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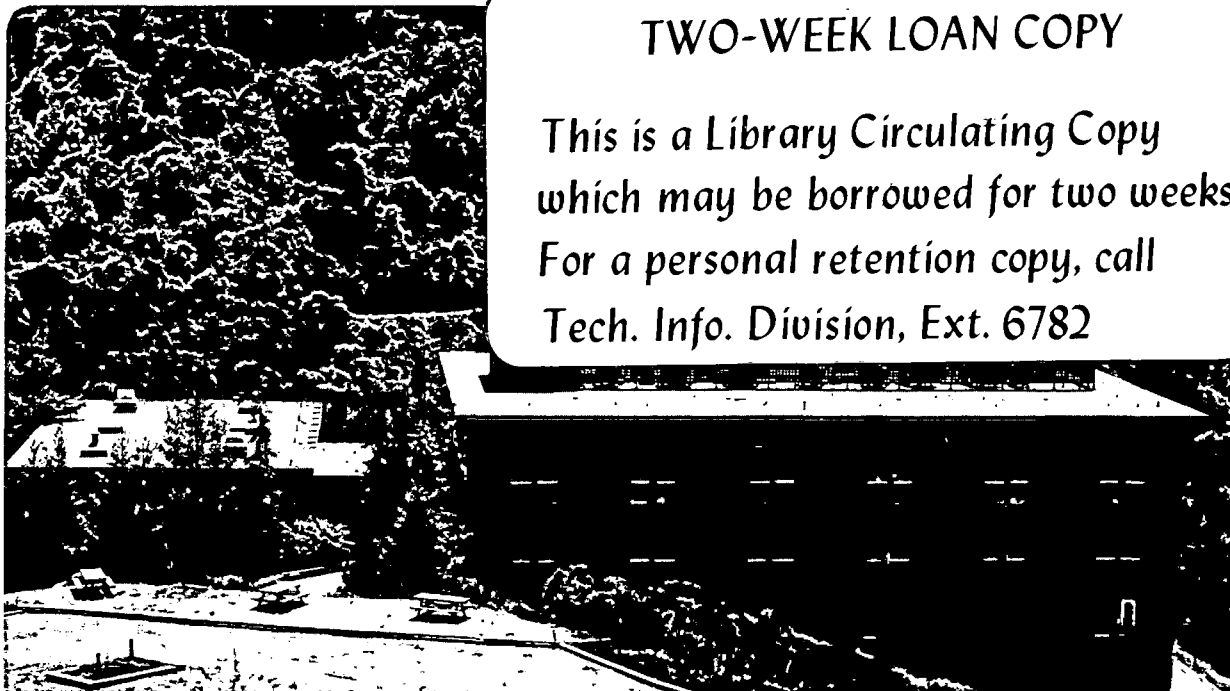
P. Perkins and K. P. C. Vollhardt

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Polymer Supported  $\eta^5$ -Cyclopentadienyl Cobalt: An  
Immobilized "Homogeneous" Fischer-Tropsch Catalyst.

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Abstract

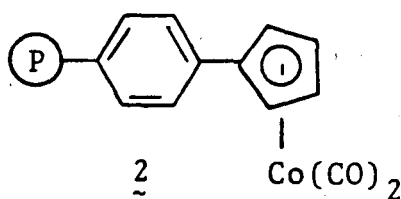
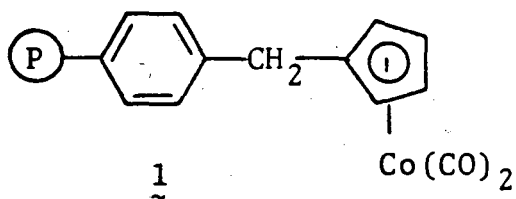
Tests of the catalytic potential of 3% divinylbenzene-cross-linked macroporous polystyrenyl- $\eta^5$ -cyclopentadienyl dicarbonyl cobalt reveal limited alkyne oligomerization capability, activity in hydroformylation, and most importantly, in Fischer-Tropsch catalysis. Control experiments provide strong evidence for the presence of a defined "homogeneous" CpCo-unit in the latter. Since  $\text{CpCo}(\text{CO})_2$  is not active under the catalytic conditions the title compound constitutes the first example of a polymer supported homogeneous catalyst with novel catalytic activity.

Sir:

The attachment of soluble, homogeneous catalysts to polymer supports has been the subject of considerable recent research activity.<sup>1,2</sup> Depending on bead and pore size, catalyst distribution, number and structure of pores, concentration and kind of attached ligands, degree of crosslinking, swelling properties of the polymer, and solvent, changes in rate and product distribution<sup>3</sup> have been observed in catalytic processes effected by these catalysts when compared with their mobile counterparts. Never, however, has there been the observation of new catalytic activity on immobilization. We wish to report that polystyrene supported  $\eta^5$ -cyclopentadienyl cobalt is catalytically active in the hydrogenation of carbon monoxide to give hydrocarbons, that this activity must be due to a defined attached homogeneous cobalt species and not to deposited metal crystallites, and that in contrast soluble  $\text{CpCo}(\text{CO})_2$  is inactive and decomposed under hydrogenating conditions. The observed data characterize the title compound as the first catalyst activated to new activity on polymer attachment and the first immobilized homogeneous Fischer-Tropsch catalyst.

We recently developed synthetic methodology en route to complex molecules employing co-oligomerizations of alkynes catalyzed by  $\text{CpCo}(\text{CO})_2$ .<sup>4</sup> In an effort to improve the efficiency of this approach, to

stabilize the metal, and to facilitate its separation, we turned to a polymer supported version of this catalyst. The method of Grubbs<sup>3a,5</sup> was used for the synthesis of two variants of polymer-supported cyclopentadiene. Treatment with  $\text{Co}_2(\text{CO})_8$  in refluxing  $\text{CH}_2\text{Cl}_2$ <sup>6</sup> followed by Soxhlet extraction of the resin with  $\text{CH}_2\text{Cl}_2$  or  $\text{C}_6\text{H}_6$  gave species 1<sup>7</sup> and 2, characterized by elemental



(P) = 1% divinylbenzene-crosslinked microporous polystyrene; 0.35 - 0.50 mmol Co/g; orange

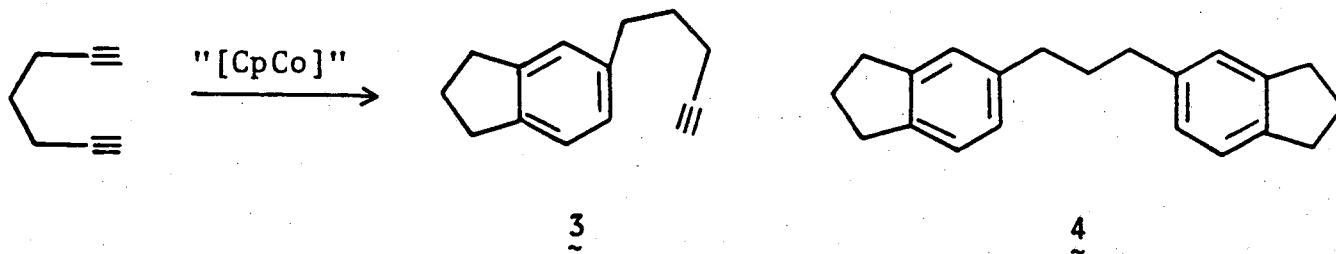
(P) = 3% divinylbenzene-crosslinked macroporous polystyrene; 0.8 - 1.0 mmol Co/g; tan.

analysis and the characteristic infrared absorptions at 2012 and 1953  $\text{cm}^{-1}$  (KBr) [cf.  $\text{CpCo}(\text{CO})_2$ : 2033, 1972 ( $\text{C}_6\text{H}_12$ ); 2017, 1954  $\text{cm}^{-1}$  (acetone)]. In a swelling solvent ( $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_6\text{H}_6$ ) both resins turned brown. Exposure to air led to slow oxidation (green color) although some resin-bound  $\text{CpCo}(\text{CO})_2$  was left even after one month's exposure (28%).

Decarbonylation of 1 and 2 could be effected by irradiation (Pyrex,  $-20^{\circ}\text{C}$ , toluene). In this reaction resin 1, in contrast to resin 2 and a more highly crosslinked species<sup>7</sup>, revealed the formation of two bridged dicobaltcarbonyl species ( $\nu_{\text{CO}}$  1790, 1773  $\text{cm}^{-1}$ ), assigned to the polymer bound analogs of  $\text{Cp}_2\text{Co}_2(\text{CO})_3^8$  and  $(\text{CpCoCO})_2^9$ , formed under similar conditions from  $\text{CpCo}(\text{CO})_2$  in solution.

Analogously, vacuum pyrolysis of either resin ( $185^{\circ}\text{C}$ ,  $10^{-3}$  Torr, 112 h) led to complete decarbonylation. Microporous polymer 1 again revealed the formation of a bridged carbonyl during the course of CO removal. Significantly (vide infra), the original species could be completely regenerated on exposure to CO pressure (IR, analysis) (110 atm,  $200^{\circ}$ , benzene).

The catalytic activity of 1 or 2 in alkyne cyclizations proved to be disappointing. For example<sup>10</sup>, whereas  $\text{CpCo}(\text{CO})_2$  (0.5 mmole) will trimerize 1,6-heptadiyne (10 mmole, refluxing purified n-octane, syringe pump addition, 88 h) to 4 in 40% yield (3 is



absent as a product), resin 1 and 2 rapidly deactivate after several turnovers to give substantial amounts of starting material, in addition to predominant formation of 3 at the expense of 4.<sup>10</sup> Strong steric inhibition is apparent, trimethylsilylated alkynes being virtually inert to catalyst.

Limited hydroformylation<sup>11</sup> and isomerization activity under mild conditions was noted with 1-pentene [resin 2 suspended in purified n-octane, 225 psi CO-H<sub>2</sub> (1:1), 140°C, ca. one turnover CO p.d.] resulting (90 h) in a mixture of c,t-2-pentene (21%), pentane (3%), 2-methylpentanal (11%), and hexanal (13%), the mass balance being made up of recovered starting material.<sup>12</sup>

Most strikingly, however, exposure of macroporous 2 in suspension (purified n-octane) to CO/H<sub>2</sub> (3:1, 75 psi at RT) at 190-200°C in a static reactor revealed pronounced methanation and Fischer-Tropsch activity. After an initiation period steady turnover of CO (ca. 0.01 mmoles/mmole Co/hr) was observed for many cycles without loss of catalytic activity. Moreover, when completely decarbonylated resin (vide supra) was employed, activity increased strongly (0.13 mmole CO/mmole Co/hr). Exposure to air eliminated catalytic activity. Interestingly, under the same conditions, resin 1 was not active.

The products (CH<sub>4</sub> and higher hydrocarbons) were identified by gas chromatography<sup>12</sup> and g.c.-mass spectroscopy. In addition, methane was ascertained by its infrared absorptions. The major oxygen containing product was water, although mass spectral evidence pointed to the presence of small amounts of CO<sub>2</sub>. A typical g.c. trace

of the octane solution after several turnovers is shown in Figure 1 ( $\text{CH}_4$ :hydrocarbon = 92:8). Deuterium gas led to  $\text{CD}_4$  and deuterated hydrocarbons (g.c. and g.c. mass spectroscopy), in addition to  $\text{D}_2\text{O}$ . A small amount of  $\text{CD}_3\text{H}$  (10% in  $\text{CD}_4$  after ca. 10 turnovers) and the appearance of a weak C-D infrared stretch in the resin ( $2168\text{ cm}^{-1}$ ) indicated some H-D-exchange with the polymer backbone.

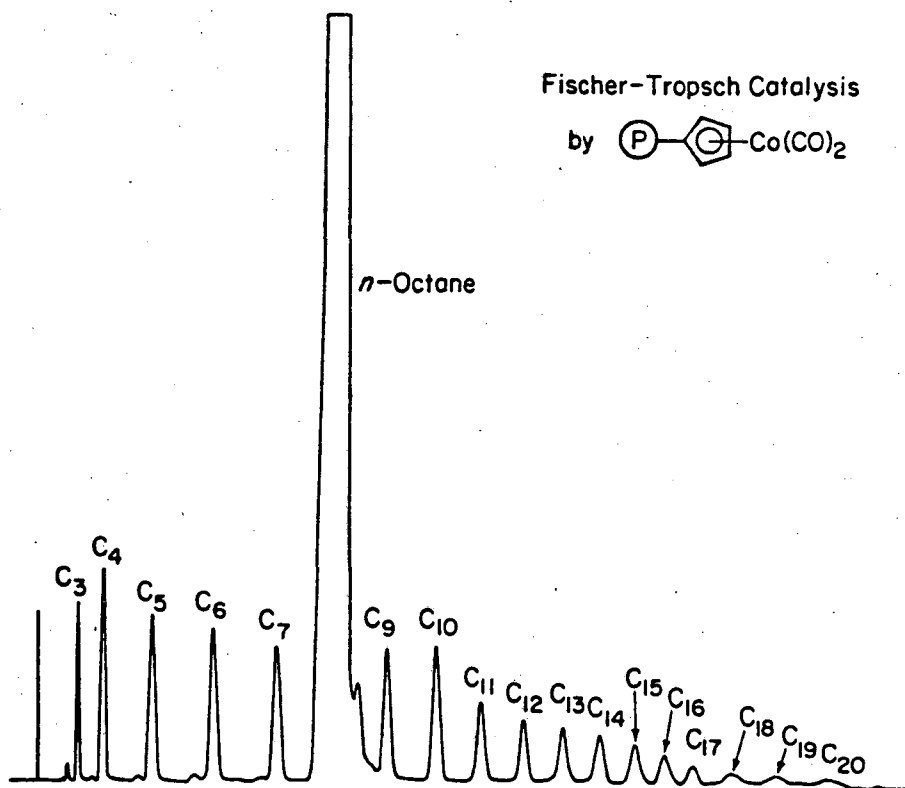


Fig. 1 Hydrocarbons from  $\text{CO}/\text{H}_2$  over 2 after 100 hr (n-octane solvent).



The following additional control experiments were run.

1. The resin (without bound cyclopentadiene) was subjected to the synthesis sequence and then exposed to Fischer-Tropsch conditions: no activity was found.
2. The suspended resin in the presence of dissolved  $\text{Co}_2(\text{CO})_8$  or  $\text{CpCo}(\text{CO})_2$  showed no activity [but formation of a cobalt mirror with  $\text{Co}_2(\text{CO})_8$ ].
3. Soluble  $\text{CpCo}(\text{CO})_2$  in n-octane gave on hydrogenation (75 psi, 190°C, 64 h) cyclopentane and cyclopentene, CO, a cobalt mirror, and methane, but no Fischer-Tropsch products.
4. After completion of a catalytic run, the resin was filtered off, resuspended in fresh n-octane and exposed to  $\text{CO}/\text{H}_2$ : the catalysis resumed at an unchanged rate. Loss of cobalt from the resin was not evident (elemental analysis). The original octane solution was inactive.
5. On pressurization with CO the completely decarbonylated catalytically active resin quantitatively regenerated the starting catalyst 2.

The data indicate that methanation and Fischer-Tropsch activity of 2 is dependent on a defined and regenerable "homogeneous" cobalt species on the resin. The reproducibility of the results, product distribution<sup>13</sup>, and regenerability of catalyst strongly argue against cobalt crystallites or heterogeneous clusters<sup>13,14</sup> being responsible for catalytic action. This conclusion is reinforced by the lack of activity of the  $\text{CpCo}(\text{CO})_2$ -resin and  $\text{Co}_2(\text{CO})_8$ -resin mixtures, the latter generating cobalt metal on the resin and the walls of the vessel.

The precise nature of the catalyst is a matter of speculation. It is perhaps of interest to note in this connection that the microporous resin <sup>1</sup> for which spectroscopic evidence suggests lack of site isolation<sup>2</sup> is inactive in Fischer-Tropsch synthesis. It appears that it is the specific chemical environment that the macroporous polystyrene provides in the vicinity of the metal that is responsible for the activity observed. The finding of H-D-exchange with the polymer-backbone suggest the intermediacy of cobalt hydrides resulting from polystyrene-C-H activation by "naked" CpCo.

The recent renaissance in research aimed at the conversion of CO to hydrocarbons<sup>17</sup> has uncovered only few homogeneous systems: some cluster based catalysts<sup>18</sup> as well as a stoichiometric mononuclear system.<sup>19,20</sup> Fischer-Tropsch activity of polymer supported catalysts in solvent suspension has never been demonstrated and could prove technologically useful in attempts to cope with the problem of heat transfer in this appreciably exothermic process. The discovery of a polymer activated novel hydrogenation system should point the way to physical experiments aimed at further structural clarification and the construction of soluble models mimicking the unique structural environment around the metal.

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