mean Ni–Ni distances in $Ni_4(\eta^5\text{-}C_5H_5)_4(\mu_3\text{-}H)_3$ (2.469 Å)[2c] and $[Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}C_5H_5)]^+[PF_6]^-$ (2.446 Å).[17]

The effective encapsulation of the 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 C_5H_5 ring is ordered), the closest inter-ring H···H contacts are estimated at ca. 2.2 Å[18] while in **1** the analogous contacts are estimated at ca. 1.9–2.2 Å,[18] depending upon the choice of ring pairs from the twofold-disordered rings. The $Ni\text{-}C_5H_5$(centroid) distances average 1.80 Å in **1** and 1.78 Å in **2** vs. 1.76 Å[2c] in the less-crowded $Ni_4(\eta^5\text{-}C_5H_5)_4(\mu_3\text{-}H)_3$ molecule.

One salient bonding feature which emerges from this work is that **1**, which corresponds to a 90-electron metal-cluster system,[19,20] is a nonconformist to the large class of octahedral metal–carbonyl clusters[21] which invariably possess an electronically equivalent configuration of 86 valence electrons[19,20] for metal–metal and metal–ligand bonding. On the basis of the assumption that the cluster molecular orbitals given by Mingos[19] for an 86-electron octahedral metal–carbonyl cluster (viz., the $[Co_6(CO)_{14}]^{4-}$ tetraanion) are also applicable to **1** and **2**,[22] 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[23] for the addition of four electrons to either a 14-electron O_h $B_6H_6^{2-}$ dianion[24,25] 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.[25–27] 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.

Acknowledgment. This research was generously supported by a grant from the National Science Foundation. M.S.P. gratefully thanks NSF for a predoctoral NSF fellowship. We are also greatly indebted to Mark A. Murphy for his assistance and Mark H. Englert and Rowland B. Randall for carrying out the magnetic susceptibility and mass spectral measurements, respectively.

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

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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[19,25] as electronically corresponding to trigonal prismane,[27] C_6H_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 $B_6H_6^{2-}$ dianion,[24] an electronic analogue of the 86-electron octahedral metal–carbonyl clusters. An octahedral C_6H_6 molecule (with two antibonding electron pairs) is expected[27b] to be "unstable with respect to at least one set of nontotally symmetric distortions of the group O_h".

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Photochemical Formation and Stereochemical Characterization of Two Electronically Equivalent but Structurally Different Series of Triangular Dicobalt–Metal Clusters, $MCo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_3(\mu_3\text{-}CO)$ [M = $Cr(\eta^6\text{-}C_6H_5Me)$, $Mn(\eta^5\text{-}C_5H_4Me)$, $Fe(\eta^4\text{-}C_4H_4)$] and $MCo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2(\mu_3\text{-}CO)$ [M = $Fe(CO)_3$, $Co(\eta^5\text{-}C_5H_4Me)$]: 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, $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$, with various photogenerated $M(CO)_x$ and $M(C_nR_n)(CO)_y$ species. The five triangularly formed, diamagnetic dicobalt–metal clusters[1] obtained by the net addition of electronically equivalent $Cr(\eta^6\text{-}C_6H_5Me)(CO)_2$, $Mn(\eta^5\text{-}C_5H_4Me)(CO)_2$, $Fe(\eta^4\text{-}C_4H_4)(CO)_2$, $Fe(CO)_4$, and $Co(\eta^5\text{-}C_5H_4Me)(CO)$ fragments to $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$ were found from spectral and X-ray diffraction analyses to divide from a structural viewpoint into two distinct series. The $MCo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_3(\mu_3\text{-}CO)$ series [composed of three members designated by M being $Cr(\eta^6\text{-}C_6H_5Me)$ (**1**), $Mn(\eta^5\text{-}C_5H_4Me)$ (**2**), and $Fe(\eta^4\text{-}C_4H_4)$ (**3**)] possesses one triply bridging and *three* doubly bridging carbonyl ligands while the $MCo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2(\mu_3\text{-}CO)$ series [consisting of two members denoted by M being $Fe(CO)_3$ (**4**) and

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(1) Based upon the conformity of each metal atom to the EAN rule, the expected diamagnetism of compounds **1**–**5** is in accordance with room-temperature magnetic susceptibility measurements by the Faraday method.

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$Co(\eta^5\text{-}C_5H_4Me)$ (**5**)] has one triply bridging but only *two* doubly bridging carbonyl ligands. It is noteworthy that these deliberately prepared, electronically equivalent metal clusters, which were conveniently photogenerated under relatively mild conditions (i.e., at room temperature) in nonoptimized 27–45% yields, were not obtainable from corresponding thermal reactions (at least under our boundary conditions). The availability of such transition-metal clusters is of particular interest in connection with their potential use as catalytic agents, viz., as homogeneous catalysts in solution and/or as highly dispersed metal crystallites obtained from the removal of ligands after attachment on solid supports.

The research presented here is an outgrowth of our work on the preparation and investigation of the physicochemical behavior of the $[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2]^n$ dimers ($n = -1, 0$),[2] from which it was found[3] that a new type of bonding tetrahedral cobalt cluster, $Co_4(\eta^5\text{-}C_5Me_5)_2(CO)_4(\mu\text{-}CO)(\mu_3\text{-}CO)_2$, could be obtained nonphotochemically from the net insertion of a $Co_2(CO)_4(\mu\text{-}CO)$ fragment across the Co–Co double bond of the neutral dimer by its reaction with dicobalt octacarbonyl. Likewise, the bonding triangular rhodium $[Rh_3(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)_2]^-$ monoanion, prepared and structurally characterized by Jones et al.[4] from the reduction of $Rh(\eta^5\text{-}C_5H_5)(CO)_2$ with sodium amalgam, was presumed to be an adduct formed by the interaction either of $Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_2$ with $Rh(CO)_2^-$ or of its dimeric monoanion with $Rh(CO)_2$. Although others[5,6] have utilized the diprotonated metal–metal double-bonded species[7] $Os_3(CO)_{10}(\mu\text{-}H)_2$[5] and $Re_2(CO)_8(\mu\text{-}H)_2$[6] and the metal–metal triple-bonded $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4$[6] to synthesize mixed-metal clusters by nonphotochemical reactions, the work presented here represents the first report (to our knowledge) of a systematic study of photochemically assisted insertion reactions across a metal–metal multiple bond.[8–10]

The photochemical procedures utilized in the preparation and purification of the molecular clusters **1–5** are similar; hence, only the preparation of the $(\eta^6\text{-}C_6H_5Me)CrCo_2$ compound **1** is outlined in detail. Its synthesis was accomplished in a designed fashion by the photolysis (quartz apparatus, 450-W Hanovia mercury vapor lamp) of $Cr(\eta^6\text{-}C_6H_5Me)(CO)_3$ (2.0 mmol) in the presence of $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$, which was initially prepared without isolation by irradiation of $Co(\eta^5\text{-}C_5Me_5)(CO)_2$ (4.0 mmol) for 6–8 h, in toluene under a N_2-swept atmosphere.[11] After termination of the 40-h photolysis with $Cr(\eta^6\text{-}C_6H_5Me)(CO)_3$, the resulting solution was concentrated under vacuum and then purified on an alumina column. The use of hexane, which eluted a mixture of starting materials, was followed by toluene, which eluted a dark brown band isolated as **1** in 37% yield. This compound, which is highly soluble in most organic solvents, is air sensitive. The following spectral data were obtained: IR ν_{CO} (toluene) 1815 (s), 1766 (m), 1622 (m) cm^{-1}; ν_{CO} (KBr) 1798 (s), 1757 (m), 1748 (m, sh), 1628 (m) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 1.59 (s, 30 H), 1.92 (s, 3 H), 4.62 (m, 2 H), 4.83 (m, 2 H), 4.95 (m, 1 H). Although the mass spectra of **1** did not exhibit the parent ion peak, its fragmentation pattern did show relatively large peaks at m/e 444 and 228, which were assigned to the $Co_2(C_5Me_5)_2(CO)_2^+$ and $Cr(C_6H_5Me)(CO)_3^+$ ions, respectively.

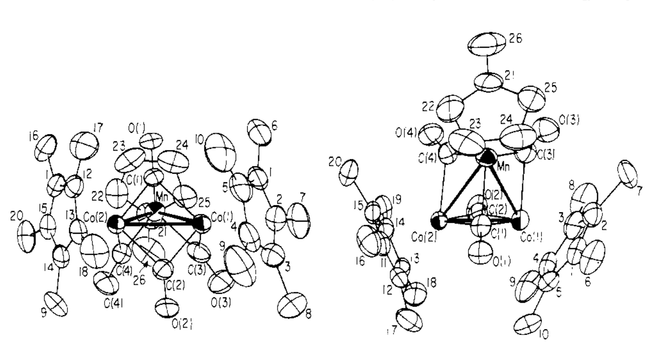

Figure 1. Two views of $(\eta^5\text{-}C_5H_4Me)MnCo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_3(\mu_3\text{-}CO)$ (**2**), which possesses an idealized C_s-m geometry. The bottom view emphasizes the molecule being formed as an addition product by the insertion of a $Mn(\eta^5\text{-}C_5H_4Me)(CO)_2$ fragment across the Co–Co double bond of $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$ to give a single-bonded metal triangle. The doubly bridging carbonyl, C(1)–O(1), of the neutral dimer is changed into a triply bridging carbonyl by coordination to the manganese atom while each of the two terminal carbonyls, C(3)–O(3) and C(4)–O(4), of the original manganese fragment is converted into an asymmetrical bridging carbonyl by its linkage to one cobalt atom. The two crystallographically independent molecules of the $(\eta^4\text{-}C_4H_4)FeCo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_3(\mu\text{-}CO)$ compound **3** possess an analogous configuration with an electronically equivalent $Fe(\eta^4\text{-}C_4H_4)$ fragment substituted in place of the $Mn(\eta^5\text{-}C_5H_4Me)$ fragment in **2**. Prominent structural features of **2** and the pseudo-mirror-related molecule B of **3** include two equivalent Mn–Co bonds of 2.561 Å (average) and a Co–Co bond of 2.487 (1) Å in **2** vs. two equivalent Fe–Co bonds of 2.512 Å (average) and a Co–Co single bond of 2.489 (2) Å in **3**. These identical Co–Co single-bond lengths in **2** and **3** are 0.15 Å longer than the Co–Co double-bond length of 2.338 (2) Å in $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$.

The $(\eta^5\text{-}C_5H_4Me)MnCo_2$ compound **2**, which is highly soluble and reasonably air stable, was similarly prepared in 33% yield from $Mn(\eta^5\text{-}C_5H_4Me)(CO)_3$ (2.3 mmol) and $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$ (1.8 mmol);[11] a very small quantity (4% yield) of the $(\eta^5\text{-}C_5H_4Me)Co_3$ compound **5** was also isolated. This tricobalt cluster, which likewise is highly soluble and reasonably air stable, was then directly prepared in 36% yield from $Co(\eta^5\text{-}C_5H_4Me)(CO)_2$ (2.0 mmol) and $Co_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_2$ (2.0 mmol) under analogous conditions. In the chromatographic separation of these two brown complexes, **5** was eluted with hexane–toluene (2:1) and **2** with toluene. Spectral measurements of **2** yielded the following data: IR ν_{CO} (hexane) 1842 (s), 1796 (m), 1781 (m), 1650 (s) cm^{-1}; ν_{CO} (KBr) 1825 (s), 1779 (m, sh), 1774 (m), 1650 (m) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 1.96 (s, 30 H), 2.24 (s, 3 H), 4.16 (m, 2 H), 4.33 (m, 2 H). Mass spectra of **2** exhibited the parent ion peak at m/e 634. Spectral measurements of **5** gave the following data: IR ν_{CO} (hexane) 1823 (s), 1780 (m), 1668 (s) cm^{-1}; ν_{CO} (KBr) 1810 (s), 1770 (m), 1663 (s) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 1.86 (s, 30 H), 2.19 (s, 3 H), 4.46 (m, 2 H), 4.93 (m, 2 H). Mass spectra of **5** displayed the parent ion peak at m/e 610.

The air-stable $(\eta^4\text{-}C_4H_4)FeCo_2$ compound **3**, which readily dissolves in organic solvents, was prepared in a Pyrex glass apparatus from $Fe(\eta^4\text{-}C_4H_4)(CO)_3$ (2.6 mmol) and $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$ (2.0 mmol) with THF as the solvent. The initial photochemical preparation of $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$ took 2 days under these conditions while its subsequent reaction with Fe-

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(6) Ashworth, T. V.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1979**, 42–5, and references cited therein.

(7) Churchill, M. R. *Adv. Chem. Ser.* **1978**, No. *167*, 36–60.

(8) Gladfelter and Geoffroy[9] stated in their recent comprehensive review of polynuclear mixed-metal clusters that photochemical techniques have only been used to produce two mixed-metal clusters, the $[MFe_2(CO)_{12}]^-$ monoanions (M = Tc, Re),[10] by photolysis of mixtures of $M_2(CO)_{10}$ (M = Tc, Re) and $Fe(CO)_5$. Since submission of this manuscript, we were informed by one of the referees of a submitted paper (Burkhardt, E. W.; Geoffroy, G. L. *J. Organomet. Chem.*, in press) on the photoassisted synthesis of $H_2FeOs_3(CO)_{13}$ and $H_2RuOs_3(CO)_{13}$ by the presumed addition of photogenerated $M(CO)_4$ fragments to the diprotonated Os–Os double-bonded part of $Os_3(CO)_{10}(\mu\text{-}H)_2$ followed by the loss of one CO.

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(11) Neither product **1** nor product **2** was formed when a mixture of either $Cr(\eta^6\text{-}C_6H_5Me)(CO)_3$ or $Mn(\eta^5\text{-}C_5H_4Me)(CO)_3$, respectively, was photolyzed with $Co(\eta^5\text{-}C_5Me_5)(CO)_2$ under the same total reaction conditions. It was later found that **4** could also be prepared directly by the irradiation of $Co(\eta^5\text{-}C_5Me_5)(CO)_2$ with $Fe_2(CO)_9$ in THF. However, it is noteworthy that IR spectra, which were used to monitor the course of the reaction, indicated the formation of a significant quantity of the neutral cobalt dimer before any $FeCo_2$ cluster **4** was detected.

$(\eta^4\text{-}C_4H_4)(CO)_3$ only required an additional 8 h. Hexane–toluene (1:1) eluted a dark brown band which gave **3** in 45% yield. The following spectral data were acquired: IR ν_{CO} (hexane) 1882 (s), 1848 (m-w), 1786 (s), 1668 (s) cm^{-1}; ν_{CO} (KBr) 1860 (s), 1824 (m), 1773 (s), 1669 (s) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 1.76 (s, 30 H), 3.84 (s, 4 H). Mass spectra of **3** exhibited a parent ion peak at *m/e* 608.

The air-sensitive $(CO_3)FeCo_2$ compound **4** was analogously obtained in a Pyrex glass apparatus from iron enneacarbonyl (1.6 mmol) and $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$ (2.2 mmol) with THF as the solvent. After the initial formation of the neutral dimer, the reaction was continued for ca. 2 days without a continuous N_2 purge of the vessel.[11] The dark red-brown band of **4** that eluted from the alumina column with toluene gave a black microcrystalline solid in 27% yield. Spectral measurements of **4** gave the following data: IR ν_{CO} (hexane) 2020 (s), 1978 (s), 1960 (s), 1837 (m), 1796 (w), 1693 (w) cm^{-1}; ν_{CO} (KBr) 2004 (s), 1962 (m, sh), 1938 (s), 1823 (m), 1786 (w), 1684 (m) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 1.38 (s), 1.52 (s). The relative intensities of these two resonances were observed to vary as a function of temperature. The highest observed peak at *m/e* 556 in the mass spectra of **4** corresponds to the parent ion peak minus two carbonyl ligands.

The first member of the $MCo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_3(\mu_3\text{-}CO)$ series to be structurally determined by X-ray crystallography[12] was the $(\eta^5\text{-}C_5H_4Me)MnCo_2$ cluster **2**. Its molecular geometry (Figure 1), which closely conforms to bilateral C_s-*m* symmetry, consists of one $Mn(\eta^5\text{-}C_5H_4Me)$ and two $Co(\eta^5\text{-}C_5Me_5)$ moieties positioned at the vertices of an isosceles triangle and linked to one another by a triply bridging carbonyl ligand and three doubly bridging carbonyl ligands as well as by direct Mn–Co and Co–Co electron-pair bonds. The IR, NMR, and mass spectral data of **2** are completely consistent with its solid-state structure. This compound provided the first example of a $M_3(\eta^5\text{-}C_5R_5)_3(\mu\text{-}CO)_3(\mu_3\text{-}CO)$-type complex which is isoelectronic and structurally analogous with a previously characterized cyclopentadienyl trimetal nitrosyl cluster, the $Mn_3(\eta^5\text{-}C_5H_5)_3(\mu\text{-}CO)_3(\mu_3\text{-}NO)$ molecule[13] of idealized C_{3v} geometry.

A subsequent spectral and X-ray diffraction analysis[12] revealed the $(\eta^4\text{-}C_4H_4)FeCo_2$ compound **3** to be a second member of the $MCo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_3(\mu_3\text{-}CO)$ series. Its molecular configuration in the solid state was determined to closely resemble that of **2** (i.e., even including an analogous asymmetry of the corresponding carbonyl ligands), thereby demonstrating the structural equivalence of the $Mn(\eta^5\text{-}C_5H_4Me)$ and $Fe(\eta^4\text{-}C_4H_4)$ fragments. The two crystallographically independent molecules of **3** were found to be similar except for different orientations (i.e., by ca. 37°) of the iron-attached cyclobutadiene rings.

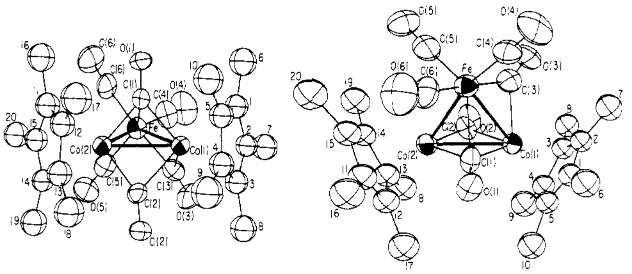

Figure 2. Molecular configuration of one of the two independent molecules of $(OC)_3FeCo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2(\mu_3\text{-}CO)$ (**4**). This molecular product may be viewed as an adduct arising from the insertion of an $Fe(CO)_4$ fragment across the Co–Co double bond of $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$ to give a single-bonded triangle of metal atoms also linked by one triply bridging and two doubly bridging carbonyl groups. One doubly bridging carbonyl ligand, C(1)–O(1), of the neutral dimer becomes the triply bridging carbonyl ligand of **4** by its coordination to the iron atoms while one terminal carbonyl, C(3)–O(3), of the $Fe(CO)_4$ fragment is changed into an asymmetrical bridging carbonyl ligand by its coordination to one cobalt atom, Co(1). The other doubly bridging carbonyl ligand, C(2)–O(2), expectedly changes from a symmetrical linkage in the neutral dimer of an idealized C_{2v}-*2mm* configuration to an unsymmetrical linkage in its bonding to the nonequivalent cobalt atoms in **4** whose molecular configuration ideally conforms only to general C_1-1 symmetry. For molecule A, the two Fe–Co single-bond lengths are 2.560 (2) and 2.577 (2) Å, and the Co–Co single-bond length is 2.476 (2) Å while for molecule B the corresponding two Fe–Co bond lengths are 2.554 (2) and 2.597 (2) Å, and the Co–Co bond length is 2.458 (2) Å.

The establishment of the $(\eta^6\text{-}C_6H_5Me)CrCo_2$ cluster **1** as a third member of this series was based primarily upon solid-state infrared spectra exhibiting the same basic carbonyl absorption pattern as those for **2** and **3**. The ^{1}H NMR and mass spectral data are in complete harmony with the stoichiometry of **1**.

An X-ray crystallographic investigation[12] of the tricarbonyliron–dicobalt cluster **4** revealed that it belongs to a structurally different $MCo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2(\mu_3\text{-}CO)$ series. The two crystallographically independent molecules were found to possess an analogous geometry (Figure 2) composed of a triangular array of one $Fe(CO)_3$ and two $Co(\eta^5\text{-}C_5Me_5)$ moieties linked to one another by a triply bridging carbonyl and two doubly bridging carbonyls (along the Co–Co and one Co–Fe edge) as well as by direct Fe–Co and Co–Co electron-pair bonds. The carbonyl bands in both the solid-state and solution infrared spectra of **4** are completely consistent with the solid-state structure while its ^{1}H NMR data are indicative of an unresolved fluxional process. The tricobalt cluster **5**, where M = $(\eta^5\text{-}C_5H_4Me)Co$, was subsequently shown from both infrared data and an X-ray diffraction examination[12] to be a second member of this series. Its solid-state configuration was determined to be analogous to that of the nonmethylated cyclopentadienyl analogue $Co(\eta^5\text{-}C_5H_5)_3(\mu\text{-}CO)_2(\mu_3\text{-}CO)$, whose structure and stereochemical nonrigidity had been previously shown by Cotton and Jamerson.[14] The only notable difference between the two structures is that the nonbridged Co–Co edge in **5** is 0.045 Å longer than that in the unsubstituted cyclopentadienyl species. This small but yet significant lengthening of one of the Co–Co bonds may be readily attributed to greater steric effects in **5**. Both the solution and solid-state IR data as well as the ^{1}H NMR and mass spectral data of **5** are consistent with its solid-state structure. Of interest is that these data indicate that **5** does *not* possess dynamic fictle behavior in solution in contrast to that found by Cotton and Jamerson[14] for $Co_3(\eta^5\text{-}C_5H_5)_3(\mu\text{-}CO)_2(\mu_3\text{-}CO)$.

The results of this systematic investigation clearly indicate that this kind of photochemical reaction provides a highly useful

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(12) (a) $(\eta^5\text{-}C_5H_4Me)MnCo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_3(\mu_3\text{-}CO)$: fw, 634; monoclinic; $P2_1/n$; a = 10.903 (4), b = 14.605 (5), c = 17.241 (4) Å, β = 94.42 (3)°, V = 2737 (2) Å^3; d_{calcd} = 1.54 g cm^{-3} for Z = 4. Least-squares refinement with anisotropic thermal parameters for the nonhydrogen atoms and fixed idealized coordinates and isotropic temperature factors for the hydrogen atoms gave $R_1(F)$ = 6.1% and $R_2(F)$ = 6.6% for 3207 independent diffractometry data [$I \geq 2\sigma(I)$]. (b) $(\eta^4\text{-}C_4H_4)FeCo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_3(\mu_3\text{-}CO)$: fw, 608; orthorhombic; $P2_1ca$; a = 14.353 (6), b = 16.069 (6), c = 22.338 (14) Å, V = 5152 (4) Å^3; d_{calcd} = 1.57 g cm^{-3} for Z = 8. Least-squares refinement of the two crystallographically independent molecules was carried out with anisotropic thermal coefficients for all nonhydrogen atoms and with fixed idealized coordinates and isotropic temperature factors for the hydrogen atoms. Since all of the parameters could not be varied at one time due to the size limitation of our full-matrix ORFLS program on the departmental Harris/7 computer, the parameters for one molecule were varied, and those for the other molecule were fixed in alternate cycles. After convergence, a final cycle was performed in which only the positional parameters for both molecules were varied along with the scale factor; the resulting $R_1(F)$ and $R_2(F)$ values were 4.7 and 5.9%, respectively, for 4422 independent diffractometry data [$I \geq 2\sigma(I)$] collected at −128 °C. (c) $(OC)_3FeCo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2(\mu_3\text{-}CO)$: fw, 612; orthorhombic; $P2_1cn$; a = 16.207 (7), b = 20.308 (7), c = 16.015 (5) Å, V = 5270 (3) Å^3; d_{calcd} = 1.54 g cm^{-3} for Z = 8. Least-squares refinement of the two crystallographically independent molecules was performed with anisotropic thermal parameters for the metal and carbonyl atoms and with isotropic thermal coefficients for the carbon atoms of the pentamethylcyclopentadienyl ligands; hydrogen atoms were included with fixed idealized coordinates and isotropic temperature factors. The final cycle converged at $R_1(F)$ = 6.0% and $R_2(F)$ = 7.5% for 4204 independent diffractometry data [$I \geq 2\sigma(I)$]. (d) $(\eta^5\text{-}C_5H_4Me)Co_3(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2(\mu_3\text{-}CO)$: fw, 610; monoclinic; $P2_1/n$; a = 10.825 (6), b = 14.545 (7), c = 16.895 (10) Å, β = 94.29 (5)°, V = 2653 (2) Å^3; d_{calcd} = 1.53 g cm^{-3} for Z = 4. Least-squares refinement with anisotropic thermal coefficients for the nonhydrogen atoms and fixed idealized coordinates and isotropic thermal temperature factors for the hydrogen atoms gave $R_1(F)$ = 4.8% and $R_2(F)$ = 6.1% for 2062 independent diffractometry data [$I \geq 2\sigma(I)$].

(13) Elder, R. C. *Inorg. Chem.* **1974**, *13*, 1037–42.

(14) Cotton, F. A.; Jamerson, J. D. *J. Am. Chem. Soc.* **1976**, *98*, 1273–4.

synthetic route for obtaining new transition-metal clusters. More detailed reports of this work, including the results of analogous reactions with related dimers (currently in progress), are forthcoming.

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Supplementary Material Available: Tables listing the crystal data and atomic parameters for compounds **2**, **3**, **4**, and **5** (34 pages). Ordering information is given on any current masthead page.

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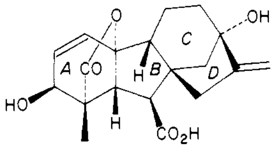
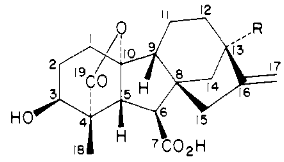
General Strategy for Gibberellin Synthesis: Total Syntheses of (±)-Gibberellin A_1[1] and Gibberellic Acid

Sir:

Extensive studies over 2 decades on the construction of the gibberellin phytohormones have provided a fund of innovative synthetic methodology,[2] and yet the completion of only two total syntheses—gibberellic acid (**1**) (~36 steps)[3] and gibberellin A_{15} (~40 steps)[4] —has been reported.[5] While the former achievement establishes a milestone in both gibberellin and synthetic chemistry, scope for more versatile and direct approaches still remains. Retrosynthetic analysis of the gibberellin molecule (Scheme I) suggests a strategy based on the construction of the C(3)–C(4) bond[6] by an aldol process,[7] C(4)–C(5) by a Michael reaction, and C(1)–C(10) through addition of an appropriate nucleophile to an enone such as **14**; reagent approach along the equatorial vector would be expected to establish the correct relative chirality of *pro*-C(10), and then geometric constraints can provide subsequent stereochemical control. We now describe the elaboration of these ideas into a very efficient strategy for gibberellin synthesis, the utility of which is demonstrated by the preparation of (±)-gibberellin A_1 (**2**)[8] in ~24 steps, and of gibberellic acid (**1**) in ~31 steps from 1,7-dimethoxynaphthalene.

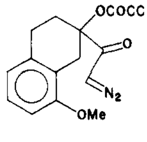


1

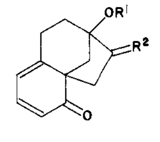


2 R = OH
3 R = H

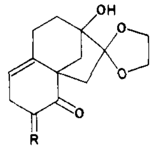
The synthesis of enone **14**, our first objective, was based on the development of earlier studies.[9] Thus, dienedione **5**, readily prepared from trifluoroacetic acid treatment of **4**,[10] was hydrolyzed [10% aqueous Na_2CO_3/MeOH/THF (1:1.5:1.8), 5 min, 25 °C, 98.5% yield] to **6**, mp 113–114 °C,[11] the cyclopentanone function of which was selectively masked [$(CH_2OH)_2$, $(CH_2Cl)_2$, Dowex 50W × 8 (10% w/w), 4 A sieves, reflux 7 h, 59% yield] to give acetal **7**, mp 129–131 °C.[12] 1,4-Reduction [K-selectride[13] (1 equiv added over 30 min), EtOH (4 equiv),[14] THF, −65 °C, 97% yield] then furnished **8**, mp 103–104 °C, which was transformed directly[15] to diazo ketone **9**, mp 118–120 °C dec, in 82% yield. Irradiation of **9** [Pyrex, Hanovia 400-W medium-pressure mercury lamp, 13% aqueous $NaHCO_3$/THF (15:4), 0 °C, 4 h] furnished a mixture of ring-contracted acids, resolved by fractional crystallization to give the less soluble [chloroform/pentane (15:4)] 6β-epimer, mp 159–161 °C (17.5% yield), and then the desired 6α-epimer, indefinite mp 152–165 °C (63% yield), methyl ester



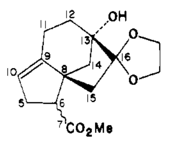
4



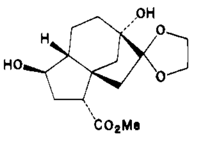
5 R^1 = $COCCl_3$, R^2 = O
6 R^1 = H, R^2 = O
7 R^1 = H, R^2 = OCH_2CH_2O



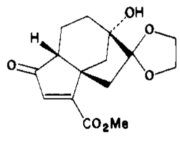
8 R = H_2
9 R = N_2



10 6β-CO_2Me
11 6α-CO_2Me

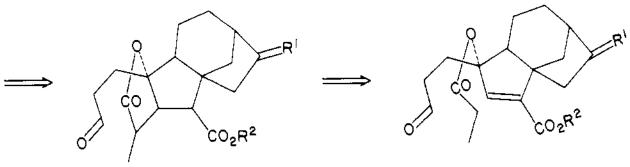


12
13 Δ^5



14

Scheme I



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[1] This work was described at the Sixth International Symposium on Synthesis in Organic Chemistry, Cambridge, England, July 1979.

[2] For recent reviews, see: (a) Fujita, E.; Node, M. *Heterocycles* **1977**, *7*, 709–752. (b) Danheiser, R. L. Ph.D. Dissertation, Harvard University, 1978. (c) Urech, R. Ph.D. Dissertation, Australian National University, 1980.

[3] (a) Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S.; Keck, G. E.; Gopalan, B.; Larsen, S. D.; Siret, P.; Gras, J.-L. *J. Am. Chem. Soc.* **1978**, *100*, 8034–8036. (b) Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S.; Siret, P.; Keck, G. E.; Gras, J.-L. *Ibid.* **1978**, *100*, 8031–8034. (c) See also: Corey, E. J.; Gorzynski Smith, J. *Ibid.* **1979**, *101*, 1038–1039. Stork, G.; Boeckmann, R. K.; Taber, D. F.; Still, W. C.; Singh, J. *Ibid.* **1979**, *101*, 7107–7109.

[4] Nagata, W.; Wakabayashi, T.; Narisada, M.; Hayase, Y.; Kamate, S. *J. Am. Chem. Soc.* **1971**, *93*, 5740–5758.

[5] Totally synthetic routes via relays, but lacking optical resolutions, have been established for gibberellin A_4 (**3**), among others (~55 steps): Mori, K.; Shiozaki, M.; Itaya, N.; Matsui, M.; Sumiki, Y. *Tetrahedron* **1969**, *25*, 1293–1321. Gibberellins A_{15} and A_{37} (~40 steps): Fujita, E.; Node, M.; Hori, H. *J. Chem. Soc., Perkin Trans. 1* **1977**, 611–621.

[6] To avoid confusion, atoms are numbered throughout on the basis of the full gibberellin skeleton: Rowe, J. R., Ed. "The Common and Systematic Nomenclature of Cyclic Diterpenes", 3rd Rev.; Forest Product Labortory, U.S. Department of Agriculture: Wisconsin, 1968.

[7] (a) The feasibility of the aldol reaction was originally demonstrated by Dolby, L. J.; Milligan, R. J. *J. Am. Chem. Soc.* **1966**, *88*, 4536–4537. (b) Subsequent studies extended the scope of the method: Dolby, L. J.; Skold, C. N. *Ibid.* **1974**, *96*, 3276–3279. (c) The approach has been further refined concurrently with the present work: Stork, G.; Singh, J. *Ibid.* **1979**, *101*, 7109–7110.

[8] MacMillan, J.; Seaton, J. C.; Suter, P. J. *Tetrahedron* **1960**, *11*, 60–66.

[9] Cossey, A. L.; Mander, L. N. *Tetrahedron Lett.* **1979**, 969–972.

[10] Blair, I. A.; Ellis, A.; Johnson, D. W.; Mander, L. N. *Aust. J. Chem.* **1978**, *31*, 405–409.

[11] Structures **4–26** represent racemic compounds and are fully consistent with their NMR, IR, and mass spectral data. All crystalline compounds afforded satisfactory microanalytical data (± <0.3%) for carbon and hydrogen. All reactions were carried out under an atmosphere of purified nitrogen, where appropriate, and yields are reported for analytically pure products.

[12] The cyclopentanone function is only slightly more reactive than the dienone carbonyl group, so care must be taken to avoid formation of the bisacetal.

[13] Fortunato, J. M.; Ganem, B. *J. Org. Chem.* **1976**, *41*, 2194–2200.

[14] In the absence of a good proton donor, some of the initially formed enol boronate added 1,4 to the substrate. Ethanol was more effective than *tert*-butyl alcohol[13] in this case.

[15] Lombardo, L.; Mander, L. N. *Synthesis* **1980**, 368–369.

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