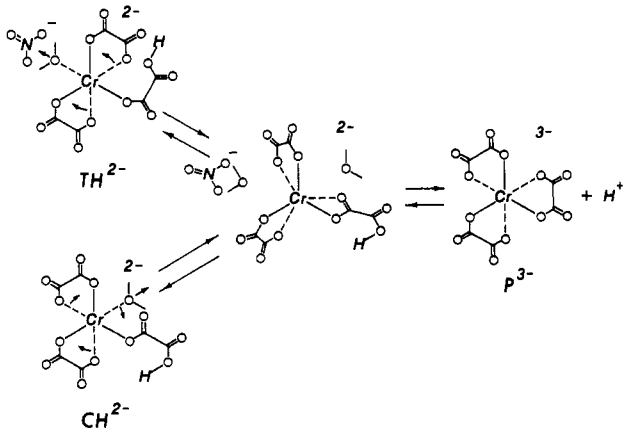
Scheme III



the data in the pH 3–5 interval alone.

Finally, we have used our values of k_1, k_{11}/k_2, and the value of $k_1k_{11}k_{31}/k_2k_{21}$ derived from the data near pH 1 to estimate k_{31}/k_{21} as 1.00 ± 0.06 at 50.0 °C and μ = 1.00 M. The small magnitude of this critical rate constant ratio implies that preferential chelation of *cis*-$Cr(ox)_2(oxH)(H_2O)^{2-}$ from pH 3 to pH 5 is due in fact to rapid chelation of its conjugate base, *cis*-$Cr(ox)_2(-ox)(H_2O)^{3-}$. This inference is in accord with the rate relationship observed for chelation of the monodentate oxalato-*O* ligands of $Cr(NH_3)_5(oxH)^{2+}$ and its conjugate base, $Cr(NH_3)_5(-ox)^+$.[18]

Nitrate Catalysis. The rate constant ratio k_{31}/k_{21} should be independent of ionic strength and reaction medium. Therefore, combined activation data at μ = 1.20 M and μ = 1.00 M may be used to estimate its associated activation parameter differences as $\Delta(\Delta H^*)$ = 1.2 ± 0.5 kcal mol^{-1} and $\Delta(\Delta S^*)$ = 4.0 ± 1.3 cal mol^{-1} K^{-1}. These values emphasize the dissociative character of nitrate-catalyzed chelation when they are compared to $\Delta(\Delta H^*)$ = 4.6 ± 0.3 kcal mol^{-1} and $\Delta(\Delta S^*)$ = 16.5 ± 0.8 cal mol^{-1} K^{-1} for k_{31}'/k_{21}'. If the activation parameters for aquation of *trans*-$Cr(ox)_2(oxH)(H_2O)^{2-}$ (k_{21}') are similar to those for aquation of the acetato-*O* ligand of *trans*-$Cr(ox)_2(OCOCH_3)(H_2O)^{2-}$ (ΔH^* = 16.3 kcal mol^{-1} and ΔS^* = −18.8 cal mol^{-1} K^{-1}),[19] nitrate-catalyzed chelation of *trans*-$Cr(ox)_2(oxH)(H_2O)^{2-}$ (k_{31}') may have activation parameters as large as ΔH^* = 21 kcal mol^{-1} and ΔS^* = −2 cal mol^{-1} K^{-1} ($k_{31}' \simeq 2 \times 10^{-2}$ M^{-1} s^{-1} at 50.0 °C).

van Eldik and Harris[21] have suggested that the nitrate ion may catalyze oxalate anation of *cis*-$Co(en)_2(H_2O)_2^{3+}$ by assisting aqua ligand dissociation. This suggestion appears quite reasonable within our substitution scheme if catalyzed water dissociation acts in concert with an associative rearrangement of the binoxalato-*O* ligand of *trans*-$Cr(ox)_2(oxH)(H_2O)^{2-}$. We suggest the detailed mechanism of Scheme III for the nitrate-catalyzed and uncatalyzed chelation processes of $Cr(ox)_2(oxH)(H_2O)^{2-}$. Here, nitrate-assisted dissociation of the aqua ligand of *trans*-$Cr(ox)_2(oxH)(H_2O)^{2-}$ leads to the (binoxalato-*O*,*O*)bis(oxalato-*O*,*O*')chromate(III) intermediate common to the chelation mechanism of *cis*-$Cr(ox)_2(oxH)(H_2O)^{2-}$ and the aquation mechanism of $Cr(ox)_3^{3-}$.[22-25] Coordination isomerization and deprotonation of the binoxalato-*O*,*O* ligand then produces $Cr(ox)_3^{3-}$ in a rapid following step. It should be noted that the higher negative charge of *trans*-$Cr(ox)_2(-ox)(H_2O)^{3-}$ should make anion-assisted water dissociation less likely. There may indeed be no nitrate-catalyzed chelation step involving this complex ion.

Nitrate catalysis by the Scheme III mechanism will not generalize to all anation processes. In this case, the nitrate ion acts to assist chelation of a potentially bidentate ligand present in the primary coordination sphere of the metal ion. A strong, secondary assist to water dissociation must come from the coordinated ligand itself to make the mechanism function. The fact that the nitrate ion catalyzes chelation, while the chloride ion and perchlorate ion do not, may be due to its particular basicity. It is sufficiently basic that it may interact strongly with the aqua ligand's protons; but it is not so basic that it will deprotonate the aqua ligand or compete favorably for the vacated coordination site.

Nitrate catalysis within this system has served as an extremely useful probe of the overall mechanism for oxalate anation. While the details of the mechanism have been developed by inference, the mathematical constraints placed upon our data evaluation by an additional anation pathway are so great that our ability to infer details has been dramatically increased. We feel that further examination of this and similar reaction systems will only serve to confirm the mechanistic details we have presented here.

Registry No. *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$, 15489-30-2; $HC_2O_4^-$, 920-52-5; $C_2O_4^{2-}$, 338-70-5.

(21) van Eldik, R.; Harris, G. M. *Inorg. Chem.* **1979**, *18*, 1997.
(22) Krisnamurty, K. V.; Harris, G. M. *J. Phys. Chem.* **1960**, *64*, 346.
(23) Bunton, C. A.; Carter, J. H.; Llewellyn, D. R.; O'Dell, A. L.; Yih, S. Y. *J. Chem. Soc.* **1964**, 4622.
(24) Banerjea, D.; Mohan, M. S. *J. Inorg. Nucl. Chem.* **1965**, *27*, 1643.
(25) Kelm, H.; Harris, G. M. *Inorg. Chem.* **1967**, *6*, 1743.

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Alkylidynetricobalt Nonacarbonyl Complexes as Hydroformylation Catalysts

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Received February 4, 1983

Several polymerizable alkylidynetricobalt nonacarbonyl complexes, $(OC)_9Co_3CC(O)OCH_2CH_2OC(O)C(CH_3)=CH_2$, $(OC)_9Co_3CC_6H_4C(O)C(CH_3)=CH_2$-*p*, and $(OC)_9Co_3CC_6H_4CH=CH_2$-*p*, were prepared in order to evaluate their derived polymers and copolymers as hydroformylation catalysts. Partial decomposition of the cluster occurs under the reaction conditions. The mono- and/or dinuclear cobalt carbonyl species that are formed appear to be the actual hydroformylation catalysts, contrary to earlier interpretation.

Introduction

Ryan, Pittman, and O'Connor,[1] during the course of investigations of the possibility of "metal cluster catalysis",[2] reported that benzylidynetricobalt nonacarbonyl (**1**) is an effective hydroformylation catalyst or catalyst precursor. The cluster complex, they said, was "recovered unchanged in high

(1) Ryan, R. C.; Pittman, C. U., Jr.; O'Connor, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 1986.

(2) Pittman, C. U., Jr.; Ryan, R. C. *CHEMTECH* **1978**, *3*, 170.

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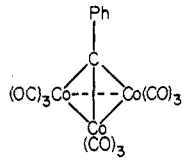

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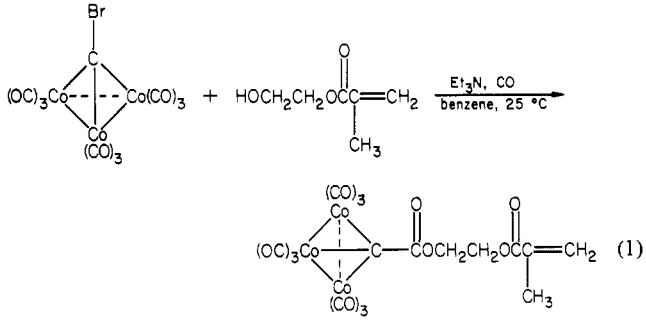
yields" following the hydroformylation reaction. For this reason and because of the fact that several reactions were carried out under relatively milder conditions than normally used for $Co_2(CO)_8$, they proposed that the active catalytic species could be the intact cluster complex.

In previous research we had developed the organic chemistry of the alkylidynetricobalt nonacarbonyl complexes[3] and, therefore, this report was of some interest to us. In view of our interest in organofunctional $RCCo_3(CO)_9$ complexes, we embarked on a project designed to produce polymerizable vinyl monomers containing the $CCo_3(CO)_9$ cluster substituents as well as polymers and copolymers prepared from these monomers. These then would be examined for their applicability as hydroformylation catalysts in the hope that useful, perhaps more selective, catalysts systems might result.

Results and Discussion

A. Synthesis Studies. Monomer preparation was straightforward. Cluster complex **2** was prepared as shown in eq 1. The synthesis is based on the known, general prep-

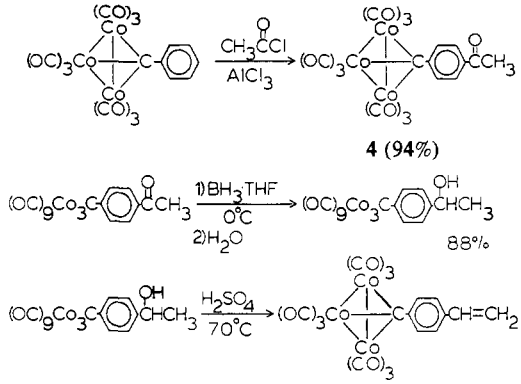


2 (70%) (1)

aration of $RO_2CCCo_3(CO)_9$ complexes by the reaction of (bromomethylidyne)tricobalt nonacarbonyl with alcohols in the presence of triethylamine.[4]

The *p*-styryl complex **3** required a three-step synthesis, as shown in Scheme I. The high-yield acylation of benzylidynetricobalt nonacarbonyl and various substituted derivatives had been studied in some detail in these laboratories.[5] Reduction of the *p*-acetyl derivatives **4** by BH_3·THF proceeded readily in high yield, and acid-induced dehydration of the resulting alcohol then gave the desired *p*-CH_2=$CHC_6H_4CCo_3(CO)_9$. The latter was less stable than the other known benzylidynetricobalt nonacarbonyl complexes, and a satisfactory combustion analysis could not be obtained. Therefore, the mono(triphenylphosphine) derivative **5** was prepared. This was a stable solid, and a satisfactory analysis was obtained.

Scheme I. Synthesis of (*p*-Vinylbenzylidyne)tricobalt Nonacarbonyl

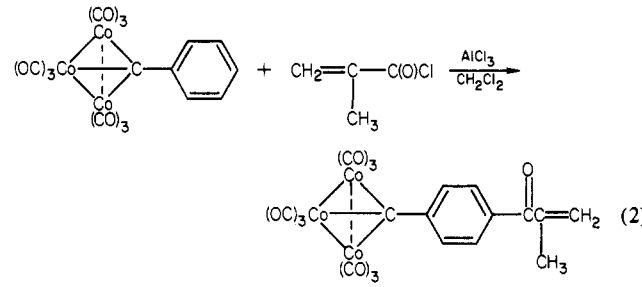


4 (94%)

88%

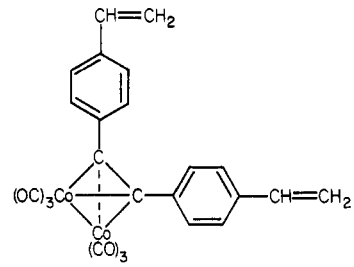
3 (78%)

A Friedel–Crafts reaction also served in the preparation of monomer **6** (eq 2).



6 (40%) (2)

In order to increase the scope of this study, the related (acetylene)dicobalt hexacarbonyl complexes **7** and **8** were



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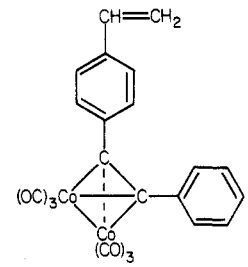

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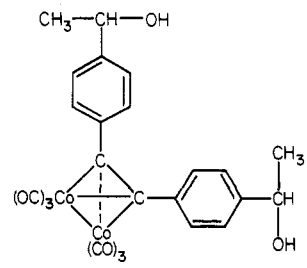
sought. The basic synthesis indicated in Scheme I could be applied here: first Friedel–Crafts acetylation of the (diphenylacetylene)dicobalt hexacarbonyl complex to give the mono- and the di-*p*-acetyl complexes;[6] then BH_3·THF reduction to the respective alcohols, **9** and **10**. The acid-cata-



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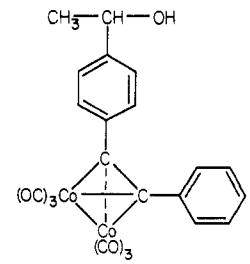

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lyzed dehydration of **9** and **10**, however, did not result in the isolation of the expected *p*-vinyl derivatives **7** and **8**. No doubt

(3) (a) Seyferth, D.; Nestle, M. O. *J. Am. Chem. Soc.* **1981**, *103*, 3320; and earlier papers of our "Organocobalt Cluster" series. (b) Review: Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97.

(4) Seyferth, D.; Rudie, C. N. *J. Organomet. Chem.* **1980**, *184*, 365.

(5) Seyferth, D.; Williams, G. H.; Wehman, A. T.; Nestle, M. O. *J. Am. Chem. Soc.* **1975**, *97*, 2107.

(6) Seyferth, D.; Nestle, M. O.; Wehman, A. T. *J. Am. Chem. Soc.* **1975**, *97*, 7417.

Table I. Conversion of 1-Hexene to 1-Heptanal and Internal Isomers Using 1:1 H_2/CO and Cobalt Carbonyl Catalyst Precursors

	expt no.									
	1	2	3	4	5	6	7	8	9	10
catalyst,[a] mmol	A, 0.133	none	A, 0.133	B, 0.134	C,[c] 0.081	C,[d] 0.020	A, 0.133	A, 0.386	A, 0.386	C,[e] 0.202
reaction time, h	22	21	26	23	24	24	24	26	25	22
temp, °C	100	100	100	100	100	100	100	100	100	100
press., psig	1025-900	1000	1015-900	1000	1000	1075-1000	1075-910	1045-940	1000-840	1000-890
1-hexene charged, mmol	30.5	32.6	32.0	32.0	31.6	32.0	31.5	31.6	31.2	31.6
decane charged, mmol	5.4	27.5	1.84	1.53	1.80	9.42	1.93	0.93	1.05	0.84
1-hexene conversion[b]	75	0[f]	84	83	82	53	85	79	85	83
1-heptanal, mmol	17.80	0	20.55	20.59	19.98	13.44	20.47	19.00	20.10	19.82
internal aldehydes, mmol	5.35	0	6.27	5.94	6.02	3.82	6.28	5.92	6.39	6.45
selectivity (normal/internal)	3.3		3.3	3.45	3.3	3.5	3.3	3.2	3.2	3.1
% of unrecovered 1-hexene converted to aldehydes	88	0	89	87	87	76	91	81	88	86
precursor recovered, %	49		59	0					59	
material balance, %	89	84[f]	90	88	88	84	91	82	88	86

[a] A = $PhCCo_3(CO)_9$, B = [(poly(carbo(2-methacryoyl)ethoxy))methylidyne] tricobalt nonacarbonyl, C = $Co_2(CO)_8$. [b] % conversion = mmol of aldehyde/mmol of 1-hexene charged. [c] Corresponds to the amount of $Co_2(CO)_8$ (or $HCo(CO)_4$) that could be generated if 40% of 0.133 mmol of $PhCCo_3(CO)_9$ decomposed to it. [d] 10% of 0.133 mmol of $PhCCo_3(CO)_9$ decomposing to $Co_2(CO)_8$ (or $HCo(CO)_4$). [e] 35% of 0.386 mmol of $PhCCo_3(CO)_9$ decomposing to $Co_2(CO)_8$ (or $HCo(CO)_4$). [f] The GLC trace indicated only 1-hexene, toluene, and decane present up to an oven temperature of 250 °C. The unrecovered 1-hexene may have been lost by evaporation during charging and workup or during depressurization of the reactor. The material balance for all of the reactions was not 100% possibly because of this loss of 1-hexene. Baking of the GLC column at 250 °C for 15 min for several of the catalytic runs did not show any higher molecular weight products.

they were formed, but they polymerized under the reaction conditions. The infrared spectra of these polymers showed the expected terminal carbonyl stretching modes for (acetylene)dicobalt hexacarbonyl complexes.

Our study of the homo- and copolymerization of the $CCo_3(CO)_9$-substituted monomers discussed above remains incomplete.[7] We were diverted from continuing these studies by the results of our introductory catalysis experiments, which are discussed below. It is sufficient to say that both **2** and **3** could be homopolymerized in degassed benzene solution at 70 °C by using azobisisobutyronitrile as a radical initiator. Monomer **2** appears to be more reactive than monomer **3**. In each case, a benzene-soluble and a benzene-insoluble polymer fraction were obtained. Monomer **6** did not polymerize under these conditions.[8]

B. Catalysis Studies. For orientational purposes, we began these studies by repeating the $PhCCo_3(CO)_9$-catalyzed hydroformylation of 1-hexene[1] (eq 3). However, in our ex-

$$CH_3(CH_2)_3CH{=}CH_2 \xrightarrow[\text{toluene}]{\substack{PhCCo_3(CO)_9 \\ 100\ ^\circ C \\ 1000\ psi\ H_2/CO}} CH_3(CH_2)_5CHO + CH_3(CH_2)_2C(C_2H_5)HCHO + CH_3(CH_2)_3C(CH_3)HCHO \quad (3)$$

periments using the conditions described, we were able to recover the $PhCCo_3(CO)_9$ complex in only moderate yield. After a 24-h reaction time at 100 °C with 850–900 psi of 1:1 H_2/CO, workup (see Experimental Section) recovered the $PhCCo_3(CO)_9$ catalyst, but never in a quantity greater than that equivalent to a 60% recovery. It seems clear that this cluster complex is not completely stable under these conditions. Table I summarizes the experimental details for these catalysis experiments.

In view of the fact that at least 40% of the charged $PhCCo_3(CO)_9$ had decomposed, it was of interest to examine the reaction mixture in more detail and, if possible, to determine the fate of the cobalt values of the unrecovered $PhCCo_3(CO)_9$. IR spectroscopy served well in this investigation. Figure 1 shows the IR spectrum of the reaction

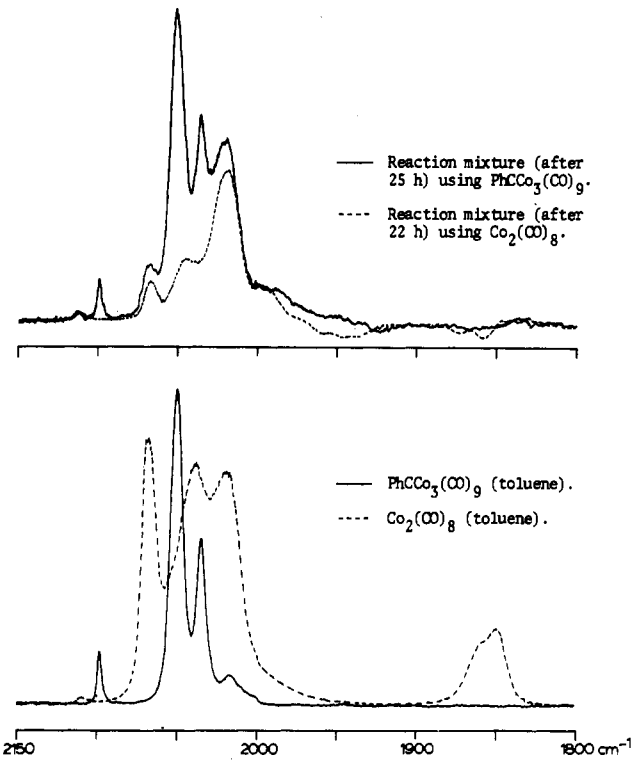

Figure 1. Infrared spectra of the reaction mixtures and the catalyst precursors of the hydroformylation of 1-hexene using cobalt carbonyl cluster precursors.

mixture after a typical catalysis experiment in which the conditions cited above were used. It is clear that cobalt carbonyl species other than $PhCCo_3(CO)_9$ were present. The IR spectra of pure $PhCCo_3(CO)_9$ and $Co_2(CO)_8$, obtained in the same solvent as the reaction mixture, also are shown in Figure 1. The observed frequencies are summarized in Table II. Those bands in the IR spectrum of the reaction mixture after the catalysis run that are not due to $PhCCo_3(CO)_9$ agree well with those observed in the IR spectrum of dicobalt octacarbonyl.

Several hydroformylation experiments were carried out by using $Co_2(CO)_8$ as the catalyst in amounts corresponding to the amount of $Co_2(CO)_8$ that could in theory have been formed if 35% of the $PhCCo_3(CO)_9$ used in the previous experiments

(7) Withers, H. P., Jr. Ph.D. Thesis, Massachusetts Institute of Technology, 1981.

(8) This is not surprising since its organic analogue, $PhC(O)C(CH_3){=}CH_2$, did not polymerize readily: Mulvaney, J. E.; Dillon, J. G.; Laverty, J. L. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 1841.

Table II. Infrared Studies of the Catalyst Precursors in the Hydroformylation Reaction Mixtures[a]

reaction mixture, catalyst precursor $PhCCo_3(CO)_9$	reaction mixture, catalyst precursor $Co_2(CO)_8$	$PhCCo_3(CO)_9$ (toluene)	$Co_2(CO)_8$ (toluene)	$HCo(CO)_4$[16]
				2123 (s)
2112 (w)	2113 (w)		2110 (w)	2107 (w)
2100 (m)		2100 (m)		
2068 (m)	2068 (m)		2069 (vs)	2062 (vs)
2051 (vs)	2046 (m)	2051 (vs)		
2036 (s)		2036 (s)	2039 (s)	2043 (vvs)
2020 (s)	2020 (s)	2018 (w)	2019 (s)	
	1999 (w, sh)			
			1860 (m, sh)	
			1850 (m)	

[a] Values listed in cm^{-1}, scanning the region from 2150 to 1800 cm^{-1}.

had decomposed to give this species. When the same reaction conditions were used, these experiments gave results analogous to those in which $PhCCo_3(CO)_9$ was the "catalyst". There was no change in selectivity, and furthermore, the IR spectra of these reaction mixtures showed only those bands (and in the same intensity) not due to $PhCCo_3(CO)_9$, which had been observed in the $PhCCo_3(CO)_9$ experiments noted above. It thus seems reasonable to conclude that enough $PhCCo_3(CO)_9$ had decomposed in those experiments to produce $Co_2(CO)_8$ (or $HCo(CO)_4$; see IR data in Table II) in amounts sufficient to catalyze the hydroformylation of 1-hexene under these conditions.

Further experiments and observations support this. A hydroformylation using a homopolymer derived from **2** as the catalyst should give some change in selectivity due to the polymeric environment if the bound cluster is the catalytically active species. Also, a lower reaction rate would be expected. In the case of many mononuclear systems, it has been shown that the polymer-immobilized catalysts result in lower reaction rates and a change in selectivity.[9] However, when the homopolymer of **2** was the catalyst used, there was no change in the selectivity and general rate, the results being quite analogous to those observed when $PhCCo_3(CO)_9$ was used as catalyst. This result supports the idea of cluster decomposition as the source of the actual catalyst. Upon fragmentation to mono- and dinuclear cobalt carbonyl species, these would no longer be bound to the polymer and thus could enter the bulk solution where catalysis could occur normally. Another observation may be significant. In the experiments in which monomeric or polymeric $RCCo_3(CO)_9$ species were used to catalyze 1-hexene hydroformylation, an induction period was observed prior to reaction; a drop in pressure did not occur until ~1 h after the reaction mixture had attained the proper reaction temperature and pressure. This very likely is a function of the rate of decomposition of the cluster to generate the catalytically active species.

Alkylidynetricobalt nonacarbonyl complexes are fairly stable, but their partial decomposition when maintained at 100 °C for longer periods of time is not surprising. Previous studies have dealt with the thermal decomposition of $RCCo_3(CO)_9$ complexes.[10,11] Of special note is the fact that $PhCCo_3(CO)_9$ was converted to the much less stable (diphenylacetylene)dicobalt hexacarbonyl when it was heated under argon in refluxing methanol solution. The yield of $(PhC_2Ph)Co_2(CO)_6$ was 63%, based on unrecovered $PhCCo_3(CO)_9$, so that significant cluster fragmentation must have occurred as well.[11] Although the mechanism of thermolysis was not defined, a decomposition course involving transfer of a RC fragment from one cluster molecule to another followed by (or concerted with) loss of a $Co(CO)_3$ fragment from the expanded cluster were the initial steps that seemed to explain the products observed.[10] Thus, in these initial steps, as well as in the thermolysis of $(PhC_2Ph)Co_2(CO)_6$, there is ample opportunity for the formation of mono- and dinuclear cobalt carbonyl species.

King and co-workers[12] have studied the use of several polynuclear cobalt carbonyl complexes, $(PhC_2Ph)Co_2(CO)_6$, $CH_3CCo_3(CO)_9$, and $(\mu_4\text{-}PhP)_2Co_4(CO)_{10}$, as catalysts for the hydrogenation of CO to alcohols at 180–200 °C and 200 atm in *p*-dioxane solution. Under these rather strenuous conditions, all three cobalt clusters were shown, by using IR spectroscopy, to produce $HCo(CO)_4$ under the reaction conditions, and each produced the same mixture of alcohols as had a $Co_2(CO)_8$ catalyst. Mignani, Patin, and Dabard[13] have used optically active (alkoxyalkylidyne)tricobalt nonacarbonyls as hydroformylation catalysts. However, no asymmetric induction in product formation was observed. This suggests that the active species does not contain a chiral entity and thus supports the idea that it is cluster decomposition products that are the actual catalysts. Japanese workers, as we discovered after this study was completed, have studied the hydroformylation of 1-hexene using $CH_3CCo_3(CO)_9$ as the catalyst.[14] They also observed, using electronic, IR, and proton NMR spectroscopy, that, under similar reaction conditions, the $CH_3CCo_3(CO)_9$ cluster decomposed, at least in part, producing $Co_2(CO)_8$ which then was the actual catalytically active species. One may conclude, on the basis of these results and those described in the present report, that a cluster fragment may have a reactivity many orders of magnitude greater than the parent complex and may be responsible for catalysis even in very small concentrations.

Experimental Section

General Comments. All reactions were carried out in flame-dried glassware under a nitrogen atmosphere.

IR spectra were obtained with a Perkin-Elmer 457A grating infrared spectrophotometer with samples in CCl_4 solution contained in 0.1-mm path length sodium chloride cavity cells. Proton magnetic resonance spectra were recorded with either a Varian Associates T60 or a Hitachi Perkin-Elmer R-24B spectrometer.

Monomer Synthesis. 1. Friedel–Crafts Reaction of $PhCCo_3(CO)_9$ with Methacryloyl Chloride. A 200-mL three-necked, round-bottomed flask equipped with a gas-inlet tube, a magnetic stir-bar, a pressure-equalizing addition funnel, and a no-air stopper was charged with 1.33 g (10 mmol) of $AlCl_3$, 60 mL of CH_2Cl_2, and 0.244 mL (2.5

(9) (a) Pittman, C. U., Jr.; Kim, B. J.; Douglas, W. M. *J. Org. Chem.* **1975**, *40*, 590. (b) Dawans, F.; Morel, D. *J. Mol. Catal.* **1977/78**, *3*, 403.
(10) Seyferth, D.; Rudie, C. N.; Merola, J. S. *J. Organomet. Chem.* **1978**, *162*, 89.
(11) Seyferth, D.; Hallgren, J. E.; Spohn, R. J.; Wehman, A. T.; Williams, G. H. XXIIIrd International Congress of Pure and Applied Chemistry, Special Lectures presented at Boston, MA, July 26–30, 1971; Vol. 6, pp 133–149.
(12) King, R. B.; King, A. D., Jr.; Tanaka, K. *J. Mol. Catal.* **1981**, *10*, 75.
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mmol) of CH_2=$C(CH_3)C(O)Cl$. To this solution was added all at once a solution of 1.036 g (2.0 mmol) of $PhCCo_3(CO)_9$[5] in 40 mL of CH_2Cl_2. The reaction mixture became deep red-brown. TLC (silica gel, pentane) showed that almost all of the starting material had reacted. After it had been stirred for 10 min, the reaction mixture was poured into 150 mL of water. The dried organic phase was evaporated at reduced pressure to leave a brown-red oil. Filtration chromatography (silicic acid) removed first two faint brown bands with pentane as eluent. Elution with CH_2Cl_2 removed a brown-red band, which upon evaporation of solvent (to 0.03 mmHg) left a black solid. Recrystallization from pentane afforded 0.48 g (40%) of black-red crystals of **6**, mp 117–118 °C. IR (CH_2Cl_2): ν(C≡O) 1650 (s) cm^{-1}; ν(C≡O) 2110 (m), 2064 (vs), 2050 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.09 (s, 3 H, CH_3), 5.73 (m, 1 H, =CH), 5.96 (m, 1 H, =CH), 7.44–7.82 (AA′XX′, 4 H, Ph). Anal. Calcd for $C_{20}H_9O_{10}Co_3$: C, 40.99; H, 1.55. Found: C, 41.23; H, 1.77.

2. Reaction of (Bromomethylidyne)tricobalt Nonacarbonyl with 2-Hydroxyethyl Methacrylate. This compound was prepared by reaction of 4.00 g (7.7 mmol) of $BrCCo_3(CO)_9$ and 0.88 mL (7.0 mmol) of CH_2=$C(CH_3)CO_2CH_2CH_2OH$ in the presence of 3.34 mL (24.0 mmol) of triethylamine in 70 mL of benzene at room temperature using the general procedure of ref 4. Carbon monoxide was bubbled through the reaction mixture during the ~50-h reaction time. Removal of volatiles left a brown oil. Filtration chromatrography separated unconverted $BrCCo_3(CO)_9$ (65 pentane/35 CH_2Cl_2 eluent) and, with use of CH_2Cl_2, the product, $(OC)_9Co_3CC(O)OCH_2CH_2OC(O)C(CH_3)$=$CH_2$: brown nuggets (from pentane at −30 °C) in 70% yield; mp 32–33 °C. IR (CCl_4): ν(C=O) 1727 (s), 1689 cm^{-1}; ν(C≡O) 2108 (s), 2069 (vs), 2051 (vs). ^1H NMR ($CDCl_3$): δ 1.87 (m, 3 H, CH_3), 4.44 (m, 4 H, CH_2), 5.48 (m, 1 H =CH), 6.03 (m, 1 H, =CH). Anal. Calcd for $C_{17}H_9O_{13}Co_3$: C, 34.14; H, 1.52. Found: C, 33.93; H, 1.61.

3. Reduction of (*p*-Acetylbenzylidyne)tricobalt Nonacarbonyl. A 100-mL three-necked flask equipped with a magnetic stir-bar, a pressure-equalizing addition funnel, a gas-inlet tube, and no-air rubber stoppers was charged with 3.19 mL of a 0.94 M solution in BH_3·THF in THF (9.0 mmol of BH_3) and 5 mL of THF and cooled in an ice-water bath. To this solution was added with stirring, dropwise over a period of 10 min, a solution of 1.275 g (2.28 mmol) of *p*-$CH_3C(O)C_6H_4CCo_3(CO)_9$[5] in 10 mL of THF. After 1 h at 0 °C, TLC indicated complete consumption of the starting material. Ten milliliters of water was added carefully to the reaction mixture and then enough hexane to produce a two-layer system. The organic phase was dried ($MgSO_4$) and evaporated at reduced pressure. Filtration chromatography (silicic acid, CH_2Cl_2) of the residue gave 0.824 g (64%) of *p*-$CH_3CH(OH)C_6H_4CCo_3(CO)_9$ as black needles (from pentane at −30 °C); mp 105–106.5 °C. IR (CCl_4): ν(C≡O) 2100 (m), 2055 (s), 2040 (s), 2014 (w), 1977 (vw) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.52 (d, J = 6 Hz, 3 H, CH_3), 2.03 (d, J = 4 Hz, 1 H, OH), 4.85 (m, 1 H, CH), 7.35 (AA′XX′, 4 H, Ph). Anal. Calcd for $C_{18}H_9O_{10}Co_3$: C, 38.46; H, 1.62. Found: C, 38.35; H, 1.72.

4. Dehydration of [*p*-(1-Hydroxyethyl)benzylidyne]tricobalt Nonacarbonyl. A 100-mL three-necked flask equipped with a magnetic stir-bar, a reflux condenser topped with a gas-inlet tube, and no-air stoppers was charged with 8.66 g (15.4 mmol) of *p*-$CH_3CH(OH)C_6H_4CCo_3(CO)_9$, 50 mg of hydroquinone, and 150 mL of benzene. The resulting solution was flushed with carbon monoxide for 15 min, and then the flask was placed in a 75 °C oil bath. A total of 0.45 mL of concentrated H_2SO_4 was added, slowly in ~0.1-mL portions, while the solution was stirred rapidly and the CO stream was maintained. The reaction, as shown by TLC, was complete within 30 min. The cooled reaction mixture was washed with two 100-mL portions of water (carefully, to avoid formation of an emulsion), and the organic layer was separated, dried, and evaporated at reduced pressure to leave a light brown, glassy solid. Filtration chromatography of the latter (silicic acid, 4:1 pentane/CH_2Cl_2), followed by careful recrystallization from pentane at −30 °C gave 6.452 g (77%) of brown flaky crystals, *p*-CH_2=$CHC_6H_4CCo_3(CO)_9$, mp 70–72 °C. IR (CCl_4): ν(C≡O) 2103 (m), 2057 (vs), 2041 (vs), 2021 (sh), 1978 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.28, 5.77, 6.75 (ABX, 3 H, CH_2=CH), 7.18–7.64 (AA′XX′, 4 H, Ph). Anal. Calcd for $C_{18}H_7O_9Co_3$: C, 39.74; H, 1.30. Found: C, 40.69; H, 1.68.

Since a better analysis could not be obtained, a mono(triphenylphosphine) derivative was prepared.

The same apparatus was charged with 1.00 g (1.84 mmol) of *p*-CH_2=$CHC_6H_4CCo_3(CO)_9$, 0.966 g (3.68 mmol) of PPh_3, and 20 mL of CH_2Cl_2. An addition funnel containing 0.138 g (1.84 mmol) of Me_3NO (dehydration product of the dihydrate using the method of Franzen[15]) in 15 mL of CH_2Cl_2 was attached and this solution was added to the cluster/phosphine solution. An immediate color change to green-brown was observed. After 5 min of stirring, 0.46 mL (7.36 mmol) of iodomethane was added by syringe and the reaction mixture was stirred for 2.5 h. The precipitate that had formed was filtered, and the filtrate was evaporated at reduced pressure. Filtration chromatography of the brown oily solid residue (silicic acid, 4:1 pentane/CH_2Cl_2), followed by recrystallization from pentane/CH_2Cl_2 gave 1.01 g (71%) of *p*-CH_2=$CHC_6H_4CCo_3(CO)_8PPh_3$: black crystals: mp 181–183 °C dec. IR (CCl_4): ν(C≡O) 2079 (s), 2039 (vs), 2026 (vs), 2013 (s), 1992 (w), 1965 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.49, 5.98, 6.86 (ABX, 3 H, CH_2=CH), 7.20–7.77 (m, 19 H, Ph). Anal. Calcd for $C_{35}H_{22}O_8PCo_3$: C, 54.01; H, 2.85. Found: C, 53.81; H, 2.89.

5. Reduction of [(*p*-Acetylphenyl)phenylacetylene]- and [Bis(*p*-acetylphenyl)acetylene]dicobalt Hexacarbonyl Complexes. The procedure used in the BH_3 reduction of *p*-$CH_3C(O)C_6H_4CCo_3(CO)_9$ was applied, using 2.932 g (5.35 mmol) of (*p*-$CH_3C(O)C_6H_4C_2C_6H_4C(O)CH_3$-*p*)$Co_2(CO)_6$[6] with 42.0 mmol of BH_3·THF in THF solution at 0 °C. TLC (silicic acid, CH_2Cl_2) showed formation of the mono-ol and the diol. After 45 min, only the latter was present. Further workup, including filtration chromatography (silicic acid, 30:70 Et_2O/CH_2Cl_2) and recrystallization from CH_2Cl_2 at −30 °C, gave (*p*-$CH_3CH(OH)C_6H_4C_2C_6H_4CH(OH)CH_3$-*p*)$Co_2(CO)_6$: brown-black crystals; mp 59–61 °C; 86% yield. IR (CCl_4): ν(C≡O) 2101 (m), 2068 (s), 2040 (s), 1940 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.50 (d, J = 6 Hz, 6 H, CH_3), 2.07 (d, J = 3 Hz, 2 H, OH), 4.85 (m, 2 H, CH), 7.40 (AA′XX′, 8 H, Ph). Anal. Calcd for $C_{24}H_{18}O_8Co_2$: C, 52.19; H, 3.29. Found: C, 52.10; H, 3.32.

The same procedure was used in the reduction of 3.00 g (5.9 mmol) of (*p*-$CH_3C(O)C_6H_4C_2C_6H_5)Co_2(CO)_6$[6] by 36.1 mmol of BH_3·THF at 0 °C. Filtration chromatography gave 2.63 g (88%) of a brown oil that could not be crystallized. Spectroscopy and analysis showed it to be (*p*-$CH_3CH(OH)C_6H_4C_2C_6H_5)Co_2(CO)_6$. IR ($CCl_4$): ν(C≡O) 2085 (m), 2050 (s), 2030 (sh), 2010 (s), 1982 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.55 (d, J = 6 Hz, 3 H, CH_3), 1.93 (d, J = 3 Hz, 1 H, OH), 4.90 (m, 1 H, CH), 7.22–7.65 (m, 9 H, Ph). Anal. Calcd for $C_{22}H_{14}O_7Co_2$: C, 51.99; H, 2.78. Found: C, 52.42; H, 2.95.

Attempted dehydration of these (diphenylacetylene)dicobalt hexacarbonyl derivatives resulted in formation of polymeric products whose IR spectra showed the presence of the $Co_2(CO)_6$ unit.

Hydroformylation of 1-Hexene with CO/H_2 with $PhCCo_3(CO)_9$, $Co_2(CO)_8$, or $(OC)_9Co_3CC(O)OCH_2CH_2(O)C(CH_3)$=$CH_2$-Derived Polymer as Catalyst. A Parr Instrument Co. 300-mL stainless-steel "Mini" pressure reactor equipped with automatic temperature control, a glass liner, its own heater, and constant-speed stirring motor was used. The reagents, solvent, and catalyst were added to the reactor in a Vacuum Atmospheres HE-43 Dri-Lab glovebox under a nitrogen atmosphere. The glass liner was charged with the catalyst, 1-hexene, and *n*-decane (internal standard), rinsing the vials with toluene (50-mL total each run), and the reactor was sealed as quickly as possible. After removal from the drybox, the reactor was placed in the heating and stirring assembly, pressurized to 1000 psi with the 1:1 H_2/CO mixture, and then the pressure was slowly released again. Repressurization, generally to 850–900 psi H_2/CO, and stirring and heating at 100 °C for a period of 24 h then followed.

After cooling, the reactor was depressurized slowly, and the contents were analyzed by GLC [F & M (Hewlett-Packard) 5750 gas chromatograph (thermal conductivity detector) equipped with a Hewlett-Packard 3380S integrator [6 ft × $^1/_4$ in. SE-30 on Chromosorb W column, 80 °C (1 min) → 200 °C, 10°/min temperature program, helium carrier gas, 80 mL/min flow rate]. Response factors were determined under the same conditions.

During the course of heating and stirring some "spillover" out of the glass liner always occurred. In the initial experiments, this material was analyzed separately. It showed no difference in composition from the material in the glass liner.

In several experiments the charged catalyst was recovered by removing the volatiles at reduced pressure and carrying out filtration chromatography on the brown-green residue (silicic acid, 4:1 pentane/CH_2Cl_2). A brown band was isolated and the material in it

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identified (IR spectrum, melting point) as the original Co cluster catalyst. An immobile green material, which was not identified, always was present on top of the silicic acid pad.

Table I summarizes the experimental details of the catalysis experiments.

Infrared Studies of Hydroformylation Reaction Mixtures. In these experiments, the cooled and depressurized reactor was opened to a nitrogen atmosphere in the drybox, and a sample of the reaction mixture was placed in a 0.1-mm path length NaCl solution cell and sealed from the atmosphere. An IR spectrum was recorded of the $\nu(C{\equiv}O)$ region (2150–1800 cm^{-1}) with a Perkin-Elmer 180 grating infrared spectrophotometer using toluene as the reference solvent. IR spectra also were recorded for pure $PhCCo_3(CO)_9$ and $Co_2(CO)_8$. Table II summarizes these IR data.

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Registry No. **1**, 13682-03-6; **2**, 86846-41-5; **3**, 83835-42-1; **4**, 29890-31-1; **5**, 86853-39-6; **6**, 86846-42-6; **7**, 86846-43-7; **8**, 86846-44-8; **9**, 86846-45-9; **10**, 86846-46-0; $BrCCo_3(CO)_9$, 19439-14-6; p-$CH_3CH(OH)C_6H_4CCo_3(CO)_9$, 86846-47-1; ($p$-$CH_3C(O)C_6H_4C_2C_6H_4C(O)CH_3$-$p$)$Co_2(CO)_6$, 29531-36-0; ($p$-$CH_3C(O)C_6H_4C_2C_6H_5$)$Co_2(CO)_6$, 29531-35-9; $Co_2(CO)_8$, 10210-68-1; $CH_2{=}C(CH_3)C(O)Cl$, 920-46-7; $CH_2{=}C(CH_3)CO_2CH_2CH_2OH$, 868-77-9; 1-hexene, 592-41-6; 1-heptanal, 111-71-7.

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Gold-197 Mössbauer Studies of Some Gold(I) Thiolates and Their Phosphine Complexes Including Certain Antiarthritic Gold Drugs[1]

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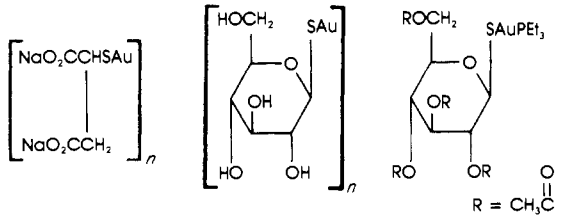
Structural information on 11 gold(I) thiolates and 12 phosphine-coordinated gold(I) thiolates has been collected by using ^{197}Au Mössbauer spectroscopy. The compounds studied include the injectable antiarthritic drugs gold sodium thiomalate (**1**), gold thioglucose (**6**), gold sodium thiosulfate (**11**), and the orally effective (phosphine)gold(I) thiolate auranofin (**15**). Isomer shifts and quadrupole coupling constants indicate that gold atoms in the 1:1 thiolates are sulfur bonded and two-coordinate. These compounds are polymeric in the solid state. This information complements previous solution studies. The Mössbauer spectra of the (phosphine)gold complexes are characteristic and consistent with a monomeric linear SAuP linkage. The spectral parameters (IS, QS) of the phosphine complexes are approximately 2 mm s^{-1} larger than those of the comparable thiolates. The structural and biological significance of these data is discussed.

Introduction

The recent discovery of the antitumor properties of *cis*-diamminedichloroplatinum(II) (*cis*-CDDP) has revived interest in the potential therapeutic applications of metals.[3] Gold compounds, however, have been used successfully, without fanfare, in the treatment of rheumatoid arthritis (RA) for over half a century.[4] Among antirheumatic drugs these chrysotherapeutic agents are unique in that they both relieve symptoms and impede the progressive course of the disease. The two compounds employed most commonly are gold sodium thiomalate (**1**) (Myochrysine) and gold thioglucose (**6**) (Solganal). These water-soluble drugs must be administered by intramuscular injection in order to be effective.



1 **6** **15**

Recently auranofin (**15**) ("Ridaura", Smith Kline & French Laboratories), a triethylphosphine-coordinated gold complex, has been found effective in treating RA when given orally and is presently undergoing extensive clinical investigation.[5] Auranofin's pharmacological[6] and pharmacokinetic[7] profile is distinctly different compared to those of **1** and **6**. Although all three compounds are gold(I) thiolates, these observed biological differences may be due to characteristic physical properties arising from the structural nature of each molecule.

The apparent ligand to gold ratio in **1** and **6** is 1, whereas the gold atom of **15** is two-coordinate as has been shown by X-ray crystallography.[8] Crystals of **1** and **6** suitable for X-ray measurements have remained elusive, so that the molecular structures of these agents are not known in detail despite their extensive clinical use. However, a number of studies (see Discussion) indicate that in solution gold sodium thiomalate (**1**) exists in aggregate form with gold atoms bridging between two sulfur atoms.[9] Similar studies of **6** have been restricted.[10]

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