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Dark and photochemical reactions of $Co_3Rh(CO)_{12}$ with diphenylacetylene. Crystal and molecular structure of the $Co_3Rh(\mu_2-CO)_2(CO)_8(\mu_4,\eta^2-PhC_2Ph)$ cluster

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Abstract

Dark and photochemical reactions of $Co_3Rh(CO)_{12}$ with diphenylacetylene yield two butterfly clusters with the alkyne inserted into the tetrametal framework. One of them is the previously unknown cluster $Co_3Rh(\mu-CO)_2(CO)_8(\mu_4,\eta^2-PhC_2Ph)$. It was characterized by X-ray crystallography (dark violet compound crystallizing in monoclinic space group $C2/c$, $a = 15.665(2)$, $b = 17.947(5)$, $c = 9.078(1)$ Å, $\beta = 93.91(1)°$, $v = 2546.1(8)$ Å^3, $Z = 4$). The ^{13}C NMR study showed that the solid state structure is retained in solution. The second product is the $Co_2Rh_2(\mu-CO)_2(CO)_8(\mu_4,\eta^2-PhC_2Ph)$ cluster obtained earlier and identified herein by its ^{13}C NMR spectrum. The formation of this cluster is evidently caused by bimolecular metal–metal exchange between cluster molecules in the course of the reaction.

Key words: Cobalt; Rhodium; Alkyne; Carbonyl; Cluster; Photochemistry

1. Introduction

The reactions of alkynes with transition metal carbonyl clusters have been the objects of considerable interest over the last two decades [1–9]. The main direction of these reactions of tetranuclear clusters is the insertion of a triple bond into tetrahedral cluster core to yield butterfly "M_4C_2" clusters. For the starting clusters containing at least two cobalt atoms, the insertion of an alkyne occurs into Co–Co bonds [2–6,9], in some cases the reaction being accompanied by destruction of the cluster [3,5,8] and metal exchange between the cluster molecules [3,10,11]. The reactions of heterometallic clusters are of especial interest because the direction of the alkyne insertion into the tetrahedral cluster core (cleavage of a certain M–M bond) depends on the composition of the cluster framework. In the present work the dark and photochemical reactions of the heterometallic $Co_3Rh(CO)_{12}$ cluster with diphenylacetylene were studied and the structures of the products obtained were established by ^{13}C NMR spectroscopy and X-ray crystallographic study.

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TABLE 1. ^{13}C NMR spectra of II in $CDCl_3$ at −53°C

δ, ppm	$^{13}C\{^1H\}$		^{13}C		Assignment	
	multiplicity	$^1J_{Rh-C}$, (Hz)	multiplicity	$^1J_{H-C}$, (Hz)		
203.9	broad signal				CO	6C
199.1	broad signal				CO	1C
192.5	broad signal				CO	1C
186.6	d	60			RhCO	1C
177.5	d	69			RhCO	1C
171.7	s		broaden		CoCPh	1C
168.6	d	16	broaden		RhCPh′	1C
150.9	s		broaden		*ipso* C(Ph)	1C
150.5	s		broaden		*ipso* C(Ph′)	1C
128.2	s		d	130	*para* C(Ph)	1C
127.9	s		d	130	*para* C(Ph′)	1C
127.7	s		d	130	*ortho* C(Ph)	2C
127.5	s		d	130	*ortho* C(Ph′)	2C
126.8	s		d	130	*metha* C(Ph and Ph′)	4C

2. Experimental section

$Co_3Rh(CO)_{12}$ was prepared by the published procedure [10]. Commercial-grade diphenylacetylene was recrystallized from hot hexane. All reactions were carried out under dry argon. IR spectra were recorded on a Specord M80 spectrophotometer, UV-Vis spectra on a Specord M40 spectrophotometer and mass spectra on a MX1301 mass spectrometer. The ^{13}C NMR spectra were recorded on a Bruker AM500 instrument using $Cr(acac)_3$ as a relaxation agent.

2.1. Dark reaction of $Co_3Rh(CO)_{12}$ (I) with PhC_2Ph

A mixture of (I) (117 mg, 0.190 mmol) and PhC_2Ph (1.054 g, 5.92 mmol) in hexane (60 ml) was stirred for 3 h at ambient temperature. The reaction was monitored by IR spectroscopy and TLC spot test. The reaction mixture obtained was subjected to initial separation by column chromatography (3 × 6 cm, Silica gel 100/250 mesh) with hexane as an eluant. The following bands were obtained in the order of elution: 1) colourless band of PhC_2Ph; 2) brown band of (I), 10 mg; 3) blue band containing mixture of $Co_3Rh(CO)_{10}PhC_2Ph$ (II) and $Co_2Rh_2(CO)_{10}PhC_2Ph$ (III); 4) yellow band containing trace amount of unidentified compounds. Subsequent careful separation of the third band (column 3 × 15 cm, Silpearl 5/40 mesh, hexane) gave a violet band of II (68 mg, 0.092 mmol) and a pink-violet band of III (48 mg, 0.061 mmol). IR spectrum of II (hexane, ν_{CO}): 2093w, 2068w, 2063vs, 2048w, 2038s, 2030vs, 1993w, 1894w, 1880w cm^{-1}. In the long-wave region of the UV-Vis spectrum of II we observed only one maximum with $\lambda = 581$ nm. It should be noted that the chromatographic bands of II and III could not be fully separated and contained admixtures of each other due to the very close chromatographic retention parameters. This should be taken into account when considering the IR spectrum of II. The ^{13}C NMR spectra of II and III are given in Tables 1 and 2. In the mass spectra of both II and III the heaviest ion $Co_2(CO)_6PhC_2Ph^+$ was registered, and we observed the consequent loss of 6 CO groups as well.

TABLE 2. ^{13}C NMR spectra of (III) in $CDCl_3$ at −53°C

$^{13}C\{^1H\}$			$^{13}C\{^1H\}$ *			Assignment	
δ, ppm	multiplicity	$^1J_{Rh-C}$, (Hz)	δ, ppm	multiplicity	$^1J_{Rh-C}$, (Hz)		
202.0	broad signal		202	broad signal		CO	6C
187.0	d	60	187.4	d	60	RhCO ax	2C
176.7	d	68	177.0	d	77	RhCO eq	2C
176.1	d	13	175.8	m		RhCPh	2C
151.2	s		151.7	s		*ipso* C(Ph)	2C
128.1	s		128.2	s		*para* C(Ph)	2C
127.6	s		127.7	s		*ortho* C(Ph)	4C
126.7	s		127.0	s		*metha* C(Ph)	4C

* Note: The data are taken from [2].

2.2. Photochemical reaction of $Co_3Rh(CO)_{12}$ (I) with PhC_2Ph

A mixture of I (37 mg, 0.060 mmol) and PhC_2Ph (1.128 g, 6.34 mmol) in hexane (60 ml) was irradiated in an annular quartz photoreactor with high-pressure Hg lamp DRL 250 W. A molybdenum-glass filter (T_{360nm} = 50%, T_{320} = 10%, T_{300} = 2%) was used to separate the 365 nm emission line. The reaction was monitored by IR spectroscopy and the TLC spot test. Irradiation was carried out up to 90% conversion of I, *ca.* 20 min. The reaction mixture obtained was separated in a manner analogous to that used in the dark synthesis. The compounds II (25 mg, 0.034 mmol) and III (9 mg, 0.012 mmol) were obtained as the main alkyne-insertion products.

2.3. Crystal structure determination

Single crystals of II suitable for an X-ray study were obtained by evaporation of the solvent from a hexane solution of II at −10°C. A black plate crystal (0.30 × 0.14 × 0.04 mm) was used in the crystallographic study. Unit cell dimensions were determined by the least-squares treatment of the setting angles of 13 reflections (40.7° < 2θ < 42.3°) measured on a Rigaku AFC5R diffractometer at 23 ± 1°C by use of graphite-monochromated Cu Kα radiation. Crystal data: $C_{24}H_{10}O_{10}Co_3Rh$, monoclinic, c-centred lattice, space group $C2/c$, a = 15.665(2), b = 17.947(5), c = 9.078(1) Å, β = 93.91(1)°, V = 2546.1(8) Å^3, Z = 4, d_{calc} = 1.925 g/cm^3, μ(Cu Kα) = 206.97 cm^{-1}. Intensities were measured on a diffractometer with a 12 kW rotating anode generator. Reflection with weak intensity (I < 10$\sigma(I)$) was scanned twice to accumulate peak counts. Background was measured at each end of the scan for

TABLE 3. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
M	−0.08335(3)	0.17575(3)	−0.29665(7)	2.51(2)
Co	0.02785(7)	0.23968(6)	−0.4400(1)	3.33(3)
O(1)	−0.2718(4)	0.1940(4)	−0.3864(8)	6.8(2)
O(2)	−0.0855(6)	0.0127(5)	−0.366(1)	11.2(3)
O(3)	0.1064(6)	0.3368(4)	−0.6476(9)	9.0(2)
O(4)	0.1580(5)	0.1303(4)	−0.4938(8)	7.8(2)
O(5)	−0.0880(5)	0.1743(4)	−0.6687(7)	7.1(2)
C(1)	−0.1988(5)	0.1898(4)	−0.3559(9)	4.3(2)
C(2)	−0.0852(6)	0.0738(6)	−0.337(1)	6.0(2)
C(3)	0.0771(6)	0.3021(5)	−0.565(1)	5.4(2)
C(4)	0.1094(6)	0.1666(5)	−0.431(1)	5.4(2)
C(5)	−0.0477(5)	0.1973(5)	−0.5683(9)	4.7(2)
C(6)	−0.0447(4)	0.2874(3)	−0.2692(7)	2.9(1)
C(7)	−0.1000(4)	0.3533(4)	−0.3056(7)	3.3(1)
C(8)	−0.0747(5)	0.4083(4)	−0.4000(10)	4.9(2)
C(9)	−0.1259(6)	0.4682(5)	−0.442(1)	6.1(2)
C(10)	−0.2026(6)	0.4754(5)	−0.382(1)	6.5(2)
C(11)	−0.2299(5)	0.4233(5)	−0.2837(9)	4.7(2)
C(12)	−0.1793(5)	0.3628(4)	−0.2474(9)	3.9(2)
H(8)	−0.0197	0.4047	−0.4374	4.9
H(9)	−0.1082	0.5034	−0.5123	6.1
H(10)	−0.2379	0.5171	−0.4071	6.5
H(11)	−0.2834	0.4292	−0.2417	4.7
H(12)	−0.1987	0.3265	−0.1811	3.9

$B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{32}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_b^*cc^* \cos\alpha)$

TABLE 4. Selected Bond Lengths and Angles *

Bond length (Å)			
M′–M	2.690(1)	O(1)–C(1)	1.161(10)
M–Co	2.521(1)	O(2)–C(2)	1.13(1)
M–Co′	2.536(1)	O(3)–C(3)	1.10(1)
M–C(1)	1.868(8)	O(4)–C(4)	1.177(10)
M–C(2)	1.87(1)	O(5)–C(5)	1.15(1)
M–C(4)	2.142(9)	C(6)–C(6′)	1.42(1))
M–C(6)	2.103(6)	C(6)–C(7)	1.490(10)
Co–C(3)	1.804(9)		
Co–C(4)	1.828(8)	C–C bonds in phenyl	
Co–C(5)	1.775(9)	group: 1.36(1)–1.392(10)	
Co–C(6)	2.161(6)		
Co–C(6′)	2.084(6)		
Bond Angle (deg)			
M′–M–Co	58.15(3)	C(3)–Co–C(4)	98.4(4)
–Co′	57.59(3)	–C(5)	98.6(4)
–C(1)	172.1(2)	–C(6)	118.2(3)
–C(2)	93.6(3)	–C(6′)	106.5(3)
–C(4′)	86.6(2)	C(4)–Co–C(5)	98.8(4)
–C(6)	72.4(2)	–C(6)	130.8(4)
Co–M–Co′	91.28(4)	–C(6′)	102.2(3)
–C(1)	118.6(2)	C(5)–Co–C(6)	106.3(3)
–C(2)	110.3(3)	–C(6′)	144.3(3)
–C(4′)	135.8(2)	C(6)–Co–C(6′)	39.0(3)
–C(6)	54.8(2)	M–C(1)–O(1)	175.0(7)
Co′–M–C(1)	116.9(3)	–C(2)–O(2)	177 (1)
–C(2)	127.6(3)	Co–C(3)–O(3)	175.5(9)
–C(4′)	45.0(2)	M′–C(4)–Co	79.0(3)
–C(6)	52.4(2)	–O(4)	132.8(7)
C(1)–M–C(2)	94.2(4)	Co–C(4)–O(4)	148.1(8)
–C(4′)	92.6(3)	–C(5)–O(5)	168.6(7)
–C(6)	99.8(3)	M–C(6)–Co	72.5(2)
C(2)–M–C(4′)	96.5(4)	–Co′	74.6(2)
–C(6)	163.3(3)	–C(6′)	107.5(2)
C(4′)–M–C(6)	91.8(3)	–C(7)	124.9(5)
M–Co–M′	64.26(3)	Co–C(6)–Co′	116.8(3)
–C(3)	161.3(3)	–C(6′)	67.6(4)
–C(4)	99.0(3)	–C(7)	118.8(4)
–C(5)	72.0(3)	Co′–C(6)–C(6′)	73.4(4)
–C(6)	52.7(2)	–C(7)	124.3(4)
–C(6′)	76.4(2)	C(6′)–C(6)–C(7)	127.1(4)
M′–Co–C(3)	132.6(3)	C(6)–C(7)–C(8)	121.1(6)
–C(4)	56.0(3)	–C(12)	122.2(6)
–C(5)	122.5(3)		
–C(6)	74.8(2)	bond angles in the	
–C(6′)	53.1(2)	phenyl group: 166.7(7)–122.9(7)	

* The primed atom is related to the unprimed one by the two-fold axis going through the mid points of M–M′ and C(6)–C(6′) bonds.

half the scan time. Corrections were made for Lorentz and polarization effects, and for absorption [12]. Three standard reflections, monitored every 150 intensity measurements, showed no significant decay during the data collection. A total of 1970 independent reflections was collected, of which 1464 with $I > 3\sigma(I)$ were used for the structural analysis.

The crystal structure was solved by the direct method [13,14]. The positional and thermal parameters of non-hydrogen atoms were refined by full matrix least-square method. The refinement of all non-hydrogen (anisotropic approximation) atoms converged at $R = 0.040$ ($R_W = 0.064$). The minimized function was $\Sigma w(|F_O| - |F_C|)^2$, where $w = \sigma(F_O)^{-2}$, its goodness of fit being 1.20. All H atoms were located on the calculated positions and included in calculation with isotropic temperature factors but no refinement was made for their parameters. Atomic coordinates and selected structural parameters are given in Tables 3 and 4.

Atomic scattering factors, with corrections for anomalous dispersion for Rh and Co [15], were taken from [16]. All calculations were performed by use of TEXSAN [17] program package.

3. Results and discussion

The mixed-metal tetrametal cluster $Co_3Rh(CO)_{12}$ readily reacts with diphenylacetylene under photochemical excitation and dark conditions

$$Co_3Rh(CO)_{12} + PhC_2Ph \longrightarrow$$

$$\underset{(II)}{Co_3Rh(CO)_{10}PhC_2Ph} + \underset{(III)}{Co_2Rh_2(CO)_{10}PhC_2Ph}$$

1. $h\nu$, $\lambda_{irr} > 320$ nm, 20 min

2. dark, 25°C, 3 h

yielding a mixture of two alkyne-tetrametal butterfly clusters II and III in different ratios in the cases of dark and photochemical reactions. The compound III was obtained earlier [5] and spectroscopically characterized [2,5]. The ^{13}C NMR spectrum of III (Table 2) is

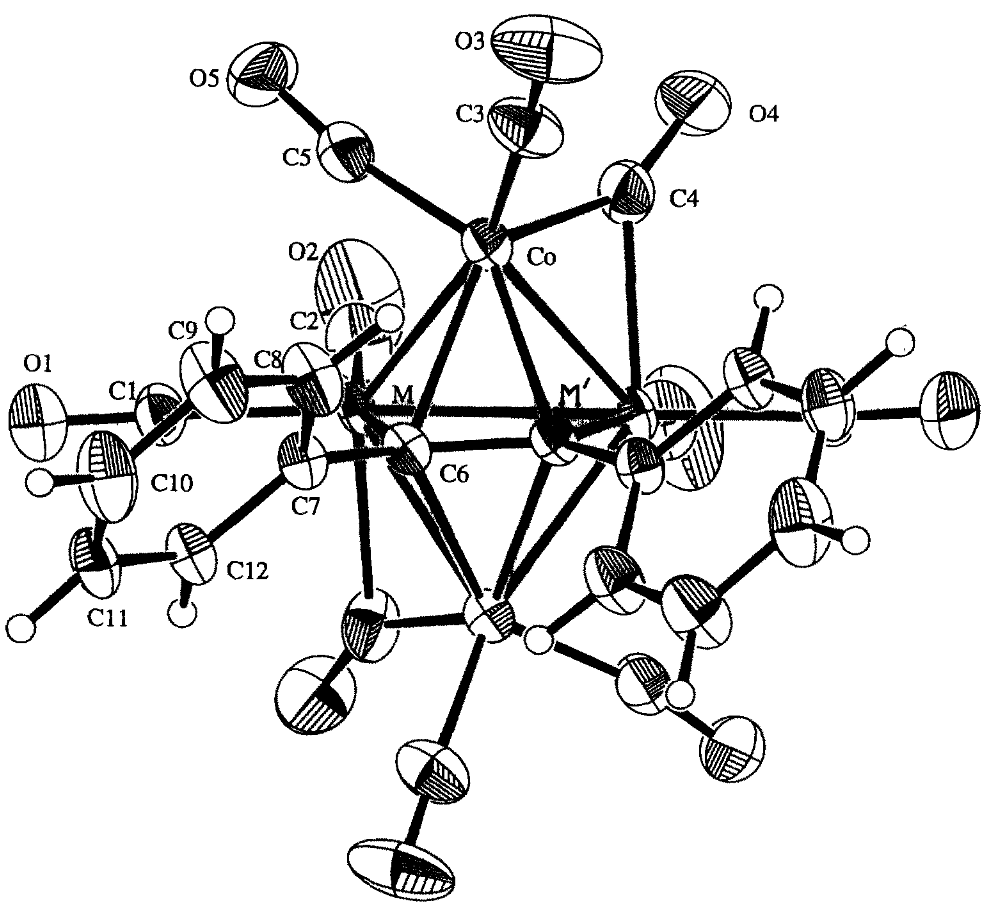

Fig. 1. ORTEP drawing of $Co_3Rh(CO)_{10}PhC_2Ph$ with 30% probability ellipsoids. Hydrogen atom is represented by a sphere with an arbitrary radius. M denotes the hybrid atom composed of 50% Co and 50% Rh atoms.

fully consistent with that given in [2]. The appearence of III among the reaction products evidently resulted from the metal substitution in the core of the starting cluster. Such a metal substitution or redistribution was earlier observed for the Co–Rh [10,11] and Co–Fe [3] clusters, the process being stimulated by the presence of substituting ligand ($P(OMe)_3$) in the reaction mixture [10]. In these cases the dark reaction of $Co_3Rh(CO)_{12}$ with three-fold excess of the ligand yields $Co_3Rh(CO)_{10}L_2$ (20%), $Co_3Rh(CO)_9L_3$ (30%), and $Co_2Rh_2(CO)_{10}L_2$ (20%). In the present work the dark reaction of $Co_3Rh(CO)_{12}$ with diphenylacetylene was found to afford 60% of $Co_3Rh(CO)_{10}PhC_2Ph$ and 40% of $Co_2Rh_2(CO)_{10}PhC_2Ph$ in a similar way. The corresponding photochemical reaction is more selective with respect to the alkyne insertion into the Co_3Rh framework yielding the compound II as the main product.

The molecular structure of II established by the X-ray crystallographic study is shown in Fig. 1. It was found that in the solid state the molecule of II has a crystallographically imposed two-fold axis: in a butterfly shaped Co_3Rh framework two of the three Co atoms are in the terminal positions of the respective wings, whereas the remaining Co and Rh atoms are in disorder on the intersection of two wings (hinge positions). These atoms are denoted as M and M′. Atomic coordinates and selected bond lengths and angles for II are given in Tables 3 and 4. The structure of II is typical of the products obtained in the reactions of alkynes with the $Co_4(CO)_{12}$ [18,19] and $Co_2Rh_2(CO)_{12}$ [5] clusters and contains butterfly cluster framework with two terminal CO ligands at each metal atom, two μ_2-bridging CO ligands and alkyne inserted into the Co–Co bond. Main structural parameters of the molecule are close to those determined for the structurally related molecules $Co_4(CO)_{10}RC_2R$ [18,19] and $Co_2Rh_2(CO)_{10}RC_2R$ [5]. The Co–Rh bond in the basal plane of Co_3RhC_2 framework in II (mean 2.529 Å) is elongated as compared to "hinge-apex" bonds in $Co_2Rh_2(CO)_{10}F_5C_6C_2C_6F_5$ (mean 2.527 Å) [5]. The same elongation is observed in $Co_4(CO)_{10}EtC_2Et$ [18] and $Co_3Ru(CO)_{10}PhC_2Ph^-$ [4]. The alkyne is inserted into the butterfly framework in a slightly asymmetrical mode (Co–C6 2.161(6), Co–C6′ 2.084(6) Å). A similar distortion is typical of the Co_4C_2 [11,18], $Co_2Rh_2C_2$ [5], Co_3RuC_2 [4] and $Co_2Ru_2C_2$ [9] clusters with the difference in the corresponding bond lengths ranging from 0.15 [18] to 0.05 Å [5]. The value of the C–C distance 1.42 Å in the alkyne moiety of II falls in the range typical of triple bonds inserted into the butterfly tetrametal clusters, which vary from 1.369 Å [5] in $Co_2Rh_2(CO)_{10}F_5C_6C_2C_6F_5$ to 1.44 Å [18] in $Co_4(CO)_{10}EtC_2Et$.

The ^{13}C NMR spectrum of II given in Table 1 is fully consistent with the structure of the molecule in the solid state. Three broad signals 203.9, 199.1, and 192.5 ppm (6 : 1 : 1) can be attributed to the CO groups bound to Co atoms and μ_2-CO ligands. These CO ligands exchange even at −53°C. In contrast, rhodium bound terminal carbonyls are rigid and appear in the spectrum as two doublets (186.6 and 177.5 ppm with $^1J_{Rh-O}$ = 60 and 69 Hz respectively), that is typical for the Rh–C coupling of terminal carbonyl groups. Similar behaviour of the CO environment was observed for $Co_2Rh_2(CO)_{10}PhC_2Ph$ [2,5]. All other signals in the spectrum can easily be assigned to carbon atoms of the inserted diphenylacetylene ligand (Table 1).

The heaviest ion registered in the mass spectra of both II and III is $Co_2(CO)_6PhC_2Ph^+$. The formation of this ion is evidently due to the thermal decomposition of II and III in the mass spectrometer chamber at elevated temperature. A possible scheme of the thermal decomposition of II and III is shown in Fig. 2.

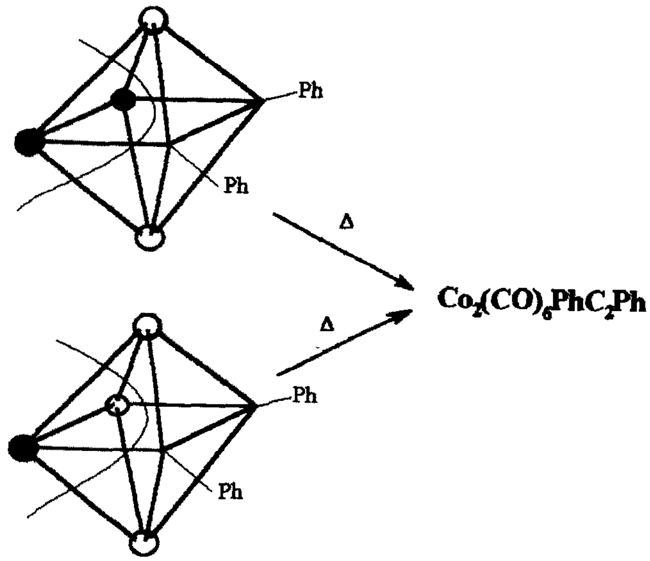

Fig. 2. Possible scheme of the thermal decomposition of $Co_3Rh(CO)_{10}PhC_2Ph$ and $Co_2Rh_2(CO)_{10}PhC_2Ph$.

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