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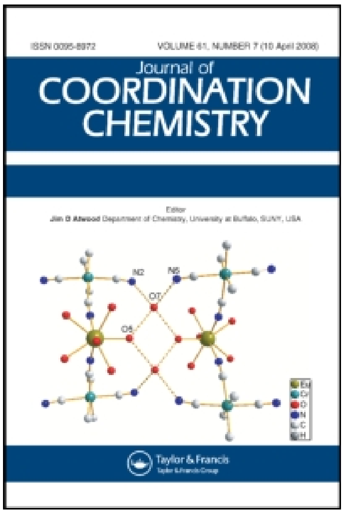

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Note

THE REACTION OF OCTACARBONYLDICOBALT AND DIPROPARGYL TEREPHTHALATE

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The reaction of octacarbonyldicobalt and dipropargyl terephthalate gave the two expected compounds $[C_6H_4\text{-}1,4\text{-}(CO_2CH_2C_2H\text{-}\mu)_2][Co_2(CO)_6]_2$ (**1**) and $[p\text{-}(HC_2CH_2OCO)C_6H_4(Co_2CH_2C_2H\text{-}\mu)][CO_2(CO)_6]$ (**2**). Both (**1**) and (**2**) were characterized by elemental analysis, IR and NMR spectra. The molecular structure of (**2**) was established by single-crystal X-ray diffraction methods.

Keywords: Synthesis; Crystal structure; Cobalt; Alkynes

INTRODUCTION

The chemistry of alkynes coordinated to cobalt has provided a very dynamic development in recent years [1 – 3]. The main driving force of this research activity has been the ability of alkynes coordinated to cobalt carbonyl or cyclopentadienyl complexes of giving highly regioselective C,C coupling reactions with CO, olefins, or acetylenes. All kinds of compounds containing

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(μ-alkyne)[$Co_2(CO)_6$] unit have been prepared. Our interest in this area prompted us to synthesize linked (μ-alkyne)[$Co_2(CO)_6$] complexes [4–8]. The coordination of $Co_2(CO)_8$ to alkyne is so fast that the regioseletivity of reaction is very low. How to perform the reaction of a diyne with $Co_2(CO)_8$ to give one (μ-alkyne)[$Co_2(CO)_6$] unit is a challenge. In this paper, we report the reaction of dipropargyl terephthalate with octacarbonyldicobalt, which affords the expected compound [*p*-($HC_2CH_2OCO)C_6H_4(CO_2CH_2C_2H$-$\mu$)][$Co_2(CO)_6$] (**2**) as main product, and the compound [C_6H_4-1,4-($CO_2CH_2C_2H$-$\mu)_2$][$Co_2(CO)_6]_2$ (**1**) in low yield.

EXPERIMENTAL

Experiments were carried out using Schlenk tube techniques under a dry, oxygen-free nitrogen atmosphere. Chromatography was carried out on columns of 160–200 silica gel mesh. $Co_2(CO)_8$ [9] and dipropargyl terephthalate [10] were prepared by literature methods using slight modifications. The NMR measurements were made with a Bruker AM400 M Hz spectrometer. A Nicolet 10 DX FT-IR spectrophotometer was used to record IR spectra, and elemental analyses were performed on a Carlo Erba 1106 instrument.

Reaction of $Co_2(CO)_8$ with Dipropargyl Terephthalate

[$Co_2(CO)_8$] (342 mg, 1 mmol) was added to 25 cm^3 of THF containing dipropargyl terephthalate C_6H_4-1,4-($COOCH_2C_2H)_2$ (484 mg, 2.0 mmol) and the mixture was stirred at room temperature for 2.5 h. A colour change from brown to purple was observed and monitoring by TLC showed the disappearance of the starting material. The solvent was removed *in vacuo* and the purple residue dissolved in a small amount of CH_2Cl_2 and chromatographed. Elution with petroleum ether (bp 60–90°C)-CH_2Cl_2 (v/v = 4/3) afforded two red bands. On evaporation of solvent, the first band was identified as the linked cluster [C_6H_4-1,4-($CO_2CH_2C_2H$-$\mu)_2$] [$Co_2(CO)_6]_2$ (**1**) (124 mg, 15.2%). *Anal.* Calc. for $C_{26}H_{10}O_{16}Co_4$(%): C, 38.36; H, 1.24. Found: C, 38.42; H, 1.25. IR (KBr disc): 2099s, 2060vs, 2027vs, (C≡O) 1717m (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.18 (s, 4H, C_6H_4), 6.14 (s, 2H, 2CH), 5.55 (s, 4H, $2CH_2$). ^{13}C NMR ($CDCl_3$): δ 198.99 (s, 6C, C≡O), 165.43 (s, 2C, 2C=O), 133.68–129.72 (d, 6C, C_6H_4), 88.20, 72.00 (d, 2C, C_2Co_2), 65.97 (s, 2C, $2CH_2$). Concentration of the second solvent and cooling to $-20^{\circ}C$ gave red crystal of the compound (**2**)

(400 mg, 75.7%). *Anal.* Calc. for $C_{20}H_{10}O_{10}Co_2$ (%): C, 45.48; H, 1.91. Found: C, 45.49; H, 1.90. IR (KBr disc): 3272 m (≡CH), 2135 w (C≡C), 2099 s, 2062 vs, 2024 vs, (C≡O), 1723 m, 1707 m (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.18 (s, 4H, C_6H_4), 6.15 (s, 1H, CH), 5.56 (s, 2H, CH_2), 4.95 (s, 2H, CH_2), 2.55 (s, 1H, ≡CH). ^{13}C NMR ($CDCl_3$): δ 198.98 (s, 3C, C≡O), 165.37, 164.90 (d, 2C, 2C=O), 133.68 – 129.72 (q, 6C, C_6H_4), 88.19, 71.97 (d, 2C, C_2Co_2), 75.32 (s, 2C, C_2H), 66.01 (s, 2C, $2CH_2$).

Crystallography of Compound (2)

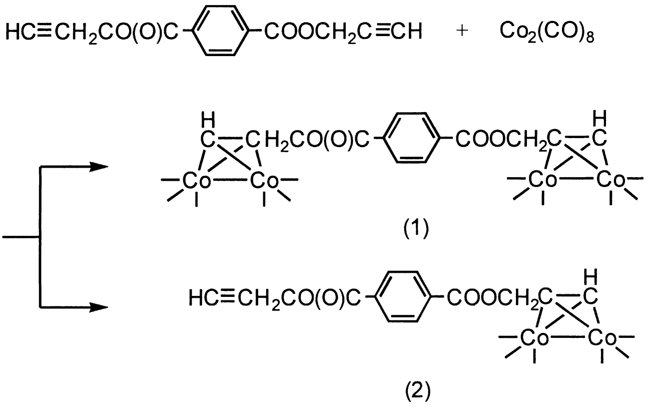
A crystal with dimensions 0.45 × 0.325 × 0.075 mm was chosen for the X-ray determination. Single-crystal X-ray diffraction data were collected on a Enraf-Nonius CAD4 diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at 20°C.

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 Enraf-Nonius Molen/VAX Software package of Molecular Structure Corporation. Full lists of crystallographic data are available from the authors upon request.

RESULTS AND DISCUSSION

The coordination of $Co_2(CO)_8$ with alkyne is so easy that regioselectivity is very low. Almost any alkyne can react with $Co_2(CO)_8$ to give (μ-alkyne)[$Co_2(CO)_6$] complexes, so how to prepare compounds that contain the (μ-alkyne)[$Co_2(CO)_6$] core and alkyne together is a problem. We have tried three procedures, (Scheme 1). Firstly, when equimolar amounts of $Co_2(CO)_8$ and dipropargyl terephthalate were dissolved in THF and stirred for 2.5 h, the main product was the linked cluster (**1**); the target compound (**2**) was in low yield. Secondly, 25 cm^3 of THF, in which $Co_2(CO)_8$ was dissolved, was slowly added to the same solvent containing an equimolar amount of dialkyne over 12 h. The solvent often blocked the vessel and the reaction paused. Finally, the third method (described above) is the most suitable. If the molar ratio of C_6H_4-1,4-$(CO_2CH_2C_2H)_2$/$Co_2(CO)_8$ increases, when chromatographed, unreacted dipropargyl terephthalate could be eluted with the target compound (**2**).

All measurements of the two complexes agree with their structures. In the IR spectra, intense absorption bands in the range of 2100 – 2020 cm^{-1} are



SCHEME 1

characteristic of carbonyls bound to cobalt, and the ester frequency is around 1720 cm^{-1}. The band at 3271 cm^{-1} and a weak absorption at 2135 cm^{-1} refer to the HC≡C unit in compound (**2**). For the ^{1}H NMR assignment, the singlet at 8.18 ppm is the resonance of four protons attached to the benzene ring; the chemical shift of the terminal alkyne proton appears downfield (6.14 ppm) because of the deshielding effect of cobalt. In ^{13}C NMR spectra, the single resonance at 199 ppm is assigned to the carbonyls.

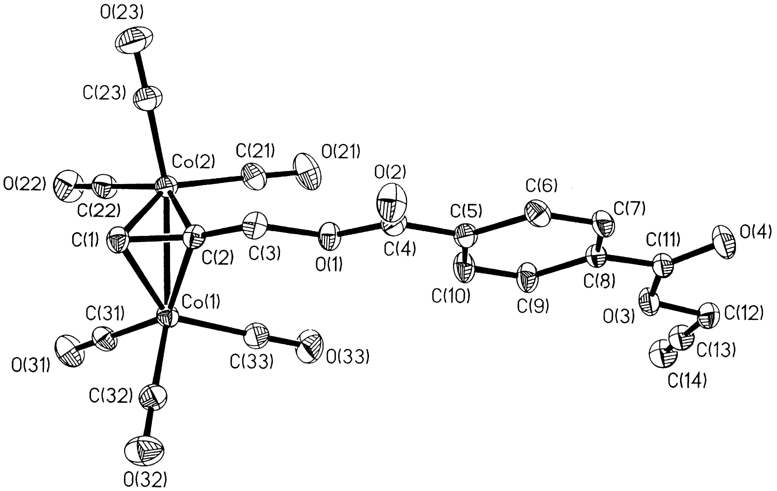


FIGURE 1 The molecular structure of compound (**2**).

TABLE I Summary of crystal data for compound (**2**)

Empirical formula	$C_{20}H_{10}O_{10}Co_2$
Formula weight	528.14
Temperature (°C)	20
Lattice parameters	$a = 7.7033(15)$, $b = 12.671(3)$, $c = 12.844(3)$ Å, $\alpha = 105.83(3)$, $\beta = 106.97(3)$, $\gamma = 105.72(3)^\circ$
V(Å^3)	1066.6(4)
Z	2
Crystal system and space group	Triclinic, PI
D_c(g cm^{-3})	1.644
F(000)	528
μ(MoK_α) (cm^{-1})	16.09
Radiation (MoK_α)(Å)	0.71073
θ_{max}(°)	25.99
No. of reflections measured	4341
No. of observations [$I > 2$ sigma (I)]	4143
No. variables	289
Goodness of fit indictor	1.014
R^a	0.056
$R_w{}^1$	0.146
Largest peak and hole in final difference map (eÅ^{-3})	0.590, −0.501

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $R_w = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^2]^{1/2}$.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for compound (**2**)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Co(1)	1299(1)	3730(1)	2147(1)	43(1)
Co(2)	4776(1)	4725(1)	2508(1)	44(1)
O(1)	2304(5)	6807(3)	2683(3)	47(1)
O(2)	1889(7)	8116(3)	1874(3)	74(1)
O(3)	2431(5)	10338(3)	7879(3)	60(1)
O(4)	2992(7)	11915(3)	7377(4)	83(1)
O(21)	6093(8)	6594(4)	4845(4)	93(1)
O(22)	6181(7)	2876(4)	2925(4)	87(1)
O(23)	7535(7)	5741(4)	1564(5)	97(2)
O(31)	1553(6)	1554(3)	2480(4)	77(1)
O(32)	−2817(6)	2861(4)	550(4)	85(1)
O(33)	1221(8)	5165(4)	4343(4)	92(1)
C(1)	2467(7)	3948(4)	1031(4)	47(1)
C(2)	2490(6)	4989(4)	1675(4)	42(1)
C(3)	2143(7)	6049(4)	1557(4)	46(1)
C(4)	2138(7)	7842(4)	2708(4)	49(1)
C(5)	2283(7)	8580(4)	3875(4)	47(1)
C(6)	2425(7)	9745(4)	4063(5)	54(1)
C(7)	2571(7)	10473(4)	5125(5)	59(1)
C(8)	2547(7)	10061(4)	6014(5)	50(1)
C(9)	2392(8)	8901(4)	5825(5)	59(1)
C(10)	2282(8)	81778(4)	4768(5)	58(1)
C(11)	2682(7)	10875(4)	7150(5)	55(1)
C(12)	2424(9)	11059(5)	8976(5)	69(2)
C(13)	2599(8)	10430(5)	9774(5)	68(2)

TABLE II (Continued)

Atom	x/a	y/b	z/c	U_{eq}
C(14)	2760(11)	9964(7)	10445(6)	90(2)
C(21)	5616(8)	5875(5)	3954(5)	62(1)
C(22)	5644(7)	3585(4)	2766(5)	57(1)
C(23)	6489(8)	5369(5)	1947(5)	62(1)
C(31)	1427(7)	2371(4)	2326(4)	53(1)
C(32)	– 1226(8)	3175(5)	1184(5)	56(1)
C(33)	1250(8)	4606(5)	3516(5)	60(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE III Selected bond lengths (Å) and angles (°) for compound (**2**)

Co(1)—C(1)	1.943(4)	O(1)—C(3)	1.450(5)	C(8)—C(11)	1.494(7)
Co(1)—C(2)	1.952(4)	O(2)—C(4)	1.193(5)	C(12)—C(13)	1.458(9)
Co(1)—Co(2)	2.4711(12)	O(3)—C(11)	1.327(6)	C(13)—C(14)	1.168(9)
Co(2)—C(2)	1.943(4)	O(3)—(12)	1.457(6)	C(4)—C(5)	1.487(7)
Co(2)—C(1)	1.948(5)	O(4)—C(11)	1.207(6)	C(2)—C(3)	1.477(6)
O(1)—C(4)	1.345(5)	C(1)—C(2)	1.344(6)		

Co(1)—C(1)—C(2)	40.37(17)	C(3)—O(1)—C(2)	108.8(3)
Co(1)—C(1)—Co(2)	50.66(15)	C(4)—O(2)—O(1)	122.7(4)
Co(1)—C(2)—Co(2)	50.45(13)	C(4)—O(2)—C(5)	124.8(4)
Co(2)—C(2)—C(1)	40.42(18)	C(4)—O(1)—C(5)	112.5(4)
Co(2)—C(2)—Co(1)	50.80(12)	C(5)—C(10)—C(6)	118.7(4)
Co(2)—C(1)—Co(1)	50.49(13)	C(5)—C(10)—C(4)	123.7(4)
O(1)—C(4)—C(3)	14.5(3)	C(5)—C(6)—C(4)	117.6(4)
O(3)—C(11)—C(12)	16.3(4)	C(6)—C(7)—C(5)	120.3(5)
C(1)—C(2)—Co(1)	70.2(3)	C(7)—C(6)—C(8)	120.8(4)
C(1)—C(2)—Co(2)	69.6(3)	C(8)—C(7)—C(9)	119.0(5)
C(1)—Co(1)—Co(2)	78.85(17)	C(8)—C(7)—C(11)	119.1(4)
C(2)—C(1)—C(3)	141.2(4)	C(8)—C(9)—C(11)	121.9(5)
C(2)—C(1)—Co(2)	70.0(3)	C(9)—C(10)—C(8)	120.2(5)
C(2)—C(3)—Co(2)	134.0(3)	C(10)—C(5)—C(9)	120.9(4)
C(2)—C(1)—Co(1)	69.4(3)	C(11)—O(4)—O(3)	123.6(5)
C(2)—C(3)—Co(1)	135.4(3)	C(11)—O(4)—C(8)	123.2(5)
C(2)—Co(2)—Co(1)	78.75(16)	C(11)—O(3)—C(8)	113.1(4)
C(12)—O(3)—C(13)	108.6(4)	C(13)—C(14)—C(12)	177.6(6)

Signals around 88 and 72 ppm are characteristic of two carbons in the C_2Co_2 core.

The molecular structure of complex (**2**) is shown in Figure 1. Crystal data atomic coordinate and selected bond lengths and angles are collected in Tables I to III. Table IV gives selected torsion angles.

The molecule contains one $(\mu\text{-}C_2H)[Co_2(CO)_6]$ unit and one alkyne connected by a $C_6H_4\text{-}1,4\text{-}(COOCH_2)_2$ chain. In the C_2Co_2 core, the Co—Co bond length is 2.471(1) Å, and the Co—C bond lengths are in the range of 1.943(4)–1.952(4) Å, all of which are comparable with those of related

TABLE IV Selected torsion angles (°) for compound (**2**)

C(4)—O(1)—C(3)—C(2)	176.0(4)	C(7)—C(8)—C(9)—C(10)	0.6(8)
C(1)—C(2)—C(3)—O(1)	175.1(6)	C(11)—C(8)—C(9)—C(10)	179.6(5)
C(3)—O(1)—C(4)—O(2)	0.4(7)	C(6)—C(5)—C(10)—C(9)	0.8(8)
C(3)—O(1)—C(4)—C(5)	179.2(4)	C(4)—C(5)—C(10)—C(9)	179.0(5)
O(2)—C(4)—C(5)—C(10)	170.1(5)	C(8)—C(9)—C(10)—C(5)	1.3(8)
O(1)—C(4)—C(5)—C(10)	9.4(7)	C(12)—O(3)—C(11)—O(4)	3.7(7)
O(2)—C(4)—C(5)—C(6)	9.7(7)	C(12)—O(3)—C(11)—C(8)	176.4(4)
O(1)—C(4)—C(5)—C(6)	170.7(4)	C(7)—C(8)—C(11)—O(4)	7.0(7)
C(10)—C(5)—C(6)—C(7)	0.4(7)	C(9)—C(8)—C(11)—O(4)	173.2(5)
C(4)—C(5)—C(6)—C(7)	179.8(4)	C(7)—C(8)—C(11)—O(3)	173.1(4)
C(5)—C(6)—C(7)—C(8)	1.1(8)	C(9)—C(8)—C(11)—O(3)	6.7(7)
C(6)—C(7)—C(8)—C(9)	0.6(7)	C(11)—O(3)—C(12)—C(13)	166.8(5)
C(6)—C(7)—C(8)—C(11)	179.2(4)	O(3)—C(12)—C(13)—C(14)	162(17)

dicobalt complexes [4–8]. The distance C(1)—C(2) is 1.344(6) Å, much longer than the distance of C(13)—C(14) (1.168(9) Å). The bond angle C(1)—C(2)—C(3) is 141.2(4)°, and the bond angle C(12)—C(13)—C(14) is 177.6(6)°; the three carbons are in a line. Differences in bond lengths and angles between the two alkynyl groups are due to the coordination of the $Co_2(CO)_6$ group. The bond distances C(4)—C(5) and C(8)—C(11) are 1.487(7) and 1.494(7) Å, slightly shorter than the normal C—C bond length (1.544 Å). Torsion angles O(2)—C(4)—C(5)—C(6) and O(4)—C(11)—C(8)—C(9) are $-9.7(7)$ and 173.2(5)°, respectively. Thus the π systems of C(4)—O(2) and C(11)—O(4) are conjugated with the π benzene system. Also from the torsion angles of the molecular chain listed in Table IV, it can be postulated that all of the carbon and oxygen atoms, except for those in the carbonyls, are located in one plane.

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