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Journal of Organometallic Chemistry 582 (1999) 252–258

Journal of Organo metallic Chemistry

Synthesis and characterization of novel organometallic compounds containing linked clusters. The molecular structure of $(CO)_8LCo_2M(\mu_3\text{-}C)C(O)OCH_2(\mu\text{-}CCH)Co_2(CO)_6$ [M = Co, W; L = CO, η^5-C_5H_5]

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Received 1 January 1999

Abstract

A novel cluster compound $(CO)_9Co_3(\mu_3\text{-}C)C(O)OCH_2(\mu\text{-}CCH)Co_2(CO)_6$ **1** and a known cluster compound $(CO)_9Co_3(\mu_3\text{-}C)CH_2CH_3$ **2** were obtained by the reaction of $Co_2(CO)_8$ with propargyl trichloroacetate. The formation of compound **2** probably involves the cleavage of the two linked clusters in compound **1**. By treating compound **1** with $NaW(CO)_3C_5H_4R$ (R = H, C(O)Me, $C(O)C_6H_4C(O)OMe$) or $NaW(CO)_3C_5H_4C(O)C_6H_4C(O)C_5H_4(CO)_3WNa$ in THF at room temperature, five new metal exchange products $(CO)_8(C_5H_4R)Co_2W(\mu_3\text{-}C)C(O)OCH_2(\mu\text{-}CCH)Co_2(CO)_6$ (R = H, **3a**; R = C(O)Me, **3b**; R = $C(O)C_6H_4C(O)OMe$, **3c**), $(CO)_7(C_5H_5)_2CoW_2(\mu_3\text{-}C)C(O)OCH_2(\mu\text{-}CCH)Co_2(CO)_6$ **4** and p-$[(CO)_6Co_2(\mu\text{-}CHC)CH_2OC(O)(\mu_3\text{-}C)Co_2W(CO)_8C_5H_4C(O)]_2C_6H_4$ **5** were obtained. The results indicate that $Co(CO)_3$ unit in different cluster cores has a different reactivity. All the compounds were characterized by C/H analyses, IR and ^{1}H-NMR. The molecular structures of **1** and **3a** were determined by X-ray structure analyses. Both **1** and **3a** are triclinic, space group, $P\bar{1}$(#2), $Z = 2$, with $a = 13.191(6)$ Å, $b = 13.324(4)$ Å, $c = 7.960(6)$ Å, $\alpha = 100.86(3)°$, $\beta = 93.49(2)°$, $\gamma = 76.46(3)°$, $V = 1335.55$ Å^3, final $R = 0.074$, $R_w = 0.104$ for **1** and $a = 8.079(2)$ Å, $b = 8.154(2)$ Å, $c = 24.102(4)$ Å, $\alpha = 82.89(2)°$, $\beta = 85.20(2)°$, $\gamma = 69.84(2)°$, $V = 1477.5(6)$ Å^3, final $R = 0.053$, $R_w = 0.058$ for **3a**.

Keywords: Synthesis; Crystal structure; Metal exchange; Linked clusters

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1. Introduction

$Co(CO)_3$ unit is the easiest leaving group in metal exchange reactions [1]. It can be replaced by other isoloble units like NiCp, $Mo(CO)_2Cp$, $Fe(CO)_3H$. By treating metal exchange reagents with $Co(CO)_3$ containing cluster compounds, various heteronuclear clusters including chiral clusters can be formed [1,2]. However, the reactivity of $Co(CO)_3$ unit in different cluster cores, to our knowledge, has not been reported.

The reaction of $Co_2(CO)_8$ with organic trihalide gives $Co_3(\mu_3\text{-}C)$ cluster [3] and the reaction of $Co_2(CO)_8$ with alkyne complex gives $Co_2(\mu\text{-}C_2)$ cluster [4]. So, by treating $Co_2(CO)_8$ with complex containing both organic trihalide and alkyne units, the novel compound containing linked $Co_3(\mu_3\text{-}C)$ and $Co_2(\mu\text{-}C_2)$ clusters (I) may be formed. From the reaction of (I) with metal ex-

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PII: S0022-328X(99)00060-1

change reagents, the reactivity of the $Co(CO)_3$ unit in $Co_3(\mu_3\text{-}C)$ and $Co_2(\mu\text{-}C_2)$ cluster cores can be studied.

In this work, we present the synthesis and metal exchange reactions of $(CO)_9Co_3(\mu_3\text{-}C)C(O)OCH_2(\mu\text{-}CCH)Co_2(CO)_6$. The results indicate that $Co(CO)_3$ unit in different cluster cores has a different reactivity.

2. Experimental

2.1. General details

All reactions and manipulations were carried out under pre-purified nitrogen atmosphere using standard Schlenk or vacuum line techniques. All solvents were dried and deoxygenated according to standard procedures [5] before use. Chromatographic separations and purification were performed on 160–200 mesh silica gel. $W(CO)_6$ was purchased from Fluka Chem. Propargyl trichloroacetate [6], $Co_2(CO)_8$ [7], $NaW(CO)_3C_5H_4R$ [8] and $NaW(CO)_3C_5H_4C(O)C_6H_4C(O)C_5H_4(CO)_3WNa$ [2e] were prepared according to the literature methods or slight modifications thereof.

IR spectra were recorded on a Nicolet FT-IR 10 DX spectrophotometer; ^{1}H-NMR were recorded on a Bruker AM-300 MHz spectrometer, C/H determinations were performed on a Carlo Erba 1106-type analyzer.

Table 1
Crystal and refinement data for **1** and **3a**

Compounds	**1**	**3a**
Empirical formula	$C_{20}H_3Co_5O_{17}$	$C_{24}H_8Co_4O_{16}W$
Formula weight	809.90	971.90
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$(#2)	$P\bar{1}$(#2)
$F(000)$	788.00	924
Lattice parameters		
a (Å)	13.191(6)	8.079(2)
b (Å)	13.324(4)	8.154(2)
c (Å)	7.960(6)	24.102(4)
α (°)	100.86(3)	82.89(2)
β (°)	93.49(2)	85.20(2)
γ (°)	76.46(3)	69.84(2)
V (Å^3)	1335.5500	1477.5(6)
Z	2	2
D_c (g cm^{-3})	2.014	2.184
μ (Mo–K$_\alpha$) (cm^{-1})	31.21	62.32
Radiation (Mo–K$_\alpha$) (Å)	0.71070	0.71069
Temperature (°C)	18	23
$2\theta_{max}$ (°)	55.1	51.9
No. observations	2336 ($I>3.00\sigma(I)$)	4672 ($I>2.00\sigma(I)$)
No. variables	389	406
R [a]	0.074	0.053
wR [b]	0.104	0.058
Goodness of fit indicator	1.25	1.48
Max. shift in final cycle	0.01	0.0006
Largest peak in final difference map (e Å^{-3})	0.63	2.19

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

2.2. Synthesis of compound 1

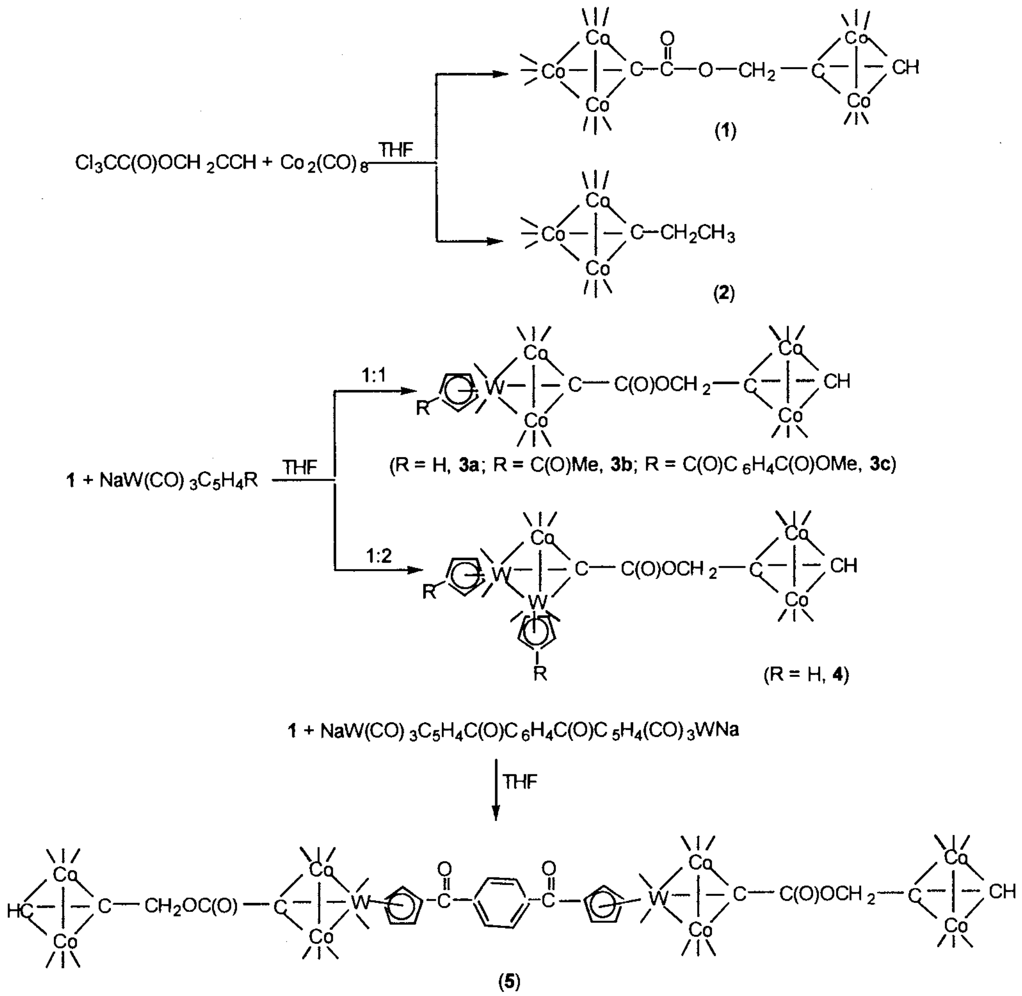
A solution of $Co_2(CO)_8$ (10.00 g, 29.2 mmol) and propargyl trichloroacetate (1.60 g, 7.9 mmol) in THF (150 cm^3) was stirred at room temperature for 24 h. After the solvent was removed at reduced pressure, the residue was chromatographed on a 3.5 × 50 cm column of silica. Elution with petroleum ether produced a red band from which 0.51 g of compound **2** as red–brown solid was obtained. Anal. Calc. for $C_{12}H_5Co_3O_9$: 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}. ^{1}H-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** as dark brown solid was obtained. yield 19.2% (based on propargyl trichloroacetate). Anal. Calc. for $C_{20}H_3Co_5O_{17}$: 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}. ^{1}H-NMR($CDCl_3$, δ): 5.55(s, 2H, CH_2), 6.10(s, 1H, CH).

2.3. Metal exchange reactions of compound 1

A solution of $NaW(CO)_3C_5H_5$ (78 mg, 0.22 mmol) and **1** (178 mg, 0.22 mmol) in THF (20 cm^3) was stirred at room temperature for 15 h. After the solvent was removed at reduced pressure, the residue was chromatographed on a 2 × 30 cm column of silica. Elution with CH_2Cl_2/petroleum ether (5:2) produced a large brown band from which 54 mg of compound **3a** as dark brown solid was obtained. Yield 25.3%. Anal. Calc. for $C_{24}H_8Co_4O_{16}W$: C, 29.63; H, 0.82%. Found: C, 29.71; H, 0.90%. IR(KBr disc): 2100m, 2081s, 2058vs, 2023vs, 2017vs, 1994vs, 1966s, 1951s, 1665m cm^{-1}. ^{1}H-NMR($CDCl_3$, δ): 5.49(s, 2H, CH_2), 5.53(s, 5H, C_5H_5), 6.10(s, 1H, CH).

The procedures for the reaction of $NaW(CO)_3C_5H_4C(O)Me$ or $NaW(CO)_3C_5H_4C(O)C_6H_4C(O)OMe$ with compound **1** were similar to that for the reaction of $NaW(CO)_3C_5H_5$ with compound **1**.

From the reaction of $NaW(CO)_3C_5H_4C(O)Me$ with **1**, 91 mg of compound **3b** as dark brown solid was obtained. Yield 40.8%. Anal. Calc. for $C_{26}H_{10}Co_4O_{17}W$: C, 30.77; H, 0.99%. Found: C, 30.89; H, 1.01%. IR(KBr disc): 2100m, 2087s, 2069s, 2028vs, 2013vs, 1994s, 1960s, 1932s, 1699m, 1659m cm^{-1}. ^{1}H-NMR($CDCl_3$, δ): 2.35(s, 3H, CH_3), 5.51(s, 2H, CH_2), 5.67(s, 2H, H(3) and H(4)), 5.97(s, 2H, H(2) and H(5)), 6.10(s, 1H, CH).



Scheme 1.

From the reaction of $NaW(CO)_3C_5H_4C(O)C_6H_4$-$C(O)OMe$ with **1**, 35 mg of compound **3c** as dark brown solid was obtained. Yield 14.0%. Anal. Calc. for $C_{33}H_{14}Co_4O_{19}W$: C, 34.92; H, 1.23%. Found: C, 34.79; H, 1.22%. IR(KBr disc): 2100m, 2048vs, 2021vs, 2001s, 1938s, 1883s, 1731m, 1662m, 1634m cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ): 3.95(s, 3H, CH_3), 5.42(s, 2H, CH_2), 5.74(s, 2H, H(3) and H(4)), 6.07(s, 2H, H(2) and H(5)), 6.09(s, 1H, CH), 7.28 ~ 8.17(m, 4H, C_6H_4).

A solution of $NaW(CO)_3C_5H_5$ (170 mg, 0.48 mmol) and **1** (178 mg, 0.22 mmol) in THF (20 cm^3) was stirred at room temperature for 24 h. The rest of the manipulations were similar to those described above. Elution with CH_2Cl_2 produced 27 mg of compound **4** as dark brown solid. Yield 10.8%. Anal. Calc. for $C_{28}H_{13}Co_3O_{15}W_2$: C, 29.63; H, 1.15%. Found: C, 29.69; H, 1.12%. IR(KBr disc): 2097s, 2087vs, 2038vs, 2005s, 1990s, 1944s, 1859s, 1663m cm^{-1}. ^{1}H-NMR($CDCl_3$, δ): 5.47(s, 2H, CH_2), 5.58(s, 10H, $2C_5H_5$), 6.11(s, 1H, CH).

A solution of $NaW(CO)_3C_5H_4C(O)C_6H_4C(O)$-$C_5H_4(CO)_3WNa$ (139 mg, 0.17 mmol) and **1** (265 mg, 0.33 mmol) in THF (20 cm^3) was stirred at room temperature for 24 h. The rest of the manipulations were similar to those described above. Elution with CH_2Cl_2 produced 53 mg of compound **5** as dark brown solid. Yield 15.0%. Anal. Calc. for $C_{56}H_{18}Co_8O_{34}W_2$: C, 32.40; H, 0.87%. Found: C, 32.54; H, 0.95%. IR(KBr disc): 2099s, 2084s, 2058vs, 2026vs, 1998vs, 1966s, 1894m, 1665m (br.) cm^{-1}. ^{1}H-NMR($CDCl_3$, δ): 5.46(s, 4H, $2CH_2$), 5.75(s, 4H, 2H(3) and 2H(4)), 6.05(s, 4H, 2H(2) and 2H(5)), 6.09(s, 2H, 2CH), 7.87(s, 4H, C_6H_4).

*2.4. X-ray crystallography of **1** and **3a***

Crystals used for X-ray determination were obtained from hexane/CH_2Cl_2 at −20°C. The crystals were mounted on a glass fiber. Preliminary examination and data collection were performed with Mo–K_α radiation ($\lambda = 0.71069$ Å) on a Rigaku RAXIS-IV imaging plate area detector (for **1**) or an Enraf–Nonius CAD4 diffractometer (for **3a**) equipped with a graphite monochromator.

The structure of compound **1** was solved by direct method and expended using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The structure of compound **3a** was solved by Patterson method and refined by the full-matrix least-squares method with anisotropic thermal parameters for the non-hydrogen atoms. All calculations were performed using the TEXSAN program system. Crystal data and experimental details are collected in Table 1.

Table 2
Positional parameters and B_{eq} for **1**

Atom	x	y	z	B_{eq} [a]
Co(1)	0.8779(1)	0.37391(10)	0.7339(2)	4.03(4)
Co(2)	0.6974(1)	0.3540(1)	0.6706(2)	4.25(4)
Co(3)	0.7482(1)	0.4272(1)	0.9634(2)	4.17(4)
Co(4)	0.6999(1)	−0.1079(1)	0.6768(2)	4.26(4)
Co(5)	0.7278(1)	−0.0418(1)	0.9851(2)	4.18(4)
O(1)	1.0620(7)	0.3576(9)	0.961(1)	7.7(3)
O(2)	0.8685(8)	0.5762(6)	0.620(1)	7.5(3)
O(3)	0.9775(8)	0.2181(8)	0.447(1)	7.0(3)
O(4)	0.6230(9)	0.5474(7)	0.525(1)	8.4(3)
O(5)	0.7386(10)	0.1917(9)	0.366(1)	8.9(3)
O(6)	0.4963(7)	0.3176(7)	0.748(1)	7.0(3)
O(7)	0.5651(9)	0.4136(8)	1.146(1)	7.8(3)
O(8)	0.8911(8)	0.413(1)	1.255(1)	9.0(4)
O(9)	0.6947(8)	0.6539(6)	0.948(1)	7.6(3)
O(10)	0.8906(7)	0.1757(6)	0.999(1)	6.3(2)
O(11)	0.8345(5)	0.1115(5)	0.7361(9)	4.2(2)
O(12)	0.5928(7)	0.0832(7)	0.547(1)	7.6(3)
O(13)	0.7897(9)	−0.2483(9)	0.369(1)	8.4(3)
O(14)	0.5349(8)	−0.2164(7)	0.715(1)	7.2(3)
O(15)	0.6276(7)	0.1821(6)	0.999(1)	6.3(2)
O(16)	0.8753(8)	−0.0423(10)	1.270(1)	8.1(3)
O(17)	0.5786(8)	−0.1261(8)	1.148(1)	7.3(3)
C(1)	0.992(1)	0.3665(9)	0.874(2)	5.6(3)
C(2)	0.8723(10)	0.4982(9)	0.664(2)	5.4(3)
C(3)	0.937(1)	0.2788(9)	0.558(2)	5.5(3)
C(4)	0.647(1)	0.4731(10)	0.584(2)	5.8(3)
C(5)	0.7228(10)	0.2538(10)	0.478(2)	5.2(3)
C(6)	0.574(1)	0.3307(9)	0.720(2)	5.0(3)
C(7)	0.634(1)	0.4157(8)	1.074(2)	5.1(3)
C(8)	0.836(1)	0.422(1)	1.145(2)	5.7(3)
C(9)	0.7148(8)	0.5670(9)	0.952(2)	5.0(3)
C(10)	0.7973(8)	0.2930(7)	0.823(1)	4.0(2)
C(11)	0.8457(9)	0.1891(7)	0.864(1)	4.1(2)
C(12)	0.8909(9)	0.0051(7)	0.753(1)	4.5(3)
C(13)	0.8185(8)	−0.0559(7)	0.796(1)	3.8(2)
C(14)	0.8186(9)	−0.1518(8)	0.826(1)	4.4(3)
C(15)	0.6325(9)	0.0085(9)	0.598(2)	4.5(3)
C(16)	0.754(1)	−0.193(1)	0.489(2)	5.5(4)
C(17)	0.599(1)	−0.1736(9)	0.701(1)	4.7(3)
C(18)	0.6651(9)	0.0941(9)	0.997(2)	4.6(3)
C(19)	0.818(1)	−0.038(1)	1.163(2)	5.5(3)
C(20)	0.636(1)	−0.0963(9)	1.079(2)	5.2(3)

[a] $B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$.

Table 3
Positional parameters and B_{eq} for **3a**

Atom	x	y	z	B_{eq} [a]
W	0.67753(5)	0.21761(4)	0.381160(19)	1.95(2)
Co(1)	0.89114(16)	0.25558(15)	0.29526(6)	2.31(8)
Co(2)	1.01555(16)	0.00689(16)	0.36802(7)	2.62(8)
Co(3)	0.9012(3)	−0.2877(2)	0.08326(8)	4.4(1)
Co(4)	0.6562(3)	−0.0286(2)	0.11095(8)	4.6(1)
O(1)	0.6023(12)	−0.1123(10)	0.4414(4)	4.8(6)
O(2)	0.3895(11)	0.2156(12)	0.3041(4)	5.0(7)
O(3)	0.5894(12)	0.5174(11)	0.2419(4)	5.2(7)
O(4)	1.1048(14)	0.1522(13)	0.1927(5)	6.5(8)
O(5)	1.0526(11)	0.4852(11)	0.3372(4)	4.9(7)
O(6)	1.3097(12)	−0.1601(13)	0.2910(5)	6.9(8)
O(7)	1.1633(13)	0.1623(14)	0.4452(5)	6.6(9)
O(8)	1.0115(13)	−0.3089(11)	0.4396(5)	5.5(7)
O(9)	0.879(2)	−0.1894(19)	−0.0377(6)	10(1)
O(10)	1.276(2)	−0.503(2)	0.0888(9)	12(2)
O(11)	0.739(2)	−0.5606(17)	0.1065(7)	11(2)
O(12)	0.3817(18)	−0.1959(17)	0.1355(6)	9(1)
O(13)	0.580(2)	0.199(2)	0.0057(6)	11(2)
O(14)	0.5144(19)	0.2406(15)	0.1873(5)	8(1)
O(15)	0.7145(10)	−0.1764(9)	0.3103(4)	3.8(5)
O(16)	0.8892(12)	−0.0998(9)	0.2426(3)	3.9(6)
C(1)	0.6352(14)	0.0034(12)	0.4188(5)	3.4(7)
C(2)	0.4969(13)	0.2175(14)	0.3318(5)	3.1(7)
C(3)	0.7056(15)	0.4135(13)	0.2632(5)	3.3(7)
C(4)	1.0230(15)	0.1864(14)	0.2325(6)	4.0(8)
C(5)	0.9902(15)	0.3981(13)	0.3207(5)	3.4(7)
C(6)	1.1984(14)	−0.0950(15)	0.3206(6)	4.2(8)
C(7)	1.1036(15)	0.1054(14)	0.4150(6)	4.0(8)
C(8)	1.0106(15)	−0.1858(15)	0.4122(5)	3.6(8)
C(9)	0.890(3)	−0.232(2)	0.0100(8)	7(1)
C(10)	1.129(3)	−0.425(2)	0.0864(10)	8(2)
C(11)	0.797(2)	−0.457(2)	0.0975(7)	6(1)
C(12)	0.490(2)	−0.131(2)	0.1250(7)	6(1)
C(13)	0.603(3)	0.110(2)	0.0458(8)	7(1)
C(14)	0.573(2)	0.1349(17)	0.1571(7)	6(1)
C(15)	0.8197(11)	0.0570(10)	0.3209(5)	2.3(6)
C(16)	0.7987(12)	−0.0832(11)	0.2912(4)	2.3(6)
C(17)	0.891(2)	−0.2425(15)	0.2108(6)	5(1)
C(18)	0.8602(16)	−0.1756(14)	0.1526(5)	3.7(8)
C(19)	0.9070(18)	−0.0753(16)	0.1112(6)	5(1)
C(20)	0.7250(16)	0.4042(15)	0.4386(6)	3.9(8)
C(21)	0.6315(16)	0.3048(13)	0.4707(5)	3.5(7)
C(22)	0.4661(15)	0.3566(14)	0.4464(6)	3.8(8)
C(23)	0.4663(14)	0.4842(13)	0.4018(6)	4.0(8)
C(24)	0.6304(18)	0.5110(13)	0.3970(6)	4.5(9)

[a] $B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$.

3. Results and discussion

The reactions described in this work are summarized in Scheme 1. $Co_2(CO)_8$ can readily react with propargyl trichloroacetate in THF at room temperature. However, the expected product **1** was formed in a low yield and no starting materials was isolated. Further investigation indicated that when this reaction was carried out at refluxing THF, compound **2** was the only product. It was reported that refluxing a xylene solution of $HCCo_3(CO)_9$ gave a mixture of $CH_3CCo_3(CO)_9$ and $CH_3CH_2CCo_3(CO)_9$. The formation of these two compounds involves the reactions of $HCCo_3(CO)_9$ with (μ-CHCH)$Co_2(CO)_6$ and (μ-$CHCCH_3$)$Co_2(CO)_6$, respectively [9]. In addition, the reaction of organic trihalide with $Co_2(CO)_8$ follows a free radical mechanism [10]. So, very probably, the two linked clusters in compound **1** are cleaved under the free radical reaction condition to give $HCCo_3(CO)_9$ and (μ-$CHCCH_3$)$Co_2(CO)_6$ after losing one molecule of CO_2 and getting two atoms of hydrogen, and then $HCCo_3(CO)_9$ reacts with (μ-$CHCCH_3$)$Co_2(CO)_6$ to give compound **2**. The two atoms of hydrogen maybe come from the solvent.

Compound **1** can react with metal exchange reagents in THF at room temperature. When **1** reacts with $NaW(CO)_3C_5H_4R$ in 1:1 molecular ratio, one unit of $Co(CO)_3$ in the $Co_3(CO)_9C$ core is substituted to give compounds **3a** ∼ **c**. When the molecular ratio is 1:2, two units of $Co(CO)_3$ in the $Co_3(CO)_9C$ core are substituted to give compound **4**. When **1** reacts with $NaW(CO)_3C_5H_4C(O)C_6H_4C(O)C_5H_4(CO)_3WNa$ in 2:1

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

Table 5
Selected bond lengths (Å) and angles(°) for **3a**

W–Co(1)	2.641(1)	Co(4)–C(19)	1.93(1)	W–Co(2)	2.695(2)
Co(4)–C(18)	1.94(1)	Co(1)–Co(2)	2.492(2)	O(1)–C(1)	1.13(1)
Co(3)–Co(4)	2.465(3)	W–C(1)	1.99(1)	W–C(15)	2.07(1)
O(5)–C(5)	1.13(1)	W–Cp	2.33	O(8)–C(8)	1.13(1)
O(10)–C(10)	1.14(2)	Co(1)–C(5)	1.81(1)	O(12)–C(12)	1.17(2)
Co(1)–C(15)	1.917(8)	Co(2)–C(8)	1.80(1)	Co(2)–C(15)	1.92(1)
C(15)–C(16)	1.48(1)	C(17)–C(18)	1.45(2)	Co(3)–C(10)	1.80(2)
C(18)–C(19)	1.32(2)	Co(3)–C(19)	1.95(1)	Co(3)–C(18)	1.95(1)
Co(4)–C(12)	1.80(2)				
C(2)–W–C(15)	76.2(4)	C(1)–W–C(15)	85.3(4)	C(15)–W–C(22)	164.4(3)
C(15)–W–Co(1)	46.1(2)	C(15)–W–Co(2)	45.3(3)	C(5)–Co(1)–C(15)	140.2(5)
C(5)–Co(1)–Co(2)	94.6(4)	C(9)–Co(3)–C(18)	140.2(6)	C(9)–Co(3)–Co(4)	97.3(6)
C(15)–Co(1)–Co(2)	49.7(3)	C(15)–Co(1)–W	51.1(3)	Co(2)–Co(1)–W	63.28(5)
C(19)–Co(3)–C(18)	39.7(5)	C(7)–Co(2)–C(15)	141.7(4)	C(19)–Co(3)–Co(4)	50.2(4)
C(18)–Co(3)–Co(4)	50.6(4)	C(8)–Co(2)–C(15)	103.4(5)	C(14)–Co(4)–C(19)	102.1(7)
C(15)–Co(2)–Co(1)	49.4(2)	C(15)–Co(2)–W	50.0(3)	Co(1)–Co(2)–W	61.06(4)
C(19)–Co(4)–C(18)	40.0(5)	C(19)–Co(4)–Co(3)	51.0(3)	C(18)–Co(4)–Co(3)	51.0(3)
C(19)–C(18)–C(17)	142(1)	O(1)–C(1)–W	176.1(9)	C(19)–C(18)–Co(3)	70.1(8)
O(2)–C(2)–W	178(1)	O(3)–C(3)–Co(1)	178(1)	O(4)–C(4)–Co(1)	176(1)
Co(4)–C(18)–Co(3)	78.4(5)	O(5)–C(5)–Co(1)	179(1)	C(18)–C(19)–Co(4)	70.6(8)
O(6)–C(6)–Co(2)	179(1)	C(18)–C(19)–Co(3)	70.3(7)	O(7)–C(7)–Co(2)	178(1)
Co(4)–C(19)–Co(3)	78.9(5)	O(8)–C(8)–Co(2)	178(1)	O(9)–C(9)–Co(3)	177(2)
O(10)–C(10)–Co(3)	176(2)	O(11)–C(11)–Co(3)	178(2)	O(12)–C(12)–Co(4)	178(2)
O(13)–C(13)–Co(4)	175(2)	O(14)–C(14)–Co(4)	178(2)	C(16)–C(15)–Co(1)	132.1(8)
C(16)–C(15)–Co(2)	120.5(6)	C(16)–C(15)–W	136.7(6)	Co(1)–C(15)–Co(2)	80.9(3)
Co(1)–C(15)–W	82.8(3)	Co(2)–C(15)–W	84.7(4)		

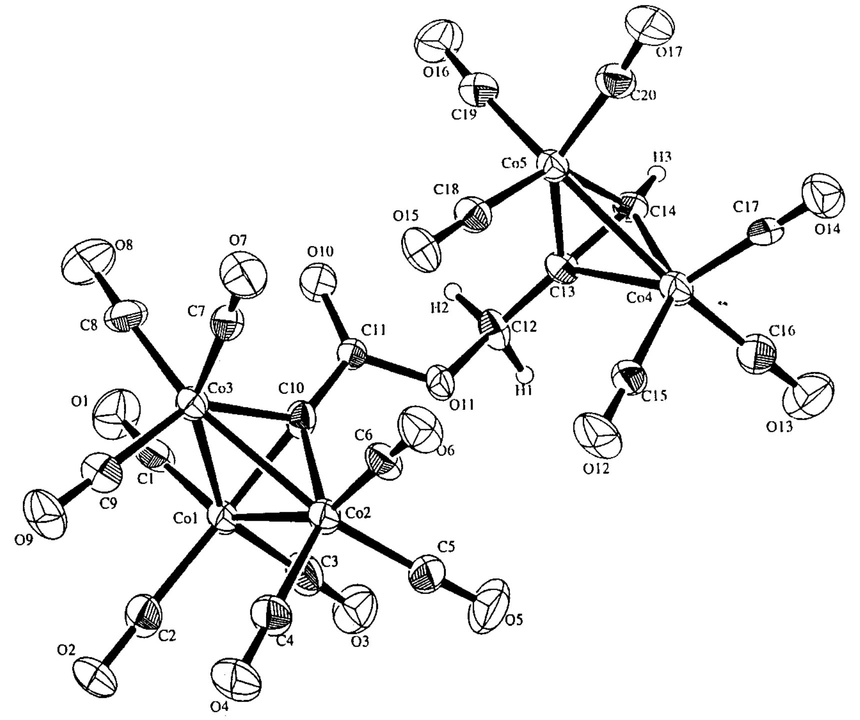


Fig. 1. The molecular structure of compound **1**.

molecular ratio, two units of $Co(CO)_3$ in two $Co_3(CO)_9C$ cores are substituted to give compound **5** in which four clusters are linked through three carbon chains.

In all these metal exchange reactions, the $Co_2(CO)_6C_2$ unit was intact. This could be seen from the ^1H-NMR spectra. For all the exchange products, the ^1H-NMR spectra show a singlet around 6.10 ppm, which should be attributed to the terminal proton in the $Co_2(CO)_6(\mu\text{-}CHCR)$ unit, just as their precursor compound **1**. If the $CoW(CO)_5(C_5H_4R)(\mu\text{-}CHCR)$ unit were formed, this signal should appear around 5.80 ppm because of the stronger deshielding effect of the tungsten fragment $[W(CO)_2(C_5H_4R)]$ [2f]. In addition, the ten protons on the two cyclopentadienyl rings in compound **4** show only one singlet at 5.58 ppm. Therefore, $Co(CO)_3$ unit in different cluster cores has a different reactivity, following the series: $Co_3C > Co_2WC > Co_2C_2$, CoW_2C.

The $Co(CO)_3$ unit in simple Co_2C_2 clusters can be exchanged by other isoloble units in refluxing THF [2f]. However, the thermal reaction of compound **1** with metal exchange reagent gave a complicated mixture rather than the expected metal exchange products. At room temperature and in THF solution, the $Co(CO)_3$ exchange in the Co_2C_2 unit can also be observed provided that the reaction time is long enough (at least 48 h) [11].

In the ^1H-NMR spectra of compounds **3b**, **3c** and **5**, the two singlets around 5.70 and 6.00 ppm are caused by the protons on the substituted cyclopentadienyl rings. The downfield singlet should be attributed to the H(2) and H(5) protons, which are close to the substituent and the upfield one should be attributed to the H(3) and H(4) protons, being remote from the substituent. Except for **2**, all the compounds show a singlet around 5.50 ppm, which should be assigned to the protons in the CH_2 unit on the carbon chain.

In the IR spectra of compounds **1**, **3a** ~ **c**, **4** and **5**, the absorption bands in the range 1859 ~ 2112 cm^{-1} are caused by the terminal carbonyls and the ones in the range 1634 ~ 1731 cm^{-1} are caused by the carbonyls (C=O) on the carbon chains or/and on the substituted cyclopentadienyl rings.

Compound **2** was identified by comparing its spectral data with the literature value [9].

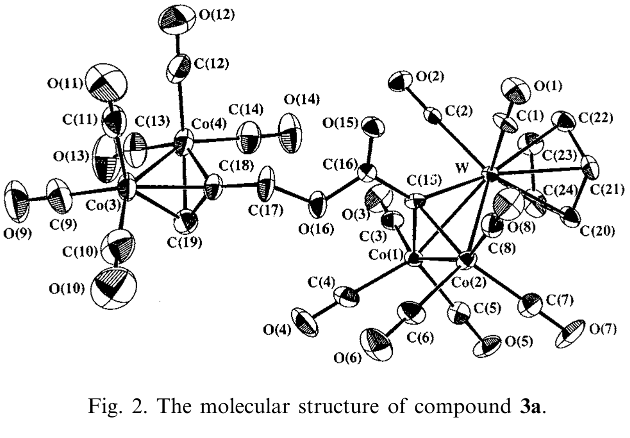


Fig. 2. The molecular structure of compound **3a**.

In order to further confirm the structures of these compounds, X-ray single-crystal structure analyses of **1** and **3a** were undertaken. The final atomic coordinates and thermal parameters of the non-hydrogen atoms for **1** and **3a** are given in Tables 2 and 3. Selected bond lengths and angles are listed in Tables 4 and 5. The molecular structures are presented in Figs. 1 and 2.

The molecule of compound **1** contains two different quasi-tetrahedral cluster cores connected through a $C(O)OCH_2$ chain. One quasi-tetrahedral cluster core consists of three cobalt atoms which form an equilateral triangle and one carbon atom which is more closely bonded to Co(2) than to Co(1) or Co(3), and the other quasi-tetrahedral cluster core consists of two cobalt atoms and two carbon atoms. Each cobalt atom bears three terminal carbonyls. However, the ones in the Co_2C_2 core are more closely coordinated by the terminal carbonyls (average Co–C bond length, 1.79 Å) than the ones in the Co_3C core (average Co–C bond length, 1.82 Å). Like in other related compounds [3c], the C(13)–C(14) bond length (1.34(1) Å) is much longer than a normal C≡C bond while the C(10)–C(11) and C(12)–C(13) bond lengths (1.47(1) and 1.49(1) Å) are much shorter than a normal C–C single bond. In the Co_3C and Co_2C_2 cores, all the geometrical parameters are in the normal range for the related compounds [3c,4a].

Generally, the structure of compound **3a** is similar to its precursor compound **1**. Instead of Co_3C core, the Co_2WC core links with Co_2C_2 core through the $C(O)OCH_2$ chain. In the Co_2WC core, each cobalt atom has three terminal carbonyls and the tungsten atom has two terminal carbonyls and one cyclopentadienyl ligand. The Co–Co distance (2.492(2) Å) is slightly longer than the corresponding value (2.468(2) Å) in compound **1**. The C(15)–C(16) bond length (1.48(1) Å) is also much shorter than a normal C–C single bond.

A metal–carbon bond is stronger than a metal–metal bond [1]. From the molecular structures of **1** and **3a**, it is clear that the $Co(CO)_3$ unit in the Co_3C core is more active than the one in the Co_2C_2 core in a metal exchange reaction. For substituting a $Co(CO)_3$ unit in the Co_2C_2 core, the cleavage of two metal–carbon bonds and one metal–metal bond is required while substituting the same unit in the Co_3C core only need to break one metal–carbon bond and two metal–metal bonds.

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC, No. 113796 for compound **1** and No. 113797 for compound **3a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ [Fax: +44-1223-336033] or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

Acknowledgements

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

References

[1] H. Vahrenkamp, Comments Inorg. Chem. 4 (1985) 253.

[2] (a) H.P. Wu, Z.Y. Zhao, Y.Q. Yin, D.S. Jin, X.Y. Huang, Polyhedron 14 (1995) 1543. (b) H.P. Wu, Y.Q. Yin, X.Y. Huang, K.B. Yu, J. Organomet. Chem. 498 (1995) 119. (c) H.P. Wu, Y.Q. Yin, Q.C. Yang, Inorg. Chim. Acta 245 (1996) 143. (d) E.R. Ding, S.M. Liu, Z.Y. Zhao, Y.Q. Yin, J. Sun, Polyhedron 16 (1997) 2387. (e) E.R. Ding, S.M. Liu, Y.Q. Yin, J. Sun, J. Chem. Res (S). 1998 (246). (f) S.L. Wu, E.R. Ding, Y.Q. Yin, J. Sun, J. Organomet. Chem. 570 (1998) 71.

[3] (a) D. Seyferth, J.E. Hallgren, P.L.K. Hung, J. Organomet. Chem. 50 (1973) 265. (b) D. Seyferth, J.E. Hallgren, R.J. Spohn, G.H. Williams, J. Organomet. Chem. 65 (1974) 99. (c) B.R. Penfold, B.H. Robinson, Acc. Chem. Res. 6 (1973) 73.

[4] (a) R.S. Dickson, P.J. Fraser, Adv. Organomet. Chem. 12 (1974) 323. (b) H.E. Amouri, M. Gruselle, Chem. Rev. 96 (1996) 1077.

[5] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, Pergamon, New York, 1980.

[6] J. Zhang, X.-N. Chen, Y.-Q. Yin, Chem. Res., in press.

[7] C.H. Wei, L.F. Dahl, Inorg. Chem. 4 (1965) 1.

[8] E.R. Ding, S.M. Liu, Y.-Q. Yin, J. Sun, Polyhedron 16 (1997) 3273.

[9] D. Seyferth, C.N. Rudie, J.S. Merola, J. Organomet. Chem. 162 (1978) 89.

[10] G. Schmid, Angew. Chem. Int. Ed. Engl. 17 (1978) 392.

[11] X.-N. Chen, J. Zhang, Y.-Q. Yin, X.-Y. Huang, J. Sun, J. Organomet. Chem. 579 (1999) 227.