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Transformation of μ_3 -acetylide cluster $\text{Co}_2(\text{CO})_6 [\mu\text{-PhC}\equiv\text{CRe}(\text{CO})_5]$ into carbyne cluster $\text{Co}_2\text{Re}(\text{CO})_{10}(\mu_3\text{-CPh})$

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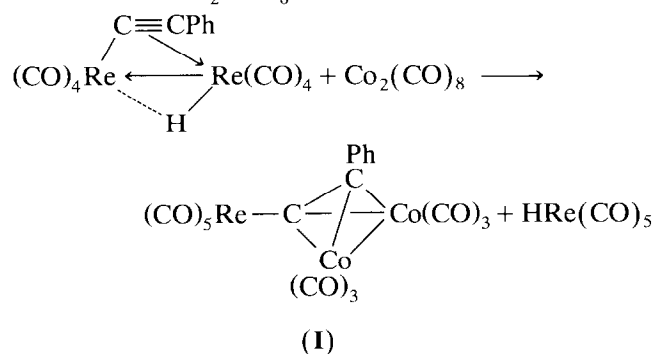
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Abstract

The acetylide complex $\text{Co}_2(\text{CO})_6[\mu\text{-PhC}\equiv\text{CRe}(\text{CO})_5]$ (**I**) undergoes nondestructive reaction with oxygen which results in the net loss of one acetylide carbon atom together with a CO ligand and accompanied by the formation of the carbyne cluster $\text{Co}_2\text{Re}(\text{CO})_{10}(\mu_3\text{-CPh})$ (**II**). According to X-ray structural data, cluster **II** is a distorted tetrahedral which contains Co–Co (2.526(4) Å) and Co–Re (2.694(4) and 2.704(3) Å) bonds.

1. Introduction

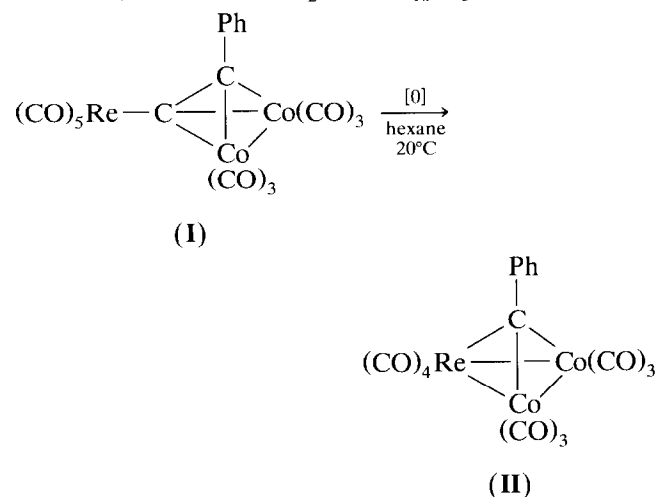
Organometallic acetylide complexes of transition metals in general, and $\text{PhC}\equiv\text{CRe}(\text{CO})_5$ in particular, [1] have been used as “building blocks” for the direct synthesis of heterometallic clusters. We have previously shown that this complex can easily be formed by treatment of the binuclear acetylide-hydride carbonyl complex of rhenium with cobalt carbonyl followed by coordination with $\text{Co}_2(\text{CO})_6$ to form cluster **I** [2].



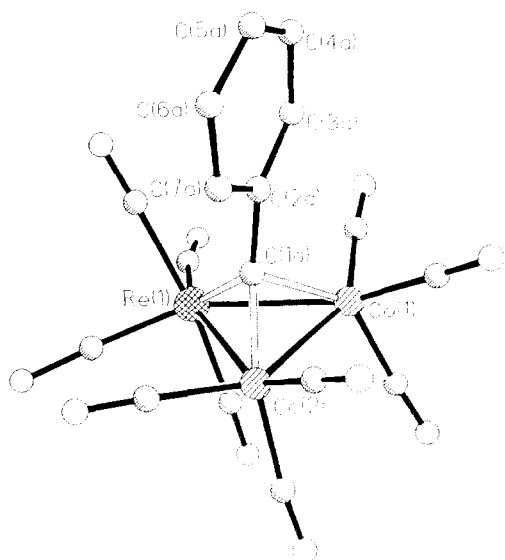
Here we report the transformation of cluster **I** into the μ_3 -carbyne cluster, the process being accompanied by the loss of an acetylide carbon atom.

2. Results and discussion

Exposure in air of $\text{Co}_2(\text{CO})_6[\mu\text{-PhC}\equiv\text{CRe}(\text{CO})_5]$ (**I**) in hexane for two days results in the formation of the new carbyne complex $\text{Co}_2\text{Re}(\text{CO})_{10}(\mu_3\text{-CPh})$ (**II**).



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Fig. 1. The molecular structure of $\text{Co}_2\text{Re}(\text{CO})_{10}(\mu_3\text{-CPh})$.

II was obtained in the form of black-red crystals stable in air.

In the IR spectra of cluster **II** bands are observed which are characteristic of terminal CO groups ($1940\text{--}2090\text{ cm}^{-1}$).

The structure of **II** has been studied by X-ray structural analysis (Fig. 1). Atomic coordinates, bond lengths and bond angles are given in Tables 1, 2 and 3 respectively. Cluster **II** is a distorted tetrahedral with a Co–Co bond ($2.526(4)\text{ \AA}$) and equal Co–Re bonds ($2.694(4)$ and $2.701(3)\text{ \AA}$). The Re(1)–C(1a) bond ($2.141(25)\text{ \AA}$)

TABLE 1. Atomic coordinates for $\text{Co}_2\text{Re}(\text{CO})_{10}(\mu_3\text{-CPh})$ ($\times 10^4$ for Co, Re, O, C)

Atom	x	y	z
Re(1)	3998(1)	2627(1)	3779(1)
Re(2)	1526(1)	–2377(1)	1052(1)
Co(1)	2075(3)	2521(2)	4892(2)
Co(2)	998(3)	1354(2)	3662(2)
Co(3)	4535(4)	–1391(2)	1794(2)
Co(4)	3604(4)	–3183(2)	1933(2)
C(1A)	1503(28)	2638(16)	3713(11)
C(2A)	654(25)	3381(13)	3442(17)
C(3A)	974(30)	4316(16)	3858(16)
C(4A)	100(37)	4953(16)	3512(20)
C(5A)	–1033(31)	4675(18)	2843(19)
C(6A)	–1335(39)	3752(22)	2395(20)
C(7A)	–471(33)	3116(20)	2788(26)
C(1B)	3990(37)	–2424(18)	1157(13)
C(2B)	4725(31)	–2706(15)	358(15)
C(3B)	4254(36)	–3638(18)	–43(15)
C(4B)	4933(52)	–3853(25)	–681(20)
C(5B)	6249(43)	–3146(26)	–915(19)
C(6B)	6765(39)	–2216(22)	–533(15)
C(7B)	5984(41)	–2003(19)	90(19)

TABLE 2. Bond lengths (\AA) in $\text{Co}_2\text{Re}(\text{CO})_{10}(\mu_3\text{-CPh})$

Re(1)–Co(1)	2.694(4)	C(3A)–C(4A)	1.434(41)
Re(1)–Co(2)	2.701(3)	C(4A)–C(5A)	1.353(40)
Re(2)–Co(3)	2.676(3)	C(5A)–C(6A)	1.449(42)
Re(2)–Co(4)	2.704(4)	C(6A)–C(7A)	1.458(49)
Co(1)–Co(2)	2.526(4)	C(2A)–C(7A)	1.330(42)
Co(3)–Co(4)	2.524(4)	C(1B)–C(2B)	1.675(39)
Re(1)–C(1A)	2.141(25)	C(2B)–C(3B)	1.409(32)
Co(1)–C(1A)	2.030(19)	C(3B)–C(4B)	1.380(51)
Co(2)–C(1A)	1.781(22)	C(4B)–C(5B)	1.423(50)
Co(3)–C(1B)	1.720(24)	C(5B)–C(6B)	1.393(45)
Co(4)–C(1B)	1.772(25)	C(2B)–C(7B)	1.415(38)
Co(3)–Co(4)	2.524(4)		
C(1A)–C(2A)	1.508(34)		
C(2A)–C(3A)	1.436(32)		

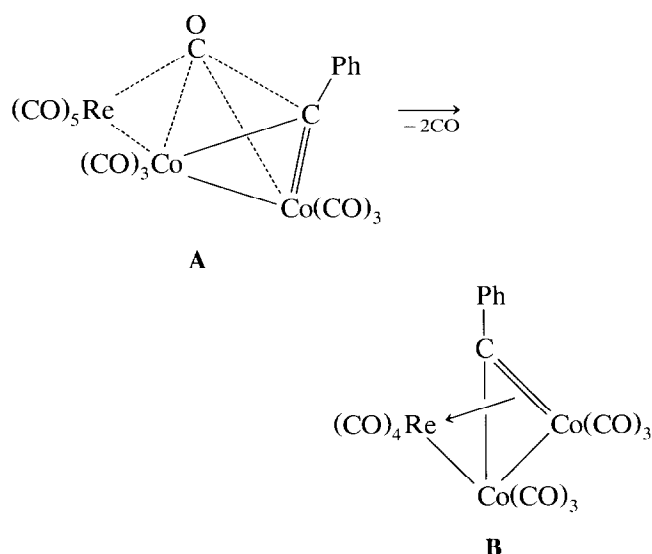
is of normal length for a single bond, however, the bond lengths Co–C(1a) do differ (Co(2)–C(1a) $1.781(22)$ and Co(1)–C(1a) $2.030(19)\text{ \AA}$). The angles ReC(1a)Co ($86.5(11)$ and $80.4(8)^\circ$) and CoC(1a)C(2a) ($136.7(15)$ and $119.1(17)^\circ$) differ respectively. This is evidence of the contribution of Co(2)–C(1a) multiple bonding.

The formation of cluster **II** is probably via oxidation of the acetylide carbon atom by traces of oxygen, in analogy with the oxidation of the cluster $\text{Co}_2(\text{CO})_6[\text{Ph-C}\equiv\text{CM}(\text{CO})_2\text{Cp}]$ ($\text{M} = \text{Fe, Ru}$) into μ_3 -carbyne clusters $\text{Co}_2\text{MCp}(\text{CO})_7(\mu_3\text{-CPh})$ [3]. We suggest that the inner carbon atom in **I**, *i.e.* the one which is attached to three metal atoms, is attacked by oxygen, and the resulting CO unit is lost subsequently by decarbonylation. This process is accompanied by scission of the

TABLE 3. Bond angles ($^\circ$) in $\text{Co}_2\text{Re}(\text{CO})_{10}(\mu_3\text{-CPh})$

Co(1)Re(1)Co(2)	55.8(1)	Co(4)Co(3)C(1B)	44.5(8)
Re(1)Co(1)Co(2)	62.2(1)	Re(2)Co(4)C(1B)	51.7(11)
Re(2)Co(3)Co(4)	62.6(1)	Re(2)C(1B)Co(3)	87.6(14)
Co(3)Re(2)Co(4)	55.9(1)	Co(3)C(1B)Co(4)	92.6(11)
Re(1)Co(2)Co(1)	61.9(1)	Co(3)C(1B)C(2B)	131.7(18)
Re(2)Co(4)Co(3)	61.5(1)	Re(2)C(1B)Co(4)	87.4(12)
Co(2)Re(1)C(1A)	41.2(6)	Re(2)C(1B)C(2B)	121.6(15)
Re(1)Co(1)C(1A)	51.6(7)	Co(4)C(1B)C(2B)	124.2(20)
Co(1)Co(2)C(1A)	52.8(6)		
Co(1)Re(1)C(1A)	48.0(5)		
Co(2)Co(1)C(1A)	44.4(6)		
Re(1)Co(2)C(1A)	52.3(8)		
Re(1)C(1A)Co(1)	80.4(8)		
Co(1)C(1A)Co(2)	82.8(9)		
Co(1)C(1A)C(2A)	119.1(17)		
Re(1)C(1A)Co(2)	86.5(11)		
Re(1)C(1A)C(2A)	131.2(14)		
Co(2)C(1A)C(2A)	136.7(15)		
Co(3)Re(2)C(1B)	39.9(6)		
Re(2)Co(3)C(1B)	52.5(11)		
Co(3)Co(4)C(1B)	42.9(8)		

C–C, Re–C, Co–C and formation of the $(\text{CO})_5\text{Re}–\text{CO}$ bond (form A).



The subsequent π -coordination of the $\text{Co}=\text{CPh}$ bond with the Re atom takes place via the loss of the second CO group, which results in form B.

3. Experimental section

All operations associated with synthesis and isolation of the initial and final complexes were carried out under argon flow, including the purification of the hydrocarbon solvents by distillation over dispersed sodium. The initial complex I was synthesized previously [2]; $\text{Co}_2(\text{CO})_8$ was obtained in accordance with established techniques [4]. IR spectra were measured, in KBr pellets with a Specord IR 75 instrument.

X-ray structural data for complex II were obtained on a Siemens P3/PC automatic diffractometer ($\lambda(\text{Mo K}\alpha)$, θ – 2θ scan). The crystal data are in Table 4. Structure II was solved by direct methods and refined in anisotropic full-matrix approximation for all non-hydrogen atoms.

3.1. $\text{Co}_2\text{Re}(\text{CO})_{10}(\mu_3\text{-CPh})$ (II)

The green solution of $\text{Co}_2(\text{CO})_6[\mu\text{-PhC}\equiv\text{CRe}(\text{CO})_5]$ (I) 0.3 g (0.42 mmol) in 50 ml of hexane was stirred in air at room temperature for 48 h until the solution had attained a stable green-brown colour. Monitoring of

TABLE 4. Crystal data of compound II

Crystal structure	Triclinic
Space group	$P\bar{1}$
a , Å	8.621(5)
b , Å	14.455(7)
c , Å	17.128(8)
β , deg	98.84(2)
V , Å ³	2019(2)
Z	4 ^a
Number of reflections measured	6171
Number of reflections used in refinement with $I \geq 4\sigma$	5258
R	0.089
R_w	0.081

^a Two independent molecules comprise the unit cell.

the reaction was by TLC. The solution was then concentrated at 60°C/0.1 Torr to a volume of 10 ml, and the residue was chromatographed on an SiO_2 column (5 × 20 cm). The zones were eluted in the following succession: cherry-brown (1) (by pentane) and green (2) (by hexane). After concentration of fraction 2 green crystals of $\text{Co}_2(\text{CO})_6[\mu\text{-PhC}\equiv\text{CRe}(\text{CO})_5]$ precipitated to an amount of 0.11 g (33%), (IR spectrum ($\nu(\text{CO})$, cm^{-1}): 1980vs, 2025vs, 2065s, 2140m). The solvent of fraction 1 was concentrated under vacuum, 5–6 ml of heptane-benzene 1:3 mixture was added and it was kept at 5°C for 24 h. The precipitated black-red crystals of II were isolated from the solution by decantation, washed in pentane and dried under vacuum. Yield of the crystals was 0.14 g (50%). IR spectrum (ν , cm^{-1}): 580w, 665w, 1940m, 1975vs, 2000s, 2032vs, 2090m).

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