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EVIDENCE FOR THE OLEFIN INSERTION MECHANISM.

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E. R. Evitt and R. G. Bergman

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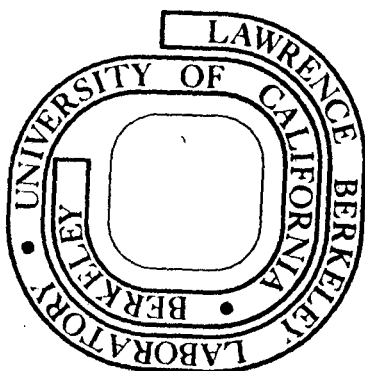
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REACTION OF A METAL ALKYL WITH ETHYLENE AS A
MODEL FOR ZIEGLER-NATTA POLYMERIZATION.
EVIDENCE FOR THE OLEFIN INSERTION MECHANISM.

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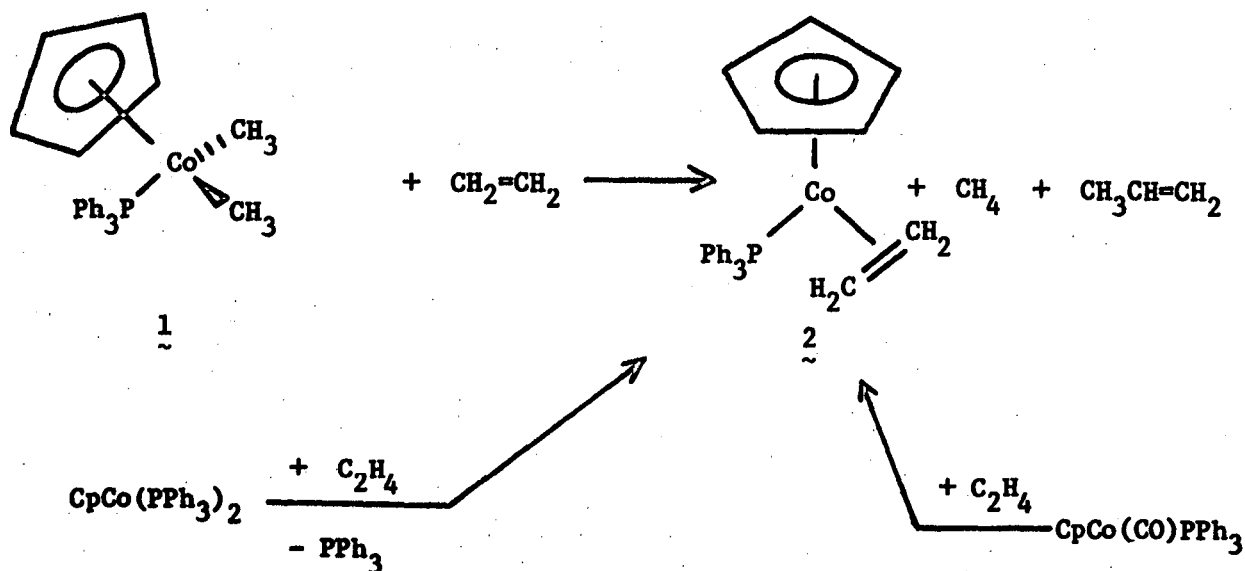
Reaction of a Metal Alkyl with Ethylene as a
Model for Ziegler-Natta Polymerization.
Evidence for the Olefin Insertion Mechanism.

Sir:

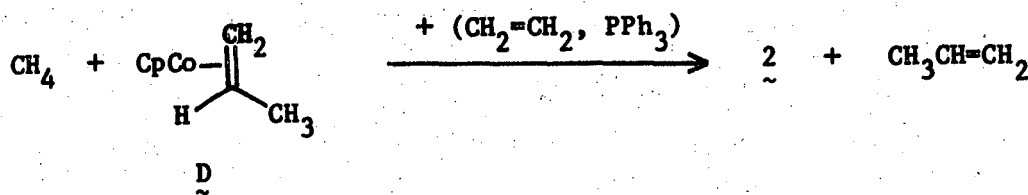
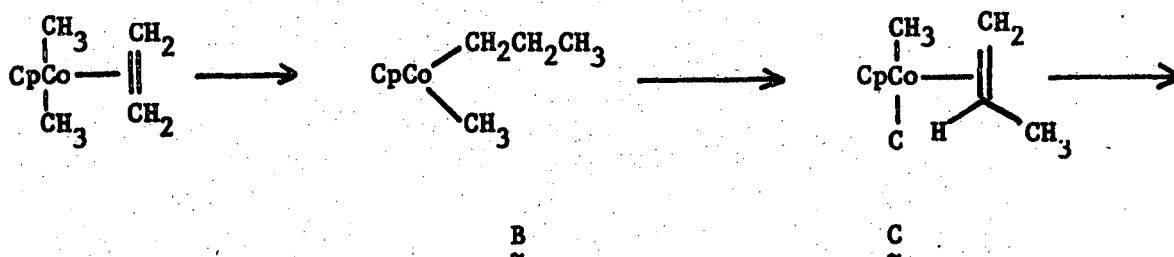
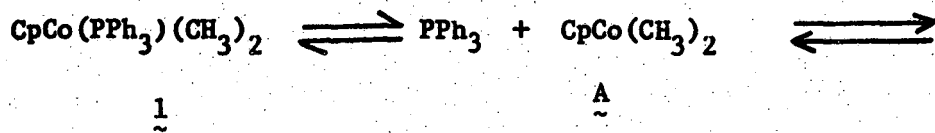
Dimerization, oligomerization and Ziegler-Natta polymerization of ethylene and other olefins are among the most important homogeneous catalytic processes.¹ It has long been assumed that these reactions involve insertion of olefin into the metal-carbon bond of an intermediate metal alkyl.^{2,3} Green, Rooney and their coworkers have pointed out recently, however, that there are no unambiguous examples in which a well-characterized metal-alkyl-olefin compound has been observed to undergo this insertion reaction.⁴ This has led them to suggest an alternative mechanism for Ziegler-Natta polymerization, which involves α -elimination to form a transient carbene complex. In this note, we wish to report that the well-characterized^{3e,5} cobalt complex 1 (Scheme I) reacts cleanly with ethylene, giving propylene and methane as products. We have carried out a labeling study which demonstrates (in agreement with the classical Ziegler-Natta mechanism) that insertion, rather than α -elimination, is the critical step in the mechanism of this reaction.

When a 0.13 M benzene- d_6 solution of 1 was heated under 4 atm (5 equivalents) of ethylene for 30 hr. at 76°C in a sealed NMR tube the absorptions characteristic of 1 (δ 4.49, 0.61 ppm) and ethylene (δ 5.27 ppm) were replaced by those from methane (δ 0.22 ppm) and propene (δ 1.58 ppm, CH_3) as well as by a new cyclopentadienyl signal (δ 5.50 ppm, 5H) and two new multiplets at δ 1.11 (2H) and 2.09 (2H) ppm. A complex with these absorptions can be isolated free of starting 1 by repeated crystallizations from benzene-hexane although it slowly decomposes in solution (N_2 atmosphere, 20°C) with loss of ethylene. η^5 -cyclopentadienylbis(triphenylphosphine)cobalt(I)⁶ and ethylene react thermally and η^5 -cyclopentadienyl(triphenylphosphine)carbonylcobalt(I)^{5a} and ethylene reaction upon photolysis (Scheme I) to give NMR absorptions identical to those observed in the reaction of ethylene with 1. The structure of this material is assigned as the new olefin complex, 2, on the basis of these observations. In a quantitative experiment, heating 2 ml of a 0.127 M benzene solution of 1 under 11 atm (20 equivalents) of ethylene at $54 \pm 1^\circ C$ for 121 hr gave: methane (91%), propene (84%), 2 (103%) and unreacted ethylene. No (< 0.5%) propane was observed.⁸

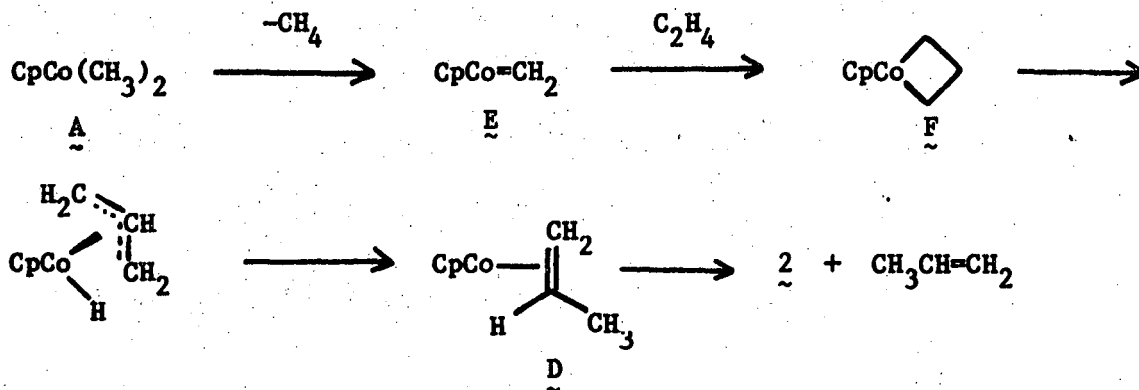
Scheme I



Scheme II



Scheme III



As in the Ziegler-Natta reaction, the observed products can be explained by either a classical mechanism involving insertion of ethylene into a metal-carbon bond (Scheme II), or by the Green-Rooney alternative involving α -elimination (Scheme III). In the former, coordination of ethylene to the unsaturated intermediate A generated by phosphine dissociation, followed by insertion into a cobalt-methyl bond, gives the propyl-methyl complex B. β -hydrogen elimination in B generates a hydrido-methyl olefin complex which reductively eliminates methane, and ethylene and phosphine displace propene from the initially formed, unsaturated, olefin complex D. In the alternative (Scheme III), intermediate A is converted to carbene complex E by α -elimination and reductive elimination of methane. Addition of ethylene to the M=C bond gives metallacycle F; this then undergoes β -elimination and a second reductive elimination, generating D which leads to 2 and propene as before (Scheme II).

Because our system involves characterisable complex 1, it has been possible to carry out a labeling experiment which clearly distinguishes these two alternatives. This involves treatment of hexadeuterated complex 1-d₆ (completely deuterated methyl groups) with undeuterated ethylene, and analysis of the isotopic distribution in the methane and propene produced. In methane formed by the insertion pathway, three of the hydrogens derive from the initial CD₃ group, and the fourth originates in the ethylene; this predicts formation of only CD₃H. Since a complete methyl group is transferred to the ethylene in the insertion route this pathway also predicts only propene-d₃ will be observed. In the α -elimination pathway the fourth hydrogen originates on the second methyl group, and thus CD₄ should be produced along with propene-d₂. Mass spectral analysis of the methane produced from this reaction⁹ showed it was identical to CD₃H synthesized by quenching a portion of the CD₃MgI used to prepare 1-d₆

with H_2O . Mass spectral analysis of the propene produced showed it to be $\geq 96\%$ propene- d_3 .¹⁰

This result clearly establishes insertion, rather than α -elimination, as the mechanism responsible for ethylene methylation by complex 1. It is still certainly possible that Ziegler-Natta polymerization takes place by the α -elimination route. However, in our opinion those in favor of this mechanism must now shoulder the burden of proof for establishing it.

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2. See, for example (a) G. Henrici-Olivé and S. Olivé, Fort. Chem. Forsch., 67, 107 (1976); (b) D. L. Thorn and R. Hoffman, J. Am. Chem. Soc., 100, 2079 (1978); (c) R. F. Heck, J. Am. Chem. Soc., 90, 5518 (1968); (d) H. A. Dieck and R. F. Heck, J. Am. Chem. Soc., 96, 1133 (1974); (e) M. P. Cooke, Jr. and R. M. Parlman, *ibid.*, 99, 5222 (1977); 97, 6863 (1975); (f) B. L. Booth, M. Gardner, and R. N. Haszeldine, J. C. S. Dalton, 1856 (1975); (g) D. E. James and J. K. Stille, J. Am. Chem. Soc., 98, 1810 (1976).
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5. (a) R. B. King, Inorg. Chem., 5, 82 (1966); (b) H. Yamazaki and N. Hagihara, J. Organomet. Chem., 21, 431 (1970).
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8. Yields are corrected for remaining $\underline{1}$. The product gases were collected with a Toepler pump, combined with an internal standard (cyclopropane), and analyzed by vapor phase chromatography. The involatile residue was dissolved in benzene- \underline{d}_6 , combined with a known amount of ferrocene, and analyzed by integrating the $\underline{1}\text{H}$ NMR spectrum of the resulting mixture. The volatile products of this reaction also include a non-thermodynamic mixture of linear butenes (1-butene, 5%; (E)-, 2-butene, 3%, (Z)-, 2-butene, 0.5%; yields relative to starting $\underline{1}$). We are currently exploring the source of these additional products.

9. Heating 2 ml of 0.14 M $\underline{1}\text{-d}_6$ ($\geq 97.6\%$ D by NMR) at $54 \pm 1^\circ\text{C}$ for 120 hr under 11 atm (27 equivalents) of ethylene. Mass spectra (50 ev), m/e (relative intensity, corrected for background and $\underline{13}\text{C}$ contributions): synthetic CD_3H : 19 (100.0), 18 (39.9), 17 (44.1), 16 (4.0), 15 (2.1), 14 (1.9); methane from $\underline{1}\text{-d}_6$ and ethylene: 19 (100.0), 18 (39.5), 17 (43.5), 16 (3.9), 15 (2.1), 14 (1.9).

10. We have discovered $\underline{1}$ decomposes slowly in benzene solution ($t_{1/2} \sim 120$ hr, 70°C) to give a mixture of methane and ethane (6:1) and as yet uncharacterized organometallic products. The methane produced by decomposing $\underline{1}\text{-d}_{21}$ (completely deuterated phosphine and methyl groups) in benzene- \underline{d}_6 is mostly CD_3H ($> 80\%$). NMR characterization of the organometallic products of the reactions of $\underline{1}$ with ethylene shows this side reaction accounts for $\leq 2\%$ of the reaction pathway under our reaction conditions.

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