Triruthenium complexes obtained in the thermal reaction of $Ru_3(CO)_{12}$ with dibenzylideneacetone

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The complexes $Ru_2(CO)_6(\mu\text{-}H)(O{=}C(CH{=}CHPh)C(H){=}CPh)$ (**5**), $Ru_3(CO)_8$-$(O{=}C(CH{=}CHPh)C(H){=}CPh)_2$ (**6**), and $Ru_3(CO)_7(O{=}C(CH{=}CPh)C(H){=}CPh)$-$(O{=}C(CH_2{-}CH_2Ph)C(H){=}CPh)$ (**7**) were obtained in the reaction of $Ru_3(CO)_{12}$ with dibenzylideneacetone PhCH=CHCOCH=CHPh. The structures of complexes **5** and **6** were established by NMR and IR spectroscopy and elemental analysis. The structure of complex **7** was established by X-ray diffraction. The structural and spectroscopic features of the complexes, as well as their possible formation and interconversion pathways are discussed.

Key words: dodecacarbonyltriruthenium, dibenzylideneacetone, five-membered oxaruthenacycles, polynuclear complexes, X-ray diffraction study, IR spectroscopy, NMR spectroscopy.

Understanding of the processes occurring upon reactions of chemical compounds is one of the main tasks of chemistry, which could be solved by isolation of the maximum number of reaction products and establishment of their possible interconversion pathways in the course of the reaction. We are studying the reactions of oxadienes with $Ru_3(CO)_{12}$. Variation of the substituents showed that the major products contain five-membered oxaruthenacycles and dihydropyran rings.[1] The features of the substituents´ nature have an impact on the structures of minor products. Introduction of new functional groups provides additional possibilities for the coordination to metal atoms and allows one to expect the formation of complexes with unusual coordination modes of an organic ligand.[2—4]

Earlier,[4] we have studied the reaction of $Ru_3(CO)_{12}$ with dibenzylideneacetone PhCH=CHCOCH=CHPh (DBA) (**1**), which, in contrast to oxadienes, contains two olefin groups. After long-term heating of the reaction mixture (until $Ru_3(CO)_{12}$ disappeared and the constant IR spectrum was obtained), complexes **2**—**4** were isolated from the reaction mixture (Scheme 1),[4] whose structures were characterized by X-ray diffraction.

The complexes contain not only the five-membered oxaruthenacycles and dihydropyran rings, but also novel unusual fragments, *viz.*, η^4-diene and η^4-oxadiene ones. Since it is known that, under drastic reaction conditions, the products formed initially undergo subsequent transformations,[5] we studied in the present work the processes occuring in the initial reaction steps.

The reaction of $Ru_3(CO)_{12}$ with DBA was performed in boiling heptane. The course of the process was monitored by following the changes in the IR spectra of the reaction mixture in the region of the metal-carbonyl stretching vibrations. The production of new complexes was controlled by the appearance of the IR absorption bands typical of each complex. Novel complexes **5**—**7** (Scheme 2) and small amounts of complexes **2** and **3** were isolated by chromatography. The structures of complexes **5** and **6** were established based on the similarity of the IR spectral characteristics with those of the complexes that have been synthesized and characterized by us earlier by X-ray diffraction (Table 1). The IR spectra of both complexes contain the bands of the metal-carbonyl stretching vibrations, which virtually coincide with their analogs (in the number, position, and relative intensity).

The ^{1}H NMR spectrum of complex **5** contains two characteristic signals for the olefinic and hydride protons appearing as doublets at δ 3.27 and −12.20 ($J = 0.9$ Hz). The signals are close to those of the complex $Ru_2(CO)_6(\mu\text{-}H)[O{=}C(CH_3)C(H){=}CPh]$ (see Table 1), whose structure was established by X-ray diffraction. Thus, complex **5** is a binuclear complex where the ruthenium atoms are linked through the M—M bond, μ-hydride bridge, and the oxadiene fragment of the ligand, which forms with one ruthenium atom the chelate five-membered oxaruthenacycle η^3-coordinated to the second ruthenium atom. The second olefin group is free of coordination.

The ^{1}H NMR spectrum of complex **6** contains one characteristic signal at δ 4.91 in the region corresponding to the signals for the protons of oxaruthenacycles involved in the η^3-coordination to the ruthenium atom. Such

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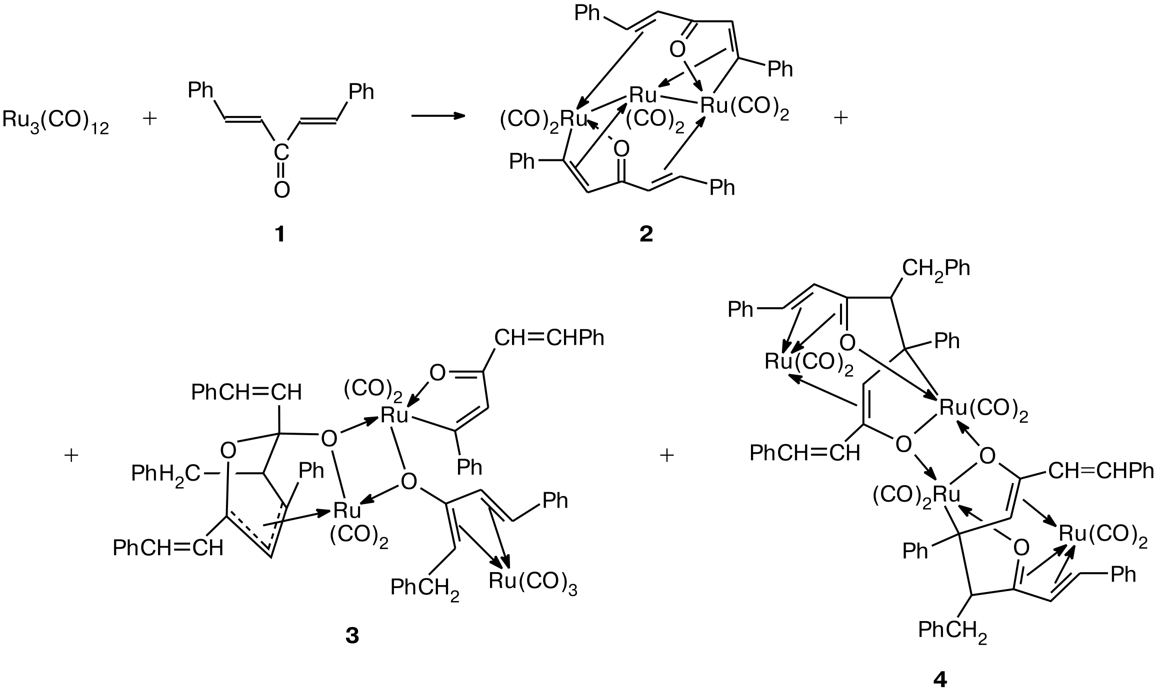
Scheme 1

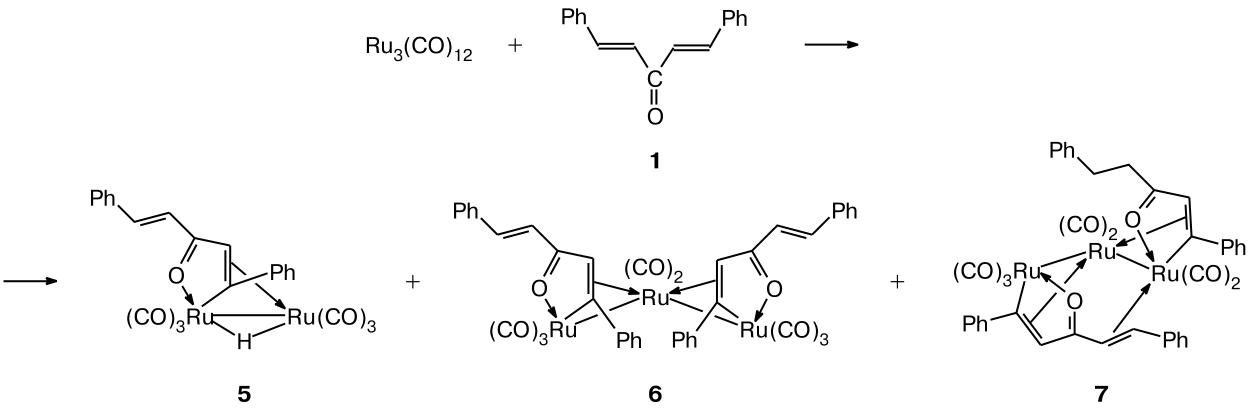


Conditions: refluxing, 4 h.

a characterisitc spectral pattern corresponds to the trinuclear complexes of a general formula $Ru_3(CO)_8[O=C(R')C(H)=CR'']_2$ (see Table 1), whose structures were established by the X-ray diffraction analysis. Thus, complex **6** contains the trinuclear metal chain where two terminal ruthenium atoms are chelated by the oxadiene fragments of the two ligands to form oxaruthenacycles. Both oxaruthenacycles η^3-coordinate to the central ruthenium atom. In contrast to complex **2**, one of each CH=CH groups of both ligands is involved in coordination. To conclude, complexes **5** and **6** formed in the initial reaction steps are analogous to those obtained in the reactions with oxadienes; the second olefin group of DBA has no effect on the behavior of the oxadiene fragment and acts only as a substituent.

Complex **7** was isolated from the reaction mixture together with complexes **5** and **6** and observed in later reaction steps.[4] The structure of complex **7** was established by the X-ray diffraction analysis, which showed that two ligand molecules are involved in the coordination to three

Scheme 2



Conditions: refluxing, 2—3 h.

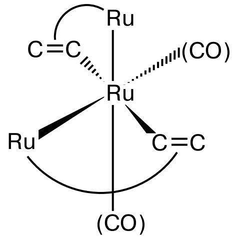
Table 1. IR and NMR spectra of the complexes obtained

Compound	IR $\nu(CO)/cm^{-1}$(hexane)	^1H NMR δ, (C_6D_6), J/Hz
$(PhCH=CH)_2CO$	1668 m, 1610 s	7.08 (d, 1 H, CH=CH, J = 16.0); 7.35—7.62 (m, 5 H, Ph); 7.74 (d, 1 H, CH=CH, J = 16.0)
$(PhCH_2CH_2)_2CO$	1684 m, 1612 s	2.76 (t, 2 H, CH_2, J = 7.8); 2.94 (t, 2 H, CH_2, J = 7.8); 7.35—7.62 (m, 5 H, Ph)
5	2098 s, 2064 v.s, 2038 s, 2016 v.s, 2008 s, 1980 m	−12.20 (d, 1 H, Ru—H, J = 0.9); 3.27 (d, 1 H, CH=C, J = 0.9); 6.86 (d, 1 H, CH=CH, J = 16.0); 6.98—7.65 (m, 11 H, Ph, CH=CH)
$Ru_2(CO)_6(\mu\text{-}H)[O=C(CH_3)C(H)=CPh]$[a,b]	2098 s, 2062 v.s, 2038 s, 2014 v.s, 2004 s, 1982 m	−12.50 (d, 1 H, Ru—H, J =1); 2.12 (s, 3 H); 3.55 (d, 1 H, CH=C, J =1); 7.0—7.6 (m, 5 H, Ph)
6	2086 s, 2074 v.s, 2024 v.s, 1998 s, 1938 w	4.91 (s, 1 H, CH=C); 6.72 (d, 1 H, CH=CH, J = 16.0); 6.62—8.10 (m, 12 H, Ph, CH=CH)
$Ru_3(CO)_8(O=C(Tol)C(H)=CPh)_2$* (**6´**)[a,b]	2088 s, 2074 v.s, 2020 v.s, 1996 s, 1934 w	2.36 (s, 3 H); 3.45 (s, 1 H); 6.8—7.1 (m, 9 H, Ph)
$Ru_3(CO)_8(O=C(Fc)C(H)=CFc)_2$* (**6″**)[a,c]	2078 s, 2064 v.s, 2008 v.s, 1980 s, 1946 w	3.64 (s, 1 H); 3.93 (m, 1 H); 4.13 (s, 5 H); 4.19 (s, 5 H); 4.29 (m, 1 H); 4.40 (m, 1 H); 4.46 (m, 1 H); 4.56 (m, 2 H); 4.63 (m, 1 H); 4.67 (m, 1 H)
7	2092 s, 2042 v.s, 2032 s, 2008 s, 1990 m, 1980 m	2.01 (s, 1 H, CH=C); 2.23 (t, 2 H, CH_2, J = 7.6); 2.83 (t, 2 H, CH_2, J = 7.6); 4.48 (s, 1 H, CH=C); 4.59 (d, 1 H, CH=C, J = 13.8); 5.66 (d, 1 H, CH=C, J = 13.8); 6.61—8.11 (m, 20 H, Ph)

[a] ^1H NMR spectra were recorded in $CDCl_3$. The data from Ref. 6. [b] The data from Ref. 1. [c] The data from Ref. 7.

metal atoms (Fig. 1, Table 2 and 3). The open metal chain contains two Ru—Ru bonds. Each ligand chelates one of the terminal ruthenium atoms to form the five-membered ruthenacycle. The oxaruthenacycles η^3-coordinate to the central ruthenium atom. This structural fragment is common for complexes **2**, **6**, and **7**. The complexes differ in the states of the olefin groups that are not involed in chelation. In complex **6**, both the olefin groups are free of coordination. In complex **2**, both the olefin groups π-coordinate to the ruthenium atom. In complex **7**, one of the olefin groups π-coordinate to the ruthenium atom (as in complex **2**) and the second olefin group is reduced to $CH_2—CH_2$. It should be noted that, upon the formation of oxaruthenacycle in the reactions of $Ru_3(CO)_{12}$ with both oxadienes and DBA, the ligand molecule loses the hydrogen atom, whereas the ligand in excess amounts act as the hydrogen acceptor and is reduced to the saturated ketones.[4] However, we have been unsuccessful earlier in isolating products from the reactions with oxadienes, which would contain the completely or partially reduced ligand as is observed in complex **7**.

Thus, the chain trinuclear clusters **2**, **6**, and **7** having similar structures were isolated in different steps of the reaction of $Ru_3(CO)_{12}$ with DBA. We assumed that the non-coordinated olefin groups of complex **6** can undergo π-coordination upon heating under the reaction conditions to form complex **2** or reduction to form complex **7**. However, the control experiments showed that complex **6** transforms upon heating into a mixture of other unidentified products (see Experimental). In order to understand the reason, we considered the spatial arrangement of the ligands around the central ruthenium atoms in complexes **2**, **6**, and **7** (see Ref. 8). The structure of complex **6** was not established by X-ray diffraction, but the structures of analogous complexes isolated in the reactions of $Ru_3(CO)_{12}$ with 1-*p*-tolyl-3-phenylprop-2-en-1-one (**6´**)[1] and 1,3-diferrocenylprop-2-en-1-one (**6″**)[7] have been determined



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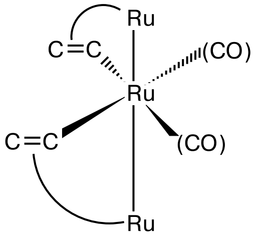

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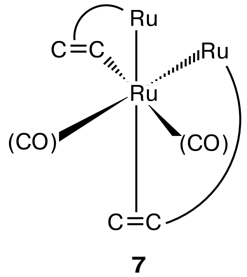


7

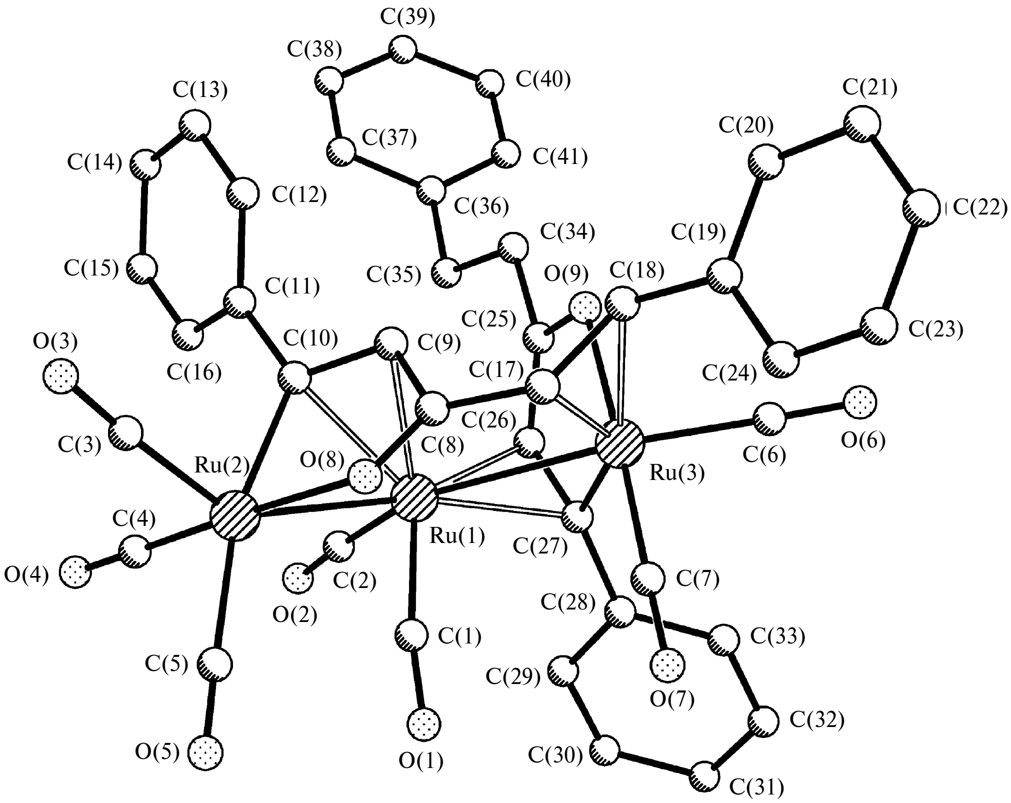


Fig. 1. Molecular structure of complex **7** (the minor part of the disordered CH_2CH_2Ph fragment and all hydrogen atoms are not shown).

earlier. Based on the analysis of the structures of two latter complexes, it was concluded that, when passing from the aryl substituent to the ferrocenyl one, the relative disposition of ligands in the coordination sphere of the central ruthenium atom remains unchanged. This allows us to assume that the passage to the styryl substituent in complex **6** will not change the spatial arrangement of ligands.

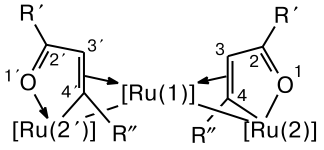
The central ruthenium atoms in complexes **2**, **6**, and **7** have a pseudo-octahedral ligand environment. The terminal ruthenium atoms are in the *trans*-position to each other in complex **6** and in the *cis*-position in complexes **2** and **7**. The π-coordinated C=C bonds in the oxaruthenacycle are in the *trans*-position to each other in complex **2** and in the *cis*-position in complexes **6** and **7**. The mutual disposition of two oxaruthenacycles relative to the central ruthenium atom is different in all complexes. Therefore, transformations of complexes cannot occur without cleavage of several bonds, which allows one to conclude that the forma-

Table 2. Principal bond lengths (*d*) for complex **7**

Bond	*d*/Å	Bond	*d*/Å
Ru(1)—Ru(2)	2.7966(8)	Ru(3)—C(17)	2.264(5)
Ru(1)—Ru(3)	2.8741(9)	Ru(3)—C(18)	2.336(5)
Ru(1)—C(9)	2.345(5)	O(8)—C(8)	1.249(5)
Ru(1)—C(10)	2.248(5)	C(8)—C(9)	1.488(7)
Ru(1)—C(26)	2.239(5)	C(9)—C(10)	1.394(6)
Ru(1)—C(27)	2.189(5)	C(17)—C(18)	1.385(6)
Ru(2)—C(10)	2.076(5)	O(9)—C(25)	1.285(6)
Ru(2)—O(8)	2.088(3)	C(25)—C(26)	1.418(7)
Ru(3)—C(27)	2.046(5)	C(26)—C(27)	1.445(6)
Ru(3)—O(9)	2.122(3)	C(34)—C(35)	1.487(9)

Table 3. Bond angles (ω) for complex **7**

Angle	ω/deg
Ru(2)—Ru(1)—Ru(3)	115.81(2)
C(10)—Ru(2)—O(8)	81.7(2)
C(8)—O(8)—Ru(2)	111.4(3)
O(8)—C(8)—C(9)	118.2(4)
C(10)—C(9)—C(8)	116.7(4)
C(9)—C(10)—Ru(2)	108.5(3)
C(18)—C(17)—C(8)	131.0(5)
C(17)—C(18)—C(19)	121.4(4)
C(27)—Ru(3)—O(9)	81.6(2)
C(25)—O(9)—Ru(3)	109.8(3)
O(9)—C(25)—C(26)	121.5(4)
C(25)—C(26)—C(27)	115.7(5)
C(26)—C(27)—Ru(3)	109.1(4)
C(35)—C(34)—C(25)	114.3(6)
C(34)—C(35)—C(36)	113.6(6)



2, 6′, 6″, 7

Table 4. Selected bond lengths and angles for complexes **2**, **6′**, **6′′**, and **7**

Complex	Bond/Å		Angle/deg	
	Ru(1)—Ru(2)	Ru(2)...Ru(2′)	ω*	φ**
2	2.840	4.276	97.7	156.3
6′	2.802	5.390	148.3	67.1
6″	2.777	5.445	157.2	91.6
7	2.797, 2.874	4.804	115.8	90.3

* The bond angle Ru(2)—Ru(1)—Ru(2′).

** The torsion angle X(1)—Ru(2)—Ru(2′)—X(1′) where X(1) is the center of the C(2)—C(3) bond and X(1′) is the center of the C(2′)—C(3′) bond.

tion of complexes occurs independently of each other. The geometric parameters characterizing the spatial differences between complexes **2**, **6**, and **7** are given in Table 4.

Thus, the reaction of $Ru_3(CO)_{12}$ with DBA affords, in the initial steps, the products that are typical of the reactions with oxadienes and the presence of the second olefin group has no impact on the reaction process. Upon a longer-term reaction, the complexes are produced, wherein additional coordination modes of the ligand are implemented.

Experimental

^1H NMR spectra were recorded on a Bruker AMX-400 (400.13 MHz) spectrometer in $CDCl_3$ and C_6D_6 using the residual signals for the incomletely deuterated $CDCl_3$ (δ_H for $CHCl_3$ is 7.25) and C_6D_6 (δ_H for C_6HD_5 is 7.25) as the internal standards. IR spectra were recorded on a Specord-75 IR spectrphotometer.

2,3,4-η³-(5-Phenyl-2-styryl-1-oxa-2-tricarbonylruthenacyclopenta-3,5-diene)-μ-hydridotricarbonylruthenium (5), bis-[2,3,4-η³-(5-phenyl-2-styryl-1-oxa-2-tricarbonylruthenacyclopenta-3,5-diene)]dicarbonylruthenium (6), and 2,3,4-η³-[η²-2-styryl-(5-phenyl-1-oxa-2-dicarbonylruthenacyclopenta-3,5-diene)]-2,3,4-η³-(2-phenylethyl-5-phenyl-1-oxa-2-tricarbonylruthenacyclopenta-3,5-diene)dicarbonylruthenium (7). ***A.*** A mixture of $Ru_3(CO)_{12}$ (320 mg, 0.5 mmol) and compound **1** (468.5 mg, 2 mmol) in heptane (150 mL) was refluxed for 2 h 20 min. After cooling to room temperature, the reaction mixture was filtered. A heptane solution was chromatographed on a silica gel column. By elution with petroleum ether, $Ru_3(CO)_{12}$ (120 mg), complex **5** (25 mg, 13.3%), complex **6** (10 mg, 3.2%), and an unidentified oily complex **X** (18 mg) were isolated. ^1H NMR for complex **X** (C_6D_6), δ: −12.27 (d, 1 H, Ru—H, J = 0.9 Hz); 3.96 (d, 1 H, CH=C, J = 0.9 Hz); 5.79 (s, 1 H, CH=C); 6.34 (s, 1 H, CH=C); 6.74 (d, 1 H, CH=CH, J = 16.0 Hz); 7.94 (d, 1 H, CH=CH, J = 16.0 Hz); 7.02—8.09 (m, 34 H, Ph, CH=CH). IR for complex **X** (hexane), ν(CO)/cm^{-1}: 2068 m, 2048 v.s, 2032 s, 2018 m, 2008 m, 1988 s, 1962 w. By elution with a petroleum ether—benzene (1 : 1) mixture, complex **7** (15 mg, 4.9%) and complexes **2** and **3** (negligible amounts) were isolated.

Complex **5**. Found (%): C, 46.02; H, 2.45. $C_{23}H_{14}O_7Ru_2$. Calculated (%): C, 45.73; H, 2.34.

Complex **6**. Found (%): C, 51.20; H, 2.69. $C_{42}H_{26}O_{10}Ru_3$. Calculated (%): C, 50.92; H, 2.65.

Complex **7**. Found (%): C, 51.20; H, 3.09. $C_{41}H_{29}O_9Ru_3$. Calculated (%): C, 51.00; H, 3.03. The fine red-orange crystals of complex **7** were obtained by recrystallization from a benzene-hexane mixture.

B. A mixture of $Ru_3(CO)_{12}$ (320 mg, 0.5 mmol) and compound **1** (468.5 mg, 2 mmol) in heptane (150 mL) was refluxed for 3 h. Same as previous, by elution with petroleum ether, $Ru_3(CO)_{12}$ (100 mg), complex **5** (5 mg, 2.6%), the oily complex **X** (20 mg), which was characterized by the spectra analogous to those of complex **X** obtained as described above, and complex **6** (20 mg, 6.4%) were obtained. By elution with a petroleum ehter—benzene (1 : 1) mixture, complex **7** (20 mg, 6.6%) and complexes **2** and **3** (negligible amounts) were isolated.

Reaction of complex 6 with dibenzylideneacetone (1). A mixture of complex **6** (12.5 mg, 0.01 mmol) and compound **1** (10 mg, 0.04 mmol) in heptane (20 mL) was refluxed for 1 h. After heating for 20 min, the IR spectrum of an unidentified compound was observed (hexane), ν(CO)/cm^{-1}: 2046 m, 2020 m, 2012 m, 1978 m, 1956 m). No traces of complexes **2** and **7** were detected. Further heating resulted in no changes in the IR spectrum.

X-ray diffraction study. The crystals of **7** · C_6H_6 ($C_{47}H_{34}O_9Ru_3$, M = 1045.95) are triclinic, space group $P\bar{1}$ 0303, at 120 K a = 7.927(2), b = 12.583(3), c = 21.065(5) Å, α = 98.877(5), β = 94.175(5), γ = 100.273(5)°, V = 2031.7(9) Å^3, Z = 2, d_{calc} = 1.710 g cm^{-3}, μ(Mo-Kα) = 11.59 cm^{-1}. The intensities of 20665 reflections (9688 independent reflections, R_{int} = 0.060) were measured on a Bruker SMART 1000 CCD autodiffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, ω-scanning, $2\theta_{max}$ = 56°, T = 120 K). The structure was solved by the direct method and refined by the full-matrix least squares method over F^2_{hkl} with the anisotropic thermal parameters for all non-hydrogen atoms. There are two solvate molecules of benzene in the structure, which are in particular positions on the inversion centers. The CH_2CH_2Ph group is disordered over two positions with population of positions 0.75/0.25. The hydrogen atoms were placed in the geometrically calculated positions and included in the refinement in the riding model. The final divergence factors are R_1 = 0.0459 (refinement over F_{hkl} for 5401 reflections with $I > 2\sigma(I)$), wR_2 = 0.0896, and S = 0.960 (refinement over F^2_{hkl} for all independent reflections). All calculations were performed using the SHELXTL software system.[9] The full tables of atomic coordinates, bond angles, and anisotropic thermal parameters were deposited in the Cambridge Crystallographic Data Centre.

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