

Boncella et al.¹⁶ have described a similar arene-ruthenium derivative (containing a phenyl group on the nitrogen and a hydrogen on the β -C atom) that was obtained from $[(C_6Me_6)Ru(PMe_3)Cl_2]$, 2 equiv of benzylideneaniline, and 2 equiv of $AgBF_4$. We suppose that the driving force for the formation of **16** (which is an isomer of **8**) is the preferred attack of electrophiles at the N (and not the β -C) atom of the $M=N=C$ unit, which would be in accord with the behavior of vinylidene-rhodium complexes toward electrophilic reagents.¹⁷

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Supplementary Material Available: A list summarizing the results of CHN analysis for complexes **5**, **6**, **8**, **10-13**, **15**, and **16** (1 page). Ordering information is given on any current masthead page.

(15) Synthesis of **16** is as follows. A solution of **8** (108 mg, 0.14 mmol) in CH_2Cl_2 (5 mL) was treated with CF_3CO_2H (11 μ L, 0.14 mmol) and stirred for 1 h at room temperature. The solution was concentrated to ca. 1 mL and chromatographed on Al_2O_3 (neutral, activity grade V) with CH_2Cl_2 . After removal of the solvent, the residue was recrystallized from CH_2Cl_2 /pentane to give orange crystals in 97% yield: mp 216 °C dec; equiv conductivity $\Lambda = 72 \text{ cm}^2 \Omega^{-1} \text{ cm}^{-1}$. IR (KBr): $\nu(NH)$ 3325 cm^{-1} . 1H NMR (90 MHz, CD_3NO_2): δ 9.58 (s, br, 1 H, NH), 8.31-7.06 (m, br, 9 H, C_6H_4 and C_6H_5), 5.62 (s, 3 H, $C_6H_3Me_3$), 2.31 (s, 9 H, $C_6H_3Me_3$), 2.24 (m, 3 H, $PCHCH_3$), 1.17 (dd, 9 H, $J(PH) = 14.5 \text{ Hz}$, $J(HH) = 7.3 \text{ Hz}$, $PCHCH_3$), 0.94 (dd, 9 H, $J(PH) = 13.1$, $J(HH) = 7.1 \text{ Hz}$, $PCHCH_3$). ^{31}P NMR (36.2 MHz, CD_3NO_2): δ 0.96 (s, P - t - Pr_3), -145.57 (sept, $J(PF) = 707.1 \text{ Hz}$, PF_6). ^{13}C NMR (22.5 MHz, CD_3NO_2): δ 191.72 (d, $J(PC) = 1.5 \text{ Hz}$, $N=C$), 174.62 (d, $J(PC) = 11.7 \text{ Hz}$, $Os-C$), 101.44 (d, $J(PC) = 2.2 \text{ Hz}$, $C_{ring}-CH_3$), 82.10 (d, $J(PC) = 2.2 \text{ Hz}$, $C_{ring}-H$), 25.36 (d, $J(PC) = 27.1 \text{ Hz}$, $PCHCH_3$), 21.15 (s, $PCHCH_3$), 19.43 (s, $PCHCH_3$), 18.59 (d, $J(PC) = 2.2 \text{ Hz}$, $C_{ring}-CH_3$), other signals for C_6H_5 and C_6H_4 carbons not mentioned.

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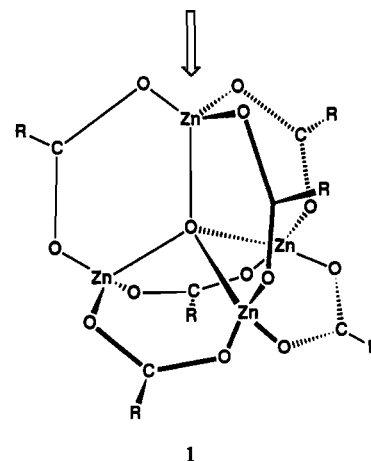
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Transition-Metal Clusters as Substituents. Synthesis, Structure, and Thermal Decomposition of $Zn_4O[(CO)_9Co_3(\mu_3-CCO_2)]_6$

The synthesis of high-nuclearity main-group-transition-element clusters in soluble molecular forms is well illustrated by recent research in the metal chalcogenide area.¹⁻³ The various approaches have included the use of zeolites⁴ and inverse micelles⁵ to induce or guide the organization. We have previously demonstrated physical association of the tailed clusters $(CO)_9Co_3(\mu_3-C(CH_2)_xOH)$ ($x = 4, 5$) in solution and in the solid state.⁶ This spontaneous association of metal clusters is also of interest in terms of developing molecular assemblies for conversion into designed materials. In the case of pyrolytic conversion of an assembled precursor, the binding forces must be much stronger

than the physical ones responsible for the association of $(CO)_9Co_3(\mu_3-C(CH_2)_xOH)$. Indeed the binding energies must approach those that hold the unwanted ligands on the metal atoms. Hence, we have begun to explore cluster association determined by the covalent bonding of a set of suitably modified clusters to an atom center or centers.⁷ One possibility is classical coordination of clusters containing a suitable ligand functional group to an oxidized metal center. The work of Seyferth and co-workers provides one compound with the desired characteristics, i.e., $(CO)_9Co_3(\mu_3-CCOOH)$.⁸

Zinc(II) forms a bis(acetato) complex, but of more interest, it also forms a tetranuclear acetate with a centered oxygen atom, i.e., $Zn_4O(MeCOO)_6$.⁹ In this compound the six acetates edge-bridge a zinc tetrahedron with an oxygen atom in the center (structure 1).¹⁰ Hence, all four zinc atoms are tetrahedrally



coordinated to four oxygen atoms leading to an environment similar to that found in the lattice of bulk zinc oxide. Indeed, the emission properties of this acetate derivative have been used to demonstrate that it behaves as if it were the smallest zinc oxide particle.¹¹ For these reasons we set out to investigate the coordination of $(CO)_9Co_3(\mu_3-CCOOH)$ to zinc.

In the event, the reaction of $(CO)_9Co_3(\mu_3-CCOOH)$ with $ZnEt_2$ cleanly produces a single deep purple-brown product, which precipitates in Et_2O . The solution infrared spectrum of the product suggests chelation via the carboxylate anion functionality,¹² and the shift in the CO stretches of the $Co_3(CO)_9$ fragments to higher frequency indicates coordination to a positive center.¹³ Further, the analysis of the crystalline material is consistent with the formulation $Zn_4O[(CO)_9Co_3(\mu_3-CCO_2)]_6$ (I).¹⁴ The overall isolated yield of this product (1-g scale) based on the cobalt cluster is 60%. The molecular weight of I is 3186.2, and the solubility of the compound in THF is impressive considering it is more than 40% by weight metal.

Crystals suitable for diffraction were grown by Et_2O diffusion into a THF solution of I, and definitive structural characterization followed crystallographic analysis via X-ray diffraction techniques.¹⁵ The structure, shown in Figure 1, is basically that of

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- (14) Anal. Calcd for $Zn_4Co_{12}C_{66}O_{67}$: Zn, 8.20; Co, 33.31; C, 24.87; O, 33.62. Found (dried under vacuum): Zn, 7.68; Co, 30.52; C, 24.77; O, 33.41.

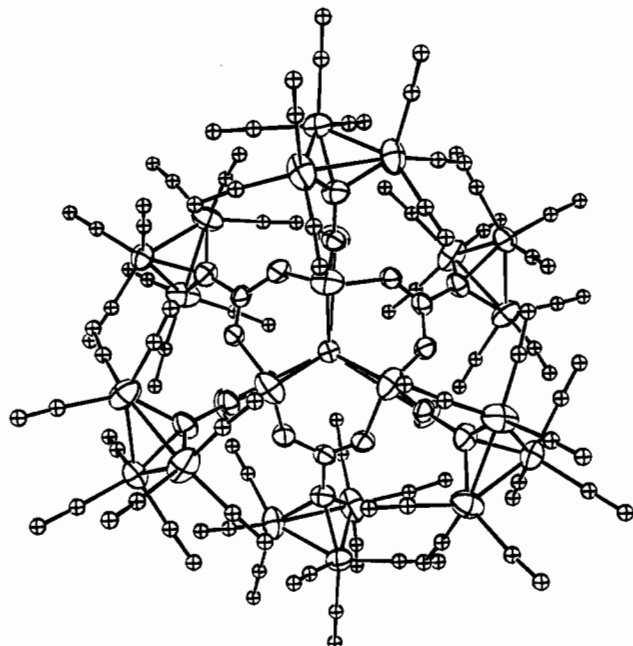


Figure 1. View of the molecular structure of **1** down the pseudo-3-fold axis. The point of view is indicated by the arrow in structure **1**. Carbonyl carbon and oxygen atoms are given arbitrarily small thermal parameters for clarity. Thermal ellipsoids for all other atoms are drawn to illustrate 50% probability surfaces. The solid-state structure is consistent with a pair of inversion-related half-molecules each consisting of four well-separated zinc (half) atoms and 12 well-separated oxygen (half) atoms surrounded by six μ_3 - $\text{CCO}_3(\text{CO})_9$ tricobalt clusters. The inversion-related tricobalt clusters are nearly coincident and were treated as fully occupied groups for the refinement.

$\text{Zn}_4\text{O}(\text{RCOO})_6$ with $\text{R} = (\text{CO})_9\text{Co}_3\text{C}$ (structure **1**).¹⁶ A detailed structural comparison between **1** and $\text{Zn}_4\text{O}(\text{MeCOO})_6$ and $(\text{C}-\text{O})_9\text{Co}_3\text{CCOOH}$ ¹⁷ is beyond the scope of this communication, but the overall dimensions of the architecture are noteworthy. Viewed as a spherical particle, compound **1** has a diameter of 15–16 Å. It is the central metal cluster (the Zn tetrahedron) that determines the octahedral spatial distribution of the transition-metal clusters. The $[(\text{CO})_9\text{Co}_3\text{COO}]^-$ ligands themselves are bulky but an extension of the cluster cone angle argument of Mingos¹⁸ shows that there is room for 10 such ligands around the oxo-tetrazinc core. Alternatively, the $(-\text{COO})_6\text{Zn}_4\text{O}$ core and $(\text{CO})_9\text{Co}_3\text{C}^-$ clusters can be considered as spheres of approximately equal radius. Thus, there should be room to pack 12 of the $(\text{CO})_9\text{Co}_3\text{C}^-$ fragments around the core. These views underline the fact that there is considerable empty space in the lattice. Although not necessarily related, note that the material crystallizes with the incorporation of a molecule of $(\text{C}_2\text{H}_5)_2\text{O}$.

Compound **1** is of interest in terms of logically building clusters of clusters, but importantly, it also serves as a potential molecular

precursor for a cobalt–zinc-based ceramic.^{19,20} Thermal gravimetric analysis establishes a $55.7 \pm 0.5\%$ weight loss between 150 and 200 °C and, subsequently, constant weight up to 400 °C. This weight loss is attributed to the loss of the 54 CO and six carboxylate ligands as CO and CO_2 (calculated loss 55.4%). In situ mass spectrometric analysis shows CO and CO_2 evolution only with the total yield of the latter at $\approx 10\%$ of the level of the former. The time–temperature profile shows that CO_2 evolution maximizes at a somewhat higher temperature than that of CO. The final product is a ferromagnetic material composed of regular particles with metallic luster. Pyrolysis of large individual crystals (≈ 1 mm) results in isotropic shrinkage of $\approx 59\%$ in all three dimensions; i.e., there is no fusion before or during loss of CO and CO_2 . The final product still exhibits shining, crystalline-like faces; however, these particles are not single crystals. Note that loss of solvent of crystallization from crystals of **1** also produces crystalline-appearing material that does not scatter X-rays. The low conversion temperatures and presumed main-group atom content may well lead to an amorphous material. The density of this material is 6.8 g/cm^3 , which when compared with typical densities of metal alloys, suggests the existence of considerable void volume. Further investigations of these materials are in progress.

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Supplementary Material Available: Tables of crystal data, atom coordinates, selected bond distances and angles, and anisotropic thermal parameters (11 pages); a table of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

- (15) Crystal data: $\text{Zn}_4\text{Co}_{18}\text{C}_{66}\text{O}_{67}(\text{C}_2\text{H}_5)_2\text{O}$; $f_w = 3261.09$; triclinic, $P\bar{1}$, $a = 15.144(4) \text{ \AA}$, $b = 15.145(4) \text{ \AA}$, $c = 16.164(4) \text{ \AA}$, $\alpha = 62.13(2)^\circ$, $\beta = 62.10(2)^\circ$, $\gamma = 60.00(2)^\circ$, $V = 2702.4(17) \text{ \AA}^3$, $Z = 1$; $D(\text{calc})_{298\text{K}} = 2.004 \text{ g cm}^{-3}$, $D(\text{obs})_{298\text{K}} = 1.92 \text{ g cm}^{-3}$; $\mu_{\text{Mo}} = 36.7$, $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$; $T = 124 \pm 2^\circ \text{C}$; Enraf-Nonius CAD4 instrument.
- (16) The structure of $\text{Co}_4\text{O}[(\text{CO})_9\text{Co}_3(\mu_3\text{-CCO}_2)]_6$, which was isolated from the reaction of $(\text{CO})_9\text{Co}_3(\mu_3\text{-CCO}_2\text{H})$ with AlCl_3 followed by hydrolysis has been reported. Schore, N. E. Presented at the 15th NSF National Organometallic Workshop, May 1991. Before becoming aware of this work, we showed that the same compound forms spontaneously from $(\text{CO})_9\text{Co}_3(\mu_3\text{-CCO}_2\text{H})$ in solution and has a structure like **1** with the Zn atoms replaced with Co atoms. Sturgeon, R. L.; Olmstead, M. M.; Schore, N. E. *Organometallics* **1991**, *10*, 1649.
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