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THE REACTION OF THE PRECURSOR $PhCCo_3(CO)_9$ WITH $NaW(CO)_3(RCp)$: CHARACTERIZATION AND CRYSTAL STRUCTURE OF THE CLUSTERS $(\mu_3\text{-}CPh)Co_2W(CO)_8(RCp)$ $(R = HCO, CH_3CO, C_2H_5OCO)$

HE-PING WU and YUAN-QI YIN*

Lanzhou Institute of Chemical Physics, Chinese Academy of Science, Lanzhou 730000,
P.R. China

and

XIAO-YING HUANG

State Key Laboratory of Structure Chemistry, Fujian Institute of Research on
Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P.R. China

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Abstract—μ_3-Phenylmethylidyne trimetal carbonyl clusters $(\mu_3\text{-}CPh)Co_2W(CO)_8(RCp)$ (**2a**: R = HCO; **3a**: R = CH_3CO; **4a**: R = C_2H_5OCO) have been obtained from a solution of the precursor $(\mu_3\text{-}CPh)Co_3(CO)_9$ refluxing with the metal exchange reagents NaW $(CO)_3(RCp)$ in THF. The results showed that electron-withdrawing groups on the cyclopentadienyl affected the activity of the metal exchange reagents $NaW(CO)_3(RCp)$ and the above reaction was accelerated thermally. The results further showed that the metal carbonyl unit $Co(CO)_3$ in the precursor $PhCCo_3(CO)_9$ can be exchanged by the organometallic group $W(CO)_2(RCp)$. The clusters were characterized by C/H analysis, IR and ^1H NMR and by crystal structure determination for cluster **3a**.

One aspect of the unconventional use of organometallic fragments as cluster building blocks is metal exchange. Metal exchange in clusters was first observed in 1971/72[1,2] without being explicitly recognized. However, only recently[3] were systematic studies begun to elucidate the scope and variability of this reaction. Some μ_3-alkylidyne-Co_2M (M = Cr, Mo, W, Fe, Ni) tetrahedral clusters were synthesized by the reaction of the precursor $RCCo_3(CO)_9$ (R = alkyl, aryl, halo, H) with Na (or K) salts of $M(CO)_3Cp$,[4,5] $Me_2AsM(CO)_3Cp$[6] and $[M(CO)_3Cp]_2$[7] through metal exchange. In these reactions, the latter species are able to attack the precursor and substitute the $Co(CO)_3$ unit. However, no μ_3-alkylidyne Co_2W derivatives containing substituted cyclopentadienyls (HCOCp, CH_3COCp, C_2H_5OCOCp) or the crystal structure of a cluster core CCo_2W have been reported up to now. In order to examine the chemical properties of the η^5-substituted cyclopentadienyl tricarbonyl derivatives of tungsten that react with $PhCCo_3$ $(CO)_9$ and to synthesize new derivatives of the clusters $RCCo_2W(CO)_8(RCp)$, we initiated a study of the reaction of the cluster $PhCCo_3(CO)_9$ with $NaW(CO)_3(RCp)$ (R = HCO, CH_3CO, C_2H_5OCO) using metal exchange reaction. Three novel clusters, $PhCCo_2W(CO)_8(RCp)$, were prepared and the crystal structure of the cluster **3a** was determined.

EXPERIMENTAL

General procedure and material

All operations were carried out under pure nitrogen using standard Schlenk and vacuum tech-

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* Author to whom correspondence should be addressed.

niques. Hexane, benzene and tetrahydrofuran were dried over sodium wire and distilled from sodium–benzophenone under nitrogen. $NaW(CO)_3(RCp)$ and $PhCCo_3(CO)_9$ were prepared according to literature methods.[8,9] Column chromatography was carried out using 160–200 mesh silica gel.

IR spectra were recorded on a Nicolet FT-IR 10 DX IR spectrophotometer; ^1H NMR spectra were recorded on a Bruker AM-400MHz spectrometer; C/H analysis determinations were performed using a 1106-type analyser.

General procedure for preparing clusters $PhCCo_2W(CO)_8(RCp)$ [R = HCO (**2a**), CH_3CO(**3a**), C_2H_5OCO (**4a**)]

To a solution of $NaW(CO)_3(RCp)$ in THF was added $PhCCo_3(CO)_9$ (**1**). The mixture was stirred for 5–8 h at 60°C. Solvent was then removed under reduced pressure. The residue was extracted in benzene and the extracts were chromatographed on a 20 × 2.5 cm silica gel column using benzene–n-hexane as eluent. Products were recrystallized in hexane–benzene at −20°C.

Compound **2a**. Yield: 21.2%. Found: C, 35.9; H, 1.3. Calc. for $C_{21}H_{10}Co_2O_9W$: C, 35.6; H, 1.4%. IR (KBr disk): ν(CO) 1689.8m, ν(CO) (terminal CO) 2071.7s, 2011.9vs, 1994.5s, 1975.2s, 1940.5s cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.55 (s, 1H, HCO), 5.78 [s, 2H, H(2), H(5)], 5.49 [s, 2H, H(3), H(4)], 7.12–7.36 (m, 5H, C_6H_5).

Compound **3a**. Yield: 20.8%. Found: C, 37.0; H, 1.5. Calc. for $C_{22}H_{12}Co_2O_9W$: C, 36.6; H, 1.7%. IR (KBr disk): ν(CO) 1685.9m, ν(CO) (terminal CO) 2069.8s, 2019.6vs, 2008.0vs, 1992.6s, 1971.4s, 1938.6m cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.30 (s, 3H, CH_3CO), 5.78 [s, 2H, H(2), H(5)], 5.17 [s, 2H, H(3), H(4)], 7.17 (t, 1H, =CH), 7.27 (d, 2H, 2 =CH), 7.31 (t, 2H, 2 =CH).

Compound **4a.** Yield: 24.7%. Found: C, 37.2; H, 1.7. Calc. for $C_{23}H_{14}Co_2O_{10}W$: C, 36.7; H, 1.9%. IR(KBr disk): ν(CO) 1720.6m, ν(CO) (terminal CO) 2069.8s, 2021.5vs, 2000.3vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.30 (s, 3H, CH_3), 4.27 (s, 2H, OCH_2), 5.82 [s, 2H, H(2), H(5)], 5.43 [s, 2H, H(3), H(4)], 7.10–7.27 (m, 5H, C_6H_5).

X-ray crystallography for **3a**

The black crystals used for X-ray determination were obtained from hexane–benzene solution at −20°C. A crystal of approximate dimensions $0.2 \times 0.16 \times 0.10$ mm^3 was used for structure determination. Data collection was performed with Mo-K_α radiation ($\lambda = 0.71069$ Å) on an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator. A total of 8572 reflections measured were collected in the range $2\theta_{max} = 49.9°$, of which 6316 reflections with $I > 3.00\sigma(I)$ were considered to be observed.

Cluster **3a** is triclinic with space group $P\bar{1}$ and lattice parameters: $a = 13.631(4)$, $b = 14.569(4)$, $c = 14.704(6)$ Å; $\alpha = 116.53(3)$, $\beta = 106.76(3)$, $\gamma = 100.62(2)°$; $Z = 4$, $V = 2329(2)$ $Å^3$, $D_c = 2.06$ g cm^{-3}, $F(000) = 1376$, $R = 0.035$, $R_w = 0.043$. The goodness of fit indicator is 0.99, maximum shift in final cycle is 0.08, largest peak in final diff. map is 0.72 e $Å^{-3}$.

The structure was solved by the Patterson method. The tungsten atom and two cobalt atoms were located by the heavy-atom method. The coordinates of the remaining non-hydrogen atoms were found from a difference map. The structure was refined by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. All calculations were performed on a MICRO VAX 3100 computer using the TEXSAN program system.

RESULTS AND DISCUSSION

The clusters mentioned above were prepared by refluxing a solution of compound **1** with $NaW(CO)_3(RCp)$ in THF for 5–8 h using metal exchange reaction. The expected clusters were obtained in yields of 20.8–24.7%. The reaction route is as follows:

$$\underset{(\mathbf{1})}{PhCCo_3(CO)_9} + NaW(CO)_3(RCp) \longrightarrow PhCCo_2W(CO)_8(RCp)$$

$$R = HCO(\mathbf{2a}), CH_3CO\ (\mathbf{3a}), C_2H_5OCO\ (\mathbf{4a})$$

These clusters are air-stable black solids. Elemental analysis, IR and ^1H NMR data of these clusters are consistent with the expected structures. According to the literature,[7] the clusters (M = W) were obtained in yields of 44% at room temperature. However, under the same reaction conditions, only trace amounts of products $PhCCo_2W(CO)_8(RCp)$ were detected by TLC. This result shows that the electron-withdrawing group C=O on the cyclopentadienyl ligand affected the reactivity of the metal exchange reagents $NaW(CO)_3(RCp)$. We found that the reaction of compound **1** with $NaW(CO)_3(RCp)$ was accelerated by heating through producing a higher yield under refluxing conditions than at room temperature. No CoW_2 clusters were found in our experiment, which is contrary to the reaction carried out by Duffy and co-workers.[7,10] Reaction results showed that one metal unit, $Co(CO)_3$, in compound **1** could be exchanged with another metal unit, $W(CO)_2(RCp)$, with electron-

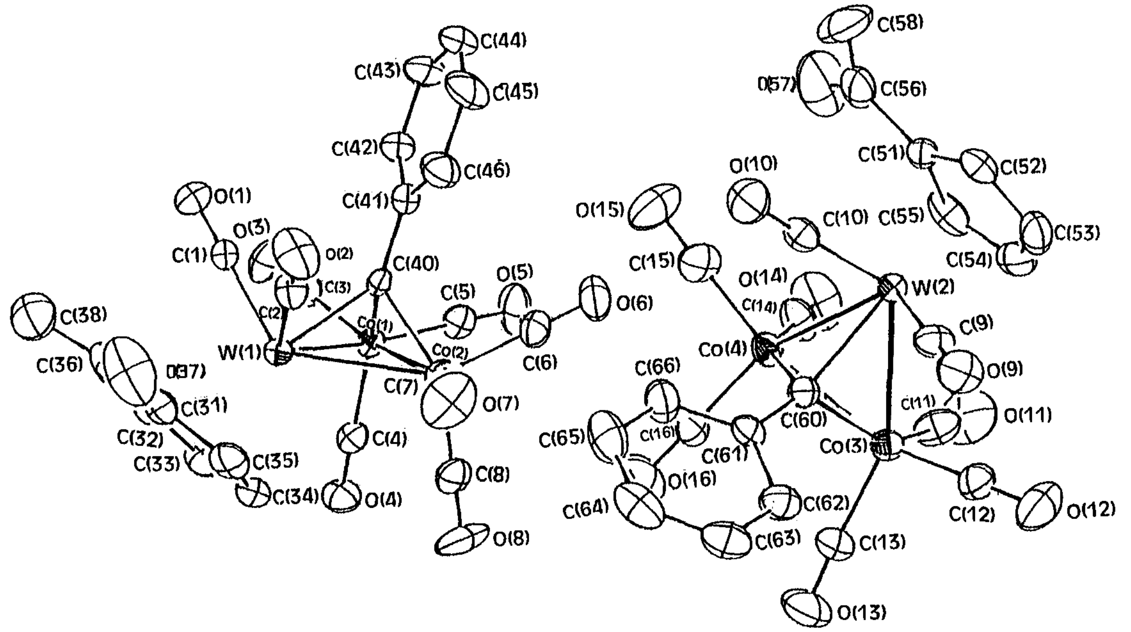
Table 1. Bond lengths (Å)

W(1)—Co(1)	2.659(1)	W(2)—Co(3)	2.663(2)
W(1)—Co(2)	2.676(2)	W(2)—Co(4)	2.669(1)
Co(1)—Co(2)	2.473(2)	Co(3)—Co(4)	2.487(2)
Co(1)—C(40)	1.941(8)	Co(3)—C(60)	1.944(8)
Co(2)—C(40)	1.935(8)	Co(4)—C(60)	1.927(8)
W(1)—C(40)	2.093(7)	W(2)—C(60)	2.086(8)
Co(1)—C_{CO}	1.79(ave)	Co(3)—C_{CO}	1.78(ave)
Co(2)—C_{CO}	1.79(ave)	Co(4)—C_{CO}	1.80(ave)
W(1)—C_{CO}	1.97(ave)	W(2)—C_{CO}	1.98(ave)
W(1)—C_{Cp}	2.281(ave)	W(2)—C_{Cp}	2.334(ave)
$(O—C)_{Co(1)}$	1.137(ave)	$(O—C)_{Co(3)}$	1.135(ave)
$(O—C)_{Co(2)}$	1.133(ave)	$(O—C)_{Co(4)}$	1.143(ave)
$(O—C)_{W(1)}$	1.145(ave)	$(O—C)_{W(2)}$	1.15(ave)
$(C_{Cp}—C_{Cp})_{W(1)}$	1.408(ave)	$(C_{Cp}—C_{Cp})_{W(2)}$	1.40(ave)
O(37)—C(36)	1.20(1)	O(57)—C(56)	1.24(1)
C(31)—C(36)	1.48(1)	C(51)—C(56)	1.48(1)
C(36)—C(38)	1.48(2)	C(56)—C(58)	1.34(1)
C(40)—C(41)	1.50(1)	C(60)—C(61)	1.48(1)

withdrawing C=O groups on cyclopentadienyls and the generality of the metal exchange reaction between tetrahedral transition metal carbonyl clusters and metal carbonyl anions.[4,7,10]

For the IR spectra of the clusters, characteristic carbonyl absorption peaks appear at 1690 (R = H), 1686 ($R = CH_3$) and 1721 cm^{-1} ($R = C_2H_5O$), respectively. A large number of more intense absorption bands at between 2070 and 1939 cm^{-1} were assigned to characteristic terminal carbonyl peaks.

For the ^1H NMR assignment of the clusters, multiplets in the range of 7.10–7.36 ppm were assigned to protons of the bridge substituent Ph. Apparent upfield singlets between 5.17 and 5.49 ppm were assigned to protons H(3) and H(4) and the downfield singlets between 5.78 and 5.82 ppm to H(2) and H(5) because of the deshielding effect of electron-



I II

Fig. 1. The crystal structure of cluster **3a** (I, II).

Table 2. Bond angles ( )

Co(1)—W(1)—Co(2)	55.22(4)	Co(3)—W(2)—Co(4)	55.61(5)
C(40)—W(1)—Co(1)	46.3(2)	C(60)—W(2)—Co(3)	46.4(2)
C(40)—W(1)—Co(1)	46.3(2)	C(60)—W(2)—Co(3)	46.4(2)
C(40)—W(1)—Co(2)	45.9(2)	C(60)—W(2)—Co(4)	45.8(2)
Co(2)—Co(1)—W(1)	62.74(5)	Co(4)—Co(3)—W(2)	62.33(6)
C(40)—Co(1)—Co(2)	50.3(2)	C(40)—Co(3)—Co(4)	49.(2)
C(40)—Co(1)—W(1)	51.3(2)	C(60)—Co(3)—W(2)	51.2(2)
Co(1)—Co(2)—W(1)	62.05(4)	Co(3)—Co(4)—W(2)	62.06(2)
C(40)—Co(2)—Co(1)	50.5(2)	C(60)—Co(4)—Co(3)	50.3(2)
C(40)—Co(2)—W(1)	50.9(2)	C(60)—Co(4)—W(2)	50.9(2)
Co(1)—C(40)—W(1)	82.4(3)	Co(3)—C(60)—W(2)	82.6(3)
Co(2)—C(40)—W(1)	83.2(3)	Co(4)—C(60)—W(2)	83.3(3)
Co(1)—C(40)—Co(2)	79.3(3)	Co(3)—C(60)—Co(4)	80.3(3)
C(41)—C(40)—Co(1)	128.9(6)	C(61)—C(60)—Co(3)	127.6(6)
C(41)—C(40)—Co(2)	125.4(6)	C(61)—C(60)—Co(4)	128.1(6)
C(41)—C(40)—W(1)	137.7(5)	C(61)—C(60)—W(2)	135.9(6)
C(1)—W(1)—C(2)	84.9(4)	C(9)—W(2)—C(10)	82.1(3)
C(1)—W(1)—C(40)	79.0(3)	C(9)—W(2)—C(60)	79.5(3)
C(2)—W(1)—C(40)	81.1(3)	C(10)—W(2)—C(40)	79.0(3)
C(1)—W(1)—Co(1)	87.9(3)	C(9)—W(2)—Co(3)	87.3(2)
C(1)—W(1)—Co(2)	124.8(2)	C(9)—W(2)—Co(4)	125.3(2)
C(2)—W(1)—Co(1)	127.3(3)	C(10)—W(2)—Co(3)	125.4(2)
C(1)—W(1)—C_{Cp}	82.9(3)–139.1(4)	C(9)—W(2)—C_{Cp}	81.5(3)–138.4(3)
C(2)—W(1)—C_{cp}	83.1(3)–140.2(3)	C(10)—W(2)—C_{Cp}	88.2(3)–144.1(3)
C(40)—W(1)—C_{Cp}	133.7(3)–163.7(3)	C(60)—W(2)—C_{Cp}	135.1(3)–165.3(3)
Co(1)—W(1)—C_{Cp}	91.8(2)–149.6(24)	Co(3)—W(2)—C_{Cp}	90.2(3)–145.8(2)
Co(2)—W(1)—C_{Cp}	90.9(3)–146.9(2)	Co(4)—W(2)—C_{Cp}	91.8(2)–145.3(3)
C_{Cp}—W(1)—C_{Cp}	34.1(3)–58.9(3)	C_{Cp}—W(2)—C_{Cp}	33.9(4)–58.3(3)
C(3)—Co(1)—C(40)	105.4(4)	C(11)—Co(3)—C(60)	108.4(4)
C(4)—Co(1)—C(40)	142.0(4)	C(12)—Co(3)—C(60)	139.8(4)
C(5)—Co(1)—C(40)	101.0(4)	C(13)—Co(3)—C(60)	99.1(4)
C(3)—Co(1)—Co(2)	154.9(3)	C(11)—Co(3)—Co(4)	152.9(3)
C(4)—Co(1)—Co(2)	99.8(3)	C(12)—Co(3)—Co(4)	93.4(4)
C(5)—Co(1)—W(1)	150.0(3)	C(13)—Co(3)—W(2)	150.1(3)
C(3)—Co(1)—C(4)	99.0(4)	C(11)—Co(3)—C(12)	100.4(5)
C(3)—Co(1)—C(5)	100.1(4)	C(11)—Co(3)—C(13)	98.3(5)
C(4)—Co(1)—C(5)	102.9(4)	C(12)—Co(3)—C(13)	104.0(5)
C(4)—Co(1)—W(1)	97.0(3)	C(12)—Co(3)—W(2)	101.7(3)
C(5)—Co(1)—Co(2)	91.7(3)	C(13)—Co(3)—Co(4)	100.8(3)
C(3)—Co(1)—W(1)	98.6(3)	C(11)—Co(3)—W(2)	91.9(3)
C(8)—Co(2)—C(40)	142.0(4)	C(16)—Co(4)—C(60)	96.5(4)
C(6)—Co(2)—C(40)	93.6(4)	C(14)—Co(4)—C(60)	146.1(4)
C(7)—Co(2)—C(40)	110.8(4)	C(15)—Co(4)—C(60)	106.4(4)
C(6)—Co(2)—Co(1)	101.1(3)	C(14)—Co(4)—Co(3)	99.5(4)
C(7)—Co(2)—Co(1)	152.7(3)	C(15)—Co(4)—Co(3)	153.4(3)
C(8)—Co(2)—Co(1)	93.0(3)	C(16)—Co(4)—Co(3)	96.7(3)
C(6)—Co(2)—W(1)	144.2(3)	C(14)—Co(4)—W(2)	104.9(3)
C(7)—Co(2)—W(1)	90.9(3)	C(15)—Co(4)—W(2)	93.9(3)
C(8)—Co(2)—W(1)	107.1(3)	C(16)—Co(4)—W(2)	147.3(3)
C(6)—Co(2)—C(7)	99.7(5)	C(14)—Co(4)—C(15)	97.7(5)
C(6)—Co(2)—C(8)	105.0(5)	C(14)—Co(4)—C(16)	102.9(5)
C(7)—Co(2)—C(8)	98.5(5)	C(15)—Co(4)—C(16)	99.0(5)
O—C—W(1)	177.35(ave)	O—C—W(2)	177.9(ave)
O—C—Co(1)	178.27(ave)	O—C—Co(3)	177(ave)
O—C—Co(2)	178.33(ave)	O—C—Co(4)	178(ave)
O(37)—C(36)—C(38)	122(1)	O(57)—C(56)—C(58)	125(1)
O(37)—C(36)—C(31)	120(1)	O(57)—C(56)—C(51)	118(2)
C(36)—C(31)—W(1)	123.5(6)	C(56)—C(51)—W(2)	122.4(6)
C(32)—C(31)—C(36)	128(1)	C(52)—C(51)—C(56)	127(1)
C(35)—C(31)—C(36)	125(1)	C(55)—C(51)—C(56)	126(1)
C(46)—C(41)—C(40)	120.8(8)	C(66)—C(61)—C(60)	121.0(8)
C(42)—C(41)—C(40)	120.8(8)	C(62)—C(61)—C(60)	123.2(8)
C_{Cp}—C_{Cp}—W(1)	71.2(5)–75.0(6)	C_{Cp}—C_{Cp}—W(2)	71.1(5)–74.6(6)
C_{Cp}—C_{Cp}—C_{Cp}	106.7(8)–108.8(9)	C_{Cp}—C_{Cp}—C_{Cp}	106.7(8)–109(1)
C_{Ph}—C_{Ph}—C_{Ph}	118.4(9)–122(1)	C_{Ph}—C_{Ph}—C_{Ph}	115.7(8)–123(1)

withdrawing C=O groups on the cyclopentadienyl ring. ^1H NMR spectra of the clusters did not exhibit a pair of apparent triplets (A_2B_2 pattern)[11,12] for cyclopentadienyl protons H(3,4) and H(2,5). Similarly, proton peaks of CH_3 and CH_2 in the CH_3CH_2O group appear as singlets instead of triplet and quartet peaks.

X-ray crystal structure analysis

Bond angles and bond lengths are listed in Tables 1 and 2. The molecular structure of cluster **3a** is presented in Fig. 1. As seen from Fig. 1, this cluster has a tetrahedral skeleton composed of carbon, tungsten and two cobalt atoms. The cobalt atom is coordinated by three terminal CO ligands, the tungsten atom by two terminal CO ligands and one substituted cyclopentadienyl ligand. There are two independent molecules in the asymmetric unit. In both molecules, all carbon atoms in the acetyl groups are co-planar with the cyclopentadienyl rings, suggesting that the π-system of the CH_3CO group is fully conjugated with the cyclopentadienyl π-system. This result was contrary to the result reported by Song *et al.*[11]

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