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Reactions of Silica-Alumina Supported Benzylidynenonacarbonyltricobalt under Hydrogen, Carbon Monoxide, and Synthesis Gas

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The cluster $C_6H_5CCo_3(CO)_9$, containing a capping $C_6H_5C\equiv$ group, was supported on SiO_2-Al_2O_3 by wet impregnation or dry mixing. The fate of the capping group was traced by monitoring the gas-phase liberation of cyclic C_6 and C_7 hydrocarbons under CO, H_2, and CO/H_2 atmospheres. For the wet-impregnated material, the presence of CO favors the cyclic C_6 product (C-C bond cleavage) and inhibits hydrogenolysis of the capping group (C-Co bond cleavage). A model accounting for this behavior proposes that CO inserts between the C-Co bond of intact surface clusters.

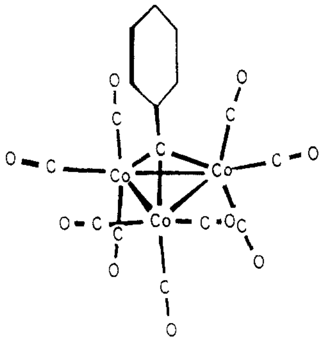
Introduction

Currently there is great interest in the nature of hydrocarbon fragments which are bound to metal surfaces.[1] Surface studies have provided evidence for surface bound CH, CH_2, C_2H_4, CCH_3, and other alkylidyne fragments bound to single crystal faces.[2] Such studies are important to the understanding of mechanisms of heterogeneous catalytic reactions over supported metals where such surface-bound fragments are proposed intermediates.[3]

Our interest has been in heterogeneous Fischer-Tropsch (F-T) synthesis over supported cobalt carbonyl clusters.[4] Surface-bound methine (CH), methylene (CH_2), and methyl (CH_3) fragments have been implicated as intermediates in the F-T synthesis.[5] Strong evidence has been presented for the formation of hydrocarbons via polymerization of methylene units on the surface of supported metal catalysts.[6] An obvious extension of our previous work was to investigate supported $RCCo_3(CO)_9$ clusters.[7] In these organometallic molecules the RC≡ group is bound to the center of a triangle of cobalt atoms, analogous to a 3-fold site on a (111) surface. As our interest is in synthesis gas chemistry, we were particularly interested in determining the fate of the capping RC≡ group for supported $RCCo_3(CO)_9$ under CO, H_2, and CO/H_2 atmospheres.

Benzylidynenonacarbonyltricobalt, **1**, was chosen for support primarily because of its moderate air and thermal stability. Therefore, the cluster core might survive thermal treatments once deposited on the support. Also, the presence of the benzene ring would serve as a chemical label that could be followed in the possible products of its reaction with CO, H_2, and CO/H_2 gases.

In spite of their moderate air and thermal stability the $RCCo_3(CO)_9$ clusters do undergo thermal, oxidative, and reductive decomposition in solution. Treatment of $C_6H_5CCo_3(CO)_9$ in refluxing methanol for 24 h under argon or air gives (diphenylacetylene)hexacarbonyldicobalt, $(PhC{\equiv}CPh)Co_2(CO)_6$, in 63% yield.[8] The cluster is stable in refluxing tetrahydrofuran, ethanol, benzene, and dioxane under nitrogen. Complete decomposition of the cluster occurs in refluxing diglyme under nitrogen in 8 h to give free diphenylacetylene in 25% yield.[9] Oxidation of the cluster with stoichiometric Ce(IV) gives diphenylacetylene in 25% yield and ethyl benzoate.[9] Hydrogenolysis of $C_6H_5CCo_3(CO)_9$ in benzene under 3-4 atm of hydrogen at 85 °C produces toluene as the sole hydrocarbon product.[10] The $C_6H_5CCo_3(CO)_9$ cluster is inert to UV irradiation in solution under hydrogen at room temperature.[11]



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In addition to the degradation studies, $C_6H_5CCo_3(CO)_9$ has been used as a homogeneous catalyst precursor. Mays et al.[12] reported that the cluster is active for the dimerization of norbornadiene. Pittman, O'Connor, and Ryan[13] reported that $C_6H_5CCo_3(CO)_9$ in benzene was active for hydroformylation of 1- and 2-pentene under synthesis gas (H_2/CO = 1 at 840 psi and 90 °C). Further, they reported that the cluster was recovered in high yield. Seyferth and Withers[14] later reported that at best only 60% of the cluster could be recovered after hydroformylation of 1-hexene under similar conditions. On the basis of IR evidence they concluded that cluster degradation occurred to produce $Co_2(CO)_8$ (or possibly $HCo(CO)_4$) as the catalytically active species. In the above experiments the fate of the capping $C_6H_5C\equiv$ group was not determined. Recently Schnelder et al.[15] reported IR and manometric studies on the interaction of $CH_3CCo_3(CO)_9$ with oxide

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supports; again, the fate of the $CH_3C\equiv$ group was not determined.

In this paper attention is focused on the fate of the capping $C_6H_5C\equiv$ group on silica–alumina supported $C_6H_5CCo_3(CO)_9$ under CO, H_2, and CO/H_2 atmospheres on catalysts prepared by pentane impregnation and moderate thermal activation under vacuum. In addition, both gas-phase products and products derived from ether extraction of the supported cluster are reported for $C_6H_5CCo_3(CO)_9/SiO_2–Al_2O_3$ prepared by mechanical mixing of the catalyst precursor and support followed by hydrogen treatment.

Experimental Section

Materials. The $C_6H_5CCo_3(CO)_9$ cluster was prepared by reaction of $HCCo_3(CO)_9$ with diphenylmercury at benzene reflux under a CO atmosphere.[16] Following work-up the crude product was purified by column chromatography (silica gel, hexane eluant) and sublimed prior to use. Purity of the sublimed product was verified by melting point, IR, and proton NMR.

Silica–alumina (425–450 m^2/g, 0.66 cm^{-3}/g) was obtained in the form of $^1/_{16}$ in. pellets from Strem Chemicals. Two forms of the support were used. For wet impregnation from pentane solution, the pellets were used. For mechanical dry mixing of the catalyst and support, the pellets were ground to a coarse powder. In both cases the supports were pretreated by heating in a Vycor tube furnace at temperatures ranging from 500 to 700 °C in flowing argon or oxygen for 18–24 h, followed by evacuation for an additional hour and then cooling to room temperature under argon flow. Water liberated in this process was trapped in a dry ice/acetone trap placed in line after the tube furnace. Water loss was found to be 6.2 wt % for supports treated at 580 °C and 7.0 wt % for supports treated at 700 °C.

All solvents used were reagent grade. Pentane used to deposit the cluster by wet-impregnation was distilled over sodium benzophenone ketyl under nitrogen and stored in a Vacuum Atmospheres drybox (HE-493).

Preparation of Supported $C_6H_5CCo_3(CO)_9$. All preparations of supported $C_6H_5CCo_3(CO)_9$ were carried out in the nitrogen-filled glovebox. The supported cluster was prepared in two ways. First, wet impregnation was carried out by dissolving $C_6H_5CCo_3(CO)_9$ (0.24 g, 0.46 mmol) in 100 mL of oxygen-free pentane. The solution was stirred, and 5 g of the pretreated support was added with stirring. The material was immediately loaded into a Parr 300-mL reactor and sealed. The solvent was removed under vacuum at room temperature over several hours, while the reactor was stirred. The supported cluster was then thermally decarbonylated by heating to 150 °C for an additional hour with stirring under vacuum. This material was then used for studies under CO, H_2, and CO/H_2 atmospheres. Second, dry mixing was carried out by grinding $C_6H_5CCo_3(CO)_9$ and pretreated support (same quantities) in a morter inside a N_2-filled drybox. This dry mix was then immediately loaded into the reactor and used for studies under a H_2 atmosphere.

Product Analysis. Sampling of gaseous products was obtained by expanding the gaseous contents of the reactor into a calibrated volume equipped with a syringe port. Gaseous product analysis was routinely obtained by GC using a Perkin-Elmer Sigma 3 gas chromatograph (FID) equipped with dual packed columns (Porapak Q, 6 ft) operated isothermally (175 °C oven, He flow 50 cm^{-3}/min). Using similar conditions response factors were measured for the following: methane, ethane, propane, *n*-butane, *n*-pentane, *n*-hexane, benzene (B), cyclohexane (C), toluene (T), and methylcyclohexane (M). The response factor for *n*-heptane was determined by extrapolation of response factors for linear C_1–C_6 hydrocarbons. The response factors used for *n*-alkanes were also used for isoalkanes.

Extraction of surface species following hydrogen treatment of dry mixed $C_6H_5CCo_3(CO)_9/SiO_2–Al_2O_3$ was obtained by stirring the solid in 10 mL of diethyl ether in a stoppered flask for 2 h, filtering, and rinsing the filtrate with additional ether. The extraction was carried out in air. The volume of the resulting pale yellow liquid was reduced to approximately 2 mL and used in subsequent GC–MS analysis. The weight loss of the solid material following extraction was 0.4 mg.

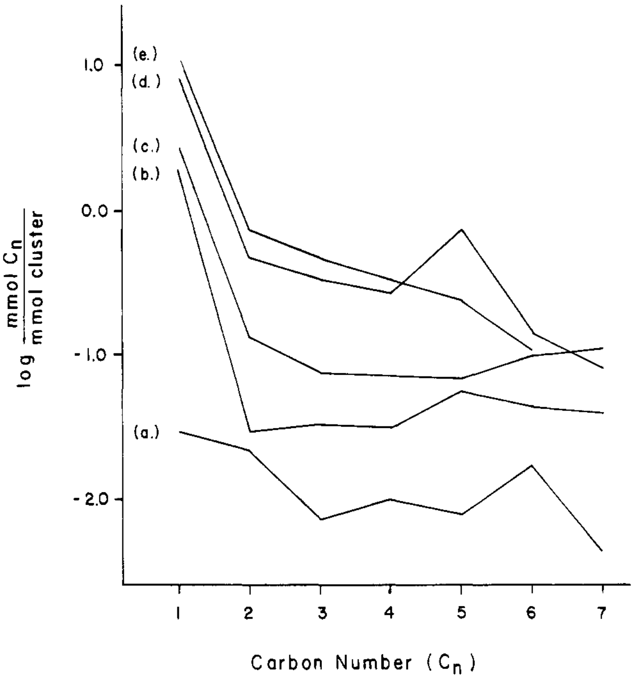

Figure 1. Product distributions for treatments of $C_6H_5CCo_3(CO)_9/SiO_2–Al_2O_3$ prepared by wet impregnation (a–c) and by dry mixing (d,e). Conditions are as follows: (a) CO, 44 psi, 150 °C, 2 h; (b) as in (a) followed by H_2, 45 psi, 150 °C, 2 h; (c) H_2, 44 psi, 150 °C, 2 h; (d) H_2, 40 psig, 150 °C, 2 h; (e) H_2, 40 psig, 150 °C, 6 h.

GC–MS analysis was performed on a HP 5995 GC/MS instrument located in the Department of Oceanography at Texas A&M University. Samples of gas (1000 μL) and liquid (1 μL) were analyzed on a 50 ft fused silica BP-1 capillary column (SGE). Product identification was facilitated by the PBM search routine and NBS/Wiley data base. GC–MS analysis of gas samples was used in the early stages of this work to assist in product identification.

Results of Wet Impregnation

The pentane solution of $C_6H_5CCo_3(CO)_9$ and $SiO_2–Al_2O_3$ pellets is dark brown. Upon removal of the solvent under vacuum, the support is red-brown in color suggesting that the cluster is absorbed intact.[17] Following thermal activation at 150 °C under vacuum the support becomes light gray. Decarbonylation is accompanied by some oxidation of the cluster analogous to the interaction of $CH_3CCo_3(CO)_9$ with silica.[15] In addition, sublimed $C_6H_5CCo_3(CO)_9$ is also observed on the cooling loop inside the reactor after thermal treatment. The amount of sublimed cluster recovered was found to depend on the pretreatment temperature of the support. Thus, 7–12 wt % recovery was found on $SiO_2–Al_2O_3$ treated at 500 °C, 18 wt % recovery at 580 °C pretreatment, and 23 wt % recovery at 700 °C pretreatment. This is not surprising since surface hydroxyl groups can attack metal carbonyls resulting in metal oxidation, proton reduction (to H_2), and CO loss.[18]

CO Treatment. Freshly activated $C_6H_5CCo_3(CO)_9/SiO_2–Al_2O_3$ was heated under 44 psi of CO to 150 °C for 2 h. The distribution of gaseous hydrocarbon products is

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(17) The red-brown coloration of the initially deposited cluster may reflect interaction of $C_6H_5CCo_3(CO)_9$ with Lewis acid sites on the support. Similar coloration is observed in solution during Friedel–Crafts acylation of 1 in the presence of aluminum halides. See: Seyferth, D.; Williams, G. H.; Wehmann, A. T.; Nestle, M. O. *J. Am. Chem. Soc.* **1975**, *97*, 2107.

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Table I. Percentage of Cyclic Hydrocarbons Derived from the $C_6H_5C\equiv$ Capping Group after Reactions of $C_6H_5CCo_3(CO)_9/SiO_2$–Al_2O_3

		mol % of $C_6H_5C\equiv$ converted to						
preparation method	treatment[a]	benzene	toluene	cyclohexane	methyl cyclohexane	total	c-C_6[b]/c-C_7	% cyclo[c] selectivity
wet impregnation	CO	1.7	0.5			2.2	3.4	100
wet impregnation	CO → H_2			3.4	3.8	7.2	0.9	82
wet impregnation	H_2			4.7	9.1	13.8	0.5	60
wet impregnation	H_2 → CO/H_2			2.4	0.7	3.1	3.4	7
wet impregnation	CO/H_2	2.3	0.3			2.6	7.6	4
dry mixed	H_2, 2 h			3.0	6.0	9.0	0.5	41
dry mixed	H_2, 6 h			0.02		0.02		<1

[a] The "→" denotes sequential reactions. Entries in the table are not cumulative and represent results of the last reaction in sequence. [b] Benzene/toluene or cyclohexane/methylcyclohexane. [c] Mol % of cyclic C_6 and C_7 cyclic hydrocarbons in the total C_6 and C_7 products.

shown in Figure 1a. The distribution is rather flat and is made up of C_1–C_5 alkanes. The C_4 and C_5 fraction contains 50 mol % branched isomers. As no C_6 or C_7 alkanes are observed, these low molecular hydrocarbons are probably derived from cracking and isomerization of residual pentane used to deposit the cluster. Benzene (B) and toluene (T) are the sole C_6 and C_7 gaseous species observed in a B/T ratio of 3.4. Taken together these cyclic hydrocarbons account for 2.2 mol % of the capping group charged (Table I). The aromatics no doubt originate from the cluster precursor; however, it cannot be determined whether they are desorbed from surface-bound intact clusters or cluster fragments. It is clear that in a hydrogen poor environment cleavage of the C–C bond in the cluster to give benzene requires less hydrogen than hydrogenolysis of three C/Co bonds to give toluene. It should also be mentioned that after thermal decarbonylation, trace amounts (less than 5 mol %) of benzene and toluene were trapped and were present in B/T ratios of about 2.5 as measured by NMR.

If the reactor is evacuated and recharged with 45 psi of H_2 and heated to 150 °C for 2 h, a product distribution shown in Figure 1b is obtained. In general, more hydrocarbons are liberated from the surface. Methane formation is particularly high (1.9 mmol of CH_4/mmol of cluster charged). Both linear and branched C_1–C_6 hydrocarbons are present. The only C_7 hydrocarbon is a branched isomer. The C_4–C_7 isomer selectivity is 32 mol %. Instead of benzene and toluene, cyclohexane (C) and methylcyclohexane (M) are present in a C/M ratio of 0.9 and account for 82 mol % of the C_6 and C_7 fractions. Together, these cycloalkanes represent an additional 5.0 mol % of the capping group charged (Table I).

In the presence of excess hydrogen, hydrogenation of the phenyl ring derived from the cap occurs readily. The presence of C_6 and C_7 aliphatic hydrocarbons and increased amounts of lower molecular weight hydrocarbons indicates that secondary reactions such as ring opening, hydrocracking, and isomerization reactions are also occurring (vide infra).

H_2 Treatment. Freshly activated $C_6H_5CCo_3(CO)_9/SiO_2$–Al_2O_3 was reacted directly with 44 psi of H_2 for 2 h at 150 °C. The distribution of gas-phase products is shown in Figure 1c. Direct hydrogenation of this material liberates significantly more hydrocarbon from the surface than hydrogenation following CO treatment. Methane is particularly high at 2.8 mmol of CH_4/mmol of cluster charged. Both linear and branched C_1–C_6 hydrocarbons are present. Isoheptanes are the only aliphatic C_7 hydrocarbons. Overall C_4–C_7 isomer selectivity is 60 mol %. Cyclohexane and methylcyclohexane are present in a C/M ratio of 0.5 and account for 60 mol % of the C_6 and C_7 fraction. Together, these cyclic hydrocarbons account for 13.8 mol % of the benzylidyne cap charged (Table I).

Although the product distribution curves in parts b and c appear similar, the direct hydrogen treatment results in an increase of gas-phase hydrocarbon products of 57 mol % compared to $C_6H_5CCo_3(CO)_9/SiO_2$–Al_2O_3 which was exposed to CO and then H_2. In particular, direct hydrogenation produces more *i*–C_7, *i*- and *n*-C_6 alkanes, and more methylcyclohexane.

The absence of *n*-heptane suggests that isoheptane derives from hydrogenation and hydrogenolysis of the capping $C_6H_5C\equiv$ group to produce methylcyclohexane which can undergo ring opening at acidic sites on the support. Selective cracking of the resulting alkanes (or alkenes) to methane occurs readily (presumably at cobalt sites) accounting for the high production of methane in parts b and c of Figure 1.

Another possibility exists for the high production of methane in Figure 1b. For $C_6H_5CCo_3(CO)_9/SiO_2$–Al_2O_3 treated first with CO and then with H_2, the direct hydrogenation of CO may account for much of the methane in this case. Consumption of hydrogen to reduce CO vs. hydrogenolysis of the capping group would explain the failure to produce substantial amounts of products derived from the capping group and the greater C/M ratio for the CO → H_2 sequence than under direct hydrogenation (Table I).

CO/H_2 Treatment. Support for some of these observations is obtained from studies of $C_6H_5CCo_3(CO)_9/SiO_2$–Al_2O_3 under CO/H_2 atmospheres. In the Fischer–Tropsch (F–T) experiments the reactor was charged with synthesis gas (H_2/CO = 2.1, 75-psi total pressure) and heated to 150 °C. Two experiments are reported. In the first, the supported cluster was treated in hydrogen as above (H_2 treatment) prior to the F–T experiment. In the second, the supported cluster was charged with the synthesis gas mixture directly after activation. The product distributions in both experiments are shown in Table II.

The supported $C_6H_5CCo_3(CO)_9$ cluster is an active Fischer–Tropsch catalyst. The prereduced material is more active as evidenced by a greater turnover number obtained at higher CO conversion. Both catalysts produce linear and branched C_1–C_7 alkanes of the same average chain length and similar isoselectivity. The most interesting feature is in the cyclic hydrocarbons which are present. The prereduced catalyst produces cyclohexane and methylcyclohexane in a C/M ratio of 3.4. These cycloalkanes make up 6.9 mol % of the C_6 and C_7 fraction (Table I). In contrast, treatment of the supported cluster directly with the synthesis gas mixture liberates benzene and toluene in a B/T ratio of 7.6. No cyclohexane or methylcyclohexane are observed in spite of the fact that hydrogen is a coreactant. The aromatics accounted for 4.1 mol % of the C_6 and C_7 fractions (Table I).

The cyclic hydrocarbons observed in the CO/H_2 experiments are thought to derive from the capping benzy-

Table II. Distribution of Gas-Phase F-T Products over $C_6H_5CCo_3(CO)_9/SiO_2-Al_2O_3$ Prepared by Wet Impregnation[a]

treatment	turnover no.[b]	mmol of hydrocarbon/mmol of cluster charged											$\bar{C}_n$[c]	% C_4-C_7 isom.
		C_1	C_2	C_3	C_4	C_5	C_6	C_7	B	T	C	M		
prereduced	12.8 (98)	13.0	2.3	2.1	1.6	1.0	0.30	0.13			0.02	0.007	1.9	50
none	11.7 (75)	11.6	1.5	1.4	1.5	1.3	0.43	0.18	0.02	0.003			1.9	55

[a] $H_2/Co = 2.1$ (75-psi total pressure), 150 °C. [b] Turnover number = $\sum nC_n$ mmol/mmol of Co charged where n is the number of carbon atoms in hydrocarbon C_n. (The present conversion at which turnovers were obtained = $10 \times \sum nC_n$ mmol/mmol of CO charged.) [c] $\bar{C}_n$ (average carbon number) = $\sum nC_n$ mmol/$\sum C_n$ mmol.

lidyne group and not from the F–T synthesis for two reasons. First, the linear and branched chain C_1-C_7 hydrocarbons formed as a result of F–T synthesis are present in quantities more than 2 orders of magnitude greater than those present under CO alone, while benzene and toluene are present in similar quantities. Secondly, it is significant that only saturated cycloalkanes are observed on the prereduced sample while only unsaturated aromatic hydrocarbons are present when the supported cluster is treated directly with synthesis gas. In both experiments, sufficient hydrogen is present in the CO/H_2 charge to completely saturate and hydrogenate all the capping group charged.

The competitive nature of CO vs. capping group hydrogenation is demonstrated by close examination of Table I. Entries one and five indicate the aromatic selectivity in the presence of CO. The benzene/toluene ratio is greater under CO/H_2 (7.6) than under CO alone (3.4). Carbon–carbon hydrogenolysis of the cap to produce benzene requires less hydrogen than C–Co hydrogenolysis to produce toluene yet benzene is favored to a greater extent under CO/H_2. Clearly hydrogen is preferentially consumed in the F–T synthesis. Similar results can be seen for the selective liberation of cycloalkanes in the presence of H_2. Direct hydrogen treatment converts 13.8 mol % of the cap with selectivity to methylcyclohexane; the C/M ratio is 0.5. Addition of CO/H_2 to the reduced material liberates an additional 3.1 mol % of the cap only now the formation of cyclohexane predominates; the C/M ratio is 3.4. Although in both cases ring hydrogenation occurs readily, the consumption of hydrogen during F–T synthesis occurs to such an extent (98% CO conversion) that C–Co hydrogenolysis is inhibited.

Results of Dry Mixing

Supported $C_6H_5CCo_3(CO)_9$ prepared by dry mixing was investigated because the measured conversion of cluster carbon derived from the wet-impregnated material after direct H_2 treatment was only 34%. Some of the cluster carbon (ligand CO) is liberated during solvent removal and thermal activation under vacuum. As was noted earlier, benzene and toluene derived from the capping group were present in the liquid-nitrogen trap after thermal decarbonylation. It was therefore desirable to prepare a system free from vacuum exposure and to see if quantitative recovery of cluster carbon could be obtained.

Upon initial mixing the white $SiO_2-Al_2O_3$ becomes peppered with the dark brown $C_6H_5CCo_3(CO)_9$. After gentle grinding the support becomes gray with uniformly distributed pink regions. This preparation apparently results in immediate breakdown of the cluster, the pink color suggesting the presence of octahedrally coordinate Co(II) ions. This material was immediately loaded into the reactor for subsequent reaction under hydrogen.

H_2 Treatment. The freshly mixed catalyst was treated directly with 40 psig of H_2 at 150 °C. Hydrogen treatment of dry mixed materials are reported for 2- and 6-h periods. The product distributions are shown in parts d and e Figure 1. In both cases, the conversion of carbon derived from the cluster to gas-phase hydrocarbon is essentially quantitative. After 2 h, the major product is methane at 8.6 of mmol CH_4/mmol of cluster charged. This methane may result from hydrogenation of the 9 CO ligands/cluster in the precursor. In addition, C_1-C_7 aliphatic hydrocarbons are present with 20 mol % isoselectivity. The only C_7 hydrocarbon present is a branched isomer. Cyclohexane and methylcyclohexane are present in a ratio of 0.5, similar to that observed on direct hydrogenation of the wet-impregnated material. The cycloalkanes account for 41 mol % of the C_6 and C_7 fraction, significantly less than the 60 mol % observed on the wet-impregnated material. Taken together these cyclic hydrocarbons represent only 9 mol % of the capping group charged compared to 13.8 mol % for the wet-impregnated material (Table I). Most the product hydrocarbon is aliphatic which suggests that extensive cracking of the capping group has occurred.

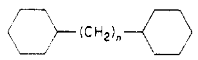
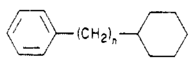
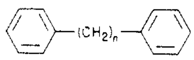
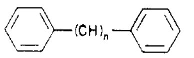
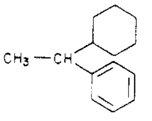
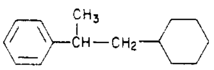
After 6 h under hydrogen over freshly mixed $C_6H_5CCo_3(CO)_9/SiO_2-Al_2O_3$, the product distribution has shifted even further toward low molecular weight hydrocarbons. The average carbon number of gaseous products is 1.3 compared to 1.6 at 2 h. Methane is present at 11.6 mmol of CH_4/mmol of cluster charged. The only alkanes present are C_1-C_6 with isomer selectivity of 33 mol %. The only cyclic hydrocarbon present is cyclohexane making up 0.1 mol % of the C_6 fraction and accounting for only 0.02 mol % of the capping group. The change in product distribution with time under hydrogen clearly demonstrates hydrocracking of the capping group at high conversion on dry mixed materials.

Surface-Extracted Species. The decomposition of the $C_6H_5CCo_3(CO)_9$ cluster during mixing was apparent. Although the gas-phase hydrocarbons resulting from H_2 treatment accounted for essentially all of the carbon charged from the cluster, it was of interest to see if any cluster degradation products were present on the surface. Diphenylacetylene has been observed in oxidative and thermal degradation studies of $C_6H_5CCo_3(CO)_9$ in solution.[9] High molecular weight degradation products would be expected to reside on the surface and not appear in the gas-phase studies.

Ether extraction of the dry mixed sample, which had been treated for 2 h under H_2, resulted in a weight loss of 0.4 mg, less than 0.1 wt % of the cluster charge. Results of GC/MS analysis of the concentrated ether extract are presented in Table III. The entries in Table III were derived from selected ion searches of species containing cyclohexyl or aromatic groups. Other species were present, primarily long-chain hydrocarbons. Species were identified by using the PBM search routine and the NBS/Wiley data base. The results are not quantitative, however, and the table includes base peak intensities as a crude measure of relative quantities. Most of the products result from diphenylacetylene in various stages of hydrogenation, but diphenylacetylene itself was not found.

In solution the formation of free diphenylacetylene from $C_6H_5CCo_3(CO)_9$ has been explained by coupling of free C_6H_5C: radicals or direct transfer of the C_6H_5C: fragment from an intact cluster (or cluster fragment) to another

Table III. GC-MS of Surface Extracted Species after Hydrogenation of Dry Mixed $C_6H_5CCo_3(CO)_9/SiO_2$-Al_2O_3

species	*n*	base peak intensity, au
	2, 3	1500, 10000
	2	1600
	3	10000
	2	680
		5300
		3600

cluster.[19] On the silica–alumina surface, the gentle grinding during dry mixing of the cluster and support apparently resulted in degradation of the cluster. It is possible that surface diphenylacetylene was generated during this process and subsequently hydrogenated to give some of the species shown in Table III.

Perhaps more interesting is the observation of two C_6 rings linked by three carbon atoms. Direct coupling of two radical capping fragments can only produce a 2-carbon link. Incorporation of additional carbon from ligand CO or cracked cap products must have occurred during mixing or following H_2 treatment. The species containing 3-carbon links are apparently present in greater yield than species containing 2-carbon links.

Discussion

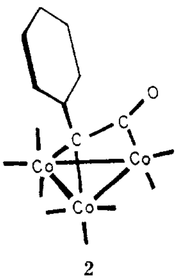
The preference for hydrogenolysis of C–C vs. C–Co bonds in $C_6H_5CCo_3(CO)_9/SiO_2$–Al_2O_3 can be ordered according to the ratio of gas-phase C_6 ring products to C_7 ring products in treatments involving H_2 over the wet-impregnated material. The order of treatments in decreasing C_6/C_7 ratio is

$$CO/H_2 > H_2 \rightarrow CO/H_2 > CO \rightarrow H_2 > H_2$$

The C_6/C_7 ratio is less than one for direct H_2 treatment where C–Co bond hydrogenolysis and phenyl ring hydrogenation occurs more readily than C–C bond hydrogenolysis.

In any treatment or sequence of treatments involving CO, the C_6/C_7 ring ratio is one or greater (Table I). The presence of CO therefore inhibits C–Co bond cleavage. Similar results have been reported for the hydrogenolysis of $(CH_3)_3CCCo_3(CO)_9$ in solution. Under H_2/CO atmosphere the hydrogenolysis is inhibited and the CO insertion product, $(CH_3)_3CH_2COH$, is observed.[10]

A possible surface intermediate which would explain the above sequence is the CO-inserted surface species **2**.



2

Migratory insertion reactions are well-known for alkylcobalt species; for example, equilibrium is rapidly established between $PhCH_2Co(CO)_4$ and $PhCH_2COCo(CO)_4$ in an atmosphere of CO at 20 °C.[20] In **2** the insertion of CO has two effects. First hydrogen attack can occur at CO or at the apical carbon atom and its substituent phenyl ring. Second the insertion may force the benzene ring to tilt toward equatorial CO ligands bound to the other metals, and so steric factors may contribute to a weakening of the phenyl carbon–apical carbon bond. Phenyl ring–apical carbon bond hydrogenolysis must occur more readily than CO hydrogenation, since neither ethylbenzene nor ethylcyclohexane are observed in the gas phase.

The formation of **2** may be faciliated by nearby Lewis acid sites (Al^{3+}) on the silica–alumina surface. Aluminum alkyls and halides can induce terminal CO ligands to shift to bridging positions in binuclear metal carbonyls.[21] In fact the cluster $PhCOCCo_3(CO)_9$ is formed from $ClCCo_3(CO)_9$ and benzene in the presence of the Lewis acid $AlCl_3$ via the formation of the acylium ion $(CO)_9Co_3CCO^+$, in which a terminal CO bound to cobalt has migrated to the capping carbon atom.[22]

The decreasing order of C_6/C_7 ring ratio may be explained in terms of **2**. Under CO/H_2 the formation of **2** on the surface stabilizes the apical carbon by forming a C–C bond, the strength stabilizes the apical carbon by forming a C–C bond, the strength of which would increase as the inserted CO is reduced to –CH(OH)– and perhaps $-CH_2-$. The phenyl carbon–apical carbon bond may be weakened upon insertion due to steric strain caused by tilting of the capping group to accommodate the inserted CO. Thus CO insertion would favor a high C_6/C_7 ring ratio. As hydrogen is preferentially consumed in CO reduction, hydrogenation of the phenyl ring is also inhibited and so benzene is liberated in preference to toluene or methylcyclohexane.

In the sequence of treatments $H_2 \rightarrow CO/H_2$, **2** is formed in the last step. In this case the C_6/C_7 ring ratio is less than that for direct CO/H_2 treatment. This is because the greater conversion of CO (98%) on the prereduced catalyst reduces the concentration of **2** on the surface. Since the material was prereduced, the amount of unreacted hydrogen (i.e., that not appearing in gas-phase products) on the surface is 60% greater than that under direct CO/H_2 treatment. Therefore, hydrogenation of the benzene ring occurs readily. Also, residual hydrogenated rings are presumably present on the surface after the prior reduction step. These species may contribute to the gas-phase products after the subsequent CO/H_2 treatment.

In the reaction sequence $CO \rightarrow H_2$, **2** is formed on the surface during exposure to CO pressure. No doubt the formation of **2** is sensitive to CO pressure and upon evacuation much of **2** would revert to surface bound **1**. Admission of H_2 then results in hydrogenation and hydrogenolysis of both surface **1** and **2** resulting in a C_6/C_7 ring ratio of 0.9.

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[19] Seyferth, D.; Rudie, C. N.; Merola, J. *J. Organomet. Chem.* **1978**, *162*, 89.

[20] Nagy-Magos, Z.; Bor, G.; Marko, L. *J. Organomet. Chem.* **1968**, *14*, 205.

[21] Shriver, D. F. *Acc. Chem. Res.* **1970**, *3*, 231.

[22] It is tempting to consider surface bound $PhCOCCo_3(CO)_9$ as a possible intermediate. This cluster has the ability to reversibly add molecular H_2 to the inserted CO (giving the alcohol) under CO/H_2 at benzene reflux. Under nitrogen at benzene reflux the alcohol releases both H_2 and CO to give **1**. Additionally $PhCOCCo_3(CO)_9$ will decarbonylate giving CO and **1**. See: Seyferth, D.; Nestle, M. O. *J. Am. Chem. Soc.* **1981**, *103*, 3320. The formation of $PhCOCC_3(CO)_9$ from **1** under CO pressure has not been observed suggesting that **2** is a more likely surface intermediate. Carbonylation reactions of $RCCo_3(CO)_9$ clusters under CO pressure result in products where CO insertion occurs between the C–Co bond of **1**. See: Tominaga, K.; Yamagami, M.; Wakamatsu, H. *Tetrahedron Lett.* **1970**, 2217.

Surface species arising from the decomposition of 1 might also be considered as precursors for the observed gas-phase cyclic hydrocarbons. These include $(PhC\equiv CPh)Co_2(CO)_6$, a known intermediate in the thermal decomposition of 1 in solution,[19] and free diphenylacetylene. Hydrogenated diphenylacetylenes were seen on the surface of the dry mixed material after H_2 treatment at quantitative conversion of the capping group. However, they were present in small quantities and could have been produced during dry mixing as was noted.

The $(PhC\equiv CPh)Co_2(CO)_6$ complex is stable under CO/H_2 in solution at room temperature for 3 months.[23] At moderate temperatures under CO pressure, $(RC\equiv CR)Co_2(CO)_6$ complexes give cyclopentadienones, R_4C_5O.[24] These high molecular weight species would be expected to reside on the surface.

At present, it is difficult to explain the cyclic C_6/C_7 ring ratios in terms of surface precursors other than 2. Further studies are in progress and include H_2, CO, and CO/H_2 treatments of materials prepared by wet impregnation of $(PhC\equiv CPh)Co_2(CO)_6$, solutions containing both $Co_2(CO)_8$ and diphenylacetylene and diphenylacetylene itself.

Acknowledgment. We gratefully acknowledge the Center for Energy and Mineral Resources at Texas A&M University for support of this work. We also thank Ms. LeaAnn Smith for preparing most of the $PhCCo_3(CO)_9$ used in this study and Dr. James Brooks and Mr. Tom McDonald for the GC–MS results.

Registry No. 1, 13682-03-6; SiO_2, 7631-86-9; Al_2O_3, 1344-28-1; H_2, 1333-74-0; CO, 630-08-0; C_6H_6, 71-43-2; $C_6H_5CH_3$, 108-88-3; c-C_6H_{12}, 110-82-7; c-$C_6H_{11}CH_3$, 108-87-2; c-$C_6H_{11}CH_2CH_2C_6H_{11}$-c, 3321-50-4; c-$C_6H_{11}CH_2CH_2CH_2C_6H_{11}$-c, 3178-24-3; $PhCH_2CH_2C_6H_{11}$-c, 1603-61-8; $PhCH_2CH_2CH_2Ph$, 1081-75-0; $PhCH{=}CHPh$, 103-29-7; c-$C_6H_{11}CH(CH_3)Ph$, 4413-16-5; c-$C_6H_{11}CH_2CH(CH_3)Ph$, 78811-31-1.

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Cyanonickel(II) Complexes as Catalysts for the Phase-Transfer-Catalyzed Carbonylation of Allyl Halides. The Isolation of the Catalytically Active Species $[Ni(CO)_3CN^-]$

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Allyl chlorides and bromides can be carbonylated to acids by cyanonickel(II) catalysts under phase-transfer-catalysis conditions. The most useful catalyst precursor is nickel cyanide, and the key catalytic species is believed to be the cyanotricarbonylnickel anion. The latter was isolated and characterized as the bis(triphenylphosphine)nitrogen(1+) salt.

Although the chemistry of transition-metal cyano complexes has been extensively investigated, few reactions are known in which such complexes function as catalysts.[1] Carbonylation reactions are especially intriguing in this regard, due to the similarity in the properties of low valent transition metal complexes containing the isoelectronic cyano and carbonyl ligands. The mechanism of the *stoichiometric* carbonylation of benzylic bromides by hexacyanodinickelate(I)[2] has been studied and is believed to proceed via the intermediacy of $[Ni(CN)_2(CO)_2]^{2-}$.[3] Carbonylation can be accompanied by reduction, coupling, or displacement of X^- by cyanide ion. The stoichiometric carbonylation $[Ni(CN)(Ph)(P)_2]$ (P = tertiary phosphine) complexes affording benzoyl cyanide has also been examined.[4]

Phase-transfer catalysis is an important technique in organic chemistry[5,6] and has in recent years been applied to metal-catalyzed reactions.[7] In carbonylation reactions catalyzed by cobalt, rhodium, iron, and ruthenium carbonyls, one can take advantage of the fact that the reactivity of hydroxide ion, under phase-transfer conditions, far exceeds that in dilute aqueous solution,[8] thus promoting the generation (and regeneration) of carbonylmetalate anions (the real catalytic species) from the neutral carbonyls or higher valent metal compounds and carbon monoxide.

Foâ and Cassar reported the carbonylation of allyl chlorides under phase-transfer conditions, using nickel tetracarbonyl as the catalyst.[9] Mixtures of unsaturated acids of *undefined* stereochemistry were obtained in 67–85% yield, after 6–10 h at 25–45 °C and 1 atm, using Aliquat 336 or benzyltriethylammonium chloride as the phase-transfer agent. It was shown that under these reaction conditions nickel tetracarbonyl is reduced by carbon monoxide and hydroxide ion to the known[10] cluster anions

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