

Hydrometallation of Alkenes and Alkynes by the Combination of Cobalt(II) Porphyrins, NaBH₄ and Oxidizing Agents

Jun-ichiro Setsune,^a Yoshihiro Ishimaru,^a Tohru Moriyama,^a and Teijiro Kitao^b

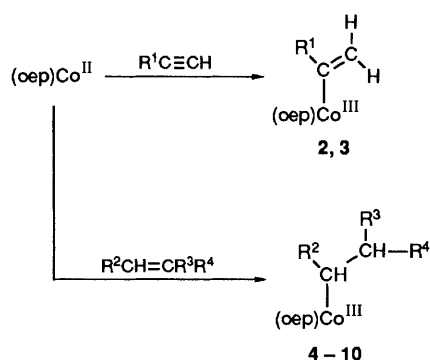
^a Department of Chemistry, Faculty of Science, Kobe University, Nada, Kobe 657, Japan

^b Department of Applied Chemistry, College of Engineering, Sakai, Osaka 591, Japan

Various organocobalt(III) porphyrins have been synthesized in good yields through the hydrometallation of a hypothetical hydridocobalt(III) porphyrin intermediate.

Cobalt porphyrins show different redox properties from those of cobaloxime and cobalamin. Co^{II} porphyrins can only be reduced to Co^I with Na–Hg and not with NaBH₄.¹ Since the NaBH₄ reduction of Co^{III} porphyrins affords stable Co^{II} porphyrins instantly, a hydridocobalt(III) porphyrin has never been isolated and investigated so far, whereas hydridocobaloxime and hydridocobalamin were shown to exist at room temperature and add to unactivated alkenes.² Hydrido-rhodium porphyrins have recently been shown to react with alkenes, alkynes and CO by novel radical chain reactions with the quite reactive Rh^{II} porphyrin as a chain carrier.³ Thus, it is of interest to see if a hydridocobalt porphyrin could be formed and react with alkenes and alkynes.

An alkyne (30 equiv.) was added to a heterogeneous mixture of (oep)Co^{II} (oep = octaethylporphyrin dianion) **1** and NaBH₄ (ca. 30 equiv.) in benzene–methanol (30:1) under argon containing a limited amount of O₂. The (oep)Co^{II} disappeared after 12 h at room temperature in the dark. Extraction with benzene and recrystallization from dichloro-methane–methanol afforded σ -(1-phenylvinyl)Co^{III}(oep) **2**, and σ -(hex-1-en-2-yl)Co^{III}(oep) **3** in 56 and 86% yields starting from phenylacetylene and hex-1-yne, respectively.[†] Evidence for these structures was the value of the ¹H–¹H coupling constants between the vinylic protons of **2** (2.2 Hz) and **3** (3.6 Hz), which were in the range typical of geminal coupling. Exactly one deuterium was transferred from NaBD₄ to the terminal position of phenylacetylene in C₆H₆–MeOH. The intensities of the two singlets at δ –0.84 and –2.67 due to the vinylic protons of the deuteriated **2** indicate that *cis*- and *trans*-addition occurs in an 8:5 ratio. It should be noted that



Conditions: NaBH₄, O₂ in C₆H₆–MeOH

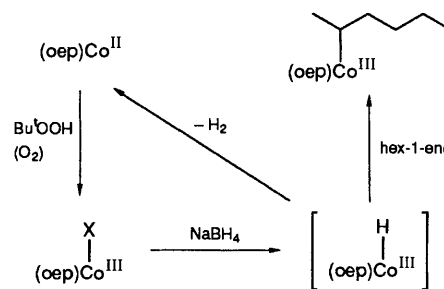
[†] Selected ¹H NMR data (CDCl₃; $\alpha, \beta, \gamma, \delta, \epsilon$ are positions relative to cobalt): **2**, δ 10.05 (porph. *meso*-H), 4.01 (porph. CH₂Me), 1.87 (porph. CH₂Me); –0.83 and –2.67 (d, 1H, *J* 2.20 Hz, β -H), 4.76 (d, 2H, γ -H), 5.70 (t, 2H, δ -H), and 6.28 (t, 1H, ϵ -H).

3, ϵ 10.08 (porph. *meso*-H), 4.01 (porph. CH₂Me), 1.87 (porph. CH₂Me); –0.96 (dt, 1H, α -H), –3.12 (d, 1H, β -H) (*J* 3.57 and 1.99 Hz), –4.29 (dt, 2H, β -H), –1.75 (quint., 2H, γ -H), –0.66 (sext., 2H, δ -H), and –0.23 (t, 3H, ϵ -H).

4, δ 9.98 (porph. *meso*-H), 4.00 (porph. CH₂Me), 1.86 (porph. CH₂Me); –3.95 (br., 1H, α -H), –6.04 (m, 1H, β -H), –4.61 (m, 1H, β -H), –5.71 (d, 3H, β -H), –1.52 (m, 1H, γ -H), –1.28 (m, 1H, γ -H), –0.71 (m, 1H, δ -H), –0.61 (m, 1H, δ -H), and –0.32 (t, 3H, ϵ -H).

phenylacetylene undergoes stereospecific *cis*-addition of hydridocobaloxime with the cobalt introduced into the benzylic carbon site.⁴ Coordination of phenylacetylene to the site *cis* to the hydride would be possible in the flexible framework of hydridocobaloxime to account for the difference in the stereochemistry.

Hydrometallation of hex-1-ene, pent-2-ene and hept-2-ene occurred similarly to afford the σ -(alkan-2-yl)Co^{III}(oep) compounds **4**,[†] **5** and **6**, in 60, 44 and 54% isolated yields, respectively, without formation of alkan-1-yl or alkan-3-yl isomers. Cyclopentene and cyclohexene also afforded σ -cycloalkylcobalt(III) complexes **7** and **8** in 63 and 70% yield, respectively, but 2-methylpent-1-ene, 1-methylcyclohexene and methyl acrylate did not give organocobalt(III) complexes under the standard reaction conditions. The regiochemistry of hydrocobaltation observed here may be explained in terms of the stability of organic radicals generated by the addition of a hydrogen radical to alkenes and alkynes. However, σ -(*tert*-alkyl)cobalt(III) porphyrins did not form owing to the steric constraints of the porphyrin ring. While the sterically congested 4-methylpent-2-ene and 3-methylcyclohexene failed to react even after 24 h under the standard reaction conditions,



Scheme 1

Table 1 Synthesis of organocobalt(III) porphyrins

Substituents				Method ^a	Yield (%)	Product
R ¹	R ²	R ³	R ⁴			
Ph	—	—	—	A	56	2
Bu	—	—	—	A	86	3
—	Bu	H	H	A	60	4
—	Bu	H	H	B	47	4
—	Bu	H	H	C	60	4
—	Me	Et	H	A	44	5
—	Me	Bu	H	A	54	6
—	Me	Pr ⁱ	H	B	17	9
—	H	Me	Pr	B	0	—
—	H	CO ₂ Me	H	A	0	—
—	—	–[CH ₂] ₃ –	H	A	63	7
—	—	–[CH ₂] ₄ –	H	A	70	8
—	—	–[CH ₂] ₃ CHMe–	H	B	47	10
—	—	–[CH ₂] ₄ –	Me	B	0	—

^a A: Ar, O₂ (0.01–0.1%), 12 h; B: Ar, BuⁱOOH (1–2 equiv.), 15 min; C: air, 15 min.

addition of *tert*-butyl hydroperoxide (1.5 equiv.) led to the formation of organocobalt(III) porphyrins **9** and **10** in 17 and 47% yield within 15 min.

The hydrocobaltation was markedly accelerated by the addition of oxidizing agents as shown above. Addition of 1.2 equiv. Bu^tOOH to the reaction with hex-1-ene under argon resulted in the rapid consumption of **1** in 15 min to give **2** in 47% yield. Compound **2** was also obtained in a similar yield within 15 min under aerobic conditions. If we started with (oep)Co^{III}Br instead of **1** under strictly anaerobic conditions, the complex **2** was generated immediately in 29% yield along with **1** in 56% yield. These facts suggest that the hydridocobalt(III) porphyrin, which would be formed through the reaction of Co^{III} porphyrins with NaBH₄ immediately liberates H₂ to give (oep)Co^{II} or undergoes insertion of alkenes and alkynes into the Co–H bond as shown in Scheme 1. Since considerable amounts of (oep)Co^{II} were formed if (oep)Co^{III}Br was treated with NaBH₄ in the presence of alkenes and alkynes, reoxidation of Co^{II} to Co^{III} with O₂ or Bu^tOOH is crucial for attaining effective conversion to organocobalt(III) porphyrins which are not so air-sensitive.

Hydridorhodium(III) porphyrins undergo insertion of alkenes *via* a quite reactive Rh^{II} porphyrin as a radical chain carrier.^{3b} However, a similar radical chain process is impossible for hydridocobalt(III) porphyrins, because the Co^{II} porphyrin is not sufficiently reactive. In fact, the regiochemistry of the hydrocobaltation observed in the present reactions and those of hydridocobalamin and hydridocobaloxime is different from that for the hydridorhodium(III) porphyrin. Thus, insertion of alkenes into hydridocobalt(III) complexes would be initiated by the homolytic cleavage of the Co–H bond followed by the H-radical addition to alkenes and recombination of the resulting organic radical with Co^{II}. This

mechanism is consistent also with the stereochemistry (for phenylacetylene) and the competitive H₂ evolution.

In conclusion, organocobalt(III) porphyrins with a secondary alkyl organo ligand have been prepared conveniently in a process, which should lead to new catalytic synthetic reactions with hydridocobalt(III) complexes as the key intermediates.⁵

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References

- 1 H. Ogoshi, E. Watanabe, N. Koketzu and Z.-I. Yoshida, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2529; D. A. Clarke, D. Dolphin, R. Grigg, A. W. Johnson and H. A. Pinnock, *J. Chem. Soc., (C)*, 1968, 881.
- 2 G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, 1967, **89**, 1999; G. N. Schrauzer and R. J. Holland, *J. Am. Chem. Soc.*, 1971, **93**, 1505; G. N. Schrauzer and R. J. Holland, *J. Am. Chem. Soc.*, 1971, **93**, 4060.
- 3 (a) J.-i. Setsune, Z.-I. Yoshida and H. Ogoshi, *J. Chem. Soc., Perkin Trans. 1*, 1982, 983; (b) R. S. Paonessa, N. C. Thomas and J. Halpern, *J. Am. Chem. Soc.*, 1985, **107**, 4333; (c) B. B. Wayland and B. A. Woods, *J. Chem. Soc., Chem. Commun.*, 1981, 700.
- 4 M. Naumberg, K. Nguyen-Van-Doung and A. Gaudemer, *J. Organomet. Chem.*, 1970, **25**, 231.
- 5 T. Okamoto and S. Oka, *Tetrahedron Lett.*, 1981, **22**, 2191; Y. Ohkatsu, M. Ohno, T. Ooi and S. Inoue, *J. Chem. Soc. Jpn., Chem. Indst. Chem.*, 1985, 387; A. Nishinaga, K. Maruyama, K. Yoda and H. Okamoto, *J. Chem. Soc., Chem. Commun.*, 1990, 876; H. Bhandal and G. Pattenden, *J. Chem. Soc., Chem. Commun.*, 1988, 1110.