*Organometallics* 1984, *3*, 180–182

# Regioselectivity of Electron-Transfer Chain Reactions of Metal Carbonyl Clusters with Polydentate Ligands. A Derivative with a Semibridging Carbonyl[1]

**Robert G. Cunninghame, Alison J. Downard,**
**Lyall R. Hanton, Simon D. Jensen, Brian H. Robinson,***
**and Jim Simpson***

*Department of Chemistry, University of Otago*
*Dunedin, New Zealand*

*Received August 17, 1983*

*Summary:* Controlled ETC reaction of dinuclear and trinuclear metal carbonyl clusters with polydentate ligands allows sequential and regioselective coordination; a novel derivative $(CF_3)_2C_2Co_2(CO)_3$(ttas) (ttas ≡ $\{o\text{-}C_6H_4[AsMe_2]\}_2AsMe$) with three arsenic atoms coordinated to one cobalt and a semibridging carbonyl group is reported.

Synthetic strategies based on the concept of electron-transfer chain (ETC) catalyzed nucleophilic substitution of metal carbonyl clusters have been proposed[2,3] and successfully implemented.[3,4] The nucleophiles have included monodentate Lewis bases[2-4] and metal carbonylate anions,[5] regioselectivity with monodentate ligands has also been achieved.[6] Regioselectivity is also feasible for polydentate ligands. Stabilization of a 17-electron site created in an ETC process (see ref 2) by the coordination of *one* donor atom of the polydentate ligand should encourage coordination of a second donor atom at the same metal atom, rather than at a different metal atom in the cluster. Besides achieving regioselectivity, ETC reactions of this type using specific electrochemical initiation rather than nonspecific chemical initiation offer the possibility of controlled syntheses of labile Lewis base derivatives. Herein we describe sequential regioselective syntheses of polydentate Lewis base complexes of $(CF_3)_2C_2Co_2(CO)_6$ and the structure of a novel derivative with a semibridging carbonyl group caused by the specific chelation at one metal atom. The generality of this synthetic strategy is explored.

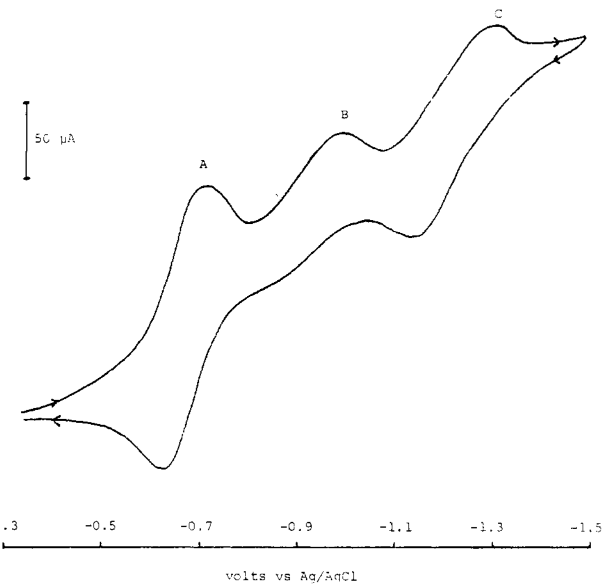


**Figure 1.** Cyclic voltammogram of $(CF_3)_2C_2Co_2(CO)_6$ and ttas (1:1 mole ratio) in $CH_2Cl_2$ at 293 K (potentials vs. Ag/AgCl standardized against $PhCCo_3(CO)_9$; scan rate 200 mV $s^{-1}$, on Pt). A is the couple $(CF_3)_2C_2Co_2(CO)_6^{0,-1}$; B and C are attributed to I and II respectively.

In order to optimize the regioselectivity, we studied the system $(CF_3)_2C_2Co_2(CO)_6$/ttas where ttas ($\{o\text{-}C_6H_4[AsMe_2]\}_2AsMe$) is a potential tridentate ligand with a "bite" that would not favor the formation of derivatives in which the Lewis base links two or more clusters.[7,8] A cyclic voltammogram for this system in $CH_2Cl_2$ is shown in Figure 1. On the addition of 1 mol equiv of ligand two new electrode processes (B and C) can be identified at $E_P{}^{red}$ = −0.95 and −1.24 V, respectively. The relative peak currents of the reactant and product couples are dependent on the concentration of ttas, scan rate, and temperature, behavior typical of rapid ETC substitution.[2,3,9] Assignments for couples B and C can be made by using the substituent parameter for an $Me_xAs$ ($x$ = 1, 2) group.[10] Thus the number of arsenic atoms coordinated to the cluster for B and C are 1 and 2, respectively, corresponding to the formation of the compounds $(CF_3)_2C_2Co_2(CO)_5$ (ttas) (I) and $(CF_3)_2C_2Co_2(CO)_4$ (ttas) (II).

These observations are consistent with the preparative and coulometric work summarized in Scheme I.[11,12] Stoichiometric reduction of II at −1.0 V gave a third product,[13] $(CF_3)_2C_2Co_2(CO)_3$(ttas) (III). This is an excellent example of controlled sequential donor coordination, and product I is not accessible by thermal or photochemical routes. The efficiency of the electrocatalytic chelation decreases along the sequence until the conversion II → III

---

(1) Electron transfer in metal carbonyl clusters. 6. Part 5: see ref 5.

(2) (a) Bezems, G. J; Rieger, P. H.; Visco, S. J. *J. Chem. Soc., Chem. Commun.* 1981, 265. (b) Arewgoda, M; Rieger, P. H.; Robinson, B. H.; Simpson, J.; Visco, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 5633.

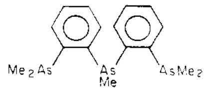
(3) Arewgoda, M.; Robinson, B. H.; Simpson, J. *J. Am. Chem. Soc.* **1983**, *105*, 1893.

(4) (a) Darchen, A.; Mahe, C.; Patin, H. *J. Chem. Soc., Chem. Commun.* **1982**, 243. (b) Bruce, M. I.; Kehoe, D. C.; Matisons, J. G.; Nicholson, B. K.; Rieger, P. H.; Williams, M. L. *Ibid.* **1982**, 442.

(5) Jensen, S. D.; Robinson, B. H.; Simpson, J. *J. Chem. Soc., Chem. Commun.*, **1983**, 1081.

(6) Arewgoda, M.; Robinson, B. H.; Simpson, J. *J. Chem. Soc., Chem. Commun.* **1982**, 284.

(7) ttas ≡



≡ $\{o\text{-}C_6H_4[As(CH_3)_2]\}_2AsCH_3$. The preferred bite for this ligand is ~81°.[8]

(8) (a) Blundell, T. L.; Powell, H. M. *J. Chem. Soc. A* **1971**, 1685. (b) Cunninghame, R. G.; Hanton, L. R., structures to be published.

(9) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 3034.

(10) Robinson, B. H.; Simpson, J., manuscript in preparation. The following relationship holds for a wide variety of cluster derivatives: $E_{1/2}(C\text{–}L) = E_{1/2}(C) - \delta_L N$ where $E_{1/2}(C\text{–}L)$ and $E_{1/2}(C)$ are the respective reduction potentials for the substituted and parent cluster, $N$ is the number of donor atoms bound to the cluster, and $\delta_L$ is the substituent parameter for the ligand. $\delta_{Me_xAs} = 0.26$ V.

(11) I: orange, $\nu$(CO) (hexane) 2093 (s), 2049 (vs), 2037 (vs), 2002 (m) $cm^{-1}$; very labile in solution and an analytically pure sample has not been isolated. II: green; mp 135 °C; Calcd for $C_{25}H_{23}O_4As_3F_6Co_2$: C, 35.55; H, 2.73. Found: C, 35.98; H, 2.77. $\nu$(CO) (hexane) 2075 (vs), 2029 (s), 1980 (s) $cm^{-1}$. The $^1H$ NMR of I and II are consistent with their assigned structures. Complex II has been structurally characterized as having equatorial/axial arsenic coordination on a single cobalt atom: space group $P2_1/c$; $a$ = 12.563 (2) Å, $b$ = 15.166 (2) Å, $c$ = 17.995 (3) Å, $\beta$ = 144.74 (1); current refinement $R$ = 0.1195; 1784 reflections $[F^2 > 3\sigma(F^2)]$.

(12) A typical[3] three-electrode system with a Pt basket working electrode was used: solvent, $CH_2Cl_2$; supporting electrolyte TBAP ($\sim 5 \times 10^{-2}$ mol $dm^{-2}$). The initial potential was −0.4 V vs. Ag/AgCl to produce I (at 0 °C to retard the rapid conversion of I → II). II was isolated in 100% yield at a potential of −0.6 V vs. Ag/AgCl. The workup procedure was that given in ref 3. The compounds are soluble in hexane and can be purified by preparative TLC using hexane/ether/$CH_2Cl_2$ (10:1:1) as eluent. The reaction of $(CF_3)_2C_2Co_2(CO)_6$ with ttas, initiated by catalytic amounts of BPK, gives II with only traces of I.

0276-7333/84/2303-0180$01.50/0 © 1984 American Chemical Society

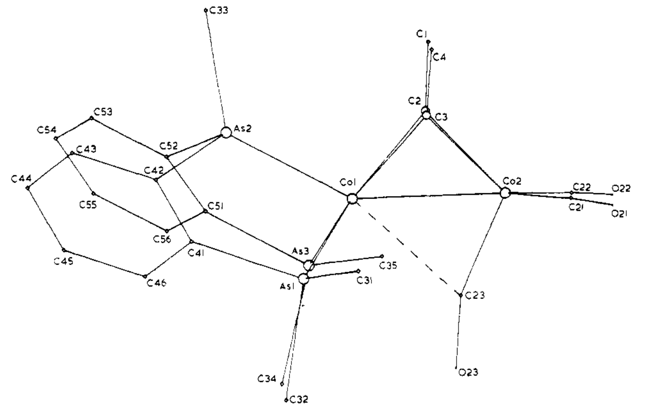
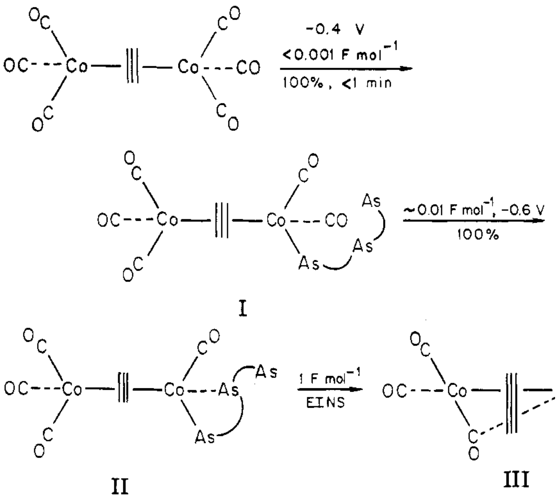


**Figure 2.** Molecular structure of III viewed down the C2–C3 bond of the acetylene ligand. The semibridging carbonyl interaction Co1–C23 is represented by a dashed line. Bond lengths (Å): Co1–Co2 = 2.454 (3), Co1–As1 = 2.311 (3), Co1–As2 = 2.280 (2), Co1–As3 = 2.316 (3), Co2–C21 = 1.77 (3), Co2–C22 = 1.78 (3), Co2–C23 = 1.79 (2), Co1–C23 = 2.33 (2), Co1–C2 = 1.92 (2), Co2–C2 = 1.94 (2), Co1–C3 = 1.93 (2), Co2–C3 = 1.92 (2), C2–C3 = 1.34 (2).

Scheme I[a]



[a] $CF_3$, Me, and Ph groups omitted for clarity.

requires 1 F $mol^{-1}$ and is simply an electron-induced nucleophilic substitution (EINS).[14]

Complex III has the structure[15] shown in Figure 2. All arsenic donor atoms chelate to a *single* cobalt atom, a configuration previously unknown in metal carbonyl cluster compounds. The coordination geometry around the substituted cobalt atom Co1 can be described in terms of a distorted octahedron, with the central arsenic atom of the ligand occupying a pseudoaxial site and the outer arsenic atoms pseudoequatorial coordination sites. In contrast, the coordination sphere of the second cobalt atom is a distorted trigonal prism with the three carbonyl ligands defining the outer triangular face of the prism and the C2–C3 bonds of the acetylene together with the notional coordination site of the "bent" Co–Co bond[16] defining the other; this latter face is shared by the Co1 octahedron. An immediate result of the quasi-prismatic arrangement of ligands around Co2 (Figure 2) is that the carbonyl and arsenic substituents of the molecule adopt an approximately staggered conformation. This is a new arrangement for dicobalt acetylene complexes[3] but is reminiscent of the configuration found in the complex $(t\text{-}Bu_2C_2)Fe_2(CO)_6$.[17] Figure 2 reveals a further unusual feature of the complex. The carbonyl ligand C23–O23 bends toward the Co1 atom such that the Co2–C23–O23 angle is reduced to 160 (2)° and the Co1–C23 contact is 2.33 (2) Å characteristic of a *semibridging carbonyl group.* These are found[18] in dinuclear and cluster metal–metal bonded systems in which the ligand environment is fundamentally unsymmetrical, either as a result of an asymmetric distribution of electron density in the molecule or due to an exceptionally cluttered environment for the affected carbonyl group. The lack of any unusually close intramolecular contacts in III precludes rationalization of the minimum energy structure on steric grounds.[19] However, the replacement of three CO ligands by donor atoms of reduced $\pi$-acceptor ability results in a buildup of charge density on Co1. We therefore believe that the molecular rearrangement accompanying the coordination of ttas is an attempt by the molecule to equalize the charge distribution between the two cobalt atoms.

Preliminary results indicate that the sequential coordination and regioselectivity achieved with ttas according to Scheme I can be extended to other polydentate ligands and polynuclear metal carbonyl substrates. Such reactions proceed via labile intermediates where the substrate is only partially ligated. Indeed, these "dangling" products analogous to I can be identified as the kinetically preferred products with all polydentate ligands and carbonyl cluster substrates so far investigated.[20,21] However the thermodynamically preferred structure, and hence the isolated compound, depends on the steric and electronic requirements of the substrate and the "bite" of the ligand. For example, the controlled ETC reaction of $PhCCo_3(CO)_9$[22] with a ligand with a flexible "bite", such as dppe, gives IV rather than a "dangling" product. The formation of IV represents a *chain-terminating step* and has a deleterious effect on the catalytic efficiency of the substitution process.[23] In contrast, dppm with a much tighter "bite" gives analogues of I by a more efficient chain-catalyzed process.

---

[13] III: purple needles: mp 206 °C; $\nu$(CO) (hexane) 2054 (s), 2031 (vs), 1990 (s) $cm^{-1}$. Calcd for $C_{24}H_{23}O_3As_3F_6Co_2$: C, 35.30; H, 2.82. Found: Found: C, 36.26; H, 3.45. These bands are very solvent dependent, and from the profile it seems that the compound may exist in two isomeric forms in solution (unpublished work). In KBr the bands are at 2024 (vs), 1979 (s), and 1865 (m) $cm^{-1}$; the latter band is assigned to the semibridging CO group. The $^1H$ and $^{13}C$ NMR spectra are complex due to the nonrigidity of the molecule in solution.

[14] A thermal reaction in THF or hexane gives product III in yields comparable to those from ETC reactions. Small yields of II are found in these reactions.

[15] Crystal data: space group *Pbca*; $a$ = 18.375 (5) Å, $b$ = 18.190 (3) Å, $c$ = 17.067 (6) Å; $V$ = 5704 Å$^3$; $Z$ = 8, $\sigma_{measd}$ = 1.87 (3) g $cm^{-3}$; $\rho_{calcd}$ = 1.90 g $cm^{-3}$. The structure was solved by direct methods. Least-squares refinement on 1896 reflections [$F^2 > 2.5\sigma(F^2)$] produced the residual $R$ = 0.056 and $R_w$ = 0.047. Details of the cystallographic work are contained in the supplementary material (Tables S1–S5).

[16] Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *J. Am. Chem. Soc.* **1980**, *102*, 156.

[17] Cotton, F. A.; Jameson, J. D.; Shults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 1774. In this structure the staggered conformation is ascribed to the minimization of intramolecular nonbonded contacts between CO groups held in close proximity by a formal Fe=Fe double bond.

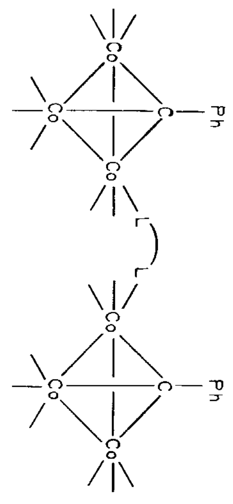
[18] Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1.

[19] All bond lengths and bond angles, both within the tri(tertiary arsine) ligand and between the arsenic atoms and Co1, lie within the ranges found in other compounds where the donor atoms occupy the corners of a triangular face.[8]

[20] The substrates include $YCCo_3(CO)_9$ (Y = Me, Ph, Cl, H), $M_3(CO)_{12}$ (Ru, Os), $R_2C_2Co_2(CO)_6$, $(CF_3)_6C_6Co_2(CO)_4$, $M_4(CO)_{12}$ (Rh, Ir), $H_4Ru_4(CO)_{12}$, and L = dppm, dppe, and ttas. Preparative BPK reactions of $Ru_3(CO)_{12}$ have been investigated by Bruce, Nicholson, and co-workers.[21]

[21] Bruce, M. I.; Hambley, T. W.; Nicholson, B. K.; Snow, M. R. *J. Organomet. Chem.* **1983**, *247*, 321.

[22] Electrolysis potential –0.38 V vs. Ag/AgCl in $CH_2Cl_2$; 90% yield; current efficiency to "dangling" intermediate <0.01 F $mol^{-1}$; $\nu$(CO) (hexane) 2078 (s), 2036 (vs), 2026 (vs), 2017 (s), 1992(m), 1967 (w) $cm^{-1}$. Structure confirmed by preliminary X-ray analysis.



IV, L-L = $Ph_2PCH_2CH_2PPh_2$

Detailed electrochemical and structural studies are underway on these systems together with an investigation of the ligand constraints leading to semibridging carbonyl coordination, but the feasibility of controlled sequential coordination of a polydentate ligand has been demonstrated. Obviously, these observations are relevant to the in situ production of labile species with catalytic potential.

**Registry No.** I, 87828-96-4; II, 87828-97-5; III, 87828-98-6; IV, 87828-99-7; $(CF_3)_2C_2Co_2(CO)_6$, 37685-63-5; $PhCCo_3(CO)_9$, 13682-03-6; Co, 7440-48-4.

**Supplementary Material Available:** Tables of crystal data (Table S1), positional and thermal parameters for non-hydrogen atoms (Table S2), positional and thermal parameters of calculated hydrogen atoms (Table S3), bond lengths and angles (Table S4), and observed and calculated structure factors (Table S5) (16 pages). Ordering information is given on any current masthead page.

---

(23) IV undergoes an electrochemically irreversible two-electron reduction at −0.71 V vs. Ag/Ag Cl.

---

## Oxidative-Addition Processes in the Reactions of $(OC)_4Fe^{-}\cdot$ with $XCY_3$ Molecules

**Richard N. McDonald,* Philip L. Schell, and William D. McGhee**

*Department of Chemistry, Kansas State University*
*Manhattan, Kansas 66506*

*Received September 29, 1983*

*Summary:* The major or exclusive product channel in the gas-phase reactions of $(OC)_4Fe^{-}\cdot$ with $ICF_3$, $BrCF_3$, $BrCCl_3$, and $CCl_4$ was halogen atom transfer, but minor amounts of product ions of oxidative addition with loss of one and two CO ligands were observed with the first two neutrals. Rate constants were determined, and mechanisms are discussed.

Although the preparation and reactions of $(OC)_4Fe^{2-}$ (Collman's reagent) are well documented,[1] the chemistry of the oxidized species $(OC)_4Fe^{-}\cdot$ has remained a mystery since, in the condensed phase, this 17-electron anion radical has only been oberved in a matrix.[2] However, various transition-metal carbonyl anion radicals ($(OC)_{x-1}M^{-}\cdot$) are available in the gas phase by dissociative electron attach-

Table I. Summary of Kinetic and Product Studies of the Reactions of $(OC)_4Fe^{-}\cdot$ with Halogenated Methanes

| rxn | ion + neutral reactant ($Y_3CX$) | products [assumed neutral] | fractn of product ion signal | $k_{total}$,[a] $cm^3\ molecule^{-1}\ s^{-1}$ | $D°(Y_3C\text{-}X)$,[b] kcal/mol | $EA(Y_3CX)$,[c] kcal/mol |
|---|---|---|---|---|---|---|
| 1 | $(OC)_4Fe^{-}\cdot + CH_3I \rightarrow$ | no reaction | | $\leqslant 10^{-13}$ | 56.1 | 5 ± 2 |
| 2a | $(OC)_4Fe^{-}\cdot + ICF_3 \rightarrow$ | $(OC)_4FeI^-$ [+ $\cdot CF_3$] | 0.88 | $4.6 \times 10^{-10}$ | 53.6 | 36 ± 5 |
| 2b | $\rightarrow$ | $(OC)_3Fe(I)CF_3^{-}\cdot$ [+ CO] + $(OC)_2Fe(I)CF_3^{-}\cdot$ [+ 2CO][d] | 0.12 | | | |
| 3a | $(OC)_4Fe^{-}\cdot + BrCF_3 \rightarrow$ | $(OC)_4FeBr^-$ [+ $\cdot CF_3$] | 0.73 | $1.7 \times 10^{-12}$ | 69.2 | 21 ± 5 |
| 3b | $\rightarrow$ | $(OC)_3Fe(Br)CF_3^{-}\cdot$ [+ CO] + $(OC)_2Fe(Br)CF_3^{-}\cdot$ [+ 2CO][d] | 0.27 | | | |
| 4 | $(OC)_4Fe^{-}\cdot + ClCF_3 \rightarrow$ | no reaction | | $\leqslant 10^{-13}$ | 85.5 | |
| 5 | $(OC)_4Fe^{-}\cdot + CCl_4 \rightarrow$ | $(OC)_4FeCl^-$ [+ $\cdot CCl_3$] | 1.00 | $7.7 \times 10^{-12}$ | 72.9 | |
| 6 | $(OC)_4Fe^{-}\cdot + BrCCl_3 \rightarrow$ | $(OC)_4FeBr^-$ [+ $\cdot CCl_3$] | 1.00 | $2.3 \times 10^{-10}$ | 54.7 | |

[a] $k_{total}$'s are estimated to be accurate to ±30%. [b] Reference 7. [c] Janousek, B. K.; Brauman, J. I. In "Gas Phase Ion Chemistry", Bowers, M. T., Ed.; Academic Press: New York 1979; Vol. 2, Chapter 10. [d] The structure assignment for the anion radical is discussed in the text.

---

(1) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342–347.

(2) Burdett, J. K. *J. Chem. Soc., Chem. Commun.* **1973**, 763–764. Breeze, P. A.; Burdett, J. K.; Turner, J. J. *Inorg. Chem.* **1981**, *20*, 3369–3378 and references therein.

© 1984 American Chemical Society