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HYDROCARBON FORMATION ON POLYMER-SUPPORTED COBALT

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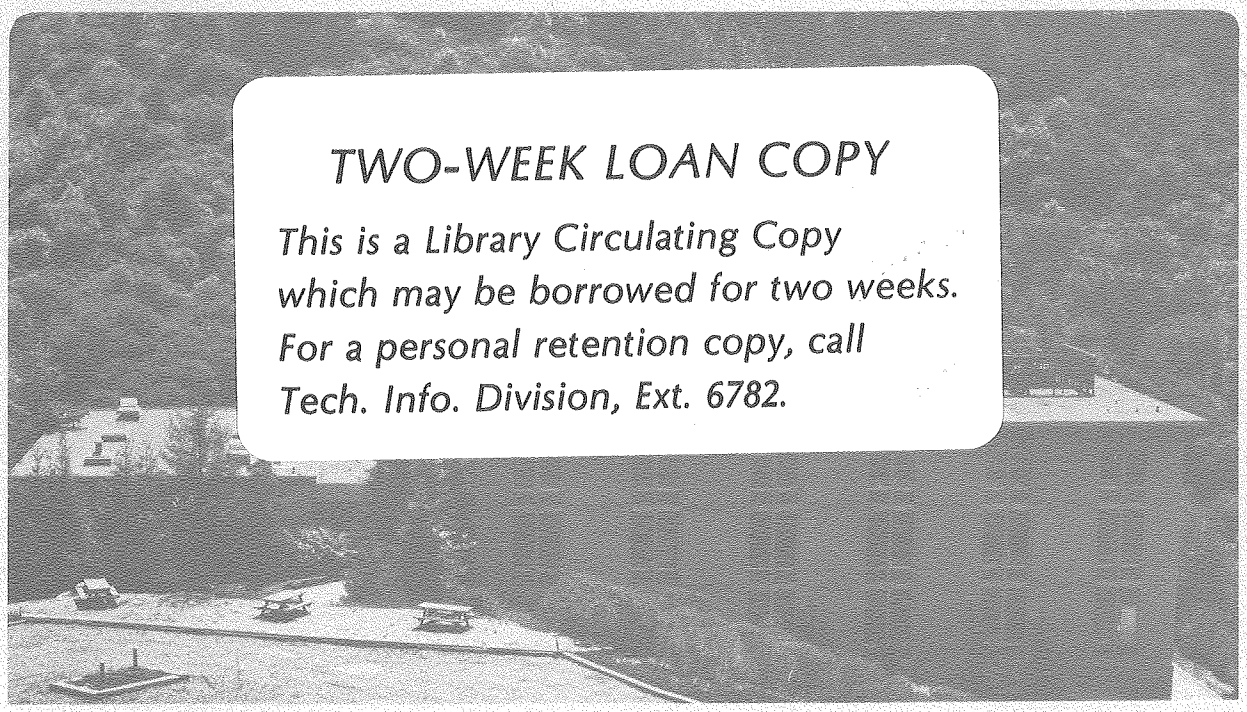

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Hydrocarbon Formation on Polymer-Supported Cobalt

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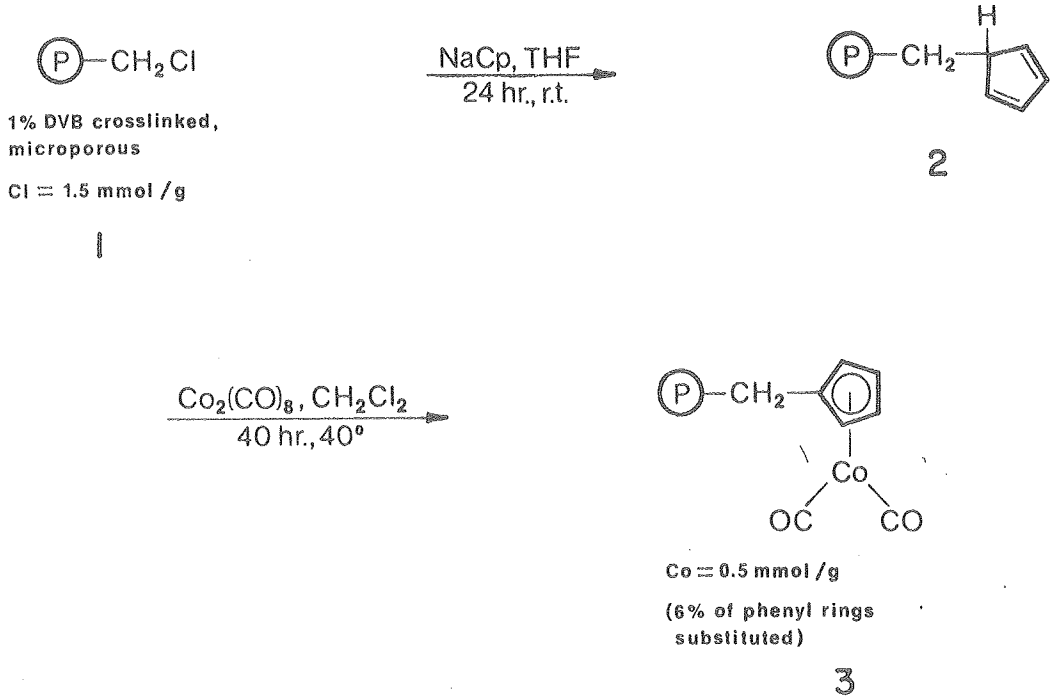
There has been considerable recent research interest in the activation of carbon monoxide en route to more complex organic molecules. Among the various reactions that have been investigated and/or newly discovered, the transition metal catalyzed reduction of CO to hydrocarbons (Fischer-Tropsch synthesis) has enjoyed particular attention (1-9). Whereas most of the successful efforts in this area have been directed toward the development of heterogeneous catalysts, there are relatively few homogeneous systems. Among these, two are based on clusters (10,11) and others are stoichiometric in metal (12-17). In this report we detail the synthesis and catalytic chemistry of polystyrene ((P)) supported η^5-cyclopentadienyl-dicarbonyl cobalt, $CpCo(CO)_2$. This material is active in the hydrogenation of CO to saturated linear hydrocarbons and appears to retain its "homogeneous", mononuclear character during the course of its catalysis.

Since cobalt on kieselguhr is one of the original Fischer-Tropsch catalysts (1-9), it appeared attractive to investigate the catalytic activity of cobalt complexes immobilized on polystyrene. Although there are many supported cobalt-based Fischer-Tropsch catalysts known (see, for example, references 18-21) no polystyrene-bound systems had been reported. During the course of our work 18% (22) and 20% (23) crosslinked analogs of (P) $CpCo(CO)_2$ were shown to exhibit limited catalytic activity and no CO activation. A preliminary disclosure of our work has appeared (24).

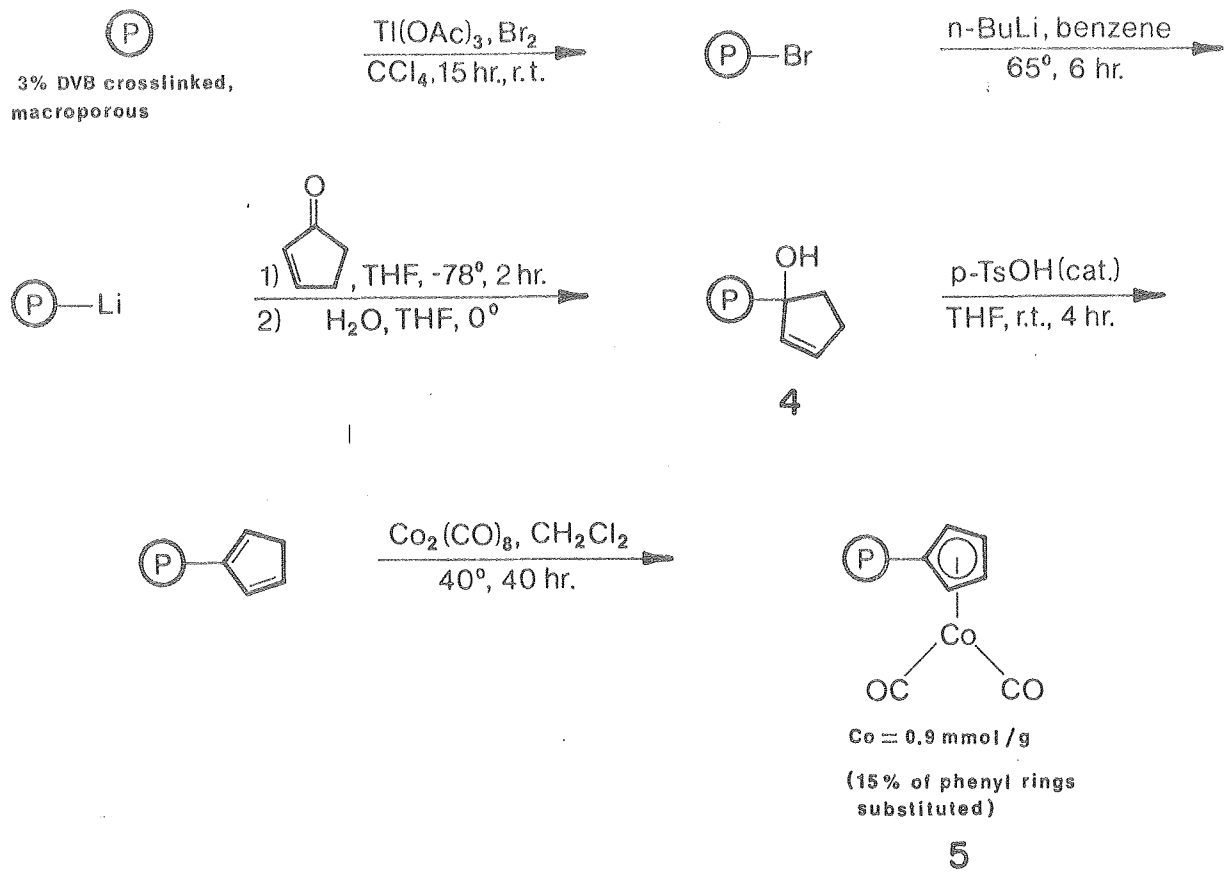
Synthesis of Polystyrene Supported Catalysts

(P) $CH_2CpCo(CO)_2$ 3 and (P) $CpCo(CO)_2$ 5 were prepared utilizing the procedures of Grubbs et al. for the syntheses of polystyrene-bound cyclopentadiene (25) and Rausch and Genetti for the synthesis of $CpCo(CO)_2$ (26). Thus, for 3, commercially available (P) CH_2Cl (1% DVB, microporous, 1.48 mmol Cl/g. resin) was treated with excess NaCp to form (P) CH_2CpH 2. This was then reacted with $Co_2(CO)_8$ to form desired compound 3 (0.3-0.5 mmol Co/g. resin, ca. 6% of phenyl rings substituted); Soxhlet extraction (benzene or CH_2Cl_2) was used in an attempt to remove non-attached species. Resin 3 showed the characteristic IR absorptions of an $M(CO)_2$ complex: 2012 and 1954 cm^{-1} (KBr); compare with $CpCo(CO)_2$: 2033 and 1972 cm^{-1} (cyclohexane); 2017 and 1954 cm^{-1} (acetone) (27).



A problem associated with this procedure is the difficulty in removing excess reagents from the microporous resin. The chloride content was fairly high (0.25 mmol/g., ca. 15% of original) in (P)CH_2CpH 2; as no chloromethyl absorbance was seen in the IR, this implied that NaCl was trapped in the resin. Elemental analysis (C, 88.90%; H, 7.47%; Cl, 0.90%; total, 97.27%) suggested the presence of other impurities, which appeared to persist even after extensive extraction with solvent (THF-ethanol).

Assuming that the hydrophobic and nonionic nature of the polystyrene matrix prevented infiltration by solvent, an alternative synthesis was devised starting with macroporous 3% crosslinked polystyrene. This resin was first washed (28) with: CH_2Cl_2, THF, THF saturated with lithium aluminum hydride, THF, twice with 1M HCl (97°C), 1M KOH (75°C), 1M HCl (75°C) three times with H_2O (75°C), DMF (40°C), twice with H_2O, 1M HCl (80°C), H_2O (80°C), methanol, methanol/CH_2Cl_2 (1/1), methanol/CH_2Cl_2 (1/3), and CH_2Cl_2. After drying in vacuo (70°C, 24 hr.), the resin was brominated using 1.05 equivalents bromine with $Tl(OAc)_3$ as a catalyst (29). Cream-white (P)Br showed 99% substitution (43.44% Br, 5.44 mmol/g.) at the para ring position (IR). If anhydrous conditions were not used in the bromination, a heterogeneous mixture of beads ranging from red-brown to white in color was obtained.



Lithiation was achieved using two portions of n-butyllithium (n-BuLi), three equivalents each, at 65°C in benzene under nitrogen atmosphere (29). The brown (P) Li was not isolated due to its extreme reactivity; bromine analysis on the final product, (P) $CpCo(CO)_2$ 5, however, proved that the lithiation at this step was essentially complete (0.1 mmol residual Br/g. resin). Upon addition of 2-cyclopentenone in THF at -78°C (1.01 equivalents, syringe pump addition over 2h), the brown color changed gradually to beige. Warming to room temperature followed by quenching with ice-cold H_2O yielded cyclopentenol derivative 4 (IR (KBr), 3425 and 1047 cm^{-1}). Some unsubstituted phenyl rings and presumably 3-(polystyryl)cyclopentanone (IR (KBr), 1730 cm^{-1}, result of conjugate addition of (P) Li to 2-cyclopentenone) were noted. Addition of excess enone gave no increase in ring substitution; faster addition or higher reaction temperature (0°C) yielded a higher proportion of cyclopentanone formation (IR).

Vacuum dehydration of 4 was unsuccessful (0.005 torr, temperatures from 65-190°C, 24 hr.) in contrast to other reports (25, 30). However, mild treatment (31) with p-toluenesulfonic acid (THF, 25°C, 4h) produced the desired (P)CpH (IR (KBr), 675 cm^{-1}, loss of bands due to 4). Higher temperature (60°C) or longer reaction times caused discoloration (black resin).

Reaction of (P)CpH with excess $Co_2(CO)_8$ (CH_2Cl_2, 40°C, 40-48 h) yielded (P)$CpCo(CO)_2$ 5 (0.8-1.0 mmol Co/g., IR (KBr), 2012 and 1953 cm^{-1}). Residual $Co_2(CO)_8$ was removed via Soxhlet extraction with benzene or CH_2Cl_2. Interestingly, reaction of 4 with $Co_2(CO)_8$ yielded 5 directly and as efficiently. Apparently, dehydration of 4 occurred under these conditions. The "overall yield" (based on cobalt incorporation) for this synthetic sequence is 15%.

The relatively low percentage of ring substitution can be attributed to several side reactions: 1,4-addition of (P)Li to 2-cyclopentenone, incomplete dehydration of 4 as evidenced by the presence of a small hydroxyl absorption (3425 cm^{-1}) in the IR spectrum of 5, and reduction of the polymer-bound cyclopentadiene in its reaction with $Co_2(CO)_8$ (26, 27, 32).

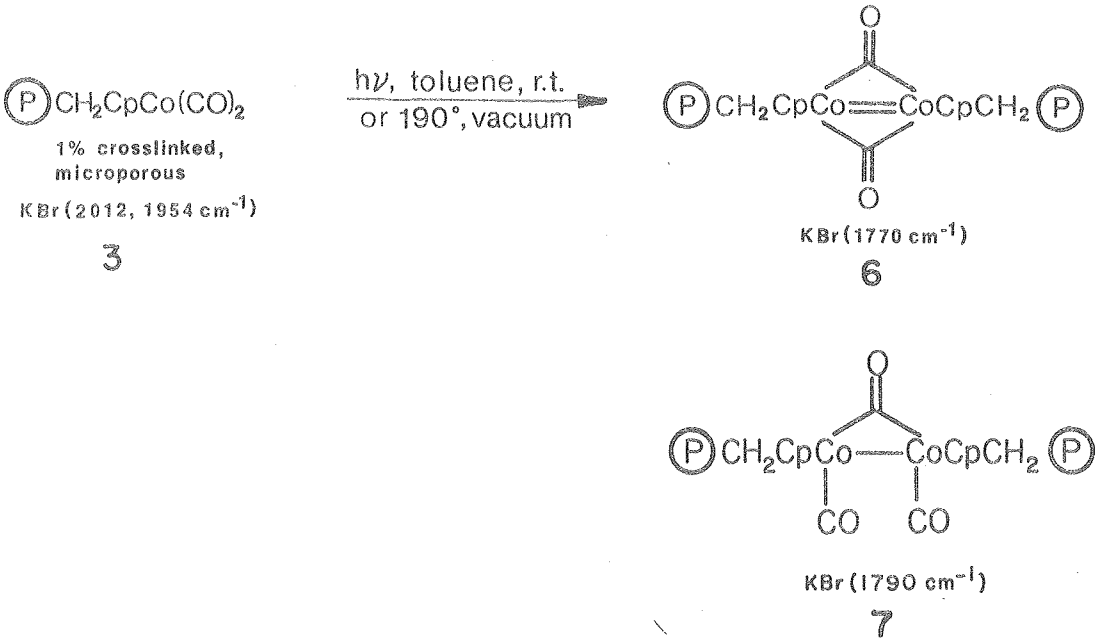
Resin 3 is light orange in color when dry; 5 is tan. Both turn dark brown in a swelling solvent. Exposure of either resin to air slowly results in a grey-green color due to oxidation, but 28% of the resin-bound $CpCo(CO)_2$ is left after one month's exposure (IR).

Thermal and Photochemical Decarbonylation

A brief investigation of the potential thermal and photolytical chemistry of resins 3 and 5 was undertaken. It was prompted by a report of the observation of site-site isolation on irradiation of 18% crosslinked 3 (22).

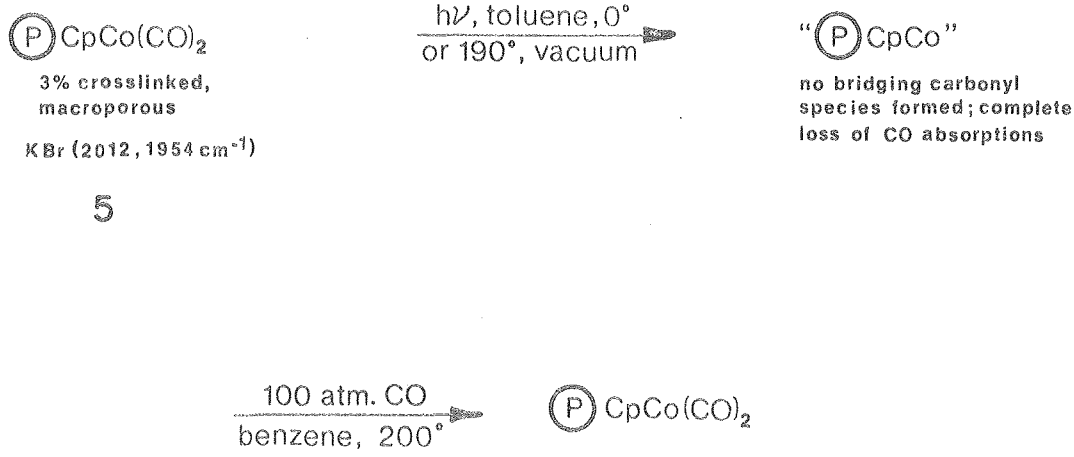
This is in contrast to soluble $CpCo(CO)_2$ which forms di- and trinuclear clusters under the same conditions (33, 34). Similar apparent prevention of the formation of higher nuclear species was noted in the decarbonylations of (P)$CH_2Fe(CO)_2H$ (22) and (P)$CH_2CpM(CO)_3H$ (M = Cr, Mo, W) (35), and in the catalytic activity of (P)$CH_2CpTiCp$ (25). However, these species are all supported by a relatively highly crosslinked polymer, and there was ample indication that lesser crosslinking enables "bimolecular" reactions of active centers (36, 37, 38, 39).

Irradiation of (P)$CH_2CpCo(CO)_2$ 3 (1% DVB, 6% ring substitution, brown color) was carried out through Pyrex (-20 to 25°C, toluene). A red-brown cast was apparent on the resin after about 15 minutes; continued irradiation resulted in a gradual change of the resin's color (green-black). A gradual loss in the terminal CO absorptions due to (P)$CH_2CpCo(CO)_2$ was seen by IR analysis (2012 and 1954 cm^{-1}), accompanied by a rise and decline of two bands in the bridging CO region (1790 and 1770 cm^{-1}). After cessation of irradiation (4h), only 6% of the resin-bound $CpCo(CO)_2$ remained; no other carbonyl-containing species were present. In analogy to $CpCo(CO)_2$, it appears that 3 forms ((P)$CH_2CpCoCO)_2$ 6 (1770 cm^{-1}) and ((P)$CH_2CpCo)_2(CO)_3$ 7 (1790 cm^{-1}) upon irradiation. Upon thermal decarbonylation (190°C, vacuum or 128°C, n-octane), 3 turned bright green in a few minutes; however, IR analysis indicated the absence of new carbonyl-containing species. Continued heating resulted in darkening of the resin, formation of a 1770 cm^{-1} absorption for 6 in the IR, development of a broad absorption covering 1700-1300 cm^{-1}, and decrease of the absorptions due to (P)$CH_2CpCo(CO)_2$. Evidently, 7 was



not formed under these conditions. No other absorptions were noted in either the thermal or photolytic decarbonylation. It can thus be concluded that the 1% DVB matrix with 6% substitution does not maintain site-site isolation.

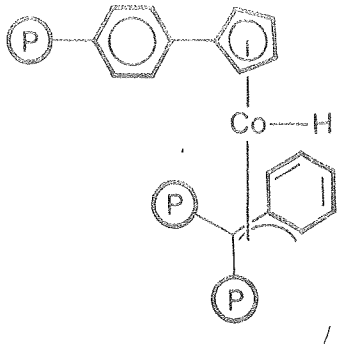
Decarbonylation of (P)CpCo(CO)$_2$ 5 (3% DVB, 15% ring substitution) via photolysis produced no color change, but a gradual disappearance of the



terminal IR carbonyl absorptions. No other CO bands were noted. Vacuum thermolysis (0.005 torr, 110-190°C) resulted in slow color changes from tan to bright green to bronze to steel gray. During this time, the only changes noted in the IR spectrum were the slow, complete disappearance of the CO absorptions due to 5 and the development of a broad absorption from 1700-1300 cm^{-1}. Again no species such as 6 and 7 were observable. Thus, resin 5 is either capable of preventing the aggregation of the coordinatively unsaturated intermediate metal centers, or the species resulting from such aggregation are kinetically unstable under the reaction conditions.

Uptake of CO (1 atm. CO, 50°C, 12 h, or 9.5 atm. CO, room temp., 40 h) by the decarbonylated resins was sluggish; under conditions comparable to the complete regeneration of $CpCo(CO)_2$ from clusters (33), only 20% regeneration of 3 and 5 was detected by IR. Quantitative recarbonylation (IR spectrum) was achieved by using 100-110 atm. CO, 200°C, benzene solvent for 24 h. No new carbonyl bearing species were detected at intermediate stages of this reaction. The strenuous conditions are necessary, as a reaction for 18 h yielded only 92% reconversion. Minimal cobalt loss from the resin had occurred by this drastic treatment (elemental analysis).

The data, although inconclusive, suggest the possibility that mononuclear cobalt species are formed in the irradiative and thermal decarbonylation of polymer-bound $CpCo(CO)_2$. These may gain coordinative saturation by interaction with the polymer backbone, possibly by π-donation from a neighboring phenyl group (22) or by some sort of oxidative addition process into a phenyl-hydrogen or benzyl-hydrogen bond. Two speculative possibilities are shown in 8 and 9.



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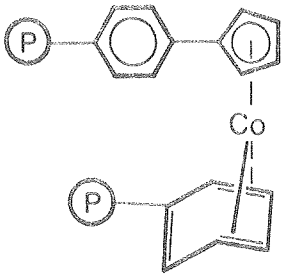

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Such structures, particularly 8, should they be present in the decarbonylated resins, might show interesting activity in the catalytic chemistry of carbon monoxide and other unsaturated small molecules. Indeed (in addition to hydrocarbon formation to be described subsequently) some, albeit limited, activity was observed in the hydroformylation reaction, included in this account, and in the catalytic trimerization of alkynes, reported elsewhere (24). Interestingly, although the latter activity was also observed by others when using a 20% crosslinked (P)$CH_2CpCo(CO)_2$, the former was not (23). On the other hand, hydroformylation activity was detected with silica gel supported $CpCo(CO)_2$ (40) and claimed for free $CpCo(CO)_2$ (41).

Hydroformylation of 1-Pentene in the Presence of (P)$CpCo(CO)_2$

There are several polymer supported transition metal hydroformylation catalysts (42). Most are attached by phosphine ligation and suffer from catalyst leaching. There are no η^5-cyclopentadienyl half sandwich systems despite the potentially, clearly advantageous presence of the relatively strong Cp-metal bond (43, 44). Resin 5 was used in the following brief study in which the potential of polystyrene-supported $CpCo(CO)_2$ to function as a hydroformylation catalyst was tested.

The reaction was conducted at 270 psig., 1/1 H_2/CO, 140°C, 90 h, using purified n-octane as the solvent and 1-pentene as the substrate. During

this time, a slow pressure drop ensued. Analysis of the solution by gas chromatography yielded: hexanal (13%), 2-methylpentanal (11%), pentane (3%), 2-pentene (21%); the balance was unreacted 1-pentene (52%). The normal to branched ratio was poor (1.1/1), indicating the failure of the resin to exert significant steric control. Olefin isomerization is evidently competitive with product formation (ratio of aldehydes to 2-pentene was 1.14/1); this would contribute to a low n/b ratio. No alcohols were observed, and no gaseous products (e.g. methane) were noted. The turnover number was low (1.68 mmol aldehyde produced per mmol Co per day), in accordance with the mild conditions used. In contrast to the reaction of 5 with alkynes (24) no loss of catalytic activity was observed on prolonged hydroformylation. This result prompted an extension of this investigation to the potential activity of 3 and 5 in the Fischer-Tropsch reaction.

Fischer-Tropsch Catalysis by Polystyrene Supported $CpCo(CO)_2$

The conditions chosen for this investigation (3/1 H_2/CO, 100 psig. (6.8 atm), 140°C) are analogous to those typically encountered in Fischer-Tropsch catalysis by heterogeneous cobalt (175-300°C, 5-30 atm.) (1). The reaction was conducted in a medium pressure glass and stainless steel reactor (static conditions), heated by an external oil bath at 190°C. The temperature inside the reactor averaged at ca. 140°C. (P) $CpCo(CO)_2$ 5 was suspended in purified n-octane to swell the resin and allow access to catalyst sites in the interior of the beads; no detectable reaction took place if the solvent was excluded. Upon reaching the reaction temperature, a slow pressure drop ensued; an induction period could not be ascertained. Analysis of the solution phase after 100h by gas chromatography showed the existence of methane and higher hydrocarbons up to $C_{25}H_{52}$ as shown in Figure 1. In addition to H_2 and CO,

methane was predominant in the gas phase (gas chromatography, mass spectra, IR). Smaller amounts of ethane, propane, butane, water, and CO_2 were also detected in the gas phase. The used catalyst had suffered a 50% loss of the absorbance intensity of the terminal CO stretches due to (P) $CpCo(CO)_2$ 5; no additional IR bands were observed. This, however, did not result in a loss of catalytic activity, as recycling the catalyst with a fresh charge

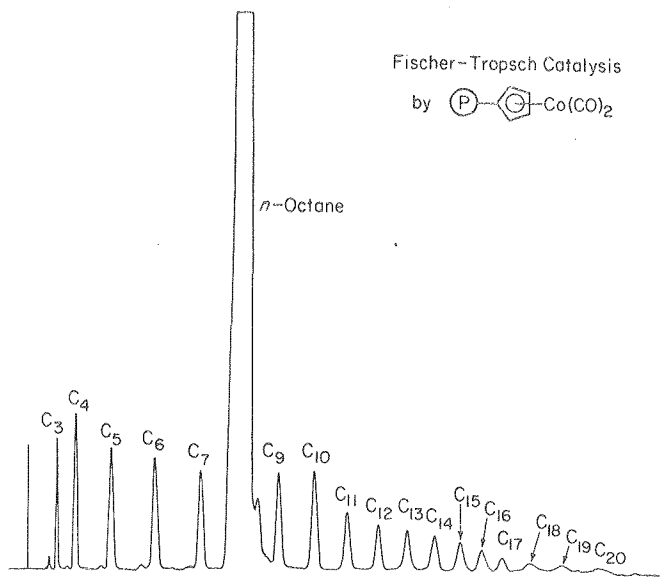

Figure I

of n-octane and H_2/CO led to a pressure drop at the same rate. The solution after reaction was colorless and (after removal of the catalyst beads) catalytically inactive; thus the catalytic activity clearly resided within the resin.

As a check to confirm that no extraneous non-polymer-attached catalytic species were present, the following experiment was performed. Polystyrene without attached cyclopentadiene was exposed to $Co_2(CO)_8$, extracted using a

Soxhlet extractor and dried in vacuo in exactly the same manner as was used to synthesize 5. When used under the above Fischer-Tropsch reaction conditions, these treated, white polystyrene beads did not discolor, release any detectable species into solution, cause a CO/H_2 pressure drop, or result in the formation of any detectable amounts of methane. These observations argue against the presence of small amounts of occluded $Co_2(CO)_8$ or $Co_4(CO)_{12}$ which could conceivably have been active or precursors to active species. It should be noted that the above clusters were reported to be essentially inactive under Fischer-Tropsch conditions (140°C, toluene, 1.5 atm., 3/1 H_2/CO, three days) leading to mere traces of methane (11). The lack of products under our conditions also indicates that, at least in the absence of resin-bound $CpCo(CO)_2$ or its derivatives, the polystyrene support did not degrade.

The extremely low turnover rate (0.011 mmol CO/mmol Co/h, production of 0.003 mmol CH_4/mmol Co/h average), stimulated attempts to increase the efficiency of the reaction. Indeed, pretreatment involving removal of CO via vacuum thermolysis of (P) $CpCo(CO)_2$ 5 to yield " (P) CpCo", followed by its use in a Fischer-Tropsch reaction, led to improved activity (turnover of 0.130 mmol CO/mmol Co/h, production of 0.053 mmol CH_4/mmol Co/h average). It appears that decarbonylation is necessary for formation of the catalytically active species.

Resin 3 was found to be more than 100 times less active than 5, hence all subsequent experiments were carried out using 5.

The number of turnovers (10) in hydrocarbon production without apparent decrease in activity proved that the reaction was indeed catalytic. The IR spectrum of the recovered resin showed small absorptions due to (P) $CpCo(CO)_2$ 5 due to some recarbonylation of " (P) CpCo". In addition, a broad distinct band at 1887 cm^{-1} was seen. The identity of the species

exhibiting this carbonyl band is still a mystery; in particular, the band position does not match that reported for any of the $CpCo(CO)_2$-derived di- and trinuclear carbonyls (vide supra). It is tempting to associate this band with some catalytic intermediate, such as the polymer-bound analogues of $CpCo(H)_2(CO)$ and $CpCo(H)(Ph)(CO)$, but this is pure speculation.

Recarbonylation of the used resin was successful at 1430 psig. CO (97.3 atm.) and 200°C; previous experiments with " (P) CpCo" (vide supra) suggested the necessity of such drastic conditions. The intensity of the (P) $CpCo(CO)_2$ absorptions returned to the original value, and an analysis of the resin showed no cobalt loss (elemental analysis).

The Fischer-Tropsch reaction with " (P) CpCo" was repeated using deuterium; GC/MS analysis after five turnovers confirmed the existence of per-deuterated hydrocarbons in solution. In addition, all the major fragment ions were of even mass, indicating that virtually no undeuterated or partially deuterated products were formed (all odd masses < 15% of the base peak). Some CD_3H was present (mass spectrum) (approximately 10% of the amount of CD_4). The IR spectrum of the resin from this reaction showed some regeneration of the attached $CpCo(CO)_2$ groups, the band at 1887 cm^{-1}, and a weak band at 2168 cm^{-1}, assigned to a C-D stretch. It appears that CD_3H arises via insertion of cobalt into a phenyl or benzyl C-H bond, exchange of the hydride with the deuterium gas to form a cobalt deuteride, and reductive elimination to form a monodeuterated phenyl ring or benzyl position ($\nu_{C-D} \sim 2140-2200$ cm^{-1}); reaction of the HD (or cobalt hydride) so produced would yield CD_3H. Both the average rate of CO consumption (0.064 mmol/mmol Co/h) and average rate of CD_4 production (0.040 mmol/mmol Co/h) were lower than the rates for the H_2/CO reaction (0.130 and 0.053 mmol/mmol Co/h, respectively) implying a possible deuterium isotope effect on the reaction.

High H_2/CO ratios in the Fischer-Tropsch reaction on metal surfaces result in the production of methane in high selectivity. In line with these observations, pure hydrogen over (P) $CpCo(CO)_2$ 5 (0.291 mmole Co) was used in one experiment (75 psig H_2 at 25°C, 68h, 140°C). This reaction produced a mixture of hydrocarbon gases (GC/MS); methane (120 μmol), ethane (1.7 μmol), propane (0.17 μmol), isobutane (ca. 0.001 μmol), and n-butane (0.09 μmol); 21% of the carbon of the original resin-bound CO was accounted for in these products. Free CO was found (26% of the original present on the resin (determined by GC)); 46% of the CO was still bound to the resin (IR). When exposed to 3/1 H_2/CO, this pretreated resin showed Fischer-Tropsch activity similar to decarbonylated 5. Thus, higher H_2/CO ratios favor methanation, as expected, and unlike many heterogeneous catalysts, there is no advantage in hydrogen pretreatment.

Further control experiments were performed to rule out the possibility of hydrocarbon production from sources other than CO. To this end, "(P) CpCo" with 2.2% residual (P) $CpCo(CO)_2$ (0.015 mmol CO) was exposed to the same partial pressure of H_2 as used above in the absence of CO under the experimental conditions. The reaction produced 0.014 mmol CH_4 total; no other hydrocarbon products were detected. It is clear that only CO, not the polystyrene support, attached catalyst, or solvent, is the carbon source for the hydrocarbon products. Further evidence in support of this statement is obtained from the mass balance on carbon in all the reactions described; starting carbon inventory based on CO and ending carbon inventory based on hydrocarbons and unreacted CO always agree to within 10%. If a contribution from another source were present (degradation of the polymer, hydrocracking of the n-octane) in significant amounts, there should be a gross discrepancy. Finally, an experiment using $^{13}CO/H_2$ and 5 furnished completely ^{13}C-labeled hydrocarbons

(g.c. mass spectrometry up to $C_{25}H_{52}$).

The ability of (P)$CpCo(CO)_2$ 5 or a derived species to catalyze the Fischer-Tropsch reaction suggested that some conditions might be found whereby soluble $CpCo(CO)_2$ might exhibit the same activity. To these ends, $CpCo(CO)_2$ was subjected to a variety of conditions: H_2, H_2/CO, 150°C, 190°C, n-octane solvent, toluene solvent, with or without added polystyrene, 2-5 days reaction time, in various permutations. Essentially complete decomposition of the complex was noted for all cases. Methane (amounting to 5-10% of the CO originally present) was produced, especially under forcing conditions (higher temperature, higher partial pressure of H_2, no added CO). Small amounts of higher hydrocarbons were detected, but the major products were cyclopentadiene, cyclopentene, and cyclopentane (1.5/88.7/9.8). A shiny coating on the walls of the glass reaction vessel (assumed to be cobalt metal) was present after reaction. Significantly, no methane or higher hydrocarbons were observed until the onset of decomposition, usually 24 h after the start of the reaction. It can be concluded that $CpCo(CO)_2$ does not possess Fischer-Tropsch activity, in accordance with the suggestions of others (10).

The observation of hydrogenated cyclopentadiene products obtained in the homogeneous reaction of $CpCo(CO)_2$ has an interesting bearing on the polymer-supported case. Were a significant amount of decomposition of "(P)CpCo" to take place by the same mechanism, one would not expect quantitative regeneration of the η^5-linkage and, in continuation, quantitative recarbonylation to form 5 as observed. Thus, it appears unlikely that polymer supported (but unbound) cobalt clusters (45), crystallites, or atoms are responsible for the observed activity. Moreover, although polystyrene seems to prevent irreversible aggregation of metal clusters (37, 46) and metal carbonyls on alumina may be reconstituted with CO after thermal or oxidative decarbonylation (47), a mechanism that involves cobalt atoms or

Product Distribution using (P)CpCo(CO)$_2$ 5
as a Fischer-Tropsch Catalyst

n-alkane	weight (mg.)	weight fraction	mmol	mol%	mmol CO consumed to form product	mol% CO consumed to form product
C_1	4.006	.321	.2504	73.4	.2504	29.7
C_2	.024	.002	.0008	.2	.0016	.2
C_3	.274	.022	.0062	1.8	.0187	2.2
C_4	.694	.056	.0120	3.5	.0479	5.7
C_5	.768	.062	.0107	3.4	.0533	6.3
C_6	1.968	.158	.0229	6.7	.1373	16.3
C_7	1.320	.106	.0132	3.9	.0924	11.0
C_9	.818	.065	.0064	1.9	.0575	6.8
C_{10}	.084	.007	.0006	.2	.0059	.7
C_{11}	.448	.035	.0029	.8	.0316	3.8
C_{12}	.422	.034	.0025	.7	.0298	3.5
C_{13}	.410	.033	.0022	.6	.0290	3.4
C_{14}	.278	.022	.0014	.4	.0200	2.4
C_{15}	.190	.015	.0009	.3	.0134	1.6
C_{16}	.150	.012	.0007	.2	.0106	1.3
C_{17}	.134	.011	.0006	.2	.0095	1.1
C_{18}	.158	.013	.0006	.2	.0112	1.3
C_{19}	.208	.017	.0008	.2	.0147	1.7
C_{20}	.110	.008	.0004	.1	.0078	.9

aggregates would require the formation of soluble species subject to leaching. Of course, it is difficult to completely rule out trace amounts of such species as being responsible for catalytic action. One would have assumed, however, that such compounds should have been formed in the attempt to use polystyrene and $CpCo(CO)_2$ or $Co_2(CO)_8$ as Fischer-Tropsch catalysts, where no activity was found. In addition, widely differing degrees of activity of 5 might have been expected depending on pretreatment of catalyst and recycle time, an effect that was not observed.

The product distribution from the Fischer-Tropsch reaction using 5 is shown above. It is similar but not identical to that obtained over other cobalt catalysts (18-21, 48, 49). The relatively low amount of methane production (73 mol%) when compared with other metals and the abnormally low amount of ethane are typical (6). The distribution of hydrocarbons over other cobalt catalysts has been found to fit the Schulz-Flory equation [indicative of a polymerization-type process (6)]. The Schulz-Flory equation in logarithmic form is

$$\log \left[\frac{M_p}{p} \right] = \log (\ln^2 \alpha) + p \log \alpha,$$

where M_p = the weight fraction of the compound containing p carbon atoms

α = the chain growth probability factor

defined as $$\alpha = \frac{r_p}{r_p + r_t}$$

r_p = rate of propagation

r_t = rate of termination

A plot of $\log(M_p/p)$ vs. p yields α from either the slope or the intercept (see Figure 2); the "goodness of fit" is indicated by the relative agreement of α obtained from the slope or the intercept. For (P) $CpCo(CO)_2$, the data yield α = 0.81 from the slope and 0.84 from the intercept; considering the fact that

a blank contribution from the n-octane solvent had to be subtracted out of C_5-C_{10}, the agreement is good. Typical values of α are 0.80-0.87 (6).

This catalyst seems to have a better selectivity towards normal paraffins than other catalysts but is not shape selective (19, 21). Isobutane/n-butane = 0.008, isopentane/n-pentane = 0.029 (gas chromatography and GC/MS); usual values are 0.1 and higher. Some compounds giving the correct masses for propene, butenes, pentenes, and hexenes were found; however, they were present in even lesser quantities than the branched paraffins.

The actual structure of the active catalyst in the above reactions is a matter of speculation. The evidence, however, points to the presence of a homogeneous but immobilized Fischer-Tropsch catalyst. Since soluble $CpCo(CO)_2$ does not possess Fischer-Tropsch activity, this activity is a unique feature of the polymer-bound system. The finding that 5 is regenerated quantitatively upon exposure of the active Fischer-Tropsch catalyst resin to CO implies that the η^5-cyclopentadienylcobalt bond remains intact throughout the Fischer-Tropsch reaction. This, along with the observation that 5 apparently enjoys some site-site isolation, disfavors the notion that (bound or unbound) clusters are responsible for catalytic action (50).

The Fischer-Tropsch activity of resin 5 and the unique reaction conditions have important consequences. The use of a reaction solvent raises the possibility of controlling heat removal in this appreciably exothermic process. The apparent homogeneous nature of the catalytic species suggests that other soluble Fischer-Tropsch catalysts may be forthcoming. Finally, (P) $CpCo(CO)_2$ 5 possesses catalytic activity not found in soluble $CpCo(CO)_2$; this demonstrates that attachment to a polymer support not only may induce changes in catalytic activity of a transition metal complex, but also might give rise to completely new activity (51, 52, 53).

The above considerations led to the expectation that it might be possible

to construct soluble analogs of 5 in which an appropriate ligand mimicked the environment imparted by the polystyrene matrix in the immediate vicinity of the metal. The results of these experiments are reported in the final section.

Homogeneous Analogs of (P) $CpCo(CO)_2$ 5

Since substitution of the Cp-ligand in $CpCo(CO)_2$ by the polystyrene chain appeared to be the origin of the special stability to the CpCo-moiety in the presence of hydrogen, it was reasoned that similar substitution by phenyl group carrying alkyl chains might have the same effect. Should these models undergo oxidative addition to benzylic (as in 8) or phenylic C-H bonds this might be readily ascertainable by structural or H-D exchange studies. Several model compounds of varying alkyl-chain length and incorporating secondary and tertiary benzylic hydrogens were synthesized in one step according to the scheme shown. The phenyl substituted alkyl halides are available by literature procedures (54, 55). Complexation to cobalt occurred most efficiently in the presence of

$$\mathrm{RBr} + \mathrm{NaCp} \xrightarrow[\mathrm{THF},\ 0^\circ]{N_2,\ 3\,hr} \xrightarrow[\substack{N_2,\ 24\,hr,\ r.t. \\ \text{cyclohexene}}]{Co_2(CO)_8,\ 1.2\ eq} \underset{\sim 60\%}{RCpCo(CO)_2} + \underset{\sim 20\%}{1,3\text{-}R_2CpCo(CO)_2}$$

$$R = C_6H_5(CH_2)_m \quad \text{or} \quad R = C_6H_5CHCH_3(CH_2)_n$$

$$m = 3\text{-}5 \qquad\qquad n = 2,4$$

a slight excess $Co_2(CO)_8$ (26) and cyclohexene. The latter alkene evidently serves to quench any intermediate $HCo(CO)_4$ (32) protecting the now valuable cyclopentadiene ligand from reduction (56). Interestingly, both mono- and bisalkylated cyclopentadienyl complexes were isolated in an approximate ratio of 6:1 by column chromatography as red-brown oils. The latter were assumed to have the 1,3-disubstitution pattern. Both sets of compounds proved to be considerably

more air and thermally sensitive than the parent system. Whereas irradiation in sealed tubes did not result in any observable change, simple heating produced insoluble clusters (33). In an effort to suppress bimolecular reactions two of the complexes [R = $C_6H_5(CH_2)_3$, $C_6H_5CHCH_3(CH_2)_2$] were subjected to flash vacuum pyrolysis at low contact times (300-450°, $2x10^{-4}$torr) (57). The resulting product mixtures contained starting material, free protonated ligand RCpH, and cobaltocenes $(RCp)_2Co$, and the pyrolysis tube was covered by a cobalt mirror. Several of the model compounds were then exposed to Fischer-Tropsch conditions similar to the ones employed in the hydrocarbon synthesis using resin 5. No activity was found until decomposition set in, producing traces of methane. Pressurization with CO/D_2, however, furnished some deuterated RCpH and recovered deuterated complex. Extensive deuteration of the latter was achieved under conditions which left the structure of the complex relatively intact (200°C, 4d, D_2/CO = 10/1, 130 psig). In the case of $RCpCo(CO)_2$ [R=$(CH_2)_4CH(CH_3)C_6H_5$] the incorporation of up to 10 deuterium atoms could be ascertained by mass spectrometry. Surprisingly, as indicated by the fragmentation pattern, very little (if any) of the deuterium label is found on the aromatic ring. The proton NMR spectrum reveals that most of the H-D exchange has occurred on the Cp ligand, its ordinarily complex AA'BB' pattern having been simplified to two broad singlet absorptions of relative combined intensity of 0.5. The aryl (5H) and aliphatic (12H) regions appear unchanged. That deuterium uptake is preferred on the RCp ligand is also suggested by the relative intensity of the $RCp\text{-}d_4Co(CO)_2$ molecular ion peak which is the signal of maximum height in the peak envelop of deuterated parent ion. It is possible that H-D exchange occurs through a cobalt hydride intermediate in an intramolecular manner as recently also postulated for a η^5-cyclopentadienyl iron hydride (58). Further exchange along the alkyl chain might occur via insertion of cobalt into ligand C-H bonds, behavior similar to that observed

with zirconocene derivatives (59). It seems likely that deuterium incorporation into resin 5 occurs through a similar mechanism. The instability of the model compounds again highlights the special stability associated with the polymer supported system. Perhaps choice of a differently substituted homogeneous analog of 5 will provide a structure endowed with the catalytic capabilities of the resin bound system. This is the subject of continuing work.

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