Journal of Organometallic Chemistry, 390 (1990) 351–360
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20864

Reactions of tungsten and molybdenum propargyl complexes with $Co_2(CO)_8$, $Co_4(CO)_{12}$, and $Cp_2Mo_2(CO)_4$. A crossover study of formation of $(CO)_3\overline{Co(\mu\text{-}RC{\equiv}CMe)W}Cp(CO)_2$

George H. Young * **and Andrew Wojcicki** *
Department of Chemistry, The Ohio State University, Columbus, OH 43210 (U.S.A.)

(Received November 28th, 1989)

Abstract

The nature of the protonation reaction of $(CO)_3\overline{Co(\mu\text{-}RC{\equiv}CCH_2MCp(CO)_3)Co}(CO)_3$ (M = Mo, W; R = Me, Ph, p-MeC_6H_4) (**2**) (obtained from $(CO)_3CpMCH_2C{\equiv}CR$ (**1**) and $Co_2(CO)_8$) to give $(CO)_3\overline{Co(\mu\text{-}RC{\equiv}CMe)M}Cp(CO)_2$ (**3**) was further investigated by a crossover experiment. Thus, reaction of an equimolar mixture of **2b** (M = W, Cp = η^5-C_5H_5, R = Ph) and **2e** (M = W, Cp = η^5-C_5H_4Me; R = p-MeC_6H_4) with CF_3COOH affords only **3b** (same M, Cp, and R as **2b**) and **3e** (same M, Cp, and R as **2e**) to show an intramolecular nature of this transformation. Reaction of $(CO)_3CpWCH_2C{\equiv}CPh$ (**1b**) with $Co_4(CO)_{12}$ was also examined and found to yield **2b** exclusively. Treatment of **1** with $Cp_2Mo_2(CO)_4$ at 0–5 °C provides thermally sensitive compounds, possibly $(CO)_2Cp\overline{Mo(\mu\text{-}RC{\equiv}CCH_2MCp(CO)_3)Mo}Cp(CO)_2$ (**5**), which decompose at room temperature to give $Cp_2Mo_2(CO)_6$ as the only isolated product.

Introduction

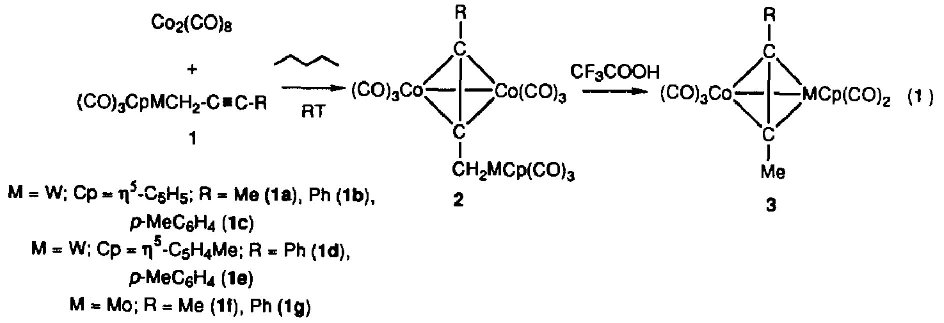
As part of an investigation of the use of transition-metal propargyl complexes as reagents for the synthesis of compounds containing heteronuclear metal–metal bonds [1,2], we recently reported the two-step synthesis of the μ-alkyne complexes $(CO)_3\overline{Co(\mu\text{-}RC{\equiv}CMe)M}Cp(CO)_2$ (M = Mo, W) (**3**). These products were formed via reaction of $Co_2(CO)_8$ with molybdenum and tungsten propargyl complexes, $(CO)_3CpMCH_2C{\equiv}CR$ (**1**), followed by protonation of the resulting alkyne-templated heterotrinuclear compounds $(CO)_3\overline{Co(\mu\text{-}RC{\equiv}CCH_2MCp(CO)_3)Co}(CO)_3$ (**2**)

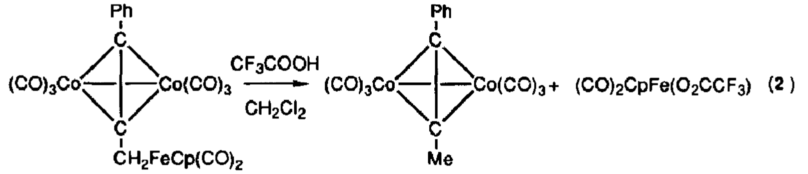
---

* Present address: B.F. Goodrich Research and Development Center, Brecksville, Ohio 44141.

0022-328X/90/$03.50

(eq. 1) [2]. By contrast, the complex $(CO)_3\overline{Co(\mu\text{-}PhC{\equiv}CCH_2FeCp(CO)_2)Co}(CO)_3$ (4), related to 2, its protonated via a different pathway (eq. 2) [2]. We now report our further findings concerning these unusual protonation reactions of **2**.





Also reported here are reactions of **1** with each of $Co_4(CO)_{12}$ and $Cp_2Mo_2(CO)_4$.

Experimental

All reactions and manipulations of air-sensitive compounds were carried out under an atmosphere of Ar by using standard procedures [3]. Chromatographic separations were effected on columns packed with alumina (150 mesh, 6% H_2O) or Florisil (60–100 mesh). Melting points were measured on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared (IR) spectra were collected on a Perkin-Elmer Model 337 spectrophotometer and were calibrated with polystyrene. ^1H NMR spectra were recorded on a Bruker AM-250 spectrometer. ^{13}C NMR spectra were recorded by Mr. Carl Engelman on a Bruker AM-250 spectrometer or by Dr. Charles Cottrell on a Bruker AM-500 spectrometer. Mass spectra were obtained by use of the fast atom bombardment (FAB) technique on a VG70-250S spectrometer by Mr. David C. Chang.

Pentane was distilled from Na under an Ar atmosphere. Dichloromethane was purified by distillation from P_4O_{10} under an Ar atmosphere prior to use. Other solvents were used without further purification. Trifluoroacetic acid, from Aldrich, and $Co_4(CO)_{12}$, from Pressure Chemical Co., were used as received. $Co_2(CO)_8$, from Strem, was crystallized first from CH_2Cl_2 and then from heptane under an atmosphere of CO. $Cp_2Mo_2(CO)_4$ [4], $(CO)_3\overline{Co(\mu\text{-}PhC{\equiv}CMe)Co}(CO)_3$ [5], $(CO)_3CpW(O_2CCF_3)$ [6], and $[(CO)_3CpW(CH_2Cl_2)]PF_6$ [7] were prepared by the literature procedures. The literature procedures [8] were used to prepare $(CO)_3CpWCH_2C{\equiv}CMe$ (**1a**), $(CO)_3CpWCH_2C{\equiv}CPh$ (**1b**), and $(CO)_3CpMoCH_2C{\equiv}CPh$ (**1g**), and were closely adapted in the synthesis of the new transition-metal propargyl complexes $(CO)_3CpWCH_2C{\equiv}CC_6H_4\text{-}p\text{-}Me$ (**1c**), $(CO)_3Cp'WCH_2C{\equiv}CPh$ ($Cp' = \eta^5\text{-}C_5H_4Me$) (**1d**), and $(CO)_3Cp'WCH_2C{\equiv}CC_6H_4\text{-}p\text{-}Me$ (**1e**) (See Table 1 for

Table 1

IR and NMR data for new tungsten propargyl complexes **1c–e** [a]

Complex	IR, ν(CO) [b], cm^{-1}	NMR, δ	
		^{1}H [c]	^{13}C{^{1}H} [c]
1c	2024, 1946, 1937	7.26–7.22, 7.09–7.06 (2m, 4H, C_6H_4), 5.53 (s, 5H, Cp), 2.33 (s, 3H, Me), 2.22 (s, 2H, CH_2)	229.03 (W–CO), 216.47 (W–CO, J(W–C) [d] = 160 Hz), 136.62 (aromatic C *ipso* to Me), 130.96, 128.75 (aromatic C's), 122.93 (aromatic C *ipso* to C≡C), 99.24 (CCH$_2$), 92.59 (Cp), 81.41 (C–Ar), 21.32 (Me), −31.46 (CH$_2$, J(W–C) = 30.5 Hz)
1d	2021, 1945, 1936	7.35–7.17 (m, 5H, Ph), 5.40 (d, J = 2.2 Hz, ring H's on C's of Cp′ β to Me), 5.36 (t, J = 23 Hz, ring H's on C's of Cp′ α to Me), 2.23 (s, 3H, Me), 2.18 (s, 2H, CH_2)	229.78 (W–CO, J(W–C) = 128.3 Hz), 217.39 (W–CO, J(W–C) = 159.0 Hz), 131.04, 128.16, 126.58 (*o*-, *m*- and *p*-C's of Ph), 125.43 (*ipso* C of Cp′), 100.44 (CCH$_2$), 93.61, 92.56, 90.45 (ring C's of Cp′), 80.75 (CPh), 13.66 (Me), −30.12 (CH$_2$, J(W–C) = 30.0 Hz)
1e	2022, 1946, 1933	7.24, 7.07 (2m, 4H, C_6H_4), 5.54–5.26 (m, 4H, ring H's of Cp′), 2.33 (*p*-MeC_6H_4), 2.23 (*Me*Cp), 2.17 (s, 2H, CH_2)	229.90 (W–CO), 217.41 (W–CO, J(W–C) = 160.0 Hz), 136.51 (aromatic C *ipso* to Me), 130.92, 128.43 (aromatic C′s), 122.33 (aromatic C *ipso* to C≡C), 110.04 (*ipso* C of Cp′), 99.48 (CCH$_2$), 93.67, 90.48 (ring C's of Cp′), 80.79 (CAr), 21.31 (*p*-*Me*C$_6$H$_4$), 13.67 (*Me*Cp), −29.97 (CH$_2$, J(W–C) = 31.0 Hz)

[a] At room temperature. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. [b] In cyclohexane solution; all absorptions of approximately equal intensity. [c] In $CDCl_3$ solution. [d] ^{183}W isotope.

spectral data of **1c–e**) by starting with $[WCp(CO)_3]^-$ [6] and the appropriate propargyl bromide. Owing to the low stability of the trinuclear metal compounds **2** even under an inert atmosphere, they were prepared in situ from $Co_2(CO)_8$ and the corresponding metal propargyl complexes as previously described [2]. The synthesis of $(CO)_3\overline{Co(\mu\text{-}PhC{\equiv}CMe)W}Cp(CO)_2$ (**3b**) was carried out as already reported [2].

Preparation of new $(CO)_3\overline{Co(\mu\text{-}RC{\equiv}CMe)W}Cp(CO)_2$ *complexes (3)*

$(CO)_3\overline{Co(\mu\text{-}p\text{-}MeC_6H_4C{\equiv}CMe)W}Cp(CO)_2$ (3c). A solution of $(CO)_3CpWCH_2$-C≡CC_6H_4-*p*-Me (**1c**) (1.31 g, 2.83 mmol) in pentane (400 mL) was added via cannula over 3 min to a stirred, room-temperature solution of $Co_2(CO)_8$ (0.969 g, 2.83 mmol) in pentane (30 mL). After 40 min formation of $(CO)_3\overline{Co(\mu\text{-}p\text{-}MeC_6H_4\text{-}C{\equiv}CCH_2WCp(CO)_3)Co}(CO)_3$ (**2c**) was complete as ascertained by IR spectroscopy. At this point CF_3COOH (0.241 mL, 0.358 g, 3.14 mmol) was added via syringe. After stirring for ca 12 h, the red reaction mixture was filtered under Ar to provide a red solid (0.134 g) and a red filtrate. The red solid was identified by IR spectroscopy as the previously reported [2] cobalt(II) trifluoroacetato complex. Chromatography of the red filtrate on an alumina column (2 × 20 cm) packed and eluted with

Table 2

IR and NMR data for new heteronuclear metal μ-alkyne complexes **3** [a]

Complex	IR, ν(CO) [b], cm^{-1}	NMR, δ	
		^{1}H [c]	^{13}C{^{1}H} [c,d]
3c	2060 (sh), 2046, 2002, 1986, 1971, 1933	7.28 (br s, 5H, Ph), 5.46, 5.30 (dd, *J* = 11.1 Hz, 4H, ring H's of Cp′), 3.00 (s, 3H,≡C*Me*), 2.17 (s, 3H, Cp*Me*)	215.55 (W–CO, *J*(W–C) [e] = 151 Hz), 213.42 (W–CO, *J*(W–C) = 163 Hz), 203.05 (br s, Co–CO), 143.85 (*ipso* C of Ph), 129.55, 128.57, 126.50 (*o*-, *m*-, and *p*-C's of Ph), 106.59 (*ipso* C of Cp′), 90.44, 90.22, 90.33, 89.88 (ring C's of Cp′), 88.80 (*C*Me), 82.20 (*C*Ph), 20.89 (≡C*Me*), 13.92 (Cp*Me*)
3d	2049, 2001, 1986, 1970, 1935	7.19, 7.10 (AA′BB′, 4H, Ar), 5.48 (s, 5H, Cp), 2.99 (s, 3H, ≡C*Me*), 2.35 (s, 3H, Ar*Me*)	214.68, 212.36(W–CO), 202.85 (br s, Co–CO), 140.29 (Ar C's *ipso* to ≡C), 136.72 (Ar C's *ipso* to Me), 129.37 (ring C's of Ar), 89.77 (Cp), 88.10 (≡*C*Me), 82.00 (≡*C*Ar), 21.22 (≡C*Me*), 20.90 (Ar*Me*)
3e	2056 (sh), 2048, 2000, 1987, 1972, 1935	7.16, 7.11 (AA′BB′, 4H, Ph), 5.43, 5.38 (2m, ring H's of Cp′), 2.97 (s, 3H, ≡C*Me*), 2.35 (s, 3H, Ar*Me*), 2.18 (s, 3H, Cp*Me*)	215.68 (W–CO), *J*(W–C) = 168 Hz), 213.64 (W–CO, *J*(W–C) = 171 Hz), 202.75, 200.30 (2 br s, Co–CO), 140.17 (Ar C's *ipso* to ≡C), 136.55 (Ar C's *ipso* to Me), 129.51, 129.35, 106.59 (*ipso* C of Cp′), 90.49, 90.21, 89.97, 89.85 (ring C's of Cp′), 88.09 (≡*C*Me), 82.78 (≡*C*Ar), 21.24 (≡C*Me*), 20.81 (Ar*Me*), 13.97 (Cp*Me*)

[a] At room temperature. Abbreviations: s, singlet; d, doublet; t, triplet, m, multiplet; sh, shoulder; br, broad. [b] In pentane solution; all absorptions of approximately equal intensity unless otherwise noted. [c] In CD_2Cl_2 solution. [d] Assignments made with the help of 2D ^{13}C–^{1}H correlation NMR. [e] ^{183}W isotope.

pentane provided a single red band which afforded $\mathrm{(CO)_3Co(\mu\text{-}\mathit{p}\text{-}MeC_6H_4C{\equiv}CMe)WCp(CO)_2}$ (**3c**) as an air-sensitive red solid (0.855 g, 52%): m.p. 151°C dec; mass spectrum (FAB), ^{184}W isotope, *m/z* (relative intensity): 578 (M^+, 9), 550 ($M^+ -$ CO, 22), 522 ($M^+ -$ 2CO, 100), 494 ($M^+ -$ 3CO, 49), 468 ($M^+ + 2 -$ 4CO, 78), 435 ($M^+ + 1 -$ 5CO, 52). See Table 2 for IR and NMR data.

$\mathrm{(CO)_3Co(\mu\text{-}PhC{\equiv}CMe)WCp'(CO)_2}$ (3d). This compound was prepared, in a manner strictly analogous to that used in the synthesis of **3c**, from $\mathrm{(CO)_3Cp'WCH_2C{\equiv}CPh}$ (**1d**) (1.31 g, 2.83 mmol) and $\mathrm{Co_2(CO)_8}$ (0.969 g, 2.83 mmol). Protonation with $\mathrm{CF_3COOH}$ (3.14 mmol) and work-up gave the red cobalt(II) trifluoroacetato complex (0.145 g) and $\mathrm{(CO_3Co(\mu\text{-}PhC{\equiv}CMe)WCp'(CO)_2}$ (**3d**) (0.721 g, 44%) as an air-sensitive red solid: m.p. 161°C dec; mass spectrum (FAB), ^{184}W isotope, *m/z* (relative intensity): 572 ($M^+ -$ 6, 25), 550 ($M^+ -$ CO, 30), 522 ($M^+ -$ 2CO, 100), 494 ($M^+ -$ 3CO, 40), 466 ($M^+ -$ 4CO, 50), ($M^+ -$ 5CO, 47). See Table 2 for IR and NMR data.

$\mathrm{(CO)_3Co(\mu\text{-}\mathit{p}\text{-}MeC_6H_4C{\equiv}CMe)WCp'(CO)_2}$ (3e). This compound was prepared, in a manner strictly analogous to that used in the synthesis of **3c**, from $\mathrm{(CO)_3Cp'WCH_2C{\equiv}CC_6H_4\text{-}\mathit{p}\text{-}Me}$ (**1e**) (0.191 g, 0.401 mmol) and $\mathrm{Co_2(CO)_8}$ (0.137 g, 0.401 mmol). Protonation with $\mathrm{CF_3COOH}$ (34 μL, 0.051 g, 0.45 mmol) and work-up gave the red cobalt(II) trifluoroacetato complex (0.034 g) and $\mathrm{(CO)_3Co(\mu\text{-}\mathit{p}\text{-}}$

$MeC_6H_4C{\equiv}CMe)WCp'(CO)_2$ (**3e**) (0.185 g, 77%) as an air-sensitive red solid: m.p. 165 °C dec; mass spectrum (FAB), ^{184}W isotope, m/z (relative intensity): 586 (M^+-6, 5), 564 (M^+- CO, 20), 536 (M^+- 2CO, 100), 508 (M^+- 3CO, 48), 480 (M^+- 4CO, 56), 452 (M^+- 5CO, 52). See Table 2 for IR and NMR data.

Crossover experiment. Protonation of an equimolar mixture of $(CO)_3Co(\mu\text{-}PhC{\equiv}CCH_2WCp(CO)_3)Co(CO)_3$ (2b) and $(CO)_3Co(\mu\text{-}p\text{-}MeC_6H_4C{\equiv}CCH_2WCp'(CO)_3)Co(CO)_3$ (2e)

The two title compounds were prepared in situ at room temperature in two separate flasks, one containing a stirred solution of $(CO)_3CpWCH_2C{\equiv}CPh$ (**1b**) (0.896 g, 2.00 mmol) and $Co_2(CO)_8$ (0.684 g, 2.00 mmol) in pentane (100 mL), and the other containing a stirred solution of $(CO)_3Cp'WCH_2C{\equiv}CC_6H_4\text{-}p\text{-}Me$ (**1e**), (0.952 g, 2.00 mmol) and $Co_2(CO)_8$ (0.684 g, 2.00 mmol) also in pentane (100 mL). Formation of **2b** and **2e** was complete in each case after 45 min as ascertained by IR spectroscopy. The two reaction solutions were then combined via cannula, and CF_3COOH (340 μL, 0.506 g, 4.44 mmol) was immediately added by syringe. The mixture was filtered and solvent was removed from the filtrate to give a red oil which was analyzed by ^1H and ^{13}C NMR spectroscopy and FAB mass spectrometry.

Attempted reaction of $(CO)_3Co(\mu\text{-}PhC{\equiv}CMe)Co(CO)_3$ with $(CO)_3CpW(O_2CCF_3)$

To a solution of $(CO)_3Co(\mu\text{-}PhC{\equiv}CMe)Co(CO)_3$ (0.064 g, 0.16 mmol) in 35 mL of pentane at room temperature was added $(CO)_3CpW(O_2CCF_3)$ 0.072 g, 0.16 mmol) as a solid. The resulting solution was stirred for 3 days, at which time no reaction was observed by IR spectroscopy.

Attempted reaction of $(CO)_3Co(\mu\text{-}PhC{\equiv}CMe)Co(CO)_3$ with $[(CO)_3CpW(CH_2Cl_2)]PF_6$

The title tungsten complex was prepared from Ph_3CPF_6 (0.221 g, 0.569 mmol) and $(CO)_3CpWH$ (0.190 g, 0.569 mmol) in CH_2Cl_2 (10 mL) at −40 °C [7]. The reaction solution was then added to $(CO)_3Co(\mu\text{-}PhC{\equiv}CMe)Co(CO)_3$ (0.229 g, 0.569 mmol) in CH_2Cl_2 (60 mL), also at −40 °C, and the resulting mixture was allowed to warm with stirring to 20 °C over 40 h. No change in the IR spectrum occurred during that time.

Reaction of $Co_4(CO)_{12}$ with $(CO)_3CpWCH_2C{\equiv}CPh$ (1b)

To a stirred solution of $(CO)_3CpWCH_2C{\equiv}CPh$ (**1b**) (0.134 g, 0.300 mmol) in benzene (50 mL) was added $Co_4(CO)_{12}$ (0.172 g, 0.300 mmol) as a solid. The resulting black mixture was refluxed for 0.5 h and solvent was removed at 35 °C to provide a dark brown residue. The IR and ^1H NMR spectra of the residue showed it to be a crude mixture of **2b** and unreacted $Co_4(CO)_{12}$. The residue was dissolved in CH_2Cl_2 (3 mL) and loaded onto a Florisil column packed in hexane. Hexane elution gave a brown band which afforded $Co_4(CO)_{12}$ (0.009 g, 5%) upon concentration. Elution with a 2% solution of THF in hexane gave a black band which rapidly changed color to red on the support. The band was collected and concentrated under vacuum to give $(CO)_3Co(\mu\text{-}PhC{\equiv}CMe)WCp(CO)_2$ (**3b**) (0.109 g, 67%) as a red solid.

Reaction of $Cp_2Mo_2(CO)_4$ with $(CO)_3CpWCH_2C{\equiv}CMe$ (1a)

A solution of $(CO)_3CpWCH_2C{\equiv}CMe$ (**1a**) (0.054 g, 0.14 mmol) in toluene (6 mL) was added via cannula over 3 min to a stirred solution of $Cp_2Mo_2(CO)_4$ (0.061 g, 0.14 mmol) in toluene (2 mL) at 4°C. The ^1H NMR spectrum of the reaction mixture was periodically recorded and showed no further changes after 4.5 h. The mixture was then concentrated under vacuum to a volume of 1.5 mL and loaded onto a jacketed column (2 × 20 cm) packed with Florisil and cooled to 0°C with ice/water. A single red band was collected on elution with pentane and was concentrated at 0°C to give an air-sensitive red solid (0.040 g, 37%): IR ν(CO) (toluene, 0°C, cm^{-1}): 2018 (s), 1979 (w), 1957 (s), 1928 (vs), 1914 (s), 1874 (w); ^1H NMR ($CDCl_3$, 0°C, ppm): δ 5.56 (s, 5H, W*Cp*), 5.32 (s, 10H, 2Mo*Cp*), 2.38 (s, 5H, CH_2 and Me). The suspected $(CO)_2CpMo(\mu\text{-}MeC{\equiv}CCH_2WCp(CO)_3)MoCp(CO)_2$ (**5a**) quantitatively decomposes to $Cp_2Mo_2(CO)_6$ in solution above 10°C and as a solid at room temperature. No tungsten-containing products resulting from this decomposition were detected.

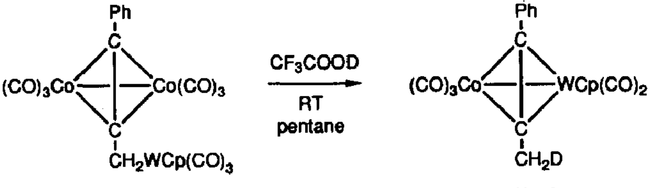
Similar reactions of $(CO)_3CpWCH_2C{\equiv}CPh$ (**1b**) and $(CO)_3CpMoCH_2C{\equiv}CPh$ (**1g**) with $Cp_2Mo_2(CO)_4$ gave comparable results.

Results and discussion

A. Mechanism of formation of $(CO)_3Co(\mu\text{-}RC{\equiv}CMe)W(CO)_2Cp$ (3)

Whereas the heterotrinuclear compounds **2** and **4** both undergo scission of the CH_2–M bond when protonated with CF_3COOH, the final products obtained are quite different. The CH_2–Fe bond in **4** is cleaved in an analogous manner to that observed in the acid-promoted cleavage of the Me–Fe bond of $(CO)_2CpFeMe$ [9], in this case affording $(CO)_3Co(\mu\text{-}PhC{\equiv}CMe)Co(CO)_3$ and $(CO)_2CpFe(O_2CCF_3)$ (eq. 2). By contrast, compounds **2** provide the heterodinuclear μ-alkyne complexes **3** via acid-promoted cleavage of the CH_2–M bond, expulsion of the $Co(CO)_3$ fragment, and replacement by the isolobal [10] $WCp(CO)_2$ moiety (eq. 1). An incompletely characterized paramagnetic compound, best formulated as a cobalt(II) trifluoroacetate [2], is formed as the co-product in all protonation reactions of **2** regardless of the identity of the R group or metal.

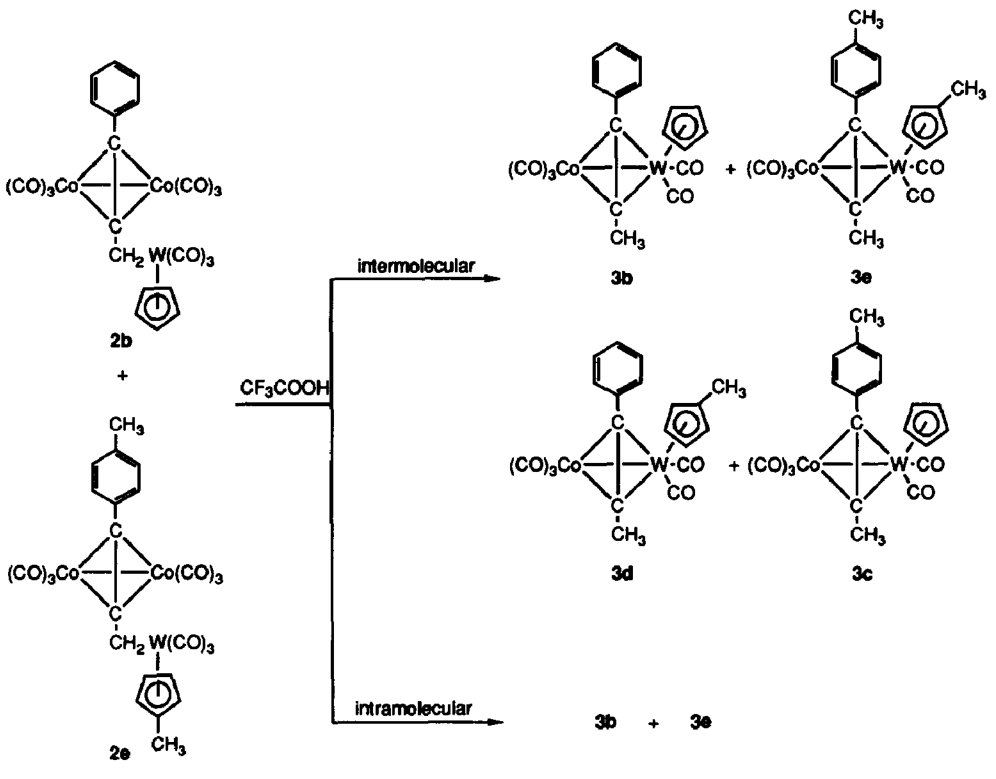
In order to learn more about the mechanism of the conversion of **2** to **3**, cleavage with deuterated acid and a crossover experiment were conducted to determine the site of addition of D^+ and the molecularity (inter or intra) of the reaction. As expected, treatment of **2b** with CF_3COOD leads to exclusive incorporation of a single D atom at the CH_2 position yielding **3b-*d*** (eq. 3) [2].



(3)

2b **3b-*d***

The mechanism of the protonation of **2** was further investigated by conducting a crossover experiment in which a mixture of the two closely related complexes $(CO)_3Co(\mu\text{-}PhC{\equiv}CCH_2WCp(CO)_3)Co(CO)_3$ (**2b**) and $(CO)_3Co(\mu\text{-}p\text{-}MeC_6H_4C{\equiv}C\text{-}CH_2WCp'(CO)_3)Co(CO)_3$ ($Cp' = \eta^5\text{-}C_5H_4Me$) (**2e**) were protonated and the products of the ensuing reaction were determined. If the scission of the CH_2–W bond occurs via an intramolecular process (i.e., without a separation into W- and



Scheme 1.

Co$_2$-containing fragments), two products, **3b** and **3e**, would be formed. However, if the scission occurs through an intermolecular pathway (i.e., with such a separation), four compounds, **3b**, **3e**, and the crossover products **3c** and **3d**, would be obtained. The two possibilities are shown in Scheme 1.

In order to determine which instrumental method would be capable of distinguishing between the possible mixtures of products, **3b**–**e** were independently synthesized and an equimolar mixture of these compounds was prepared and examined by ^{1}H and ^{13}C NMR spectroscopy and FAB mass spectrometry. The NMR spectra of a mixture of these four complexes did not provide sufficient differentiation of appropriate resonances. By contrast, FAB mass spectrometry was capable of distinguishing between the possible product mixtures, and thus elucidated the molecularity of the reaction. The mass spectra of the individual complexes are available as supplementary material from the authors.

The mass spectrum of an equimolar mixture of **3b**–**e** is shown in Fig. 1. The clusters of spectral lines about each labelled peak are due to the isotopic distribution of W, and their intensities reflect their natural abundance. In the following discussion all peaks will be assigned relative to the most abundant of these isotopes, ^{184}W. For reasons that are not clear, compounds **3** frequently give peaks of $M^+ - 6$ ions * that are more intense than the corresponding M^+ peaks. This is also observed in the spectrum of the equimolar mixture of **3b**–**e**. Thus, the peak at m/z 586 is attributed to the $M^+ - 6$ fragment of **3e**, and the relatively more intense peak at

---

* These ions most probably are formed by reaction with the Magic Bullet matrix.

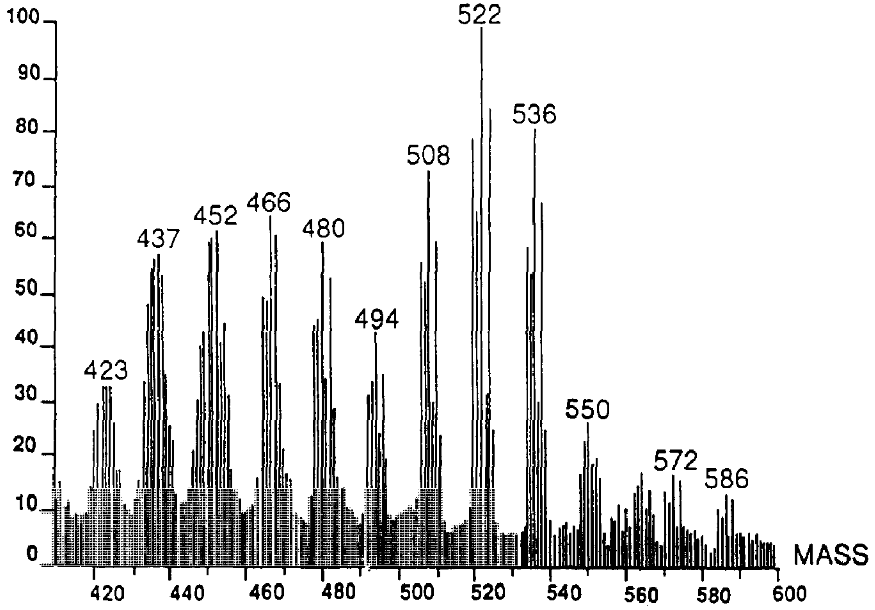


Fig. 1. FAB mass spectrum of an equimolar mixture of **3b**–**e**.

m/z 572 is due to the equivalent $M^+ - 6$ fragments of the isomeric **3c**,**d**. Next, a peak appears at *m/z* 564 which is due to the M^+ ion of **3b** and the M^+–CO ion of **3e** of the same mass. From this point on, successive differences of *m/z* 14 between the peak clusters are observed as a result of the mass difference between the $M^+ - x$CO ($x = 1$–5) peaks from isomers **3c**,**d**, and the peaks due to the overlap of $M^+ - x$CO with $M^+ - y$CO ($y = x + 1$, 0–4) of **3e** and **3b**, respectively.

The spectrum of the equimolar four-product mixture was then compared to that obtained in the crossover experiment from the protonation of an equimolar mixture of **2b** and **2e** (Fig. 2). It is obvious upon inspection of the spectra in Figs. 1 and 2 that the crossover products **3c**,**d** were not formed in the protonation of **2b** and **2e**, since there are no peaks differing by *m/z* 14 in the mass spectrum of the crossover reaction mixture. Therefore, the cleavage of the CH_2–W bond in **2** occurs via an intramolecular route.

The nature of this intramolecular pathway is not obvious. Since protonation at tungsten (and at molybdenum, in the analogous reactions of **2f**,**g**) would be expected to result in reductive elimination of $-CH_2-$ and $-H$ to give $(CO)_3Co(\mu$-RC≡CMe$)Co(CO)_3$ and $(CO)_3CpW(O_2CCF_3)$, that route is an unlikely one. It would then appear that H^+ adds to cobalt or carbon of the Co_2C_2 fragment. This may lead to scission of the Co–Co or Co–C bond to weaken the attachment of one cobalt carbonyl-containing fragment on the way to its extrusion and replacement by the isolobal $WCp(CO)_2$. Unfortunately, the reaction could not be followed by ^1H NMR spectroscopy owing to the formation of the paramagnetic cobalt(II) trifluoroacetate.

An intramolecular pathway for the conversion of **2** to **3** on protonation is consistent with our observations of the lack of reactivity of $(CO)_3Co(\mu$-PhC≡CMe$)Co(CO)_3$ toward each of $(CO)_3CpW(O_2CCF_3)$ and $[(CO)_3CpW(CH_2Cl_2)]PF_6$. If the conversion proceeded via the formation of $(CO)_3Co(\mu$-RC≡CMe$)$-$Co(CO)_3$ and $(CO)_3CpW(O_2CCF_3)$ or $[(CO)_3CpW(\text{solvent})]^+$, then a further reaction between these products would be required to yield **3**.

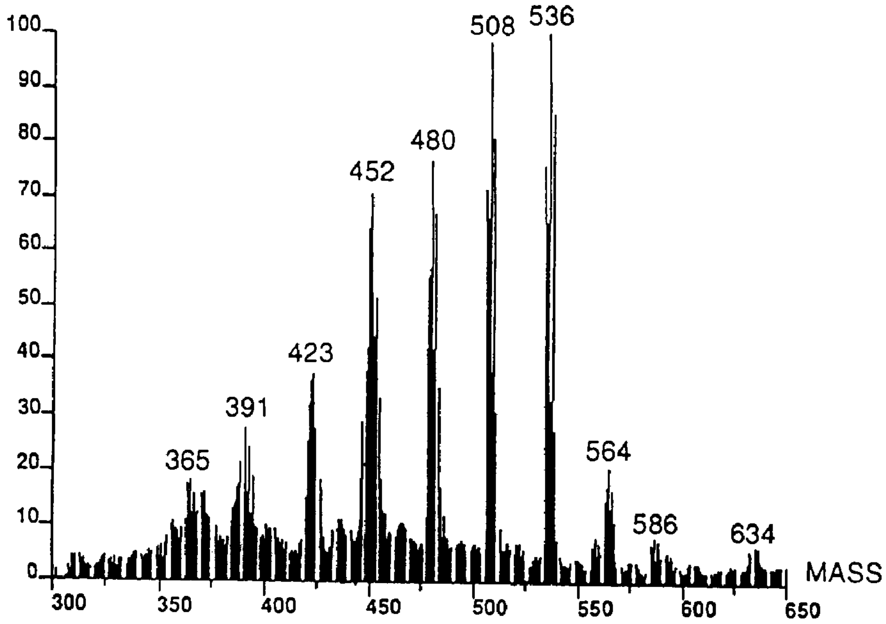
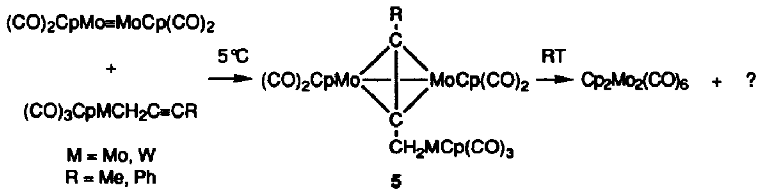


Fig. 2. FAB mass spectrum of the crossover reaction mixture.

B. Reactions of $(CO)_3CpMCH_2C{\equiv}CR$ (1) with $Co_4(CO)_{12}$ and $Cp_2Mo_2(CO)_4$

Although alkynes react with $Co_4(CO)_{12}$ to give numerous products depending on reaction conditions [11], the reaction of **1b** with $Co_4(CO)_{12}$ provided only the previously described **2b**. Alkynes are also known to react with $Cp_2Mo_2(CO)_4$ to give the stable compounds $(CO)_2CpMo(\mu\text{-}RC{\equiv}CR)MoCp(CO)_2$ [4]. Therefore related complexes were expected to be formed upon reaction of **1** with $Cp_2Mo_2(CO)_4$. However, stirring solutions of **1** and $Cp_2Mo_2(CO)_4$ in toluene at room temperature caused the immediate formation of $Cp_2Mo_2(CO)_6$ as the only isolable product. On the other hand, if the temperature was kept between 0 and 5 ° C, a slower reaction was evident. This reaction was followed by IR and ^1H NMR spectroscopy and shown to reach completion after 4.5 h.

After work-up of the reaction mixture at 0 ° C as described in the Experimental section, compounds of suspected formulation $(CO)_2CpMo(\mu\text{-}RC{\equiv}CCH_2MCp(CO)_3)MoCp(CO)_2$ (**5**) were isolated. These compounds decompose as solids or in solution at room temperature, and no attempt was made at their unequivocal characterization. However, the chemical shift of the CH_2 group (2.83 ppm) and the observation of two types of Cp ligands (5.56, s, 5H, W*Cp*; 5.32, s, 10H, 2Mo*Cp*) in **5a** seem to favor the structure shown below (eq. 4). It appears likely that **5** decompose to $Cp_2Mo_2(CO)_6$ by abstraction of CO from the $MCp(CO)_3$ group. The fate of the W or Mo atom was not determined.



(4)

Acknowledgements

We gratefully acknowledge financial support of the National Science Foundation (Grant CHE-8420806). FAB mass spectra were obtained at The Ohio State University Chemical Instrument Center (funded in part by National Science Foundation Grant 79-10019).

References

1 G.H. Young, A. Wojcicki, M. Calligaris, G. Nardin and N. Bresciani-Pahor, J. Am. Chem. Soc., 111 (1989) 6890.
2 T.H. Wido, G.H. Young, A. Wojcicki, M. Calligaris and G. Nardin, Organometallics, 7 (1988) 452.
3 D.F. Shriver, The manipulation of Air-Sensitive Compounds, McGraw-Hill, New York, 1969.
4 M.D. Curtis and R.J. Klingler, J. Organomet. Chem., 161 (1978) 23.
5 G. Cetini, O. Gambino, R. Rossetti and E. Sappa, J. Organomet. Chem., 8 (1967) 149.
6 T.S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3 (1956) 104.
7 W. Beck and K. Schloter, Z. Naturforsch. B, 33 (1978) 1214.
8 (a) J.O. Kroll and A. Wojcicki, J. Organomet. Chem., 66 (1974) 95. (b) J.-L. Roustan and C. Charrier, C.R. Seances Acad. Sci., Ser. C., 268 (1969) 2113.
9 N. De Luca and A. Wojcicki, J. Organomet. Chem., 193 (1980) 359.
10 R. Hoffmann, Angew. Chem., Int. Ed. Engl., 21 (1982) 711.
11 (a) R.S. Dickson, P.J. Fraser, Adv. Organomet. Chem., 12 (1974) 323. (b) R.S. Dickson and G.R. Tailby, Aust. J. Chem., 23 (1970) 229. (c) U. Krüerke and W. Hübel, Chem. Ber., 94 (1961) 2829.