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\* Address correspondence to these authors at the Department of Chemistry, University of Kansas.

Ian H. Williams, Dale Spangler, Douglas A. Femec  
Gerald M. Maggiora,\* Richard L. Schowen\*

Departments of Chemistry and Biochemistry  
University of Kansas, Lawrence, Kansas 66045  
and NRCC Lawrence Berkeley Laboratory  
Berkeley, California 94720

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### Clusterification of Reactive Species Generated through Chemical Reduction of Metallocenes: Synthesis and Stereochemical Characterization of a New Hexameric Series of Metal-Cyclopentadienyl Clusters, $[\text{Ni}_6(\eta^5\text{-C}_5\text{H}_5)_6]^n$ ( $n = 0, +1$ )

Sir:

In the course of efforts to systematize our knowledge of different modes of metal-cluster formation and the interrelationships among coordination geometries, electronic structures, and reactivity patterns of polynuclear metal clusters, we have uncovered a synthetic route to several new series of metal-cyclopentadienyl oligomers, formulated generally as  $\text{M}_x(\text{C}_5\text{H}_5)_y\text{H}_z$ . The reaction scheme involves reduction of the metallocenes  $\text{M}(\eta^5\text{-C}_5\text{H}_5)_2$  ( $\text{M} = \text{Fe, Co, Ni}$ ) to highly reactive species whose clusterification to a complex mixture of products is accompanied by formation of the cyclopentadienide anion. Reported herein is a preliminary account of the reductive chemistry of nickelocene which has resulted in the isolation and physicochemical characterization of two nickel cyclopentadienyl hexamers,  $\text{Ni}_6(\eta^5\text{-C}_5\text{H}_5)_6$  (**1**) and its one-electron oxidized species  $[\text{Ni}_6(\eta^5\text{-C}_5\text{H}_5)_6]^+[\text{PF}_6]^-$  (**2**), which are unprecedented (to our knowledge) as polynuclear metal-cyclopentadienyl clusters possessing no other ligands.

Previously reported cyclopentadienyl-metal clusters formed from cyclopentadienyl complexes under reducing conditions have invariably been hydride-containing species.<sup>1-3</sup> These include  $\text{Co}_4(\eta^5\text{-C}_5\text{H}_5)_4(\mu_3\text{-H})_4$ <sup>1</sup> and  $\text{Ni}_4(\eta^5\text{-C}_5\text{H}_5)_4(\mu_3\text{-H})_3$ ,<sup>2</sup> which are formed by the reductions of  $\text{Co}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-NO})_2$  and  $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)\text{NO}$ , respectively, with  $\text{LiAlH}_4/\text{AlCl}_3$ , and  $\text{Rh}_3(\eta^5\text{-C}_5\text{H}_5)_3(\mu_3\text{-C}_5\text{H}_5)(\mu_3\text{-H})$ ,<sup>3</sup> which was prepared by the reduction of  $\text{RhCl}_3$  with  $(\text{C}_5\text{H}_5)\text{MgBr}$ . Prior chemical reductions of  $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2$  with either  $\text{Na}(\text{Hg})/\text{ROH}$ <sup>4</sup> or  $\text{K}/\text{liquid NH}_3$ <sup>5</sup> have yielded only such materials as  $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_5\text{H}_7)$  and nickel metal, respectively. Geiger and co-workers<sup>6</sup> have carried out an extensive electrochemical investigation of several metallocenes. Two of their observations relevant to our work are the following: (1) the nickelocene monoanion (which decomposes to unidentified

products) generated in a cyclic voltammetric experiment has a room-temperature half-life of ca. 1 s; and (2) the exhaustive electrolytic "reduction of nickelocene is mechanistically very complex",<sup>6b</sup> with resulting solutions exhibiting several polarographic waves indicative of a mixture of electroactive species.

Our reductions of  $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2$  and its ring-alkylated derivatives<sup>7</sup> were accomplished (in yields exceeding 80%, based upon recovery of this starting material) by treatment of a THF solution of vacuum-sublimed nickelocene with an equimolar amount of sodium naphthalenide in THF.<sup>8</sup> After removal of solvent from the resulting reddish brown solution, extractions of the residue with various organic solvents produced solutions which were chromatographed on alumina. This procedure produced 5-7 intensely colored air-sensitive bands,<sup>9,10</sup> depending upon the rate of addition of the reducing agent and the temperature of the reaction. To date, analyses of mass spectral, <sup>1</sup>H NMR, IR, and electrochemical measurements on these fractions and their oxidized species along with X-ray diffraction examinations have shown the existence of five different kinds of cyclopentadienyl-nickel clusters, viz.,  $\text{Ni}_2(\text{C}_5\text{H}_5)_2(\mu\text{-C}_5\text{H}_5)$ ,<sup>11</sup>  $\text{Ni}_3(\text{C}_5\text{H}_5)_4$ ,  $\text{Ni}_4(\text{C}_5\text{H}_5)_4\text{H}_x$  ( $x = 1, 3^2$ ),  $\text{Ni}_5(\text{C}_5\text{H}_5)_5\text{H}_3$ , and  $\text{Ni}_6(\text{C}_5\text{H}_5)_6$ .

The first such fraction to be adequately characterized was the hexameric  $\text{Ni}_6(\eta^5\text{-C}_5\text{H}_5)_6$  species (**1**). Deep red-brown solutions of **1** in  $\text{CH}_2\text{Cl}_2$  and THF yielded (after removal of solvent) a black amorphous solid which is insoluble in hexane, only slightly soluble in benzene or acetone, and moderately soluble in dichloromethane or THF. Although amorphous powders or solutions of **1** are air sensitive, the compound in the crystalline state is reasonably air stable. A solid-state (KBr) infrared spectrum displayed absorption bands characteristic of  $\pi$ -bonded  $\text{C}_5\text{H}_5$  rings. The initial formulation of **1** as a hexamer was made from a mass spectrum (70-eV ion source; inlet temperature 200 °C), which showed a well-defined parent molecular ion envelope for  $\text{Ni}_6\text{C}_{30}\text{H}_{30}$  ( $m/e$  738 for <sup>58</sup>Ni). Cyclic voltammograms<sup>12</sup> of **1** in  $\text{CH}_2\text{Cl}_2/0.1$  M TBAH indicated four one-electron couples at  $E_{1/2}$  values (vs. SCE) of  $[\text{Ni}_6]^- -0.97$  V  $[\text{Ni}_6]^0 -0.26$  V  $[\text{Ni}_6]^+ +0.19$  V  $[\text{Ni}_6]^{2+} +1.00$  V  $[\text{Ni}_6]^{3+}$ , where  $[\text{Ni}_6]$  is an abbreviation for **1**.

Chemical oxidation of **1** with a 1:1 molecular ratio of  $\text{AgPF}_6$  in diethyl ether produced (in 93% yield) the brown-colored  $[\text{Ni}_6(\eta^5\text{-C}_5\text{H}_5)_6]^+[\text{PF}_6]^-$  (**2**), which is relatively soluble in acetone. Further oxidation of **2** with  $\text{AgPF}_6$  in acetone solution yielded an insoluble black precipitate (presumably the  $[\text{PF}_6]^-$  salt of the dication) which is slightly soluble in dimethyl sulfoxide. In contrast to **1**, solutions of **2** (e.g., in acetone) are not noticeably attacked by air after minutes of exposure. Magnetic susceptibility measurements of **2** by the Faraday method ( $\mu_{\text{eff}} = 3.94\text{-}3.97 \mu_B$  from 100 to 300 K) indicate the presence of three unpaired electrons,<sup>13,14</sup> this expected paramagnetic character was corroborated from a solid-state room-temperature EPR spectrum.

(7) Analogous reductions of 1,1'-dimethyl- and 1,1'-dibenzyl-substituted nickelocenes gave less air-sensitive fractions from chromatography. However, attempted crystallizations of these materials have to date been unsuccessful.

(8) Preliminary experiments show that  $\text{Na}(\text{Hg})$  in polar aprotic solvents also reduces nickelocene to a mixture of deep brown oligomers.

(9) Final yields of pure individual products ranged from 1-10% because of severe problems with insolubility and band tailing. Fractions often had to be rechromatographed in order to secure adequate purity for characterization. Moderate success has recently been achieved in our laboratories through the utilization of gel permeation chromatography.<sup>10</sup>

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(12) Cyclic voltammetric measurements were performed under ambient conditions on **1** in  $\text{CH}_2\text{Cl}_2$  solutions (0.10 M TBAH as supporting electrolyte) with a gold disk working electrode at a scan rate of 500 mV/s. Analogous cyclic voltammetric measurements on **2** in  $\text{CH}_3\text{CN}$  solutions (0.10 M TBAH) exhibited five one-electron couples at  $E_{1/2}$  values (vs. SCE) of  $[\text{Ni}_6]^{2-} -1.74$  V  $[\text{Ni}_6]^- -1.01$  V  $[\text{Ni}_6]^0 -0.42$  V  $[\text{Ni}_6]^+ +0.26$  V  $[\text{Ni}_6]^{2+} +0.80$  V  $[\text{Ni}_6]^{3+}$  at a scan rate of 500 mV/s. Evidence for chemical reversibility of the waves is given by their approximate conformity to the criterion  $|i(\text{peak, anodic scan})| = |i(\text{peak, cathodic scan})|$ .

(13)  $\text{Ni}_4(\eta^5\text{-C}_5\text{H}_5)_4(\mu_3\text{-H})_3$  also contains three unpaired electrons ( $\mu_{\text{eff}} = 4.10 \mu_B$  at 295 K)<sup>2a</sup> which were shown from a molecular orbital investigation by Hoffmann et al.<sup>14</sup> to occupy a low-lying triply degenerate  $t_1$  orbital.

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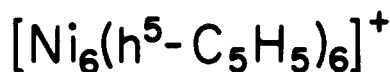
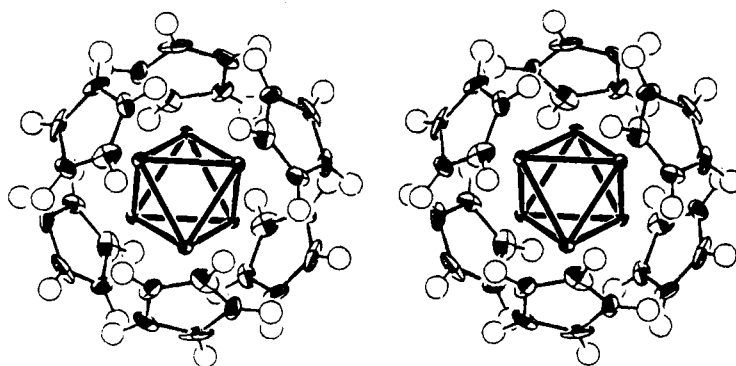
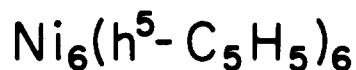
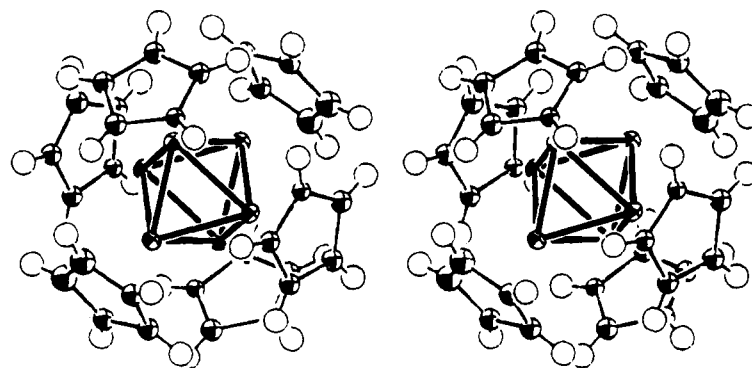
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**Figure 1.** Stereoscopic views of the neutral  $\text{Ni}_6(\eta^5\text{-C}_5\text{H}_5)_6$  molecule and the  $[\text{Ni}_6(\eta^5\text{-C}_5\text{H}_5)_6]^+$  monocation of the  $[\text{PF}_6]^-$  compound (2). Hydrogen atoms are included to emphasize the high degree of ring crowding in these hexameric clusters. The nickel core of the neutral parent molecule, which has crystallographic  $D_{2h}$  site symmetry, is slightly but significantly distorted from a regular  $O_h$  octahedral geometry to an observed tetragonal  $D_{4h}$  geometry. On the other hand, the nickel core of the monocation, which possesses crystallographic  $S_6\text{-}\bar{3}$  site symmetry, experimentally conforms to a regular  $O_h$  octahedral geometry.

Both the stoichiometries and atomic arrangements of **1** and **2** were ascertained from X-ray crystallographic studies.<sup>15</sup> Their nearly identical geometries (Figure 1) consist of six nickel atoms located at the corners of an octahedron with a  $\eta^5$ -cyclopentadienyl ligand coordinated to each nickel atom. In **2**, the crystallo-

graphically ordered, well-behaved  $\text{PF}_6^-$  anion has  $S_6\text{-}\bar{3}$  site symmetry with its one independent P-F bond length of normal value, 1.586 (7) Å.

A small tetragonal distortion of the nickel octahedron in **1** from a regular cubic  $O_h$  geometry to a tetragonal  $D_{4h}$  geometry is indicated from the 12 Ni-Ni edge bond lengths, of which only three are independent. This slight axial compression of the nickel core along one trans(Ni-Ni) axis is evidenced by the eight identical Ni-Ni bond lengths of 2.411 (2) Å being smaller than the other four experimentally equivalent Ni-Ni bond lengths, of which two are 2.435 (3) Å and the other two 2.438 (2) Å. This deformation is also reflected in one smaller trans(Ni-Ni) distance of 3.373 (4) Å vs. the two identical trans(Ni-Ni) distances of 3.446 (3) Å. On the other hand, the nickel core of **2** experimentally conforms to a regular  $O_h$  octahedron in that the two independent Ni-Ni distances of 2.419 (2) and 2.428 (2) Å are statistically equivalent. The one independent trans(Ni-Ni) distance is 3.427 (3) Å.

Of special interest from a bonding viewpoint is that for the neutral parent **1** and its monocation the weighted mean Ni-Ni distances of 2.419 and 2.423 Å, respectively, are experimentally equivalent. These values are significantly shorter than the nearest Ni-Ni neighbor distances in both cubic close-packed nickel (2.492 Å)<sup>16</sup> and hexagonal close-packed nickel (2.492 Å)<sup>16</sup> as well as the

(15) (a)  $\text{Ni}_6(\text{C}_5\text{H}_5)_6$  (fw, 742.8): octahedral-shaped crystal obtained from slow evaporation of a  $\text{CS}_2/\text{CH}_2\text{Cl}_2$  solution; tetragonal,  $P4_2/mnm$  ( $D_{4h}^{14}$ );  $a = b = 9.367$  (4),  $c = 15.053$  (6) Å,  $V = 1320.8$  (8) Å<sup>3</sup>;  $\rho_o = 1.85$  g/cm<sup>3</sup> (floatation) vs.  $\rho_c = 1.87$  g/cm<sup>3</sup> for  $Z = 2$ . Our ultimate choice of the centrosymmetric  $P4_2/mnm$  space group, which requires molecular site symmetry of  $D_{2h}\text{-}mmm$ , was based upon least-squares refinement (with anisotropic thermal parameters for two independent nickel atoms and isotropic temperature factors for eight independent carbon atoms and with fixed contributions for eight hydrogen atoms) to  $R_1(F)$  and  $R_2(F)$  values of 4.1 and 5.2%, respectively, for 410 independent data [ $I > 2\sigma(I)$ ]. The resulting molecular site symmetry of  $D_{2h}$  requires that Ni(I) and Ni(II) possess  $C_{2v}\text{-}mm2$  and  $C_s\text{-}m$  site symmetry, respectively. Each of the  $\text{C}_5\text{H}_5$  rings attached to these two nickel atoms was best modeled by a twofold crystal disorder. (b)  $[\text{Ni}_6(\text{C}_5\text{H}_5)_6]^+[\text{PF}_6]^-$  (fw, 887.8): truncated cubic crystal obtained from slow evaporation of an acetone solution; cubic,  $P2_1/a\bar{3}$  ( $T_h^8$ );  $a = 14.315$  (3) Å,  $V = 2933.5$  (13) Å<sup>3</sup>;  $\rho_o = 1.98$  g/cm<sup>3</sup> (floatation) vs.  $\rho_c = 2.01$  g/cm<sup>3</sup> for  $Z = 4$ . The required  $S_6\text{-}\bar{3}$  site symmetry for each monocation and each  $\text{PF}_6^-$  anion gives rise to the crystallography independent unit being composed of one Ni, one  $\text{C}_5\text{H}_5$  ring, one P, and one F atom. Least-squares refinement with anisotropic thermal parameters for all nonhydrogen atoms together with fixed hydrogen-atom contributions gave  $R_1(F) = 5.7\%$  and  $R_2(F) = 5.9\%$  for 589 independent reflections [ $I > 2\sigma(I)$ ].

mean Ni–Ni distances in  $\text{Ni}_4(\eta^5\text{-C}_5\text{H}_5)_4(\mu_3\text{-H})_3$  (2.469 Å)<sup>2c</sup> and  $[\text{Ni}_3(\eta^5\text{-C}_5\text{H}_5)_3(\mu_3\text{-C}_5\text{H}_5)]^+[\text{PF}_6]^-$  (2.446 Å).<sup>17</sup>

The effective encapsulation of the  $\text{Ni}_6$  cores by the cyclopentadienyl rings in both hexamers (Figure 1) is indicated from the gear-like interlocking of the cyclopentadienyl hydrogen atoms. In **2** (for which the independent  $\text{C}_5\text{H}_5$  ring is ordered), the closest inter-ring H···H contacts are estimated at ca. 2.2 Å<sup>18</sup> while in **1** the analogous contacts are estimated at ca. 1.9–2.2 Å,<sup>18</sup> depending upon the choice of ring pairs from the twofold-disordered rings. The Ni– $\text{C}_5\text{H}_5$ (centroid) distances average 1.80 Å in **1** and 1.78 Å in **2** vs. 1.76 Å<sup>2c</sup> in the less-crowded  $\text{Ni}_4(\eta^5\text{-C}_5\text{H}_5)_4(\mu_3\text{-H})_3$  molecule.

One salient bonding feature which emerges from this work is that **1**, which corresponds to a 90-electron metal-cluster system,<sup>19,20</sup> is a nonconformist to the large class of octahedral metal–carbonyl clusters<sup>21</sup> which invariably possess an electronically equivalent configuration of 86 valence electrons<sup>19,20</sup> for metal–metal and metal–ligand bonding. On the basis of the assumption that the cluster molecular orbitals given by Mingos<sup>19</sup> for an 86-electron octahedral metal–carbonyl cluster (viz., the  $[\text{Co}_6(\text{CO})_{14}]^{4-}$  tetraanion) are also applicable to **1** and **2**,<sup>22</sup> the additional three electrons in **2** or four electrons in **1** would populate either two or three of the 11 antibonding metal–cluster MOs (of representations  $t_{1u}$ ,  $t_{2u}$ ,  $t_{1g}$ , and  $e_g$  under  $O_h$  symmetry) or possibly antibonding metal–ligand MOs. The fact that **2** contains three unpaired electrons points to their occupation of a triply degenerate orbital. If the assumed energy-level ordering given by Glidewell<sup>23</sup> for the addition of four electrons to either a 14-electron  $O_h$   $\text{B}_6\text{H}_6^{2-}$  dianion<sup>24,25</sup> or an 86-electron  $O_h$  metal–carbonyl cluster is also valid for **1** and **2**, then the four additional electrons in **1** will likewise populate the  $t_{2u}$  level to give a  $^3T_{1g}$  ground state. The 90-electron  $O_h$  system should then undergo a Jahn–Teller distortion; a first-order vibronic deformation can give rise to the experimentally determined  $D_{4h}$  hexanickel configuration for **1** (as well as a  $D_{2h}$  one) with the four electrons still remaining antibonding with respect to the nickel core. A corresponding  $^4A_{2u}$  ground state for a half-filled  $t_{2u}$  level in **2** is completely consistent with the observed undistorted  $O_h$  nickel core as well as with the determined magnetic moment at room temperature.

A 90-electron octahedral metal core is electronically unstable relative to a 90-electron trigonal-prismatic metal core which corresponds to an *arachno* square antiprism and is the geometry expected from the Wade bonding scheme.<sup>25–27</sup> Hence, the

locked-in octahedral nickel architecture found for both **1** and **2** is presumed to be a consequence of less steric overcrowding of the cyclopentadienyl ligands than that estimated for an analogous trigonal-prismatic nickel core. The importance of nonbonded ligand–ligand repulsion forces in these hexamers is also consistent with the observed bond-length invariance of the octahedral nickel framework (instead of an expected decrease in average length predicted from MO considerations) upon oxidation of **1** to **2**. The resulting bonding implication that **1** is an “electron-rich” cluster is in harmony with its electrochemical behavior.

A full presentation of this work will be made upon completion of current studies involving both further physicochemical characterization of these remarkable hexameric species and their chemical reactivity with carbon monoxide and other small molecules.

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**Supplementary Material Available:** Two tables listing the atomic parameters of **1** and **2** (3 pages). Ordering information is given on any current masthead page.

Michael S. Paquette, Lawrence F. Dahl\*

Department of Chemistry, University of Wisconsin—Madison  
Madison, Wisconsin 53706

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**Photochemical Formation and Stereochemical Characterization of Two Electronically Equivalent but Structurally Different Series of Triangular Dicobalt–Metal Clusters,  $\text{MCo}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-CO})_3(\mu_3\text{-CO})$  [ $\text{M} = \text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{Me})$ ,  $\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{Me})$ ,  $\text{Fe}(\eta^4\text{-C}_4\text{H}_4)$ ] and  $\text{MCo}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-CO})_2(\mu_3\text{-CO})$  [ $\text{M} = \text{Fe}(\text{CO})_3$ ,  $\text{Co}(\eta^5\text{-C}_5\text{H}_4\text{Me})$ ]: A Rational Synthesis of Mixed-Metal Clusters by Photogenerated Metal-Fragment Addition across a Metal–Metal Multiple-Bonded Dimer**

Sir:

In order to illustrate the apparent diversity and scope of photochemically generating a desired variety of related mixed-metal clusters by the net insertion of organometallic fragments across metal–metal multiple-bonded species, we report herein the results of a designed synthetic procedure which has produced a particular electronically equivalent class of mixed-metal clusters by a series of reactions of a given double-bonded metal–metal dimer,  $\text{Co}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-CO})_2$ , with various photogenerated  $\text{M}(\text{CO})_x$  and  $\text{M}(\text{C}_n\text{R}_n)(\text{CO})_y$  species. The five triangularly formed, diamagnetic dicobalt–metal clusters<sup>1</sup> obtained by the net addition of electronically equivalent  $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{CO})_2$ ,  $\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2$ ,  $\text{Fe}(\eta^4\text{-C}_4\text{H}_4)(\text{CO})_2$ ,  $\text{Fe}(\text{CO})_4$ , and  $\text{Co}(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})$  fragments to  $\text{Co}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-CO})_2$  were found from spectral and X-ray diffraction analyses to divide from a structural viewpoint into two distinct series. The  $\text{MCo}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-CO})_3(\mu_3\text{-CO})$  series [composed of three members designated by M being  $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{Me})$  (**1**),  $\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{Me})$  (**2**), and  $\text{Fe}(\eta^4\text{-C}_4\text{H}_4)$  (**3**)] possesses one triply bridging and three doubly bridging carbonyl ligands while the  $\text{MCo}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-CO})_2(\mu_3\text{-CO})$  series [consisting of two members denoted by M being  $\text{Fe}(\text{CO})_3$  (**4**) and

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(26) A 90-electron trigonal-prismatic metal cluster (i.e., with no antibonding cluster valence electrons) may be regarded from the Wade–Mingos representation<sup>19,25</sup> as electronically corresponding to trigonal prismane,<sup>27</sup>  $\text{C}_6\text{H}_6$  (a valence isomer of benzene), which has nine occupied bonding skeletal MOs in contrast to seven occupied bonding and eleven empty antibonding skeletal MOs possessed by the octahedral  $\text{B}_6\text{H}_6^{2-}$  dianion,<sup>24</sup> an electronic analogue of the 86-electron octahedral metal–carbonyl clusters. An octahedral  $\text{C}_6\text{H}_6$  molecule (with two antibonding electron pairs) is expected<sup>27b</sup> to be “unstable with respect to at least one set of nontotally symmetric distortions of the group  $O_h$ ”.

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