(2-Indenyl)ferrocene (4): yield 0.36 g (12%). Anal. Calcd for $C_{19}H_{16}Fe$ (M_r 300.18): C, 76.02; H, 5.37. Found: C, 76.37; H, 5.21. ^1H NMR ($CDCl_3$): δ 3.62 (s, CH_2), 4.06 (s, C_5H_5), 4.28 ("t", J = 1.8 Hz, C_5H_4), 4.52 ("t", J = 1.8 Hz, C_5H_4), 6.79 (s, CH), 7.08–7.30 (m, 3 ArH), 7.39 (d, ^3J = 7.2 Hz, 1 ArH). ^{13}C NMR ($CDCl_3$): δ 39.80 (CH_2), 66.40 (C_5H_4), 68.99 (C_5H_4), 69.39 (C_5H_5), 80.88 (C_5H_4-indenyl), 119.88, 123.44, 123.68, 123.86, 126.54 (sp^2 indenyl-CH), 142.53, 145.96, 146.41 (sp^2 indenyl-C).

Synthesis of Bis(1-ferrocenyl-3,4-dimethylcyclopentadienyl)ferrocene (5). To a stirred solution of (3,4-dimethylcyclopenta-1,3-dienyl)ferrocene (278 mg, 1 mmol) in THF at 0 °C was added dropwise BuLi (0.4 mL, 2.5 M in hexane), followed after 30 min by $FeCl_2$ (63 mg, 0.5 mmol). After 12 h at room temperature the volatiles were removed in vacuo, the solid was washed with 25 mL of *n*-hexane, and the product was extracted with CH_2Cl_2. The CH_2Cl_2 was stripped in vacuo and the remaining orange solid recrystallized from toluene/*n*-hexane: yield 230 mg (38%). Anal. Calcd for $C_{34}H_{34}Fe_3$ (M_r 610.2): C, 66.93; H, 5.62. Found: C, 66.94; H, 5.66. ^1H NMR (C_6D_6): δ 1.71 (s, CH_3), 3.71 (s, CH in $C_5H_2(CH_3)_2$), 3.94 (s, C_5H_5), 4.13 ("t", J = 1.7 Hz, CH in C_5H_4), 4.22 ("t", J = 1.7 Hz, CH in C_5H_4). ^{13}C NMR (C_6D_6): δ 12.13 (CH_3), 65.85 (CH in Cp), 67.82 (CH in Cp), 69.21 (CH in Cp), 69.55 (C_5H_5), 81.72 (C in Cp), 82.92 (C in Cp), 84.11 (C in Cp).

Reaction of the Dilithio Salt of 2 with $FeCl_2$. To a stirred solution of 1,1′-bis(3,4-dimethylcyclopenta-1,3-dienyl)ferrocene (200 mg, 0.54 mmol) in THF at 0 °C was added dropwise BuLi (0.43 mL, 2.5 M in hexane), followed after 30 min by $FeCl_2$ (68 mg, 0.54 mmol). After 12 h at room temperature the volatiles were removed in vacuo, the solids were washed with 25 mL of *n*-hexane, and the product was extracted with CH_2Cl_2. After evaporation of the solvent an orange powder stayed behind. Anal. Calcd for the polymer $(C_{24}H_{26}Fe_2)_x$: C, 67.46; H, 6.15. Found: C, 66.20; H, 5.86. ^1H NMR ($CDCl_3$): δ 1.45 (bs, 6 H), 3.64 (bs, 2 H), 5.00 (b, 2 H), 5.08 (b, 2 H).

Crystal Structure Determination of Compound 2. Crystals of compound 2 were grown by slowly cooling a diethyl ether solution. Crystallographic data, positional and thermal parameters, and bond distances and angles of 2 are collected in Tables I–III. All software used is included in the SHELXTL PLUS (PC-Version) package.[18] The lack of systematic absences determined the triclinic crystal system. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. An absorption correction was applied (ψ scans[19]). The structure was solved by direct methods and refined by full-matrix least squares. The distribution of the E statistics seemed to indicate the acentric space group *P1*, in which the structure was initially solved and refined. Choosing the centrosymmetric alternative $P\bar{1}$, however, gave chemically more reasonable results and was therefore considered the correct solution. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were localized on the final Fourier map and fixed isotropic.

Acknowledgment. I wish to thank Prof. H. Vahrenkamp for generous support and a reviewer for valuable comments on the X-ray structure.

Registry No. 1, 140175-32-2; 2, 140175-33-3; 3, 140175-34-4; 3a, 140175-36-6; 4, 140175-35-5; 5, 140201-41-8; dilithioferrocene, 33272-09-2; 3,4-dimethylcyclopentenone, 84627-96-3; 1-indanone, 83-33-0; 2-indanone, 615-13-4.

Supplementary Material Available: A table giving the structure determination summary and complete lists of bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates (7 pages). Ordering information is given on any current masthead page.

OM9105942

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[18] Sheldrick, G. M. SHELXTL-PLUS (PC-Version), Universität Göttingen, 1990.

[19] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 359.

Cluster-Bound Ketenylidenes as Precursors to Dicarbide Ligands: Synthesis and Characterization of $[PPN][Fe_3Co_3(C_2)(CO)_{18}]$

Michael P. Jensen, David A. Phillips,[†] Michal Sabat,[‡] and Duward F. Shriver*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

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The triiron acetylide cluster compound $[PPN][Fe_3(CO)_9CCOAc]$ (1) [PPN = bis(triphenylphosphine)nitrogen(1+), $(Ph_3P)_2N^+$] reacts with $[Fe(CO)_4]^{2-}$ to produce the metalated acetylide cluster $[PPN]_2[Fe_3(CO)_9CCFe(CO)_4]$ (2). Further metalation of 2 with excess $Co_2(CO)_8$ produces a hexametallic dicarbido cluster $[PPN][Fe_3Co_3(C_2)(CO)_{18}]$ (5). The reaction proceeds by formation of two intermediate compounds, the dicarbide-containing cluster compound $[PPN]_2[Fe_4Co_2(C_2)(CO)_{18}]$ (3) and the acetylide $[PPN][Fe_2Co(CO)_9CCFe(CO)_4]$ (4). Compound 4 also forms in moderate yield directly from 1, and the reaction of 5 with $[Fe_2(CO)_8]^{2-}$ regenerates 3. $[PPN][Fe_3Co_3(C_2)(CO)_{18}]$ (5) was the subject of a single-crystal X-ray structure determination. The compound crystallizes in the space group $P2_1/c$ (No. 14), with a = 15.878 (2) Å, b = 29.774 (4) Å, c = 11.930 (1) Å, β = 90.32 (1)°, V = 5640 (2) Å^3, and Z = 4. Refinement of 568 variables on 5217 observed [$I > 3\sigma(I)$] reflections converged to R = 4.4% and R_w = 5.6%. The structure of the cluster anion 5 consists of two metal triangles at either end of the dicarbide bond, with the metal triangles in a nonparallel configuration. Extended Hückel MO calculations indicate that the nonparallel configuration of the metal triangles in solution gives rise to the observed diamagnetic ground state.

Introduction

Carbido clusters have been intensively investigated as models for adsorbed surface carbides that occur in heterogeneous chemistry such as the Fischer–Tropsch process.[1] Carbides have been incorporated into a wide range

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[†] Permanent address: Department of Chemistry, Wabash College, Crawfordsville, IN 47933.

[‡] Current address: Department of Chemistry, University of Virginia, Charlottesville, VA 22901.

[1] (a) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (b) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (c) Rofer-DePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447. (d) Biloen, P.; Sachtler, W. M. H. *Adv. Catal.* **1981**, *30*, 165. (e) Herrmann, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117.

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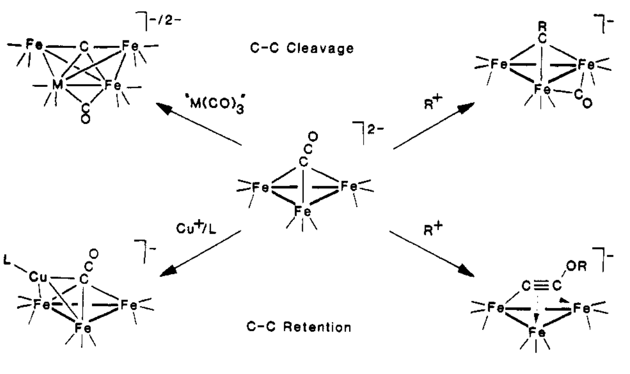
Scheme I



of clusters, including not only metal carbonyls[2] but also alkoxide[3] and early metal halide[4] structures. The chemistry of metal cluster carbides is well developed,[5] and theoretical studies supply insight into the observed structures, bonding, and reactivity.[6]

Clusters containing the related dicarbido (C_2) moiety are rare in comparison. Aside from the alkyne-like complexes $L_nMC{\equiv}CML_n$ [L_nM = $Cp^*{}_2Sc$,[7a] $(tBu_3SiO)_3Ta$,[7b] $(tBuO)_3W$,[7c-e] $CpW(CO)_3$,[7f] $CpCr(CO)_3$,[7g] $(CO)_5Mn$,[7h] $(CO)_5Re$,[7i-k] $CpRu(CO)_2$,[7l] $(R_3P)_2PtI$,[7m] R_3PAu,[7n,o] etc.[7p]], acetylide-like complexes such as $(PhMe_2P)_2Pt[C_2W_2(OtBu)_5]_2$[7c,d] and $[(Ph_2P)Ru_2(CO)_6]_2C_2$,[8] and a number of bis(carbido) clusters,[9] only ten organometallic dicarbide cluster complexes are known.[10-12] The ligand is encapsulated by a continuous polymetallic framework in most of these complexes. Examples of open dicarbide metal clusters are $Co_6(C_2)(CO)_{18}$[11g-j] and $Co_6(C_2)(CO)_{14}S$.[11k] Molecular orbital calculations on dicarbido clusters indicate that the C–C bond length correlates with the degree of metal-to-ligand back-bonding.[13]

Dicarbides are more familiar in solid-state chemistry. A number of binary carbides contain $(C_2)^{n-}$ ions, including the salts MC_2 (M = Ca, Sr, Ba) and the f-block phases M_2C_3 and MC_2.[14] The dicarbide bond lengths vary considerably, from 1.19 Å in insulating CaC_2 to 1.314 Å in metallic ThC_2 and 1.340 Å in UC_2. Dicarbides are also found in octahedral cavities of gadolinium halides, with bond lengths of 1.36–1.47 Å.[15]

One reason for the paucity of organometallic dicarbides is the lack of widely applicable synthetic routes. Dicarbido complexes are obtained through redox condensation of carbides with a second carbide source [e.g., $Co_3(CO)_9CCl$], pyrolytic decomposition of a carbido cluster, or reaction of a polynuclear carbonylate with C_2Cl_4 and C_2Cl_6. In the present work, we investigated the utility of the ketenylidene ligand (CCO) as a precursor to dicarbido cluster complexes.

The ketenylidenes $[M_3(CO)_9(CCO)]^{2-}$ (M = Fe, Ru, Os)[16] form a variety of carbide clusters through addition of electrophilic transition metal fragments.[17] For example (Scheme I), the reaction of $[M_3(CO)_9(CCO)]^{2-}$ and [Mn-

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(2) (a) Tachikawa, M.; Muetterties, E. L. *Prog. Inorg. Chem.* **1981**, *28*, 203. (b) Longoni, G.; Ceriotti, A.; Della Pergola, R.; Manassero, M.; Perego, M.; Piro, G.; Sansoni, M. *Phil. Trans. R. Soc. London A* **1982**, *308*, 47. (c) Bradley, J. S. *Adv. Organomet. Chem.* **1983**, *22*, 1. (d) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Nicholls, J. N.; Vargas, M. D. *J. Organomet. Chem.* **1983**, *249*, 255. (e) Vargas, M. D.; Nicholls, J. N. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 123. (f) Gubin, S. P. *Pure Appl. Chem.* **1986**, *58*, 567. (g) Whitmire, K. H. *J. Coord. Chem.* **1988**, *17*, 95.

(3) Chisholm, M. H. *J. Organomet. Chem.* **1987**, *334*, 77.

(4) Corbett, J. D. *Pure Appl. Chem.* **1984**, *56*, 1527.

(5) (a) Bradley, J. S.; Ansell, G. B.; Hill, E. W. *J. Am. Chem. Soc.* **1979**, *101*, 7417. (b) Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4541. (c) Davis, J. H.; Beno, M. A.; Williams, J.; Zimmie, J.; Tachikawa, M.; Muetterties, E. L. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 668. (d) Holt, E. M.; Whitmire, K. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 5621. (e) Bradley, J. S.; Hill, E. W.; Ansell, G. B.; Modrick, M. A. *Organometallics* **1982**, *1*, 1634. (f) Hriljac, J. A.; Swepston, P. N.; Shriver, D. F. *Organometallics* **1985**, *4*, 158. (g) Bogdan, P. L.; Woodcock, C.; Shriver, D. F. *Organometallics* **1987**, *6*, 1377. (h) Etienne, M.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 2324.

(6) (a) Housecroft, C. E.; Fehlner, T. P. *Organometallics* **1983**, *2*, 690. (b) Wijeyeskeva, S. D.; Hoffmann, R.; Wilker, C. N. *Organometallics* **1984**, *3*, 962. (c) Harris, S.; Bradley, J. S. *Organometallics* **1984**, *3*, 1086. (d) Housecroft, C. E. *J. Organomet. Chem.* **1984**, *276*, 297. (e) Halet, J.-F.; Saillard, J.-Y.; Lissillour, R.; McGlinchey, M. J.; Jaouen, G. *Organometallics* **1986**, *5*, 139. (f) Brint, P.; O'Guill, K.; Spalding, T. R. *Polyhedron* **1986**, *5*, 1791. (g) Chisholm, M. H.; Clark, D. L.; Huffman, J. C.; Smith, C. A. *Organometallics* **1987**, *6*, 1280. (h) Halet, J.-F.; Evans, D. G.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1988**, *110*, 87. (i) Hriljac, J. A.; Harris, S.; Shriver, D. F. *Inorg. Chem.* **1988**, *27*, 816.

(7) (a) St. Clair, M.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1991**, *10*, 525. (b) Neithamer, D. R.; LaPointe, R. E.; Wheeler, R. A.; Richeson, D. S.; Van Duyne, G. D.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1989**, *111*, 9056. Vibrational data and theoretical calculations support a dimetallacumulene structure, $L_3M{=}C{=}C{=}ML_3$. It should be noted that this compound is derived from a mononuclear ketenylidene, $(tBu_3SiO)_3TaCCO$. (c) Blau, R. J.; Chisholm, M. H.; Folting, K.; Wang, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 4552. (d) Blau, R. J.; Chisholm, M. H.; Folting, K.; Wang, R. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1582. (e) Listemann, M. L.; Schrock, R. R. *Organometallics* **1985**, *4*, 75. This complex is actually a bis(carbyne), $L_3W{\equiv}CC{\equiv}WL_3$. (f) Ustynyuk, N. A.; Vinogradova, V. N.; Kravtsov, D. N.; Oprunenko, Y. F.; Piven, V. A. *Metalloorg. Khim.* **1988**, *1*, 884. (g) Ustynyuk, N. A.; Vinogradova, V. N.; Kravtsov, D. N. *Metalloorg. Khim.* **1988**, *1*, 85. (h) Davies, J. A.; El-Ghanam, M.; Pinkerton, A. A.; Smith, D. A. *J. Organomet. Chem.* **1991**, *409*, 367. (i) Heidrich, J.; Steimann, M.; Appel, M.; Beck, W.; Phillips, J. R.; Trogler, W. C. *Organometallics* **1990**, *9*, 1296. (j) Beck, W.; Niemer, B.; Breimair, J.; Heidrich, J. *J. Organomet. Chem.* **1989**, *372*, 79. (k) Appel, M.; Heidrich, J.; Beck, W. *Chem. Ber.* **1987**, *120*, 1087. (l) Koutsantonis, G. A.; Selegue, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 2316. (m) Ogawa, H.; Onitsuka, K.; Joh, K.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H. *Organometallics* **1988**, *7*, 2257. (n) Nast, R.; Schneller, P.; Hengefield, A. *J. Organomet. Chem.* **1981**, *214*, 273. (o) Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 411. (p) Frank, K. G.; Selegue, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 6414.

(8) Bruce, M. I.; Snow, M. R.; Tiekink, E. R. T.; William, M. L. *J. Chem. Soc., Chem. Commun.* **1986**, 701.

(9) For example, Hayward, C. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 7347. See also ref 10.

(10) Reference 13 contains a useful table with structural information and references to a large number of dicarbido, bis(carbido), and poly(carbido) clusters.

(11) (a) Arrigoni, A.; Ceriotti, A.; Della Pergola, R.; Longoni, G.; Manassero, M; Masciocchi, N.; Sansoni, M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 322. (b) Arrigoni, A.; Ceriotti, A.; Della Pergola, R.; Longoni, G.; Manassero, M; Sansoni, M. *J. Organomet. Chem.* **1985**, *296*, 243. (c) Ceriotti, A.; Longoni, G.; Manassero, M.; Masciocchi, N.; Resconi, L.; Sansoni, M. *J. Chem. Soc., Chem. Commun.* **1985**, 181. (d) Albano, V. G.; Braga, D.; Ciani, G.; Martinengo, S. *J. Organomet. Chem.* **1981**, *213*, 293. (e) Albano, V. G.; Chini, P.; Martinengo, S.; Sansoni, M.; Strumolo, D. *J. Chem. Soc., Dalton Trans.* **1978**, 459. (f) Ceriotti, A.; Longoni, G.; Manassero, M.; Masciocchi, N.; Piro, G.; Resconi, L.; Sansoni, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1402. (g) Bor, G.; Marko, L.; Marko, B. *Chem. Ber.* **1962**, *95*, 333. (h) Allegra, G.; Peronaci, E. M.; Ercoli, R. *Chem. Commun.* **1966**, 549. (i) Matheson, T. W.; Robinson, B. H.; Tham, W. S. *J. Chem. Soc. A* **1971**, 1457. (j) Brice, M. D.; Penfold, B. R. *Inorg. Chem.* **1972**, *11*, 1381. (k) Gervasio, G.; Rossetti, R.; Stanghellini, P. L.; Bor, G. *Inorg. Chem.* **1984**, *23*, 2073.

(12) (a) Two papers contain references to unpublished work concerning the dicarbide clusters $[Ru_2Fe_2(C_2)(CO)_9Cp_2]$[7l] and $[(Ph_2P)_2Ru_5(C_2)(CO)_{11}X_2]$ (X = Cl, SMe).[12b] (b) Bruce, M. I. *J. Organomet. Chem.* **1990**, *400*, 321.

(13) Halet, J.-F.; Mingos, D. M. P. *Organometallics* **1988**, *7*, 51.

(14) (a) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, England, 1984; pp 947–53 and references therein. (b) Li, J.; Hoffmann, R. *Chem. Mater.* **1989**, *1*, 83.

(15) (a) Miller, G. J.; Burdett, J. K.; Schwarz, C.; Simon, A. *Inorg. Chem.* **1986**, *25*, 4437. (b) Schwanitz-Schuller, U.; Simon, A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40*, 710. (c) Warkentin, E.; Masse, R.; Simon, A. *Z. Anorg. Allg. Chem.* **1982**, *491*, 323.

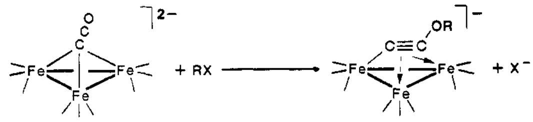
(16) (a) Kolis, J. W.; Holt, E. M.; Drezdzon, M. A.; Whitmire, K. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 6134. (b) Kolis, J. W.; Holt, E. M.; Shriver, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 7307. (c) Sailor, M. J.; Shriver, D. F. *Organometallics* **1985**, *4*, 1476. (d) Went, M. J.; Sailor, M. J.; Bogdan, P. L.; Brock, C. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1987**, *109*, 6023.

(17) (a) Kolis, J. W.; Holt, E. M.; Hriljac, J. A.; Shriver, D. F. *Organometallics* **1984**, *3*, 469. (b) Hriljac, J. A.; Holt, E. M.; Shriver, D. F. *Inorg. Chem.* **1987**, *26*, 2943. (c) Jensen, M. P.; Henderson, W.; Johnston, D. H.; Sabat, M.; Shriver, D. F. *J. Organomet. Chem.* **1990**, *394*, 121.

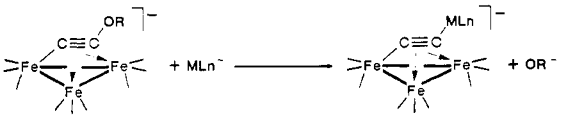
$(CO)_3(CH_3CN)_3]^+$ generates $[MnM_3C(CO)_{13}]^-$. In this process the ketenylidene C–CO bond is broken, and the resulting carbonyl is retained on the metals. The ketenylidene C–C bond also cleaves when $[Fe_3(CO)_9(CCO)]^{2-}$ reacts with H^+ or Me^+ at C_α (C_α–C_β–O) to form alkylidyne complexes, $[Fe_3(CO)_{10}(\mu_3\text{-}CR)]^-$ (R = H, Me).[16,18] These examples of facile C_α–C_β bond scission support description of the ketenylidene ligand as a "carbide mimic",[16a] in which a three-coordinate carbide is stabilized by interaction with a carbonyl.[19] Although the C_α–C_β bond is broken readily in these reactions, this bond appears to be strong, as judged by vibrational data,[20] the short C_α–C_β bond lengths of 1.26 (4)–1.30 (2) Å, and spin–spin coupling constants ($^1J_{C-C}$) of 74–96 Hz. Electrophilic ketenylidene clusters react at C_β without C–C bond cleavage.[21]

Some clarification of these diverse reactivity patterns is provided by addition of Cu^+ to the iron ketenylidene to form $[Fe_3CuI(CO)_9(CCO)]^{2-}$, which is the first characterized example of a μ_4-CCO ligand.[22] The Cu(I) center, unlike other electrophiles, fails to disrupt the ketenylidene ligand. This result is attributed to the lack of available d electrons for dπ–pπ* back-bonding and the inability of Cu^+ to bond strongly enough to C_α to compensate for C_α–C_β scission. Therefore, the ketenylidene C–C bond is demonstrably stable in the absence of particular driving forces that assist cleavage, and the CCO ligand is a viable precursor to C_2 products. Recent work has been directed at effecting ligand transformations with retention of the C_α–C_β bond.[23]

One transformation necessary to form dicarbido ligands is C_β–O bond cleavage. The first step in this process (eq 1) is formation of acetylide clusters with a good leaving group, such as acetate on $[Fe_3(CO)_9CCOAc]^-$. Bridging acetylides generally are susceptible to nucleophilic attack,[24] and when the acetylide substituent is a good leaving group, the nucleophile becomes the substituent on a new acetylide cluster;[25] in the present research the added nucleophile is a metal complex, and the resulting acetylide carbons are bonded solely to metals. Subsequent cluster expansion about the pendant metal then leads to higher nuclearity dicarbido compounds. The application of this overall strategy to the synthesis of $[PPN][Fe_3Co_3(C_2)(CO)_{18}]$ (5) is described below.



(1a)



(1b)

Experimental Section

All manipulations were performed under prepurified nitrogen using standard Schlenk techniques, in a Vacuum Atmospheres drybox or on a high-vacuum line.[26] Solvents were collected by distillation under nitrogen from appropriate drying agents (CH_2Cl_2 from P_2O_5; Et_2O and THF from sodium/benzophenone; pentane sequentially from H_2SO_4 and 4A sieves; *i*-PrOH from Mg/I_2). CD_2Cl_2 for NMR experiments was freeze–pump–thaw degassed and distilled under vacuum from P_2O_5.

Infrared spectra were recorded on a Bomem MB series benchtop FTIR spectrometer at 2-cm^{-1} resolution using solutions in 0.1-mm path length CaF_2-window cells or Fluorolube mulls of solids between KBr plates. ^{13}C NMR spectra were recorded on a Varian XLA-400 spectrometer (100.577 MHz) and were internally referenced to solvent with positive chemical shifts lying downfield from TMS. Liquid secondary ion mass spectra were obtained by Dr. D. L. Hung of the Northwestern University Analytical Services Laboratory on a VG70/250SE spectrometer by Cs^+ ion bombardment of samples in *m*-nitrobenzyl alcohol matrices. Elemental analyses were performed by Analytische Laboratorien, Engleskirchen, Germany.

$[PPN][Fe_3(CO)_9CCOAc]$ was prepared by literature synthesis.[18] (PPN)Cl (Aldrich, Alfa) and $Na_2[Fe(CO)_4]\cdot 1.5$diox (diox = dioxane) (Aldrich) were used as received. $Co_2(CO)_8$ (Strem) was stored cold under nitrogen and sublimed at ambient temperature immediately prior to use.

Synthesis of $[PPN]_2[Fe_3(CO)_9CCFe(CO)_4]$ (2). Samples of $[PPN][Fe_3(CO)_9CCOAc]$ (I) (1.300 g, 1.25 mmol), (PPN)Cl (1.46 g, 2.54 mmol), and $Na_2[Fe(CO)_4]\cdot 1.5$diox (0.540 g, 1.56 mmol) were slurried in 10 mL of THF, and the slurry was stirred for 72 h. The slurry was then filtered through a thick Celite pad on a fine-porosity frit. A minimum of fresh THF was used to complete the washing of solutes through the frit. The filtrate was evaporated to dryness under vacuum. The isolated oils were redissolved in 4 mL of CH_2Cl_2, and 8 mL of pentane was layered on the solution and allowed to slowly mix to produce brick red crystals of 2. The crystals were isolated by filtration and washed successively with *i*-PrOH and Et_2O. Yield: 0.725 g (0.429 mmol, 34%). The isolated solids contain approximately 4% $[PPN]_2[Fe_3(CO)_9(CCO)]$ as judged by NMR spectroscopy; therefore, elemental analysis of 2 was not performed. IR, ν(C≡O) (THF, cm^{-1}): 2030 vw, 2003 m, 1961 vs, 1956 s, sh, 1926 m, 1911 m, 1873 w, sh. IR, ν(C≡C) (mull, cm^{-1}): 1646 vw. MS (*m*/*e*): mass = 764 (parent + matrix − 1); loss of one carbonyl; 664 and 636 (unassigned); then 585 (parent − CO + 1); successive loss of eight carbonyls.

The ketenylidene complex remaining on the Celite pad was recovered and identified spectroscopically. Yield: 0.920 g (0.599 mmol, 47%). This gives an overall cluster yield of 82%.

Synthesis of $[PPN][Fe_3Co_3(C_2)(CO)_{18}]$ (5) from 2. $[PPN]_2[Fe_3(CO)_9CCFe(CO)_4]$ (2) (0.150 g, 0.089 mmol) and excess $Co_2(CO)_8$ (0.070 g, 0.205 mmol) were dissolved in 5 mL of CH_2Cl_2 to give a dark yellow-black solution. After the solution was stirred for several minutes, the solvent was removed under vacuum. The resulting black oils were extracted with Et_2O to give a dark solution and light gray solids. The solids were removed by filtration and discarded. The filtrate was evaporated to dryness under vacuum to give crude 5 as an oily black solid. Slow diffusion of 7 mL of pentane into a 3-mL Et_2O solution of the solid gave

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[18] Hriljac, J. A.; Shriver, D. F. *J. Am. Chem. Soc.* **1987**, *109*, 6010.

[19] Lavigne, G. In *Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990; Chapter 5.

[20] Sailor, M. J.; Went, M. J.; Shriver, D. F. *Inorg. Chem.* **1988**, *27*, 2666.

[21] (a) Seyferth, D.; Williams, G. H. *J. Organomet. Chem.* **1972**, *38*, C11. (b) Seyferth, D.; Hallgren, J. E.; Eschbach, C. S. *J. Am. Chem. Soc.* **1974**, *96*, 1730. (c) Sievert, A. C.; Strickland, D. S.; Shapley, J. R.; Steinmetz, G. R.; Geoffroy, G. L. *Organometallics* **1982**, *1*, 214. (d) Shapley, J. R.; Strickland, D. S.; St. George, G. M.; Churchill, M. R.; Bueno, C. *Organometallics* **1983**, *2*, 185. (e) Holmgren, J. S.; Shapley, J. R. *Organometallics* **1984**, *3*, 1322. (f) Holmgren, J. S.; Shapley, J. R. *Organometallics* **1985**, *4*, 793. (g) Mlekuz, M.; D'Agostino, M. F.; Kolis, J. W.; McGlinchey, M. J. *J. Organomet. Chem.* **1986**, *303*, 361. (h) Ching, S.; Holt, E. M.; Kolis, J. W.; Shriver, D. F. *Organometallics* **1988**, *7*, 892.

[22] Gunale, A. S.; Jensen, M. P.; Stern, C. L.; Shriver, D. F. *J. Am. Chem. Soc.* **1991**, *113*, 1458.

[23] (a) Jensen, M. P.; Sabat, M.; Johnston, D. H.; Jones, L. M.; Shriver, D. F. *J. Organomet. Chem.* **1990**, *383*, 279. (b) Jensen, M. P.; Sabat, M.; Shriver, D. F. *J. Cluster Sci.* **1990**, *1*, 75. (c) Jensen, M. P.; Shriver, D. F. Unpublished results.

[24] Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113.

[25] Similar results occur when the ketenylidene analgoue $H_3Os_3(CO)_9(BCO)$ reacts with BX_3: Workman, D. P.; Jan, G.-Y.; Shore, S. G. *Inorg. Chem.* **1990**, *29*, 3518.

[26] (a) Shriver, D. F.; Drezdzon, M. A. *Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley Interscience: New York, 1986. (b) *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. L.; Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.

Table I. Summary of the Crystal Structure Data

formula	$C_{56}H_{30}NO_{18}P_2Co_3Fe_3$
M_r	1411.14
cryst size, mm	0.48 × 0.27 × 0.12
cryst system	monoclinic
space group	$P2_1/c$ (No. 14)
a, Å	15.878 (2)
b, Å	29.774 (4)
c, Å	11.930 (1)
β, deg	90.32 (1)
V, Å^3	5640 (2)
Z	4
d_{calcd}, g cm^{-3}	1.66
μ(Mo Kα), cm^{-1}	16.67
radiation (λ, Å)	graphite-monochromated Mo Kα (0.710 69)
scan type	ω
2θ range, deg	4–46
scan width, deg	0.85 + 0.35 tan θ
no. of unique data	7837
no. of unique data with $I > 3\sigma(I)$	5217
no. of params	568
$R(F)$	0.044
$R_w(F)$	0.056
GOF	1.55

gray-black microcrystals, which were isolated by filtration and washed with 5 mL of pentane. Yield: 0.080 g (0.057 mmol, 64%). Anal. Found (calc) for $Fe_3Co_3P_2O_{18}NC_{56}H_{30}$: Fe, 11.75 (11.87); Co, 12.30 (12.53); C, 47.48 (47.66); H, 2.22 (2.14). IR, ν(C≡O) (THF, cm^{-1}): 2081 w, 2041 s, sh, 2033 vs, 2026 vs, 2008 m, 2001 m, 1990 m, 1957 w, 1928 vw, sh, 1824 w, br. MS (m/e): mass = 873 (parent); successive loss of 11 carbonyls.

Synthesis of [PPN][$Fe_3Co_3(C_2)(CO)_{18}$] (5) from 1. [PPN][$Fe_3(CO)_9CCOAc$] (1) (0.075 g, 0.072 mmol) and 1 equiv of $Co_2(CO)_8$ (0.025 g, 0.073 mmol) were dissolved in 8 mL of THF to produce a brown solution. After being stirred for several minutes, the solution was evaporated to dryness in vacuo. The resulting brown oils were extracted with 10 mL of Et_2O. The resulting brown solution was filtered from the remaining light gray-brown solids. Solvent was removed from the filtrate, and the solids were redissolved in THF. Additional $Co_2(CO)_8$ (0.025 g, 0.073 mmol) dissolved in 2 mL of THF was added by cannula. The solution was stirred for several minutes. The solvent was then stripped off. The residue was extracted with Et_2O, and the resulting solution was filtered from dark black-brown solids. The filtrate was worked up as above to give crystalline 5, identified by the spectral features reported above. Yield: 0.040 g (0.028 mmol, 37%).

Isolation of [PPN]$_2$[$Fe_4Co_2(C_2)(CO)_{18}$] (3). A sample of [PPN]$_2$[$Fe_3(CO)_9CCFe(CO)_4$] (2) (0.075 g, 0.044 mmol) was dissolved with $Co_2(CO)_8$ (0.025 g, 0.073 mmol) in 5 mL of CH_2Cl_2. The yellow-black solution was stirred for several minutes, and then the solvent was stripped off under vacuum. The remaining solids were extracted twice with 10-mL aliquots of Et_2O, and the extracts were discarded. The remaining black solids were redissolved in 4 mL of CH_2Cl_2 and layered with 6 mL of Et_2O. The layers diffused to produce a 20-mg mixture of small black crystals of 3 and large pale white crystals of [PPN][$Co(CO)_4$]. The crystals were isolated by filtration and manually separated under N_2 in a drybox. IR, ν(C≡O) (CH_2Cl_2, cm^{-1}): 2053 vw, 1992 vs, 1950 m, br, 1924 w, sh, 1769 w, br. MS (m/e): mass = 870 (parent), successive loss of 12 carbonyls.

X-ray Crystal Structure Determination of [PPN][$Fe_3Co_3(C_2)(CO)_{18}$] (5). A single crystal of 5 was grown by slow diffusion of pentane into a CH_2Cl_2 solution of the cluster prepared from 1. The crystal was mounted on a glass fiber in air and transferred to the cold (−120 °C) N_2 stream of an Enraf-Nonius CAD4 diffractometer. A summary of the data collection is given in Table I. Unit cell parameters were determined by least-squares refinement on the setting angles of 25 independent reflections. A monoclinic unit cell was indicated, and the space group $P2_1/c$ was uniquely assigned on the basis of systematic absences. Absorption corrections were performed with the program DIFABS.[27] Transmission factors ranged from 0.84 to 1.14. The data were corrected for Lorentz and polarization effects. A decay correction was not applied, as the intensities of four standard reflections, monitored every 3 h throughout the data collection, showed no significant variation.

All calculations were performed using the TEXSAN 4.0 software package[28] run on a Micro VAX 3600 computer. The structure was determined by direct methods (SHELXS 86)[29] and difference Fourier techniques. Least-squares refinements were run initially with isotropic thermal parameters and then with anisotropic parameters for all atoms except those of the PPN phenyl rings. Hydrogen atoms were located on a difference map and added without refinement to the calculations. The identities of individual metals of the cluster anion could not be unambiguously determined from peak heights on the initial difference map and are therefore assigned to conform with other data. Redistribution of the metals did not significantly affect refinement. The largest feature in the final difference map had an amplitude of 0.70 e/Å^3. Final positional parameters are listed in Table II. Pertinent bond lengths and angles are given in Table III.

Molecular Orbital Calculations. Extended Hückel calculations[30] were performed using the CACAO program package.[31] Literature values were used for Fe and Co orbital parameters.[32] Idealized eclipsed geometries were used with all M–M = 2.500 Å, M–CO = 1.790 Å, C–O = 1.140 Å, M–C_2 = 1.950 Å, and C–C = 1.370 Å. All carbonyls were in ideal terminal positions, with equatorial carbonyls 98° apart and 3° above the M_3 plane and with axial carbonyls 82° below the M_3 plane.

The structural distortion of 5 was modeled by tipping the metal triangles in increments of 2.5° each to a total of 17.5°. The axes of rotation passed through the centers of the M_3 triangles perpendicular to the C_2 bond and a line bisecting one M–M–M angle. A further translation of the metal triangles perpendicular to the axis of rotation of 0.05 Å for each 2.5° of rotation was necessary to prevent undue variation of the M–C_2 distances. This had the effect of moving one metal on each triangle directly toward the other while moving the other four away. The resulting geometric features are summarized in Table V.

Tilting angles greater than 15° closed the distance between opposing equatorial carbonyl oxygens on the proximal metals below 2.00 Å. As there is no contribution from carbonyl atoms to the frontier orbitals of the studied complexes, and the O···O′ overlap is small at 17.5°, the calculated HOMO–LUMO gap at that angle is assumed to be unaffected by the proximity of the CO ligands.

Results and Discussion

General Observations. An overview of the reactions studied in the course of this work is given in Scheme II. The ketenylidene-derived acetylide cluster [PPN][$Fe_3(CO)_9CCOAc$] (1) is converted to a dicarbido compound [PPN][$Fe_3Co_3(C_2)(CO)_{18}$] (5) via the metalated acetylide derivative [PPN]$_2$[$Fe_3(CO)_9CCFe(CO)_4$] (2), which reacts with 2 equiv of $Co_2(CO)_8$ to give 5 in THF or CH_2Cl_2. A second dicarbido complex [PPN]$_2$[$Fe_4Co_2(C_2)(CO)_{18}$] (3) and an acetylide cluster, [PPN][$Fe_2Co(CO)_9CCFe(CO)_4$] (4), are intermediates in the formation of 5. Alternately, compound 1 reacts with $Co_2(CO)_8$ to yield 5 directly but in diminished yield. The isolation of the intermediate compounds as pure crystalline solids is hindered by the presence of other species. The solubility of 4 is nearly

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[27] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

[28] Swepston, P. N. *TEXSAN, Version 4.0, the TEXRAY Structure Analysis Progam Package*; Molecular Structure Corp.: College Station, TX, 1987.

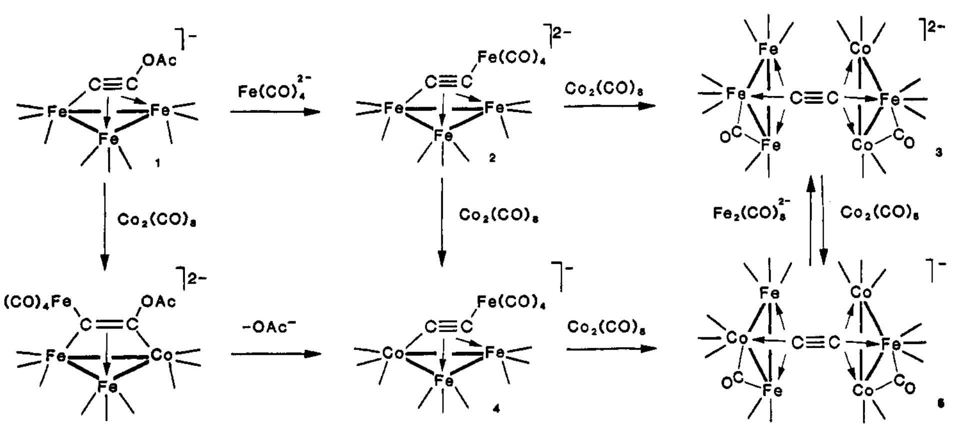
[29] Sheldrick, G. M. *SHELXS86: A Program for Crystal Structure Determination*; University of Gottingen: Gottingen, Germany, 1986.

[30] (a) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179. (b) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 3489. (c) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *37*, 2872. (d) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

[31] Mealli, C.; Proserpio, D. M. *J. Chem. Educ.* **1990**, *67*, 3399.

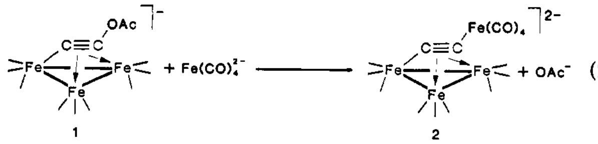
[32] Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.

Scheme II



identical to that of 5, and 3 is not easily separated from the large quantity of $[Co(CO)_4]^-$ generated by metal substitution reactions. Black crystals of 3 were obtained in a mixture with off-white $[PPN][Co(CO)_4]$ on occasion. Compound 4 was not isolated, but its identity inferred from in situ spectroscopic data. Compounds 2 and 5 are easily isolated and are fully characterized.

Formation of $[PPN]_2[Fe_3(CO)_9CCFe(CO)_4]$ (2). The potent nucleophile $Na_2[Fe(CO)_4]$[33] reacts with 1 in THF over a 3-day period to produce the new metalated cluster $[PPN]_2[Fe_3(CO)_9CCFe(CO)_4]$ (2) (eq 2). The yield is



(2)

moderated by a competing reaction at the acyl carbonyl of 1 to give $[PPN]_2[Fe_3(CO)_9(CCO)]$. Fortunately, 2 is almost completely separable from the ketenylidene complex due to low solubility of the latter in THF.

^{13}C NMR spectroscopy confirmed the formulation of 2 (Figure 1). Two resonances in a 9.0:4.0 intensity ratio observed at 219.9 and 219.0 ppm arise from the carbonyls on the cluster framework and on the pendant iron. Signals at 201.6 and 114.8 ppm are assigned to C_α and C_β, respectively. Preparation of 2 from a sample of 1 enriched with 30% ^{13}C at all cluster carbons revealed spin–spin coupling between the acetylide carbons, with $^1J_{C-C} = 23$ Hz. The C_β resonance is coupled to the four dynamically equivalent carbonyls of the substituent metal also, $^2J_{C-C} = 8$ Hz. The ^{13}C spectrum compares well with those of other triiron acetylides (Table IV) such as the close analogue $[PPN][Fe_3(CO)_9CCFe(CO)_2Cp]$, which has acetylide resonances at 206.3 and 99.0 ppm with $^1J_{C-C} = 22$ Hz.[23b]

We demonstrated previously that $PMePh_2$ displaces acetate from 1 to form the phosphonium acetylide cluster $Fe_3(CO)_9CCPMePh_2$.[23a] The phosphine attacks C_α to form an alkyne complex, which quickly loses acetate and rearranges to the isolated product.[34] This mechanism was confirmed by carrying out the reaction with a sample of 1 selectively enriched with ^{13}C at C_β but not C_α. The ^{13}C NMR spectrum of the resulting compound revealed that the isotope label was transferred to C_α in the product, indicating $PMePh_2$ adds selectively to C_α of 1. The intermediate phosphonium alkyne was isolated from addition of the phosphine to $[PPN][Fe_3(CO)_9CCOEt]$ and its structure verified by X-ray crystallography.[23a]

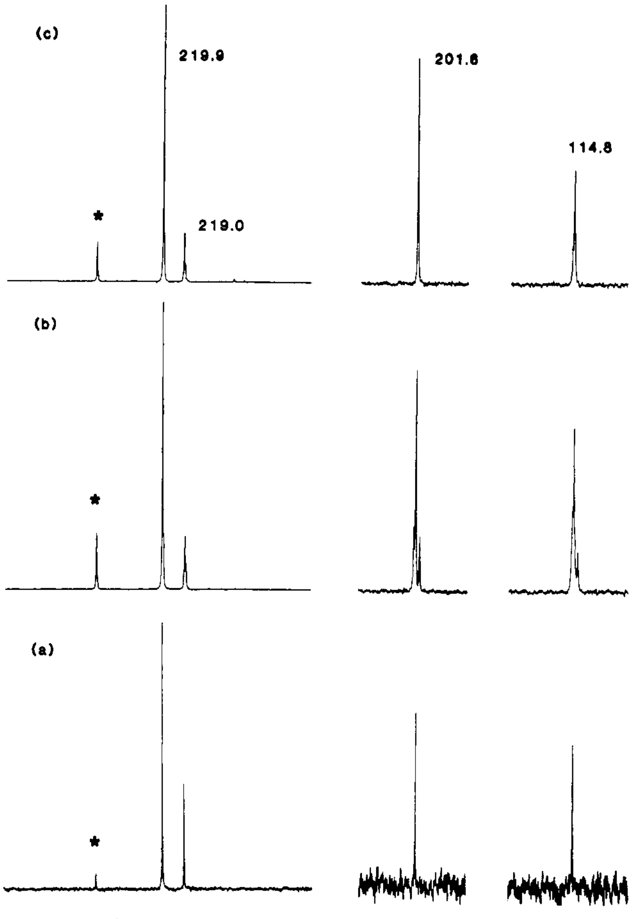


Figure 1. ^{13}C NMR spectra of $[PPN]_2[Fe_3(CO)_9CCFe(CO)_4]$ (2) prepared from (a) unenriched 1, (b) 1 enriched to ~30% ^{13}C at all cluster carbons, and (c) 1 enriched with ^{13}C at the carbonyls and C_β but not C_α. The resonance marked with an asterisk is due to the carbonyls of $[PPN]_2[Fe_3(CO)_9(CCO)]$.

In the present research, ^{13}C NMR indicates that $[Fe(CO)_4]^{2-}$ attaches to C_α of selectively labeled 1 in only 56% of the product. Thus, nucleophilic addition to C_β occurs at 44% of the overall rate. Alkynes with leaving groups are susceptible to attack at any of three sites, reacting at either carbon or on the displaceable substituent.[35] All three reactions occur on 1 at nearly equivalent rates. The difference in site preference between the phosphine and

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(33) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 2515.

(34) See also: (a) Suades, J.; Dahan, F.; Mathieu, R. *Organometallics* **1988**, *7*, 47. (b) Boyar, E.; Deeming, A. J.; Felix, M. S. B.; Kabir, S. E.; Adatia, T.; Bhusate, R.; McPartlin, M.; Powell, H. R. *J. Chem. Soc., Dalton Trans.* **1989**, 5.

(35) Miller, S. I.; Dickstein, J. I. *Acc. Chem. Res.* **1976**, *9*, 358.

Table II. Positional Parameters for $[PPN][Fe_3Co_3(C_2)(CO)_{18}]$ (5)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co1	0.70622 (6)	0.10930 (3)	0.73703 (7)	C51	0.7612 (5)	0.1502 (2)	0.1967 (6)
Co2	0.73447 (6)	0.15864 (3)	0.34427 (7)	C52	0.7897 (5)	0.2094 (3)	0.3741 (6)
Co3	0.69489 (6)	0.08089 (3)	0.40096 (8)	C53	0.6288 (5)	0.1808 (2)	0.3316 (6)
Fe1	0.62847 (6)	0.17917 (3)	0.67272 (8)	C61	0.6281 (5)	0.0817 (2)	0.2826 (7)
Fe2	0.59163 (6)	0.10302 (3)	0.59278 (8)	C62	0.6682 (5)	0.0273 (3)	0.4517 (6)
Fe3	0.84441 (6)	0.10731 (3)	0.43068 (8)	C111	0.0586 (4)	0.0737 (2)	0.8483 (6)
P1	0.1547 (1)	0.10362 (5)	0.8193 (1)	C112	0.0122 (5)	0.0842 (2)	0.9422 (6)
P2	0.1974 (1)	0.17812 (5)	0.9771 (1)	C113	−0.0624 (5)	0.0594 (3)	0.9627 (7)
O11	0.6040 (4)	0.0904 (2)	0.9377 (5)	C114	−0.0874 (5)	0.0267 (3)	0.8930 (7)
O12	0.7695 (3)	0.0193 (2)	0.6872 (4)	C115	−0.0412 (6)	0.0160 (3)	0.7999 (7)
O13	0.8533 (4)	0.1549 (2)	0.8358 (5)	C116	0.0323 (5)	0.0399 (2)	0.7777 (6)
O21	0.7706 (3)	0.2403 (2)	0.6369 (4)	C121	0.2401 (4)	0.0676 (2)	0.8572 (5)
O22	0.5085 (3)	0.2394 (2)	0.5624 (5)	C122	0.2267 (5)	0.0286 (2)	0.9152 (6)
O23	0.6018 (5)	0.2040 (2)	0.9078 (5)	C123	0.2942 (5)	0.0021 (2)	0.9497 (6)
O24	0.4592 (4)	0.1406 (2)	0.7269 (6)	C124	0.3739 (5)	0.0139 (2)	0.9234 (6)
O31	0.4637 (4)	0.1076 (2)	0.4169 (5)	C125	0.3890 (5)	0.0523 (3)	0.8674 (7)
O32	0.5430 (4)	0.0159 (2)	0.6834 (6)	C126	0.3211 (6)	0.0795 (3)	0.8320 (7)
O41	0.9690 (4)	0.1199 (2)	0.2520 (5)	C131	0.1568 (4)	0.1121 (2)	0.6704 (5)
O42	0.9233 (4)	0.0289 (2)	0.5344 (5)	C132	0.1940 (5)	0.0811 (3)	0.6008 (7)
O43	0.9136 (3)	0.1705 (2)	0.5950 (5)	C133	0.1883 (6)	0.0868 (3)	0.4830 (8)
O44	0.8137 (4)	0.0373 (2)	0.2569 (6)	C134	0.1447 (5)	0.1231 (3)	0.4395 (7)
O51	0.7782 (4)	0.1448 (2)	0.1059 (5)	C135	0.1089 (5)	0.1536 (2)	0.5103 (6)
O52	0.8251 (4)	0.2421 (2)	0.3927 (4)	C136	0.1139 (4)	0.1484 (2)	0.6249 (5)
O53	0.5639 (3)	0.1953 (2)	0.3210 (5)	C211	0.1172 (4)	0.2003 (2)	1.0674 (5)
O61	0.5854 (4)	0.0806 (2)	0.2055 (5)	C212	0.0348 (4)	0.2050 (2)	1.0257 (5)
O62	0.6531 (4)	−0.0096 (2)	0.4747 (5)	C213	−0.0270 (5)	0.2239 (2)	1.0929 (6)
N	0.1550 (3)	0.1510 (2)	0.8787 (4)	C214	−0.0064 (4)	0.2369 (2)	1.2015 (6)
C1	0.6978 (4)	0.1360 (2)	0.5910 (5)	C215	0.0725 (4)	0.2316 (2)	1.2434 (6)
C2	0.7363 (4)	0.1307 (2)	0.4901 (5)	C216	0.1354 (4)	0.2129 (2)	1.1766 (5)
C11	0.6441 (5)	0.0981 (2)	0.8616 (7)	C221	0.2570 (4)	0.2239 (2)	0.9226 (5)
C12	0.7450 (4)	0.0550 (2)	0.7060 (6)	C222	0.2658 (5)	0.2638 (2)	0.9805 (6)
C13	0.7965 (5)	0.1372 (2)	0.7966 (6)	C223	0.3175 (5)	0.2985 (3)	0.9386 (7)
C21	0.7157 (5)	0.2161 (2)	0.6526 (5)	C224	0.3582 (5)	0.2925 (3)	0.8413 (7)
C22	0.5567 (4)	0.2160 (2)	0.6025 (6)	C225	0.3516 (5)	0.2538 (3)	0.7815 (7)
C23	0.6097 (6)	0.1943 (3)	0.8151 (7)	C226	0.2989 (5)	0.2192 (2)	0.8215 (6)
C24	0.5256 (5)	0.1377 (2)	0.6851 (7)	C231	0.2687 (4)	0.1456 (2)	1.0637 (6)
C31	0.5174 (5)	0.1059 (2)	0.4809 (7)	C232	0.2356 (5)	0.1126 (2)	1.1284 (7)
C32	0.5635 (4)	0.0497 (2)	0.6477 (7)	C233	0.2938 (5)	0.0837 (3)	1.1887 (7)
C41	0.9208 (5)	0.1152 (2)	0.3215 (7)	C234	0.3754 (5)	0.0896 (3)	1.1789 (7)
C42	0.8918 (5)	0.0598 (3)	0.4964 (6)	C235	0.4097 (6)	0.1231 (3)	1.1171 (8)
C43	0.8863 (4)	0.1460 (3)	0.5299 (6)	C236	0.3545 (5)	0.1518 (3)	1.0554 (7)
C44	0.7903 (5)	0.0622 (3)	0.3256 (7)				

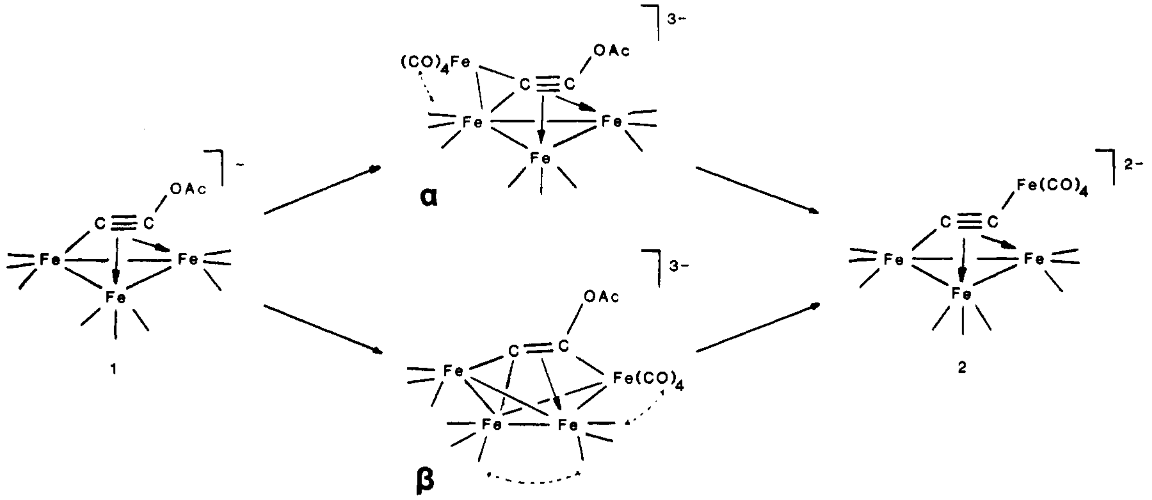

Figure 2. Postulated mechanism for $[Fe(CO)_4]^{2-}$ addition to $(PPN)[Fe_3(CO)_9CCOAc]$ (1), showing intermediate C_α and C_β adducts. Dashed lines indicate intramolecular CO exchange proposed to account for ^{13}C enrichment of pendant iron carbonyls.

the metalate must result from relative stabilities of the initial α and β adducts, with steric interaction between the added fragment and the cluster framework likely playing a significant role.

A curious transfer of carbonyl ligands from the cluster to the added metalate occurs during formation of 2, giving rise to a reproducible intensity ratio of 6.92:2.08 (2) for carbonyl resonances in the ^{13}C NMR spectra of isotopically enriched cluster. Relaxation was efficient in these cases as indicated by comparison of expected and observed intensity ratios for the acetylide carbon signals and the combined carbonyl resonances; these typically agreed to within 4%. If this ligand transfer is predominantly intramolecular, attack of the nucleophile to form simple alkyne- and vinylidene-like S_N2 transition states is improbable. The coordinative unsaturation of $[Fe(CO)_4]^{2-}$ may permit initial incorporation into the cluster framework and partial CO exchange (Figure 2). Stable analogues of

Table III. Bond Lengths (Å) and Selected Bond Angles (deg) for $[PPN][Fe_3Co_3(C_2)(CO)_{18}]$ (5)

Bond Lengths			
Fe1–Fe2	2.527 (1)	Fe3–C44	2.026 (8)
Fe1–Co1	2.536 (1)	Co2–C51	1.830 (8)
Fe2–Co1	2.504 (1)	Co2–C52	1.782 (9)
Fe3–Co2	2.535 (1)	Co2–C53	1.809 (8)
Fe3–Co3	2.524 (1)	Co3–C61	1.762 (9)
Co2–Co3	2.493 (1)	Co3–C62	1.760 (8)
Fe1–C1	1.956 (6)	Co3–C44	1.852 (8)
Fe2–C1	1.951 (6)	C11–O11	1.136 (8)
Co1–C1	1.919 (6)	C12–O12	1.155 (7)
Fe3–C2	1.987 (6)	C13–O13	1.142 (8)
Co2–C2	1.928 (6)	C21–O21	1.146 (8)
Co3–C2	1.938 (6)	C22–O22	1.138 (8)
C1–C2	1.362 (8)	C23–O23	1.151 (9)
Co1–C11	1.818 (8)	C24–O24	1.171 (8)
Co1–C12	1.770 (7)	C31–O31	1.143 (9)
Co1–C13	1.800 (9)	C32–O32	1.141 (8)
Fe1–C21	1.787 (8)	C41–O41	1.140 (8)
Fe1–C22	1.787 (8)	C42–O42	1.140 (8)
Fe1–C23	1.784 (9)	C43–O43	1.149 (8)
Fe1–C24	2.054 (8)	C44–O44	1.167 (8)
Fe2–C24	1.841 (7)	C51–O51	1.130 (8)
Fe2–C31	1.778 (9)	C52–O52	1.146 (8)
Fe2–C32	1.776 (8)	C53–O53	1.123 (8)
Fe3–C41	1.800 (8)	C61–O61	1.140 (8)
Fe3–C42	1.781 (8)	C62–O62	1.157 (8)
Fe3–C43	1.779 (8)		
Bond Angles			
Fe1–Co1–Fe2	60.18 (4)	Co1–C13–O13	179.0 (7)
Fe1–Fe2–Co1	60.52 (4)	Fe1–C21–O21	178.0 (7)
Co1–Fe1–Fe2	59.29 (4)	Fe1–C22–O22	176.6 (6)
Co2–Co3–Fe3	60.69 (4)	Fe1–C23–O23	176.6 (9)
Co2–Fe3–Co3	59.05 (4)	Fe1–C24–O24	134.7 (6)
Fe3–Co2–Co3	60.26 (4)	Fe2–C24–O24	144.4 (7)
Fe1–C1–C2	140.6 (5)	Fe2–C31–O31	173.2 (7)
Fe2–C1–C2	110.0 (4)	Fe2–C32–O32	177.9 (7)
Co1–C1–C2	136.5 (5)	Fe3–C41–O41	179.5 (8)
Fe1–C1–Co1	81.7 (2)	Fe3–C42–O42	177.3 (7)
Fe1–C1–Fe2	80.6 (2)	Fe3–C43–O43	179.0 (7)
Co1–C1–Fe2	80.6 (2)	Fe3–C44–O44	136.1 (6)
Co2–C2–C1	138.0 (5)	Co2–C51–O51	179.4 (7)
Co2–C2–C1	114.9 (5)	Co2–C52–O52	179.6 (8)
Fe3–C2–C1	138.4 (5)	Co2–C53–O53	177.8 (6)
Co2–C2–Co3	80.3 (2)	Co3–C61–O61	177.5 (7)
Co2–C2–Fe3	80.7 (2)	Co3–C62–O62	173.2 (7)
Fe3–C2–Co3	80.0 (2)	Co3–C44–O44	142.8 (7)
Co1–C11–O11	178.2 (8)	Fe1–C24–Fe2	80.7 (3)
Co1–C12–O12	178.9 (6)	Fe3–C44–Co3	81.1 (3)

both structures are known.[36] The diagrammed intermetallic CO fluxionality combined with the relative rates of C_α and C_β addition predicts a carbonyl resonance intensity ratio of 6.98:2.02, close to the observed value.

Electron-transfer reactions must be considered with the highly reduced $[Fe(CO)_4]^{2-}$ anion. However, production of 2 by a radical mechanism would require cleavage of acetate anion from a $[Fe_3(CO)_9(C_2)]^-$ radical rather than separation of an acyl radical from $[Fe_3(CO)_9(CCO)]^{2-}$. This unlikely event fails to account for either the CO transfer or the preference for C_α addition. Furthermore, $Na[CpFe(CO)_2]$ reacts with 1 much more rapidly to produce $[PPN][Fe_3(CO)_9CCFe(CO)_2Cp]$ with negligible ketenylidene formation; this is best ascribed to nucleophilicity, as the strong ion pairing of $Na_2[Fe(CO)_4]$[33] slows reactivity and the greater steric bulk of $CpFe(CO)_2^-$ hinders attack at the acyl of 1. Treatment of 1 with sodium benzophenone ketyl rapidly generates ketenylidene.[23c] The same reaction may occur here with the metalate serving as the reductant, but electron transfer would have to be unusually slow to permit formation of 2. Electron transfer does not occur when $[Fe(CO)_4]^{2-}$ reacts with more conventional electrophiles.[33] Although this pathway is not disproven here, the results are more suggestive of nucleophilic behavior.

Table IV. Selected ^{13}C NMR Data for Unsaturated Ligands on Iron and Cobalt Carbonyl Frameworks[a]

compd	$\delta(C_\alpha)$, ppm	$\delta(C_\beta)$, ppm	$^1J_{CC}$, Hz	ref
$[PPN]_2[Fe_3(CO)_9(CCO)]$[b]	90.1	182.2	74	16b
$[PPN][Fe_2Co(CO)_9(CCO)]$[c]	82.8	172.5	79.4	21h
$[PPN][Fe_3(CO)_{10}(CMe)]$[b]	286.2			16b
$[Fe_2Co(CO)_{10}(CH)]$[c]	269.8			21h
$Fe_2Co(CO)_9CCSiMe_3$[d]	202.60	97.43	g	39f
$Fe_2Co(CO)_7(dmpm)CCOMe$[e]	156.6	160.4	43.5	42
$[PPN][Fe_3(CO)_9CCFe(CO)_2Cp]$	206.3	99.0	22	23b
$[PPN][Fe_3(CO)_9CCOAc]$ (1)	172.9	132.2	39	18
$[PPN]_2[Fe_3(CO)_9CCFe(CO)_4]$ (2)	201.6	114.8	23	i
$[PPN]_2[Fe_4Co_2(C_2)(CO)_{18}]$ (3)[f]	279.4	285.7[h]	g	i
$[PPN][Fe_2Co(CO)_9CCFe(CO)_4]$ (4)[f]	193.1	142.2	27	i
$[PPN][Fe_3Co_3(C_2)(CO)_{18}]$ (5)	293.7	285.9[h]	34	i

[a] CD_2Cl_2 solution, room temperature or as noted. [b] CD_3CN, −40 °C. [c] CD_2Cl_2, −90 °C. [d] $CDCl_3$, room temperature. [e] CD_2Cl_2, −60 °C. [f] CD_2Cl_2, −70 °C, prepared in situ. [g] Not observed. [h] $(CO)_9FeCo_2C$. [i] This work.

Additional characterization of 2 is provided by infrared spectroscopy. In particular, the position of the strongest $\nu(C{\equiv}O)$ bands some 30 cm^{-1} lower than those of 1 reflects increased negative charge on the cluster. A weak absorption at 1646 cm^{-1} is assigned to acetylide bond stretching. Absorptions due to carbonyls on the pendant iron overlap with those of the cluster, preventing definitive assignment of specific bands and determination of local symmetry at that site.

Although an X-ray crystal structure determination was not performed, spectroscopic similarities between 2 and $[PPN][Fe_3(CO)_9CCFe(CO)_2Cp]$ suggest equivalent structures, and the latter complex is known to be typical of trimetallic carbonyl acetylide clusters.[23b] Therefore, 2 is considered to be an acetylide complex.

Reaction of 2 with $Co_2(CO)_8$. Dicobalt octacarbonyl is an efficient reagent for cluster expansion[37] of 2. The affinity of $Co_2(CO)_8$ for alkynes to form $Co_2(CO)_6(RC{\equiv}CR')$ species is well-known,[38] and similar addition to metal acetylides has been documented.[39] In some cases condensation occurs, forming closed cluster frameworks about the acetylide ligand. Therefore, the acetylide bond of 2 should act as a template for cluster building on the pendant iron. This expectation was met but with added complexity.

When 2 is dissolved with excess $Co_2(CO)_8$ in THF or CH_2Cl_2, the product formed is $[PPN][Fe_3Co_3(C_2)(CO)_{18}]$ (5) (eq 3). This cluster arises from the anticipated $Co_2(CO)_6$ ligation plus a metal substitution that exchanges isoelectronic $[Co(CO)_n]^+$ and $Fe(CO)_n$ fragments. Closer

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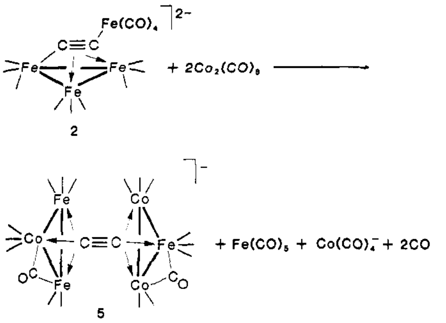
(36) (a) Weatherell, C.; Taylor, N. J.; Carty, A. J.; Sappa, E.; Tiripicchio, A. *J. Organomet. Chem.* **1985**, *291*, C9. (b) Ewing, P.; Farrugia, L. J. *J. Organomet. Chem.* **1987**, *320*, C47. (c) Sappa, E.; Tiripicchio, A.; Carty, A. J.; Toogood, G. E. *Prog. Inorg. Chem.* **1987**, *35*, 437. (d) Ewing, P.; Farrugia, L. J. *Organometallics* **1989**, *8*, 1246. (e) Chi, Y.; Lee, G.-H.; Peng, S.-M.; Wu, C.-H. *Organometallics* **1989**, *8*, 1574. (f) Chi, Y.; Wu, C.-H.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1991**, *10*, 1677. (g) Rumin, R.; Robin, F.; Petillon, F. Y.; Muir, K. W.; Stevenson, I. *Organometallics* **1991**, *10*, 2274.

(37) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169.

(38) Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323.

(39) (a) Yasufuku, K.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2664. (b) Yasufuku, K.; Aoki, K.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1616. (c) Carriedo, G. A.; Riera, V.; Miguel, D.; Manotti Lanfredi, A. M.; Tiripicchio, A. *J. Organomet. Chem.* **1984**, *272*, C17. (d) Bruce, M. I.; Duffy, D. N.; Humphrey, M. G. *Aust. J. Chem.* **1986**, *39*, 159. (e) Bruce, M. I. *Pure Appl. Chem.* **1986**, *58*, 553. (f) Seyferth, D.; Hoke, J. B.; Rheingold, A. L.; Cowie, M.; Hunter, A. D. *Organometallics* **1988**, *7*, 2163. (g) Weidmann, T.; Weinrich, V.; Wagner, B.; Robl, C.; Beck, W. *Chem. Ber.* **1991**, *124*, 1363.



(3)

spectroscopic inspection of the reaction of **2** with 1 equiv of $Co_2(CO)_8$ revealed that two intermediates are generated: the expected dicarbido compound [PPN][$Fe_4Co_2(C_2)(CO)_{18}$] (**3**) and the acetylide complex [PPN][$CoFe_2(CO)_9C$-$CFe(CO)_4$] (**4**). These clusters form in roughly equimolar amounts under the conditions employed. Both compounds were observed to react with a second equivalent of $Co_2(CO)_8$ to give **5**. The conversions of **2** to **3** and **4** to **5** are thought to be effected by coordination of $Co_2(CO)_8$ to the acetylide ligand, triggering condensation of a second metal triangle. The reactions taking **2** to **4** and **3** to **5** are further examples of a metal substitution reaction observed in other work with similar trimetallic clusters.[21h,40] Because the general nature of this reaction was previously established, yields of the side products $Fe(CO)_5$ and [PPN][$Co(CO)_4$] were not determined.

Reaction of **1** with $Co_2(CO)_8$ also yields **5**. The mechanism of this transformation is obscure but apparently involves formal addition of a $[Co(CO)_n]^-$ species to the cluster with explusion of the unique iron. The relatively strong Fe–C_α σ bond [$d_{\mathrm{Fe-C}}$ = 1.809 (6) Å][18] remains intact, giving **4** when acetate is lost from the unobserved alkyne. Minor side reactions give other uncharacterized products, limiting the eventual yield of **5**.

The transformation of **3** to **5** is reversed by 1 equiv of $[PPN]_2[Fe_2(CO)_8]$.[41] Thus, incorporation of cobalt by metal substitution must occur in the original triiron cluster framework, and **5** consists of one $CoFe_2$ triangle and one Co_2Fe group on either end of the C_2 ligand. The structures of compounds **3** and **5** are therefore assumed to be identical and to strongly resemble $Co_6(C_2)(CO)_{18}$.[11j]

In keeping with the proposed isostructural relationship between **3** and **5**, the infrared spectra of the two compounds are very similar, with the $\nu(C\equiv O)$ bands of the dianion **3** shifted 30–45 cm^{-1} lower than those of the monoanion **5**. Both spectra contain a broad band some 220 cm^{-1} lower than the strongest modes, indicating that one or more carbonyls bridge two metals. The $\nu(C\equiv C)$ band of **5**, expected to be symmetry allowed but weak, was not located. This mode lies at 1411 cm^{-1} in $Co_6(C_2)(CO)_{14}S$;[11k] if a similar value applies to **5**, the band is likely obscured by absorptions from the PPN^+ counterion. The infrared spectrum of **4** includes $\nu(C\equiv O)$ bands at 2074 vw, 2028 vs, 2017 s, and 1990 m cm^{-1} in CH_2Cl_2 solution.

The dicarbido cluster compound **5** was further characterized by ^{13}C NMR spectroscopy. The presence of three quadrupolar ^{59}Co nuclei ($I = {}^7/_2$, 100% abundance) hampered investigation, but synthesis from ^{13}C-enriched **1** and variable-temperature techniques were sufficient to overcome this obstacle. The spectrum of **5** at room temperature (Figure 3) consists of a wide envelope from 200 to 225 ppm ascribed to terminal CO ligands, two broad signals at 240 and 245 ppm apparently due to bridging carbonyls, and two broad resonances at 285.9 and 293.7 ppm assigned to the dicarbide ligand. The observation of two broad ligand resonances confirms the unsymmetrical structure with cobalt in both metal triangles. The downfield resonance sharpens more rapidly with decreasing temperature, prompting their assignment to the carbon adjacent to the monocobalt triangle. In spectra recorded at −70 °C, satellites due to spin–spin coupling are resolved, with $^1J_{C-C}$ = 34 Hz.

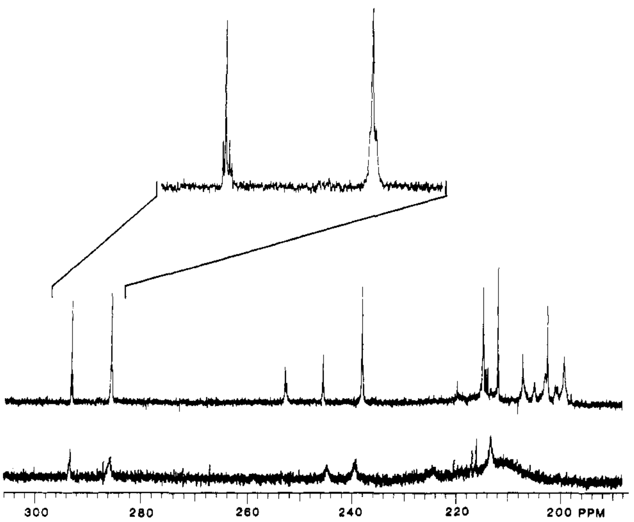


Figure 3. ^{13}C NMR spectra of [PPN][$Fe_3Co_3(C_2)(CO)_{18}$] (**5**), prepared from **1** enriched to ~30% ^{13}C at all cluster carbons, recorded at room temperature (bottom) and at −70 °C (top). Resonances due to the $[PPN]^+$ counterion are not shown.

Since clusters **3** and **4** escaped routine isolation, ^{13}C NMR spectroscopy was used to probe the initial reaction of enriched **2** with $Co_2(CO)_8$ in situ. A spectrum of the reaction mixture, recorded at −70 °C, contains two pairs of ligand resonances. Signals at 285.7 and 279.4 ppm are attributed to the dicarbide ligand of **3**. The downfield resonance is assigned to the carbon bound to the Co_2Fe triangle on the basis of greater quadrupolar broadening. Unfortunately, neither resonance was sufficiently narrow to observe coupling. Two other signals at 193.1 and 142.2 ppm correspond respectively to C_α and C_β on **4**, with $^1J_{C-C}$ = 27 Hz. The downfield resonance is broad at room temperature, indicating a σ bond between C_α and cobalt, as determined for other $CoFe_2$ acetylide clusters.[39f,42] The C_β chemical shift is temperature dependant, having a value of 149.4 ppm under ambient conditions.

At present, there are few data on NMR features of dicarbido ligands against which the ^{13}C spectrum of **5** can be meaningfully compared. To our knowledge, no spectra have been reported for any of the cluster dicarbides listed in ref 11. The spectrum of enriched *trans*-$(Ph_2MeP)_2Pt[C_2W_2(OtBu)_5]_2$[7c,d] contains resonances at 302 and 233 ppm, with $^1J_{C-C}$ = 18 Hz. This compound, described as either a dicarbido complex or as dimetallaacetylide, is not isostructural with **5**. The C_4 carbons of $[Co_3(CO)_9]_2C_4$[43] resonate at 213.2 ppm (Co_3-*C*-C-$)_2$ and 131.8 ppm (Co_3-C-*C*-$)_2$.[44] The C_2 ligand resonances of **5** fall in the wide range of chemical shifts observed for μ_3-alkylidyne carbons.[45] The absence of diagnostic spectral features for

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(40) (a) Epstein, R. A.; Withers, H. W.; Geoffroy, G. L. *Inorg. Chem.* **1979**, *18*, 942. (b) Horwitz, C. P.; Holt, E. M.; Shriver, D. F. *Organometallics* **1985**, *4*, 1117. (c) Ching, S.; Jensen, M. P.; Sabat, M.; Shriver, D. F. *Organometallics* **1989**, *8*, 1058.

(41) Strong, H.; Krusic, P. J.; San Filipo, J. *Inorg. Synth.* **1990**, *28*, 203.

(42) Ching, S.; Sabat, M.; Shriver, D. F. *Organometallics* **1989**, *8*, 1047.

(43) Dellaca, R. J.; Penfold, B. R.; Robinson, B. H.; Robinson, W. T.; Spencer, J. L. *Inorg. Chem.* **1970**, *9*, 2204.

(44) Aime, S. *Inorg. Chim. Acta* **1982**, *62*, 51.

(45) Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97.

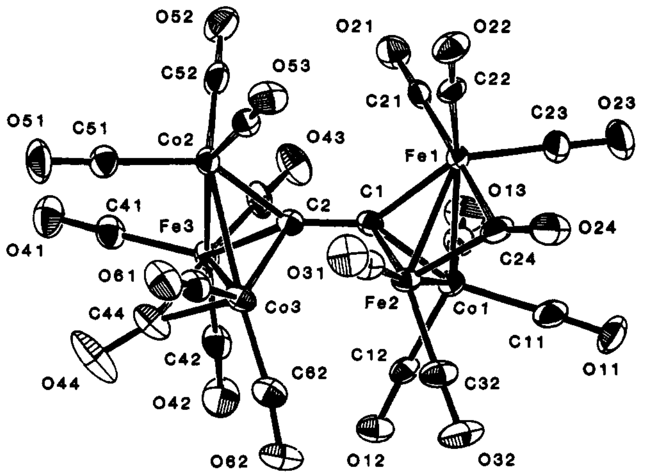

Figure 4. ORTEP diagram of the cluster anion of 5, $[Fe_3Co_3(C_2)(CO)_{18}]^-$, with ellipsoids drawn at 30% probability.

the dicarbide ligand of 5 prompted an X-ray crystal structure determination.

Structure and Bonding in 5. The structure of 5 as determined by X-ray crystallography (Figure 4) consists of two distorted M_3C tetrahedra linked by the dicarbide bond. The identities of metals could not be determined from diffraction data so they are tentatively assigned positions that are compatible with the spectroscopic data. The length of the dicarbide bond is 1.362 (8) Å, equivalent to the distance of 1.37 (1) Å found in $Co_6(C_2)(CO)_{18}$[11j] and $Co_6(C_2)(CO)_{14}S$.[11k] The former cluster closely resembles 5, featuring two parallel $(CO)_9Co_3$ triangles oriented orthogonally to the dicarbide ligand in a slightly staggered arrangement. However, in 5 the metal planes are tipped toward one another, placing Fe2 and Co3 only 2.899 (1) Å apart. This distance is too large for a bond between first-row metals, but the metals are close enough to alter the coordination of the CO ligands. The carbonyls are pushed away, and the two equatorial ligands lying closest to the opposing metal triangles (C31–O31 and C62–O62) are slightly bent, displaying M–C–O angles of 173.2 (7)°. The axial carbonyls (C24–O24 and C44–O44) bridge asymmetrically to other metals. Both metal frameworks are nearly perfect equilateral triangles in spite of these bridges. Because of the tipping, the disposition of the metals about the dicarbido carbons varies greatly. The

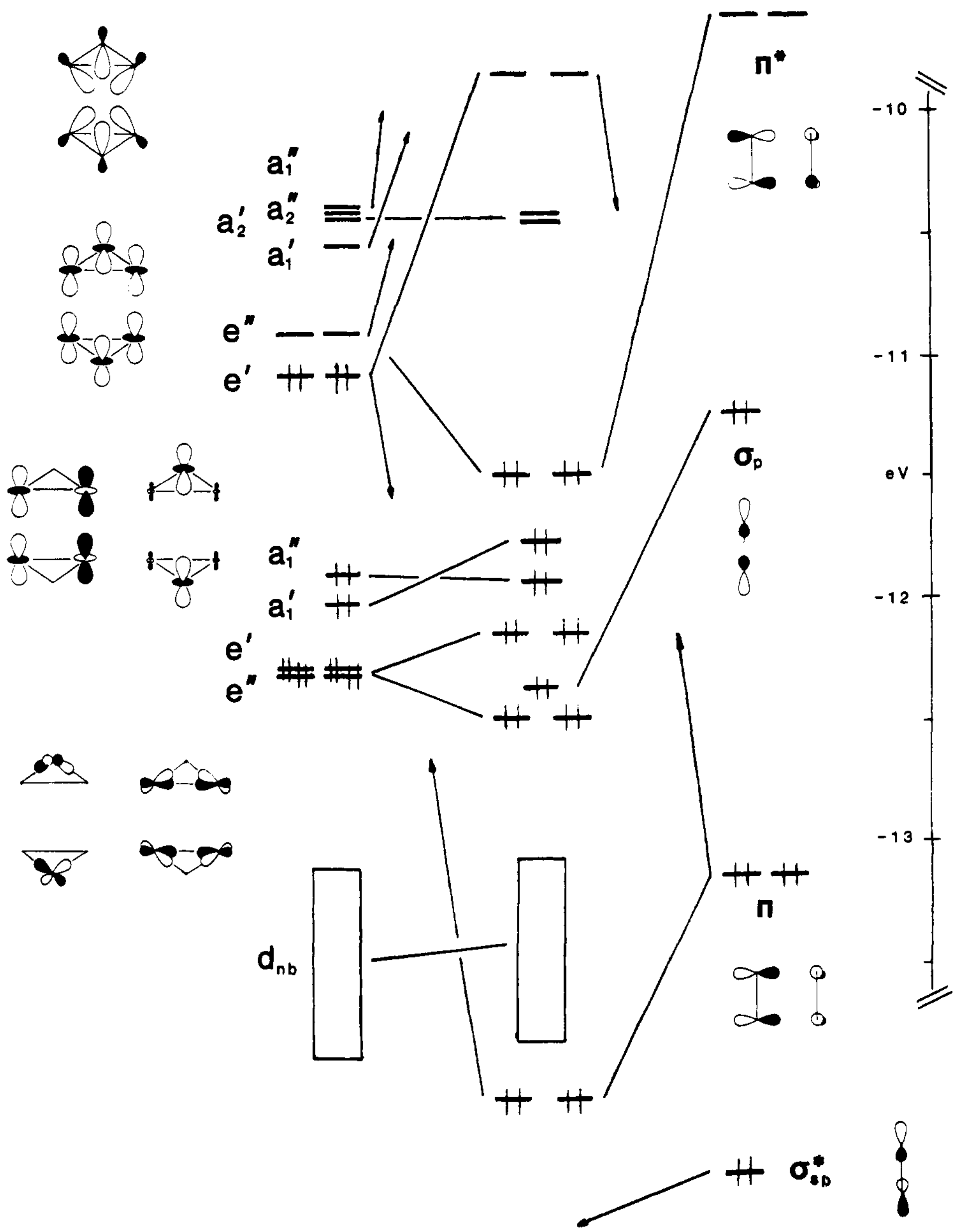

Figure 5. Partial interaction diagram for D_{3h} $Co_6(C_2)(CO)_{18}$, with ligand and in-phase metal a′ and e′ orbitals.

Table V. Summary of Geometric and Electronic Parameters for the $M_6(C_2)(CO)_{18}$ Model

	M_1–M_2–M_3 tilt, deg							
	0	2.5	5.0	7.5	10.0	12.5	15.0	17.5
M1–C1, Å	1.950	1.945	1.942	1.939	1.938	1.937	1.936	1.937
M2,3–C1, Å	1.950	1.953	1.958	1.964	1.971	1.980	1.991	2.003
M1···M1′, Å	3.992	3.866	3.741	3.615	3.491	3.367	3.245	3.124
∠M1–C1–C1′, deg	132.3	129.9	127.6	125.4	123.2	121.0	119.0	116.9
∠M2,3–C1–C1′, deg	132.3	133.4	134.6	135.7	136.8	137.8	138.8	139.7
$\Delta E_{\text{tot.}}$(calc), eV								
$[Co_6(C_2)(CO)_{18}]^{2+}$	0.00	–0.05	–0.06	+0.02	+0.04	+0.21	+1.55	+5.13
$[Fe_3Co_3(C_2)(CO)_{18}]^-$	0.00	–0.04	–0.03	+0.06	+0.09	+0.30	+1.62	+5.21

M–C–C bond angles range from 110.0 (4) to 140.6 (5)°, and the metal–dicarbide distances vary somewhat from 1.919 (6) Å (Co1–C1) to 1.987 (6) Å (Fe3–C2). Resonances in the μ_2-CO region of the ^{13}C NMR spectrum of 5 suggest this structure is retained in solution, even at room temperature. Tilting of π ligands on $M_3(CO)_9$ faces is generally facile,[46] so the structural distortion of 5 might be dismissed as uncompelling. However, consideration of the bonding in 5 indicates that the tilt may be enforced by a second-order Jahn–Teller effect.

The open dicarbide cluster $Co_6(C_2)(CO)_{18}$ is expected to have 96 valence electrons (2 × 48),[47] and this is in fact the case when the $(C_2)^{2-}$ ligand is counted as an eight-electron donor. However, $[Fe_3Co_3(C_2)(CO)_{18}]^-$ (anion of 5), with two fewer valence electrons, is a stable, diamagnetic compound. As the first step in clarifying this difference in structure and electron count, extended Hückel calculations were performed on an idealized eclipsed D_{3h} geometry of $Co_6(C_2)(CO)_{18}$. The resulting interaction diagram (Figure 5) is readily interpreted by comparison to the electronic structures of face-capped C_{3v} $M_3(CO)_9(\mu_3\text{-L})$ complexes.[46c] Orbitals on each of the three-metal triangular faces the form two sets of a_1 + e orbitals. The filled lower set is metal–metal bonding. The empty second set interacts with donor orbitals on the capping ligand, for example, the a_1 lone pair and e π bonds of ketenylidene, $(CCO)^{2-}$.[16d] A lone metal–metal antibonding orbital of a_2 symmetry is generally left as the LUMO in the resulting complex.

The coordination of $(C_2)^{2-}$ in eclipsed $Co_6(C_2)(CO)_{18}$ is similar; however, in-phase and out-of-phase combinations of orbitals across the two opposing metal triangles give rise to two sets of six orbitals with $a_1' + a_1'' + e' + e''$ symmetry. The filled lower set again comprises the six metal–metal bonds. The partially filled upper set accepts electrons from the filled σ^*_{sp} (a_1''), π (e′), and σ_p (a_1') $(C_2)^{2-}$ dicarbide orbitals. The metals also donate into the empty π^* (e″) ligand orbitals. The resulting back-bonding accounts for the lengthened $(C_2)^{2-}$ bond, 1.37 (1) Å.[11j] This bond length is still considerably shorter than those of most encapsulated dicarbides, in which donation from the σ_p orbital and back-donation into the π^* set appears to be more favorable.[13] Consistent with this difference, the calculated overlap population of 1.14 for the dicarbide bond lies above the values of 0.88–1.11 calculated for dicarbides enclosed in larger Co_8L_{16} and $Co_{10}L_{16}$ frameworks. Therefore, the dicarbide is less activated by Chatt–Dewar–Duncanson bonding in the lower nuclearity open compounds $Co_6(C_2)(CO)_{18}$ and 5. The carbon atoms of the ligand thus each retain a substantial negative charge calculated to be –0.36 e⁻. As in the capped trinuclear cluster compounds, the LUMO is a_2' metal–metal antibonding. The LUMO

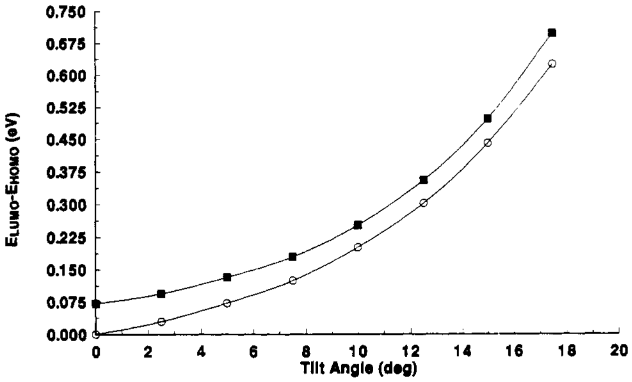

Figure 6. Plot of calculated HOMO–LUMO gap vs M_3 tilt for hypothetical C_{2v} $[Co_6(C_2)(CO)_{18}]^{2+}$ (circles) and C_s $[Fe_3Co_3(C_2)(CO)_{18}]^-$ (boxes).

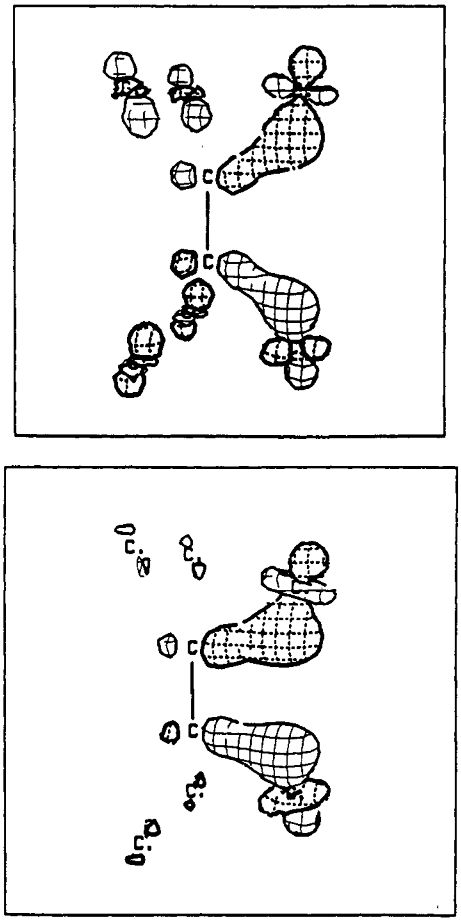

Figure 7. CACAO drawings of the LUMO for $[Co_6(C_2)(CO)_{18}]^{2+}$ at 0° (top) and at 15° tilt (bottom).

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(46) (a) Seyferth, D.; Williams, G. H.; Hallgren, J. E. *J. Am. Chem. Soc.* **1973**, *95*, 266. (b) Seyferth, D.; Williams, G. H.; Traficante, D. D. *J. Am. Chem. Soc.* **1974**, *96*, 604. (c) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456. (d) D'Agostino, M. F.; Mlekuz, M.; Kolis, J. W.; Sayer, B. G.; Rodger, C. A.; Halet, J.-F.; Saillard, J.-Y.; McGlinchey, M. J. *Organometallics* **1986**, *5*, 2345.

(47) (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1975**, *18*, 1. (b) Mingos, D. M. P. *Adv. Organomet. Chem.* **1977**, *15*, 1. (c) Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305.

lies 1.05 eV above the HOMOs and just 0.01 eV below the corresponding a_2'' orbital.

Calculations on C_s $[Fe_3Co_3(C_2)(CO)_{18}]^-$ in the same geometry lead to analogous results, but with the degenerate e′ and e″ sets slightly split because of the low symmetry of the heterometal triangles. However, the calculated splitting (0.07 eV) is too small to give a diamagnetic ground state at room temperature. Accordingly, we explored the possibility that the tilt of the two M_3 planes observed for **5** might increase the HOMO–LUMO separation. The distortion observed for **5** was modeled by tilting the metal planes of $C_s[Fe_3Co_3(C_2)(CO)_{18}]^-$ and $D_{3h}[Co_6(C_2)(CO)_{18}]^{2+}$ as described above. This immediately lowers the symmetry of the latter to C_{2v} but leaves the symmetry of the mixed-metal compound unchanged. The calculated total energy is virtually unaffected for both compounds, indicating such tipping is facile. Calculations performed on arrangements tilted up to 17.5° indicated a greatly increasing HOMO–LUMO separation with increasing tilt (Figure 6). Although this simple analysis ignores the rearrangement of carbonyl ligands, these results indicate that the observed diamagnetism results from the tilt of the two metal triangles. The gap results primarily from destabilization of the LUMO (Figure 7). The shifts of other frontier orbitals are minor by comparison, especially for those lacking involvement of the ligand π system.

These calculations also suggest **5** could display reversible redox behavior. Unfortunately, chemical reduction with a variety of reagents leads to destructive cluster fragmentation. The opposite approach, reversible oxidation of $Co_6(C_2)(CO)_{18}$, may be more feasible.

Conclusions

Conversion of a cluster-bound ketenylidene ligand to dicarbides by cluster expansion of a metalated acetylide has been achieved, indicating that ketenylidenes might be general precursors to C_2-containing metal clusters, just as they are useful precursors for metal cluster carbides. Analyses of metalate attack and $Co_2(CO)_8$ addition to the acetylide clusters indicate these reactions are mechanistically complex. NMR spectral properties of two dicarbide complexes have been recorded. A further distorted example of a rare structural type has been identified, and the electronic basis for this distortion has been described.

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Supplementary Material Available: Complete listings of thermal parameters and hydrogen atomic coordinates for **5** (4 pages). Ordering information is given on any current masthead page.

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Preparation and Properties of Chiral Titanocene and Zirconocene Dichloride Complexes of a Chiral Ligand

Arnold L. Rheingold,[†] N. P. Robinson,[‡] John Whelan,[‡] and B. Bosnich*[,‡]

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue,
Chicago, Illinois 60637, and Department of Chemistry and Biochemistry, University of Delaware,
Newark, Delaware 19716

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The ligand (*S,S*)-2,3-butylene-1,1′-bis(indene) was prepared from diindenylmagnesium and the dimesylate of (*R,R*)-2,3-butanediol after conventional synthetic methods had failed. Reaction of the dilithium salt of (*S,S*)-2,3-butylene-1,1′-bis(indene) with $TiCl_4{\cdot}2THF$ in THF under high-dilution conditions gave [Ti((*S,S*)-2,3-butylene-1,1′-bis(indenyl))Cl_2], which, upon PtO_2/H_2 reduction, gave [Ti((*S,S*)-chiracene)Cl_2] as a mixture of kinetically formed isomers. These consisted of the *R,R*, *R,S*, and *S,S* diastereomers. Upon irradiation, a photostationary state consisting of 85% of the *R,R* isomer and 15% of the *R,S* isomer was obtained. The desired pure (*R,R*)-[Ti((*S,S*)-chiracene)Cl_2] complex was isolated, and its crystal structure was determined by X-ray diffraction. It was found that this complex was configurationally stable under normal conditions, confirming our initial expectations. The circular dichroism spectra of the *R,R* and *R,S* isomers have been recorded and discussed, and a connection between the photostationary state and thermodynamic equilibrium of the isomers is suggested. The corresponding zirconium complexes were obtained in low yield. There is a strong kinetic preference for the (*R,S*)-[Zr((*S,S*)-chiracene)Cl_2] isomer. This isomer was isolated, and its structure was determined by X-ray diffraction. The photostationary state is different from that of the titanium analogue. It consists of a mixture of *R,R* and *S,S* diastereomers.

With appropriate substitution cyclopentadienyl ligands form chiral complexes when bound to a metal. Of particular current interest are chiral species derived from $[Cp_2MX_2]$ complexes (Cp = cyclopentadienyl; M = Ti(IV), Zr(IV), Hf(IV)). These chiral complexes have been employed as precursors for a variety of stereoselective transformations. Among these are asymmetric catalytic hydrogenation of olefins,[1] a variety of stoichiometric asymmetric transformations,[2,5] and stereoselective polym-

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[†] University of Delaware.

[‡] The University of Chicago.

(1) Pino, P.; Galimberti, M. *J. Organomet. Chem.* **1989**, *370*, 1. Waymouth, R.; Pino, P. *J. Am. Chem. Soc.* **1990**, *112*, 4911. Halterman, R. L.; Vollhardt, K. P. C. *Tetrahedron Lett.* **1986**, *27*, 1461. Halterman, R. L.; Vollhardt, K. P. C.; Welker, M. E.; Bläser, D.; Boese, R. *J. Am. Chem. Soc.* **1987**, *109*, 8105. Halterman, R. L.; Vollhardt, K. P. C. *Organometallics* **1988**, *7*, 883. Cesarotti, E.; Ugo, R.; Kagan, H. B. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 779. Cesarotti, E.; Ugo, R.; Vitiello, R. *J. Mol. Catal.* **1981**, *12*, 63. Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501.

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