# Stereochemistry and Bonding of the Tris(benzene)tricobalt Dicarbonyl Monocation, [Co3($\eta^6$-C6H6)3($\mu_3$-CO)2]+: A Comparative Analysis of Its 48-Electron Co3(CO)2 Core with the 46-Electron Co3(CO)2 Core of Co3($\eta^5$-C5Me5)3($\mu_3$-CO)2 and Resulting Electronic Implications

## William L. Olson and Lawrence F. Dahl*

*Contribution from the Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706. Received September 12, 1985*

**Abstract:** A structural-bonding analysis of the 48-electron [Co3($\eta^6$-C6H6)3($\mu_3$-CO)2]+ monocation (**1**) was performed in order to provide an operational test that the corresponding 46-electron Co3($\eta^5$-C5Me5)3($\mu_3$-CO)2 (**2**), whose common Co3(CO)2 core contains *two* fewer valence electrons, has greater metal–metal bonding character. The greenish-brown cobalt–benzene trimer (**1**), initially prepared in 1958 and characterized then only by elemental analysis and an IR spectrum, was isolated as the tetraphenylborate salt and characterized by spectroscopic (IR and $^1$H NMR), electrochemical, and X-ray diffraction measurements. The *mean* Co–Co bond length in **1** was compared with those in eight other 48-electron [Co3($\eta^5$-C5R5)3($\mu_3$-X)($\mu_3$-Y)]$^n$ clusters containing Co3XY cores (for which X = CO, CS, NO; Y = O, NO, NR, S) with either C5H5 (four), C5H4Me (three), or C5Me5 (one) ligands. It was found both in **1** and in six of the seven bicapped triangular cobalt clusters containing sterically innocent C5H5 or C5H4Me ligands that the *mean* Co–Co bond distance correlates with the size of the *larger* capping atom of the triply bridging X and Y ligands and thus is relatively insensitive to whether the capping ligand is a $\pi$-donor (e.g., NH, NR) or a $\pi$-acceptor (e.g., NO, CO). The fact that the *mean* Co–Co distance of 2.399 Å for the benzene-coordinated Co3(CO)2 core of **1** is virtually identical with the *mean* Co–Co distances of 2.399–2.406 Å for the *four* C5H5- or C5H4Me-coordinated tricobalt clusters with similar-sized C,N- or N,N-capping atoms provides convincing evidence that the benzene ligands in **1** are also sterically innocent. The steric non-innocence of the C5Me5 ligands in **2** is indicated in the 48-electron Co3($\eta^5$-C5Me5)3($\mu_3$-CO)($\mu_3$-NH) by the *mean* Co–Co distance of 2.428 Å which is 0.025 Å larger than those in the other two 48-electron C5H4Me-coordinated Co3(CO)(NR) and Co3(NO)(NH) cores. Of prime interest was a comparison of the structural features of the common Co3(CO)2 core in the 46-electron C5Me5-containing **2** and the 48-electron C6H6-containing **1**. The only major structural difference of statistical significance is the 0.029 Å *greater mean* Co–Co distance in **1**; this enlargement of the trimetal framework in **1** must have an electronic origin because any inherent steric effect of the more bulky C5Me5 ligands in **2** would give rise to a *smaller mean* Co–Co bond length in **1** than in **2**. The assumption that the C5Me5 ligands in **2** would analogously cause a sterically induced increase of 0.025 Å in the mean Co–Co bond length leads to the conclusion that the addition of two electrons to a 46-electron Co3(CO)2 core with sterically innocent C5R5 ligands would produce an estimated *increase* of 0.05–0.06 Å in the *mean* Co–Co distance. These bond-length arguments, which point to the HOMOs containing the two added electrons in the 48-electron **1** possessing considerable tricobalt antibonding character, are in complete harmony with the results of nonparametrized Fenske–Hall MO calculations carried out on **1** under an assumed $D_{3h}$ geometry. These combined experimental–theoretical studies provide convincing evidence that the transformation of an electron-deficient 46-electron M3(CO)2 core to a normal 48-electron one involves a "net" destabilization of the relatively weak metal–metal interactions which is counterbalanced by a "net" stabilization of the much stronger trimetal–carbonyl interactions. Although a cyclic voltammogram of **1** displayed a reversible reduction couple tentatively assigned to a one-electron process, an effort to obtain the neutral 49-electron species by chemical reduction was unsuccessful. [Co3($\eta^6$-C6H6)3($\mu_3$-CO)2]+[BPh4]$^-$·CH2Cl2: formula weight = 871; orthorhombic; *Pbca*; *a* = 18.902 (6) Å, *b* = 22.778 (10) Å, *c* = 17.882 (10) Å, *V* = 7674 Å$^3$ at *T* = 295 K; *D*(calcd) = 1.49 g/cm$^3$ for *Z* = 8 with *F*(000) = 3568. Least-squares refinement converged at $R_1$(*F*) = 5.75%, $R_2$(*F*) = 5.54% for 1196 independent diffractometry data (*I* > 2.5$\sigma$(*I*)).

In 1958 Chini and Ercoli[1] reported the synthesis of the tris(benzene) and tris(toluene)tricobalt dicarbonyl monocations of formula [Co3($\eta^6$-C6H$_{6-x}$Me$_x$)3(CO)2]+ (*x* = 0, 1), which were isolated as the I$^-$, [Co(CO)4]$^-$, [BPh4]$^-$, and Reinecke [Cr(SC-N)4(NH3)2]$^-$ salts. These clusters, prepared from the thermal reaction of Co2(CO)8 and AlBr3 with either benzene or toluene, were characterized by elemental analysis and IR spectroscopy. In that same year the preparation of the benzene derivative of this monocation, isolated as the [ClO4]$^-$, Reinecke, and picrate salts, was independently reported by Fischer and Beckert[2] from the thermal reaction of Hg[Co(CO)4]2 with benzene in the presence of AlCl3. Both groups proposed that the basic structure of the 48-electron [Co3(C6H6)3(CO)2]+ monocation was analogous to that of the paramagnetic (49-electron) Ni3($\eta^5$-C5H5)3(CO)2 molecule also reported in 1958 by Fischer and Palm.[3] The architectural formulation of the trinickel molecule as Ni3($\eta^5$-C5H5)3($\mu_3$-CO) with two triply bridging carbonyl ligands was subsequently established from a photographic X-ray diffraction

study by Hock and Mills[4] in 1961; its structure was recently refined by diffractometry data for a comparative structural-bonding analysis[5] of the isostructural 48-electron CoNi2($\eta^5$-C5H5)3($\mu_3$-CO)2. The predicted structural analogy[1,2] of the [Co3($\eta^6$-C6H6)3($\mu_3$-CO)2]+ monocation to Ni3($\eta^5$-C5H5)3($\mu_3$-CO)2 has been accepted and quoted by others.[6,7]

Our particular interest in the [Co3($\eta^6$-C6H6)3(CO)2]+ monocation (**1**) arose from our recent synthesis and stereochemical characterization by spectroscopic and X-ray diffraction analysis of Co3($\eta^5$-C5Me5)3($\mu_3$-CO)2[8] (**2**), an electronically unsaturated (46-electron) structural analogue of the Fischer–Palm Ni3($\eta^5$-

(1) Chini, P.; Ercoli, R. *Gaz. Chim. Ital.* **1958**, *88*, 1170–1182.
(2) Fischer, E. O.; Beckert, O. *Angew. Chem.* **1958**, *70*, 744.
(3) Fischer, E. O.; Palm, C. *Chem. Ber.* **1958**, *91*, 1725–1731.

(4) Hock, A. A.; Mills, O. S. *Advances in the Chemistry of Coordination Compounds*; Kirschner, S., Ed.; Macmillan: New York, 1961; pp 640–648.
(5) Byers, L. R.; Uchtman, V. A.; Dahl, L. F. *J. Am. Chem. Soc.* **1981**, *103*, 1942–1951.
(6) Silverthorn, W. E. *Adv. Organomet. Chem.* **1975**, *13*, 47–137.
(7) Kemmitt, R. D. W.; Russell, D. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. V, p 263.
(8) (a) Olson, W. L.; Schugart, K.; Fenske, R. F.; Dahl, L. F. *Abstracts of Papers*, 187th National Meeting of the American Chemical Society, St. Louis, Missouri; American Chemical Society: Washington, DC, 1984; INOR 279. (b) Olson, W. L.; Stacy, A. M.; Dahl, L. F., previous paper in this issue.

$C_5H_5)_3(\mu_3\text{-}CO)_2$[3] and corresponding $Ni_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2$.[9] A previous theoretical analysis of a then unknown 46-electron $M_3(\eta^5\text{-}C_5R_5)_3(\mu_3\text{-}CO)_2$ cluster (M = Co, Rh; R = H) by Hoffmann and colleagues[10] suggested that such an electron-deficient molecule under $D_{3h}$ symmetry (with no molecular distortions) should have a triplet spin ground state with two unpaired electrons in two doubly degenerate e'' orbitals of trimetal antibonding character and metal–CO bonding character. Although extensive magnetic susceptibility measurements (with a SQUID magnetometer) over a 4–300 K range showed that **2** does not have two unpaired electrons in the solid state,[11] this inorganic analogue of the cyclopropenyl monoanion[12] was found from a variable-temperature ¹H NMR study to exhibit in solution a temperature-dependent equilibrium between singlet and triplet spin states. Cyclic voltammetric measurements showed **2** to undergo a one-electron reversible reduction (to a 47-electron monoanion). The crystal structure of **2** was determined from room temperature (and low-temperature) X-ray diffractometry measurements to possess $C_{3h}\text{-}3/m$ crystallographic site symmetry. No detectable evidence was found (from the sizes, shapes, and orientations of the atomic thermal ellipsoids) for a threefold-averaged structure consisting of a $Co_3(CO)_2$ core significantly deformed from a $D_{3h}$ geometry, by which the residual paramagnetic character of the molecule in the crystalline state could be readily rationalized.

In order to assess whether the three symmetry-equivalent Co–Co' bond lengths of 2.370 (1) Å in the 46-electron **2** reflect multiple metal–metal bond character, we decided to perform an operational test to determine the effects of the addition of valence electron(s) on the geometry of the $Co_3(CO)_2$ core. Since preliminary attempts to crystallize the 47-electron monoanion of **2** for an X-ray structural determination were unsuccessful, we turned our attention to the 48-electron $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+$ monocation[1,2] which (to our knowledge) is the only other species (besides **2** and the previously mentioned toluene-coordinated monocation[1]) possessing a $Co_3(CO)_2$ core. The formal transformation of **2** into **1**, by which the "net" addition of two valence electrons makes **1** electronically equivalent with the hypothetical 48-electron $[Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2]^{2-}$ dianion, involves the replacement of three neutral five-electron-donating pentamethylcyclopentadienyl rings by three six-electron-donating benzene rings coupled with the loss of one electron by oxidation to the monocation. A meaningful bonding interpretation of geometrical variations between the $Co_3(CO)_2$ cores of **1** and **2** requires **1** and **2** to possess similar MO energy-level diagrams in accordance with the presumed isolobal nature[13] of the $Co(\eta^5\text{-}C_5Me_5)^-$ and $Co(\eta^6\text{-}C_6H_6)$ fragments. The other major boundary conditions which must be met in order to relate bond-length changes between **1** and **2** to their electronic configurations are that electronic effects dominate over steric effects in giving rise to an equilibrium geometry and that the relatively weak metal–metal interactions, which are considerably smaller than the metal–ligand interactions, are still sufficiently strong to produce significant structural variations upon a change in MO configuration. The resulting stereochemical-bonding information on these and related $[Co_3(\eta^5\text{-}C_5R_5)_3(\mu_3\text{-}X)(\mu_3\text{-}Y)]^n$ clusters[14-20] (presented
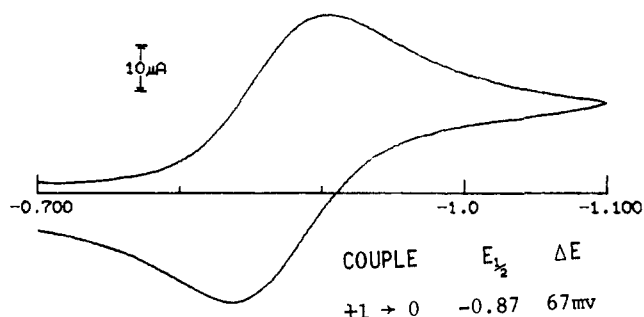


**Figure 1.** Cyclic voltammogram of $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+$-$[BPh_4]^-\cdot CH_2Cl_2$ in acetonitrile/0.1 M $[N(n\text{-}Bu)_4]^+[PF_6]^-$ at a platinum disk electrode with a scan rate of 100 mV/s. The indicated reversible reduction couple of the bulk monocation (**1**) at an $E_{1/2}$ value of –0.87 V (vs. SCE) with $\Delta E = 67$ mV has been tentatively assigned as a one-electron process, corresponding to a one-electron reduction of **1** to a chemically unstable, 49-electron neutral species.

herein) provides a self-consistent basis that all of these boundary conditions have been satisfied.

This paper reports the synthesis (by the Chini-Ercoli method[1]) and physicochemical characterization (including X-ray diffraction analysis) of the $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+$ monocation (**1**) prepared as the tetraphenylborate salt and crystallized with one dichloromethane solvent molecule. Also given are the results of a MO calculation of **1** via the nonparametrized Fenske–Hall model.[21] These experimental and theoretical studies of **1** in conjunction with those[8] of **2** provide convincing evidence that the transformation of an electron-deficient 46-electron $M_3(CO)_2$ core to a normal 48-electron one involves a "net" destabilization of the relatively weak metal–metal bonds which is counterbalanced by a "net" stabilization of the much stronger trimetal–carbonyl bonds.

## Experimental Section

**Materials and Techniques.** Unless otherwise stated, all reactions and manipulations were performed under an atmosphere of prepurified nitrogen via standard Schlenk tube techniques or within a Vacuum Atmospheres glovebox. The following solvents were dried and distilled immediately before use: benzene ($CaH_2$), methanol (Mg), diethyl ether (potassium benzophenone), acetonitrile ($CaH_2$), and dichloromethane ($P_2O_5$). Both acetone-$d_6$ (molecular sieves) and acetonitrile-$d_3$ ($CaH_2$) were freeze–thaw–degassed three times and then vacuum-distilled before use. Aluminum bromide was prepared in accordance with a literature method.[22] All other reagents were purchased from major chemical suppliers and used without further purification.

**Preparation of $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+[BPh_4]^-$.** This compound was prepared by the method of Chini and Ercoli.[1] In a typical reaction, a solution of $Co_2(CO)_8$ (4.7 g, 13.7 mmol) in 50 mL of benzene was slowly added under vigorous stirring to a 250-mL round-bottomed flask containing $AlBr_3$ (7.32 g, 27.4 mmol) and 50 mL of benzene. The reaction which gave rise to a yellow-brown suspension was stirred at room temperature until no further evolution of carbon monoxide was observed. The reaction flask was then fitted with a reflux condenser and placed in a water bath (at 60 °C) which was slowly warmed over a 4-h period to a final temperature of 80 °C. Vacuum removal of the benzene from the resulting greenish brown solution yielded a tan residue which was washed with two 50-mL portions of cold methanol followed by equivalent amounts of cold diethyl ether (–78 °C). The extracts were discarded, and the remaining dark brown solid was dried to give 4.1 g of the impure bromide salt of the $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+$ monocation.

Isolation of the desired tetraphenylborate salt was accomplished by the dissolving of 0.2 g of the above dark brown precipitate in 50 mL of

(9) Maj, J. J.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1982**, *104*, 3054–3063.

(10) (a) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456–3467. (b) Pinhas, A. R.; Albright, T. A.; Hofmann, P.; Hoffmann, R. *Helv. Chim. Acta* **1980**, *63*, 29–49.

(11) Stacy, A. M., private communication to L. F. Dahl, Nov. 1984.

(12) (a) Breslow, R. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 565–570. (b) Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1981**, *14*, 69–76.

(13) (a) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711–724. (b) Elian, M.; Chen, M. M. L.; Mingos, M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148–1155. (c) Bursten, B. E.; Fenske, R. F. *Inorg. Chem.* **1979**, *18*, 1760–1765.

(14) Co₃(η⁵-C₅H₅)₃(μ₃-CO)(μ₃-O): Uchtman, V. A.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 3763–3769.

(15) (a) Co₃(η⁵-C₅H₅)₃(μ₃-NO)₂: Kubat-Martin, K. A.; Rae, A. D.; Dahl, L. F. *Abstracts of Papers*; 187th National Meeting of the American Chemical Society St. Louis, Missouri; American Chemical Society: Washington, DC, 1984; INOR 137; *Organometallics* **1985**, *4*, 2221–2223. (b) Co₃(η⁵-C₅H₄Me)₃(μ₃-NO)₂: Kubat-Martin, K. A.; Rae, A. D.; Dahl, L. F. *Organometallics* **1985**, *4*, 2221–2223.

(16) Co₃(η⁵-C₅H₄Me)₃(μ₃-CO)(μ₃-NC(O)NH₂): Bedard, R. L.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 5924–5932.

(17) [Co₃(η⁵-C₅H₄Me)₃(μ₃-NO)(μ₃-NH)]⁺[BPh₄]⁻: Bedard, R. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 5942–5948.

(18) Co₃(η⁵-C₅Me₅)₃(μ₃-CO)(μ₃-NH): Bedard, R. L.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 5924–5932.

(19) Co₃(η⁵-C₅H₅)₃(μ₃-CO)(μ₃-S): Frisch, P. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *94*, 5082–5084.

(20) Co₃(η⁵-C₅H₅)₃(μ₃-CS)(μ₃-S): Werner, H.; Leonhard, K.; Kolb, O.; Röttinger, E.; Vahrenkamp, H. *Chem. Ber.* **1980**, *113*, 1654–1662.

(21) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768–775.

(22) Nicholson, D. G.; Winter, P. K.; Fineberg, H. *Inorg. Synth.* **1950**, *3*, 30–36.

methanol. After filtration, 0.3 g of NaBPh₄ (0.87 mmol) dissolved in a minimum amount of a 50% methanol/water mixture (v/v) was added. The brown-green precipitate which formed immediately upon mixing was filtered, washed with water and then diethyl ether, and dried under vacuum to give 75 mg (~20% yield) of $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+$-$[BPh_4]^-$.

A proton NMR spectrum (acetone-$d_6$), performed on a Bruker WP-270 spectrometer, gave resonances at $\delta$ 6.27 (s, 18 H), 6.76 (m, 4 H), 6.91 (m, 8 H), 7.33 (br s, 8 H).

Solid-state (KBr) infrared spectra carried out on a Beckman Model 4240 spectrophotometer exhibited a strong, broad carbonyl band at 1671 cm⁻¹, which is in agreement with the value of 1675 cm⁻¹ obtained from a solid-state (KBr) spectrum by Chini and Ercoli.[1]

**Electrochemical Measurements.** Cyclic voltammetric studies were performed with a Bioanalytical Systems 100 Electrochemical analyzer equipped with a PAR electrochemical cell which was operated inside a Vacuum Atmospheres glovebox under an atmosphere of recirculating, purified nitrogen. The cell consisted of three electrodes, viz., a platinum disk working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE).

Tetra-*n*-butylammonium hexafluorophosphate (TBAH) supporting electrolyte was prepared via a published method,[23] recrystallized from absolute ethanol, and oven-dried before use. Supporting electrolyte concentration was maintained at 0.1 M, and $iR$ compensation for solution resistance was made before measurement of the current vs. voltage curves.

**Electrochemical Behavior of 1.** Cyclic voltammetric measurements on **1** in acetonitrile solution show only one apparent reversible +1/0 reduction couple (Figure 1) at −0.87 V (vs. SCE reference electrode). Its reversible character is indicated by the peak separation of 67 mV and by the anodic and cathodic peak currents being approximately equal throughout the scan-rate range investigated (viz., 20–100 mV/s). An attempt to verify the tentative assignment of this reduction of the bulk monocation (**1**) as a one-electron process to give the neutral 49-electron species was made from an IR monitoring of the chemical reaction of **1** with a stoichiometric quantity of cobaltocene. Addition of a 1:1 molar ratio of solid $Co(\eta^5\text{-}C_5H_5)_2$ to a stirred solution of **1** in THF at room temperature under a nitrogen atmosphere resulted in a rapid change of the solution from a brownish-green color to a light-red color. Infrared spectra taken before and immediately after addition of the reducing agent showed a large decrease in the single carbonyl band at 1696 cm⁻¹ of **1** with no new carbonyl band indicative of a reduced species being observed at a lower frequency. Decomposition was complete after 5 min with formation of a greyish white precipitate. Our inability to obtain the reduced species is not surprising in light of the original report by Chini and Ercoli[1] that attempts with different chemical agents to reduce the monocation to a neutral species resulted in decomposition of **1** with formation of cobalt metal.

**Structural Determination of $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+[BPh_4]^-\cdot CH_2Cl_2$.** Suitable crystals were obtained by slow evaporation of a saturated dichloromethane solution. A needle-shaped crystal (of approximate dimensions 0.10 × 0.12 × 0.40 mm) was mounted inside a Lindemann glass capillary which then was hermetically sealed. A Syntex (Nicolet) PĪ diffractometer with Mo Kα radiation was used to obtain intensity data at room temperature (ca. 22 °C) by the $\theta$–$2\theta$ scan technique. Details of crystal alignment and data-collection parameters along with a listing of utilized crystallographic programs are given elsewhere.[24]

Axial photographs revealed orthorhombic $D_{2h}$ Laue symmetry. Cell dimensions, derived from least-squares analysis of 15 well-centered reflections with $15 \leq 2\theta \leq 25°$, are $a = 18.902$ (6) Å, $b = 22.778$ (10) Å, $c = 17.882$ (10) Å. On the basis of $V = 7674$ Å³ and formula weight = 871 for $C_{45}H_{40}Co_3O_2BCl_2$, the calculated density is 1.49 g/cm³ for $Z = 8$ with $F(000) = 3568$. The centrosymmetric space group *Pbca* was uniquely defined by the observed systematic absences of {0*kl*} for *k* odd, {*h0l*} for *l* odd, and {*hk*0} for *h* odd.

Intensities were measured for one independent *hkl* octant over a range of $3° \leq 2\theta \leq 45°$. The intensities of two standard reflections, monitored after every 50 data points, exhibited nonsignificant variations (less than 3%) during data collection. $\psi$ scans showed no significant fluctuations in intensities, and hence an absorption correction was not made. Data reduction gave 1196 independently observed reflections with $I > 2.5\sigma(I)$.

The crystal structure (involving one cation, one anion, and one CH₂Cl₂ as the crystallographically independent unit) was solved by the use of MULTAN[25] followed by successive Fourier syntheses which located all the

## Table I. Positional Parameters for $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+[BPh_4]^-\cdot CH_2Cl_2$

| atom | x | y | z |
|---|---|---|---|
| Co1 | 0.153 25 (14) | 0.120 02 (10) | 0.769 35 (15) |
| Co3 | 0.173 28 (14) | 0.031 40 (12) | 0.701 19 (14) |
| Co2 | 0.191 38 (14) | 0.034 88 (12) | 0.835 89 (14) |
| Cl1 | −0.069 03 (41) | −0.079 57 (36) | 0.657 87 (53) |
| Cl2 | −0.116 42 (43) | −0.107 83 (45) | 0.805 12 (58) |
| O1 | 0.044 80 (74) | 0.030 95 (61) | 0.788 93 (82) |
| O2 | 0.302 87 (74) | 0.088 85 (51) | 0.747 13 (68) |
| C3 | −0.072 49 (140) | −0.055 73 (117) | 0.750 96 (90) |
| C1 | 0.106 07 (126) | 0.045 15 (85) | 0.777 86 (112) |
| C2 | 0.242 30 (113) | 0.075 99 (75) | 0.756 93 (99) |
| B | −0.142 85 (124) | 0.261 65 (100) | 0.946 46 (120) |
| C11 | 0.167 55 (98) | 0.195 62 (53) | 0.703 01 (71) |
| C12 | 0.203 24 (48) | 0.202 76 (47) | 0.770 36 (115) |
| C13 | 0.167 69 (92) | 0.195 42 (54) | 0.837 76 (72) |
| C14 | 0.096 44 (94) | 0.180 94 (52) | 0.837 80 (71) |
| C15 | 0.059 37 (46) | 0.173 52 (50) | 0.771 70 (116) |
| C16 | 0.096 06 (96) | 0.181 09 (56) | 0.703 78 (71) |
| C21 | 0.177 70 (105) | 0.055 42 (61) | 0.951 61 (65) |
| C22 | 0.248 62 (100) | 0.059 41 (56) | 0.932 40 (75) |
| C23 | 0.281 96 (49) | 0.012 61 (87) | 0.897 40 (77) |
| C24 | 0.244 38 (98) | −0.038 18 (59) | 0.881 61 (64) |
| C25 | 0.173 70 (97) | −0.043 55 (54) | 0.900 00 (78) |
| C26 | 0.140 55 (51) | 0.004 22 (87) | 0.935 46 (79) |
| C31 | 0.211 53 (91) | 0.045 77 (52) | 0.590 84 (67) |
| C32 | 0.247 20 (48) | −0.001 55 (76) | 0.621 92 (79) |
| C33 | 0.211 24 (91) | −0.048 67 (52) | 0.652 28 (66) |
| C34 | 0.136 90 (89) | −0.047 43 (52) | 0.650 87 (67) |
| C35 | 0.100 51 (48) | −0.000 21 (78) | 0.619 85 (81) |
| C36 | 0.138 19 (92) | 0.046 44 (52) | 0.589 81 (67) |
| C41 | −0.131 29 (105) | 0.285 10 (51) | 0.859 29 (57) |
| C42 | −0.061 03 (82) | 0.286 86 (56) | 0.837 05 (91) |
| C43 | −0.043 66 (55) | 0.304 71 (58) | 0.764 99 (109) |
| C44 | −0.096 56 (102) | 0.320 80 (51) | 0.715 17 (59) |
| C45 | −0.167 03 (82) | 0.319 53 (55) | 0.735 57 (86) |
| C46 | −0.183 89 (57) | 0.301 35 (56) | 0.808 79 (104) |
| C51 | 0.386 87 (67) | 0.190 54 (54) | 0.988 53 (71) |
| C52 | 0.373 07 (61) | 0.201 65 (47) | 0.913 45 (87) |
| C53 | 0.398 12 (72) | 0.163 66 (66) | 0.858 77 (54) |
| C54 | 0.436 97 (69) | 0.114 55 (57) | 0.879 18 (74) |
| C55 | 0.451 63 (64) | 0.102 25 (47) | 0.953 44 (90) |
| C56 | 0.425 92 (73) | 0.141 12 (63) | 1.008 30 (54) |
| C61 | −0.101 96 (67) | 0.198 19 (46) | 0.951 51 (83) |
| C62 | −0.116 06 (58) | 0.156 47 (68) | 0.895 35 (65) |
| C63 | −0.082 88 (75) | 0.101 94 (58) | 0.895 48 (67) |
| C64 | −0.035 09 (67) | 0.088 51 (45) | 0.951 95 (84) |
| C65 | −0.020 71 (55) | 0.129 26 (65) | 1.007 69 (64) |
| C66 | −0.054 11 (71) | 0.183 46 (54) | 1.006 95 (63) |
| C71 | −0.230 40 (49) | 0.250 90 (70) | 0.968 47 (67) |
| C72 | −0.279 77 (78) | 0.294 38 (48) | 0.953 50 (64) |
| C73 | −0.350 89 (67) | 0.284 35 (50) | 0.967 57 (69) |
| C74 | −0.374 28 (47) | 0.231 55 (63) | 0.996 48 (70) |
| C75 | −0.323 68 (77) | 0.187 86 (44) | 1.011 41 (66) |
| C76 | −0.252 16 (67) | 0.197 40 (57) | 0.997 52 (68) |

non-hydrogen atoms. Least-squares refinement was then carried out with RAELS[26] under the following boundary conditions: (1) The cobalt, boron, and the carbonyl carbon and oxygen atoms were refined with individual positional and anisotropic thermal parameters; (2) the carbon atoms of each benzene ring and likewise of each phenyl ring were constrained to a regular hexagonal $D_{6h}$ geometry with fixed C–C bond lengths of 1.40 Å and refined with six variable parameters; the thermal motion of each ring was described by a TLX model[27] (with 15 variables); (3) the one carbon and two chlorine atoms of the dichloromethane molecule of crystallization were refined with individual positional and anisotropic thermal parameters, but weighted slack constraints were imposed requiring a minimization of the difference (ideally zero) between the two C–Cl bond lengths; and (4) coordinates for the hydrogen atoms of the benzene and phenyl rings and coordinates for the hydrogen atoms of the dichloromethane solvate were miraged at idealized trigonal planar and idealized tetrahedral locations, respectively, with all C–H distances fixed

(23) Lange, W.; Müller, E. *Chem. Ber.* **1930**, *67*, 1058–1070.

(24) Byers, L. R.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 277–284.

(25) Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declercq, J.-P., MULTAN-78, Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368–376.

(26) Rae, A. D. *RAELS, A Comprehensive Least-Square Program*; University of New South Wales: Kensington, 1976. Adapted for a Harris/7 computer by A. D. Rae, University of Wisconsin—Madison, 1983.

(27) (a) Rae, A. D. *Acta Crystallogr., Sect. A* **1975**, *A31*, 570–574. (b) Schomaker, V.; Trueblood, K. N. *Acta Crystallogr., Sect. B* **1968**, *B24*, 63–76.

7660 *J. Am. Chem. Soc., Vol. 108, No. 24, 1986*

*Olson and Dahl*

**Table II.** Interatomic Distances and Bond Angles for
$[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+[BPh_4]^-\cdot CH_2Cl_2$

### A. Intracation Distances (Å)

| | | | |
|---|---|---|---|
| Co1–Co2 | 2.386 (4) | Co2–C21 | 2.130 (11) |
| Co1–Co3 | 2.385 (4) | Co2–C22 | 2.108 (11) |
| Co2–Co3 | 2.426 (4) | Co2–C23 | 2.095 (11) |
| Co1–C1 | 1.930 (20) | Co2–C24 | 2.106 (11) |
| Co1–C2 | 1.972 (20) | Co2–C25 | 2.147 (11) |
| Co2–C1 | 1.930 (22) | Co2–C26 | 2.135 (11) |
| Co2–C2 | 1.945 (19) | Co3–C31 | 2.121 (11) |
| Co3–C1 | 1.892 (22) | Co3–C32 | 2.124 (11) |
| Co3–C2 | 1.929 (20) | Co3–C33 | 2.145 (11) |
| C1–O1 | 1.219 (19) | Co3–C34 | 2.122 (11) |
| C2–O2 | 1.195 (17) | Co3–C35 | 2.124 (12) |
| Co1–C11 | 2.106 (11) | Co3–C36 | 2.121 (11) |
| Co1–C12 | 2.108 (11) | Co1–Bz1[a] | 1.606 |
| Co1–C13 | 2.124 (11) | Co2–Bz2 | 1.602 |
| Co1–C14 | 2.137 (11) | Co3–Bz3 | 1.609 |
| Co1–C15 | 2.153 (11) | | |
| Co1–C16 | 2.114 (11) | | |

### B. Intracation Bond Angles (deg)

| | | | |
|---|---|---|---|
| Co1–C1–O1 | 133.3 (18) | C1–Co1–C2 | 87.3 (9) |
| Co2–C1–O1 | 132.4 (17) | C1–Co2–C2 | 88.1 (9) |
| Co3–C1–O1 | 135.3 (18) | C1–Co3–C2 | 89.7 (9) |
| Co1–C2–O2 | 135.2 (14) | Co2–Co1–Bz1 | 148.8 |
| Co2–C2–O2 | 134.5 (15) | Co3–Co1–Bz1 | 150.0 |
| Co3–C2–O2 | 134.2 (15) | Co1–Co2–Bz2 | 145.4 |
| Co1–C1–Co2 | 76.3 (8) | Co3–Co2–Bz2 | 155.1 |
| Co1–C1–Co3 | 77.3 (8) | Co1–Co3–Bz3 | 146.0 |
| Co2–C1–Co3 | 78.8 (9) | Co2–Co3–Bz3 | 154.5 |
| Co1–C2–Co2 | 75.0 (7) | | |
| Co1–C2–Co3 | 75.4 (8) | | |
| Co1–C2–Co3 | 77.5 (8) | | |

### C. Intraanion Distances (Å) and Bond Angles (deg)

| | | | |
|---|---|---|---|
| B–C41 | 1.657 (23) | C41–B–C51 | 113.1 (16) |
| B–C51 | 1.686 (22) | C41–B–C61 | 105.8 (14) |
| B–C61 | 1.642 (23) | C41–B–C71 | 112.8 (15) |
| B–C71 | 1.718 (24) | C51–B–C61 | 112.0 (14) |
| | | C51–B–C71 | 104.8 (14) |
| | | C61–B–C71 | 108.4 (15) |

### D. CH₂Cl₂ Solvate Distances (Å) and Bond Angles (deg)

| | | | |
|---|---|---|---|
| C3–Cl1 | 1.747 (16) | Cl1–C3–Cl2 | 109.4 (15) |
| C3–Cl2 | 1.741 (16) | | |

[a] Bz*n* denotes the centroid of benzene ring *n* attached to Co*n* (*n* = 1, 2, 3).



**Figure 2.** The $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+$ monocation (of crystallographic $C_1$—1 site symmetry) crystallized as the tetraphenylborate salt.

at 1.0 Å. These hydrogen atoms were assigned the same isotropic temperature factor and included as fixed-atom contributors in the least-squares refinement.
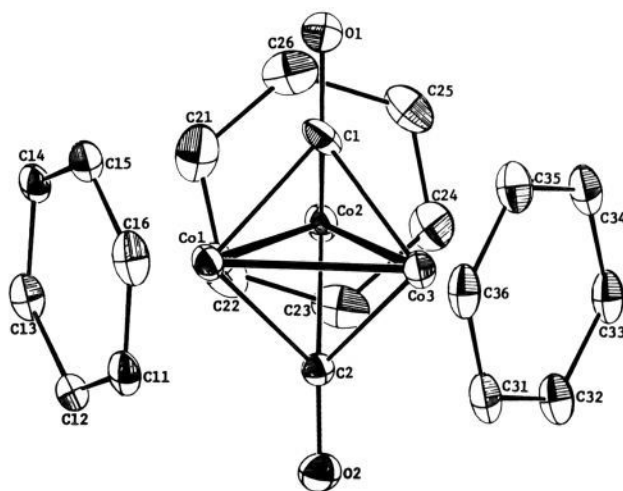
The resulting full-matrix refinement, for which the data-to-parameter ratio was 1196/216 = 5.5/1, converged at $R_1(F) = 5.75\%$ and $R_2(F) = 5.54\%$[28] with no variable shift-to-error ratio on the last cycle being greater than 0.01. The goodness-of-fit value was 1.32. A final electron-density difference map exhibited no unusual features. Atomic scattering factors including anomalous dispersion corrections were taken from the *International Tables for X-Ray Crystallography*.[29]

Final atomic coordinates for all non-hydrogen atoms are given in Table I. Interatomic distances and bond angles are presented in Table II. Calculated coordinates and isotropic temperature factors for all hydrogen atoms, anisotropic thermal parameters for all non-hydrogen atoms, appropriate least-squares planes and perpendicular displacements of selected atoms from these planes, and a listing of calculated and observed structure factor amplitudes are available as supplementary material.

**Molecular Orbital Calculations of 1.** The nonempirical Fenske–Hall MO model, which has been previously described and widely applied to a variety of transition-metal complexes,[30] was utilized. Since this method

has no adjustable parameters, the calculated results (eigenvectors and associated eigenvalues) are completely determined by the assumed geometry of the monocation and the atomic basis set.

Clementi's double-$\zeta$ HF functions[31] for neutral atoms were used for carbon and oxygen. The 1s and 2s functions were curve-fit to single-$\zeta$ forms by use of the maximum overlap criterion.[32] For hydrogen, a single exponent of 1.16 (whose value corresponds to the minimum energy exponent of methane) was chosen. Cobalt functions were taken from the tables of Richardson et al.[33] Single-$\zeta$ functions were utilized for all core and valence cobalt orbitals except for the 3d for which double-$\zeta$ functions were employed.

In these calculations, mean interatomic distances for the determined geometry of the monocation (1) were used (e.g., Co–Co = 2.399 Å; Co–CO = 1.93 Å) with the benzene rings reoriented in order to make the entire configuration conform to $D_{3h}$—3/*m2m* symmetry.

Local right-handed coordinate systems were chosen at each cobalt atom with the z axis directed toward the centroid of the cobalt triangle, the x axis located in the plane of the cobalt triangle, and the y axis perpendicular to this cobalt plane. A local left-handed coordinate system was chosen at each of the two bridging carbon atoms with the z axis directed toward the centroid of the cobalt triangle and the y axis in the tricobalt plane oriented toward Co3. A right-handed master coordinate system was chosen at the centroid of the cobalt triangle with the z axis perpendicular to the tricobalt plane and the x axis in the tricobalt plane oriented toward Co1. These coordinate systems used in the calculations are the same as those previously employed in Fenske–Hall MO calculations[8] on the 46-electron $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ and its reduced derivatives and in earlier Fenske–Hall MO calculations[34] on a number of other $[Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}X)(\mu_3\text{-}Y)]^n$ clusters (M = Fe, Co, Ni).

## Results and Discussion

**Crystal Structure of $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+[BPh_4]^-\cdot CH_2Cl_2$. (a) General Structural Features.** The crystal structure consists of discrete $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+$ monocations and $[BPh_4]^-$ monoanions which are well separated from each other. The lack of any specific ion-pair interactions is evidenced by no interionic distances being less than the sum of corresponding van der Waals atomic radii (e.g., all H···H contacts are ≥2.4 Å). However, an analysis revealed that one hydrogen atom of the dichloromethane molecule of crystallization is weakly hydrogen-bonded to one of the carbonyl oxygen atoms, O1, of the monocation. This relatively

(28) The unweighted and weighted discrepancy factors used are $R_1(F) = [\sum||F_o| - |F_c||/\sum|F_o|] \times 100$ and $R_2(F) = [\sum w_i||F_o| - |F_c||^2/\sum w_i|F_o|^2]^{1/2} \times 100$. All least-squares refinements were based on the minimization of $\sum w_i||F_o| - |F_c||^2$ with individual weights of $w_i = 1/\sigma^2(F_o)$ assigned on the basis of the estimated standard deviations of the observed structure factors. The standard deviation in an observation of unit weight ("goodness-of-fit") is defined by $[\sum w_i(|F_o| - |F_c|)^2/(m-n)]^{1/2}$.

(29) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 149, pp 155–157.

(30) (a) Fenske, R. F. *Prog. Inorg. Chem.* **1976**, *21*, 179–208. (b) Fenske, R. F. *Pure Applied Chem.* **1971**, *27*, 61–71. (c) Gordon, D.; Fenske, R. F. *Inorg. Chem.* **1982**, *21*, 2907–2915. (d) Kostic, N. M.; Fenske, R. F. *Organometallics* **1983**, *2*, 1319–1325. (e) Matachek, J. R.; Angelici, R. J.; Schugart, K. A.; Haller, K. J.; Fenske, R. F. *Organometallics* **1984**, *3*, 1038–1044.

(31) Clementi, E. *J. Chem. Phys.* **1964**, *40*, 1944–1945.

(32) Radtke, D. D. Ph.D. Dissertation, University of Wisconsin, Madison, WI, 1966.

(33) Richardson, J. W.; Nieuwpoort, W. C.; Powell, R. R.; Edgell, W. F. *J. Chem. Phys.* **1962**, *36*, 1057–1061.

(34) Rives, A. B.; You, X.-Z.; Fenske, R. F. *Inorg. Chem.* **1982**, *21*, 2286–2294.

**Table III.** Relationship of Mean Cobalt–Cobalt Distance to Size of the Larger Capping E Heteroatom of the Two Triply Bridging X and Y Ligands in $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+$ (1) and Other 48-Electron $[Co_3(\eta^5\text{-}C_5R_5)_3(\mu_3\text{-}X)(\mu_3\text{-}Y)]^n$ Clusters

| cluster | covalent radius (Å)[j] of larger E atom | mean Co–Co dist (Å) | crystallographic site sym | ref |
|---|---|---|---|---|
| E = C and O | | | | |
| $Co_3(C_5H_5)_3(CO)(O)$ | 0.77 | 2.365 (4) | $C_{3h}$—3/m (CO and O disordered) | a |
| E = C and N | | | | |
| $Co_3(C_5H_4Me)_3(CO)(NR)$ (where R = C(O)NH_2) | 0.77 | 2.400 | $C_1$—1 | b |
| $Co_3(C_5Me_5)_3(CO)(NH)$ | 0.77 | 2.428[k] | $C_s$—m | c |
| E = C and C | | | | |
| $[Co_3(C_6H_6)_3(CO)_2]^+$ | 0.77 | 2.399 | $C_1$—1 | d |
| E = N and N | | | | |
| $Co_3(C_5H_5)_3(NO)_2$ | 0.75 | 2.399 (3) | $C_{3h}$—3/m | e |
| $Co_3(C_5H_4Me)_3(NO)_2$ | 0.75 | 2.403 | $C_1$—1 | f |
| $[Co_3(C_5H_4Me)_3(NO)(NH)]^+$ | 0.75 | 2.406 | $C_1$—1 | g |
| E = S and C | | | | |
| $Co_3(C_5H_5)_3(CO)(S)$ | 1.02 | 2.452 (2) | $C_{3h}$—3/m (CO and S disordered) | h |
| $Co_3(C_5H_5)_3(CS)(S)$ | 1.02 | 2.44 (1) | $C_{3h}$—3/m (CS and S disordered) | i |

*a* Reference 14. *b* Reference 16. *c* Reference 18. *d* This work. *e* Reference 15. *f* Reference 15. *g* Reference 17. *h* Reference 19. *i* Reference 20. *j* Estimated covalent radii are 0.77 Å for C, 0.75 Å for N, 0.73 Å for O, and 1.02 Å for S.[43] *k* This 0.025 Å larger value for the mean Co–Co distance is attributed to steric overcrowding of the terminal $C_5Me_5$ ligands in sharp contrast to the normal values for the mean Co–Co distances in the related triangular metal clusters with sterically innocent $C_5H_5$, $C_5H_4Me$, or $C_6H_6$ ligands.

weak but definite C3—H2···O1 interaction is consistent with the determined C3···O1 separation of 3.04 Å and an estimated H2···O1 separation of ca. 2.4 Å (based upon an idealized hydrogen position).

**(b) Stereochemistry of the Tetrafluoroborate Monoanion and CH_2Cl_2 Solvate.** The tetrahedral configuration of the $[BPh_4]^-$ monoanion exhibits no unusual features, and the mean B–C bond length of 1.67 Å is in agreement with those for this anion from other structural determinations.[16,35] The mean C–Cl bond length of 1.74 Å and the Cl–C–Cl′ bond angle of 109.4 (15)° for the dichloromethane molecule of crystallization are also normal values.

**(c) Stereochemistry of the $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+$ Monocation (1).** Its configuration, depicted in Figure 2, consists of a triangular array of cobalt atoms, each symmetrically coordinated to a benzene ring, with two triply bridging carbonyl ligands above and below the cobalt framework. Figure 3, which displays the architectural dimensions for the $Co_3(CO)_2$ core of **1**, shows a small but significant deviation of the three Co–Co′ distances from an equilateral triangle. The observed distortion toward an isosceles cobalt triangle (of $C_{2v}$-2mm symmetry) gives rise to one long Co–Co′ distance of 2.426 (4) Å and two short Co–Co′ distances of 2.385 (4) and 2.386 (4) Å. The individual Co–CO bond lengths of range 1.892 (22)–1.972 (20) Å are not sufficiently precise to determine whether the entire $Co_3(CO)_2$ core is deformed from a regular $D_{3h}$—3/m2m geometry toward a $C_{2v}$—2mm, $C_2$—2, or $C_s$—m geometry. This small tricobalt deformation may be a consequence of composite electronic–steric effects.[36]

The nearly symmetrical coordination in **1** of each benzene ligand to its cobalt atom is evidenced by the 2.095 (11)–2.153 (11) Å range for the 18 independent Co–C(ring) bond lengths. The mean Co–C(ring) bond length of 2.12 Å is comparable to that of 2.15 Å for the mesitylene ligand in the 48-electron $Co_3(\eta^6\text{-}C_6H_3Me_3)(CO)_6(\mu_3\text{-}CPh)$[37] but expectedly shorter than that of 2.26 Å for the eclipsed $C_6Me_6$ ligands in the 20-electron $[Co(\eta^6\text{-}C_6Me_6)_2]^+$ monocation (as the $[PF_6]^-$ salt).[38] Other transition-metal clusters known to contain an analogous triangular
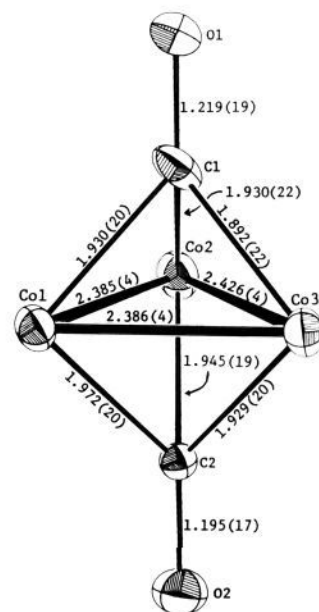


**Figure 3.** Dimensions of the $Co_3(CO)_2$ core of the 48-electron $[Co(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+$ monocation showing its small distortions from an idealized $D_{3h}$—3/m2m geometry.

$M_3(\eta^6\text{-}C_6R_6)_3$ fragment (R = Me, H) are relatively rare. Those crystallographically characterized include three structurally analogous $[M_3(\eta^6\text{-}C_6Me_6)_3(\mu_2\text{-}Cl)_6]^{n+}$ cations[39-41] (M = Zr, Nb), viz., the crystal-disordered 50-electron $[Nb_3(\eta^6\text{-}C_6Me_6)_3(\mu_2\text{-}Cl)_6]^+$ monocation (as the chloride salt),[39] the 49-electron $[Nb_3(\eta^6\text{-}C_6Me_6)_3(\mu_2\text{-}Cl)_6]^{2+}$ dication (as the dimeric $[TCNQ]_2^-$ salt),[40] and the 46-electron $[Zr_3(\eta^6\text{-}C_6Me_6)_3(\mu_2\text{-}Cl)_6]^{2+}$ dication (as the $[Al_2Cl_7]^-$ salt).[41]

The close conformity of the overall architecture of this 48-electron monocation with those of the 49-electron Fischer–Palm molecule and its subsequent off-spring and in particular with that recently determined[8] for the 46-electron $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2$ (**2**) has satisfied our initial goal in allowing a valid comparative analysis of its $Co_3(CO)_2$ core with that of **2** (vide infra).

**Comparative Analysis of the Mean Co–Co Distance of 1 with Those in Other 48-Electron $[Co_3(\eta^5\text{-}C_5R_5)_3(\mu_3\text{-}X)(\mu_3\text{-}Y)]^n$ Clusters**

(35) (a) Cobbledick, R. E.; Einstein, F. W. B. *Acta Crystallogr.* **1979**, *B35*, 2041–2044. (b) Hoffmann, K.; Weiss, E. *J. Organomet. Chem.* **1974**, *67*, 221–228.

(36) This small distortion is *not* uncommon for a completely bonding 48-electron system with sterically innocent ligands. Analogous variations in the three individual metal–metal distances were found in other closely related bicapped tricobalt clusters, e.g., 2.399 (3)–2.428 (3) Å in the $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ monocation,[17] 2.382 (1)–2.414 (1) Å in $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$,[16] and 2.395 (1)–2.414 (1) Å in $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)_2$.[15b]

(37) (a) Brice, M. D.; Dellaca, R. J.; Penfold, B. R.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1971**, 72–73. (b) Dellaca, R. J.; Penfold, B. R. *Inorg. Chem.* **1972**, *11*, 1855–1858 and references therein.

(38) Thompson, M. R.; Day, C. S.; Day, V. W.; Mink, R. I.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 2979–2986.

(39) Churchill, M. R.; Chang, S. W.-Y. *J. Chem. Soc., Chem. Commun.* **1974**, 248–249.

(40) Goldberg, S. Z.; Spivack, B.; Stanley, G.; Eisenberg, R.; Braitsch, D. M.; Miller, J. S.; Abkowitz, M. *J. Am. Chem. Soc.* **1977**, *99*, 110–117.

(41) Stollmaier, F.; Thewalt, U. *J. Organomet. Chem.* **1981**, *208*, 327–334.

**Table IV.** Comparison of Selected Mean Distances and Bond Angles Under $C_{3h}$—$3/m$ Symmetry[a] for the $Co_3(CO)_2$ Cores of the 46-Electron $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2$ (2) and the 48-Electron $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+$ Monocation (1)

| | | | difference[b] | |
|---|---|---|---|---|
| core dimension | 2 | 1 | $\Delta = \bar{x}_1 - \bar{x}_2$ | $|\Delta|/\sigma$[c] |
| | | A. Distance (Å) | | |
| Co–Co | 2.370 | 2.399 | 0.029* | 12.2 |
| Co–CO | 1.951 | 1.933 | −0.018 | 1.8 |
| OC⋯CO | 2.78 | 2.69 | −0.09 | 3.1 |
| Co–C(ring) | 2.108 | 2.123 | 0.015 | 3.5 |
| Co–$C_nR_n$(centroid) | 1.73 | 1.61 | −0.12 | |
| | | B. Bond Angles (deg) | | |
| Co–C–O | 135.5 (2) | 134.2 | −1.3 | 1.9 |
| Co–C(O)–Co′ | 74.7 (3) | 76.7 | 2.4 | 5.2 |
| OC–Co–CO | 91.0 (4) | 88.4 | −2.6 | 4.6 |

[a] The $Co_3(CO)_2$ cores of 2 and 1 have crystallographic site symmetry $C_{3h}$—$3/m$ and $C_1$—$1$, respectively. [b] The asterisk denotes a dimensional difference, $\bar{x}_1 - \bar{x}_2$, which is considered to be significantly meaningful on an arbitrary basis that $|\Delta|/\sigma \geq 6$. [c] $|\Delta|/\sigma = |\bar{x}_1 - \bar{x}_2|/[\sigma(\bar{x}_1)^2 + \sigma(\bar{x}_2)^2]^{1/2}$, where the standard deviations of the means, $\sigma(\bar{x}_1)$ and $\sigma(\bar{x}_2)$, are obtained from the individual $\sigma_i$'s of the $n$ measurements (Table II) by $\sigma(\bar{x}_i) = \sigma_i/n^{1/2}$.
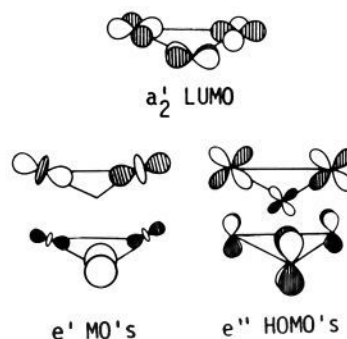
**and Resulting Implications.** Of particular relevance is a comparison given in Table III of the mean Co–Co bond length in 1 with those in eight other structurally determined 48-electron $[Co_3(\eta^5\text{-}C_5R_5)_3(\mu_3\text{-}X)(\mu_3\text{-}Y)]^n$ clusters[14-20] containing $Co_3XY$ cores (for which X = CO, CS, NO and Y = O, NR, S) with either $C_5H_5$ (four), $C_5H_4Me$ (three), or $C_5Me_5$ (one) ligands. Table III reveals that (with one exception[42]) the mean Co–Co bond distances in the 48-electron bicapped triangular metal clusters containing sterically innocent ligands may be simply correlated (within 0.01 Å) with the covalent radius[43] of the larger capping atom of the triply bridging X and Y ligands. Of special interest is that the mean Co–Co distance of 2.399 Å for the benzene-coordinated $Co_3(CO)_2$ core of 1 is virtually identical (within 0.007 Å) with the mean Co–Co distances for the four $C_5H_5$- or $C_5H_4Me$-coordinated tricobalt clusters with similar-sized C,N- or N,N-capping atoms, viz., $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ (2.400 Å),[16] $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}NO)_2$ (2.399 (3) Å),[15a] $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)_2$ (2.403 Å),[15b] and the $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ monocation (2.406 Å) as the $[BPh_4]^-$ salt.[17,44] These experimentally equivalent values for the mean Co–Co distances, which are in harmony with the nearly equivalent covalent radii of carbon (0.77 Å) and nitrogen (0.75 Å), provide convincing evidence that the benzene ligands in 1 are also sterically innocent. The 0.025 Å larger mean Co–Co distance of 2.428 Å for the $C_5Me_5$-coordinated $Co_3(CO)(NH)$ core is readily ascribed to steric overcrowding of the bulky $C_5Me_5$ ligands. This small but significant bond-length increase indicates that the $C_5Me_5$ ligands in 2 may likewise produce a similar enlargement of its mean Co–Co bond length (vide infra).

**Comparative Analysis of the 48-Electron $[Co_3(\eta^6\text{-}C_6H_6)(\mu_3\text{-}CO)_2]^+$ Monocation (1) with the 46-Electron $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2$ (2).** The structural differences between these two electronically different species containing a common $Co_3(CO)_2$ core are presented in Table IV. On going from 2 to 1, the only major structural change of statistical significance (Table IV) is the increase in the mean Co–Co distance of 0.029 Å (corresponding to a highly significant shift-to-error $(|\Delta|/\sigma)$ of 12.2).[45-48]



**Figure 4.** Pictorial representations of the major cobalt orbitals contributing to the frontier MOs of 1 (viz., the e′ of MOs of −13.65 eV, the completely filled e″ HOMOs of −13.25 eV, and the a′₂ LUMO of −11.03 eV).

This resultant increase in the mean Co–Co bond length must have an electronic origin in that any inherent steric effect of the more bulky $C_5Me_5$ ligands in 2 would give rise to a smaller mean Co–Co bond-length difference between 1 and 2. Hence, the assumption (vide supra) that the bulky $C_5Me_5$ ligands in 2 would sterically increase the mean Co–Co bond length by ca. 0.025 Å leads to the conclusion that the geometrical effect of adding two electrons to a 46-electron $Co_3(CO)_2$ core with sterically innocent $C_5R_5$ ligands would involve an actual increase of the mean Co–Co distance by approximately 0.05–0.06 Å. This estimated bond-length change due to the added two electrons is entirely consistent with similarly small changes of 0.03 Å in the average metal–metal distances of the 49-electron Fischer–Palm $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ (Ni–Ni, 2.389 Å)[5] upon either a one-electron reduction to its 50-electron monoanion (Ni–Ni, 2.421 Å)[9] or a formal one-electron oxidation by replacement of one nickel with one cobalt atom to give the crystal-disordered 48-electron $CoNi_2(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ (M–M, 2.356 Å).[5] It is apparent that these small variations in metal–metal bond length upon change in electronic configuration reflect the weakness of the metal–metal interactions relative to the strong metal–ligand interactions in these triangular metal clusters.

**Correlation of Experimental Data with Molecular Orbital Results.** The above analysis attributes the observed increase in mean Co–Co bond length of the $Co_3(CO)_2$ core on going from 2 to 1 to the two added electrons in 1 occupying a MO which possesses considerable tricobalt antibonding character. These bond-length arguments are in complete harmony not only with the results of the nonparametrized Fenske–Hall MO calculations on 1 but also with the results of previous Fenske–Hall MO calculations (reported

(42) The fact that the mean Co–Co distance of 2.365 (4) Å for $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}O)$ is smaller than the expected value of 2.40 Å (based upon the size of the larger capping carbon atom) may possibly be a consequence of the markedly greater electronegative effect of the smaller capping oxygen atom.

(43) (a) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd ed.; Harper & Row: New York, 1983; pp 258–259. (b) Porterfield, W. W. *Inorganic Chemistry: A Unified Approach*; Addison-Wesley: Reading, MA, 1984; p 168.

(44) Of significance is that in these five clusters with triply bridging atoms of similar size the mean Co–Co bond length is insensitive to the nature of one of the triply bridging ligands as either a π-donor (e.g., NH, NR) or π-acceptor (e.g., NO, CO).

(45) In other electronically equivalent triangular or tetrahedral metal clusters possessing sterically innocent terminal ligands and bridging atoms of similar size, the mean metal–metal distances normally agree within 0.01–0.02 Å even though the variations in the individual metal–metal distances within a given metal cluster may be substantial. For example, the 50-electron $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}S)_2$ consists of two independent molecules in the crystalline state with the $Co_3S_2$ core of each molecule possessing one nonbonding and two bonding Co–Co distances.[46] Although the corresponding individual Co–Co distances of 2.492 (2), 2.497 (2), and 3.151 (2) Å for one molecule are significantly different from those of 2.457 (2), 2.488 (2), and 3.221 (2) Å for the other molecule, the mean Co–Co distances of 2.713 and 2.722 Å are in good agreement. It is also noteworthy that these mean values for the two independent diamagnetic molecules of this $C_5H_4Me$-coordinated $Co_3S_2$ core closely conform with the values of 2.687 (3) and 2.691 (4) Å determined by two independent structural analyses[47,48] at room temperature for the three identical Co–Co distances in the 50-electron paramagnetic $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2$ which has crystallographic $C_{3h}$—$3/m$ site symmetry. The essential invariance of the mean metal–metal distance to different distortions in a given metal cluster containing metal atoms with identical ligands is attributed to compensatory bond-length variations which essentially preserve a balancing of the charge densities of the metal atoms.

(46) (a) Pulliam, C. R.; Englert, M. H.; Dahl, L. F. *Abstracts of Papers*, 190th National Meeting of the American Chemical Society, Chicago, Illinois, American Chemical Society: Washington, DC, 1985; INOR 387. (b) Pulliam, C. R.; Englert, M. H.; Dahl, L. F., to be published.

(47) Frisch, P. D.; Dahl, L. F. *J. Am. Chem. Soc.* 1972, 94, 5082–5084.

(48) Kamijo, N.; Watanabe, T. *Acta Crystallogr., Sect. B* 1979, B35, 2537–2542.

elsewhere[8]) on the hypothetical cyclopentadienyl analogue of the 46-electron **2** (in which $C_5H_5$ rings were substituted for the $C_5Me_5$ rings of **2** in order to simplify the calculations). The important metal orbital contributions to the frontier MO's found for both **1** and **2** are displayed in Figure 4. A comparison of their energy-level patterns and associated orbital characters[49] reveals that the half-filled doubly degenerate $e''$ HOMO's[50] (under $D_{3h}$ symmetry) in the 46-electron **2** correspond in the 48-electron **1** to the completely filled $e''$ HOMOs (under $D_{3h}$ symmetry) which are only 0.40 eV above the next highest filled doubly degenerate $e'$ MOs but 2.2 eV below the nondegenerate LUMO of $a_2'$ representation. An examination of these frontier MOs shows that they are primarily trimetallic. For **1** the two $e''$ HOMOs are each composed of a total of 56% $3d_{yz}$, 14% $3d_{xy}$, and 2% $4p_y$ AO character for the three cobalt atoms, 6% $e_1(bz)$ character for the three benzene ligands, and 14% $2\pi(CO)$ character for the two carbonyl ligands. The corresponding total percent orbital character for each of the doubly degenerate $e'$ MOs is 91% Co $3d_{z^2}$ and 3% Co $3d_{x^2-y^2}$, while for the nondegenerate $a_2'$ LUMO the total percent orbital character is 88% Co $3d_{xz}$ and 12% $e_1(bz)$.

Of prime importance is that these nonparametrized Fenske–Hall MO calculations clearly show that the half-filled $e''$ HOMOs[50]

in **2** and the corresponding filled $e''$ HOMOs in **1** are mainly comprised of cobalt AOs, which are tricobalt antibonding, and carbonyl $2\pi(CO)$ orbitals, which form bonding interactions with the cobalt atoms. These findings are also entirely self-consistent with the initial theoretical results from extended-Hückel calculations by Hoffmann and colleagues,[10] who showed an energy-correlation diagram for a then unknown 46-electron $D_{3h}$ $Rh_3$-$(\eta^5-C_5H_5)_3(\mu_3-CO)_2$ molecule with the pictorial representation of the half-filled $e''$ HOMO possessing trimetal antibonding character per se but trimetal–dicarbonyl bonding character.

Furthermore, the MO scheme for **1** clearly indicates that the addition of one electron to **1** to give the neutral 49-electron $Co_3(\eta^6-C_6H_6)_3(\mu_3-CO)_2$ molecule would involve occupation of the nondegenerate $a_2'$ MO which experimentally should give rise to a ca. 0.03-Å enlargement[5,9] of the tricobalt framework without any marked triangular distortion (i.e., no first-order Jahn–Teller vibronic effect). This prediction is expectedly in agreement with previous experimental–theoretical studies[5,9,10,34] for the closely related 49-electron Fischer–Palm molecule and its reduced and formally oxidized species. In conclusion, it is gratifying that the combined experimental–theoretical results reported herein provide a coherent, integrated picture for these triangular metal clusters.

**Supplementary Material Available:** Calculated coordinates and isotropic temperature factors for all hydrogen atoms, anisotropic thermal parameters for all non-hydrogen atoms, and selected least-squares planes for $[Co_3(\eta^6-C_6H_6)_3(\mu_3-CO)_2]^+[BPh_4]^-\cdot CH_2Cl_2$ (5 pages); listing of the observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

(49) On the basis of the chosen local coordinate axial systems for the cobalt atoms being identical (as defined in the experimental section) in the Fenske–Hall MO calculations on **1** and **2**, the orbital character of the frontier $e''$, $e'$, and $a_2'$ MOs (under $D_{3h}$ symmetry) may consist of cobalt valence AOs: $e''$ ($3d_{yz}$, $3d_{xy}$, $4p_y$); $e'$ ($3d_{z^2}$, $3d_{x^2-y^2}$, $3d_{xz}$, $4s$, $4p_x$, $4p_z$); $a_2'$ ($3d_{xz}$, $4p_x$).

(50) Application of the Fenske–Hall MO method[21] to the hypothetical cyclopentadienyl $Co_3(\eta^5-C_5H_5)_3(\mu_3-CO)_2$ analogue of **2** was carried out for an undistorted $D_{3h}$ geometry and two types of distorted $C_{2v}$ geometries. Under assumed $D_{3h}$ symmetry corresponding to the 46-electron **2** possessing a triplet spin state, the degenerate energy levels of the half-filled $e''$ HOMOs are 2.38 eV higher than those of the highest filled MOs of $e'$ representation but 4.29 eV lower than the level of the $a_2'$ LUMO. Each of the doubly degenerate $e''$ HOMOs consists of a total of 34% $3d_{yz}$, 8% $3d_{xy}$, and 8% $4p_y$ AO character for the three cobalt atoms, 20% $e_1(Cp)$ character for the three $C_5H_5$ ligands, and 22% $2\pi(CO)$ character for the two carbonyl ligands. The corresponding total percent character for each of the two $e'$ MOs was calculated to be 41% Co $3d_{z^2}$, 10% Co $3d_{x^2-y^2}$, 10% Co $3d_{xz}$, and 9% Co $4p_x$, 22% $e_1(Cp)$, and 5% $2\pi(CO)$, while for the $a_2'$ LUMO the calculated values are 65% Co $3d_{xz}$ and 34% $e_1(Cp)$.