CHEMISTRY LETTERS, pp. 1173-1176, 1992.

Preparation of Novel σ-Bonded Organozirconium(IV) Porphyrins and Photoreduction to the Zirconium(II) Complex by Visible Light

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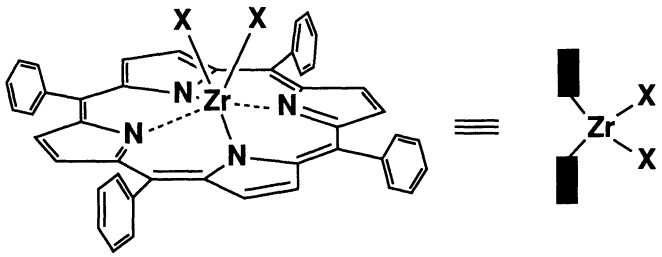
Reaction of (5, 10, 15, 20-tetraphenylporphinato)zirconium diacetate ((TPP)Zr(OAc)$_2$) with organo-lithium or -magnesium compounds gave the corresponding σ-bonded organozirconium(IV) porphyrins ((TPP)ZrR$_2$, R = Me, Et, *n*-Bu, and Ph). Irradiation of (TPP)ZrMe$_2$ with visible light resulted in a clean generation of the low-valent zirconium(II) porphyrin complex.

Despite the increasing interest in organometallic complexes of early transition metals, the chemistry of their porphyrin complexes still remains in an undeveloped state. We have recently discovered that zirconium(IV) porphyrins serve as novel, efficient catalysts for regio- and stereoselective carboalumination of alkynes, where (porphinato)zirconium complexes carrying σ-bonded zirconium - alkyl groups are the active species.[1] Thus, the reactivities of the zirconium - carbon bonds in organozirconium porphyrins are of fundamental interest.

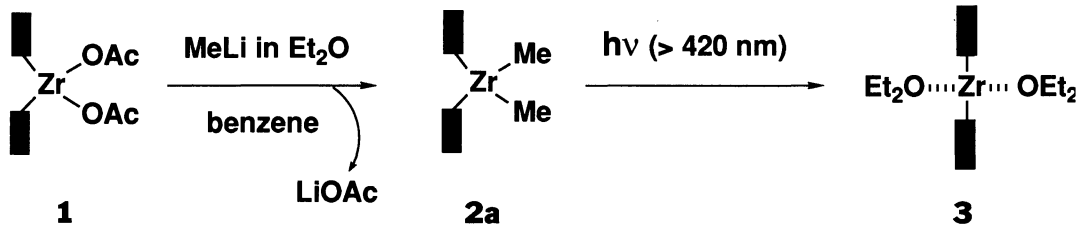
In the present communication, we wish to report successful preparation of some σ-bonded dialkyl- and diaryl-zirconium(IV) porphyrins (**2**), and a clean generation of the novel low-valent zirconium(II) species (**3**) by photoreduction of the dimethyl complex (**2a**) with visible light (Scheme 1).[2]



Zirconium(IV) porphyrins

1 : X = OAc **2a** : X = Me **2c** : X = *n*-Bu
2b : X = Et **2d** : X = Ph

A typical example of the preparation of **2** was given below. To a 10-mL Pyrex round-bottomed flask fitted with a three-way stopcock containing a benzene suspension (2 mL) of **1** ((TPP)Zr(OAc)$_2$,[3] 0.041 g / 0.05 mmol) was added under dry nitrogen an ether solution of methyllithium (0.45 mmol) at room temperature, where **1** was immediately dissolved to give a clear reddish brown solution. The flask was wrapped in aluminum foil, and the content was stirred in the dark for 1 h at room temperature, then evaporated to dryness under reduced pressure. The ^{1}H NMR spectrum of the residue in C_6D_6 is shown in Fig. 1,[4] where a singlet signal due to the Zr-O_2CCH_3 groups of **1**



1 2a 3

Scheme 1.

(δ0.37 ppm (6H)) is not observed,[3] while a new singlet signal assignable to the two methyl groups bound to Zr appears in the highly upfield region (δ-2.98 ppm (6H)) due to the strong shielding effect of the porphyrin ligand. The signals due to the *ortho*-protons of the peripheral phenyl rings (Ph-*o*) are observed at two different positions (δ8.52 (4H) and 8.14 (4H)), similarly to **1**,[3] demonstrating the *cis* coordination of the two axial methyl groups to the zirconium porphyrin moiety (**2a**).

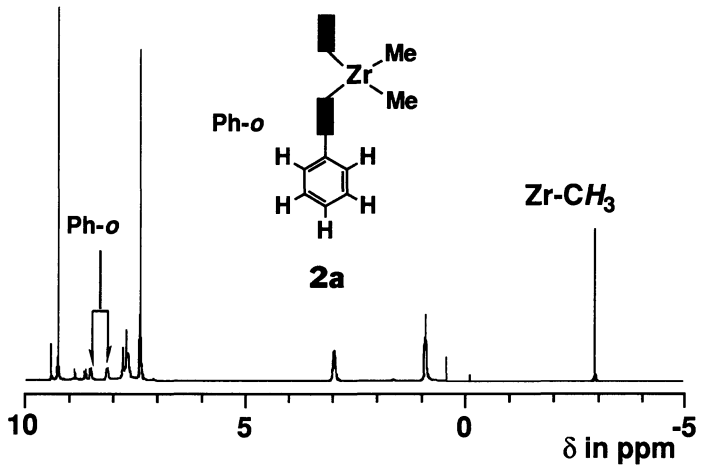


Fig. 1. ^{1}H NMR spectrum of the reaction mixture of **1** and MeLi in C_6D_6/Et_2O at room temperature under N_2.

Similarly, di-*n*-butyl- and diphenyl-zirconium(IV) porphyrins (**2c** and **2d**) were prepared by using *n*-BuLi and PhLi, respectively, in place of MeLi.[4] Use of organomagnesium compounds such as EtMgBr and *n*-Bu_2Mg-TMED[5] for the reaction with **1** also resulted in the formation of diethylzirconium(IV) porphyrin (**2b**) and **2c**, respectively.[4] It is interesting to note that the complexes **2b** and **2c** whose alkyl groups bear β-hydrogens were stable even at room temperature, distinct from the zirconocene analogs (Cp_2ZrR_2). For example, Cp_2ZrEt_2 and $Cp_2Zr(n\text{-}Bu)_2$ have been reported to be stable only at a very low temperature such as -78 °C, while they easily undergo β-hydrogen elimination followed by reductive elimination upon warming to room temperature, giving the corresponding Cp$_2$Zr(II) - olefin complexes.[6]

Of much interest to note is a clean photoreduction of (TPP)$ZrMe_2$ (**2a**) into the low-valent zirconium(II) species. When a benzene solution of **2a**, prepared from **1** and MeLi (1/5), was irradiated with visible light (> 420 nm)[7] at room temperature, the color of the solution gradually turned to green. In the ^{1}H NMR spectrum in C_6D_6 after 3-h irradiation (Fig. 2), the signal due to the Zr-Me groups of **2a** (δ-2.98 ppm in Fig. 1) completely disappeared, while the two signals due to the *ortho*-protons of the peripheral phenyl rings (Ph-*o*) turned to a single resonance at δ8.64 (8H) ppm, indicating that the two faces of the complex became structurally equivalent to each other. From these observations, the zirconium species thus formed is con-

cluded to be the novel, low-valent zirconium(II) porphyrin complex (**3**).[8] The high susceptibility of **2a** to visible light is quite interesting, considering its high thermal stability: no decomposition of **2a** even when heated at 50 °C for 5 h. Since the signals of ether in Fig. 2 are observed to shift from the original positions,[9] the zirconium(II) porphyrin (**3**) is considered to be coordinated by ether. When 1-methylimidazole (MeIm) was added to this system, the upfield shift for the signals of ether disappeared, and the **3**-MeIm complex was formed.[10] On the other hand, no such axial ligand exchange was observed when trimethylphosphine or *tert*-butylacetylene was added even in large excess to the **3**-Et_2O complex. It was also noted that the zirconium(II) porphyrin (**3**) was easily demetallated by H_2O to give the free base porphyrin ($TPPH_2$), although zirconium(IV) porphyrins such as **1** are not completely demetallated even upon treatment with conc. H_2SO_4.

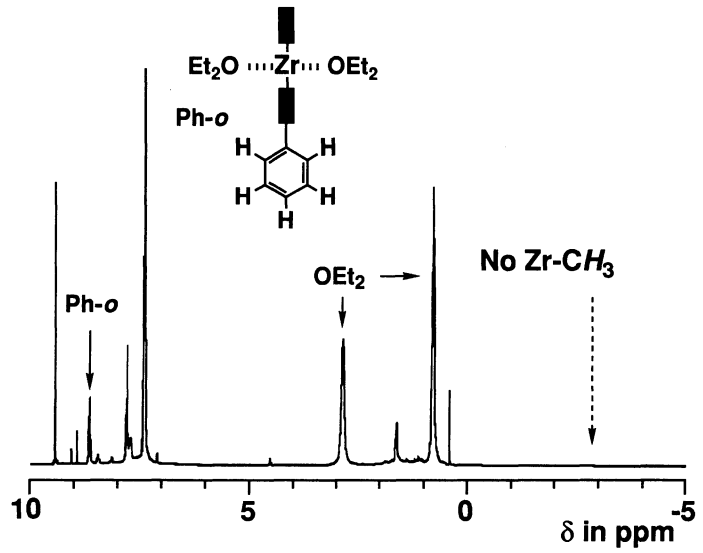


Fig. 2. ^1H NMR spectrum of the reaction mixture of **1** and MeLi in C_6D_6/Et_2O after 3-h irradiation with a xenon arc light (> 420 nm) at room temperature under N_2.

In conclusion, the unique thermal and photochemical reactivities were observed for the zirconium - carbon bonds in σ-bonded organozirconium(IV) porphyrins. For the visible light - induced reduction of dimethylzirconium(IV) porphyrin to the zirconium(II) species, photoexcitation of the porphyrin ligand is considered to be responsible. Utilization of these new zirconium porphyrin complexes for organic syntheses is now under investigation.

References

1) K. Shibata, T. Aida, and S. Inoue, *Tetrahedron Lett.*, **33**, 1077 (1992).
2) As for the porphyrin complexes of low-valent group IV metals, Ti(II) porphyrins have been recently reported, which were prepared by the $LiAlH_4$ reduction of dichlorotitanium(IV) porphyrins in the presence of diphenylacetylene. L. K. Woo, J. A. Hays, R. A. Jacobson, and C. L. Day, *Organometallics*, **10**, 2102 (1991).
3) Preparation of **1**, see Ref. 1. ^1H NMR (δ in ppm) in C_6D_6: 9.27 (s, pyrrole-β, 8H), 8.75, 8.22 (dd, Ph-*o*, 4H × 2), 7.65 - 7.85 (m, Ph-*m, p*, 12H), 0.37 (s, Zr-O_2CCH_3, 6H). UV-Vis (CH_2Cl_2) λ_{max} / nm: 396.0, 417.5, 540.5, 531.5. The X-ray crystallography of (OEP)$Zr(OAc)_2$ (OEP: octaethylporphinato) has demonstrated the *cis*-coordination of the two axial acetate ligands to the zirconium porphyrin moiety: G. A. Taylor and M. Tsutsui, "Porphyrins and Metalloporphyrins," ed by K. M. Smith, Elsevier, Amsterdam (1975), p. 295.

4) ^{1}H NMR (δ in ppm) for **2a** in C_6D_6: 9.27 (s, pyrrole-β, 8H), 8,52, 8.14 (dd, Ph-*o*, 4H × 2), 7.7 - 7.9 (m, Ph-*m, p*, 12H), -2.98 (s, C*H*$_3$, 6H). For Zr-Et of **2b**: -2.34 (t, CH_2CH_3, 6H), -3.19 (q, Zr-C*H*$_2$, 4H). For Zr-*n*-Bu of **2c**: 0.42 (t, $(CH_2)_3CH_3$, 6H), 0.04 (m, Zr-$(CH_2)_2CH_2$, 4H), -2.51 (m, Zr-CH_2CH_2, 4H), -3.15 (t, Zr-C*H*$_2$, 4H). For Zr-Ph of **2d**: 6.38 (d, Ph-*p*, 2H), 6.28 (m, Ph-*m*, 4H), 3.97 (d, Ph-*o*, 4H).

5) Prepared as reported in: M. H. Gitlitz and W. J. Considine, *J. Organomet. Chem.*, **23**, 281 (1970).

6) T. Takahashi, T. Seki, Y. Nitto, and M. Saburi, *J. Am. Chem. Soc.*, **113**, 6266 (1991) and references cited therein.

7) With a 500-W xenon arc lamp through glass filters to cut out heat and light with the wavelength shorter than 420 nm.

8) ^{1}H NMR (δ in ppm) for **3** in C_6D_6 containing Et_2O ([**3**] / [Et_2O] = 1 / 14): 9.44 (s, pyrrole-β, 8H), 8.64 (m, Ph-*o*, 8H), 7.7 - 7.8 (m, Ph-*m, p*, 12H), 2.85 (br., ether CH_2), 0.79 (br., ether CH_3).

9) ^{1}H NMR (δ in ppm) for Et_2O in C_6D_6: 3.51 (CH_2) and 1.35 (CH_3).

10) ^{1}H NMR (δ in ppm) for the **3**-MeIm complex ([**3**] / [MeIm] = 1 / 21) in C_6D_6: 9.45 (s, pyrrole-β, 8H), 8.64 (m, Ph-*o*, 8H), 7.7 - 7.8 (m, Ph-*m, p*, 12H), 6.8 (br., MeIm 2, 5-H), 6.06 (br. s., MeIm 4-H), 2.45 (br. s., MeIm N-CH_3). For MeIm in C_6D_6: 7.48 (2-H), 7.24 (5-H), 6.51 (4-H) and 2.75 (N-CH_3).

(Received April 4, 1992)