_3$-[(diphenylphosphinomethyl)phenylphosphido-P(Ru^1),P´(Ru^2,Ru^3)]-$μ_3$-[(*trans*-2-ferrocenylethen-1´-yl)-3-ferrocenyl-1-indenyloxy-$C^{1´,2´}$(Ru^2),O(Ru^1),$C^{1,2,3,3a,7a}$(Ru^3)]-*triangulo*-triruthenium (7). IR (cyclohexane), ν(CO)/cm^{-1}: 2013 s, 1981 s, 1961 s, 1936 w. ^1H NMR (C_6D_6), δ: –16.69 (ddd, 1 H, HRu, $^2J_{H,P}$ = 16.0 and 8.8 Hz; $^4J_{H,H}$ = 4.0 Hz); 4.10 (s, 5 H, C_5H_5); 4.29 (s, 5 H, C_5H_5); 3.70—4.80 (m, 10 H, C_5H_4 + CH_2); 5.50 (dd, 1 H, HC=, $^3J_{H,H}$ = 11.0 Hz, $^3J_{H,P}$ = 4.0 Hz); 6.12 (d, 1 H, HC=, $^3J_{H,H}$ = 11.0 Hz); 6.80—8.20 (m, 19 H, C_6H_5 + C_6H_4). ^{31}P NMR (C_6D_6), δ: 40.5 (d, 1 P, $^2J_{P,P}$ = 70.9 Hz); 196.2 (d, 1 P, $^2J_{P,P}$ = 70.9 Hz).

X-ray diffraction study of complexes 2, 3, and 4. The crystallographic data and the principal details of the refinement of compounds **2—4** are given in Table 4. All structures were solved by direct methods and refined by the full-matrix least-squares method based on F^2_{hkl}. Since the transmission coefficient μ for compounds **2—4** has low values, absorption was ignored.

In the course of refinement of the structure of **2**, four peaks about the inversion center were revealed in a difference electron density synthesis. These peaks correspond to the disordered solvent molecule of the unknown nature. The positions and the thermal parameters of the nonhydrogen atoms in complex **2** were refined anisotropically. The hydrogen atoms were placed in geometrically calculated positions and refined using the riding model.

The crystal structure of **3** contains the toluene and *n*-hexane molecules of solvation. One of the toluene molecules occupies the special position on the twofold axis. The second toluene molecule and the *n*-hexane molecule occupy close positions with the occupancies of 0.3 and 0.7, respectively. One of the phenyl substituents (C(24)—C(29)) of the organic ligand in complex **3** is disordered over two positions with an occupancy ratio of 0.7 : 0.3 (Figure 2 shows only one orientation of this fragment with the higher occupancy). All nonhydrogen atoms in complex **3** were refined anisotropically. All hydrogen atoms, except for the disordered phenyl substituent, were revealed from difference electron density syntheses and refined with isotropic thermal parameters.

The crystal structure of **4** contains toluene molecules of solvation (in the special position on the twofold axis) and benzene molecules of solvation (disordered around the inversion center). The ruthenium, phosphorus, and oxygen atoms in complex **4** were refined with anisotropic thermal parameters. The carbon atoms were refined isotropically. The H(8) and H(9) atoms were revealed from a difference electron density synthesis and refined with isotropic thermal parameters. The remain-

Table 4. Crystallographic data and details of X-ray diffraction study and the refinement of compounds **2—4**

Parameter	**2**	**3**	**4**
Molecular formula	$C_{52}H_{32}O_7P_2Ru_3$	$C_{56.8}H_{50.2}O_6P_2Ru_3$	$C_{54.5}H_{41}O_7P_2Ru_3$
Molecular weight	1133.93	1193.92	1173.02
Space group	$P2_1/n$	C2/c	C2/c
Temperature/K	293(2)	100(2)	293(2)
a/Å	14.672(6)	32.904(1)	22.449(5)
b/Å	20.397(6)	17.6737(5)	15.003(3)
c/Å	15.551(5)	23.4148(7)	30.190(6)
β/deg	104.54(3)	133.377(1)	104.15(3)
V/Å^3	4505(3)	9897.1(5)	9860(3)
Z	4	8	8
d_{calc}/g cm^{-3}	1.672	1.603	1.580
Diffractometer	Siemens P3/PC	SMART 1000 CCD	Enraf Nonius CAD4
Radiation		Mo-Kα (λ = 0.71073 Å)	
μ/cm^{-1}	11.17	10.20	10.24
Scan mode	θ-2θ	φ and ω	θ-2θ
$2θ_{max}$/deg	58	62	40
Number of independent reflections (R_{int})	12022 (0.0840)	15202 (0.0473)	3209 (0.1199)
R_1 (based on F for reflections with $I > 2σ(I)$)	0.0595 (7761)	0.0391 (10625)	0.0591 (1365)
wR_2 (based on F^2 for all reflections)	0.1672	0.1008	0.1584
Number of parameters in the refinement	577	782	343
GOF	1.033	0.937	0.953
Weighting scheme		$w^{-1} = σ^2(F_o^2) + (aP)^2 + bP$, where $P = 1/3(F_o^2 + 2F_c^2)$	
a	0.0992	0.0573	0.0644
b	1.7864	0.0000	0.0000

ing hydrogen atoms in complex **4** were placed in geometrically calculated positions and refined using the riding model.

All calculations were carried out on a personal computer with the use of the known program packages.[16—18]

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