Inorg. Chem. **1993,** *32,* 995–1000 **995**

Clusters as Ligands. Comparison of the Reactivity of $(CO)_9Co_3(\mu_3\text{-}CR)$ (R = COOH, $p\text{-}C_6H_4(CH_2)_2COOH$) Leading to the Formation of $Zn[p\text{-}C_6H_4(CH_2)_2CO_2]_2$ vs $M^{II}{}_4O[(CO)_9Co_3CCO_2]_6$ (M = Zn, Co)

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Received August 25, 1992

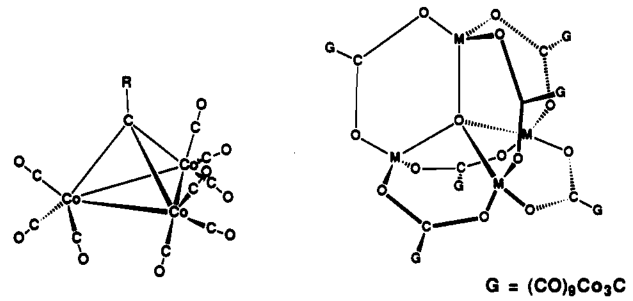
In order to explore the notion of cluster-substituted ligands as a route to large cluster assemblies, the gram-scale synthesis and purification along with spectroscopic and crystallographic characterization of two cluster-substituted carboxylate ligand precursors, $(CO)_9Co_3\{\mu_3\text{-}C[1,4\text{-}C_6H_4(CH_2)_2COOH]\}$, I, and $(CO)_9Co_3(\mu_3\text{-}CCOOH)$, II, were carried out [I·toluene, space group triclinic $P\bar{1}$, $a = 9.348(1)$ Å, $b = 11.954(1)$ Å, $c = 13.862(1)$Å, $\alpha = 92.83(2)°$, $\beta = 100.67(2)°$, $\gamma = 109.51(1)°$, $V = 1424.3$ Å^3, d(calcd) = 1.59 g/cm^3, $Z = 2$; II, space group triclinic $P\bar{1}$, $a = 7.906(1)$ Å, $b = 8.673(1)$ Å, $c = 12.915(4)$ Å, $\alpha = 83.73(2)°$, $\beta = 86.94(2)°$, $\gamma = 68.30(1)°$, $V = 817.8$ Å^3, d(calcd) = 1.98 g/cm^3, d(obs) = 1.97 g/cm^3, $Z = 2$]. Although the spectroscopic characterization of II has been previously reported, its instability in solution at room temperature has not been recognized. Thus, we report its spontaneous conversion to $Co_4O[(CO)_9Co_3CCO_2]_6$, III, which is a metal cluster analogue of classical $M^{II}{}_4O[RCO_2]_6$ "basic" metal carboxylates normally formed by sublimation of $M^{II}[RCO_2]_2$. The reaction of I, which is stable in solution, with $^1/_2$ $ZnEt_2$ yields $Zn[(CO)_9Co_3CC_6H_4(CH_2)_2CO_2]_2$, which is analogous to the product formed from either acetic acid or $C_6H_5(CH_2)_2COOH$ with the same reaction stoichiometry. In contrast, the reaction of II with $ZnEt_2$ in a 1:1 stoichiometry forms $Zn_4O[(CO)_9Co_3CCO_2]_6$, IV, in high yield at room temperature. The differing chemistry of II is attributed to the direct electronic interaction of the tricobalt cluster with the carboxylate fragment in II. IR spectra and cyclic voltammetry are used to detail the nature of this electronic coupling. Although both III and IV undergo quasi-reversible cluster ligand dissociation in THF, the reaction is more extensive for the former compound and ultimately leads to degradation of the tricobalt cluster.

Introduction

The utilization of transition metals to modify the reactivity of organic ligands[1,2] and to act as ligand assembly points[3] are approaches that continue to be profitably exploited. We have suggested that transition metal clusters can be viewed as bulky, π donating ligands to main group atom centers.[4,5] As a logical extension of these observations, the derivatization of a transition metal cluster so that it can function as a ligand in binding to more highly oxidized metal centers has much to recommend it. Thus, we suggest that the combination of coordination chemistry and transition metal organometallic cluster chemistry constitutes a systematic approach to the construction of large metal structures. The literature contains a number of related mononuclear ligand systems, i.e., $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CO_2M$ (M = K, Li, $SnPh_3$),[6] $[Co(n\text{-}Pr\text{-}salen)K(CO_2)(THF)]_m$,[7] $Mo_2[(\eta^5\text{-}C_5H_4CO_2)Fe(\eta^5\text{-}C_5H_5)]_4(ax\text{-}CH_3CN)(ax\text{-}DMSO)](DMSO)_2$,[8] $W_2(O_2CBu^t)_3(\eta^5\text{-}C_5H_4CO_2)Fe(\eta^5\text{-}C_5H_4CO_2)W_2(O_2CBu^t)_3$[9] and a polynuclear system.[10]

For our initial studies, the cluster fragment we have chosen is the well known capped tricobalt fragment $(CO)_9Co_3C$ whereas the ligand functionality we have chosen is $[\text{-}COO]^-$ (Chart I).

Chart I



G = $(CO)_9Co_3C$

I, R = $-C_6H_4-CH_2CH_2COOH$

II, R = COOH

III, M = Co

IV, M = Zn

The reasons are obvious. It is already known that the capped tricobalt cluster fragment, $(CO)_9Co_3C$, is both a versatile electronic donor and acceptor[11-15] and metal carboxylate chemistry is well developed in terms of both metal and structure type.[16] On the other hand, the examination of such a cluster as a classical carboxylate ligand has not been explored previously.

A non trivial problem in carrying out the desired syntheses is the sensitivity of the $(CO)_9Co_3C$ fragment to basic conditions. Thus, we were required to work with the acid form of the carboxylate functionality. To begin, we set out to make a simple $Zn(RCO_2)_2$ complex which, as discussed below, was straightforward for all acids except the one for which the carboxylic acid

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group was conjugated to the cluster. Further, we found that the latter cluster acid undergoes spontaneous decomposition in solution. This observation explains some puzzling observations in the literature[17] and further limits its use as a ligand. A preliminary report of part of this work has appeared.[18]

Results

Isolation of I and II. To approach the problem posed in a systematic fashion we desired two ligand types. For the first, or base-line ligand, we wanted a ligand in which the cluster fragment was electronically isolated from the ligand functionality. For the second, and more interesting ligand, we desired good electronic communication between the cluster and ligand functionality. Compound I, $(CO)_9Co_3[\mu_3\text{-}CC_6H_4(CH_2)_2COOH]$, was prepared according to reaction (1) using a modification of the Friedel–

$$Co_3(CO)_9(\mu_3\text{-}CCl) + C_6H_5(CH_2)_2COOH \xrightarrow{1.\ 3AlCl_3/2.\ H_2O} (CO)_9Co_3[\mu_3\text{-}CC_6H_4(CH_2)_2COOH]\ (I) + HCl \quad (1)$$

Crafts methodology of Dolby and Robinson.[14] Excess $AlCl_3$ and increased reaction temperature were effective in increasing the yield to useable levels. Clean separation of excess 3-phenyl propanoic acid from I was achieved with gel permeation chromatography. Compound II, $[Co_3(CO)_9(\mu_3\text{-}CCOOH)$, is a byproduct of this reaction and was separated from I by utilizing the more facile formation of acylium cation $[(CO)_9Co_3CCO]^+$ from II relative to I.[19,20]

Compound II is a known compound which is most efficiently formed by the published method developed in Seyferth's laboratory.[11] However, it also forms as a by-product during the synthesis of I and as the major product when a very large excess of $AlCl_3$ is used. Presumably this is due to the formation of $[(CO)_9Co_3CCO]^+$ in the reaction. Hence, reaction (2) also constitutes a convenient alternative route to II when the chloro compound is on hand. To a large extent this is known chemistry.[21-28]

$$Co_3(CO)_9(\mu_3\text{-}CCl) \xrightarrow{1.\ 3AlCl_3/2.\ H_2O} (CO)_9Co_3[\mu_3\text{-}CCOOH]\ (II) + HCl \quad (2)$$

Physical and Structural Properties of I and II. *Infrared Spectra.* The complete IR spectra of I and II are important for following their reactions and are given in Table I and in Figure 3 in the supplementary material. Both acids exhibit absorptions for the monomer and hydrogen bonded dimer with relative intensities that depend on medium and concentration. The solubility of acid I is larger than that of II.

Comparison of the spectra of shows that the acid C=O frequencies of II are shifted to lower energies relative to I. This shift is attributed to the electronic effects of substituent R in the acid RC(O)OH. In I the two methylene groups effectively block π interactions between the carbonyl and $C_6H_4CCo_3(CO)_9$ group whereas in II both the known σ-inductive and π-mesomeric donor effects of the cluster[29] leads to lower CO frequencies. This interpretation is confirmed by an examination of the absorptions of the metal bound carbonyls in the attached tricobalt cluster. In going from I to II all absorptions increase in frequency. Indeed it is known that the value of the highest frequency A_1 mode correlates well with the donor/acceptor properties of the $CCo_3(CO)_9$ fragment towards a group attached to the carbyne carbon atom.[26,30] Thus, we expect II to be the weaker acid and to form a more basic carboxylate.

Table I. Comparison of Infrared Spectra of I–IV[a]

	I	II	III	IV
-OH Stretching and overtone or combination	[b]3425w, 2958w, 2925m, 2855w	[b] 3041sh, m, 2932m, 2843sh, 2788m, 2625m, 2517m		
Stretching of cobalt carbonyls	[b]2101m, 2042vs, 2035sh,s, 2022sh,m	[b] 2111w, 2058vs, 2048vs, **2032s, 2018ms, 2005m**	[b] 2111m, 2025sh, s,2038sh, s, 2042vs	[b] 2111m, 2077sh, s, 2059sh, s, 2044vs
	[c] **2101m, 2052vs, 2038s, 2020.5sh,m**	[c] 2109w, **2066vs**, 2047s	[c] 2109 w, 2071s, **2043 vs**	[c] 2109 w, 2070s, **2042vs**
Stretching of CO in carboxylic acid or carboxylate	[b]**1712m, dimer**	[b] **1640w, dimer**	[b]**1539m(a)**, 1386s(s)	[b]**1557m(a)**, 1387s(s)
	[c] **1750vw, 1712m, dimer**	[c] **1686w, monomer, 1644m, dimer,1606w**	[c]**1538w(a), 1385w(s)**	[c]**1557w(a), 1386w(s)**
Other modes of vibration	1409w, 1302w, 1263w, 674w, 615m, 533m, 475w, 438w	[b] 1413vw, 1281w, 1058vw, 950vw, 778vw, 721w, 545w, 530w, 506sh, mw, 498m, 475vw, 449vw, 431vw	[b]1338w, 1087vw, 791vw, 754w, 729w, 555w, 529w, 516w, 501m, 470w, 440vw **415w**	[b]1342w,1086vw, 794 vw, 755w, 728w, 556w, 528w, 516w, 501m, 469w) 437vw **411w**

[a] Numbers in bold type are useful as characteristic frequencies. [b] In KBr pellet (4000–400 cm^{-1}). [c] In CH_2Cl_2 (2200–1200 cm^{-1}).

pH Measurements. Direct pH measurements of approximately equimolar solutions of I and II have been carried out. Values of 4.1 and ≈6.4 were obtained for I and II, respectively, in 50% acetone/H_2O. The latter value is approximate because of decomposition (slow relative to the time of measurement) under these conditions. These measurements are consistent with considering II as being the precursor to a more basic carboxylate than either I or acetic acid.

Cyclic Voltammetry. The reversible reduction of a number of derivatives of $Co_3(CO)_9(\mu_3\text{-}CR)$ in acetone has been reported previously;[26,30] however, I and II have not been investigated in this manner. These two compounds behave as expected and the data are given in Table II. Note that the reduction potentials are solvent dependent[31] but, when the reduction potential of $Co_3(CO)_9(\mu_3\text{-}CCl)$ is used as a common reference point, the A_1 carbonyl stretching frequencies and reduction potentials of I and II fit the previously published correlation.[30] As expected conjugation of the [-COOH] group with the metal cluster lowers

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Table II. Cyclic Voltammetry Data for I and II[a]

compd	$E_{1/2}$(Red) (V)	ΔE_p (mV)	i_a/i_c	E_{pa}(Ox) (V)	i_a/i_c
I	−0.70[b]	146	1.0	1.18	irreversible
	−0.76[c]	140	1.0	none	
II	−0.63[b]	150	1.0	0.91	irreversible
	−0.66[c]	150	1.0	none	
$(CO)_9Co_3CCl$	−0.59[b]	120	1.0	multipeaks	irreversible
	−0.73[c]	225	1.0	multipeaks	irreversible

[a] Scan rate: 20 mV. [b] In acetonitrile. [c] In 1,2-dichloroethane.

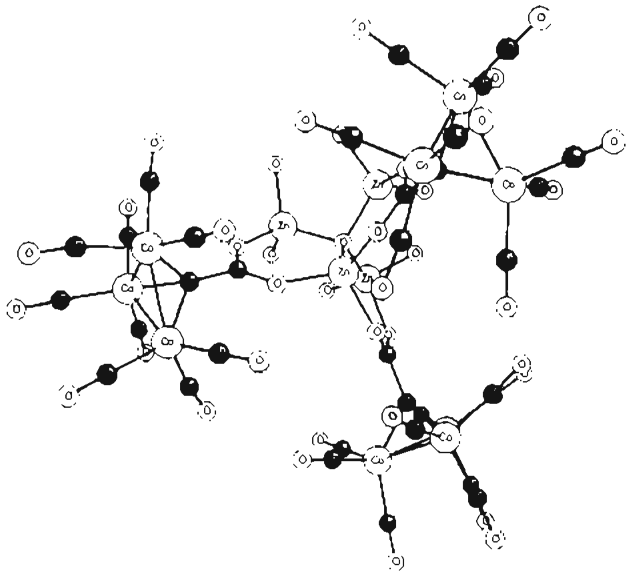

Figure 1. Schematic representation of the molecular structures of $M^{II}{}_4O[(CO)_9Co_3CCO_2]_6$, M = Co(III), Zn(IV). The three $[(CO)_9Co_3C]$ fragments lying to the rear of the drawing have been removed for the clarity.

the reduction potential of the metal cluster which is again consistent with considering II as the precursor to a better carboxylate ligand. Curiously, over a period of time, sweeping the potential between −1.4 to 1.5 V vs Ag/AgCl results in the precipitation of $[(CO)_9Co_3C]_2$[32] from I but not from II.

Solid State Structures. Crystallographic data for non-cluster metallocarboxylates are available[6,7] and crystallographic information is available for one cluster-carboxylic acid, i.e., $H_3Os_3(CO)_9CCOOH$[33] (Figure 1). The ORTEP diagrams for I and II and the associated structural parameters are given in the supplementary tables. The structures, although helpful in solving the structures of larger assemblies, are unexceptional. Although a comparison of the structural parameters obtained for I and II corroborate the greater positive character of the metals of II relative to I and the correspondingly greater negative charge of the carboxylate moiety of II, the differences are barely outside of the error of the measurements (see the supplementary material).

Reaction Properties of I and II. ***Solution Behavior.*** Both clusters I and II are stable in the solid state however the solution behavior is strikingly different. The cluster I is soluble and stable in nonpolar solution. The cluster II is soluble in polar solvents such as ether, THF, CH_2Cl_2, acetone, and methanol, however, it is unstable in solution, particularly in the presence of air, and $Co_4O[(CO)_9Co_3CCO_2]_6$, III, spontaneously precipitates (Reaction (3); Chart I). Thus, the attempted crystallization of II in

$$22(CO)_9Co_3CCOOH + 7O_2 \rightarrow 3Co_4O[(CO)_9Co_3CCO_2]_6\downarrow + 44CO + 11H_2O \quad (3)$$

air gives III as the major product. Decomposition of the reaction mixture in a pure degassed solvent is much slower but proceeds to the same final product. Under otherwise identical conditions, the addition of a small amount of a simple carboxylic acid, e.g. acetic acid, inhibits the formation of III and leads to the precipitation of pure crystalline II in high yield. Both a solution of III and the solid has essentially the same color as that of II; however, decomposition into III causes an apparent decrease in solubility of the sample. Sturgeon et al.[17] have reported reaction (2) as a route to III as it indeed ultimately is under their conditions. Their structural determination of III is unambiguous; however, we find their reported IR spectrum and solubility characteristic of II rather than III.

Reaction with $ZnEt_2$. For comparative purposes, we investigated the reaction of CH_3COOH and $C_6H_5(CH_2)_2COOH$ with $ZnEt_2$. The first reaction has been examined previously[34] but only in a 1:1 stoichiometry. Reaction with a 2:1 ratio of reactants in Et_2O rapidly led to the clean precipitation of white $Zn(RCO_2)_2$ for both acids. Further addition of $ZnEt_2$ to give an overall 1:1 stoichiometry caused the initially formed precipitate to dissolve yielding a clear solution. The spectroscopic characterization of these reaction products leads to the following conclusions.

$$ZnEt_2 + 2RCOOH \rightarrow Zn(RCO_2)_2\downarrow + C_2H_6\uparrow \quad (4)$$

$$ZnEt_2 + RCOOH \rightarrow \text{“}EtZn(RCO_2)\text{”} + C_2H_6\uparrow \quad (5)$$

The latter product, "$EtZn(RCO_2)$", is the same as that identified previously;[34] however, based on new data we must formulate it differently. That is, we find no evidence for a species $EtZn(RCO_2)$ but rather suggest, based on the spectroscopic evidence, that the product is $\{[ZnEt_2]_{2/3}[Zn'Et'_2]_{1/3}[Zn(RCO_2)_2]\}_{3n}$ where $ZnEt_2$ and $Zn'Et'_2$ are inequivalent and n is unknown.

The reaction of I is strictly analogous to that described for the simple carboxylic acids and leads to red-brown $Zn(RCO_2)_2$ when a 2:1 stoichiometry is used. Again, further addition of $ZnEt_2$ leads to a red-brown solution. Thus, in the absence of conjugation between the metal cluster and the acid functionality, the cluster substituted acid behaves as a simple carboxylic acid.

However, when II reacts with $ZnEt_2$ in Et_2O in any mole ratio, IV (Chart I) begins to precipitate immediately and C_2H_6 is observed in the gas phase. In a 1:1 ratio, a deep purple-brown product containing cobalt is cleanly formed in high yield according to reaction (6). Although one might expect the initial reaction of II with $ZnEt_2$ to be similar to that of I and the other carboxylic acids, the only isolated product is the oxo-cluster.

$$(CO)_9Co_3CCOOH + ZnEt_2 \rightarrow Zn_4O[(CO)_9CCO_2]_6\downarrow + C_2H_6\uparrow + \ldots \quad (6)$$

Structural Properties of III and IV. ***Infrared Spectra.*** The large clusters III and IV exhibit the very characteristic[16,35] IR pattern of a metal–metal bridging carboxylate in the region 1500 to 1700 cm^{-1} (Table I and Figure 3-supplementary material). The expected antisymmetric [1539(1) for III and 1557(1) for IV cm^{-1}] and symmetric [1386(1) cm^{-1} for both III and IV] stretching modes are seen in both in solid state and in solution. Consistent with the fact that the carboxylate fragment in III and IV are buried within the molecules, the band positions are insensitive to solvent. However, solid state or solution IR provides an easy means to distinguish between II and III or IV in the region 1500 to 1700 cm^{-1} (see Table I and Figure 3-supplementary material). Another reproducible, but less understandable, difference in the solution IR spectra of II and III or IV lies in the metal bound CO stretching region. Although the energies are nearly the same for the two types of compounds in the same solvent, the most

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intense band changes from that at 2066 cm^{-1} in II to that at 2042 cm^{-1} in both III and IV. This provides another means of following the spontaneous conversion of II to III.

Solid State Structures.[17,18] The core of each molecule consists of six carboxylate moieties edge-bridging an oxygen atom centered $[M(II)]_4$, M = Co, Zn, tetrahedron. The metal–metal edges of this tetrahedral central metal oxo cluster core determine the octahedral spatial distribution of the carbon capped tricobalt clusters. Hence, these compounds are direct analogues of classical $M^{II}_4O[RCO_2]_6$ "basic" metal carboxylates which are known for M = Zn, Co and Be.[36–42] Note that all four M(II) centers are approximately tetrahedrally coordinated to four oxygen atoms and that $Zn_4O[MeCO_2]_6$ has been described previously as a compound containing the smallest particle of zinc oxide.[43]

Table II-supplementary material provides a comparison of selected averaged structural parameters for compounds II, III, and IV as well as $Zn_4O(CH_3CO_2)_6$. The structural data for III and IV show no significant differences between the $(CO)_9Co_3C$ fragments in the large clusters and those of I and II. As they are effectively isostructural, III and IV are very similar. Both contain crystallographically imposed inversion centers and, consequently, have disordered cubane-like cores composed of two interpenetrating M_4O tetrahedrons. This cube is compressed along a body diagonal so that each M_4O tetrahedron has three long and one short M–O interactions. On the other hand, both $Zn_4O(CH_3CO_2)_6$ and its beryllium counterpart have a regular tetrahedral cores[36] that are not disordered.

Reaction Properties of III and IV. ***Solution Behavior.*** It was noted that both carboxylate stretching modes of III are unobservable in dry THF. However, if the THF is removed after a short period of time and the residue redissolved CH_2Cl_2 the known spectrum of III was again observed. If left in THF, III eventually degrades with loss of the cobalt carbonyl cluster to uncharacterized products. A possible explanation for this observation is that the carboxylate ligands dissociate when III is dissolved in THF.

To examine both III and IV for evidence of ligand dissociation we have treated solutions with $Mo_2(CH_3CO_2)_4$. From on-going work[44] we know that $Mo_2(CH_3CO_2)_4$ reacts within minutes with II to form the very deep blue-black compound $Mo_2[(CO)_9Co_3CCO_2]_4$. Hence, as a trap for II, or some fragment of it, formation the dimolybdenum cluster derivative can serve as a qualitative measure of the extent III and IV fragment in solution. In THF, III in the presence of $Mo_2(CH_3CO_2)_4$ almost immediately develops a dark blue color whereas IV, under the same conditions, only develops a purplish cast over a period of 24 h. In CH_2Cl_2 III develops a blue color at a ≈10× slower rate. Thus, the cluster ligand $[(CO)_9Co_3CCO_2]^-$ dissociates from both III and IV and more readily from the former. This dissociation is promoted by the coordinating solvent THF.

Discussion

In order to form classical coordination complexes with cluster substituted ligands it is necessary to avoid reaction conditions that will destroy the cluster. In the case of I and II a basic environment cannot be tolerated, hence, the ligands must be used in their protonated forms. To make the cluster substituted zinc carboxylates we have employed the direct reaction of the acid form of I and II with $ZnEt_2$ using the elimination of ethane as the driving force. Because of the isolation of the acid group from the metal cluster in I, it behaves as a normal carboxylic acid. However, in II the electronic perturbation of the acid group by the tricobalt cluster opens a low energy pathway to into the basic carboxylate IV. Furthermore, the high basicity of $[(CO)_9Co_3CO_2]^-$ apparently makes solutions of II prone to oxidative degradation to III, the Co^{II} analogue of IV. These differences must be related to the nature of the electronic interaction between the metal cluster and carboxylic acid group. Hence, it is worthwhile to look more closely at the differing behavior of I and II.

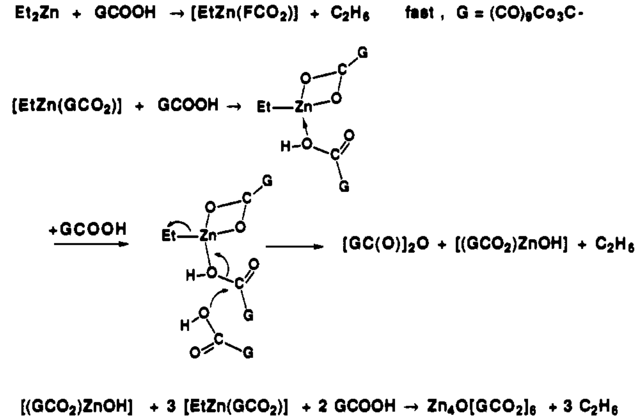

Figure 2. Proposed reaction pathway for the formation of IV from the reaction of II with $ZnEt_2$.

It is known that $Zn(RCO_2)_2$ can be converted into $Zn_4O(RCO_2)_6$ by sublimation[36,45] and the conversion of $Be(CH_3CO_2)_2$ to $Be_4O(CH_3CO_2)_6$ at 150–200 °C is accompanied by the formation of $(CH_3CO)_2O$.[16] However, a pathway to IV proceeding via $Zn[(CO)_9Co_3CCO_2)]_2$ is unlikely as if the simple carboxylate were formed during the reaction it would be expected to precipitate. Further, the reaction forming the oxo-cluster and the anhydride would still be expected to have a significant energy barrier. Thus, there must be a fundamental difference in the reaction of $ZnEt_2$ with II relative to I.

Based on these observations we postulate the schematic pathway given in Figure 2. This reaction pathway is based on the assumption that the substituent effect of the cluster sufficiently reduces the Brönsted acidity of II so that elimination of ethane is slow relative to the rate of formation of the anhydride and zinc oxo precursor shown. The proposed initial steps are consistent with the suggestion of Inoue et al.[34] That is, in their system, coordination to the zinc center is postulated in order to explain the greater reactivity of the Et group of "$EtZn(RCO_2)$" vs that of EtZnOMe. The overall stoichiometry of the reaction scheme shown in Figure 2 is

$$8(CO)_9Co_3CCOOH + 4ZnEt_2 \rightarrow Zn_4O[(CO)_9CCO_2]_6 + (CO)_9Co_3CC(O)O(O)CCCo_3(CO)_9 \quad (7)$$

In this regard, some additional observations are pertinent. First, when the reaction is carried out under the most rigorous conditions for the exclusion of air and H_2O, the maximum isolated yield of IV is 70% based on cobalt. The theoretical yield based on the stoichiometry reaction (7) is 75%. On the other hand, less rigorous conditions *and* a 1:1 ratio of II to $ZnEt_2$ leads to significantly higher yields. That is, reaction (8) now plays a role permitting

$$(CO)_9Co_3CC(O)O(O)CCCo_3(CO)_9 + H_2O \rightarrow 2(CO)_9Co_3CCOOH \quad (8)$$

a 100% theoretical yield for a 1:1 ratio of II and $ZnEt_2$ in the

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presence of adventitious water. Second, when the filtrate from reaction (6) was reduced to dryness without removing excess $ZnEt_2$, a solid state IR of the dark solid showed another carboxylate band (1535 cm^{-1}, KBr), not due to III, superimposed on those of IV. This compound or mixture is very unstable (pyrophoric in the solid state) and a solution of this material, on standing at room temperature, decomposes continuously. However, on exposure of the solution of this intermediate to air, IV was the only product detected by IR. It is possible that this secondary product is $(CO)_9Co_3CC(O)O(O)CCCo_3(CO)_9$ or an adduct of the anhydride with $ZnEt_2$.

Although the mechanistic postulates are just that, the observations demonstrate that the substituent effect exerted by a metal cluster can have substantial consequences on the reaction chemistry of the substituted functionality. As the metal cluster, the ligand functionality, and the higher oxidation state metal core can all be varied, this work establishes a potentially general approach to very large metal-main group atom architectures.

Experimental Section

General Methods. Reactions and manipulations were conducted under N_2 using standard Schlenk tube techniques. Glassware was oven-dried before use. Solvents were distilled from drying agents under nitrogen as follows: sodium benzophenone ketyl for hexane, diethyl ether and tetrahydrofuran (THF); P_2O_5 for CH_2Cl_2. Acetonitrile was distilled over CaH_2 under N_2. Reagent grade acetone and CCl_4 as well as $AlCl_3$ were used as received from Aldrich. $Co_2(CO)_8$ was from Strem and used directly. $(CO)_9Co_3CCl$ used in the syntheses detailed below was prepared by published methods[45] and purified using a silica gel column before use. Bio-Beads S-X8 were purchased from BIO-RAD Laboratories, Richmond, CA. Spectral data were obtained on the following instruments: ^1H and ^{13}C NMR; GN-300; Varian 500; FT-IR; Nicolet 205; NMR shifts are referenced to residual solvent signals: CD_2Cl_2, 5.32; $(CD_3)_2CO$, 2.04. Mass measurements were obtained on a Finnigan-MAT 8400; FAB matrix (50% *p*-nitrobenzyl alcohol and 50% glycerol). A Carle Model 311 gas chromatograph with molecular sieves and Porapak columns in series and argon carrier gas was used to identify H_2 and small hydrocarbons. A Corning Model 200 pH meter with a glass electrode was used for the pH measurements. Cinnamic acid was used as the standard acid (p*K*a = 4.44). Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN and M-H-W Laboratories, Phoenix, AZ. The cyclic voltammetry was carried out with PAR and BAS equipment. The working electrode was a platinum disk and the auxiliary electrode was a platinum wire. The supporting electrolyte was 0.1 M tetraethylammonium perchlorate and the concentrations in acetonitrile of the compounds investigated were typically 10^{-3} M. Potentials were measured with respect to a Ag/AgCl reference electrode calibrated against the reversible ferrocene(+1/0) couple in acetonitrile. The scan rates for the cyclic voltammograms were varied between 20 and 500 mV s^{-1}.

Preparation of $(CO)_9Co_3[\mu_3\text{-}CC_6H_4CH_2CH_2COOH]\cdot C_6H_5CH_3$ (I). A 250-mL two-neck round-bottom flask containing a purple solution of 5.00 g (10.5 mmol) $Co_3(CO)_9(\mu_3\text{-}CCl)$ and 1.58 g (10.5 mmol) of hydrocinamic acid in 80 mL of 1,2-dichloroethane (DCE) was equipped with reflux device and bubbler. The flask was refluxed at 110 °C while stirring under a N_2 atmosphere. A suspension of $AlCl_3$ in DCE (5.00 g, 37.5 mmol) was added slowly through the second neck over a period of 15 min with a syringe. The purple solution gradually turned brown with the generation of HCl which was expelled by bubbler. Sampling the reaction mixture showed the gradual disappearance of the purple band at high R_f and growth of a product that gave of a small brown band with R_f = 0.2–0.3 on TLC (CH_2Cl_2). After completion of the reaction, the viscous mixture was diluted with DCE and washed in a 250 mL separation funnel with 10% HCl twice and then water in order to remove unreacted $AlCl_3$. This DCE solution was dried over concentrated sulfuric acid and the volume reduced to 30 mL. This solution was passed through a bio-beads column with hexane in order to get rid of excess 3-phenylpropanoic acid. The deep brown band contained no residual 3-phenylpropanoic acid. An acidic silica gel column with DCE and acetone as consecutive eluants was used to remove some of the cobalt carbonyl impurities. In order to remove II, the solution from the column was reduced to dryness under vacuum and treated with 1 mL mixture of concentrated H_2SO_4 and 80% H_3PO_4 in (2:1/v:v). This mixture was extracted quickly with dry toluene and the toluene fraction centrifuged to remove tiny mineral acid droplets suspended in the solution. The clean brown solution was concentrated again and put into a refrigerator at —20 °C. Overnight cooling gave red-brown prismatic crystals. The crystals were collected, washed quickly with degassed distilled water to get rid of a trace sulfonated toluene, and then washed with cool hexane. The crystals which were used for the X-ray diffraction studies were picked from this toluene solution (Table III). The sample for elemental analysis and the spectroscopic measurements was dried in vacuo and gave 2.48 g of pure material corresponding to a yield of 40% based on total cobalt. Anal. Calcd for $Co_3C_{19}O_{11}H_9$: Co, 9.99; C, 38.67; O, 29.83; H, 1.54. Found (dried under vacuum): C, 38.89; H, 1.77. Spectroscopic data: ^1H NMR (CD_3COCD_3, 20 °C, δ): 2.66 (t, 2H, J_{HH} = 7.8 Hz), 2.90 (t, 2H, J_{HH} = 7.8 Hz), 7.25 (d, 2H, J_{HH} = 8.1 Hz), 7.52 (d, 2H, J_{HH} = 8.1 Hz); ^{13}C NMR(CD_3Cl, 20 °C, δ): 30.56 (CH_2), 35.18 (CH_2), {119.20, 128.60, 128.70, 128.86, 128.99, 140.46} (Ph), 178.74 (COOH), 200.21 (br, CO); IR (see Table I); MS (CI): (M + 1) 591.

Table III. Crystallographic Data

a. $[(CO)_9Co_3CC_6H_4CH_2CH_2COOH]_2$, I	
$C_{26}H_{16}Co_3O_{11}$	fw 682.22
$a = 9.348(1)$ Å	space group $P\bar{1}$ (No. 2)
$b = 11.954(1)$ Å	$\lambda = 0.710\,73$ Å
$c = 13.862(4)$ Å	$\rho_{calcd} = 1.59$ g/cm^{-3}
92.83(2), 100.67(2), 109.51(1) deg	$\mu = 30.72$ cm^{-1}
$V = 1424.3$ Å^3	transm coeff = 0.808–0.999
$Z = 2$	$R_1 = 0.045$
$T = 21 \pm 1$ °C	$R_2 = 0.039$
b. $[(CO)_9Co_3CCOOH]_2$, II	
$C_{11}HCo_3O_{11}$	fw 485.92
$a = 7.906(1)(1)$ Å	space group $P\bar{1}$ (No. 2)
$b = 8.673(1)$ Å	$\lambda = 0.710\,73$ Å
$c = 12.915(1)$ Å	$\rho_{obsd} = 1.98$, $\rho_{calcd} = 1.97$ g/cm^{-3}
83.73(2), 86.94(2), 68.30(1) deg.	$\mu = 30.72$ cm^{-1}
$V = 817.8$ Å^3	transm coeff = 1.01–0.94
$Z = 2$	$R_1 = 0.024$
$T = 21 \pm 1$ °C	$R_2 = 0.027$

[a] $R_1 = \sum|F_o - F_c|/\sum|F_o|$, $R_2 = (\sum w(F_o - F_c)^2/\sum w(F_o)^2)^{1/2}$.

Preparation of $(CO)_9Co_3CCOOH$ (II). In a typical reaction $Co_3(CO)_9(\mu_3\text{-}CCl)$ 12.3 g (25.18 mmol) was dissolved in 200 mL of degassed CH_2Cl_2 in a 500 mL Schlenk flask and $AlCl_3$ 10.3 g (77.27 mmol) was added rapidly and stirred under N_2 for 12 min. Note that the timing is important. Reaction times of more than 2 h results in the loss of all acid II. At this time TLC(CH_2Cl_2) of the reaction mixture showed disappearance of the purple band due to $Co_3(CO)_9(\mu_3\text{-}CCl)$ at high R_f position and appearance of a new dark brown band (R_f = 0) covered by a purple-brown band (R_f = 0.3). The color changed from purple to yellow brown and the reaction mixture thickened with some precipitation. To this mixture was added another 150 mL CH_2Cl_2 followed immediately by addition dropwise of 50 mL 38% HCl while the reaction flask was cooled with an ice/water bath. When the mixture stopped bubbling and cooled down, 38% HCl and water were used alternatively to wash it until the blue color in aqueous phase disappeared. The organic layer was separated after washing and 1 mL acetic acid or an equal amount hydrocinamic acid was added. Following a wash with 50 mL water, this solution was dried over $MgSO_4$ for several hours and filtered. At this stage, TLC (CH_2Cl_2 as eluant) showed acid II as the major component (purple-brown band; R_f = 0.3) with a very pale brown impurity band at higher R_f. Evaporation of the filtrate yielded dark, triangular, thick plate-like crystals (Table III). The total amount of crystalline material obtained was 7.20 g corresponding to a yield of 60%. Experiments without the added acetic acid yielded microcrystals and an insoluble precipitate. Anal. Calcd for $Co_3C_{11}O_{11}H$: Co, 36.38; C, 27.19; H, 0.21. Found: Co, 37.25; C, 27.31; H, <0.5. Density (fluid displacement; CBr_4 in CCl_4): 1.97 g/cm^3 obsd, 1.98 g/cm^3 calcd (see supplementary material). Spectroscopic data: IR (See Table I). MS (negative FAB) (M – 28) 458. No parent ion was detected. NMR: ^1H (CD_2Cl_2, 20 °C, δ) 11.5 (br, w); ^{13}C (CD_2Cl_2, 20 °C, δ) 202.5. Note that the acid proton shift reported previously[21] is incorrect and indicates a wet sample. A single crystal suitable for X-ray diffraction was chosen directly from synthetic crystalline by slow evaporation of the filtrate in the air without recrystallization.

It is important to note that the crude II, obtained by the hydrolysis of $[(CO)_9Co_3CCO]^+$ using dilute HCl or water is contaminated by a non-water soluble cobalt containing impurity. This species has a high R_f value and is much more air and moisture sensitive than II [IR (hexane, cm^{-1}): 2081 (m), 2064 (s), 2029 (m), 2012 (m). R_f = 0.8 in CH_2Cl_2]. Presumably this impurity arises from the sacrificial decomposition of some of the tricobalt cluster which is required to provide the tenth CO for the formation of $[(CO)_9Co_3CCO]^+$.[22] This impurity decomposes in water to form a pale pink gel-like cobalt hydroxide.

Preparation of $Co_4O[(CO)_9Co_3CCO_2]_6$ (III). 0.200 g (0.0412 mmol) of crystalline acid II was dissolved in 20 mL reagent grade acetone in a Schlenk tube. The tube was opened to the air through the side arm and kept at room temperatures. After two days a TLC showed the disappearance of the acid II band and appearance of the carboxylate III band ($R_f = 0$) and the solution was slowly evaluated to dryness. The solid was collected and washed with ether and hexane before drying again. The total weight of solid is 0.171 g (0.0541 mmol) corresponding to yield (96% based on total cobalt).

In order to check the reported synthesis of III[17] 0.0313 g (0.00657 mmol) of $(CO)_9Co_3CCl$ was dissolved in a minimum amount of methylene chloride. To the solution 0.0263 g (0.0197 mmol) of powdery $AlCl_3$ was added. The reaction mixture turned to brown-yellow in 30 min and was poured over cracked ice in the air. The aqueous layer was found to have pH = 2–3. The purple brown organic layer was washed with copious water and then dried with $MgSO_4$. The IR of this solution was that of the authentic II with a weak impurity peak in 2096 cm^{-1}. The IR spectrum in the solid state for the solid resulting from removal of the solvent under vacuum showed was identical to that of II. Thus, the principal product of the reaction is II and III is only formed on decomposition as described above. This is contrary to the conclusions of Sturgeon et al.[17] However, we note that the previously reported solid state IR spectrum of III is actually that of II, i.e., the band reported is the C=O stretch of the acid and no indication of the characteristic carboxylate absorptions of III is given. Further, the material labeled as III is described as soluble in benzene whereas authentic III is virtually insoluble in this solvent.

Preparation of $Zn_4O[(CO)_9Co_3CCO_2]_6$ (IV). A typical synthesis was carried out in a two neck 250 mL Schlenk flask equipped with a 50 mL filtration funnel and a magnetic stirring bar. To the filtration funnel was loaded 2.70 g (5.56 mmol) $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$ which was then sealed by a rubber septum. 125 mL Et_2O was continuously added to the funnel by syringe and the intense purple-brown filtrate was collected in the reaction flask. When the filtrate became pale and only a very minor amount of black impurity was left on the funnel, the funnel was removed and replaced with a rubber septum. 5.56 mL (5.56 mmol) ZnEt2 in hexane (1 M) was added drop-wise into the stirring filtrate in the flask over a period of 10 min. Black microcrystals begin precipitating out of solution immediately and precipitation is complete after another 20 min. Analysis of the head gas by gas chromatography show the presence of C_2H_6. The microcrystals were filtered, collected and washed with cool Et_2O using the second neck of the flask. Before washing the microcrystals were pyrophoric. Both solid and solution IR showed that this microcrystals were pure $Zn_4O[(CO)_9Co_3(\mu_3\text{-}CCO_2)]_6$. The microcrystals were redissolved in THF and diffusion of Et_2O over night resulted in well formed crystals with ideal or truncated rhombohedral shapes. Total weight of recrystallized material was 1.84 g corresponding to a 61% yield based on the formula $Zn_4O[(CO)_9Co_3(\mu_3\text{-}CCO_2)]_6\cdot(C_2H_5)_2O$. IR (Table I); Anal. Calcd for $Zn_4Co_{18}C_{66}O_{67}$: 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.

Reaction of RCOOH with $ZnEt_2$. ***a. $ZnEt_2$:$PhCH_2CH_2COOH$ = 1:2.*** To a Schlenk tube containing 1.5 g (10 mmol) of solid hydrocinamic acid was added 20 mL distilled diethyl ether. The homogeneous solution thus formed was purged with dry N_2. To this solution was added dropwise 5 mL (5 mmol) 1 M $ZnEt_2$ solution by syringe. The clean solution immediately became cloudy with precipitation of a white solid. The reaction mixture was filtered and the precipitate was washed with diethyl ether three times and dried under vacuum. The IR and the ^1H NMR spectra are consistent with those expected for anhydrous $Zn(PhCH_2CH_2CO_2)_2$. The yield of 1.81 g corresponds to ≈100% yield. IR (2200–1200 cm^{-1}): 1544 vs, 1450 s. ^1H NMR(CD_2Cl_2, 20 °C, δ): 2.67 (t, 2H, J_{HH} = 7.8 Hz), 2.93 (t, 2H, J_{HH} = 7.6 Hz), 7.23 (m, 5H).

b. $ZnEt_2$:CH_3COOH = 1:2. In the same manner as in part (a) 0.6 g (10 mmol) of acetic acid was reacted with 5 mL (5 mmol) 1 M $ZnEt_2$. The white product weighted 0.90 g corresponding to a 99% yield. The IR spectra and the ^1H NMR spectra identifies the product as the known compound $Zn(CH_3CO_2)_2$.[46] IR (2200–1200 cm^{-1}): 1549 vs, 1455 s. ^1H NMR (CD_2Cl_2, 20 °C, δ): 2.09 (s, 3H).

c. $ZnEt_2$:$PhCH_2CH_2COOH$ = 1:1. To a Schlenk tube containing 0.75 g (10 mmol) of solid hydrocinamic acid was added 20 mL distilled diethyl ether. The homogeneous solution thus formed was purged with N_2. To this solution was added dropwise 5 mL (5 mmol) 1 M $ZnEt_2$ solution by syringe. The clean solution immediately became cloudy and white $Zn(OOCCH_2CH_2Ph)_2$ formed on addition of the first half $ZnEt_2$ as expected from above. The second half mole of $ZnEt_2$ caused the white precipitate to redissolve. The resulting clear solution was evaporated to give a thick oil-like material extremely soluble in most of organic solvents. The IR spectra show a single set of bridging carboxylate bands. But both ^1H and ^{13}C NMR show a single type of carboxylate but two types of Zn bound ethyl group (Et′ and Et) in a ratio of 1:2. Integration shows an Et to $PhCH_2CH_2$ (acid) ratio of 1:1. IR (2200–1200 cm^{-1}): 1598 s, 1440 s. ^1H NMR (CD_2Cl_2, 20 °C): Zn–CH_2–CH_3: 0.49 (q, 2H, J_{HH} = 8.0 Hz), 1.42 (t, 3H, J_{HH} = 7.8 Hz) ; Zn–CH_2'–CH_3': 0.52 (q, 2H, J_{HH} = 8.0 Hz), 1.47 (t, 3H, J_{HH} = 7.8 Hz); $PhCH_2CH_2COOZn$: 2.79 (t, 2H, J_{HH} = 7.4 Hz), 3.02 (t, 2H, J = 7.2 Hz), 7.36 (m, 4H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C, δ): Zn–CH_2–CH_3: –0.208 (CH_2), 12.53 (CH_3); Zn–CH_2'–CH_3': –1.68 (CH_2'), 12.66 (CH'_3); $PhCH_2CH_2COOZn$: 32.01 (CH_2), 39.51 (CH_2), (126.7, 128.8, 128.9, 141.1) (Ph, m); COO^-: 182.1.

d. $ZnEt_2$:CH_3COOH = 1:1. In the same manner as in part (c) 0.30 g (10 mmol) of acetic acid was reacted with 5 mL (5 mmol) 1 M $ZnEt_2$ solution by syringe. The IR spectra show that this material has two sets of bridging carboxylate bands. Again both ^1H and ^{13}C NMR show a single type of carboxylate but two types of Zn bound ethyl groups (Et′ and Et) in a ratio of 1:2. Integration demonstrates an Et to Me (acid) ratio of 1:1. IR (CH_2Cl_2, 2200–1200 cm^{-1}): 1615 s, 1600 s, 1446 s, 1410 s. ^1H NMR (CD_2Cl_2, 20 °C, δ): Zn–CH_2–CH_3: 0.266 (CH_2, q, J = 8.1 Hz), 1.193 (CH_3, t, J = 8.1 Hz) ; Zn–CH_2'–CH_3': 0.31 (q, 2H, J_{HH} = 8.1 Hz), 1.25 (t, 2H, J = 8.6 Hz); CH_3COOZn: 2.18 (s, 3H), $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2, 75 MHz): Zn–CH_2–CH_3: –0.795 (CH_2), 12.22 (CH_3); Zn–CH_2'–CH_3': –1.75 (CH_2'), 12.55 (CH_3); CH_3COOZn: 25.02; COO^-: 180.9.

e. $ZnEt_2$:$(CO)_9Co_3CC_6H_4(CH_2)_2COOH$ = 1:2. To a Schlenk tube containing 0.1200 g (0.203 mmol) of crystalline $(CO)_9Co_3CC_6H_4(CH_2)_2COOH$ was added 10 mL distilled diethyl ether. The homogeneous red-brown solution thus formed was purged with N_2. To this solution was added dropwise 0.102 mL (0.102 mmol) 1 M $ZnEt_2$ solution by syringe. The brown solution became cloudy and a dark precipitate formed. The reaction mixture was filtrated and the precipitation was washed with ether three times before being pumped to dryness again. This precipitate was insoluble in CH_2Cl_2. This reaction can be conducted in toluene media with the same product including solvate toluene. The FT-IR solid spectra show a single set of bridging carboxylate bands but, because of solubility problems, only ^1H NMR solvate toluene signal could be recorded. The compound is identified as $Zn[(CO)_9Co_3CPhCH_2CH_2CO_2]_2\cdot C_6H_5CH_3$. IR (KBr, 2200–1200 cm^{-1}): 2102 m, 2045 vs, 1957 w, 1544 m, 1450 m. Anal. Calcd for $ZnCo_6C_{45}O_{22}H_{24}$: C, 40.47; H, 1.81. Found: C, 40.69; H, 2.36.

f. $ZnEt_2$:$(CO)_9Co_3CC_6H_4(CH_2)_2COOH$ = 1:1. To a Schlenk tube containing 0.1200 g (0.203 mmol) of $(CO)_9Co_3C_6H_4(CH_2)_2COOH$ was added 10 mL distilled diethyl ether. The homogeneous red-brown solution thus formed was purged with N_2. To this solution was added dropwise 0.203 mL (0.203 mmol) 1 M $ZnEt_2$ solution by syringe. The first half of $ZnEt_2$ resulted in the precipitation of $Zn[(CO)_9Co_3CPhCH_2CH_2CO_2]_2$. The second half caused most of the brown precipitate to redissolve. The solution thus formed was pumped to dryness. The IR spectra showed a single set of bridging carboxylate bands. ^1H NMR exhibited broader signals than the analogous systems prepared from the smaller acids and described above. However, the species formed in solution is presumed to be similar. IR (KBr, 2200–1200 cm^{-1}): 2102 m, 2045 vs, 1957 w, 1566 m, 1514 m. ^1H NMR (CD_2Cl_2, 20 °C, δ): $(CO)_9Co_3CPhCH_2CH_2COOZnx$: 2.73 (br, 2H), 2.97 (br, 2H), 7.19 (d, 2H, J_{HH} = 6.6 Hz), 7.52 (d, 2H, J_{HH} = 6.6 Hz), but weak signals and overlapping solvent peaks prevented assignment of the the Zn–Et resonances.

Acknowledgment. We thank the NSF for support of this work and Mr. Paul Lindenfeld for his development of our synthesis of acid II. We thank Prof. A. G. Lappin for advice on the CV experiments and Prof. A. L. Rheingold for the crystallographic identification of $[(CO)_9Co_3C]_2$. W.C. thanks the Department of Chemistry for a Reilly Fellowship.

Supplementary Material Available: Figures showing the IR spectra of I-IV in solution and in the solid state and ORTEP drawings, text giving a description of the structures, and tables of crystal and refinement data, atomic coordinates, thermal parameters, and selected bond distances and bond angles (18 pages). Ordering information is given on any current masthead page.

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