

## Formation of Organocobalt Porphyrin Complexes by Reactions of Cobalt(II) Porphyrins with Azoisobutyronitrile and Organic Substrates

Alexei A. Gridnev,<sup>a</sup> Steven D. Ittel,<sup>b</sup> Michael Fryd<sup>c</sup> and Bradford B. Wayland\*<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323, USA

<sup>b</sup> DuPont, Central Research and Development, Experimental Station, E328/327 Wilmington, DE 19880-0328, USA

<sup>c</sup> DuPont, Marshall Laboratory, 3500 Grays Ferry Ave., Philadelphia, PA 19146, USA

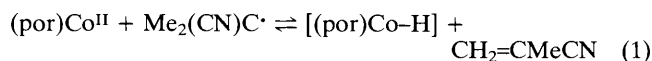
Reaction of a cobalt(II) porphyrin with azoisobutyronitrile (AIBN) at 333 K provides a convenient source of a transient cobalt hydride that reacts with alkenes and alkynes to form secondary alkyl and vinyl complexes, respectively or alternatively with organic halides and epoxides in the presence of donor molecules to form primary alkyl and  $\beta$ -hydroxyalkyl complexes.

Cobalt catalysed chain transfer in free radical polymerization of methacrylates is expanding in commercial significance as a source of macromonomers.<sup>1</sup> During mechanistic studies of this process using AIBN as the free radical initiator source and cobalt(II) porphyrins as the chain transfer catalyst it was recognized that a transient cobalt hydride formed in the reaction could be trapped by organic substrates to form organocobalt porphyrin complexes. Alkyl complexes of cobalt

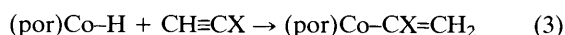
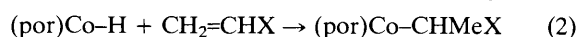
porphyrins are usually formed by reaction of the Co<sup>I</sup> derivative,  $[(\text{por})\text{Co}]^-$ , with alkyl halides.<sup>2,3</sup> Hydride reducing agents such as NaBH<sub>4</sub> are generally ineffective in reducing Co<sup>II</sup> to Co<sup>I</sup> so that the standard procedure involves sodium amalgam reduction to Co<sup>I</sup> and subsequent reaction with the alkyl halide. Setsune *et al.* have recently demonstrated a clever alternative approach for producing organocobalt complexes by reaction of Co<sup>II</sup> porphyrins with NaBH<sub>4</sub> and alkenes or

alkynes in the presence of oxidizing agents.<sup>4,5</sup> This approach produces a transient and currently unobserved cobalt porphyrin hydride that either adds to the alkene and alkyne or eliminates dihydrogen to reform a Co<sup>II</sup> porphyrin. Regeneration of Co<sup>III</sup> porphyrin by the oxidizing agent and reaction with BH<sub>4</sub><sup>-</sup> provides a continuous source of the transient hydride.

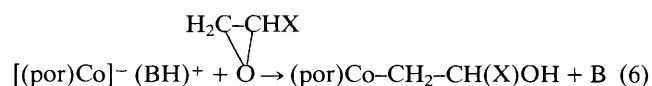
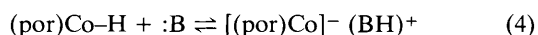
The approach to forming organocobalt porphyrins reported here utilizes the reaction between cobalt(II) porphyrins and the alkyl radical from AIBN [Me<sub>2</sub>(CN)C<sup>•</sup>] as a continuously generated source of the transient cobalt hydride [eqn. (1)].



This hydride subsequently reacts with alkene or alkyne to produce organo cobalt derivatives [eqns. (2) and (3)]. Trans-



fer of a hydrogen atom from the cobalt hydride to the unsaturated substrate to produce the most stable alkyl radical dictates the stereoselectivity for the organocobalt complexes (Table 1).<sup>4</sup> Use of a weak donor solvent like dimethylformamide (DMF) or addition of donor molecules for reaction (1) results in some deprotonation of the transient hydride to form a Co<sup>I</sup> porphyrin species [eqn. (4)] which in the presence of an organohalide or epoxide reacts on to yield organocobalt derivatives [eqns. (5) and (6)] (Table 1). Regioselectivity for epoxide reactivity reactions [eqn. (6)] is directed by formation of the most stable Co-alkyl bond.



The general reaction procedure consists of preparing a solution of the cobalt(II) porphyrin [tetra(4-methoxyphenyl)porphyrinatocobalt(II)] with an excess of AIBN and organic substrate in a vacuum adapted reaction tube which is subsequently degassed, sealed and heated at 333 K. Chloroform or benzene are used as solvents for reactions of alkenes and alkynes, and DMF solvent is used for reactions of alkyl halides and epoxides. Isolation and purification of the organocobalt derivatives is accomplished by established procedures.<sup>2,3</sup>

**Table 1** Representative organocobalt(III) porphyrins obtained from the reaction of a cobalt(II) porphyrin with AIBN and organic substrates ( $T = 333 \text{ K}$ )

Organic substrate	Solvent	Product <sup>a</sup>	Yield <sup>b</sup>
CH <sub>2</sub> =CH(CO <sub>2</sub> Me)	CHCl <sub>3</sub>	(por)CoCHMeCO <sub>2</sub> Me	70
CH <sub>2</sub> =CHCMe <sub>2</sub> OH	CHCl <sub>3</sub>	(por)CoCH <sub>2</sub> CH <sub>2</sub> CMe <sub>2</sub> OH	95
CH <sub>2</sub> =CHPh	CHCl <sub>3</sub>	(por)Co-CHMePh	50
CH≡C(Ph)	CHCl <sub>3</sub>	(por)Co-CPh=CH <sub>2</sub>	60
MeI	DMF	(por)Co-Me	95
EtI	DMF	(por)Co-Et	95
CH <sub>2</sub> OCH <sub>2</sub> Et	DMF	(por)-CH <sub>2</sub> CH(OH)Et	65

<sup>a</sup> (por) = tetra(4-methoxyphenyl)porphyrin dianion. <sup>b</sup> Yield is based on the conversion of the cobalt(II) porphyrin for a mole ratio of organic substrate to cobalt of ca. 30.

Homogeneous solutions of cobalt(II) porphyrins and AIBN in a variety of solvent media provide a controlled source of cobalt porphyrin hydride and cobalt(I) porphyrin species which through reaction with organic substrates provide a general one-pot method for obtaining organocobalt porphyrin complexes. Efficient trapping of the transient cobalt hydride by alkenes supports the suggestion that these reactions are viable intermediate steps in the catalytic cycle for chain transfer in radical polymerization of olefins.<sup>1,6,7</sup>

This programme is supported by a grant from the US National Science Foundation and by a grant from DuPont for support of A. A. G.

Received, 5th March 1993; Com. 3/01316B

## References

- G. W. Parshall and S. D. Ittel, *Homogeneous Catalysis*, Wiley Interscience, New York, 2nd edn., 1992, pp. 85-6.
- M. Perree-Fauvet, A. Gaudemer, P. Boucly and J. Devynek, *J. Organomet. Chem.*, 1976, **120**, 439.
- M. Ogoshi, E. Watanabe, N. Koketsu and Z. Yoshida, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2529.
- J. Setsune, Y. Ishimaru, T. Moriyama and T. Kitao, *J. Chem. Soc., Chem. Commun.*, 1991, 555.
- J. Setsune, Y. Ishimaru, T. Moriyama and T. Kitao, *J. Chem. Soc., Chem. Commun.*, 1991, 556.
- N. S. Enikolopyan, B. R. Smirnov, G. V. Ponomarev and I. M. Belgovskii, *J. Polym. Sci., Polym. Chem. Ed.*, 1981, **19**, 879.
- A. A. Gridnev, I. M. Belgovskii and N. S. Enikolopyan, *Dokl. Chem. (Engl. Transl.)*, 1986, **289**, 281.