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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

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To cite this Article Zhang, Jie , Chen, Xue-Nian , Yin, Yuan-Qi and Wang, Wen-Ling(1999) 'THE REACTION OF OCTACARBONYLDICOBALT AND PROPARGYL TRICHLOROACETATE', *Journal of Coordination Chemistry*, 48: 4, 459 – 464

To link to this Article: DOI: 10.1080/00958979908023585

URL: <http://dx.doi.org/10.1080/00958979908023585>

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Note

THE REACTION OF OCTACARBONYLDICOBALT AND PROPARGYL TRICHLOROACETATE

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(Received 30 November 1998)

The reaction of octacarbonyldicobalt and propargyl trichloroacetate gave the expected unknown compound $(\text{CO})_9\text{Co}_3(\mu_3\text{-C})\text{C}(\text{O})\text{OCH}_2(7\mu\text{-CCH})\text{Co}_2(\text{CO})_6$ (**1**) and the unexpected known compound $(\text{CO})_9\text{Co}_3(\mu_3\text{-C})\text{CH}_2\text{CH}_3$ (**2**). Both (**1**) and (**2**) were characterized by elemental analysis and ¹H NMR spectra. The molecular structure of (**1**) was determined by single-crystal X-ray diffraction methods.

Keywords: Synthesis; crystal structure; cluster compound

INTRODUCTION

Compounds containing linked clusters are usually prepared by reactions of ready-made simple clusters with reagents that can offer carbon chains.^{1–3} In a very few cases, they are formed by direct cluster construction of a ready-made carbon chain.⁴ It is well known that the reaction of octacarbonyldicobalt with an organic trihalide gives $\text{Co}_3(\mu_3\text{-C})$ clusters^{5,6} and the reaction

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of octacarbonyldicobalt with an alkyne complex gives $\text{Co}_2(\mu\text{-C}_2)$ clusters.⁷ Thus, by treating octacarbonyldicobalt with a compound containing both organic trihalide and alkyne units, a new compound containing linked $\text{Co}_3(\mu_3\text{-C})$ and $\text{Co}_2(\mu\text{-C}_2)$ clusters is very likely to be formed. In this paper, we report the reaction of octacarbonyldicobalt with propargyl trichloroacetate, which gives the expected compound $(\text{CO})_9\text{Co}_3(\mu_3\text{-C})\text{C}(\text{O})\text{OCH}_2(\mu\text{-CCH})\text{Co}_2(\text{CO})_6$ (**1**) and the unexpected compound $(\text{CO})_9\text{-Co}_3(\mu_3\text{-C})\text{CH}_2\text{CH}_3$ (**2**).

EXPERIMENTAL

The reaction and manipulations were performed under an atmosphere of pure nitrogen by using standard Schlenk or vacuum line techniques. Solvents were treated according to the standard procedures for preparing anhydrous and deoxygenated solvents.⁸ Column chromatography was carried out by using silica gel of 160–200 mesh. $\text{Co}_2(\text{CO})_8$ ⁹ and propargyl trichloroacetate¹⁰ were prepared by literature methods or slight modifications thereof. Infrared spectra were recorded on a Nicolet FT-IR 10 DX spectrophotometer; ¹H NMR spectra were recorded on a Bruker AM-300 MHz spectrometer and elemental analyses were performed on a Carlo Erba 1106 analyzer.

Reaction of $\text{Co}_2(\text{CO})_8$ with Propargyl trichloroacetate

A solution of $\text{Co}_2(\text{CO})_8$ (10.00 g, 29.2 mmol) and propargyl trichloroacetate (1.60 g, 7.9 mmol) in THF (150 cm³) was stirred at room temperature for 24 h. After the solvent was removed under reduced pressure, the residue was chromatographed on a 3.5 × 50 cm column of silica. Elution with petroleum ether (60–90°) produced a red band from which 0.51 g of compound (**2**) as a red brown solid was obtained. Calcd. for $\text{C}_{12}\text{H}_5\text{Co}_3\text{O}_9$ (%): C, 30.64; H, 1.06. Found: C, 30.49; H, 1.01. IR (KBr disc): 2982w, 2940w, 2883w, 2805w, 2103s, 2037vs, 2002vs, 1967m, 1457w, 1415w, 1367w, 1150m, 1053w, 1042w, 647m cm⁻¹. ¹H NMR (CDCl_3): δ 3.66–3.77 (q, 2H, CH_2), 1.49–1.55 (t, 3H, CH_3). Further elution with petroleum ether/ CH_2Cl_2 (1 : 1) produced a large brown band from which 1.23 g of compound (**1**) dark brown solid was obtained with 19.2% yield (based on propargyl trichloroacetate). Calcd. for $\text{C}_{20}\text{H}_3\text{Co}_5\text{O}_{17}$ (%): C, 29.63; H, 0.37. Found: C, 29.83, H, 0.28. IR (KBr disc): 2112m, 2098s, 2053vs, 2025vs, 2008vs, 2002vs, 1976m, 1675m cm⁻¹. ¹H NMR (CDCl_3): δ 6.10 (s, H, CH), 5.55 (s, 2H, CH_2).

Crystallography of Compound (1)

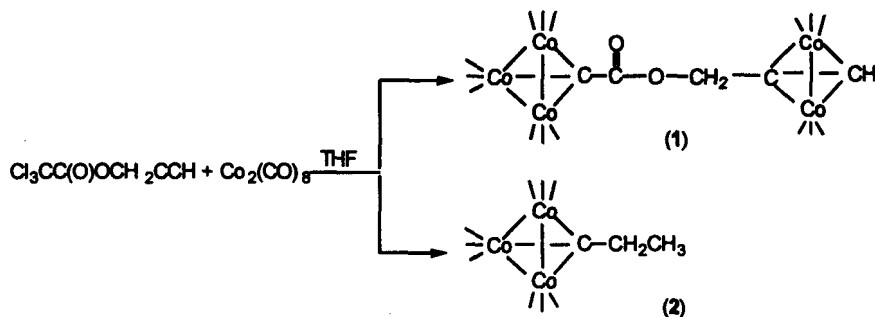
Deep red crystals used for X-ray determination were obtained from hexane/ CH_2Cl_2 (2:1) at -20°C . A crystal of approximate dimensions $0.8 \times 0.7 \times 0.6$ mm was chosen and mounted on a glass fibre. The single-crystal X-ray diffraction data were collected on a Rigaku RAXIS-IV imaging plate area detector with graphite-monochromated MoK_α radiation ($\lambda = 0.71070 \text{ \AA}$) using the $\omega-2\theta$ scan technique at 18°C .

The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation. Full list of crystallographic data are available from the authors upon request.

RESULTS AND DISCUSSION

Stirring a THF solution of $\text{Co}_2(\text{CO})_8$ and propargyl trichloroacetate at room temperature can cause a reaction (Scheme 1). However, the expected compound (1) is formed only in low yield. Further investigation indicates that when this reaction is performed in refluxing THF, compound (2) is the only product.

It is reported that refluxing a xylene solution of $\text{HCCo}_3(\text{CO})_9$ can give a mixture of $\text{CH}_3\text{CCo}_3(\text{CO})_9$ and $\text{CH}_3\text{CH}_2\text{CCo}_3(\text{CO})_9$; the formation of these two compounds involves the reaction of $\text{HCCo}_3(\text{CO})_9$ with $(\mu\text{-CHCH})\text{-Co}_2(\text{CO})_6$ and $(\mu\text{-CHCCH}_3)\text{Co}_2(\text{CO})_6$ respectively.¹¹ From this, it may be deduced that in the reaction of $\text{Co}_2(\text{CO})_8$ with propargyl trichloroacetate,



SCHEME 1

the product (1) decomposes to give $\text{HCCO}_3(\text{CO})_9$ and $(\mu\text{-CHCCH}_3)\text{Co}_2(\text{CO})_6$ after losing one molecular of CO and gaining two atoms of hydrogen, and then $\text{HCCO}_3(\text{CO})_9$ reacts with $(\mu\text{-CHCCH}_3)\text{Co}_2(\text{CO})_6$ to give (2). Investigations about how this process takes place are still in progress.

Both compounds (1) and (2) are well characterized by elemental analysis, IR and ^1H NMR. The spectroscopic data of compound (2) fit the literature values well.¹¹ In the IR spectra of (1), absorption bands in the range 1976–2112 cm^{-1} are caused by terminal carbonyls and that at 1675 cm^{-1} is caused by the carbonyl (C=O) on the carbon chain. ^1H NMR spectra of (1) are simple, with only two singlets at 6.10 and 5.55 ppm corresponding to the protons on the CH and CH_2 units, respectively.

The molecular structure of compound (1) is shown in Figure 1. Crystal data and selected bond lengths and angles for compound (1) are collected in Tables I and II.

The molecular compound (1) contains two different clusters $(\text{CO})_9\text{Co}_3(\mu_3\text{-C})$ and $(\text{CO})_6\text{Co}_2(\mu\text{-C}_2)$ connected by a $\text{C}(\text{O})\text{OCH}_2$ chain.

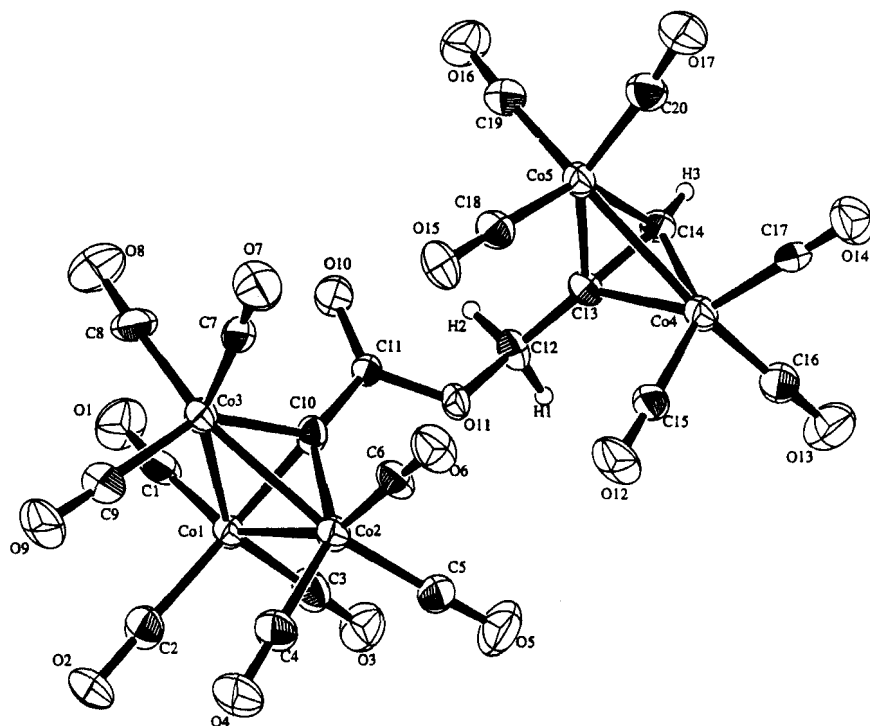


FIGURE 1 The molecular structure of compound (1).

TABLE I Summary of crystal data for compound (1)

Formula	C ₂₀ H ₃ Co ₅ O ₁₇
F.W.	809.90
Lattice parameters	$a = 13.191(6)$, $b = 13.324(4)$, $c = 7.960(6)$ Å $\alpha = 100.86(3)$, $\beta = 93.49(2)$, $\gamma = 76.46(3)^\circ$ $V = 1335.55$ Å ³
Z	3
Space group	$P\bar{1}$
D_c (g cm ⁻³)	2.014
$F(000)$	788.00
μ (MoK α) (cm ⁻¹)	31.21
Radiation (MoK α) (α)	0.71070
Temp. (°C)	18
Scan type	$\omega-2\theta$
$2\theta_{\max}$ (°)	55.1
No. of reflections measured	3071
No. of observations ($I > 3.00\sigma(I)$)	2336

TABLE II Selected bond lengths (Å) and angles (°) for compound (1)

Co(1)–Co(2)	2.468(2)	Co(1)–Co(3)	2.468(2)	Co(1)–C(10)	1.92(1)
Co(2)–Co(3)	2.467(2)	Co(2)–C(10)	1.881(9)	Co(3)–C(10)	1.914(10)
Co(4)–Co(5)	2.483(2)	Co(4)–C(13)	1.98(1)	Co(4)–C(14)	1.95(1)
Co(5)–C(13)	1.94(1)	Co(5)–C(14)	1.95(1)	C(10)–C(11)	1.47(1)
C(12)–C(13)	1.49(2)	C(13)–C(14)	1.34(1)		
Co(2)–Co(1)–Co(3)	59.98(7)	Co(2)–Co(1)–C(10)	48.8(3)	Co(3)–Co(1)–C(10)	49.8(3)
Co(1)–Co(2)–Co(3)	60.01(6)	Co(1)–Co(2)–C(10)	50.3(3)	Co(3)–Co(2)–C(10)	50.0(3)
Co(1)–Co(3)–Co(2)	60.01(6)	Co(1)–Co(3)–C(10)	50.2(3)	Co(2)–Co(3)–C(10)	48.9(3)
Co(5)–Co(4)–C(13)	49.9(3)	Co(5)–Co(4)–C(14)	50.6(4)	C(13)–Co(4)–C(14)	40.0(4)
Co(4)–Co(5)–C(13)	51.3(3)	Co(4)–Co(5)–C(14)	50.5(3)	C(13)–Co(5)–C(14)	40.4(4)
Co(1)–C(10)–Co(2)	80.9(4)	Co(1)–C(10)–Co(3)	80.0(4)	Co(1)–C(10)–C(11)	121.5(8)
Co(2)–C(10)–Co(3)	81.1(3)	Co(2)–C(10)–C(11)	139.5(7)	Co(4)–C(13)–Co(5)	78.8(4)
Co(4)–C(13)–C(12)	134.4(8)	Co(4)–C(13)–C(14)	69.0(7)	Co(5)–C(13)–C(14)	70.4(7)
C(12)–C(13)–C(14)	140(1)	Co(4)–C(14)–Co(5)	78.9(4)	Co(4)–C(14)–C(13)	70.9(6)
Co(5)–C(14)–C(13)	69.1(7)				

In the Co₃C core, all three Co–Co bond lengths are 2.468(2) Å, and the average Co–C bond length is 1.91 Å. These values are close to corresponding values found in the simple Co₃C cluster.¹ In the Co₂C₂ core, the Co–Co bond length is 2.483(2) Å, the C–C bond length is 1.34(1) Å, and the average Co–C bond length is 1.96 Å. They are all in the normal range for related alkyne–dicobalt complexes.¹²

Acknowledgements

We are grateful to the Laboratory of Organometallic Chemistry at the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, for financial support of our work.

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