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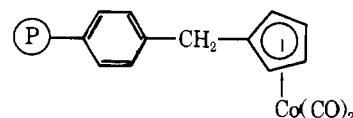
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Polymer-Supported η^5 -Cyclopentadienylcobalt. An Immobilized "Homogeneous" Fischer–Tropsch Catalyst

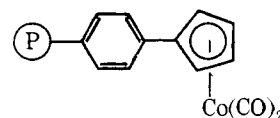
Sir:

The attachment of soluble, homogeneous catalysts to polymer supports has been the subject of considerable recent research activity.^{1,2} Depending on bead and pore size, catalyst distribution, number and structure of pores, concentration and kind of attached ligands, degree of cross-linking, swelling properties of the polymer, and solvent, changes in rate and product distribution³ 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 η^5 -cyclopentadienylcobalt 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 CpCo(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 cooligomerizations of alkynes catalyzed by CpCo(CO)₂.⁴ 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^{3a,5} was used for the synthesis of two variants of polymer-supported cyclopentadiene. Treatment with Co₂(CO)₈ in refluxing CH₂Cl₂⁶ followed by Soxhlet extraction of the resin with CH₂Cl₂ or C₆H₆ gave species **1**⁷ and **2**, characterized by elemental analysis and the



1, P = 1% divinylbenzene–cross-linked microporous polystyrene; 0.35–0.50 mmol of Co/g; orange



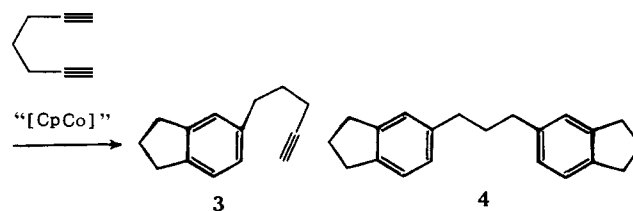
2, P = 3% divinylbenzene–cross-linked macroporous polystyrene; 0.8–1.0 mmol of Co/g; tan

characteristic infrared absorptions at 2012 and 1953 cm⁻¹ (KBr) [cf. CpCo(CO)₂: 2033, 1972 (C₆H₁₂); 2017, 1954 cm⁻¹ (acetone)]. In a swelling solvent (CH₂Cl₂, C₆H₆) both resins turned brown. Exposure to air led to slow oxidation (green color), although some resin-bound CpCo(CO)₂ was left even after 1 month's exposure (28%).

Decarbonylation of **1** and **2** could be effected by irradiation (Pyrex, –20 °C, toluene). In this reaction, resin **1**, in contrast to resin **2**, and a more highly cross-linked species,⁷ revealed the formation of two bridged dicobalt carbonyl species (ν_{CO} 1790, 1773 cm⁻¹) assigned to the polymer-bound analogues of Cp₂Co₂(CO)₃⁸ and (CpCoCO)₂,⁹ formed under similar conditions from CpCo(CO)₂ in solution.

Analogously, vacuum pyrolysis of either resin (185 °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 °C, benzene).

The catalytic activity of **1** or **2** in alkyne cyclizations proved to be disappointing. For example,¹⁰ whereas CpCo(CO)₂ (0.5 mmol) will trimerize 1,6-heptadiyne (10 mmol, 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**.¹⁰ Strong steric inhibition is apparent, trimethylsilylated alkynes being virtually inert to catalyst.

Limited hydroformylation¹¹ and isomerization activity under mild conditions was noted with 1-pentene [resin **2** sus-

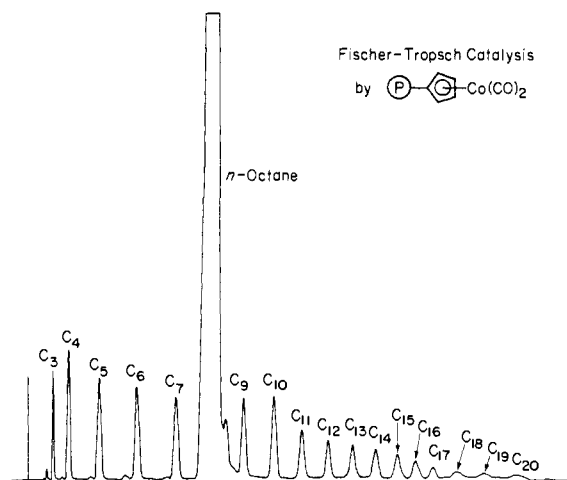


Figure 1. Hydrocarbons from CO-H₂ over **2** after 100 h (*n*-octane solvent).

pended in purified *n*-octane, 225 psi of CO-H₂ (1:1), 140 °C, ca. one turnover of CO p.d.] resulting (90 h) in a mixture of *cis,trans*-2-pentenenes (21%), pentane (3%), 2-methylpentanal (11%), and hexanal (13%), the mass balance being made up of recovered starting material.¹²

Most strikingly, however, exposure of *macroporous 2* in suspension (purified *n*-octane or toluene) to CO-H₂ (3:1, 75 psi at room temperature) 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 mmol/mol of Co per h) was observed for many cycles without loss of catalytic activity. Increasing the CO-H₂ pressure increased hydrocarbon production. Moreover, when completely decarbonylated resin (*vide supra*) was employed, activity increased strongly (0.13 mmol of CO/mmol of Co per h). A small fraction of **2** was regenerated under these conditions without apparent adverse effect on catalytic activity (over at least five turnovers). Reaction of the decarbonylated system with H₂ alone gave no catalytic reaction. Exposure to air eliminated catalytic activity. Under the same conditions, resin **1** produced some methane, but was less active by ca. two orders of magnitude.

The products (CH₄ and higher hydrocarbons) were identified by gas chromatography¹² and GC-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 CO₂. A typical GC trace of the octane solution after several turnovers is shown in Figure 1 (CH₄-hydrocarbon, 92:8). Deuterium gas led to CD₄ and highly deuterated hydrocarbons (GC and GC-mass spectroscopy), in addition to D₂O. A small amount of CD₃H (10% in CD₄ after ca. 10 turnovers) and the appearance of a weak C-D infrared stretch in the resin (2168 cm⁻¹) indicated some H-D exchange with the polymer backbone. This experiment (in addition to some of the following controls) rules out solvent or polystyrene as the source of hydrocarbons.

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 Co₂(CO)₈ or CpCo(CO)₂ showed no activity [but formation of a cobalt mirror with Co₂(CO)₈]. (3) Soluble CpCo(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 CO-H₂: 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 (IR, analysis) regenerated the starting catalyst **2**.

The data indicate that methanation and Fischer-Tropsch activity of **2** are dependent on a defined and regenerable "homogeneous" cobalt species on the resin. The reproducibility of the results, product distribution,¹³ and regenerability of catalyst strongly argue *against* cobalt crystallites or heterogeneous clusters^{13,14} being responsible for catalytic action. This conclusion is reinforced by the lack of activity of the CpCo(CO)₂-resin and Co₂(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 **1**, for which spectroscopic evidence suggests lack of site isolation,² 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 suggests 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 hydrocarbons¹⁷ has uncovered only few homogeneous systems: some cluster based catalysts¹⁸ as well as a stoichiometric mononuclear system.^{19,20} 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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Evidence for a Possible Trans Oxidative Addition of Hydrogen to an Iridium Complex

Sir:

In all cases so far reported, oxidative addition of dihydrogen to metal complexes occurs in a cis fashion.¹ We report herein evidence for a possible case of trans addition of dihydrogen together with other observations on the stereochemistry of some iridium trihydrides.

Treatment of a solution of carbonylhydridotris(triphenylphosphine)iridium(I) (**1**) with H₂ results in formation of an equilibrium mixture of the two isomeric trihydrides **3** and **4**.² Kinetic evidence suggests that **3** and **4** are in equilibrium by repetitive reductive elimination and oxidative addition of H₂,

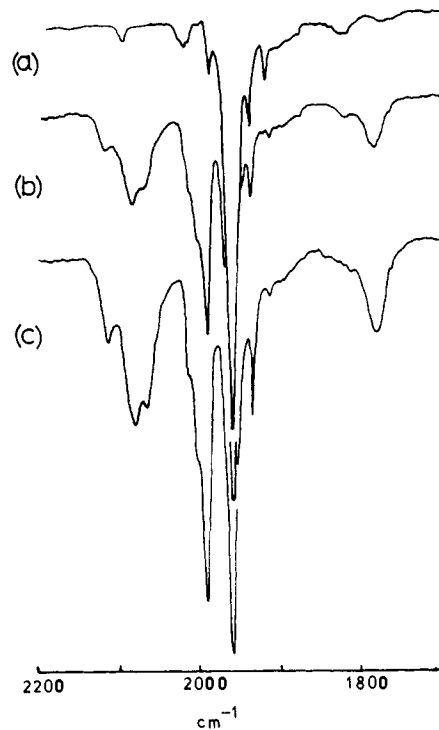
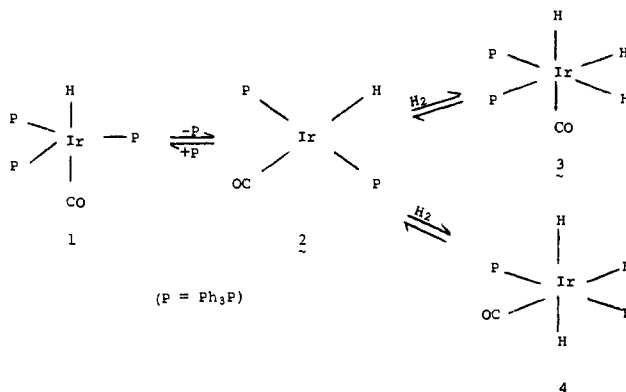


Figure 1. Infrared spectra of P₃(CO)IrD: (a) before addition of H₂, (b) after bubbling H₂ for 45 min, (c) after bubbling H₂ for 90 min. Reactions were run at 20 °C in CH₂Cl₂.



each pure isomer being converted to the equilibrium mixture at room temperature in a few hours. It is also reasonable to assume from kinetic evidence that the reaction proceeds through the square planar intermediate **2**.^{2,3}

Treatment of a solution of deuterio-**1** with bubbling dihydrogen resulted in the infrared spectral changes shown in Figure 1. The most striking feature of these spectra is the appearance of rather large amounts of a product containing trans hydrogens ($\nu_{\text{Ir-H}}$ 1780 cm⁻¹)⁷ in addition to the expected product, **5**, with D trans to CO ($\nu_{\text{Ir(III)CO}}$ 1985 cm⁻¹)⁸ and a

