96055-91-3; $W_2Cp*_2H_6(PMe_3)$, 102630-12-6; $[WCp*(CO)_2H]_2$, 86307-89-3; $[WO_2(O\text{-}t\text{-}Bu)]_2Cp^2$, 95045-00-4; $[WCl_4]_2Cp^2$, 102615-30-5; $[WMe_4]_2Cp^2$, 102615-31-6; $[WH_4]_2Cp^2$, 102630-13-7; $[WH_5(PMe_3)]_2Cp^2$, 102630-14-8; $[W_2H_6(Pme_3)]Cp^2$, 102615-32-7; $[W_2Cp*_2H_9]BF_4$, 102615-34-9; $[WCp*Cl_4]_2$, 102615-35-0; $WCp*Cl_4PMe_3$, 96055-86-6; $WCp*Me_4$, 96055-89-9; $W(C_3Et_3)(OCMe_2CMe_2O)(O\text{-}t\text{-}Bu)$, 102615-36-1; $ZnMe_2$, 544-97-8; $[WCl_4(PMe_3)]_2Cp^2$, 95045-02-6; 3,7-decadiyne, 33840-20-9.

Supplementary Material Available: Tables of final atomic coordinates, thermal parameters, and structure factor tables for the structures determined at −50 and −180 °C and selected bond distances and angles in the −180 °C structure (46 pages). Ordering information is given on any current masthead page.

A Heteronuclear μ-Alkyne Complex, $[\mu\text{-}(CF_3)_2C_2]CoMo(CO)_5(\eta\text{-}C_5H_5)$

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Exchange of a $Co(CO)_3$ unit in $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_6$ (1) by the isoelectronic fragment $Mo(CO)_2Cp$ is effected by the addition of an electron to 1 in the presence of $[Mo(CO)_3Cp]_2$ or by the thermal reaction between 1 and $Mo(CO)_3Cp^-$. $(CO)_3Co[\mu\text{-}(CF_3)_2C_2]Mo(CO)_2Cp$ (2) crystallized in space group $P2_1/c$ (Z = 8, a = 16.903 (3) Å, b = 12.110 (2) Å, c = 18.149 (3) Å, β = 111.32 (1)°), and its X-ray crystal structure was refined to R = 0.0348 and R_w = 0.0387 for 3510 reflections ($I > 3\sigma(I)$). Insertion of a $Mo(CO)_2Cp$ group does not significantly distort the μ-alkyne–M_2 geometry of 1; Co–Mo = 2.692 Å. A PPh_3 derivative was also characterized. 2 undergoes chemically reversible one-electron reductions at two separate redox centers. The thermal or photochemical reaction between 1 and $[Mo(CO)_3Cp]_2$ does not give 2, and, while an electron assists the synthesis, it is not a catalyzed reaction. A novel reaction of 1 with the radical initiator AIBN gives $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5[NC(CH_3)_2CN_2C(CH_3)_2CN]$.

Metal carbonyl anions can function as nucleophiles in electron transfer chain (ETC) catalyzed reactions with metal carbonyl clusters.[1] One potential advantage of these reactions is that heteronuclear metal clusters can be synthesized under relatively mild conditions, obviating the problems of thermal instability encountered in thermal metal exchange reactions. It was of interest to establish whether metal fragment exchange would occur where the metal–metal backbone is clamped by an electronically demanding organic group; in this instance, a μ-alkyne group. The complex $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_6$ (1) is a good ETC substrate,[2] with a relatively stable radical anion, and a reaction with a metal nucleophile would give a rare example[3] of a heterodinuclear monoalkyne complex; an example is $(CO)_3Co[\mu\text{-}R_2C_2]NiCp$.[4] In this paper we describe the synthesis, structure, and reactivity of $(CO)_3Co[\mu\text{-}(CF_3)_2C_2]Mo(CO)_2Cp$ (2).

Experimental Section

All reactions were carried out in argon-degassed solvents, dried, and purified as outlined before[2] and under an Ar atmosphere. $[Mo(CO)_3Cp]_2$,[6] $K[Mo(CO)_3Cp]$,[7] $Na[Mo(CO)_3Cp]$,[8] 1,[9] and PPN^+Cl^-[10] were prepared by literature procedures. Benzophenone ketyl (BPK) was prepared as a THF solution as described elsewhere.[11] 2,2′-Azobis(2-methylpropionitrile) (AIBN) was used as received (Aldrich).

Conventional current–voltage curves were recorded on a PAR 174 Analyzer equipped with a PAR 175 Universal Programmer and a Bryans X-Y recorder (scan rates < 1 V s^{-1}) or Tectronix Storage oscilloscope or on an interfaced Apple //e microcomputer. Standard cells were used for the transient and bulk electrochemistry, and all measurements and electrode reactions were carried out under Ar with TBAP (CH_2Cl_2, THF) or TEAP (acetone) as supporting electrolytes. Electrodes were rigorously cleaned, and all potentials are with respect to Ag/AgCl referenced against ferrocene.[11] The cyclic voltammograms were simulated at 200 mV s^{-1} by using programs based on Feldberg's statements.[12] Reductions (electrochemically or alkali metal) for ESR measurements were carried out by the methods described elsewhere.[13] Infrared spectra were recorded on Nicolet FT or Perkin-Elmer 225 spectrometers and NMR on 60-MHz JEOL or 90-MHz Perkin-Elmer spectrometers with internal Me_4Si standard.

Preparation of 2. (i) Reaction with $[Mo(CO)_3Cp]_2$ in THF. A 98.2-mg (0.200-mmol) sample of $[Mo(CO)_3Cp]_2$ was added to a solution of 89.2 mg (0.199 mmol) of 1 in 20 cm^3 of THF. A purple solution of BPK was added, via an air-tight syringe, in 0.1-cm^3 portions until all of 1 was consumed (monitored by IR); during this time the solution changed from red to yellow-green. At this stage an IR spectrum showed ν(CO) bands at 2069, 2024, 2010, and 2006 cm^{-1} as well as bands due to $Mo(CO)_3Cp^-$ and $[Mo(CO)_3Cp]_2$. The THF solution was reduced to dryness in vacuo to give a green solid. Extraction of this solid with hexane gave an orange-red solution plus a residue, and chromatographic separation of the solution on silica gel plates (hexane/ether/CH_2Cl_2, 10:1:1) gave three bands; orange (1), pink ($[Mo(CO)_3Cp]_2$), and orange-red. The last band was removed and eluted with CH_2Cl_2, and the residue after removal of the CH_2Cl_2 was crystallized from hexane/CH_2Cl_2 to yield orange-red crystals of 2 (17%). Anal. Calcd for $C_{14}H_5CoF_6MoO_5$: C, 32.21; H, 0.97. Found: C, 32.53; H, 0.97. Mass spectrum (70 eV): m/e (relative

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[1] Jensen, S. D.; Robinson, B. H.; Simpson, J. *J. Chem. Soc. Chem. Commun.* **1983**, 1081.

[2] Arewgoda, C. M.; Robinson, B. H.; Simpson, J. *J. Am. Chem. Soc.* **1983**, *105*, 1893.

[3] Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135.

[4] (a) Freeland, B. H.; Hux, J. E.; Payne, N. C.; Tyers, K. G. *Inorg. Chem.* **1980**, *19*, 693. (b) Muetterties, E. L.; Pretzer, W. R.; Thomas, M. G.; Beier, B. F.; Thorn, D. L.; Day, V. W.; Anderson, A. B. *J. Am. Chem. Soc.* **1978**, *100*, 2090. (c) Jaouen, G.; Marinetti, A.; Saillard, J.-Y.; Sayer, B. G.; McGlinchey, M. J. *Organometallics* **1982**, *1*, 225.

[5] Davidson, J. L. *J. Chem. Soc., Dalton Trans.* **1983**, 1667.

[6] King, R. B. In *Organometallic Synthesis*; Academic Press: New York, 1965; Vol. 1, p 109.

[7] Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263.

[8] (a) Hayter, R. G. *Inorg. Chem.* **1963**, *2*, 1031. (b) Darensbourg, M. Y.; Jimenez, P.; Sackett, J. R.; Hanckel, J. M.; Kump, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 1521.

[9] Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323.

[10] Ruff, J. K.; Schlientz, W. J. *Inorg. Synth.* **1974**, *15*, 84.

[11] Downard, A. J.; Robinson, B. H.; Simpson, J. *Organometallics*, in press.

[12] Feldberg, S. W. *Electroanal. Chem.* **1969**, *3*, 199.

[13] Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* **1977**, *16*, 405.

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intensity based on ion at 132 as 100%), 524 (7, M^+), 496 (17, $M^+ - CO$), 468 (17, $M^+ - 2CO$), 440 (9, $M^+ - 3CO$), 412 (11, $M^+ - 4CO$), 384 (6, $M^+ - 5CO$); another series starting at 505 ($M^+ - F$), 477 (3, $M^+ - F - CO$), 449 (3, $M^+ - F - 2CO$), 421 (1, $M^+ - F - 3CO$), 393 (1, $M^+ - F - 4CO$), 365 (1, $M^+ - F - 5CO$). IR (hexane, cm^{-1}): $\nu(CO)$ 2085 (s), 2045 (vs), 2027 (vs), 2014 (vs), 1993 (s). ^1H NMR ($CDCl_3$): δ 5.47 (s). UV (CH_2Cl_2): λ 493 nm (ϵ 2.8 × 10^3 mol^{-1} dm^2), 344 (4.1 × 10^4 mol^{-1} dm^2).

Hexane (40 cm^3) was added to the residue from the above reaction and the solution acidified with H_3PO_4 (20%). This led to vigorous gas evolution. The hexane layer was washed twice with water and dried over $MgSO_4$. The aqueous layer was extracted with CH_2Cl_2 and the dried CH_2Cl_2 extract combined with the hexane layer. At this point the solution was a red-brown color, but there was noticeable decomposition with time. Solvent was removed from the extracts, and chromatographic separation gave an 8% yield of 2 and a small amount of blue $(CF_3)_2C_2Co_4(CO)_{10}$.[9] The aqueous layer contained only Co(II) salts.

(ii) Reaction with $Mo(CO)_3Cp^-$ in THF. Na/K alloy was added, over a period of 30 min, to a vigorously shaken THF solution (40 cm^3) of $[Mo(CO)_3Cp]_2$ (49 mg, 0.1 mmol). Shaking was continued for a further 30 min to give complete reaction to $Mo(CO)_3Cp^-$. This solution was transferred under Ar to another 100 cm^3 flask and 1 (45 mg, 0.1 mmol) added to the solution. The solution was then heated to reflux temperature for ~30 min at which stage the solution was a dark green-brown color and no $Mo(CO)_3Cp^-$ remained; black insoluble material was noted after ~15 min. The solvent was stripped and the residue extracted twice with hexane (15 cm^3). Separation of the product from the hexane solution was achieved by using silica gel paper, the fourth band yielding 28 mg (0.05 mmol) of 2 (53%). The other major band was unreacted 1.

Other BPK-Intiated Reactions. (i) Reaction with $[Mo(CO)_3Cp]^-$. In a typical reaction a freshly prepared THF solution of $K^+Mo(CO)_3Cp^-$ or the sodium salt (20 cm^3, 0.40 mmol) was added to 90 mg (0.20 mmol) of 1. An immediate color change from orange-red to dark yellow-green was observed, and the $\nu(CO)$ spectrum indicated that some $[Mo(CO)_3Cp]_2$ had formed but that most of 1 was unreacted. No other reaction occurred at ambient temperatures. When the yellow-green solution above is treated with successive aliquots of BPK until no 1 remains, there is a reaction to give a solution with the same IR spectrum as that noted for the BPK-induced reaction with $[Mo(CO)_3Cp]_2$. Workup as for the $[Mo(CO)_3Cp]_2$ reaction gave 2 in slightly less yield without significant amounts of soluble compounds other than the reactants.

(ii) Reaction with $[Mo(CO)_3Cp]_2$ in Benzene. This reaction was carried out by the procedure used with THF as solvent. The BPK was prepared in benzene (the solubility is less than in THF, and greater amounts of BPK solution were used). When the BPK was added, there was a gradual disappearance of the $\nu(CO)$ spectrum of 1 with the appearance of bands at 2073, 2027, 2018, and 2000 cm^{-1} which correspond to those found in the THF preparation of 2. The solvent was stripped in vacuo, but extraction of the residue with hexane did not give 2 (or soluble products other than reactants).

Thermal and Photolytic Reactions of 1 with $[Mo(CO)_3Cp]_2$. (i) THF. 1 (147 mg, 0.33 mmol) and $[Mo(CO)_3Cp]_2$ (162 mg, 0.33 mmol) were heated under reflux in THF (20 cm^3) for 7 h. During this time the solution became brown in color and 1 reacted. TLC and IR analyses showed that 2 was not present at this stage of the reaction but that a brown compound was being formed (R_f 0 in CH_2Cl_2 and hexane). The IR spectrum in THF had $\nu(CO)$ bands at 2078, 2039, 2010, and 1991 cm^{-1} other than those due to unreacted starting compounds. The solvent was removed in vacuo and the residue extracted with hexane to yield two bands on a silica gel plate (hexane/CH_2Cl_2, 10:1, eluant) and a major insoluble portion. Extraction of the second band yielded ~3 mg of 2 (IR); the first band was unreacted $[Mo(CO)_3Cp]_2$. The reaction was repeated, but the reaction residue was extracted with THF rather than hexane. Again the IR showed the same $\nu(CO)$ as before but no 2. However, decomposition was rapid with no indication of the formation of 2. The yellow decomposition product dissolved in acetone, but it did not contain carbonyl groups.

(ii) Benzene. A solution of 1 (45 mg, 0.10 mmol) and $[Mo(CO)_3Cp]_2$ (25 mg, 0.05 mmol) in benzene (10 cm^3) was heated under reflux for 6 h. Chromatographic separation on silica gel (hexane/CH_2Cl_2, 10:1) gave three soluble products and decomposition material. The first product band (orange-brown), yield 2.5 mg, gave a mass spectrum with highest m/e at 534 and $\nu(CO)$ at 2074 (vs), 2024 (s), 2011 (s), 1993 (vw), and 1975 (vw) cm^{-1}; the product did not contain molybdenum (shown by the isotopic composition). The second band (green) gave 15 mg of $[\mu\text{-}(CF_3)_2C_2Co_2(CO)_3(\eta\text{-}C_6H_6)]$ confirmed by reference to an authentic sample.[14] A yield of 6.5 mg of 2 was recovered from the third band. It should be noted that the product distribution in this thermal reaction was variable[14b] although small amounts of 2 and the benzene derivative were always obtained. No products containing both Co and Mo, other than 2, were detected.

(iii) CH_2Cl_2. No reaction between 1 and $[Mo(CO)_3Cp]_2$ occurred after 3 h heating under reflux. However, after 10 h of heating the solution had become very dark in color, but TLC and IR analyses showed that the soluble products were the reactants; there was extensive non-carbonyl-containing decomposition material.

(iv) Cyclohexane. A stirred solution of 1 (22.1 mg, 0.49 mmol) and $[Mo(CO)_3Cp]_2$ (12.3 mg, 0.26 mmol) in cyclohexane (20 cm^3) at 15 °C was irradiated (125-W Hg) for 20 h. No gas evolution occurred, and by this stage the $[Mo(CO)_3Cp]_2$ had decomposed. The reaction data over this 20-h period (IR, TLC) showed that no 2 had formed and that no other soluble compounds other than reactants had been present.

Attempted Electrochemical Preparation of 2. A solution of 1 (2 × 10^{-4} mol dm^{-3}) in CH_2Cl_2 (20 cm^3)/TBAP (0.1 mol dm^{-3}) was reduced at −0.4 V for 1 h at Pt with the whole apparatus enclosed under Ar.[11] During this period the color changed from the typical red of 1 to a green-brown which is due to the radical anion $1^{\bullet-}$ [$\nu(CO)$ 2043 (w), 2008 (vs), 1991 (s) cm^{-1}]. Solid $[Mo(CO)_3Cp]_2$ was added to the reduced solution and the solution stirred. The color changed to brown at this point, but the $\nu(CO)$ spectrum showed that no reaction had occurred; this was confirmed by TLC analysis. The potential was progressively decreased to −0.8 V so as to reduce $[Mo(CO)_3Cp]_2$. The solution darkened in color, and new species slowly formed [principal $\nu(CO)$ bands at 2081, 2060, and ~2012 cm^{-1}] other than $[Mo(CO)_3Cp]^-$. When the current had decreased to <10% of the initial value, the electrolyte solution was removed from the cell and the solvent stripped in vacuo. The residue was chromatographed on silica gel plates (CH_2Cl_2/ether, 1:1) giving unreacted $[Mo(CO)_3Cp]_2$ and two partially resolved brown bands (the one of lower R_f was the major band). These bands were removed and the compounds eluted with CH_2Cl_2. In both cases, however, the compounds rapidly decomposed under Ar, in both solid and solution, and it has not been possible to characterize them other than by IR spectra [major product, $\nu(CO)$ 2081 (m), 2041 (s), 2018 (vs), 1979 (m) cm^{-1}; minor, $\nu(CO)$ 2093 (w), 2059 (s), 2020 (vs), 1997 (s) cm^{-1}]. The $\nu(CO)$ spectra of the products corresponded to those given above for the new species formed at −0.8 V. 2 was not produced in the reaction.

Similar reactions were carried out in methyl cyanide and acetone, but there was complete decomposition.

Reaction of 1 with AIBN. The following reaction includes $[Mo(CO)_3Cp]_2$ as it was designed to give 2. 1 (0.038 g) and $[Mo(CO)_3Cp]_2$ (0.021 g) were dissolved in hexane (15 cm^3), and 1 mg of AIBN was added. There was no reaction at 293 K, so the solution was heated under reflux for 6 h with additional AIBN being added at hourly intervals. After 1 h new $\nu(CO)$ bands at 2043, 2027, 2018, and 1954 cm^{-1} appeared, which increased with time, but both IR spectra and TLC showed that 2 was not formed at any stage in the reaction. The hexane was stripped and the residue separated on silica gel plates (hexane/CH_2Cl_2/ether, 10:1:1). A red-brown band appeared below the reactant bands, and workup of this band gave $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5[NC(CH_3)_2CN_2C(CH_3)_2CN]$ as red-brown crystals. Anal. Calcd for $C_{17}H_{12}Co_2F_6N_4O_5$: C, 34.93; H, 2.05. Found: C, 35.62; H, 2.63. Mass spectrum (70 eV): m/z 556 ($M^+ - CO$) (calcd 556) and sequential loss of four COs from the parent ion (there is a concomitant breakdown pattern due to 1). IR (hexane, cm^{-1}): $\nu(CO)$

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(14) (a) Jensen, S. D.; Robinson, B. H.; Simpson, J., to be submitted for publication. (b) Details are given in: Jensen, S. D. M.Sc. Thesis, University of Otago, 1985.

Table I. Crystal Data, Data Collection, and Refinement of 2

Crystal Data

cryst system: monoclinic	formula: $C_{14}H_5O_5F_6CoMo$
space group: $P2_{1/c}$	fw: 522.06 g mol^{-1}
a = 16.903 (3) Å	D_{calcd} = 2.01 g cm^{-1}
b = 12.110 (2) Å	Z = 8
c = 18.149 (3) Å	$F(000)$ = 2015.90
β = 111.32 (1)°	cryst size: 1 × 0.3 × 0.15 mm
V = 3460.8 Å^3	μ(Mo Kα) = 16.41 cm^{-1}

Data Collection and Refinement

diffractometer: Nicolet P$\bar{3}$
temp: 293 ± 1 K
radiatn: Mo Ka (λ = 0.710 69 Å)
scan type: θ–2θ
data limits: $0 < 2\theta < 40°$
reflctns measd: $\pm h,k,l$
cryst decay: <2%[a]
total obsd data: 4255
absorpn correctn: empirical[b]
max transmissn = 0.777
min transmissn = 0.678
unique data: 3510 ($I > 3\sigma(I)$)
no. of variables: 245
$R(\sum||F_o| - |F_c||/|F_o|) = 0.0348$
$R_w[\sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|] = 0.0387$
$w = [2.4705/(\sigma^2(F) + 0.000\,273F^2)]$

[a] Standard reflections (0,6,1), (7,0,–2), and (0,0,8) measured after every 100 reflections. [b] See ref 16.

2097 (w), 2062 (vs), 2045 (s), 2027 (m), 2014 (sh). The compound is soluble in organic solvents, but these solutions rapidly decompose at ambient temperature.

Reaction of 2 with Excess $(CF_3)_2C_2$. 2 dissolved in ether (1.0 cm^3) was placed in a thick-walled glass tube with a constricted neck and evacuated in conjunction with several freeze–thaw cycles. Excess $(CF_3)_2C_2$ gas was condensed into the tube, and the tube was sealed and shaken for 3 days at ambient temperature. The tube was broken open and the solution analyzed by TLC and IR spectra. Both techniques showed that no reaction had occurred.

Preparation of 3. A hexane solution (4 cm^3) of 2 (6 mg, 0.012 mmol) and PPh_3 (6 mg, 0.023 mmol) was boiled for 30 min. The solvent was stripped in vacuo and the residue chromatographed on foil-backed silica gel paper (Merck F60 254) to remove unreacted PPh_3. The single red band was removed and eluted with CH_2Cl_2; recrystallization from hexane gave deep red crystals of $PPh_3(CO)_2Co[\mu\text{-}(CF_3)_2C_2]Mo(CO)_2Cp$ (3) (quantitative yield). Anal. Calcd for $C_{31}H_{20}CoF_6MoO_4P$: C, 49.21; H, 2.65. Found: C, 49.42; H, 2.89. IR (hexane, cm^{-1}): ν(CO) 2052 (w), 2035 (m), 2018 (ms), 2004 (s), 1979 (vs), 1962 (sh, w). ^{1}H NMR ($CDCl_3$): δ 5.27 (s, 5 H), 7.25–7.55 (m, 15 H).

Crystal Structure Determination of 2. Crystals of 2, prepared as described above, were grown from hexane–CH_2Cl_2 solutions, and an orange-red rhombus was selected for data collection. Precession photography using Cu Kα radiation indicated a monoclinic system, identified as the space group $P2_1/c$ (No. 14)[15] from the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$. Data were collected at 20 ± 1 °C on a Nicolet P-$\bar{3}$, four-circle, fully automated diffractometer. The cell dimensions and orientation matrices were calculated from 25 accurately centered reflections. Relevant details of the crystal, data collection, solution, and refinement are summarized in Table I. Data were processed and empirical absorption corrections applied by using programs from the SHELXTL package.[16]

Table II. Final Positional and Equivalent Thermal Parameters for 2

atom	x/a	y/b	z/c	U_{eq},[a] Å^2
		Molecule 1		
Mo(1)	0.9007 (1)	0.8049 (1)	1.2308 (1)	0.036
Co(1)	0.7663 (1)	0.7807 (1)	1.0951 (1)	0.041
C(111)	0.9123 (5)	0.6211 (5)	1.0965 (4)	0.065
C(112)	0.8805 (3)	0.7179 (4)	1.1244 (3)	0.041
C(113)	0.8799 (3)	0.8286 (4)	1.1084 (3)	0.039
C(114)	0.9143 (4)	0.8959 (5)	1.0589 (3)	0.052
F(11)	0.8999 (4)	0.5277 (3)	1.1272 (3)	0.118
F(12)	0.9958 (3)	0.6246 (4)	1.1127 (3)	0.114
F(13)	0.8780 (3)	0.6060 (3)	1.0179 (2)	0.093
F(14)	0.8937 (3)	1.0015 (3)	1.0568 (2)	0.087
F(15)	0.9980 (2)	0.8949 (4)	1.0832 (3)	0.112
F(16)	0.8854 (3)	0.8647 (3)	0.9833 (2)	0.082
C(11)	0.8868 (4)	0.9715 (6)	1.2225 (3)	0.049
O(11)	0.8806 (3)	1.0639 (4)	1.2191 (3)	0.078
C(12)	1.0232 (4)	0.8265 (5)	1.2453 (3)	0.055
O(12)	1.0925 (3)	0.8368 (5)	1.2563 (3)	0.087
C(13)	0.8868 (5)	0.6481 (6)	1.2995 (4)	0.067
C(14)	0.9633 (5)	0.6984 (6)	1.3421 (4)	0.069
C(15)	0.9488 (5)	0.8012 (6)	1.3671 (3)	0.064
C(16)	0.8607 (5)	0.8151 (6)	1.3403 (4)	0.069
C(17)	0.8223 (4)	0.7203 (7)	1.2985 (4)	0.067
C(18)	0.7103 (4)	0.8960 (6)	1.1171 (4)	0.060
O(18)	0.6753 (3)	0.9654 (5)	1.1334 (3)	0.094
C(19)	0.7158 (4)	0.6621 (6)	1.1178 (4)	0.062
O(19)	0.6849 (4)	0.5853 (5)	1.1317 (3)	0.106
C(110)	0.7211 (4)	0.7743 (5)	0.9876 (4)	0.055
O(110)	0.6933 (3)	0.7706 (4)	0.9215 (3)	0.082
		Molecule 2		
Mo(2)	0.3338 (1)	0.7216 (1)	0.6635 (1)	0.043
Co(2)	0.4467 (1)	0.7157 (1)	0.5901 (1)	0.052
C(211)	0.2632 (5)	0.7574 (7)	0.4671 (4)	0.082
C(212)	0.3273 (4)	0.7586 (5)	0.5481 (3)	0.052
C(213)	0.3755 (4)	0.8379 (5)	0.5970 (4)	0.060
C(214)	0.3845 (7)	0.9585 (7)	0.5924 (6)	0.108
F(21)	0.2391 (3)	0.6607 (5)	0.4392 (3)	0.134
F(22)	0.1914 (3)	0.8078 (6)	0.4623 (3)	0.158
F(23)	0.2863 (4)	0.8098 (6)	0.4156 (3)	0.175
F(24)	0.4442 (4)	1.0004 (4)	0.6542 (4)	0.165
F(25)	0.3162 (5)	1.0111 (4)	0.5806 (5)	0.198
F(26)	0.4073 (5)	0.9855 (5)	0.5307 (4)	0.186
C(21)	0.4116 (5)	0.8103 (6)	0.7501 (4)	0.080
O(21)	0.4577 (5)	0.8628 (6)	0.8021 (4)	0.144
C(22)	0.2383 (6)	0.8415 (7)	0.6496 (5)	0.096
O(22)	0.1890 (5)	0.8987 (7)	0.6435 (6)	0.108
C(23)	0.2790 (5)	0.5445 (5)	0.6285 (4)	0.067
C(24)	0.2252 (4)	0.6021 (6)	0.6559 (4)	0.075
C(25)	0.2708 (5)	0.6283 (7)	0.7379 (4)	0.082
C(26)	0.3517 (5)	0.5855 (7)	0.7585 (4)	0.078
C(27)	0.3568 (5)	0.5325 (5)	0.6911 (4)	0.066
C(28)	0.5420 (5)	0.7274 (7)	0.6800 (5)	0.079
O(28)	0.5995 (4)	0.7358 (6)	0.7343 (3)	0.126
C(29)	0.4401 (4)	0.5725 (7)	0.5653 (4)	0.064
O(29)	0.4346 (3)	0.4814 (5)	0.5474 (3)	0.089
C(210)	0.4832 (5)	0.7665 (7)	0.5148 (5)	0.087
O(210)	0.5059 (4)	0.7964 (6)	0.4669 (4)	0.133

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The structure was solved by direct methods by using the program Multan,[17] with stereochemical information for the $Mo(CO)_2$, $Co(CO)_3$, and $(CF_3)_2C_2$ fragments included in the normalization procedure. The highest ranked of the resulting E maps revealed the location of the metal atoms for the two unique molecules in the asymmetric unit. The remaining non-hydrogen atoms were found in a series of difference Fourier syntheses and least-squares refinements by using SHELX76.[18] Refinement with all non-hydrogen atoms assigned isotropic thermal parameters converged with R = 0.097. Hydrogen atoms on the cyclopentadiene ring were included in calculated positions (C–H = 1.08 Å), and all non-hydrogen atoms were assigned anisotropic thermal parameters. The two independent molecules were refined in alternating blocked-matrix cycles, and a weighting scheme was introduced. The function minimized was $(|F_o| - |F_c|)^2$. Refinement of this model converged with R = 0.0349 and R_w = 0.0387. Scattering factors for the Co and Mo atoms were taken from

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(15) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1969; Vol. 1.

(16) Sheldrick, G. M., SHELXTL, University of Gottingen, 1981.

(17) Main, P.; Woolfson, M. M.; Germain, G. MULTAN-78 suite of programs.

(18) Sheldrick, G. M., SHELX-76, University of Cambridge, 1976.

Cromer and Mann[19] with corrections for anomalous dispersion from Cromer and Liberman.[20] Final positional and equivalent thermal parameters are given in Table II, and remaining crystallographic data are deposited in supplementary Tables S1–S5.

Results and Discussion

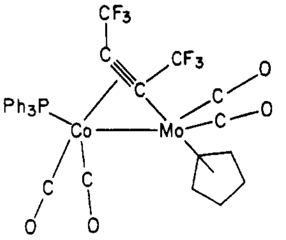
BPK-intitiated reaction of 1 with $[Mo(CO)_3Cp]_2$ in THF, or the thermal reaction between 1 and the anion $Mo(CO)_3Cp^-$ in THF without BPK, gave the orange-red air-stable complex 2. Optimum yields were obtained by (2),

$$2[(CF_3)_2C_2]Co_2(CO)_6 + [Mo(CO)_3Cp]_2 \xrightarrow{BPK} 2\{(CO)_3Co[(CF_3)_2C_2]Mo(CO)_2Cp\} + 2Co(CO)_4^- \quad (1)$$

$$[(CF_3)_2C_2]Co_2(CO)_6 + Mo(CO)_3Cp^- \xrightarrow{\Delta} (CO)_3Co[(CF_3)_2C_2]Mo(CO)_2Cp + Co(CO)_4^- \quad (2)$$

the lower variable yields via (1) being the result of an electron-induced rather than electron-catalyzed reaction by BPK; the mechanism is outlined later in the discussion. Other routes to 2 explored in this work are given in the Experimental Section. 2 was characterized by analysis, spectroscopic data, and crystal structure. In the mass spectrum successive loss of CO from the parent ion $CoMo(C_5H_5)(C_4F_6)(CO)_5^+$ is accompanied by a parallel sequential loss from $CoMo(C_5H_5)(C_4F_5)(CO)_5^+$, but there was no evidence of fragments arising from Co–Mo scission suggesting a strong Co–Mo interaction. All five ν(CO) bands predicted for a molecule of C_1 symmetry are found, and the ^1H (η-C_5H_5) resonance at 5.47 ppm is comparable to that for $[Mo(CO)_3Cp]_2$ at 5.27 ppm. The energy of the totally symmetric A_1 stretching mode at 2085 cm^{-1}, intermediate between 2122 cm^{-1} for 1 and 2020 cm^{-1} for $[\mu$-$(CF_3)_2C_2]Mo_2(CO)_4Cp_2$, indicates that there is more electron density on the cobalt atom than in 1 (see redox properties). It is interesting that the ν(C≡C) mode in 2 (1550 cm^{-1}) is ~50 cm^{-1} lower in energy than that in 1 and $[\mu$-$(CF_3)_2C_2]_2MoCo(CO)_3Cp$;[5] there is no apparent structural reason for this observation.

Reaction of 2 with PPh_3 in hexane gave $(Ph_3P)(CO)_2Co[\mu$-$(CF_3)_2C_2]Mo(CO)_2(\eta$-$C_5H_5)$ (3). Coordination



3

of PPh_3 to the cobalt atom is shown by the absence of ^{31}P coupling to the ^1H (η-C_5H_5) resonance at 5.27 ppm; in the complex $MoCo[(CF_3)_2C_2]_2(CO)_2Cp(PEt_3)$ where the phosphine is coordinated to Mo, J_{PH} = 1.6 Hz.[5] Further, the strong ν(CO) band at 1993 (s) cm^{-1} assigned to the $Mo(CO)_2$ group in 2 is only shifted to lower energy by 14 cm^{-1} whereas the A_1 mode of the $Co(CO)_3$ group shifts 33 cm^{-1}, a shift normally found on the formation of $[(\mu$-$CF_3)_2C_2]Co_2(CO)_5L$ derivatives.[2]

Davidson[5] has prepared a number of Co–Mo bis(μ-alkyne) and metallacyclopentadiene complexes, and it seemed that a reaction between $(CF_3)_2C_2$ and 2 would provide an alternative route to them. However, this was not the case, indicating that 2 is not an intermediate in the formation of the bis(alkyne) complexes.

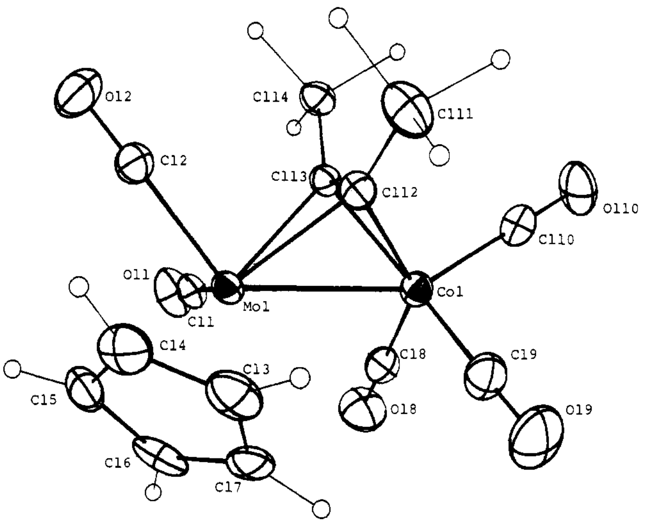


Figure 1. View of 2 (molecule 1) showing the atom numbering scheme used in the text (view approximately along the acetylene C≡C bond). Hydrogen and fluorine atoms are represented as spheres of arbitrary radius.

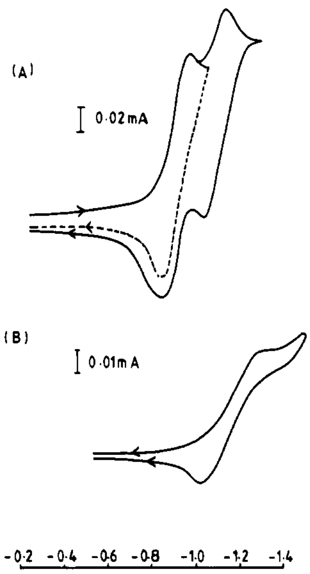


Figure 2. Cyclic voltammograms of 2 (A) and 3 (B) in acetone at 200 mV s^{-1} at Pt at 293 K (volts vs. Ag/AgCl; dashed line, CV switched at –1.0 V).

Molecular Structure of 2. Crystals of 2 consist of discrete molecules with the closest intermolecular contact, not involving hydrogen atoms, between O(21)···O(210), 3.04 Å. Figure 1 shows a general view of one of the two unique molecules in the assymmetric unit and defines the atom numbering scheme. Atoms of the second molecule are numbered similarly with all atom numbers prefixed by the Figure 2. Selected intramolecular bond lengths and angles are collected in Table III. Parameters for molecule 1 of 2 will be used in the subsequent discussion; small differences in bond lengths and angles between the two independent molecules can best be ascribed to crystal packing effects.

Molecules of 2 consist of a quasi-tetrahedral $CoMoC_2$ core with the C≡C bond of the acetylene in a perpendicular orientation, inclined at an angle of 91.5° to the Co–Mo bond. The Co and Mo atoms are linked by a Co–Mo bond of length 2.692 Å. It is interesting to note in this context that the mean of the sum of the Co–Co and Mo–Mo distances in the homometallic analogues of 2, $Ph_2C_2Co_2(CO)_6$ (d_{Co-Co} = 2.476 (2) Å)[21] and $Ph_2C_2Mo_2$-

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[19] Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

[20] Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

Table III. Selected Bond Lengths and Angles for 2

molecule 1		molecule 2	
	Bond Lengths (Å)		
Mo(1)···Co(1)	2.692 (1)	Mo(2)···Co(2)	2.696 (1)
Mo(1)···C(112)	2.116 (5)	Mo(2)···C(212)	2.105 (6)
Mo(1)···C(113)	2.138 (5)	Mo(2)···C(213)	2.135 (7)
Mo(1)···C(11)	2.031 (7)	Mo(2)···C(21)	1.962 (7)
Mo(1)···C(12)	2.007 (7)	Mo(2)···C(22)	2.116 (9)
Mo(1)···C(13)	2.329 (7)	Mo(2)···C(23)	2.332 (6)
Mo(1)···C(14)	2.303 (7)	Mo(2)···C(24)	2.302 (8)
Mo(1)···C(15)	2.306 (6)	Mo(2)···C(25)	2.298 (9)
Mo(1)···C(16)	2.324 (8)	Mo(2)···C(26)	2.324 (8)
Mo(1)···C(17)	2.345 (8)	Mo(2)···C(27)	2.347 (6)
Co(1)···C(112)	1.960 (5)	Co(2)···C(212)	1.950 (6)
Co(1)···C(113)	1.935 (5)	Co(2)···C(213)	1.940 (6)
Co(1)···C(18)	1.812 (7)	Co(2)···C(28)	1.834 (7)
Co(1)···C(19)	1.793 (7)	Co(2)···C(29)	1.784 (8)
Co(1)···C(110)	1.821 (7)	Co(2)···C(210)	1.80 (1)
C(111)···C(112)	1.455 (9)	C(211)···C(212)	1.476 (8)
C(112)···C(113)	1.371 (7)	C(212)···C(213)	1.359 (8)
C(113)···C(114)	1.481 (9)	C(213)···C(214)	1.47 (1)
C(11)···O(11)	1.123 (8)	C(21)···O(21)	1.170 (9)
C(12)···O(12)	1.121 (9)	C(22)···O(22)	1.06 (1)
C(18)···O(18)	1.127 (9)	C(28)···O(28)	1.109 (8)
C(19)···O(19)	1.138 (9)	C(29)···O(29)	1.14 (1)
C(110)···O(110)	1.119 (8)	C(210)···O(210)	1.13 (1)
	Bond Angles (deg)		
Co(1)–Mo(1)–C(112)	46.2 (1)	Co(2)–Mo(2)–C(212)	45.9 (2)
Co(1)–Mo(1)–C(113)	45.5 (1)	Co(2)–Mo(2)–C(213)	45.5 (2)
Co(1)–Mo(1)–C(11)	90.2 (1)	Co(2)–Mo(2)–C(21)	91.2 (3)
Co(1)–Mo(1)–C(12)	128.4 (2)	Co(2)–Mo(2)–C(22)	127.3 (3)
C(112)–Mo(1)–C(113)	37.6 (2)	C(212)–Mo(2)–C(213)	37.4 (2)
C(11)–Mo(1)–C(12)	88.1 (3)	C(21)–Mo(2)–C(22)	88.9 (3)
Mo(1)–Co(1)–C(112)	51.2 (2)	Mo(2)–Co(2)–C(212)	50.8 (2)
Mo(1)–Co(1)–C(113)	52.0 (1)	Mo(2)–Co(2)–C(213)	51.7 (2)
Mo(1)–Co(1)–C(18)	92.8 (2)	Mo(2)–Co(2)–C(28)	96.3 (3)
Mo(1)–Co(1)–C(19)	101.0 (2)	Mo(2)–Co(2)–C(29)	99.3 (3)
Mo(1)–Co(1)–C(110)	150.6 (2)	Mo(2)–Co(2)–C(210)	149.9 (3)
C(112)–Co(1)–C(113)	41.2 (2)	C(212)–Co(2)–C(213)	40.9 (2)
C(18)–Co(1)–C(19)	103.7 (3)	C(28)–Co(2)–C(29)	104.7 (3)
C(18)–Co(1)–C(110)	102.7 (3)	C(28)–Co(2)–C(210)	102.4 (4)
C(19)–Co(1)–C(110)	99.4 (3)	C(29)–Co(2)–C(210)	98.5 (4)
Mo(1)–C(112)–Co(1)	82.6 (2)	Mo(2)–C(212)–Co(2)	83.3 (2)
Mo(1)–C(112)–C(111)	139.6 (4)	Mo(2)–C(212)–C(211)	138.0 (6)
Mo(1)–C(112)–C(113)	72.1 (3)	Mo(2)–C(212)–C(213)	72.5 (4)
Co(1)–C(112)–C(111)	132.1 (4)	Co(2)–C(212)–C(211)	131.9 (6)
Co(1)–C(112)–C(113)	68.4 (3)	Co(2)–C(212)–C(213)	69.2 (4)
Mo(1)–C(113)–Co(1)	82.6 (2)	Mo(2)–C(213)–Co(2)	82.7 (2)
Mo(1)–C(113)–C(112)	70.3 (3)	Mo(2)–C(213)–C(212)	70.1 (4)
Mo(1)–C(113)–C(114)	138.8 (3)	Mo(2)–C(213)–C(214)	138.4 (7)
Co(1)–C(113)–C(112)	70.4 (3)	Co(2)–C(213)–C(212)	69.9 (4)
Co(1)–C(113)–C(114)	132.9 (3)	Co(2)–C(213)–C(214)	132.3 (7)
C(111)–C(112)–C(113)	133.6 (6)	C(211)–C(212)–C(213)	134.9 (6)
C(112)–C(113)–C(114)	133.8 (6)	C(212)–C(213)–C(214)	135.5 (6)
Mo(1)–C(11)–O(11)	178.6 (4)	Mo(2)–C(21)–O(21)	179.4 (8)
Mo(1)–C(12)–O(12)	177.2 (5)	Mo(2)–C(22)–O(22)	177 (1)
Co(1)–C(18)–O(18)	177.1 (7)	Co(2)–C(28)–O(28)	179.2 (8)
Co(1)–C(19)–O(19)	178.4 (7)	Co(2)–C(29)–O(29)	178.3 (5)
Co(1)–C(110)–O(110)	179.8 (2)	Co(2)–C(210)–O(210)	178.6 (8)

$(CO)_4(\eta^5\text{-Cp})_2$ (d_{Mo-Mo} = 2.956 (1) Å),[22] is 2.72 Å. Furthermore, the metal–metal separation observed here compares favorably with values reported for trinuclear clusters with Co–Mo bonds, such as $PhCCo_2Mo(CO)_8(\eta^5\text{-Cp})$[23] ($d_{Co-Mo}$ = 2.677 (1) Å). The only Co–Mo bond length reported for a dinuclear complex is 2.998 (1) [2.969 (1)] Å[24] for the two unique molecules of the cyclooctatetraene-bridged complex $(\eta^5\text{-Cp})Co(\mu\text{-}C_8H_8)Mo(CO)_3$, where extension of the Co–Mo vector is ascribed to the necessity to accommodate the bridging $\mu\text{-}C_8H_8$ ligand.

Table IV. Comparison of Structural Parameters for Dicobalt, Cobalt–Molybdenum, and Dimolybdenum Acetylene Complexes

	$Ph_2C_2Co_2$-$(CO)_6$[a]	$(CF_3)_2C_2CoMo$-$(CO)_5(\eta^5\text{-Cp})$[b]	$Ph_2C_2Mo_2$-$(CO)_4$-$(\eta^5\text{-Cp})_2$[c]
d_{M-M}/Å	2.476 (2)	2.692 (1)	2.956 (1)
$d_{M-C(acet)}$/Å	2.022 (10)	2.116 (5)	2.203 (4)
		(M = Mo)	
	1.960 (10)	2.138 (5)	2.192 (4)
	1.952 (8)	1.960 (5)	2.185 (4)
		(M = Co)	
	1.948 (8)	1.935 (5)	2.148 (4)
$d_{C\equiv C(acet)}$/Å	1.36 (1)	1.371 (7)	1.329 (6)
C—C≡C/deg	140 (1)	133.6 (6)	135.4 (4)
	140 (1)	133.8 (6)	133.8 (4)

[a] Reference 21. [b] This work. [c] Reference 22.

The overall structure of 2 is related to that of 1, by replacement of the $Co(CO)_3$ moiety by the isolobal $Mo(CO)_2(\eta^5\text{-Cp})$ unit. The coordination geometry about the cobalt atom is distorted octahedral, with the equatorial plane of the octahedron containing the two acetylene carbon atoms C(112) and C(113) and the C(18)–O(18) and C(19)–O(19) carbonyl ligands. The cobalt atom is displaced by 0.3 Å from this mean basal plane toward the pseudoaxial carbonyl group C(110)–O(110). Despite the proximity of the sterically demanding $Mo(CO)_2(\eta^5\text{-Cp})$ fragment, there is no evidence for any significant change in the geometry of the $Co(CO)_3$ moiety in comparison to that observed in a variety of $R_2C_2Co_2$ complexes.[2,21]

The $Mo(CO)_2(\eta^5\text{-Cp})$ moiety adopts a configuration reminiscent of that found in the $LMo_2(CO)_2(\eta^5\text{-Cp})_2$ molecules (L = allene,[25] $NCNMe_2$[26]) and in the nonbridging fragments of the highly assymmetric $R_2C_2Mo_2(CO)_4(\eta^5\text{-Cp})_2$ molecules.[22] The greater steric requirement of the cyclopentadienyl ligand has the effect of decreasing the C(11)–Mo(1)–C(12) angle to 88.1° compared to the corresponding C–Co(1)–C angles of the $Co(CO)_3$ group in the range 98.5–104.7°. As a result, the traditional "sawhorse" structure of the parent dicobalt acetylene is destroyed. There is however no evidence to suggest that steric crowding in the Co-Mo system is sufficiently great to cause semibridging of the Co–Mo bond as occurred with the analogous $R_2C_2Mo_2(CO)_4(\eta^5\text{-Cp})_2$ systems.[22] The pseudoaxial carbonyl C(12)–O(12) on the Mo atom is clearly not affected by interactions with the η^5-Cp ligand as the "axial" carbonyls on the adjacent metal centers are almost completely eclipsed (the dihedral angle C(12)–Mo(1)–Co(1)–C(110) is 1.5°).

The acetylene coordinates to the heterometallic system in the anticipated cis-bent, perpendicular conformation. The M–C_{ac} distances do not deviate significantly from those reported for the progenitor homonuclear systems (Table IV). The C(112)–C(113) bond is 1.371 (7) Å long which corresponds well to the values reported for other $R_2C_2Co_2$ complexes[2,21] but is longer than the values 1.329–1.337 Å reported for $R_2C_2Mo_2$ species.[22] In contrast, the angles subtended by the CF_3 substituents [C(111)–C(112)–C(113) = 113.6 (6)° and C(112)–C(113)–C(114) = 133.8 (6)°]parallel the observations from the di-

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(21) Gregson, D.; Howard, J. A. K. *Acta Crystallogr. C: Cryst. Sci. Commun.* **1983**, *C39*, 1024.

(22) (a) Bailey, W. I.; Cotton, F. A.; Jamerson, J. D.; Kolb, J. R. *J. Organomet. Chem.* **1976**, *121*, C23. (b) Bailey, W. I.; Chisholm, M. H.; Cotton, D. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764.

(23) Beurich, H.; Vahrenkamp, H. *Angew* Chem., *Int. Ed. Engl.* **1978**, *17*, 863.

(24) Salzer, A.; Egolf, T.; Linowsky, L.; Petter, W. *J. Organomet. Chem.* **1981**, *221*, 339.

(25) Bailey, W. I.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 802.

(26) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 807.

molybdenum rather than the dicobalt precursors. Electronic considerations dictate that the high acetylene "bend back" angle and the relatively long C≡C vector, observed here, are mutally exclusive in terms of the occupancy of the π and π^* orbitals.[27] It would therefore appear that the molecular parameters observed for the acetylene ligand in 2 are the result of a subtle balance between the steric and electronic requirements of the overall metal–ligand system.

Redox Properties of 2 and 3. Two closely spaced quasi-reversible polarographic reduction waves ($E_{3/4} - E_{1/4}$ = 85 and 100 mV, respectively) are observed at $E_{1/2}$ = −0.92 and −1.11 V for 2 in acetone. Cyclic voltammograms in acetone at Pt or Hg show (Figure 2) two chemically reversible couples (i_{pa}/i_{pc} = 1), but charge transfer is not diffusion-controlled for the first wave (ΔE_p is 90 mV).

The combined polarographic reduction currents correspond to a two-electron charge transfer, and this was confirmed by coulometry. Because of the small peak separation it was not possible to selectively reduce at the individual waves, but the individual polarographic currents are consistent with successive one-electron transfers. Cyclic voltammograms were satisfactorily simulated[12] by assuming that the two reduction products, formed by one-electron transfer, were each stable on the electrochemical time scale with $k_s(1)$ (heterogeneous rate constant for the first transfer) = 9×10^{-3} cm s^{-1} and $k_s(2) = 2 \times 10^{-2}$ cm s^{-1}.

Two possibilities for the electron-transfer process are (a) one-electron reduction at two noninteracting redox centers and (b) successive one-electron reduction at one redox center. The different k_s values are consistent with a charge transfer involving two redox centers of disparate molecular configuration. Comparative reduction potentials ($E_{1/2}$) for 1 and 2 are shown in equ 3 and 4. The more

$$1 + e \xrightarrow{-0.52\ V} 1^{\bullet -} \xrightarrow{-1.16\ V} 1^{2-} \qquad (3)$$

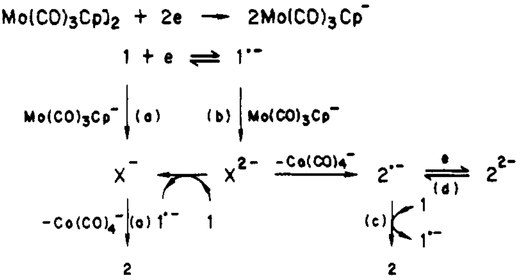
$$2 + e \xrightarrow{-0.92\ V} 2^{\bullet -} \xrightarrow{-1.11\ V} 2^{2-} \qquad (4)$$

negative primary reduction potential for 2 ($E_{1/2}$ = −0.92 V), compared to 1, is consistent with increased electron density on the metal framework through substitution of a net electron acceptor, $Co(CO)_3$, by a poorer acceptor fragment, $Mo(CO)_2Cp$. This should also decrease the potential for the reduction of a dianion relative to 1; in all carbonyl clusters studied so far[28] charge transfer to a radical anion is chemically irreversible and at a potential more than 0.5 V negative of $E_{1/2}$ for the primary charge transfer. For the reasons above we prefer option a where the first electron enters a LUMO orbital centered on the metal/alkyne framework and the second transfers to the Mo–(η-C_5H_5) group.

$$(CO)_3Co[\mu\text{-}(CF_3)_2C_2]Mo(CO)_2Cp \underset{}{\overset{-0.92\ V}{\rightleftharpoons}} (CO)_3Co^{\bullet -}[\mu\text{-}(CF_3)_2C_2]Mo(CO)_2Cp \overset{-1.11\ V}{\rightleftharpoons} (CO)_3Co^{\bullet -}[\mu\text{-}(CF_3)_2C_2]Mo(CO)_2Cp^{\bullet -} \qquad (5)$$

Support for this electron-transfer sequence comes from the electrochemistry of 3. With this molecule only one quasi-reversible two-electron reduction wave is observed (Figure 2) at $E_{1/2}$ = ∼−1.15 V; i_{pa} is marginally greater than i_{pc} at 200 mV s^{-1}, but the ratio i_{pa}/i_{pc} is dependent on scan rate. These observations are explicable in terms of (5). Coordination of Ph_3P to the cobalt atom should decrease $E_{1/2}$ by ∼0.2 V,[29] and thus the two waves merge; a slow ECE reaction following the first charge transfer, common[11] in the electrochemistry of cluster/phosphine derivatives, would cause the observed variation of i_{pa}/i_{pc} with scan rate.

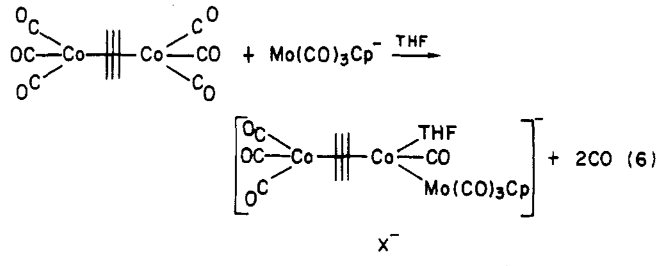
Scheme I



Alkali-metal or electrolytic reduction of 2 in an ESR cavity gave a weak signal at $\langle g \rangle \approx 2.00$ which is likely to be due to an organic decomposition product, but we could not detect a paramagnetic species showing coupling to cobalt or molybdenum. Note that an ESR signal from $2^{\bullet -}$ is expected to be extremely broad given the number of isotopes of Mo with $I > {}^1/_2$ and the esr characteristics of cluster radical anions.[28]

Pathway to 2. Synthesis of 2 using BPK (reaction 1) arose from an expectation that metal carbonyl anions could function as nucleophiles in electron transfer chain catalyzed pathways. A mechanism for the ETC pathway is shown in Scheme I (X is the initial product of nucleophilic substitution).

A detailed analysis of the i–E responses over a wide scan range from CH_2Cl_2 or THF solutions containing 1 and $Mo(CO)_3Cp^-$ did not reveal waves attributable to 2 showing that the chain length, if indeed it is an ETC reaction, is very short.[30] Similarly, the controlled potential reduction of 1 in the presence of $[Mo(CO)_3Cp]_2$ did not give 2. Direct exchange of $Co(CO)_4^-$ and $Mo(CO)_3Cp^-$ clearly takes place at elevated temperatures in THF (but not benzene) presumably via prior coordination of $Mo(CO)_3Cp$ (pathway a). Indeed, the common green intermediate noted in both the BPK and thermal reaction with ν(CO) at 2069, 2024, 2010, and 2006 cm^{-1} could be attributed to intermediate X and the ubiquitous THF could also assist in CO dissociation. The difficulty with this assignment is that an A_1 ν(CO) mode at 2069 cm^{-1} suggests that *two* CO groups of 1 are replaced,[2] and it may be that both THF and $Mo(CO)_3Cp^-$ are coordinated (eq 6).



The thermal reaction between $Mo(CO)_3Cp^-$ and 1 is negligible at room temperature, so the initiation of reaction 1 by BPK is not simply a reduction of $[Mo(CO)_3Cp]_2$ to produce the anion. We suggest that BPK does initiate the ETC cycle pathway b via an activated radical anion $1^{\bullet -}$, but as noted above, the chain is truncated to the extent that it is an electron-induced rather than ETC-catalyzed reaction and the yield is poor. Providing the rates of electron transfer for pathways c and d are comparable, the accessibility of a second reversible couple (pathway d) could truncate the whole cycle. The small concentration

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[27] Hoffman, D. M.; Hoffman, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858.

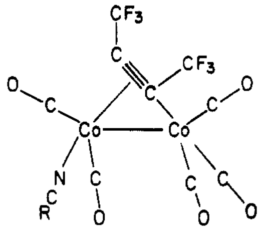
[28] Lindsay, P. N. T.; Peake, B. M.; Robinson, B. H.; Simpson, J.; Honrath, U.; Vahrenkamp, H.; Bond, A. M. *Organometallics* **1984**, *3*, 413.

[29] Arewgoda, C. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J.; Visco, S. *J. Am. Chem. Soc.* **1982**, *104*, 5633.

[30] Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771.

of $1^{\cdot -}$ generated electrochemically would prevent an efficient reaction by this means of activation.

We had considered that the preparation of 2 might involve carbonyl radicals,[31] but there was no evidence for this suggestion. Instead, the product from an AIBN-initiated reaction using 1 and $[Mo(CO)_3Cp]_2$ was the new labile derivative $[(CF_3)_2C_2]Co_2(CO)_5[NCC(CH_3)_2N_2C(CH_3)_2CN]$ (4). This formulation is based on analysis, mass spectra, and IR spectra. A structure in which the nitrile is coordinated in a pseudoequatorial position is suggested by the identical profile and energy of the ν(CO) bands of 4 and those of $[(CF_3)_2C_2]Co_2(CO)_5(NCCH_3)$.[2]



4, R ≡ CMe$_2$N$_2$CMe$_2$CN

Conclusion

While this particular synthesis to give 2 does not represent another example of a ETC-catalyzed attack on a carbonyl substrate by a metal carbonyl nucleophile, it is clear that heteronuclear carbonyl complexes are accessible via this route even when the metal–metal bond in the reactant is "clamped" by an organic moiety. In the system described herein the chain is terminated because of a second reversible reductive charge transfer in the product. We are currently studying other systems where this problem is not met.

Registry No. 1, 37685-63-5; 2, 102735-96-6; 3, 102735-97-7; 4, 102735-98-8; AIBN, 78-67-1; BPK, 119-61-9; $[Mo(CO)_3Cp]_2$, 12091-64-4; PPh_3, 603-35-0; Co, 7440-48-4; Mo, 7439-98-7.

Supplementary Material Available: Tables of positional and thermal parameters, structure factors, bond lengths and angles, and least-squares plane for 2 and a view of the second molecule of 2 (27 pages). Ordering information is given on any current masthead page.

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[31] A radical pathway has been demonstrated in the synthesis of some FeCo clusters. Horwitz, C. P.; Holt, E. M.; Shriver, D. F. *Organometallics* 1985, *4*, 1117.

Tungsten Carbonyl Isocyanide Carbene Complexes: A Structural and Spectroscopic Study of Three Types of Metal–Carbon Bonds in the Same Molecule

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The syntheses, spectroscopic characterization, and X-ray structural determinations of $(CO)_4W(C(OCH_3)(C_6H_5))(CNC_6H_4\text{-}p\text{-}CH_3)$ (**1**) and $(CO)_4W(C(OCH_3)(C_6H_5))(CNC(CH_3)_3)$ (**2**) are reported. Data from related complexes are also presented in order to compare differences in metal–carbon bonding in W–CO, $W–C_{CAR}$, and $W–C_{CNR}$ bonds in the complexes. The X-ray crystal structures of both molecules reveal that the carbene ligand is cis to the isocyanide ligand with W–CO distances significantly shorter than the other W–C distances in each complex. Crystal data for **1**: space group *Pbca* (No. 61); $Z = 8$, $a = 21.172$ (3) Å, $b = 22.463$ (3) Å, $c = 8.322$ (2) Å; $V = 3957.9$ (9) Å^3; $R = 0.038$, $R_w = 0.030$. Crystal data for **2**: space group $P2_1/n$ (No. 14); $Z = 4$, $a = 16.709$ (2) Å, $b = 9.425$ (2) Å, $c = 12.823$ (2) Å; $\beta = 111.52$ (3)°; $V = 1875.8$ (5) Å^3; $R = 0.047$, $R_w = 0.045$. Carbonyl force constants, ^{13}CO chemical shifts, tungsten–carbon coupling constants, and metal–carbon bond lengths all indicate that carbon monoxide is as an overwhelming π acid in the molecules. Both isocyanide ligands appear to be much weaker π acceptors, while phenylmethoxycarbene is primarily a σ donor.

Introduction

Carbonyl, isocyanide, and carbene ligands all possess donor lone pairs and exhibit orbitals with proper symmetry for potential overlap with occupied t_{2g} orbitals on a pseudooctahedrally coordinated low-valent transition-metal center. Thus all three ligand types are capable of dative bonding, an observation which has led many investigators to speculate on their comparative σ donor/π acceptor abilities.[1] Zerovalent transition-metal carbonyl carbenes have been the subject of theoretical, crystallographic, and spectroscopic studies,[2] while zerovalent transition-metal carbonyl isocyanides have been studied theoretically, spectroscopically, and electrochemically.[3]

Each ligand experiences different effects upon coordination, and while generalizations are probably not entirely appropriate, carbon monoxide is usually found to be more reactive when coordinated to zerovalent metals,[4] while coordinated isocyanides are ordinarily stabilized.[5] Of the

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(1) (a) Mills, O. S.; Redhouse, A. D. *J. Chem. Soc. A* **1968**, 642. (b) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127. (c) Guy, M. P.; Guy, J. T.; Bennett, D. W. *J. Mol. Struct.* (*Theochem.*) **1985**, *122*, 95.

(2) (a) Guy, J. T., Jr.; Guy, M. P.; Bennett, D. W. *J. Mol. Struct.* (*Theochem.*), in press. (b) Schubert, U. *Coord. Chem. Rev.* **1984**, *55*, 261. (c) Bodner, G. M.; Kahl, S. B.; Bork, K.; Storhoff, B. N.; Wuller, J. E.; Todd, L. J. *Inorg. Chem.* **1973**, *12*, 1071. (d) Kohler, F. H.; Kalder, H. J.; Fischer, E. O. *J. Organomet. Chem.* **1976**, *113*, 11.

(3) (a) Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* **1975**, *14*, 247. (b) King, R. B.; Saran, M. S. *Inorg. Chem.* **1974**, *13*, 74. (c) Treichel, P. M.; Firsich, D. W.; Essenmacher, G. P. *Inorg. Chem.* **1979**, *18*, 2405.

(4) Fischer, E. O.; Shubert, U.; Kleine, W.; Fischer, H. *Inorg. Synth.* **1979**, *19*, 164.