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Tricobalt Carbonyl Clusters Containing C_n ($n = 2, 4, 6$) Ligands

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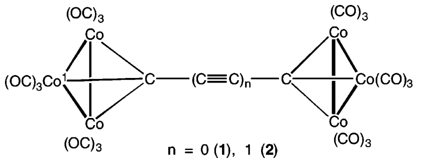
Treatment of $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_7$ with zinc dust in refluxing thf afforded $Co_6(\mu_6\text{-}C_2)(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_{12}$ (**5**), containing two Co_3 triangles which are linked by a short Co−Co bond and the C_2 ligand. The Pd(0)/Cu(I)-catalyzed reactions of $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_7$ or $Co_3(\mu_3\text{-CBr})(CO)_9$ with $Co_3\{\mu_3\text{-C}(C{\equiv}C)_nAu(PPh_3)\}(\mu\text{-dppm})(CO)_7$ ($n = 1, 2$, respectively) gave $\{Co_3(\mu\text{-dppm})(CO)_7\}_2(\mu_3{:}\mu_3\text{-CC}{\equiv}\text{CC})$ (**6**) and the unsymmetrical C_6 derivative $\{(OC)_9Co_3\}\{\mu_3{:}\mu_3\text{-C}(C{\equiv}C)_2C\}\{Co_3(\mu\text{-dppm})(CO)_7\}$ (**4**). The former reacted further with dppm to give $\{Co_3(\mu\text{-dppm})(CO)_7\}_2(\mu_3{:}\mu_3\text{-CC}{\equiv}\text{CC})(\mu\text{-dppm})$ (**7**), in which the two Co_3 clusters are bridged by the third dppm ligand.

Introduction

Interest in compounds containing unsaturated C_n chains end-capped by transition-metal−ligand groups arises out of the propensity for electronic interactions (electron or hole transport) between the metal centers through the carbon chain.[1−3] This is particularly apparent when the metal−ligand groupings are redox active, and much recent interest in systems containing Mn,[4] Re,[5] Fe,[6,7] Ru,[8] Ru_2,[9] and Pt[10] has been summarized in recent reviews.[11]

Complexes containing C_2 or C_4 groups linking two metal cluster moieties have been known for many years.[12−14] The molecular structures of both monoclinic[15] and trigonal[16] phases of $\{(OC)_9Co_3\}_2(\mu_3{:}\mu_3\text{-}C_2)$ (**1**) confirm the presence of a C−C bond, measured at 1.37(2) and 1.426(9) Å, respectively. Each carbon atom is also attached to a triangular $Co_3(CO)_9$ cluster with mean Co−Co and Co−C separations of 2.457(1) and 1.95(1) Å, respectively. The X-ray structure of the analogous C_4 cluster (**2**)[13c] shows that the C_4 ligand linking the two $Co_3(CO)_9$ clusters has C−C separations of 1.37(1) and 1.24(2) Å, together with mean Co−Co and Co−C distances of 2.47(1) and 1.92(1) Å. In this complex, the carbon chain geometry is consistent with



n = 0 (**1**), 1 (**2**)

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(1) Ward, M. D. *Chem. Ind.* **1996**, 568.

(2) Harriman, A. D.; Ziessel, R. *Coord. Chem. Rev.* **1998**, *171*, 331.

(3) (a) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178−180*, 431. (b) Paul, F.; Lapinte, C. In *Unusual Structures annd Physical Properties in Organometallic Chemistry*; Gielen, M.; Willem, R.; Wrackmeyer, B.; Eds.; Wiley: Chichester, U.K., 2002; p 220.

(4) (a) Fernandez, F. J.; Alfonso, M.; Schmalle, H. W.; Berke, H. *Organometallics* **2001**, *20*, 3122. (b) Kheradmandan, S.; Heinze, K.; Schmalle, H. W.; Berke, H. *Angew. Chem.* **1999**, *111*, 2412; *Angew. Chem., Int. Ed.* **1999**, *38*, 2270. (c) Keradmandan, S.; Venkatesan, K.; Blacque, O.; Schmalle, H. W.; Berke, H. *Chem. Eur. J.* **2004**, *10*, 4872.

(5) (a) Brady, M.; Weng, W.; Zhou, Y.; Seyler, J. W.; Amoroso, A. J.; Arif, A. M.; Böhme, M.; Frenking, G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 11922. (b) Falloon, S. B.; Szafert, S.; Arif, A. M.; Gladysz, J. A. *Chem. Eur. J.* **1998**, *4*, 1033. (c) Bartik, T.; Weng, W.; Ramsden, J. A.; Szafert, S.; Falloon, S. B.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.*, **1998**, *120*, 11071. (d) Dembinski, R.; Bartik, T.; Bartik, B.; Jarger, M.; Gladysz, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 810. (e) Meyer, W. E.; Amoroso, A. J.; Horn, C. R.; Jaeger, M.; Gladysz, J. A. *Organometallics* **2001**, *20*, 1115. (f) Brady, M.; Weng, W.; Zhou, Y.; Seyler, J. W.; Amoroso, A. J.; Arif, A. M.; Böhme, M.; Frenking, G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 775.

(6) (a) Akita, M.; Chung, M.-C.; Terada, M.; Miyauti, M.; Tanaka, M.; Moro-oka, Y. *J. Organomet. Chem.* **1998**, *565*, 49. (b) Akita, M.; Sugimoto, S.; Hirakawa, H.; Kato, S.; Terada, M.; Tanaka, M.; Moro-oka, Y. *Organometallics* **2001**, *20*, 1555. (c) Akita, M.; Terada, M.; Moro-oka, Y. *Organometallics* **1992**, *11*, 1825. (d) Chung, M.-C.; Sakurai, A.; Akita, M.; Moro-oka, Y. *Organometallics* **1999**, *18*, 4684. (e) Akaita, M.; Sakurai, A.; Chung, M.-C.; Moro-oka, Y. *J. Organomet. Chem.* **2003**, *670*, 2. (f) Akita, M.; Moro-oka, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 420.

(7) (a) Coat, F.; Guillevic, M.-A.; Toupet, L.; Paul, F.; Lapinte, C. *Organometallics* **1997**, *16*, 5988. (b) Guillemot, M.; Toupet, L.; Lapinte, C. *Organometallics* **1998**, *17*, 1928. (c) Coat, F.; Paul, F.; Lapinte, C.; Toupet, L.; Costuas, K.; Halet, J.-F. *J. Organomet. Chem.* **2003**, *683*, 368. (d) Le Narvor, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, 7129.

(8) (a) Bruce, M. I.; Low, P. J.; Costuas, K.; Halet, J.-F.; Best, S. P.; Heath, G. A. *J. Am. Chem. Soc.* **2000**, *122*, 1949. (b) Bruce, M. I.; Ellis, B. G.; Low, P. J.; Skelton, B. W.; White, A. H. *Organometallics* **2003**, *22*, 3184.

(9) (a) Ren, T.; Xu, G.-L. *Comments Inorg. Chem.* **2002**, *23*, 355. (b) Ren, T.; Zou, G.; Alvarez, J. C. *Chem. Commun.* **2000**, 1197.

(10) (a) Peters, T. B.; Bohling, J. C.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1999**, 18, 3261. (b) Mohr, W.; Stahl, J.; Hampel, F.; Gladysz, J. A. *Inorg. Chem.* **2001**, *40*, 3263. (c) Bohling, J. C., Peters, T. B.; Arif, A. M.; Hampel, F.; Gladysz, J. A. In *Coordination Chemistry at the Turn of the Century*; Ondrejovic, G., Sirota, A., Eds.; Slovak Technical University Press: Bratislava, Slovakia, 1999; p 47. (d) Owen, G. R.; Stahl, J.; Hampel, F.; Gladysz, J. A. *Organometallics* **2004**, *23*, 5889. (e) Owen, G. R.; Hampel, F.; Gladysz, J. A. *Organometallics* **2004**, *23*, 5893. (f) Zheng, Q.; Hampel, F.; Gladysz, J. A. *Organometallics* **2004**, *23*, 5896. (g) Mohr, W.; Stahl, J.; Hampel, F.; Gladysz, J. A. *Chem. Eur. J.* **2003**, *9*, 3324.

(11) (a) Low, P. J.; Bruce, M. I. *Adv. Organomet. Chem.* **2002**, *48*, 71. (b) Bruce, M. I.; Low, P. J. *Adv. Organomet. Chem.* **2004**, *50*, 179.

(12) Allegra, G.; Ercoli, R.; Peronaci, E. M. *Chem. Commun.* **1966**, 549.

(13) (a) Dellaca, R. J.; Penfold, B. R.; Robinson, B. H.; Robinson, W. T.; Spencer, J. L. *Inorg. Chem.* **1970**, *9*, 2197. (b) Robinson, B. H.; Spencer, J. L.; Hodges, R. *Chem. Commun.* **1968**, 1480. (c) Dellaca, R. J.; Penfold, B. R.; Robinson, B. H.; Robinson, W. T.; Spencer, J. L. *Inorg. Chem.* **1970**, *9*, 2204. (d) Palyi, G.; Varada, G.; Schmiedeknecht, K. *C1 Mol. Chem.* **1985**, *1*, 297. (e) Mlekuz, M.; D'Agostino, M. F.; Kolis, J. W.; McGlinchey, M. J. *J. Organomet. Chem.* **1986**, *303*, 361. (f) Seyferth, D.; Hallgren, J. E.; Spohn, R. J.; Williams, G. H.; Nestle, M. O.; Hung, P. L. K. *J. Organomet. Chem.* **1974**, *65*, 99. (g) Beveridge, A. D.; Clark, H. C. *J. Organomet. Chem.* **1968**, *11*, 601. (h) Bor, G.; Marko, L.; Marko, B. *Chem. Ber.*, **1961**, *95*, 333. (i) Le Coustemer, G.; Mollier, Y. *J. Chem. Soc., Chem. Commun.* **1980**, 38. (j) Varadi, G.; Palyi, G. *Inorg. Chim. Acta* **1976**, *20*, L33.

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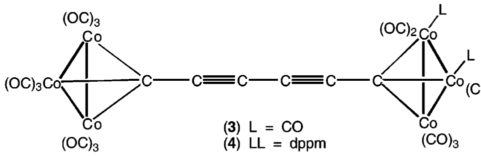
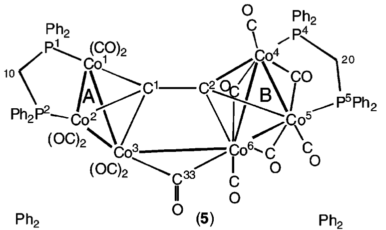
"partial π-delocalization", while the carbonyl groups shield the C≡C triple bond so that it does not react with $Co_2(CO)_8$, for example. The next higher ethynologue, $\{Co_3(CO)_9\}_2(\mu_3{:}\mu_3\text{-}CC{\equiv}CC{\equiv}CC)$ (**3**), has not yet been described, although the $Co_2(CO)_6$ derivative has been obtained and structurally characterized by two groups.[17,18] In connection with our studies on complexes containing carbon chains end-capped by metal cluster moieties, much of which has been centered on compounds containing the $Co_3(\mu\text{-dppm})(CO)_7$ end group,[19] we have attempted to obtain complexes analogous to **1** and **2** containing these end groups. This paper describes the results of our search and the structures and properties of three complexes which we have characterized, together with the asymmetric bis-cluster compound $\{(OC)_9Co_3\}(\mu_3{:}\mu_3\text{-}CC{\equiv}CC{\equiv}CC)\{Co_3(\mu\text{-dppm})(CO)_7\}$ (**4**).

Results and Discussion

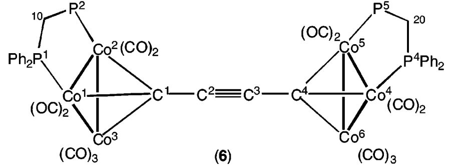
Treatment of $Co_3(\mu_3\text{-Br})(\mu\text{-dppm})(CO)_7$ with zinc dust in refluxing thf afforded a Co_6 cluster identified as $Co_6(\mu_6\text{-}C_2)(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_{12}$ (**5**) by a single-crystal X-ray structure determination, together with small amounts of $Co_3(\mu_3\text{-}CCO_2H)(\mu\text{-dppm})(CO)_7$.[20,21] In **5**, the two Co_3 clusters have been linked by a further long Co−Co bond (2.6788(6) Å) at the expense of loss of one of the CO ligands. This Co−Co bond is bridged by a CO group, while the C_2 fragment also links the two clusters by interacting with all six metal atoms. The two dppm ligands bridge Co−Co edges of the triangular faces and adopt a conformation which places them in mutually orthogonal orientations; in one Co_3 cluster the three basal Co−Co edges are also bridged by CO ligands.



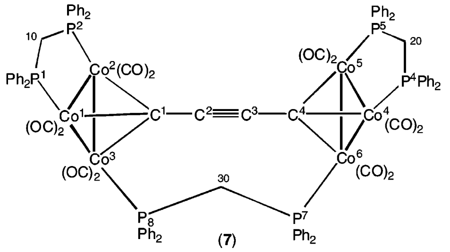
(**3**) L = CO
(**4**) LL = dppm



(**5**)



(**6**)



(**7**)

The C_4 complex $\{Co_3(\mu\text{-dppm})(CO)_7\}_2(\mu_3{:}\mu_3\text{-}CC{\equiv}CC)$ (**6**), obtained in 63% yield by the Pd(0)/Cu(I)-catalyzed elimination of $AuBr(PPh_3)$ from an equimolar mixture of $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_7$ and $Co_3\{\mu_3\text{-}CC{\equiv}CAu(PPh_3)\}(\mu\text{-dppm})(CO)_7$,[22] reacts further with dppm to give $\{Co_3(\mu\text{-dppm})(CO)_7\}_2(\mu_3{:}\mu_3\text{-}CC{\equiv}CC)(\mu\text{-dppm})$ (**7**) in 87% yield.[23] The unsymmetrical complex $\{(OC)_9Co_3\}\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_2C\}\{Co_3(\mu\text{-dppm})(CO)_7\}$ (**4**) was formed similarly in 72% yield from $Co_3(\mu_3\text{-CBr})(CO)_9$ and $Co_3(\mu_3\text{-}CC{\equiv}CC{\equiv}CAu(PPh_3))\}(\mu\text{-dppm})(CO)_7$.[24] All of the complexes were identified by elemental microanalyses and mass spectrometry.

The IR spectra of **3**−**7** each contained terminal ν(CO) absorptions between 2063 and 1933 cm^{-1}, with weak bands between 1875 and 1785 cm^{-1} arising from the bridging CO groups in **5**. Comparison of the spectra of **2** (2107 w, 2090 s, 2065 vs, 2037 s, 1983 vw cm^{-1}) and **6** is instructive, the stronger absorptions in particular showing a pronounced shift to lower wavenumbers, consistent with increased back-bonding from the more electron-rich dppm-substituted clusters. For **3**, ν(CO) bands

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[14] (a) Worth, G. H.; Robinson, B. H.; Simpson, J. *Organometallics* **1992**, *11*, 3863. (b) Robinson, B. H.; Tham, W. S. *J. Organomet. Chem.* **1968**, *16*, P45. (c) Matheson, T. W.; Robinson, B. H.; Tham, W. S. *J. Chem. Soc. A* **1971**, 1457.

[15] Brice, M. D.; Penfold, B. R. *Inorg. Chem.* **1972**, *11*, 1381.

[16] Geiser, U.; Kini, A. M. *Acta Crystallogr.* **1993**, *C49*, 1322.

[17] Seyferth, D.; Spohn, R. J.; Churchill, M. R.; Gold, K.; Scholer, F. *J. Organomet. Chem.* **1970**, *23*, 237.

[18] (a) Robinson, B. H.; Spencer, J. L. *J. Organomet. Chem.* **1971**, *30*, 267. (b) Dellaca, R. J.; Penfold, B. R. *Inorg. Chem.* **1971**, *10*, 1269.

[19] (a) Bruce, M. I.; Smith, M. E.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2003**, *670*, 170. (b) Bruce, M. I.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *J. Organomet. Chem.* **2003**, *683*, 398. (c) Antonova, A. B.; Bruce, M. I.; Ellis, B. G.; Gaudio, M.; Humphrey, P. A.; Jevric, M.; Melino, G.; Nicholson, B. K.; Perkins, G. J.; Skelton, B. W.; Stapleton, B.; White, A. H.; Zaitseva, N. N. *Chem. Commun.* **2004**, 960.

[20] Zinc dust (excess) was added to a solution of $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_9$ (50 mg, 0.06 mmol) in thf (6 mL), and the mixture was heated at the reflux point for 4 h. The filtered solution was evaporated, and a CH_2Cl_2 extract of the residue was separated by preparative tlc (acetone/hexane 3/7). The first black band (R_f 0.46) contained $Co_3(\mu_3\text{-CH})(\mu\text{-dppm})(CO)_9$ (5.3 mg, 11%), and the second green band (R_f 0,31) afforded $Co_3(\mu_3\text{-}CCO_2H)(\mu\text{-dppm})(CO)_9$ (2.9 mg, 6%), both identified by comparison with authentic samples. A slow-moving brown-purple band (R_f 0.21) yielded $Co_6(\mu_6\text{-}C_2)(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_{12}$ (**5**; 16.3 mg, 37%), obtained as dark crystals (CH_2Cl_2/MeOH). Anal. Found: C, 51.70; H, 2.92. Calcd ($C_{65}H_{44}Co_6O_{13}P_4$; M_r = 1510): C, 51.65; H, 2.91. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2045 s, 2015 vs, 1991 m, 1875 vw, 1848 vw, 1819 vw, 1785 vw. ^1H NMR: δ 2.84, 4.39 (2 × m, 2 × 2H, dppm), 7.37−7.87 (m, 40H, Ph). ^{31}P NMR: δ 32.25, 44.8 (2 × s (br)). ES MS (positive ion, MeOH + NaOMe, m/z): 1533, $[M + Na]^+$. ES MS (negative ion, MeOH + NaOMe, m/z): 1509, $[M - H]^-$; 1491, $[M - H - CO]^-$.

[21] Bruce, M. I.; Kramarczuk, K. A.; Perkins, G. J.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *J. Cluster Sci.* **2004**, *15*, 119.

[22] A mixture of $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_9$ (34 mg, 0.04 mmol), $Co_3\{\mu_3\text{-}CC{\equiv}CAu(PPh_3)\}(\mu\text{-dppm})(CO)_9$ (50 mg, 0.04 mmol), $Pd(PPh_3)_4$ (6 mg, 0.005 mmol), and CuI (1 mg, 0.005 mmol) in thf (4 mL) was stirred at room temperature for 2 h. After removal of solvent under reduced pressure, the residue was taken up in CH_2Cl_2 and separated by preparative tlc (acetone/hexane 3/7). One major brown band (R_f 0.28) was collected to give dark brown crystals of $\{(OC)_7(\mu\text{-dppm})Co_3\}_2(\mu_3{:}\mu_3\text{-}CC{\equiv}CC)$ (**6**; 40 mg, 63%). Anal. Found: C, 52.30; H, 2.66. Calcd ($C_{68}H_{44}Co_6O_{14}P_4$; M_r = 1562): C, 52.27; H, 2.84. IR (Nujol, cm^{-1}): ν(C≡C) 2113 w. IR (CH_2Cl_2): ν(CO) 2063 m, 2049 m, 2009 vs (br), 1975 (sh), 1961 (sh). ^1H NMR: δ 3.59, 4.08 (2 × m, 2 × 2H, dppm), 7.06−7.45 (m, 40H, Ph). ^{13}C NMR: δ 40.8 (s (br), CH_2), 96.1 (C_β), 128.0−132.6 (m, Ph), 204.1, 217.45 (2 × s (br), CO). ^{31}P NMR: δ 31.1 (dppm). ES MS (positive ion, MeOH, m/z): 1562, M^+; 1534−1478, $[M - nCO]^+$ (n = 1−3). ES MS (negative ion, MeOH + NaOMe, m/z): 1561, $[M - H]^-$.

[23] A solution containing **6** (70 mg, 0.045 mmol) and dppm (17.2 mg, 0.045 mmol) in thf (7 mL) was treated with Me_3NO (6.8 mg, 0.09 mmol), and the mixture was stirred at room temperature for 1 h. After removal of solvent under reduced pressure, a dichloromethane extract of the residue was purified by preparative tlc (acetone/hexane 3/7). The major purple band (R_f 0.31) contained $\{(OC)_7(\mu\text{-dppm})Co_3\}_2(\mu_3{:}\mu_3\text{-}CC{\equiv}CC)(\mu\text{-dppm})$ (**7**; 73.6 mg, 87%), which formed dark red crystals (CH_2Cl_2/MeOH). Anal. Found: C, 57.64; H, 3.40. Calcd ($C_{91}H_{66}Co_6O_{12}P_6$; M_r = 1891): C, 57.74; H, 3.49. IR (Nujol): ν(C≡C) 2133 vw. IR (CH_2Cl_2): ν(CO) 2012 vs, 1993 s (sh), 1982 m, 1962 m, 1933 (sh) cm^{-1}. ^1H NMR: δ 3.37, 3.54, 3.81 (3 × m, 3 × 2H, dppm), 7.13−7.37 (m, 60H, Ph). ^{13}C NMR: δ 30.65 (s (br), CH_2), 95.75 (C_β), 128.1−132.7 (m, Ph), 202.6, 213.1 (2 × s (br), CO). ^{31}P NMR: δ 31.2 (dppm). ES MS (positive ion, MeOH, m/z): 1891, M^+; 1863, 1835, $[M - nCO]^+$ (n = 1, 2).

are at 2099 m, 2058 vs, 2039 m, 2016 vs, 1971 (sh), and 1954 (sh) cm^{-1} and a weak band at 2115 cm^{-1} is assigned to ν(CC). For **4**, ν(CC) is at 2115 cm^{-1} and the ν(CO) bands are found between 2099 and 1954 cm^{-1} (cf. 2089 cm^{-1} and between 2064 and 1974 cm^{-1}, respectively, for $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu\text{-}C(C{\equiv}C)_2C\}$[19a]).

In the ^{1}H and ^{31}P NMR spectra, resonances at δ_H ca. 2.85 and 4.35 (CH$_2$), δ_H 7.0−7.9 (Ph), and δ_P 31−32 are assigned to the dppm ligands. In the case of **5**, two ^{31}P resonances are found at δ_P 32.25 and 44.8, which can be assigned to the dppm ligands on the non-CO-bridged and CO-bridged Co$_3$ clusters, respectively, by comparison with related complexes. For **6** and **7**, ^{13}C NMR spectra could be obtained and showed the dppm CH$_2$ (δ_C ca. 40) and Ph (δ_C ca. 128−132.5), together with the inner carbons of the C$_4$ chains at δ_C 96.13 (**6**) or 95.75 (**7**). The Co−CO ligands are found as broad singlets at δ_C ca. 203 and 215. Three ^{13}C resonances from the C$_6$ chain in **4** are found at δ 95.8, 112.5, and 123.0, with the CO ligands of the two clusters at δ 199.2 (Co$_3$(CO)$_9$) and 201.5, 209.4 (Co$_3$(dppm)(CO)$_7$). As is often the case, the carbons attached to the Co$_3$ clusters were not found, probably as a result of broadening by the cobalt quadrupole. The electrospray mass spectra (ES MS) were measured in solutions containing NaOMe to aid ionization and contained cations such as [M + Na]$^+$ and [M − *n*CO]$^+$ or anions such as [M − H − *n*CO]$^-$, consistent with their compositions.

Molecular Structures. The molecular structures of **5**−**7** have been determined by single-crystal X-ray diffraction studies: **5** modeled as its 3CH$_2$Cl$_2$ solvate, **6** as 4PhMe and 2CH$_2$Cl$_2$·2C$_6$H$_6$ solvates, as well as the unsolvated form, results from the latter being presented in Figure 2 and the main text. In addition, the structure of **2** has been redetermined from a specimen obtained during the course of another study.[25]

In **5** (Figure 1), the two Co$_3$ clusters have been linked by a further long Co−Co bond (2.6788(6) Å) at the expense of loss of one of the CO ligands. This Co−Co bond is bridged by a CO group, while the C$_2$ fragment also links the two clusters by interacting with all six metal atoms. The two dppm ligands bridge Co−Co edges of the triangular faces and adopt a conformation which places them in mutually orthogonal orientations (interplanar dihedral angle 89.79(4)°); in one Co$_3$ cluster the three basal Co−Co edges are also bridged by CO ligands. The Co−Co separations in the two Co$_3$ fragments of **5** (labeled **A** and **B** here) fall into four types and range between 2.4069 and 2.5412(6) Å. The shortest, Co(4)−Co(5) in cluster **B**, is bridged by both CO and one dppm ligand, while the two other CO-bridged edges are longer, at 2.4682 and 2.4806(6) Å. In the other Co$_3$ cluster **A**, the dppm-bridged edge is 2.4991(7) Å, some 0.093 Å longer than Co(4)−Co(5). Surprisingly, the two nonbridged Co(1,2)−Co(3) bonds differ by 0.04 Å, reflective of a more general asymmetry about the Co(3,6)C(1,2) plane. Somewhat longer Co−P bonds (2.2348, 2.2416(8) Å) are found for cluster **B** as compared to those for for cluster **A** (2.1929, 2.2243(8) Å). This is a result of these Co atoms being also involved in bonding to the bridging CO ligands and hence not back-bonding as efficiently into the phosphorus ligand. Both sets of values may be compared with those found in the prototypical complex Co$_3$(μ_3-CH)(μ-dppm)(CO)$_7$, which has Co−Co separations of 2.462(2) Å (dppm-bridged) and 2.452, 2.474(2) Å and Co−P distances of 2.162(2) Å.[21]

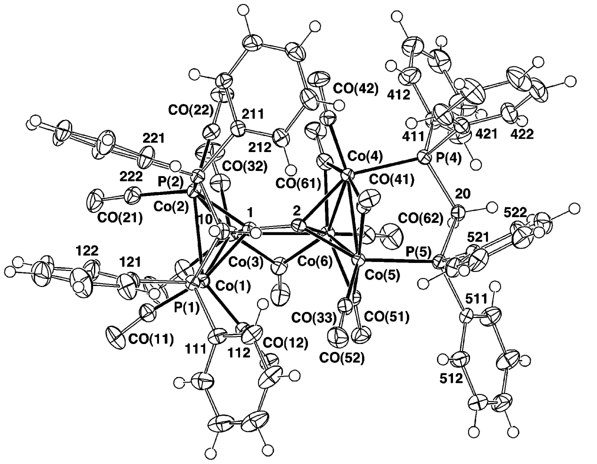

Figure 1. Plot of a molecule of Co$_6$(μ_6-C$_2$)(μ-dppm)$_2$(μ-CO)(CO)$_{12}$ (**5**), showing the atom-numbering scheme. Selected distances (Å) and angles (deg): Co(1)−Co(2) = 2.4991(7), Co(1)−Co(3) = 2.5079(6), Co(2)−Co(3) = 2.5412(6), Co(3)−Co(6) = 2.6788(6), Co(4)−Co(5) = 2.4069(7), Co(4)−Co(6) = 2.4682(6), Co(5)−Co(6) = 2.4806(6), Co(1)−P(1) = 2.1929(9), Co(2)−P(2) = 2.2243(8), Co(4)−P(4) = 2.2348(9), Co(5)−P(5) = 2.2416(8), Co(1,2,3)−C(1) = 1.927(3), 1.873(2), 2.001(3), Co(4,5,6)−C(2) = 1.946(3), 1.938(2), 2.024(3), C(1)−C(2) = 1.367(3); Co(1,2,3)−C(1)−C(2) = 136.3(2), 141.4(2), 102.2(2), Co(4,5,6)−Co(2)−Co(1) = 138.1(2), 143.4(2), 115.7(2).

The most interesting feature of the structure of **5** is the C$_2$ ligand, which interacts with all six metal atoms (Co−C = 1.873−2.024(3) Å). The somewhat unsymmetrical bonding appears to result from formation of shorter bonds to the cobalt atoms also supporting the dppm ligand, separations to atoms Co(3,6) being considerably longer at 2.001 and 2.024(3) Å as well as from the Co(3)−Co(6) interaction and its CO bridge. In Co$_3$(μ_3-CH)(μ-dppm)(CO)$_7$, the Co−C distances are between 1.836 and 1.898(9) Å, with no particular relationship to whether the Co is bonded to dppm.[21] The C(1)−C(2) bond length is 1.367(3) Å, the same as that in the monoclinic phase (1.37(2) Å)[15] but shorter than that found in the trigonal phase of **1** (1.426(9) Å).[16]

Complexes **6** and **7** (Figures 2 and 3) are derived from **2** by replacement of two CO ligands by two and three dppm ligands, respectively. In the former, the Co−Co edges bridged by dppm are somewhat longer, at 2.4826 and 2.4755(8) Å, than the other two in each cluster (2.4501−2.4672(6) Å) while, in comparison, the basal Co$_3$ triangle in **2** is considerably expanded (Co−Co(av) = 2.522(10) Å). The Co−P distances are in the range 2.178−2.187(1) Å, there being no essential difference from those found in **5** above. The third dppm ligand in **7** bridges the nonbonded Co(3)−Co(6) vector with Co−P distances of 2.216 and 2.242(1) Å. In this molecule, one of the non-dppm-bridged Co−Co bonds in each cluster is considerably longer (2.4948-

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[24] A solution containing Co$_3$(μ_3-CBr)(CO)$_9$ (41.6 mg, 0.08 mmol), Co$_3${μ_3-CC≡CC≡CAu(PPh$_3$)}(μ-dppm)(CO)$_9$ (100 mg, 0.08 mmol), Pd(PPh$_3$)$_4$ (9 mg, 0.008 mmol), and CuI (1 mg, 0.006 mmol) in thf (7 mL) was left at room temperature for 1 h. After removal of solvent, the residue was taken up in CH$_2$Cl$_2$ and purified by preparative tlc (acetone/hexane 3/7). The major brown band (R_f 0.57) afforded $\{(OC)_9Co_3\}(\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_2C)\text{-}\{Co_3(\mu\text{-dppm})(CO)_7\}$ (**8**; 70.8 mg, 72%) as small red platelike crystals. Anal. Found: C, 44.88; H, 1.68. Calcd (C$_{47}$H$_{22}$Co$_6$O$_{16}$P$_6$; M_r = 1258): C, 44.83; H, 1.75. IR (CH$_2$Cl$_2$, cm^{-1}): ν(C≡C) 2115 vw. IR (CH$_2$Cl$_2$): ν(CO) 2099 m, 2058 vs, 2039 m, 2016 s, 1971 (sh), 1954 m. ^{1}H NMR: δ 3.54, 4.37 (2 × m, 2 × 1H, dppm), 7.30−7.40 (m, 20H, Ph). ^{13}C NMR: δ 44.65 (t, *J*(CP) = 19 Hz, dppm), 95.8, 112.5, 123.0 (carbon chain), 128.55−135.3 (m, Ph), 199.2 (s (br), Co$_3$(CO)$_9$), 201.5, 209.4 (2 × s (br), Co$_3$(CO)$_7$(dppm)). ^{31}P NMR: δ 35.2 (s (br), dppm). ES MS (positive ion, MeOH + NaOMe, *m/z*): 1281, [M + Na]$^+$. ES MS (negative ion, MeOH + NaOMe, *m/z*): 1289, [M + OMe]$^-$; 1230, [M + OMe − CO]$^-$. A red band (R_f 0.50) contained $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_4C\}$ (5.2 mg, 8%), identified by comparison with an authentic sample.[19a]

[25] A serendipitous preparation of **2** enabled a structural determination to be made that was considerably more precise than that described over 30 years ago.[13,15] Structural parameters from the present determination are used in the discussion above.

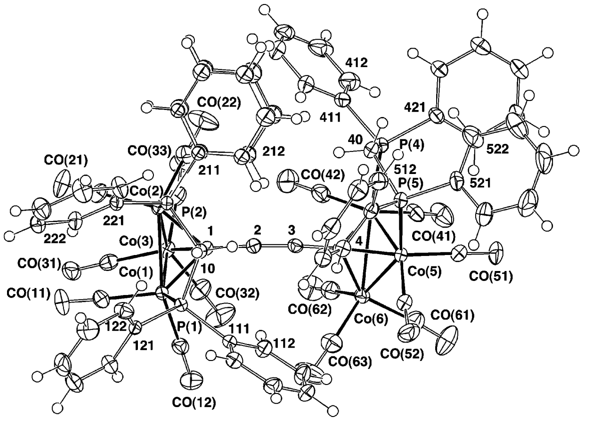

Figure 2. Plot of a molecule of $\{Co_3(\mu\text{-dppm})(CO)_7\}_2(\mu_3{:}\mu_3\text{-}CC{\equiv}CC)$ (**6**), showing the atom-numbering scheme. Selected distances (Å) and angles (deg): Co(1)−Co(2) = 2.4826(6), Co(1)−Co(3) = 2.4501(7), Co(2)−Co(3) = 2.4590(7), Co(4)−Co(5) = 2.4755(8), Co(4)−Co(6) = 2.4672(6), Co(5)−Co(6) = 2.4697(8), Co(1)−P(1) = 2.183(1), Co(2)−P(2) = 2.178(1), Co(4)−P(4) = 2.180(1), Co(5)−P(5) = 2.187(1), Co(1,2,3)−C(1) = 1.895(3), 1.902(3), 1.958(3), Co(4,5,6)−C(4) = 1.921(3), 1.896(4), 1.952(3), C(1)−C(2) = 1.381(5), C(2)−C(3) = 1.232(4), C(3)−C(4) = 1.370(4); Co(1,2,3)−C(1)−C(2) = 136.4(2), 135.0(2), 123.6(3), C(1)−C(2)−C(3) = 171.8(4), C(2)−C(3)−C(4) = 169.9(4), C(3)−C(4)−Co(4,5,6) = 129.4(3), 141.6(3), 123.8(3).

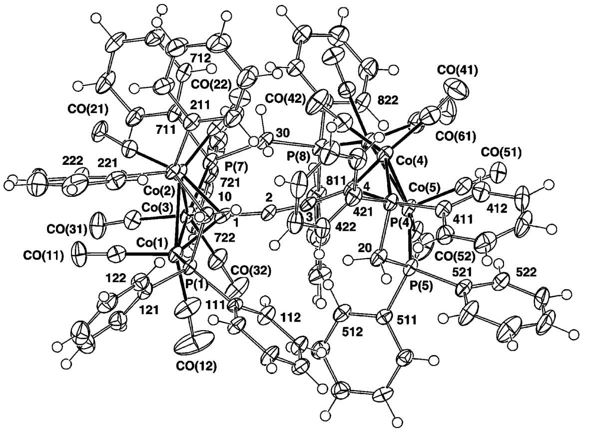

Figure 3. Plot of a molecule of $\{Co_3(\mu\text{-dppm})(CO)_7\}_2(\mu_3{:}\mu_3\text{-}CC{\equiv}CC)(\mu\text{-dppm})$ (**7**), showing the atom-numbering scheme. Selected distances (Å) and angles (deg): Co(1)−Co(2) = 2.4983(10), Co(1)−Co(3) = 2.4654(9), Co(2)−Co(3) = 2.4948(9), Co(4)−Co(5) = 2.4827(9), Co(4)−Co(6) = 2.5097(9), Co(5)−Co(6) = 2.4723(9), Co(1)−P(1) = 2.199(1), Co(2)−P(2) = 2.186(1), Co(3)−P(7) = 2.216(2), Co(4)−P(4) = 2.217(1), Co(5)−P(5) = 2.201(2), Co(6)−P(8) = 2.242(3), Co(1,2,3)−C(1) = 1.923(5), 1.920(4), 1.960(4), Co(4,5,6)−C(4) = 1.937(5), 1.930(4), 1.946(5), C(1)−C(2) = 1.396(7), C(2)−C(3) = 1.236(7), C(3)−C(4) = 1.387(7); Co(1,2,3)−C(1)−C(2) = 141.7(4), 129.2(4), 124.0(3), C(1)−C(2)−C(3) = 168.3(5), C(2)−C(3)−C(4) = 172.0(5), C(3)−C(4)−Co(4,5,6) = 126.1(3), 141.9(4), 127.6(3).

(9), 2.5097(9) Å) than the other two (2.4654, 2.4723(9) Å); the dppm-bridged Co−Co bonds are 2.4983 and 2.4827(9) Å.

The Co−C bonds in **6** range between 1.895 and 1.921(3) Å for Co(1,2,4,5), i.e., those attached to dppm, while the remaining Co−C bonds are longer (1.958, 1.952(3) Å). The four-carbon chain has interatomic distances of 1.381(5), 1.232(4), and 1.370(4) Å, suggesting some delocalization of the π-electron density along the chain. Angles at the two central carbons are 171.8(4) and 169.9(4)°, indicating a larger than normal distortion away from linearity. In **2**, the geometry is somewhat different, with slightly longer C−Co bonds (average 1.964(10) Å), C−C separations of 1.412 and 1.258(4) Å, and angles at the central carbons of 178.9(3)°. In **7**, the range of Co−C distances (1.920−1.960(4) Å) does not show any dependence on the nature of the dppm attachment. Again the C−C distances along the chain (1.396, 1.236, 1.387(7) Å) show evidence of electron delocalization, with angles at C(2) and C(3) of 168.3 and 172.0(5)°, respectively.

Table 1. Redox Chemistry of Cobalt Clusters[a]

complex	$E_1°$/V	$E_2°$/V	$\Delta E°$/mV	K_C
1[b]	−0.77	−0.41	360	1.21×10^6
2[b]	−0.68	−0.39	210	3.54×10^3
5	−1.18	+0.22	1400	
6[c]	−1.45	−1.21	240	1.14×10^4
7	−1.33	+0.06	1390	

[a] Conditions: 10^{-3} M complex, 0.1 M $[NBu_4]PF_6$ in CH_2Cl_2, referenced to $FeCp_2/[FeCp_2]^+ = +0.46$ V, three-electrode cell equipped with Pt-disk working electrode, Pt-gauze auxiliary electrode, and Pt-wire pseudo-reference electrode, scan rate 0.2 V s^{-1}. [b] References 26 and 27. [c] $E_3° = +0.85$ V.

In these three complexes, it is instructive to compare the torsion angles between the two dppm-bridged Co−Co vectors in each complex, as indicated by Co(3)−C(1)−C(2 or 4)−Co(6) values of −6.2(2), −50.4(2), and 41.7(3)° for **5**−**7**, respectively. While the simplest explanation for this varying twisting would appear to be steric interference between the dppm Ph substituents, also involving the equatorial CO groups to a degree, an electronic effect cannot be ruled out in the case of **5**, in which the basal Co−Co bonds are also CO-bridged. In the CCo_3 clusters, the presence of bridging CO groups has been interpreted in terms of a more electron-rich cluster, as found, for example, in the cases of $Co_3(\mu\text{-CCl})(CO)_9$ and its PCy_3-substituted analogues.[25]

Electrochemistry. Earlier extensive electrochemical studies of **1** and **2** have shown that each undergoes two distinct one-electron-reduction processes, a shift of the first to more negative potentials occurring as the carbon chain is lengthened from C_2 to C_4.[26,27] The reduction products are generally unstable at room temperature, and electron-transfer-catalyzed substitution of CO groups by ligands such as tertiary phosphines does not occur (in contrast to the situation with mono-cluster species).[26,28] At low temperatures, chemically reversible processes are found. Spectroscopic studies have been interpreted as showing conversion of the initial reduced species to a CO-bridged isomer which can be oxidized to the neutral **1**.[26] In their CVs (Table 1), the two 1e waves are separated by ca. 360 mV for **1** and by ca. 200 mV for **2**, with comproportionation constants, K_C, of 1.21×10^6 and 3.54×10^3, respectively. Both results suggest that there is effective electronic communication between the two sites of reduction, the CCo_3 clusters, dependent upon the separation between the clusters (separation between CCo_3 centers ca. 4.6 Å in **1** and ca. 7.1 Å in **2**). For **2**, a reversible oxidation is found at ca. +0.85 V.

The CVs of **5**−**7** are also given in Table 1. For **5** and **7**, only one reduction wave is found, assigned to the cluster core. An oxidation wave for **5** at +0.22 V, assigned to $[Co(CO)_4]^-$, together with some minor waves may indicate that these processes are not fully reversible at room temperature. Two 1e processes are found for **6**, which may be compared with the

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(26) (a) Worth, G. H.; Robinson, B. H.; Simpson, J. *Organometallics* **1992**, *11*, 3863. (b) Brooksby, P. A.; Duffy, N. W.; McQuillan, A. J.; Robinson, B. H.; Simpson, J. *J. Organomet. Chem.* **1999**, *582*, 183.

(27) (a) Osella, D.; Gambino, O.; Nervi, C.; Ravera, M.; Bertolino, D. *Inorg. Chim. Acta* **1993**, *206*, 155. (b) Osella, D.; Milone, L.; Nervi, C.; Ravera, M. *J. Organomet. Chem.* **1995**, *488*, 1.

(28) Dawson, P. A.; Robinson, B. H.; Simpson, J. *J. Chem. Soc., Dalton Trans.* **1979**, 1762.

two processes observed for the non-phosphine-substituted complex **2** at −0.62 and −0.82 V (separation 210 mV). It is more difficult to reduce **6** than it is to reduce **2** ($E = -1.21$, -1.45 V, $\Delta E = 240$ mV), and no oxidation wave is found. Addition of the bis-tertiary phosphine ligand to the Co_3 cluster is expected to increase the electron density within the CCo_3 core, in comparison with **2**, as also shown by the ν(CO) values, resulting in a system which is more difficult to reduce. The magnitude of the ΔE values (210 mV for **2** vs 240 mV for **6**, with K_C in the order **1** > **6** > **2**) suggests that electronic communication between the cluster cores through the carbon chain is marginally more pronounced in **6** than in **2**. For **7**, on the other hand, which is easier to reduce than **6** ($E = -1.33$ V), only one process is found, although a second, oxidation, event is found at +0.06 V.

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Supporting Information Available: Full details of the crystal structure determinations of **2** and **5**−**7** (CCDC 278100−278103, 281788) as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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