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Synthesis and molecular structures of $Co_2(CO)_{6-n}(PPh_3)_n[\mu\text{-}C_2(CH_2R)_2]$ ($R = CH_2OH$ or CH_2SCMe_3) derivatives containing chelated $[CpFe(CO)_2]_2Sn$ or $W(CO)_4$ fragments

A.A. Pasynskii [a],*, Y.V. Torubaev [a], F.S. Denisov [a], A.Y. Lyakina [b], R.I. Valiullina [a],
G.G. Alexandrov [a], K.A. Lyssenko [c]

[a] *N.S. Kurnakov Institute of General and Inorganic Chemistry RAS, Leninsky Prosp. 31, Moscow V-71, 117907, Russia*
[b] *Higher Chemical College RAS, Miusskaya pl. 9, Moscow, Russia*
[c] *A.N. Nesmeyanov Institute of Organoelement Compounds RAS, ul. Vavilova 28, Moscow V-334, 117813, Russia*

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Dedicated to Professor Stanisław Pasynkiewicz, an outstanding chemist and good friend, on the occasion of his 70th birthday

Abstract

Reaction of $[Co_2(CO)_6][\mu\text{-}C_2(CH_2OH)_2]$ with $[CpFe(CO)_2]_2Sn(OMe)_2$ or interaction of $[Co_2(CO)_5(PPh_3)][\mu\text{-}C_2(CH_2SCMe_3)_2]$ with $W(CO)_5(THF)$ gives mixed-metal chelate derivatives $[Co_2(CO)_6][\mu\text{-}C_2(CH_2O)_2]Sn[CpFe(CO)_2]_2$ and $[(Ph_3P)Co_2(CO)_5][\mu\text{-}C_2(CH_2SCMe_3)_2][W(CO)_4]$, respectively, characterized by X-ray diffraction analysis. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Cobalt; Iron; Tin; Tungsten; Acetylene π-complex; Mixed-metal cluster; Chelate; X-ray analysis

1. Introduction

The planned syntheses of mixed-metal compounds is important for the preparation of mixed-metal catalysts or precursors of complex materials. One method is to use transition metal complexes as ligands to another metal atom. From this, it was interesting to prepare mixed-metal derivatives of dicobalt–carbonyl complexes of functionally substituted acetylenes, where another metal atom would be chelated by functional groups of the coordinated acetylene.

It is known that the geometry of the C≡C–C fragment in π-coordinated acetylenes depends on the number of electrons, formally donated by the triple C≡C bond to the metal core. As we have shown recently, in the case of diphenylacetylene or butyne-2-diol-1,4, 2e-π-coordination with the $CpMn(CO)_2$ fragment results in a decrease in the C–C≡C angle from 180° to 153° (av.) only [1]. On the other hand, the 4e-π-coordination of the bridging acetylene with a $Co_2(CO)_6$ fragment reduces the C–C≡C angle to about 140° (for example, 144° in butyndiol complex $[Co_2(CO)_6][\mu\text{-}C_2(CH_2OH)_2]$ (**1**) [2]). As a result, the hydroxymethyl groups at acetylene's carbon atoms are getting closer and can promote the formation of a seven-membered chelate cycle with another metal atom. Recently complexes such as $[Co_2(CO)_6][\mu\text{-}C_2(CH_2O)_2]SiPh_2$ [3] were synthesized for a chelated silicon atom and characterized by X-ray analysis along with $\{[Co_2(CO)_6][\mu\text{-}C_2(CH_2O)_2]\text{-}SiPh_2\}_2$, in which two acetylenic fragments of the dicobalt complex **1** and two bridging Ph_2Si groups formed a 14-membered cycle (of course, the Si atom was only a model of the metal atom) [4].

On the other hand, the synthesis and structure of $–CH_2SMe$ derivative of the acetylenic complex $[(Ph_2PCH_2Ph_2P)Co_2(CO)_4][\mu\text{-}C_2(CH_2SMe)_2]Mo(CO)_4$ containing a seven-membered chelate cycle was re-

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* Corresponding author. Fax: +7-095-9541279.
E-mail address: aapas@ionchran.rinet.ru (A.A. Pasynskii)

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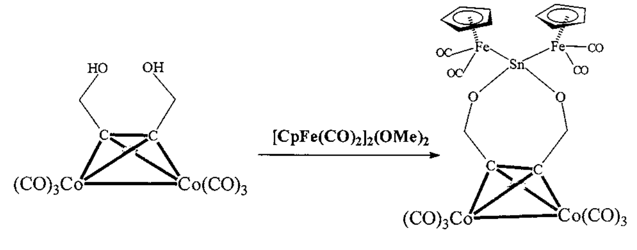
ported [5]. But in this case, the structure of the initial compound (without the $Mo(CO)_4$ fragment) was unknown, so it was difficult to follow the influence of the chelated metal-containing fragment onto the $C_2(CH_2)_2$ core geometry.

Here we used the mixed-metal fragment $Sn[CpFe(CO)_2]_2$ instead of $SiPh_2$ for the chelating of **1** on one side, and the recently, the structurally characterized complex $[(Ph_3P)Co_2(CO)_5][\mu\text{-}C_2(CH_2SCMe_3)_2]$ (**2**) [6] for the chelating of $W(CO)_4$ fragment on the other side.

2. Results and discussion

Interaction of **1** with $[CpFe(CO)_2]_2Sn(OMe)_2$ gives $[Co_2(CO)_6][\mu\text{-}C_2(CH_2O)_2]Sn[CpFe(CO)_2]_2$ (**3**) as dark-red crystals, easily hydrolyzed in a benzene solution in air.



In the elemental unit of crystal **3**, two isomers are presented with a boat (**3b**) and a chair (**3a**) conformation of seven-membered SnO_2C_4 cycles (Figs. 1 and 2). The Sn–Fe bonds are shortened in comparison with the sum of covalent radii of atoms due to the additional π-interaction, resulting also in the decrease of the Fe–Sn–Fe angle to 126° (av.). But the $Co_2C_2(CH_2)_2$ core geometry in isomers is nearly the same as in **1** (Co–Co, 2.468(2); C–C, 1.335(12) (av.); Co–C, 1.97(1) (av.)) although the C≡C–C angles are diminished to 138.5° (av.) as in the above-mentioned Ph_2Si derivatives [3]. This means that the nature of the chelated fragment or the conformation of the chelate cycle only slightly affects the coordinated acetylenic core.

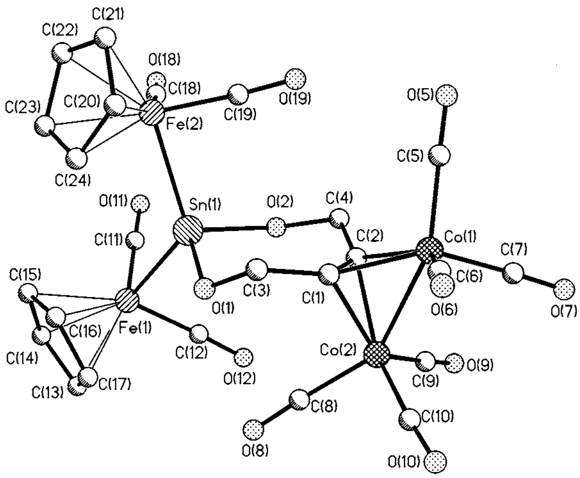


Fig. 1. Molecular structure of $[Co_2(CO)_6][\mu\text{-}C_2(CH_2O)_2]Sn[CpFe(CO)_2]_2$ (**3a**).

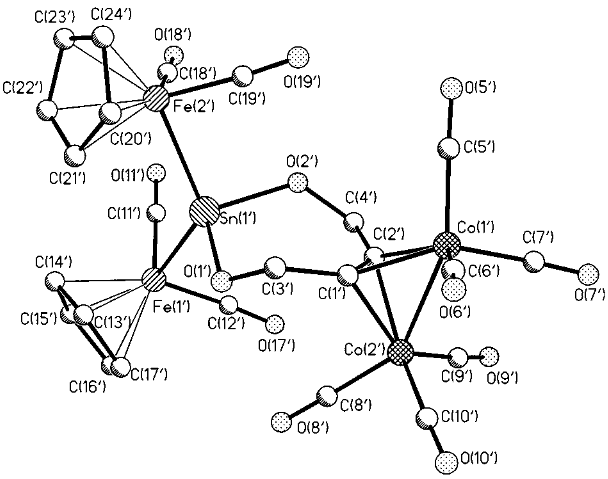
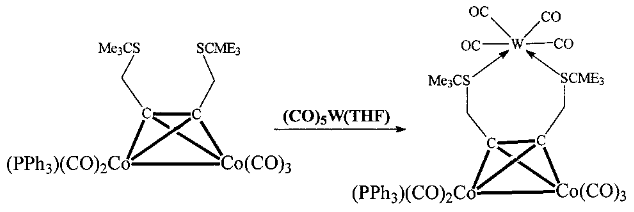


Fig. 2. Molecular structure of $[Co_2(CO)_6][\mu\text{-}C_2(CH_2O)_2]Sn[CpFe(CO)_2]_2$ (**3b**).

The interaction of **2** with $W(CO)_5(THF)$ results in $(Ph_3P)Co_2(CO)_5](\mu\text{-}C_2(CH_2SCMe_3)_2)[W(CO)_4]$ (**4**), obtained in the form of black crystals investigated by X-ray diffraction analysis (Co–Co, 2.490(2) Å; C≡C, 1.350(5) Å; C≡C–C, 139(5)° (av.)) (Fig. 3).



The seven-membered cycle WS_2C_4 in this structure could be described as a distorted chair in which the W

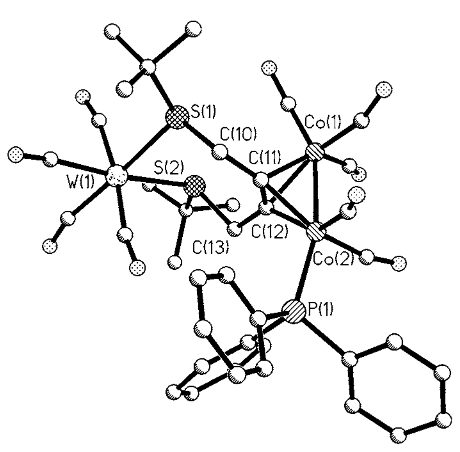


Fig. 3. Molecular structure of $[(Ph_3P)Co_2(CO)_5][\mu\text{-}C_2(CH_2SCMe_3)_2][W(CO)_4]$ (**4**).

atom and the two acetylene atoms (C(11) and C(12)) are shifted to different sides from the plane of four atoms (S(1)C(10)C(13)S(2)) by 1.84 and − 0.67 Å, respectively.

The geometry of the acetylenic fragment in this cycle is close to that found in the initial **2**, on one side, and in the known complex $[(Ph_2PCH_2Ph_2P)Co_2(CO)_4][\mu\text{-}C_2(CH_2SMe)_2]Mo(CO)_4$ [4], on the other side. As we have shown recently, there is no substantial change in the Co_2C_2 and C≡C–C geometry with the substitution of one or two OH groups in **1** by $SCMe_3$ groups, nor with the substitution of one CO group by the PPh_3 ligand as well [6].

So we can conclude that the substitution of carbonyl groups by terminal and bridging phosphines, varying of functional groups in acetylene or chelating of this groups with other metal atoms, almost has no effect on the Co_2C_2 and C≡C–C geometry in dicobalt–acetylene π-complexes, which is determined mainly by a 4e-π-interaction of the C≡C bond with two cobalt atoms. The role of this factor was shown in our recent study of the transformation of the 2e-π-donated acetylene in $CpMn(CO)_2[HOCH_2C{\equiv}CCH_2SCMe_3]$ (the derivative of $CpMn(CO)_2[C_2(CH_2OH)_2]$ having a C≡C–C angle of 153° [2]), under the action of $W(CO)_5THF$ with formation of the vinylketothiolate ligand chelated with $W(CO)_4$ in $CpMn(CO)_2[CH_2{=}CH(CO)CH_2SCMe_3]\text{-}W(CO)_4$ [7].

3. Experimental

All manipulations were carried out under an argon atmosphere. Solvents were dried and distilled before use. Commercial $Co_2(CO)_8$ was recrystallized from pentane. Commercial 1,4-butyndiol (Fluka) was used without additional purification. The complexes $[Co_2(CO)_6][\mu\text{-}C_2(CH_2OH)_2]$ and $[(Ph_3P)Co_2(CO)_5][\mu\text{-}C_2(CH_2SCMe_3)_2]$ were prepared by early published methods [6]. A high-pressure mercury lamp DRT-2 (200 W) was used for the photochemical reaction. The IR spectra were recorded on a Specord 75 IR spectrometer in KBr pellets.

3.1. Preparation of $[Co_2(CO)_6][\mu\text{-}C_2(CH_2O)_2]\text{-}Sn[Cp'Fe(CO)_2]_2$ (**3**)

Metallic sodium (0.1 g, 4 mmol) was added to 50 ml of a stirred mixture of benzene–methanol (1:5). After complete dissolving of sodium, 1.08 g (2 mmol) of crystalline $[CpFe(CO)_2]_2SnCl_2$ was added to the reaction mixture and stirred for 2 h. Then 0.74 g (2 mmol) of $[Co_2(CO)_6][\mu\text{-}C_2(CH_2OH)_2]$ was added and stirred for 1.5 h. The resulting dark-red solution was filtered and evaporated in a vacuum water pump until the first crystals appeared on the surface of the flask. A total of 20 ml of heptane was added and the reaction mixture was allowed to crystallize at room temperature. Black crystalline precipitate was separated, washed in heptane and dried in vacuo. Yield 0.7 g (42.0%). Elemental analysis for $C_{24}H_{14}Co_2Fe_2O_{12}Sn$ (842.60): Anal. Calc. (%): C, 34.21; H, 1.67: found (%): C, 33.46; H, 1.57. IR (KBr) $\nu = 2092$ (vs), 2050 (vs), 2020 (vs), 2010 (vs), 1954 (vs), 1035 (s), 990 (s), 854 (m), 579 (m) cm^{-1}.

3.2. Preparation of $[(Ph_3P)Co_2(CO)_5][\mu\text{-}C_2\text{-}(CH_2SCMe_3)_2][W(CO)_4]$ (**4**)

A solution of $W(CO)_6$ (0.19 g, 0.54 mmol) in 30 ml of THF, stirred by a magnetic mixer and cooled by running water in the quartz Schlenk vessel, was irradiated by UV light for 4 h. Initially, the colorless reaction mixture became yellow–green after which 0.2 g (0.27 mmol) of solid **2** was added. The color immediately changed to cherry-red. Solvent was evaporated in vacuo, oily residue was dissolved in a 30 ml of ether–hexane (2:1) mixture, then evaporated to half the initial volume and kept at − 10°C overnight. Dark-red crystals were separated, washed in hexane and dried in vacuo. Yield 0.1 g (36%). Elemental analysis for $C_{39}H_{37}Co_2O_9PS_2W$ (4) (1046.53): Anal. Calc. (%): C, 44.76; H, 3.56; S, 6.13: found (%): C, 44.26; H, 3.23; S, 5.72. Monocrystals were used for X-ray study. IR (KBr): $\nu = 2050$ (s), 2000 (vs), 1970 (s), 1950 (s), 1880 (vs), 1860 (vs), 1800 (vs), 1420 (m), 1140 (m), 1080 (m), 730 (s), 680 (s), 550 (m) cm^{-1}.

Table 1
Crystal data and structure refinement for **3** and **4**

Compound	**3**	**4**
Empirical formula	$C_{24}H_{14}Co_2Fe_2O_{12}Sn$	$C_{39}H_{37}Co_2O_9PS_2W$
Formula weight	842.60	1046.53
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Temperature (K)	293(2)	293(2)
Wavelength (Å)	Mo–K_α ($\lambda = 0.71073$)	Mo–K_α ($\lambda = 0.71073$)
a (Å)	13.576(9)	12.57(1)
b (Å)	16.697(8)	18.11(2)
c (Å)	24.118(10)	19.02(2)
β (°)	92.61(4)	92.49(8)
V (Å^3)	5461(5)	4325(7)
Z	8	4
$\rho_{calc.}$ (g cm^{-3})	2.050	1.607
F(000)	3280	2072
Theta range for data collection (°)	1.48–50.00	1.55–41.84
No. of independent reflections	9554	5100
No. of observed reflections	7518 [$I>2\sigma(I)$]	1426 [$I>3\sigma(I)$]
R	0.0610	0.0840
R_w	0.1665	0.1696
Largest difference peak and hole (e Å^{-3})	1.399 and −1.072	1.068 and −1.480

Table 2
Selected bond lengths (Å) and angles (°) for **3** and **4**

3(isomer **a**)		**3** (isomer **b**)		**4**	
Bond lengths					
Sn(1)–O(1)	2.030(6)	Sn(1′)–O(1′)	2.028(6)	Co(1)–Co(2)	2.472(2)
Sn(1)–O(2)	2.045(6)	Sn(1′)–O(2′)	2.037(6)	Co(1)–C(2)	1.79(1)
Sn(1)–Fe(1)	2.521(2)	Sn(1′)–Fe(1′)	2.532(2)	Co(1)–C(7)	1.971(9)
Sn(1)–Fe(2)	2.544(2)	Sn(1′)–Fe(2′)	2.538(2)	Co(1)–C(8)	1.98(1)
Co(2)–C(2)	1.957(9)	Co(1′)–C(1′)	1.954(9)	Co(2)–C(7)	1.96(1)
Co(2)–C(1)	1.987(9)	Co(1′)–C(2′)	2.006(8)	Co(2)–C(8)	1.935(9)
Co(2)–Co(1)	2.468(2)	Co(1′)–Co(2′)	2.468(2)	C(7)–C(8)	1.33(1)
Co(1)–C(1)	1.953(9)	Co(2′)–C(2′)	1.947(8)	S(1)–W(1)	2.54(2)
Co(1)–C(2)	1.981(9)	Co(2′)–C(1′)	1.973(8)	S(2)–W(1)	2.58(2)
C(1)–C(2)	1.341(12)	C(2′)–C(1′)	1.329(12)		
Bond angles					
O(1)–Sn(1)–O(2)	104.3(2)	O(1′)–Sn(1′)–O(2′)	102.8(2)	S(1)–W(1)–S(2)	79.8(7)
Fe(1)–Sn(1)–Fe(2)	125.93(6)	Fe(1′)–Sn(1′)–Fe(2′)	126.08(5)	C(7)–C(8)–C(9)	142.0(9)
C(1)–C(2)–C(4)	139.2(8)	C(2′)–C(1′)–C(3′)	136.8(8)	C(6)–C(7)–C(8)	140(1)
C(2)–C(1)–C(3)	138.2(8)	C(1′)–C(2′)–C(4′)	139.5(8)		

3.3. Single-crystal structure determination of **3** and **4**

The crystals of **3** and **4** were mounted in air on glass fiber using epoxy resin. All X-ray data for **3** and **4** were obtained from a Siemens P3/PC and CAD-4 four-circle diffractometers, respectively. The DIFABS [8] method was used for absorption correction of two at the stage of an isotropic approximation. Two reflections were monitored periodically, as a check for crystal decomposition or movement. No significant variation in these standards was observed; therefore, no correlation was applied. Details of crystal parameters, data collection, and structure refinement are given in Table 1.

Structures of **3** and **4** were solved using direct methods to locate all non-hydrogen atoms and refined by the least-squares method in anisotropic approximation. Computations were performed using the SHELXL and SHELXS program package for PC [9,10]. Selected bond lengths and angles for **3** and **4** are given in Table 2.

4. Supplementary material

Details of the crystal structures for compounds **3** and **4** are available from the Cambridge Crystallographic Data Centre, CCDC nos. 136992 and 136991, respectively. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit @ccdc.cam.ac.uk).

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