affords $Re_7C(CO)_{21}^{3-}$ (isolated yield 40%), although a four-fold excess of sodium is needed under these conditions. Prolonged pyrolysis (30 h) of $H_2Re_6C(CO)_{18}^{2-}$ in triglyme (200 °C) affords $Re_8C(CO)_{24}^{2-}$ (yield 30%) as the only identifiable product without the formation of any observable $Re_7C(CO)_{21}^{3-}$. Treatment of $H_2Re_6C(CO)_{18}^{2-}$ with $Re_2(CO)_{10}$ ($Re_6$:$Re_2$ = 1:1) and heating the mixture in triglyme (190–200 °C) afford only $Re_8C(CO)_{24}^{2-}$ in ca. 80% isolated yield.

In the conversion of $H_2Re_6C(CO)_{18}^{2-}$ to the two larger clusters, the hydride ligands may be removed in one of three forms: as $H_2$, as two hydride ions ($H^-$), or as two protons ($H^+$). Since it is necessary to employ the appropriate quantity of reducing or oxidizing agent (sodium and/or $Re_2(CO)_{10}$) with $H_2Re_6C(CO)_{18}^{2-}$ to provide $Re_7C(CO)_{21}^{3-}$ or $Re_8C(CO)_{24}^{2-}$, respectively, loss of the hydride ligands as $H_2$ is the probable pathway. This would generate the formal intermediate "$Re_6C(CO)_{18}^{2-}$", which should react further in the manner observed. However, if they were removed as hydrides, a neutral intermediate (e.g., "$Re_6C(CO)_{18}$") would be generated, and this is not likely to be reduced to $Re_8C(CO)_{24}^{2-}$ in the presence of $Re_2(CO)_{10}$ only. The final possibility, removal as $2H^+$, would provide a more reduced species (e.g., "$Re_6C(CO)_{18}^{4-}$"), and the formation of $Re_7C(CO)_{21}^{3-}$ from $H_2Re_6C(CO)_{18}^{2-}$ is not likely to require the use of sodium as we have found.

**Interconversion of $Re_7C(CO)_{21}^{3-}$ and $Re_8C(CO)_{24}^{2-}$.** The similar reaction temperature required for the preparation of $Re_7C(CO)_{21}^{3-}$ and $Re_8C(CO)_{24}^{2-}$ suggests the possibility of their interconversion under appropriate conditions. In fact, the interaction of $Re_7C(CO)_{21}^{3-}$ with $Re_2(CO)_{10}$ (1:2.5 mole ratio) in triglyme (190 °C) produces $Re_8C(CO)_{24}^{2-}$ in ca. 80% yield (eq 5). Conversely, the

$$Re_7C(CO)_{21}^{3-} \underset{Na + CO}{\overset{Re_2(CO)_{10}}{\rightleftarrows}} Re_8C(CO)_{24}^{2-} \tag{5}$$

reduction of $Re_8C(CO)_{24}^{2-}$ with excess sodium under a carbon monoxide atmosphere at 160 °C forms $Re_7C(CO)_{21}^{3-}$ in good yield (70%), presumably transforming the $Re(CO)_3$ cap into $Re(CO)_5^-$ under these strongly basic conditions. These results suggest that if $Re_7C(CO)_{21}^{3-}$ is generated in the direct synthesis of $Re_8C(CO)_{24}^{2-}$ (eq 3), it is easily converted to the octanuclear carbide dianion due to the high mole ratio of $Re_2(CO)_{10}$ present. More generally the conversion of $Re_7C(CO)_{21}^{3-}$ into $Re_8C(CO)_{24}^{2-}$ provides an experimental realization of the formal "capping reaction" shown in eq 6. Analogous capping reactions with a variety of platinum metal caps $ML_n^+$ have been successful and are described in a companion paper.[16]

$$Re_7C(CO)_{21}^{3-} + \text{"}Re(CO)_3^{+}\text{"} \rightarrow Re_8C(CO)_{24}^{2-} \tag{6}$$

**Registry No.** $Re_2(CO)_{10}$, 14285-68-8; $[Et_4N]_2[Re_4(CO)_{16}]$, 111525-55-4; $[(Ph_3P)_2N]_2[Re_4(CO)_{16}]$, 111525-56-5; $[Et_4N]_3[Re_7C(CO)_{21}]$, 99900-74-0; $[(Ph_3P)_2N]_3[Re_7C(CO)_{21}]$, 107021-61-4; $Na_3[Re_7C(CO)_{21}]$, 111525-57-6; $[Et_4N]_2[Re_8C(CO)_{24}]$, 83267-48-5; $[(Ph_3P)_2N]_2[Re_8C(CO)_{24}]$, 111525-58-7; $[Et_4N]_2[H_2Re_6C(CO)_{18}]$, 85601-12-3; Na, 7440-23-5.

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# Reactions of Transition-Metal–Propargyl Compounds with Dicobalt Octacarbonyl. New Heterobinuclear μ-Alkyne Complexes

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Reactions of transition-metal–propargyl complexes $[M]CH_2C{\equiv}CR$ with $Co_2(CO)_8$ in pentane at room temperature afford the trinuclear products $(CO)_3Co(\mu\text{-}RC_2CH_2[M]Co(CO)_3$ ([M] = $CpFe(CO)_2$, R = Ph (**1a**), Me (**1b**); [M] = $Mn(CO)_5$, R = Ph (**2**); [M] = $CpW(CO)_3$, R = Ph (**3a**), Me (**3b**); [M] = $CpMo(CO)_3$, R = Ph (**4**)) as purple solids of different degrees of stability (**1a**, **1b**, and **2** ≫ **3a**, **3b**, and **4**). Treatment of **1a** and **2** with $CF_3CO_2H$ and alumina, respectively, leads to cleavage of the M–$CH_2$ bond with the formation of $(CO)_3Co(\mu\text{-}PhC_2Me)Co(CO)_3$ and $CpFe(CO)_2OC(O)CF_3$ (from **1a**). By contrast, **3a**, **3b**, and **4** react with $CF_3CO_2H$ and alumina surprisingly to give heterobinuclear μ-alkyne complexes, $Cp(CO)_2M(\mu\text{-}RC_2Me)Co(CO)_3$ (**5a**, **5b**, and **6**, respectively) as air-stable, red solids. Complexes **1**–**6** were characerized by a combination of elemental analyses, FAB mass spectrometry, and IR and $^1H$ and $^{13}C$ NMR spectroscopy; the structure of **5a** was determined by single-crystal X-ray analysis. Crystal data: monoclinic, space group $P2_1/n$ with $a$ = 8.825 (2) Å, $b$ = 15.003 (2) Å, $c$ = 14.035 (2) Å, $\beta$ = 93.42 (1)°, and $Z$ = 4. The structure was solved and refined to $R$ = 0.0249 and $R_w$ = 0.0268 by using 3918 independent reflections. The alkyne $PhC_2Me$ is transversely bridging the Co–W bond (2.693 (1) Å), and its Me substituent is trans to Cp.

## Introduction

Dicobalt octacarbonyl readily reacts with terminal and internal alkynes ($RC{\equiv}CR'$) to yield binuclear complexes of the type $(CO)_3Co(\mu\text{-}RC_2R')Co(CO)_3$ (I) which feature a transversely bridging alkyne ligand.[1] Corresponding reactions of $Co_2(CO)_8$ with organo–transition-metal complexes containing C≡C bonds have received relatively little attention. Rosenblum et al.[2] studied the reaction of di-

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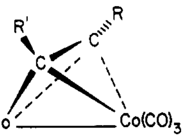

I

ferrocenylacetylene ($FcC{\equiv}CFc$) with $Co_2(CO)_8$ which affords $(CO)_3Co(\mu\text{-}FcC_2Fc)Co(CO)_3$. Yasufuku and Yamazaki[3] and Riera, Tiripicchio, and co-workers[4] examined the behavior of $Co_2(CO)_8$ toward several transition-metal acetylide complexes. The complexes $CpFe(CO)(L)C{\equiv}CR$ ($L = CO$, $R = Me$; $L = PPhMe_2$, $R = Ph$) and $Mn(CO)_4(PCy_3)C{\equiv}CPh$ yielded $(CO)_3Co(\mu\text{-}RC_2Fe(CO)(L)Cp)Co(CO)_3$ and $(CO)_3Co(\mu\text{-}PhC_2Mn(CO)_4(PCy_3)Co(CO)_3$, respectively, with $(CO)_3Co(\mu\text{-}PhC_2Fe(CO)(PPhMe_2)Cp)Co(CO)_3$ reacting further to a trinuclear $(CO)_3Co(PhC_2FeCp)Co(CO)_3$ of uncertain structure. The complex $(CO)_3Co(\mu\text{-}PhC_2Fe(CO)_2Cp)Co(CO)_3$ afforded only the incompletely characterized $(CO)_3Co(PhC_2FeCp)Co(CO)_3$. Recently, a reexamination of the last-mentioned reaction by Bruce and co-workers[5] resulted in the isolation of $(CO)_3Co(\mu\text{-}PhC_2Fe(CO)_2Cp)Co(CO)_3$ instead, which was characterized by X-ray crystallography. This complex and its $RuCo_2$ analogue are converted by $O_2$ to the trinuclear clusters $CpM(CO)Co_2(CO)_6(\mu_3\text{-}CPh)$ (M = Fe, Ru).[6]

Transition-metal–propargyl complexes ($[M]CH_2C{\equiv}CR$) have not been investigated with respect to their reactivity toward $Co_2(CO)_8$. Because of a considerable current interest in binuclear and polynuclear metal–alkyne complexes,[7] and in order to fill the aforementioned void, we have examined reactions of $Co_2(CO)_8$ with several metal–propargyl complexes. We thought that the presence of three metals in expected products of the type $(CO)_3Co(\mu\text{-}RC_2CH_2[M])Co(CO)_3$ might lead to some interesting chemistry that would be different from the chemistry of the alkyne complexes $(CO)_3Co(\mu\text{-}RC_2R')Co(CO)_3$. Indeed, we observed that some trinuclear compounds $(CO)_3Co(\mu\text{-}RC_2CH_2[M])Co(CO)_3$ react with acids to lose one $Co(CO)_3$ fragment and generate heterobinuclear alkyne-bridged complexes. In this paper we report results of our study, including the complete characterization by single-crystal X-ray diffraction of the heterobinuclear complex $Cp(CO)_2W(\mu\text{-}PhC_2Me)Co(CO)_3$ obtained in this manner.

## Experimental Section

**General Procedures and Measurements.** All reactions and manipulations of air-sensitive compounds were carried out under an atmosphere of $N_2$ or Ar by using standard procedures.[8] Elemental analyses for C and H were performed by Galbraith Laboratories, Inc., Knoxville, TN. Mn and Co were analyzed by using literature procedures.[9,10] Chromatographic separations and purifications were effected on columns packed with alumina (ca. 150 mesh, 6–10% $H_2O$) or Florisil (60–100 mesh). Melting points were measured in vacuo on a Thomas-Hoover melting point apparatus and are uncorrected. Molecular weights in solution were determined with a Knauer Dampfdruck osmometer by Dr. G. Carturan. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 337 or 283B spectrophotometer and were calibrated with polystyrene. $^1H$ NMR spectra were obtained on a Varian Associates EM-360L or a Bruker AM-250 spectrometer. $^{13}C$ NMR spectra were recorded on a Bruker WP-80, WH-300, or AM-250 spectrometer. $^2H$ NMR spectra were collected on a Bruker AM-500 spectrometer by Dr. Charles Cottrell. Mass spectra were obtained by use of the fast atom bombardment (FAB) technique on a Kratos MS-30 or VG70-250S spectrometer by Mr. C. R. Weisenberger or Mr. D. C. Chang. Bulk magnetic susceptibility measurements were done by the method of Evans[11] in acetone-$d_6$ solution on a Bruker AM-500 spectrometer by Dr. Cottrell.

**Materials.** THF and diethyl ether were distilled from Na and benzophenone under an atmosphere of $N_2$ or Ar immediately before use. Pentane and hexane were purified by distillation from Na under $N_2$. Dichloromethane was distilled from $P_4O_{10}$ prior to use. Petroleum ether (bp 35–60 °C) and other solvents were used as received.

Trifluoroacetic acid (99%) was distilled prior to use, whereas trifluoroacetic acid-$d$ (99 atom % D) was used as received from Aldrich. $Co_2(CO)_8$, from Strem, was crystallized first from $CH_2Cl_2$ and then from heptane under an atmosphere of CO. The metal–propargyl complexes $CpFe(CO)_2CH_2C{\equiv}CMe$,[12] $CpFe(CO)_2CH_2C{\equiv}CPh$,[13] $Mn(CO)_5CH_2C{\equiv}CPh$,[13] $CpMo(CO)_3CH_2C{\equiv}CPh$,[14] $CpW(CO)_3CH_2C{\equiv}CMe$,[15] and $CpW(CO)_3CH_2C{\equiv}CPh$[15] were prepared according to the literature.

**Reactions of Metal–Propargyl Complexes with $Co_2(CO)_8$.** These reactions were carried out at room temperature in pentane solution with ca. 1:1 molar ratio of the metal–propargyl complex and $Co_2(CO)_8$. A detailed description of the reaction between $CpFe(CO)_2CH_2C{\equiv}CPh$ and $Co_2(CO)_8$ is provided to illustrate the procedure. Other reactions and workup were conducted similarly with the following modifications. Chromatography on alumina (10% $H_2O$) was used only for the iron complexes; reaction products of $Mn(CO)_5CH_2C{\equiv}CPh$ with $Co_2(CO)_8$ and of $CpW(CO)_3CH_2C{\equiv}CPh$ with $Co_2(CO)_8$ were found to react with alumina and were therefore purified by chromatography on Florisil. Reaction products of $CpMo(CO)_3CH_2C{\equiv}CPh$ with $Co_2(CO)_8$ and of $CpW(CO)_3CH_2C{\equiv}CMe$ with $Co_2(CO)_8$ decomposed on both alumina and Florisil columns and during attempts at crystallization. They were isolated by evaporation to dryness of the reaction solutions and were not purified.

Percent yields, physical properties, mass spectra, and analytical data for all isolated products are presented below. IR and NMR data are given in Table I.

**(i) $CpFe(CO)_2CH_2C{\equiv}CPh$.** A solution of 1.08 g (3.70 mmol) of $CpFe(CO)_2CH_2C{\equiv}CPh$ in 100 mL of pentane was added dropwise with stirring over 15 min to 1.26 g (3.68 mmol) of $Co_2(CO)_8$ dissolved in 20 mL of pentane. Gas was evolved as the mixture changed color from orange to dark purple. After additional stirring (total reaction time 1 h), solvent was removed under reduced pressure to yield a purple crystalline residue. Chromatography on a 2 × 25 cm column of alumina eluting with pentane first removed a small pink band (IR 2095 (s), 2055 (s), 2025 (s),

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**Table I. IR and NMR Data for New Complexes**[a]

| | | NMR, $\delta$ | |
|---|---|---|---|
| complex | IR $\nu$(CO),[b] $cm^{-1}$ | $^1H$[c] | $^{13}C\{^1H\}$[c] |
| **1a** | 2090 (st), 2048 (st), 2028 (st), 2015 (st), 1970 (st) | 7.46–7.18 (m, Ph), 4.69 (s, Cp), 3.17 (s, $CH_2$)[e] | 216.5 (FeCO), 200.3 (CoCO), 139.9, 129.0, 128.7, 127.1 (Ph), 114.0 ($CCH_2$), 93.5 (*C*Ph), 85.4 (Cp), 6.1 ($CH_2$)[e] |
| **1b** | 2091 (st), 2048 (st), 2025 (st), 2003 (st), 1960 (st) | 4.86 (s, Cp), 3.03 (s, $CH_2$), 2.78 (s, Me)[e] | 216.7 (FeCO), 200.3 (CoCO), 111.6 ($CCH_2$), 94.1 (*C*Me), 85.5 (Cp), 22.2 (Me), 6.0 ($CH_2$)[e] |
| **2** | 2112 (w), 2082 (me), 2049 (st), 2028 (st), 2013 (st), 1999 (me), 1970 (w)[d] | 7.50–7.18 (m, Ph), 2.19 (s, $CH_2$)[e] | 211.1 (MnCO), 200.1 (CoCO), 139.1, 129.2, 128.8, 127.3 (Ph), 110.2 ($CCH_2$), 92.3 (*C*Ph), 11.4 ($CH_2$)[e] |
| **3a** | 2086 (st), 2068 (st), 2045 (st), 2024 (st), 2009 (st), 1944 (st), 1932 (st) | 7.64–7.25 (m, Ph), 5.33 (s, Cp), 3.48 (s, $CH_2$) | 229.0, 220.3 (WCO), 200.5 (CoCO), 140.1, 129.0, 128.5, 127.6 (Ph), 112.1 ($CCH_2$), 93.1 (*C*Ph), 92.3 (Cp), 7.9 ($CH_2$) |
| **3b** | 2081 (st), 2066 (me), 2040 (st), 2019 (st), 1943 (st), 1933 (st) | 5.58 (s, Cp), 3.68 (s, $CH_2$), 2.99 (s, Me) | |
| **4** | 2086 (st), 2069 (st), 2045 (st), 2025 (st), 1953 (st), 1941 (st) | 7.48–7.29 (m, Ph), 5.33 (s, Cp), 3.20 (s, $CH_2$) | |
| **5a**[f] | 2049 (st), 2000 (st), 1985 (st), 1976 (st), 1937 (st) | 7.22 (s, Ph), 5.18 (s, Cp), 3.01 (s, Me) | 214.5, 212.1 (WCO), 203.3, 202.4 (CoCO), 143.7, 129.6 (Ph), 89.8 (Cp), 88.7 (*C*Me), 81.8 (CPh), 21.4 (Me) |
| **5b**[g] | 2042 (st), 1995 (st), 1978 (st), 1972 (st), 1933 (st) | 5.43 (s, Cp), 2.72 (s, 2Me) | 213.9 (WCO), 203.5 (CoCO), 89.5 (Cp), 86.4 (*C*Me), 20.3 (Me) |
| **6** | 2049 (st), 1999 (st), 1986 (st), 1943 (st) | 7.28 (m, Ph), 5.37 (s, Cp), 2.81 (s, Me) | 227.9, 225.8 (MoCO), 204.7, 204.4, 200.1 (CoCO), 143.4 129.2, 128.7, 126.7 (Ph), 95.5 (*C*Me), 92.0 (Cp), 89.1 (*C*Ph), 21.4 (Me) |

[a] At room temperature. Abbreviations: st, strong; me, medium; w, weak; s, singlet; m, multiplet. [b] *In pentane solution unless otherwise* noted. [c] In $CD_2Cl_2$ solution unless otherwise noted. [d] In cyclohexane solution. [e] In $CDCl_3$ solution. [f] **5a**–*d*: $^2H$ NMR ($CH_2Cl_2$) $\delta$ 2.95 ($CH_2D$); $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 20.5 (t, $J(^{13}C{-}D)$ = 20 Hz, $CH_2D$). [g] **5b**–*d*: $^2H$ NMR ($CH_2Cl_2$) $\delta$ 2.60 ($CH_2D$); $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 20.3 (s, Me), 20.0 (t, $J(^{13}C{-}D)$ = 20 Hz, $CH_2D$).

1990 (w) $cm^{-1}$), which yielded 0.018 g of an incompletely characterized material when evaporated to dryness. Further elution with pentane gave a large green band, which was collected and evaporated to dryness to afford 1.71 g (80%) of dark purple crystals of $(CO)_3Co(\mu\text{-}PhC_2CH_2Fe(CO)_2Cp)Co(CO)_3$ (**1a**): mp 109 °C; mass spectrum, *m/z* (relative intensity) 578 ($M^+$, 0.8), 401 ($Co_2(CO)_6CH_2C_2Ph^+$, 6.0), 177 ($CpFe(CO)_2^+$, 2.8), 121 ($CpFe^+$, 2.6), 59 ($Co^+$, 100.0). Anal. Calcd for $C_{22}H_{12}Co_2FeO_8$: C, 45.71; H, 2.09. Found: C, 46.11; H, 2.10.

**(ii) $CpFe(CO)_2CH_2C{\equiv}CMe$.** Product $(CO)_3Co(\mu\text{-}MeC_2CH_2Fe(CO)_2Cp)Co(CO)_3$ (**1b**) was obtained in 86% yield as a purple solid: mp 68 °C dec; mass spectrum, *m/z* (relative intensity) 516 ($M^+$, 1.2), 339 ($Co_2(CO)_6CH_2C_2Me^+$, 11.5), 177 ($CpFe(CO)_2^+$, 3.4), 59 ($Co^+$, 100.0). Anal. Calcd for $C_{17}H_{10}Co_2FeO_8$: C, 39.57; H, 1.95. Found: C, 40.03; H, 2.49.

**(iii) $Mn(CO)_5CH_2C{\equiv}CPh$.** Product $(CO)_3Co(\mu\text{-}PhC_2CH_2Mn(CO)_5)Co(CO)_3$ (**2**) was obtained in 71% yield as a purple solid: mp 86–88 °C dec; mass spectrum, *m/z* (relative intensity) 596 ($M^+$, 72.6), 568 ($M^+ - CO$, 26.5), 540 ($M^+ - 2CO$, 52.9), 512 ($M^+ - 3CO$, 100.0). Anal. Calcd for $C_{20}H_7Co_2MnO_{11}$: C, 40.30; H, 1.19; Mn, 9.22. Found: C, 40.14, H, 1.25; Mn, 9.02.

**(iv) $CpW(CO)_3CH_2C{\equiv}CPh$.** Product $(CO)_3Co(\mu\text{-}PhC_2CH_2W(CO)_3Cp)Co(CO)_3$ (**3a**) was obtained in 66% yield as a purple solid: mp 103 °C dec; mass spectrum, $^{184}W$ isotope, *m/z* (relative intensity) 734 ($M^+$, <0.5), 401 ($Co_2(CO)_6CH_2C_2Ph^+$, 3.0), 59 ($Co^+$, 100.0). Anal. Calcd for $C_{23}H_{12}Co_2O_9W$: C, 37.63; H, 1.65; Co, 16.06. Found: C, 37.65; H, 1.87; Co, 17.50, 17.42.

**Reactions of Trinuclear $MCo_2$ Complexes with Alumina.** **(i) $(CO)_3Co(\mu\text{-}PhC_2CH_2W(CO)_3Cp)Co(CO)_3$ (3a).** To a solution of 0.097 g (0.13 mmol) of **3a** in 45 mL of pentane was added 3.06 g of alumina (10% $H_2O$), and the resulting mixture was stirred for 9 h at room temperature. Gas evolution was observed as a dark purple solution turned red. The mixture was filtered, and the alumina was washed with diethyl ether (2 × 16 mL). After the filtrate and the washings had been combined, the volatiles were removed. Chromatography of the residue on a Florisil column (2 × 20 cm) eluting with 90:10 petroleum ether–diethyl ether removed a large red band, which was collected and evaporated to dryness to yield 0.042 g (56%) of $Cp(CO)_2W(\mu\text{-}PhC_2Me)Co(CO)_3$ (**5a**). The product was crystallized from pentane to give dark red needles: mp 99–101 °C; mass spectrum, $^{184}W$ isotope, *m/z* (relative intensity) 536 ($M^+ - CO$, 64.8), 508 ($M^+ - 2CO$, 100.0). Anal. Calcd for $C_{19}H_{13}CoO_5W$: C, 40.45; H, 2.32; Co, 10.4; mol wt (cyclohexane), 564. Found: C, 40.20; H, 2.47; Co, 10.4; mol wt (cyclohexane), 544 ± 12. IR and NMR data are given in Table I.

Continued elution with 50:50 petroleum ether–diethyl ether removed a small orange band, from which 0.018 g of a solid material was obtained upon solvent evaporation: IR ($C_6H_6$) 2105 (m), 2065 (s), 2025 (s), 2003 (s), 1970 (sh), 1925 (m) $cm^{-1}$. This solid was not further characterized.

**(ii) $(CO)_3Co(\mu\text{-}PhC_2CH_2Mn(CO)_5)Co(CO)_3$ (2).** A reaction similar to the preceding one was carried out between 0.101 g (0.170 mmol) of **2** and 3.10 g of alumina (10% $H_2O$) in pentane for 33 h at room temperature. Chromatography on Florisil eluting with petroleum ether and 95:5 petroleum ether–diethyl ether led to the isolation of the following species in the order of their elution: $(CO)_3Co(\mu\text{-}PhC_2Me)Co(CO)_3$ (0.036 g, 63% conversion), characterized by comparison of its IR and $^1H$ NMR spectra with those of an authentic sample prepared according to the literature;[16] unreacted **2** (0.017 g); and a lavender solid (0.027 g; IR (hexane) 2118 (m), 2095 (m), 2075 (m), 2058 (s), 2019 (vs), 1910 (w) $cm^{-1}$), which was not further characterized.

**Reactions of Trinuclear $MCo_2$ Complexes with $CF_3CO_2H$.** **(i) $(CO)_3Co(\mu\text{-}PhC_2CH_2W(CO)_3Cp)Co(CO)_3$ (3a).** To a solution of 0.276 g (0.376 mmol) of **3a** in 40 mL of $CH_2Cl_2$ was added via syringe 0.030 mL (0.045 g, 0.39 mmol) of $CF_3CO_2H$. The resulting mixture was stirred at room temperature for 8 h, during which time its color changed from purple to red and gas was evolved. The mixture was filtered to separate a red powder (0.017 g), which was washed with $CH_2Cl_2$ (2 × 3 mL) and dried, dec pt ~145 °C; IR (Nujol) 1710 (sh), 1670 (m, br), 1202 (m), 1148 (m) $cm^{-1}$; $\mu_{eff}$ dependent on mol wt (e.g., 2.50 or 2.89 $\mu_B$, assuming mol wt 285, as for $Co(O_2CCF_3)_2$, or 381, as for $Co(O_2CCF_3)_2(H_2O)_4$); qualitative analysis for Co.[10]

Chromatography of the filtrate on a Florisil column (2 × 16 cm) as described for the corresponding reaction of **3a** with alumina afforded 0.134 g (63%) of $Cp(CO)_2W(\mu\text{-}PhC_2Me)Co(CO)_3$ (**5a**).

This reaction was also carried out by treating a pentane solution of **3a**, prepared in situ from $CpW(CO)_3CH_2C{\equiv}CPh$ and $Co_2(CO)_8$ (vide supra), with ca. 1 equiv of $CF_3CO_2H$ (or $CF_3CO_2D$). The

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[16] Cetini, G.; Gambino, O.; Rossetti, R.; Sappa, E. *J. Organomet. Chem.* **1967**, *8*, 149.

**Table II. Crystal Data, Data Collection, and Refinement of 5a**

| | |
|---|---|
| **Crystal Data** | |
| mol formula | $C_{19}H_{13}CoO_5W$ |
| mol wt | 564.1 |
| cryst system | monoclinic |
| space group | $P2_1/n$ |
| $a$, Å | 8.825 (2) |
| $b$, Å | 15.003 (2) |
| $c$, Å | 14.035 (2) |
| $\beta$, deg | 93.42 (1) |
| $V$, Å$^3$ | 1854.9 (6) |
| $Z$ | 4 |
| $D_{\mathrm{calcd}}$, g cm$^{-3}$ | 2.02 |
| $F(000)$ | 1072 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 72.5 |
| cryst size, mm | 0.21 × 0.30 × 0.33 |
| **Data Collection and Refinement** | |
| diffractometer | Enraf-Nonius CAD4 |
| temp, K | 294 ± 1 |
| radiatn | Mo K$\alpha$, graphite monochromated ($\lambda$ = 0.710 69 Å) |
| scan type | $\omega/2\theta$ |
| scan speed, deg min$^{-1}$ | variable (0.78–5) |
| scan range,[a] deg in $\omega$ | $1.3 + 0.35 \tan\theta$ |
| aperture width, mm | $1.0 + \tan\theta$ |
| aperture height, mm | 4 |
| $2\theta$ range, deg | 6–60 |
| reflectns measd | $\pm h,k,l$ |
| orientation monitors[b] | 3 |
| intensity monitors[c] | 4 |
| total obsd data | 5791 |
| absorpn correctn | empirical, $\Psi$ scans of four close-to-axial |
| transmissn factors | 0.645–0.999 |
| unique data ($I > 3\sigma(I)$)[d] | 3918 |
| no. of variables | 235 |
| minimized function | $\sum w\Delta^2$ [e] |
| $R$ ($\sum\Delta)/\sum\lvert F_o\rvert$)[e] | 0.0249 |
| $R_w$ ($[\sum w\Delta^2/\sum wF_o^2]^{1/2}$)[e] | 0.0268 |
| $w$ | 1 |
| error in observn of unit wt | 1.81 |
| largest parameter shift/error | 0.02 |

[a] Extended by 25% on both sides for background measurements. [b] Measured after each 400 reflections; new orientation matrix if angular change >0.1. [c] Measured after each 4000 s. [d] Standard deviation from counting statistics. [e] $\Delta = \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert$.

**Table III. Positional and Equivalent Thermal Parameters of Non-Hydrogen Atoms of 5a with Estimated Standard Deviations in Parentheses**

| atom | $x$ | $y$ | $z$ | $B$,[a] Å$^2$ |
|---|---|---|---|---|
| W | 0.06936 (2) | 0.19285 (1) | 0.07757 (1) | 2.405 (3) |
| Co | 0.21270 (7) | 0.31446 (5) | −0.02580 (5) | 3.12 (1) |
| O(1) | 0.4955 (6) | 0.3553 (4) | −0.1138 (4) | 8.5 (2) |
| O(2) | −0.0294 (6) | 0.3492 (3) | −0.1734 (4) | 7.0 (1) |
| O(3) | 0.1956 (9) | 0.4657 (4) | 0.1044 (4) | 9.6 (2) |
| O(4) | 0.2102 (6) | 0.0175 (3) | 0.1646 (4) | 6.0 (1) |
| O(5) | 0.2226 (5) | 0.2898 (4) | 0.2543 (3) | 5.8 (1) |
| C(1) | 0.3837 (7) | 0.3397 (5) | −0.0811 (5) | 4.9 (1) |
| C(2) | 0.0643 (7) | 0.3368 (4) | −0.1158 (4) | 4.1 (1) |
| C(3) | 0.2019 (9) | 0.4059 (5) | 0.0563 (5) | 5.4 (2) |
| C(4) | 0.1582 (6) | 0.0816 (4) | 0.1330 (4) | 3.7 (1) |
| C(5) | 0.1682 (6) | 0.2539 (4) | 0.1905 (4) | 3.7 (1) |
| C(6) | 0.4584 (6) | 0.1909 (5) | 0.0842 (4) | 4.8 (1) |
| C(7) | 0.3012 (5) | 0.2066 (4) | 0.0403 (3) | 3.05 (9) |
| C(8) | 0.2111 (5) | 0.1799 (3) | −0.0384 (3) | 2.65 (8) |
| C(9) | 0.2337 (5) | 0.1299 (3) | −0.1255 (3) | 2.90 (9) |
| C(10) | 0.1150 (6) | 0.1151 (4) | −0.1931 (4) | 3.7 (1) |
| C(11) | 0.1380 (7) | 0.0699 (4) | −0.2776 (4) | 4.5 (1) |
| C(12) | 0.2812 (8) | 0.0378 (4) | −0.2946 (4) | 4.9 (1) |
| C(13) | 0.3988 (7) | 0.0505 (4) | −0.2286 (5) | 4.7 (1) |
| C(14) | 0.3757 (6) | 0.0953 (4) | −0.1443 (4) | 4.0 (1) |
| C(15) | −0.1509 (6) | 0.1108 (4) | 0.0473 (5) | 4.2 (1) |
| C(16) | −0.1521 (6) | 0.1439 (4) | 0.1407 (4) | 3.9 (1) |
| C(17) | −0.1613 (6) | 0.2360 (4) | 0.1360 (4) | 4.1 (1) |
| C(18) | −0.1666 (6) | 0.2612 (4) | 0.0404 (5) | 4.5 (1) |
| C(19) | −0.1601 (5) | 0.1829 (5) | −0.0154 (4) | 4.7 (1) |

[a] *Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as* $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

rest of the procedure was similar to that described above and yielded comparable results.

**(ii) $(CO)_3Co(\mu\text{-}MeC_2CH_2W(CO)_3Cp)Co(CO)_3$ (3b).** A solution of 0.271 g (0.703 mmol) of $CpW(CO)_3CH_2C{\equiv}CMe$ in 125 mL of pentane was added over 4 min to a stirred solution of 0.241 g (0.705 mmol) of $Co_2(CO)_8$ in 25 mL of pentane at room temperature. After ca. 40 min the reaction was complete (ascertained by IR spectroscopy). The mixture was then treated with 0.060 mL (0.089 g, 0.78 mmol) of $CF_3CO_2H$ and stirred overnight to yield a red solid and a red solution, which were separated by filtration. The red solid was shown (IR spectrum) to be identical with that formed in the reaction of $(CO)_3Co(\mu\text{-}PhC_2CH_2W(CO)_3Cp)Co(CO)_3$ (3a) with $CF_3CO_2H$. The solution was chromatographed on alumina (10% $H_2O$) to afford a red band from which 0.212 g (60% yield) of $Cp(CO)_2W(\mu\text{-}MeC_2Me)Co(CO)_3$ (5b), mp 145 °C dec, was obtained upon evaporation of the solvent: mass spectrum, $^{184}W$ isotope, $m/z$ 502 ($M^+$), 475 ($M^+ + H - CO$). Anal. Calcd for $C_{14}H_{11}CoO_5W$: C, 32.47; H, 2.34. Found: C, 33.49; H, 2.19.

The corresponding reaction of the title complex with $CF_3CO_2D$ gave comparable results.

**(iii) $(CO)_3Co(\mu\text{-}PhC_2CH_2Mo(CO)_3Cp)Co(CO)_3$ (4).** The procedure employed was strictly analogous to that for the preceding reaction and used $CpMo(CO)_3CH_2C{\equiv}CPh$ in place of $CpW(CO)_3CH_2C{\equiv}CMe$. Workup of the reaction mixture afforded red solid with IR absorptions at 1710, 1670, 1202, and 1148 cm$^{-1}$ and $Cp(CO)_2Mo(\mu\text{-}PhC_2Me)Co(CO)_3$ (6), also a red solid: mp 52 °C dec; mass spectrum, $^{98}Mo$ isotope, $m/z$ (relative intensity) 478 ($M^+ + 2H$), 450 ($M^+ + 2H - CO$), 422 ($M^+ + 2H - 2CO$, 100.0), 394 ($M^+ + 2H - 3CO$), 366 ($M^+ + 2H - 4CO$), 362 ($M^+ + 2H - PhC_2Me$), 338 ($M^+ + 2H - 5CO$).

**(iv) $(CO)_3Co(\mu\text{-}PhC_2CH_2Fe(CO)_2Cp)Co(CO)_3$ (1a).** Trifluoroacetic acid (0.08 mL, 1 mmol) was added by syringe to a solution of 0.400 g (0.692 mmol) of 1a in 65 mL of $CH_2Cl_2$ with stirring at room temperature. The reaction mixture was stirred for 18 h and then filtered to separate a purple solid from a brown solution. The purple solid was triturated with acetone (1 mL), and the resulting mixture was filtered. The red-brown filtrate was concentrated to yield 0.056 g (28%) of $CpFe(CO)_2OC(O)CF_3$, characterized by comparison of its IR and $^1H$ NMR spectra with those reported in the literature.[17]

The brown solution from the first filtration was chromatographed on alumina (6% $H_2O$) eluting with petroleum ether to separate a red band from a slower moving brown band. These bands yielded, respectively, upon collection and evaporation to dryness, 0.144 g (52%) of $(CO)_3Co(\mu\text{-}PhC_2Me)Co(CO)_3$ and 0.090 g (22% recovery) of unreacted 1a.

**Crystallographic Analysis of $Cp(CO)_2W(\mu\text{-}PhC_2Me)Co(CO)_3$ (3a).** Crystals of 3a suitable for X-ray diffraction were grown from pentane. Cell dimensions and space group were established in a routine manner on an Enraf-Nonius CAD4 diffractometer at room temperature by using graphite-monochromated Mo K$\alpha$ radiation. The same instrument was then used to collect intensity data. Crystal data, data collection, and refinement are summarized in Table II. The structure was solved by the heavy-atom method. After anisotropic refinement, the calculated positions of hydrogen atoms all occurred in positive electron density regions. Final full-matrix least-squares refinement, with the fixed contribution of hydrogen atoms ($B$ = 5 Å$^2$), converged to $R$ = 0.0249. Scattering factors, anomalous dispersion terms, and programs were taken from Enraf-Nonius SDP.[18] Final

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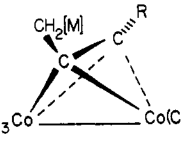
(17) (a) King, R. B.; Kapoor, R. N. *J. Organomet. Chem.* **1968**, *15*, 457. (b) De Luca, N.; Wojcicki, A. *Ibid.* **1980**, *193*, 359.

(18) *Structure Determination Package*, Enraf-Nonius: Delft, Holland, 1981.

positional and equivalent thermal parameters are given in Table III. Listings of anisotropic thermal parameters, hydrogen atom coordinates, and structure factors are available as supplementary material.[19]

## Results and Discussion

**Synthesis and Characterization of Trinuclear $MCo_2$ Complexes.** Reactions between transition-metal-propargyl complexes and $Co_2(CO)_8$ were conducted in pentane solution at room temperature. They reached completion after 30–60 min as evidenced by the disappearance of the IR $\mu$(C=O) band of $Co_2(CO)_8$ at 1868 $cm^{-1}$. The isolated purple products **1**–**4** exhibit varying degrees of stability and were purified and handled accordingly.



**1** [M] = $CpFe(CO)_2$ ; R = Ph (a), Me (b)
**2** [M] = $Mn(CO)_5$ ; R = Ph
**3** [M] = $CpW(CO)_3$ ; R = Ph (a), Me (b)
**4** [M] = $CpMo(CO)_3$ ; R = Ph

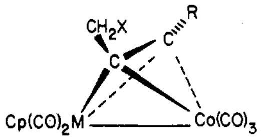
Complexes **1a**, **1b**, and **2** are stable in solution under an inert atmosphere and can be purified by chromatography on alumina (**1a**, **1b**) or Florisil (**2**). By contrast, the tungsten and molybdenum complexes **3a**, **3b**, and **4** decompose in solution even in the absence of $O_2$. Decomposition of **3a** in pentane is observable by IR spectroscopy after ca. 15 min and is essentially complete after 40 h. The principal decomposition products are $Co_4(CO)_{12}$ and a black unidentified solid (IR (pentane) $\nu$(CO) 2072, 2050, 2020, 2005, 1860 $cm^{-1}$). Complexes **3b** and **4** are even less stable than **3a** and could not be purified by chromatography on various supports or by crystallization. Nevertheless, a comparison of the spectroscopic (IR, NMR) properties of the crude reaction mixtures with those of the stable $MCo_2$ complexes confirms the identity of **3b** and **4**. All products are stable in the solid under an inert atmosphere. Further details of stability and purification of these $MCo_2$ complexes are provided in the Experimental Section.

The characterization of new trinuclear complexes was accomplished by a combination of elemental analyses, FAB mass spectrometry, and IR and $^1H$ and $^{13}C\{^1H\}$ NMR spectroscopy. The IR spectra in the $\nu$(CO) region show a marked similarity to the spectra of various complexes $(CO)_3\overline{Co(\mu\text{-}RC_2R')Co}(CO)_3$[16] supplemented with the absorption bands of the carbonyl groups belonging to the fragment [M]. Carbonyl ligands of Co and M are also observed as separate signals in the $^{13}C\{^1H\}$ NMR spectra of **1a**, **1b**, **2**, and **3a**. The remaining parts of the $^{13}C\{^1H\}$ NMR spectra of these products show signals of all inequivalent carbon nuclei and are completely consistent with the assigned structures.[20] $^1H$ NMR data are straightforward and also in full accord with these assignments.

**Reactions of Trinuclear $MCo_2$ Complexes with Acids.** Whereas the iron complexes **1a** and **1b** can be chromatographed on alumina without significant decomposition, the other $MCo_2$ products react with this support. To learn more about these reactions, each of **2** and **3a** was stirred with alumina in pentane, and soluble products were isolated and characterized. The reaction of **2** afforded $(CO)_3\overline{Co(\mu\text{-}PhC_2Me)Co}(CO)_3$, which is derived by acid cleavage of the Mn–$CH_2$ bond in the trinuclear complex. No Mn-containing product(s) could be identified. Complex **3a** reacted with alumina to give a new heterobinuclear product, $Cp(CO)_2\overline{W(\mu\text{-}PhC_2Me)Co}(CO)_3$ (**5a**). This compound results from scission of the W–$CH_2$ bond by acid and replacement of one $Co(CO)_3$ by the isoelectronic $W(CO)_2Cp$.

To explore further the behavior of these trinuclear products toward acid, complexes **1**–**4** were treated with $CF_3CO_2H$ under homogeneous conditions. For **1a**, such treatment resulted only in the cleavage of the Fe–$CH_2$ bond to furnish $(CO)_3\overline{Co(\mu\text{-}PhC_2Me)Co}(CO)_3$ and $CpFe(CO)_2OC(O)CF_3$ (eq 1). In contrast, the tungsten and molybdenum complexes **3a**, **3b**, and **4** afforded **5a**, **5b**, and **6**, respectively, as well as a red noncarbonyl solid that is

$$\mathbf{1a} + CF_3CO_2H \rightarrow$$
$$(CO)_3\overline{Co(\mu\text{-}PhC_2Me)Co}(CO)_3 + CpFe(CO)_2OC(O)CF_3 \quad (1)$$



**5** M = W ; R = Ph (a), Me (b); X = H, D (d)
**6** M = Mo; R = Ph; X = H

sparingly soluble in $H_2O$. This material has been partially characterized by IR spectroscopy[17a] and paramagnetism as an impure cobalt(II) trifluoroacetato complex. The reaction would therefore appear to proceed as shown in eq 2 for **3a**.

$$\mathbf{3a} + CF_3CO_2H \rightarrow \mathbf{5a} + \text{“}Co^{II}(O_2CCF_3)_n\text{”} \quad (2)$$

Treatment of **3a** and **3b** with $CF_3CO_2D$ affords **5a**-*d* and **5b**-*d*, respectively, to demonstrate that the added hydrogen indeed originates from the reactant acid. However, the process leading to the substitution of a $Co(CO)_3$ group in the dimetallatetrahedrane $Co_2C_2$ core of **5** by $W(CO)_2Cp$ is not obvious.[21] This interesting reaction is under mechanistic investigation.

**Spectroscopic Characterization of Heterobinuclear $\mu$-Alkyne Complexes.** The new heterobinuclear $\mu$-alkyne complexes **5a**, **5b**, and **6** are red solids, stable to air for several hours at ambient temperatures. They were characterized by a combination of elemental analyses, FAB mass spectrometry, and IR and $^1H$ and $^{13}C\{^1H\}$ NMR spectroscopy (Table I). The structure of **5a** was determined by X-ray diffraction analysis.

All five $\nu$(CO) bands predicted for molecules of $C_1$ symmetry are found in the IR spectra of **5a** and **5b**. The spectrum of **6** shows only four $\nu$(CO) absorptions, but that at 1986 $cm^{-1}$ is broad and probably consists of two unresolved bands. Thus, these data provide no evidence for the presence of isomers in solution. Isomerism might be expected for **5a** and **6**, where the alkyne Me group can be positioned cis on trans with respect to the Cp ligand. This

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[19] See paragraph at end of paper regarding supplementary material.

[20] For $^{13}C\{^1H\}$ NMR spectra of $(CO)_3\overline{Co(\mu\text{-}RC_2R')Co}(CO)_3$ see: Aime, S.; Milone, L.; Rossetti, R.; Stranghellini, P. L. *Inorg. Chim. Acta* **1977**, *22*, 135.

[21] However, some analogy may be found between the reaction in point and the replacement of a $Co(CO)_3AsMe_2$ fragment by $W(CO)_3Cp$ in a heteronuclear cluster; see: Richter, F.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 53.

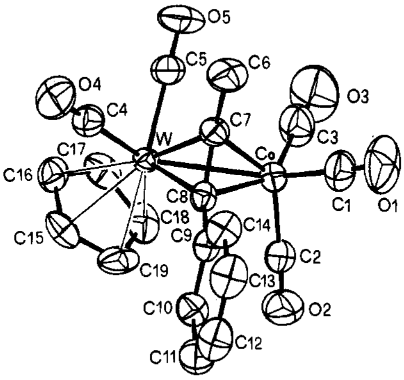

**Figure 1.** ORTEP plot of **5a** showing atom numbering scheme. Atoms are drawn at the 50% probability level. Hydrogen atoms are omitted.

point will be considered again with the description of the molecular structure of **5a**.

The $^1$H NMR spectra consist of the resonances of the Ph, Cp, and Me groups, all of which show unexceptional chemical shifts. The spectrum of **5a** in $CD_2Cl_2$ solution is invariant over the temperature range of +40 to −70 °C, again suggesting the presence of only one WCo species in solution. In the $^{13}C\{^1H\}$ NMR spectra of **5a**, **5b**, and **6**, separate resonances are identified for CoCO and WCO or MoCO. The assignment of these signals is rendered straightforward by the broad shape of the CoCO resonances owing to quadrupolar coupling with the $^{59}$Co nucleus.[22] The remaining signals can be readily assigned to various inequivalent carbon atoms of the $\mu$-alkyne and Cp groups.

Complexes **5a** and **5b** represent the first WCo members of a group of heterobinuclear $\mu$-alkyne compounds of the type $L_nM(\mu\text{-}RC_2R')M'L'_m$. For MoCo, a recently prepared and fully characterized complex, $Cp(CO)_2Mo(\mu\text{-}CF_3C_2CF_3)Co(CO)_3$,[23] is known, in addition to **6**. Other similar complexes containing a $Co(CO)_3$ moiety include $CpNi(\mu\text{-}RC_2R')Co(CO)_3$,[24] $(CO)_4Mn(\mu\text{-}RC_2R')Co(CO)_3$,[25] and $(CO)_3Rh(\mu\text{-}RC_2R')Co(CO)_3$.[26]

**Crystal and Molecular Structure of $Cp(CO)_2W(\mu\text{-}PhC_2Me)Co(CO)_3$ (5a).** Crystals of **5a** consist of discrete molecules with normal van der Waals contacts. The closest nonhydrogen intermolecular distance, 3.147 (7) Å, is between O(2) and O(5) ($x - {}^1/_2$, ${}^1/_2 - y$, $z - {}^1/_2$). The molecular structure with the atom numbering scheme is shown in Figure 1. Selected bond distances and angles are given in Table IV.

**Table IV. Selected Bond Distances (Å) and Angles (deg) for 5a with Estimated Standard Deviations in Parentheses**

| | | | |
|---|---|---|---|
| | Bond Distances | | |
| Co–W | 2.693 (1) | W–C(17) | 2.331 (4) |
| Co–C(1) | 1.778 (5) | W–C(18) | 2.351 (4) |
| Co–C(2) | 1.796 (4) | W–C(19) | 2.348 (4) |
| Co–C(3) | 1.797 (5) | O(1)–C(1) | 1.138 (5) |
| Co–C(7) | 2.000 (4) | O(2)–C(2) | 1.136 (5) |
| Co–C(8) | 2.027 (4) | O(3)–C(3) | 1.127 (6) |
| W–C(4) | 1.983 (4) | O(4)–C(4) | 1.144 (5) |
| W–C(5) | 1.986 (4) | O(5)–C(5) | 1.127 (5) |
| W–C(7) | 2.151 (3) | C(6)–C(7) | 1.503 (5) |
| W–C(8) | 2.120 (3) | C(7)–C(8) | 1.381 (5) |
| W–C(15) | 2.319 (4) | C(8)–C(9) | 1.458 (5) |
| W–C(16) | 2.313 (4) | | |
| | Bond Angles | | |
| W–Co–C(1) | 144.8 (2) | Co–W–C(5) | 85.4 (1) |
| W–Co–C(2) | 99.1 (1) | Co–W–C(7) | 47.2 (1) |
| W–Co–C(3) | 97.3 (2) | Co–W–C(8) | 48.0 (1) |
| W–Co–C(7) | 52.1 (1) | C(4)–W–C(5) | 86.0 (2) |
| W–Co–C(8) | 51.0 (1) | Co–C(1)–O(1) | 177.9 (5) |
| C(1)–Co–C(2) | 104.8 (2) | Co–C(2)–O(2) | 178.6 (4) |
| C(1)–Co–C(3) | 101.3 (2) | Co–C(3)–O(3) | 177.0 (5) |
| C(1)–Co–C(7) | 93.3 (2) | W–C(4)–O(4) | 179.6 (4) |
| C(1)–Co–C(8) | 100.1 (2) | W–C(5)–O(5) | 178.8 (4) |
| C(2)–Co–C(3) | 104.1 (2) | Co–C(7)–C(6) | 130.0 (3) |
| C(2)–Co–C(7) | 136.5 (2) | W–C(7)–C(6) | 138.9 (3) |
| C(2)–Co–C(8) | 97.1 (2) | C(6)–C(7)–C(8) | 139.1 (4) |
| C(3)–Co–C(7) | 110.7 (2) | Co–C(8)–C(9) | 125.8 (2) |
| C(3)–Co–C(8) | 144.7 (2) | W–C(8)–C(9) | 143.9 (3) |
| C(7)–Co–C(8) | 40.1 (1) | C(7)–C(8)–C(9) | 136.0 (3) |
| Co–W–C(4) | 126.4 (1) | | |

Molecules of **5a** have a quasi-tetrahedral core that approaches a dimetallatetrahedrane structure.[27] The C≡C bond (1.381(5) Å) is inclined at an angle $\theta$ of 87.7° to the Co–W bond (2.693 (1) Å). This geometry is quite similar to that of $Cp(CO)_2Mo(\mu\text{-}CF_3C_2CF_3)Co(CO)_3$: Co–Mo = 2.692 (1) Å, C≡C = 1.371 (7) Å, and $\theta$ = 88.5°.[23]

The value of the Co–W distance accords with a single metal–metal bond. Because of the bridging support of the alkyne ligand, this distance is shorter than that found in trinuclear complexes such as $RuCoW(CO)_8Cp(\mu_3,\eta^2\text{-}C{=}CHBu\text{-}t)$, 2.723 (3) Å,[28] and $Co_2W(CO)_6Cp(\mu_3\text{-}CMe)(\mu\text{-}PPh_2)$, 2.730 (1) and 2.792 (1) Å.[29]

Both cobalt and tungsten atoms achieve distorted octahedral environments if the $\mu$-$PhC_2Me$ and Cp ligands are considered to occupy two and one coordination sites, respectively. The two pseudooctahedra share the $\mu$-$C_2$ edge (C(7)–C(8)) and the Co–W axis. The atoms C(1) and C(4) occupy pseudoaxial positions.

The average Co–C($\mu$-$C_2$) distance of 2.01 (2) Å is comparable, within experimental error, to the mean values found in $(CO)_3Co(\mu\text{-}RC_2R)Co(CO)_3$ complexes (R = Ph, 1.97 (1) Å; R = $CO_2Me$, 1.92 (2) Å; R = *t*-Bu, 1.987 (2) Å),[30] as well as to the average value of 1.95 (1) Å in $Cp(CO)_2Mo(\mu\text{-}CF_3C_2CF_3)Co(CO)_3$.[23] Similarly, the average W–C($\mu$-$C_2$) distance of 2.14 (2) Å compares well with the values found in $W_2(\mu\text{-}RC_2R)$ alkoxide derivatives (R = H, 2.10 (2) Å, R = Me, 2.13 (8) Å).[31] It is interesting to note that these W–C distances are close to those reported for $W(\eta^2\text{-}RC_2R)$ complexes (R = H, Me 2.06 (2)–2.09 (2) Å).[32]

The lack of data for strictly related complexes does not allow any detailed discussion to be made of the geometry of the coordinated alkyne ligand as a function of the different nature of the bridged metal atoms and alkyne substituents. We can only observe that in the closest

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**Table V. Intramolecular Nonbonded Distances (Å) Involving Alkyne Substituents in 5a**[a]

| | | | |
|---|---|---|---|
| C(6)···C(1) | 3.259 (5) | C(9)···C(1) | 3.456 (5) |
| O(1) | 3.745 (5) | C(2) | 3.451 (5) |
| C(4) | 3.223 (6) | C(4) | 3.797 (5) |
| O(4) | 3.624 (5) | | |
| C(5) | 3.183 (5) | C(10)···C(2) | 3.536 (5) |
| O(5) | 3.581 (6) | O(2) | 3.752 (5) |
| | | C(19) | 3.726 (6) |

[a] Only distances shorter than 3.9 Å are given.

analogue so far reported, Cp(CO)$_2\overline{\text{Mo}(\mu\text{-CF}_3\text{C}_2\text{CF}_3)\text{Co}}$(CO)$_3$,[23] the alkyne C–C distance (1.371 (7) Å) compares well with the C(7)–C(8) bond length of 1.381 (5) Å in **5a**, in spite of the different electron-withdrawing character of the two alkynes. The C–C–CF$_3$ bond angles (average 133.7 (1)°) in the MoCo complex are significantly narrower than the C–C–Ph and C–C–Me angles (136.0 (3) and 139.1 (4)°, respectively) in **5a**. However, all of these values are in the typical ranges of bond lengths (1.3–1.4 Å) and angles (130–150°) found in binuclear complexes in which the metal–metal bond is transversely spanned by an alkyne ligand.[27]

As expected from intramolecular steric interactions, the Cp ring is forced to the side opposite the alkyne ligand, which in turn adopts the usual cis-bent structure. The atoms C(6), C(9) and C(7), C(14) are nearly eclipsed (torsion angles C(6)–C(7)–C(8)–C(9) = −9.6° and C(7)–C(8)–C(9)–C(14) = 0.7°).

This brings us to the most noteworthy structural aspect of the molecule, namely, the orientation of the PhC$_2$Me fragment with respect to the rigid dimetal moiety. Of the two possible isomers, i.e. one with Me trans to Cp and the other with Me cis to Cp, only the former is present in the crystal, together with its enantiomer. One might think that this arrangement derives from intraligand steric repulsions; however, inspection of nonbonded distances involving the alkyne substituents (Table V) shows that the Me carbon atom C(6) forms closer contacts than the Ph carbon atom C(9). The Me group is nestled among C(1), C(4), and C(5) at a short distance of 3.22 Å (av). Models indicate that transposition of the Me and Ph groups should relieve these repulsive steric interactions. Since there is no electronic reason for the observed geometry, it may be that the trapping of the Me group stabilizes this isomer or that its formation is kinetically favored.

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**Registry No.** **1a**, 111635-09-7; **1b**, 111635-10-0; **2**, 111635-11-1; **3a**, 111635-12-2; **3b**, 111635-13-3; 4, 111635-14-4; **5a**, 111635-15-5; **5a**-*d*, 111689-07-7; **5b**, 111635-16-6; **5b**-*d*, 111635-18-8; **6**, 111635-17-7; CpFe(CO)$_2$CH$_2$C≡CPh, 33114-75-9; Co$_2$(CO)$_8$, 10210-68-1; CpFe(CO)$_2$CH$_2$C≡CMe, 34822-36-1; Mn(CO)$_5$CH$_2$C≡CPh, 23626-46-2; CpW(CO)$_3$CH$_2$C≡CPh, 32993-03-6; Co(O$_2$CCF$_3$)$_2$, 6185-58-6; (CO)$_3\overline{\text{Co}(\mu\text{-PC}_2\text{Me})\text{Co}}$(CO)$_3$, 53556-74-4; CpW(CO)$_3$CH$_2$C≡CMe, 32877-63-7; CpMo(CO)$_3$CH$_2$C≡CPh, 32877-62-6; CpFe(CO)$_2$OC(O)CF$_3$, 37048-23-0.

**Supplementary Material Available:** Listings of anisotropic thermal parameters and hydrogen atom coordinates for complex **5a** (3 pages); a listing of structure factors for complex **5a** (16 pages). Ordering information is given on any current masthead page.

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# Structural Studies of Iron Phosphonate Complexes, ($\eta^5$-C$_5$H$_5$)(CO)$_2$FeP(O)(OEt)$_2$, and Its Reactivity

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The structure of ($\eta^5$-C$_5$H$_5$)(CO)$_2$FeP(O)(OEt)$_2$ has been determined by X-ray diffraction. It crystallized in the triclinic space group $P\bar{1}$ with unit cell parameters $a$ = 15.494 (4) Å, $b$ = 13.668 (3) Å, $c$ = 7.890 (2) Å, $\alpha$ = 85.78 (2)°, $\beta$ = 80.26 (2)°, $\gamma$ = 64.77 (1)°, and $D_{\text{calcd}}$ = 1.464 g cm$^{-3}$ for $Z$ = 4. One of the main features of the molecule of the complex is the unequal coordination of the two carbonyl groups: one is trans and the other is gauche to the phosphoryl group in the Newman projection along the P–Fe bond and the bond length between Fe and CO is shorter in the trans CO than in the gauche CO. Thus, the trans CO is linked to the Fe atom more strongly than the gauche CO. $^{13}$C NMR measurements in a chloroform at room temperature revealed that the two carbonyl groups can be resolved. The carbonyl groups of the complex cannot be displaced by P($n$-Bu)$_3$ or P(OEt)$_3$ under refluxing conditions in benzene and cannot be oxidized to CO$_2$ by Me$_3$NO. The iron phosphonate complex reacts readily with a Lewis acid, R$^+$ (R$^+$ = Me$^+$, CPh$_3$$^+$, H$^+$), to afford the corresponding iron phosphite complex, [($\eta^5$-C$_5$H$_5$)(CO)$_2$FeP(OR)(OEt)$_2$]$^+$.

## Introduction

Transition-metal phosphonate complexes are of interest because the pentavalent phosphorus atom is covalently bonded to the transition metal. Phosphonate complexes are usually prepared by reacting trialkyl phosphite, P(OR)$_3$, with complexes containing a labile nucleophilic ligand, X (eq 1).[4]

$$\text{L}_n\text{M–X} + \text{P(OR)}_3 \rightarrow \text{L}_n\text{M–P(O)(OR)}_2 + \text{RX} \quad (1)$$

Although the reaction mechanism of the Arbuzov-like dealkylation reaction has been investigated,[5,6] X-ray

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