S. G. Sligar, I. C. Gunsalus, M. Goutermann, and C. R. Connell, *ibid.*, **98**, 2672 (1976).
(17) Y. Imai and R. Sato, *J. Biochem.*, **62**, 464 (1967).
(18) D. Mansuy, P. Gans, J.-C. Chottard, and J.-F. Bartoli, *Eur. J. Biochem.*, **76**, 607 (1977).
(19) D. Mansuy, P. Beaune, T. Crestell, C. Bacot, J.-C. Chottard, and P. Gans, *Eur. J. Biochem.*, **86**, 573 (1978).
(20) W. Nastainczyk, H. H. Ruf, and V. Ullrich, *Eur. J. Biochem.*, **60**, 615 (1975).
(21) D. Mansuy, W. Duppel, H. H. Ruf, and V. Ullrich, *Z. Physiol. Chem.*, **355**, 1341 (1974).
(22) A. R. Dahl and E. Hodgson, *Chem. Biol. Interact.*, **21**, 137 (1978).
(23) This procedure has been used to obtain the visible spectra of model complexes of CO-[16] and NO-iron(II)-cytochromes P 450: J. O. Stern and J. Peisach, *FEBS Lett.*, **62**, 364 (1976).
(24) The 459-nm peak is not due to the complex $Fe^{III}(TPP)(n\text{-}BuS^-)_2$,[25] which could be formed by oxidation of the iron by oxygen traces, since an EPR study at 110 K of the experiment failed to reveal any significant formation of Fe^{III}(TPP) low-spin complex.[25] Moreover, the addition of n-BuS$^-$ to Fe^{III}(TPP)(Cl) and Fe^{II}(TPP), under identical conditions, does not lead to the 459-nm peak formation.
(25) H. H. Ruf and P. Wende, *J. Am. Chem. Soc.*, **99**, 5449 (1977).
(26) (a) J. T. Groves, G. A. McClusky, R. E. White, and M. J. Coon, *Biochem. Biophys. Res. Commun.*, **81**, 154 (1978); (b) E. G. Hrycay, J. Gustafsson, M. Ingemal-Sundberg, and L. Ernster, *ibid.*, **66**, 209 (1975); (c) V. Ullrich, H. H. Ruf, and P. Wende, *Croat. Chem. Acta*, **49**, 213 (1977).
(27) D. Mansuy, M. Lange, J.-C. Chottard, and J.-F. Bartoli, *Tetrahedron Lett.*, **33**, 3027 (1978).

D. Mansuy,* J.-P. Battioni, J.-C. Chottard
Laboratoire de Chimie de l'Ecole Normale Supérieure
24, rue Lhomond, 75231 Paris Cedex 05, France

V. Ullrich*
Department of Physiological Chemistry
Universität des Saarlandes
665 Homburg/Saar, West Germany

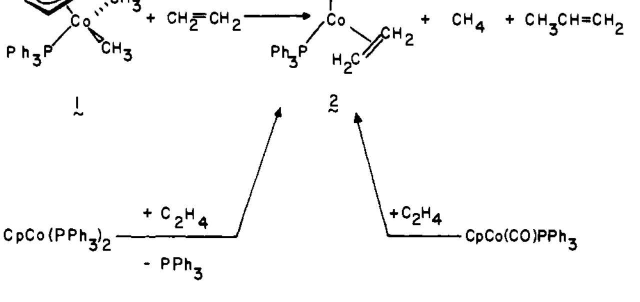
Received January 19, 1979

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

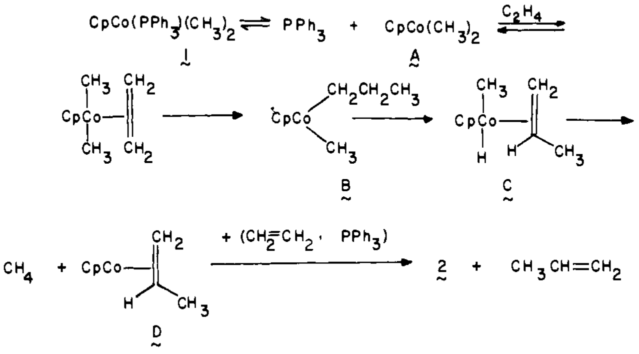
Sir:

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 and his co-workers have pointed out recently, however, that there are no unambiguous examples—in either early or late transition metal complexes—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 apparent insertion reactions which involves α-elimination to form a transient carbene complex. In this note, we 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 view) that insertion, rather than α-elimination, is the critical step in the mechanism of this reaction.

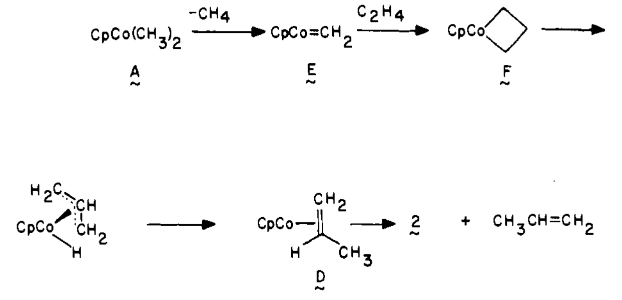
Scheme I



Scheme II



Scheme III



When a 0.13 M benzene-d_6 solution of **1** was heated under 4 atm (5 equiv) of ethylene for 30 h at 76 °C in a sealed NMR tube, the absorptions characteristic of **1** (δ 4.49, 0.61 ppm) and ethylene (5.27) were replaced by those from methane (0.22) and propene (1.58, CH_3), as well as by a new cyclopentadienyl signal (5.50, 5 H) and two new multiplets at 1.11 (2 H) and 2.09 (2 H) 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 react upon photolysis (Scheme I) to give NMR absorptions identical with those observed in the reaction of ethylene with **1**. The structure of this material is assigned as the new olefin complex,[7] **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 equiv) of ethylene at 54 ± 1 °C for 121 h gave methane (91%), propene (84%), **2** (103%), and unreacted ethylene. No (<0.5%) propane was observed.[8]

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 into 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 characterizable complex **1**, it

0002-7863/79/1501-3973$01.00/0

is possible to carry out labeling experiments which clearly distinguish these two alternatives. This involves treatment of appropriately labeled **1** with labeled and unlabeled 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 methyl group and the fourth originates in the ethylene. A complete methyl group is also transferred to the ethylene. In the α-elimination pathway the fourth hydrogen originates on the second methyl group, and a methylene group is transferred to the ethylene.

When **1**-d_{21} (completely deuterated phosphine and methyl groups) was treated with ethylene, mass spectral analysis of the product methane[9,10] showed that it was identical with CD_3H synthesized by quenching a portion of the CD_3MgI, used to prepare **1**-d_{21}, with H_2O. Similar analysis of the propene produced showed it to be ≥96% propene-d_3. In a second experiment, reaction of **1**-d_{21} with ethylene-d_4 gave 95% CD_4. These results demonstrate that (a) the new methane hydrogen is derived from the ethylene and from no other hydrogen source in the system (cyclopentadienyl ring, solvent, phosphine) and (b) a complete methyl group is transferred to the ethylene. This 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 and/or other apparent insertion reactions take 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.

Acknowledgment. We are grateful for support of this work by the National Science Foundation (Grant No. CHE78-08706) and the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. W-7405-Eng-48.

References and Notes

(1) (a) L. S. Reich and A. Schindler, "Polymerizations by Organometallic Compounds", Wiley-Interscience, New York, 1966; (b) D. G. H. Ballard, *J. Polym. Sci.*, **13,** 2191 (1975); (c) M. M. Taqui Khan and A. E. Martell, "Homogeneous Catalysis by Metal Complexes", Vol. II, Academic Press, New York, 1974, pp 110–117.

(2) See, for example, (a) G. Henrici-Olivé and S. Olivé, *Fortschr. Chem. Forsch.*, **67,** 107 (1976); (b) D. L. Thorn and R. Hoffman, *J. Am. Chem. Soc.*, **100,** 2079 (1978); (c) R. F. Heck, *ibid.*, **90,** 5518 (1968); (d) H. A. Dieck and R. F. Heck, *ibid.*, **96,** 1133 (1974); (e) M. P. Cooke, Jr., and R. M. Parlman, *ibid.*, **99,** 5222 (1977), and **97,** 6863 (1975); (f) B. L. Booth, M. Gardner, and R. N. Haszeldine, *J. Chem. Soc., Dalton Trans.*, 1856 (1975); (g) D. E. James and J. K. Stille, *J. Am. Chem. Soc.*, **98,** 1810 (1976).

(3) For some apparent examples of insertion of alkynes into metal–carbon σ bonds, see (a) H. C. Clark and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 92 (1970); (b) M. H. Chisholm and H. C. Clark, *Acc. Chem. Res.*, **6,** 202 (1973); (c) S. J. Tremont and R. G. Bergman, *J. Organomet. Chem.*, **140,** C12 (1977); (d) H. G. Alt, *ibid.*, **127,** 349 (1977); (e) E. R. Evitt and R. G. Bergman, *J. Am. Chem. Soc.*, **100,** 3237 (1978).

(4) (a) K. J. Ivin, J. J. Rooney, C. D. Stewart, M. L. H. Green, and R. Mahtab, *J. Chem. Soc., Chem. Commun.*, 604 (1978); (b) M. L. H. Green and R. Mahtab, *J. Chem. Soc., Dalton Trans.*, 262 (1979).

(5) (a) R. B. King, *Inorg. Chem.*, **5,** 82 (1966); (b) H. Yamazaki and N. Hagihara, *J. Organomet. Chem.*, **21,** 431 (1970).

(6) (a) P. V. Rinze, J. Lorberth, H. Noth, and B. Stutle, *J. Organomet. Chem.*, **19,** 399 (1969); (b) A. Misano, *Inorg. Synth.*, **12,** 12 (1970).

(7) The rhodium analogue has recently been characterized by X-ray crystallographic methods: W. Porgio and M. Zocchi, *J. Am. Chem. Soc.*, **100,** 2048 (1978).

(8) Yields are corrected for remaining **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-d_6, combined with a known amount of ferrocene, and analyzed by integrating the ^1H NMR spectrum of the resulting mixture. The volatile products of this reaction also include a nonthermodynamic mixture of linear butenes (1-butene, 5%; (*E*)-2-butene, 3%; (*Z*)-2-butene, 0.5%; yields relative to starting **1**). We are currently exploring the source of these additional products.

(9) Heating 2 mL of 0.14 M **1**-d_{21} (≥97.6 atom % D in methyl, ≥98.4% in phosphine phenyl; by NMR) in benzene-h_6 at 54 ± 1 °C for 120 h under 11 atm (27 equiv) of ethylene. Mass spectra (50 eV), *m/e* (relative intensity, corrected for background and ^{13}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 **1**-d_{21} and ethylene, 19 (100.0), 18 (39.5), 17 (43.5), 16 (3.9), 15 (2.1), 14 (1.9).

(10) At higher temperature, **1** decomposes slowly in benzene solution ($t_{1/2} \sim$ 120 h, 70 °C) to give a mixture of methane and ethane (6:1) and as yet uncharacterized organometallic products. The methane produced by decomposing 1-d_{21} (completely deuterated phosphine and methyl groups) in benzene-d_6 is mostly CD_3H (>80%). This side reaction accounts for ≤2% of the products formed under the milder ethylene reaction conditions.

Eric R. Evitt, Robert G. Bergman*
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, California 91125
Department of Chemistry, University of California
and the Molecular and Materials Research Division
Lawrence Berkeley Laboratory, Berkeley, California 94720

Received February 17, 1979

Titanium(III) Porphyrins and Their Dioxygen Adducts

Sir:

There is wide current interest in the reactions of low-valent metalloporphyrin complexes with molecular oxygen.[1] We report here a convenient synthetic procedure for the isolation of coordinatively unsaturated titanium(III) porphyrins, some mechanistic implication for their autoxidation, and the stabilization of a reversible titanium(III)-dioxygen adduct by immobilization in a host crystal lattice.

Stirring a suspension of $Ti(F)_2(TPP)$[2,3] with zinc amalgam in dry, oxygen-free benzene gives a pink solution from which the five coordinate d^1 complex Ti(F)(TPP), **1**, can be isolated as purple crystals.[4,5] Hyperfine splittings in the EPR spectrum of **1** in CH_2Cl_2 at room temperature (Figure 1) indicate substantial interaction of the unpaired electron with the axial fluoride ligand and weaker interactions with the four equivalent porphyrin nitrogens (Table I).[6] Consistent with the presence of a vacant coordination site in **1**, changes in the EPR and UV-visible spectra are observed upon addition of ligands

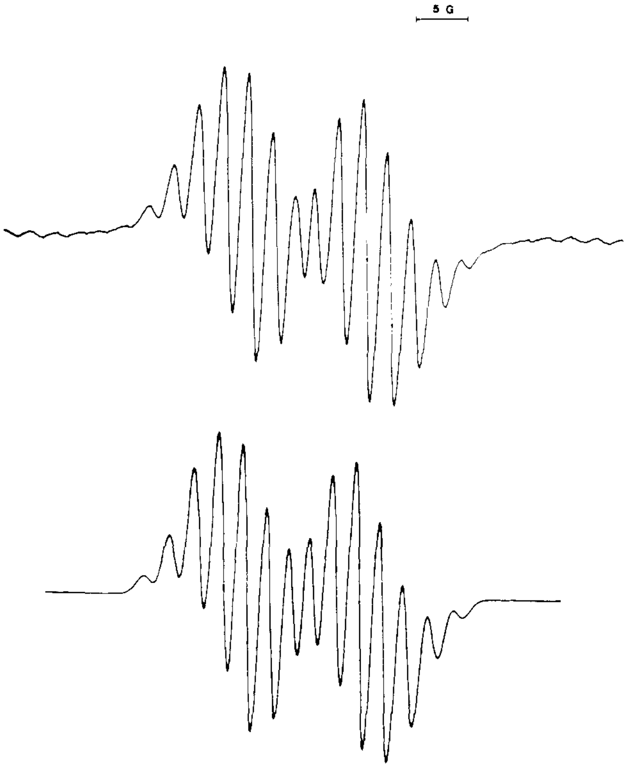


Figure 1. Experimental (top) and simulated (bottom) EPR spectra of Ti(F)(TPP) in dichloromethane at 25 °C.

0002-7863/79/1501-3974$01.00/0