CHEMISTRY LETTERS, pp. 667-670, 1989.

Reversible Binding of Acetylene to Cationic Cobalt(III) Octaethylporphyrin

Jun-ichiro SETSUNE,* Mitsuhiro IKEDA, Yoshihiro ISHIMARU, and Teijiro KITAO
Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Sakai, Osaka 591

Acetylene is reversibly inserted into a Co-N bond of bis(aquo)-octaethylporphyrinatocobalt(III) perchlorate, $(OEP)Co^{III}(H_2O)_2ClO_4$ (1), in CH_2Cl_2 solution, generating a d^6 high spin (S = 2) complex. Addition of 2,6-lutidine to a mixture of 1 and acetylene gave a σ-vinylcobalt(III) complex, $(OEP)Co^{III}-CH=CH-L^+ClO_4$ [L = 2,6-lutidine], whereas pyridine replaced the acetylene ligand to afford $(OEP)Co^{III}(py)_2ClO_4$. These results suggest the intermediacy of a Co^{III} acetylene π-complex.

As far as metalloporphyrins are concerned, alkene and alkyne π-complexes so far characterized are only limited to $(Por)Ru^{II}(H_2C=CH_2)$,1) $(Por)Os^{II}(H_2C=CH_2)$,1b) and $(Por)Mo^{II}(PhC\equiv CPh)$.2) Whereas these π-complexes are all in a low oxidation state as is generally the case with transition metal π-complexes,3) a tri-valent metalloporphyrin π-complex, (OEP4))$Rh^{III}(H_2C=CH_2)CF_3CO_2$, has recently been shown to take place in equilibrium with a σ-complex, $(OEP)Rh^{III}-CH_2CH_2OCOCF_3$, under acidic conditions5) and discussed in relation to the proposed Co^{III} alkene π-complex intermediate in the coenzyme B_{12} dependent rearrangement of ethylene glycol to acetaldehyde catalyzed by dioldehydrase.6) This work demonstrates new aspects of the chemistry of metalloporphyrin π-complexes. That is, $(OEP)Co^{III}(H_2O)_2ClO_4$ reversibly binds acetylene in CH_2Cl_2 solution and a Co^{III} alkyne π-complex which has turned out to be too reactive to be observed spectroscopically undergoes intramolecular attack of porphyrin nitrogen on the ligated alkyne to give novel N,Co-bridged Co^{III} porphyrins. On the other hand, the intermolecular attack of 2,6-lutidine afforded various σ-vinylcobalt(III) porphyrins.

Introduction of purified acetylene gas into CH_2Cl_2 solution of $(OEP)Co^{III}(H_2O)_2ClO_4$ (1)7) resulted in the immediate color change from reddish brown to green. Addition of n-hexane to this reaction mixture afforded precipitates, the visible spectrum of which showed absorption maxima at 398, 544, and 592 nm, however, reverted rapidly to that of 1 in the absence of acetylene with showing four isosbestic points at 387, 471, 570, and 633 nm as shown in Fig. 1. ^1H-NMR spectrum of the mixture of 1 and excess acetylene in CD_2Cl_2 at 0 °C shows two 2H-signals due to meso protons at 11.6 and -9.0 ppm which are absent in the spectrum of the meso-deuterated analogue, eight 2H-signals due to CH_2 protons at 38.1, 30.9, 30.3, 28.1, 23.0, 20.3 (overlapped), and 19.3 ppm, and four 6H-signals due to CH_3 protons at 10.2, 10.0, 9.5, and 3.9 ppm (see Fig. 2). However, signals derived from acetylene could not be detected over the range of ±200 ppm. The splitting pattern and

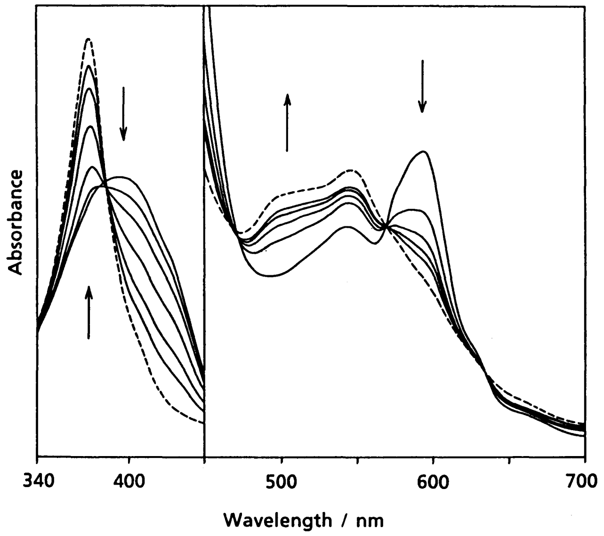


Fig. 1. UV-Vis spectral change recorded at 1 minute's interval after the dissolution of 2 in CH_2Cl_2 (------- : after 30 min).

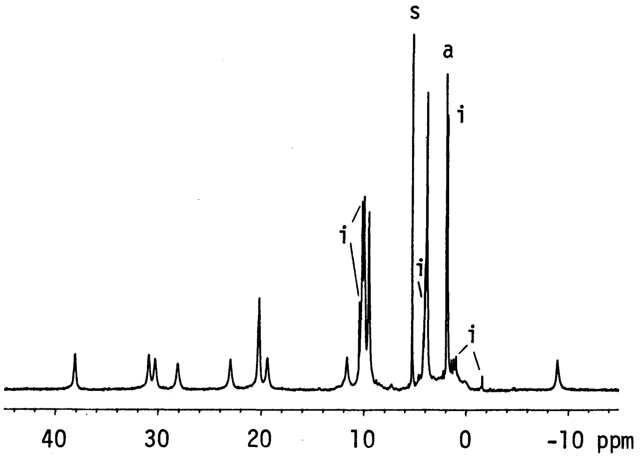


Fig. 2. ^1H-NMR spectrum of a mixture of 1 and acetylene in CD_2Cl_2 at 0 °C (a: acetylene, s: solvent, i: diamagnetic impurities).

chemical shift range of this spectrum is quite similar to that of d^6 high spin (S = 2) N-methyl(OEP)$Fe^{II}Cl$.[8] In fact, the magnetic moment (μ_{eff} = 5.2 μ_B) of this acetylene adduct (2) measured by Evans method in $CDCl_3$ at 0 °C is close to the spin only value (4.9 μ_B) for the d^6 high spin state (S = 2).

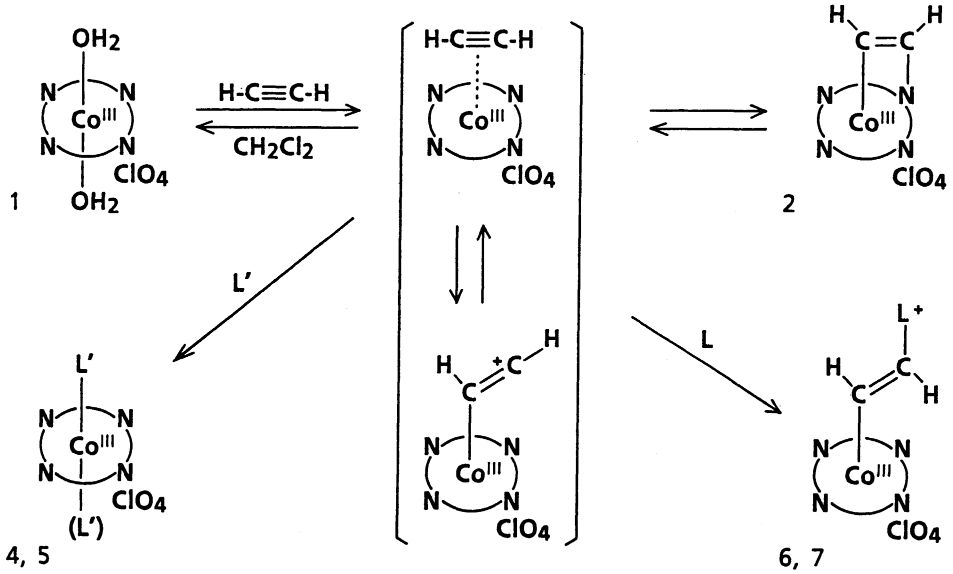
Addition of pyridine and 2,6-lutidine (5 equiv.) to the mixture of 1 and acetylene caused immediate color change from green to pink red, to give (OEP)$Co^{III}(py)_2$-ClO_4 (4)[7a] and (OEP)Co^{III}-CH=CH-$N^+(C_7H_9)ClO_4$ (6)[9] in 67% and 64% yield, respectively. Similar reactions occurred in case of triphenylphosphine and tri(o-tolyl)-phosphine. The latter attacked the coordinated acetylene to give a σ-vinyl complex, (OEP)Co^{III}-CH=CH-$P^+(C_7H_7)_3ClO_4$ (7),[10] in 84% yield while the former brought about axial ligand exchange to give (OEP)$Co^{III}(PPh_3)ClO_4$ (5)[11] in 77% yield.

It is true that the observed NMR spectrum of 2 is also like those of N-methyl-(OEP)Co^{II} complexes which are in a d^7 high spin state (S = 3/2),[12] but the fact that all the reaction products (1, 4, 5, 6, 7) derived from 2 are in a tri-valent state is only rationalized by the high spin Co^{III} structure with a Co,N-etheno bridge for 2. We have recently found that methyl propiolate reacts with 1 to give a d^6 low spin (S = 0) complex (3) which has the Co,N-etheno bridged structure with a carbomethoxy group on the cobalt side and is stable enough to be isolated.[13] The propensity to release acetylene and the high spin electronic structure of 2 in contrast to the low spin (S = 0) and stable nature of 3 is accounted for by the greater electronic repulsion between the metal d_{yz} orbital (taking a mirror plane as a xz plane) and the π-orbital of the etheno bridge in 2 than in 3.

Addition of methyl propiolate to a mixture of 1 and 2,6-lutidine gave rise to a σ-vinyl complex, (OEP)Co^{III}-$C(CO_2CH_3)$=CH-$N^+(C_7H_9)ClO_4$ (8),[14] in 77% yield. However, the Co,N-bridged complex 3 could not be converted into 8 by the treatment with 2,6-lutidine. Although a similar reaction of 1 with phenyl acetylene in the presence of 2,6-lutidine gave (OEP)Co^{III}-CH=$C(C_6H_5)$-$N^+(C_7H_9)ClO_4$ (9)[15] in 50% yield, the reaction products in the absence of the amine were too unstable to be characterized. The trans addition of cobalt and 2,6-lutidine to alkynes was verified by the vicinal coupling constant between two vinylic protons (J = 13 Hz for 6 and 14 Hz for 7) and the similarity of the ^{1}H-chemical shifts of the 2,6-lutidine moiety of 6, 8, and 9. The direction of the addition of cobalt and 2,6-lutidine to the mono-substituted alkynes was determined through ^{13}C-^{1}H correlation NMR study between the vinylic proton (-1.22 ppm for 8 and -0.51 ppm for 9) and the vinylic β-carbon (115.8 ppm for 8 and 128.5 ppm for 9) which was distinguishable from the α-carbon because Co-bound carbons are generally unobservable in the ^{13}C-NMR.[13)]

These results are strongly indicative of intermediacy of a Co^{III} acetylene π-complex which undergoes nucleophilic attack on the coordinated acetylene by nitrogen intramolecularly to give 2 and 3, intermolecularly to give 6, 8, and 9, and axial ligand exchange to give 4 and 5. The observed regioselectivity in case of the mono-substituted alkynes is accounted for by assuming a Co^{III} σ-vinyl carbonium ion intermediate that is electronically equivalent to the π-complex through σ-π conjugation.

Cationic macrocyclic Co^{III} and Rh^{III} complexes have been known to react with alkenes and alkynes to give σ-alkyl and σ-vinyl complexes.[6b,6c,7a,16)] In these reactions were postulated Co^{III} and Rh^{III} π-complexes which have recently been observed directly by ^{1}H-NMR spectroscopy as diamagnetic species.[5,6g)] However, our result points out, for the first time, that a macrocycle nitrogen of a Co^{III} complex takes part in the bonding with acetylene, leading to a novel high spin Co^{III} species which reversibly release acetylene by way of a Co^{III} π-complex.



L' = py, PPh3; L = 2,6-lutidine, tri(o-tolyl)phosphine;

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education , Science, and Culture, Japan.

References

1) a) J. P. Collman, P. J. Brothers, L. McElwee-White, E. Rose, and L. J. Wright, J. Am. Chem. Soc., 107, 4570 (1985); b) J. P. Collman, P. J. Brothers, L. McElwee-White, and E. Rose, ibid., 107, 6110 (1985).

2) A. De Cian, J. Colin, M. Schappacher, L. Ticard, and R. Weiss, J. Am. Chem. Soc., 103, 1850 (1981).

3) M. Herverhold, "Metal π-Complexes Vol.II," Elsevier, Amsterdam (1972).

4) OEP denotes octaethylporphyrin dianion.

5) B. B. Wayland, S. L. Van Voorhees, and K. J. Del Rossi, J. Am. Chem. Soc., 109, 6513 (1987).

6) a) R. H. Abeles and D. Dolphin, Acc. Chem. Res., 9, 114 (1976); b) R. B. Silverman, D. Dolphin, T. J. Carty, E. K. Krodel, and R. H. Abeles, J. Am. Chem. Soc., 96, 7096 (1974); c) R. B. Silverman and D. Dolphin, ibid., 98, 4626 (1976); d) B. T. Golding and S. Sakrikar, J. Chem. Soc., Chem. Commun., 1972, 1183; e) B. T. Golding, H. L. Holland, U. Horn, and S. Sakrikar, Angew. Chem., Int. Ed. Engl., 9, 959 (1970); f) K. L. Brown, M. M. L. Chu, and L. L. Ingraham, Biochemistry, 15, 1402 (1976); g) K. L. Brown and S. Ramamurthy, Organometallics, 1, 413 (1982).

7) a) H. Sugimoto, N. Ueda, and M. Mori, Bull. Chem. Soc. Jpn., 54, 3425 (1981); b) A. Salehi, W. A. Oertling, G. T. Babcock, and C. K. Chang, J. Am. Chem. Soc., 108, 5630 (1986).

8) A. L. Balch, Y.-W. Chan, G. N. La Mar, L. Latos-Grazynski, and M. W. Renner, Inorg. Chem., 24, 1437 (1985).

9) 6: ^{1}H-NMR ($CDCl_3$, 270 MHz) H_{meso} 10.24 (s); $H_{lut(\gamma)}$ 7.36 (t); $H_{lut(\beta)}$ 6.61 (d); CH_2 4.06 (dq); CH_3 1.87 (t); lutidine α-CH_3 -0.06 (s); $H_{vinyl(\alpha)}$ 0.01 (d)(J = 13 Hz); $H_{vinyl(\beta)}$ -0.87 (d) ppm. ^{13}C-NMR ($CDCl_3$, 67.8 MHz) $C_{lut(\alpha)}$ 153.1; $C_{py(\beta)}$ 143.9; $C_{lut(\gamma)}$ 143.6; $C_{py(\alpha)}$ 142.6; $C_{lut(\beta)}$ 125.6; C_{vinyl} 118.0; C_{meso} 99.4; CH_2 19.8; lutidine α-CH_3 19.4; CH_3 18.4 ppm.

10) 7: ^{1}H-NMR ($CDCl_3$, 270 MHz) H_{meso} 10.11 (s); H_p 7.25 (t); H_m 6.77 (m); H_o 5.28 (dd)(J_{P-H} = 15 Hz); CH_2 4.01 (q); CH_3 1.80 (t); $H_{vinyl(\alpha)}$ 1.23 (dd)(J_{vic} = 14 Hz, J_{P-H} = 21 Hz); tolyl o-CH_3 0.17 (s); $H_{vinyl(\beta)}$ -0.96 (dd) (J_{P-H} = 26 Hz). ^{13}C-NMR ($CDCl_3$, 67.8 MHz) $C_{py(\beta)}$ 144.1; $C_{py(\alpha)}$ 142.5; C_o 141.8, 126.7 (J_{C-P} = 9, 13 Hz); C_p 134.3 (J_{C-P} = 2 Hz); C_m 133.3, 132.8 (J_{C-P} = 11, 12 Hz); C_{vinyl} 115.4 (J_{C-P} = 84 Hz); C_{ipso} 105.5 (J_{C-P} = 67 Hz); C_{meso} 99.4; tolyl o-CH_3 21.0 (J_{C-P} = 5 Hz); CH_2 19.9; CH_3 18.5 ppm.

11) 5: ^{1}H-NMR ($CDCl_3$, 270 MHz) H_{meso} 10.16 (s); H_p 7.08 (m); H_m 6.56 (m); H_o 3.97 (m); CH_2 3.91 (q); CH_3 1.80 (t) ppm.

12) L. Latos-Grazynski, Inorg. Chem., 24, 1104 (1984); K. Aoyagi, H. Toi, Y. Aoyama, and H. Ogoshi, Chem. Lett., 1987, 467; K. Fukui, H. Ohoya, N. Hirota, K. Aoyagi, and H. Ogoshi, Chem. Phys. Lett., 104, 15 (1987).

13) J.-i. Setsune, M. Ikeda, and T. Kitao, J. Am. Chem. Soc., 109, 6515 (1987).

14) 8: ^{1}H-NMR ($CDCl_3$, 270 MHz) H_{meso} 10.33 (s); $H_{lut(\gamma)}$ 7.32 (t); $H_{lut(\beta)}$ 6.54 (d); CH_2 4.08 (dq); CH_3 1.88 (t); OCH_3 1.44 (s); lutidine α-CH_3 0.09 (s); H_{vinyl} -1.22 (s) ppm. ^{13}C-NMR ($CDCl_3$, 67.8 MHz) CO 162.8; $C_{lut(\alpha)}$ 154.2; $C_{py(\beta)}$ 144.2; $C_{lut(\gamma)}$ 144.0; $C_{py(\alpha)}$ 143.2; $C_{lut(\beta)}$ 125.0; C_{vinyl} 115.8; C_{meso} 100.4; OCH_3 49.4; CH_2 19.8; lutidine α-CH_3 18.6; CH_3 18.4 ppm.

15) 9: ^{1}H-NMR ($CDCl_3$, 270 MHz) H_{meso} 10.07 (s); $H_{lut(\gamma)}$ 7.59 (t); H_p 6.86 (t); $H_{lut(\beta)}$ 6.77 (d); H_m 6.55 (t); CH_2 3.99 (q); H_o 3.40 (d); CH_3 1.84 (t); lutidine α-CH_3 0.20 (s); H_{vinyl} -0.51 (s) ppm. ^{13}C-NMR ($CDCl_3$, 67.8 MHz) $C_{lut(\alpha)}$ 152.8; $C_{lut(\gamma)}$ 144.4; $C_{py(\beta)}$ 144.4; $C_{py(\alpha)}$ 142.9; C_{ipso} 133.6; C_{vinyl} 128.5; C_p 127.4; $C_{o,m}$ 126.9, 126.8; $C_{lut(\beta)}$ 126.4; C_{meso} 99.8; lutidine α-CH_3 20.0; CH_2 19.8; CH_3 18.3 ppm.

16) M. C. Weiss, and V. L. Goedken, J. Am. Chem. Soc., 98, 3389 (1976); D. Cummins, E. D. Mckenzie, and A. Segnitz, J. Organometal. Chem., 87, C19 (1975); H. Ogoshi, J.-i. Setsune, Y. Nanbo, and Z.-I. Yoshida, ibid., 159, 328 (1978).

(Received January 20, 1989)