

# Novel $\eta^1$ -alkynyl zirconium porphyrin complexes: synthesis and characterization of (por)Zr( $\eta^1$ -C $\equiv$ CR)<sub>3</sub>Li(THF) [por = octaethylporphyrinato (oep) or tetraphenylporphyrinato dianion (tpp)]; R = Ph, SiMe<sub>3</sub>]

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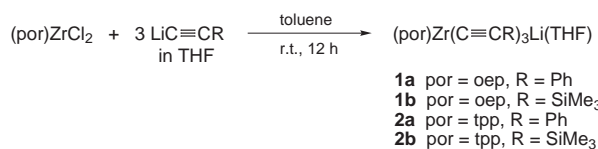
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Received (in Cambridge, UK) 10th March 1999, Accepted 21st April 1999

Reaction of (por)ZrCl<sub>2</sub> [por = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion (oep) or 5,10,15,20-tetraphenylporphyrinato dianion (tpp)] with 3 equiv. of LiC $\equiv$ CR (R = Ph and SiMe<sub>3</sub>) produces novel alkynyl zirconium(IV) porphyrin complexes (por)Zr( $\eta^1$ -C $\equiv$ CR)<sub>3</sub>Li(THF) in which three alkynyl ligands are coordinated to the zirconium center in a piano stool fashion and the Li<sup>+</sup> ion is bound to the pocket formed by three alkynyl ligands; treatment of (por)Zr( $\eta^1$ -C $\equiv$ CPh)<sub>3</sub>Li(THF) with anhydrous HCl produces a C–C bond coupled product H<sub>2</sub>C=CPh(C $\equiv$ CPh) and HC $\equiv$ CPh quantitatively.

Although early transition metal porphyrin complexes have received considerable attention in recent years,<sup>1</sup> the chemistry still remains in large part undeveloped. We<sup>2</sup> and others<sup>3,4</sup> have prepared organometallic zirconium porphyrin complexes and investigated their chemistry. As part of our work on organometallic zirconium porphyrin complexes, we are interested in alkynyl zirconium porphyrin complexes. Alkynyl metal complexes have been known to be involved in linear- and cyclo-oligomerization of terminal alkynes by various d-block<sup>5</sup> and f-block<sup>6</sup> metals. Alkynyl ligands  $\sigma$ -bonded to a metal center are also able to coordinate to other metal centers by using  $\pi$ -electrons of the C $\equiv$ C groups. A variety of bridging fashions have been found in alkynyl bridged multinuclear complexes.<sup>7</sup> However, there are few transition metal alkynyl complexes containing three alkynyl ligands coordinated to a single metal center.<sup>8</sup> Here we report the synthesis and characterization of novel alkynyl zirconium porphyrin complexes. They are not only the first well-characterized alkynyl metalloporphyrin complexes<sup>9</sup> but also rare examples of trialkynyl transition metal complexes.

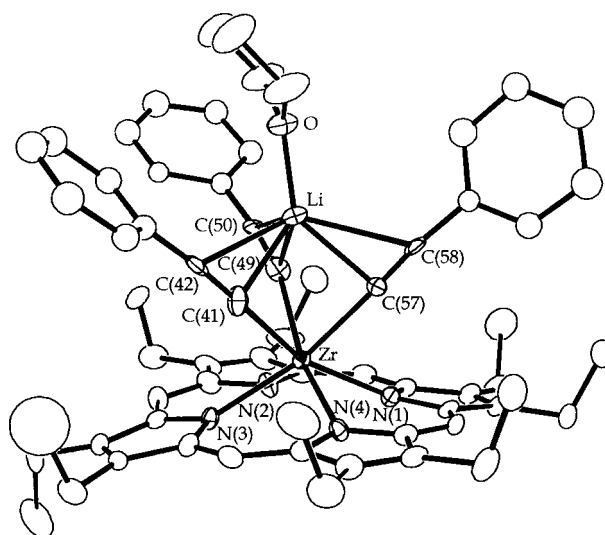
Alkynyl zirconium porphyrin complexes **1a,b**, **2a,b** were synthesized in high yields by the reactions of (por)ZrCl<sub>2</sub> with 3 equiv. of LiC $\equiv$ CR.<sup>†</sup>



The <sup>1</sup>H NMR signals for the phenyl and the SiMe<sub>3</sub> protons of the alkynyl ligands coordinated to the (por)Zr moiety in **1a–2b** are shifted to higher field owing to the ring current of the porphyrin ligand. The diastereotopic methylene signals for the oep ligand in **1a** and **1b** indicates that the environments of the two sides of the porphyrin are different in these complexes. In addition, the significant upfield shift of the signals for one THF molecule implies that the THF molecule is located above the porphyrin ring current. The THF molecule is easily displaced by an excess of diethyl ether, as judged by NMR spectroscopy.

The structure of **1a** has been confirmed by X-ray crystallography (Fig. 1).<sup>‡</sup> Three alkynyl groups are attached to the

zirconium on one side of the (oep)Zr unit. The coordination geometry around the zirconium is best described as a 4 : 3 piano stool with the porphyrin occupying the square base. The Li<sup>+</sup> is coordinated by three C $\equiv$ C bonds of the alkynyl ligands and one THF molecule in a pseudotetrahedral coordination geometry. The overall structure of **1a** is consistent with that in solution. The crystal structure of **1a** also suggests that the larger upfield shifted <sup>1</sup>H NMR signals for the THF molecule in **1a** than those in **1b** are due to the additional ring current of the three phenyl groups. The Zr–N bond distances range from 2.253(3) to 2.272(4) Å with an average value of 2.259(7) Å. The Zr atom is displaced 1.008 Å from the mean N<sub>4</sub> plane. The Zr–C bond distances in **1a** [2.305(10), 2.329(10) and 2.334(10) Å] are somewhat longer than those in (oep)Zr(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> [2.285(4), 2.289(4) Å],<sup>3a</sup> but shorter than those in (oep)ZrMe<sub>2</sub> [2.352(4), 2.334(4) Å].<sup>3b</sup> The Zr–C bond distances in **1a** are significantly longer than those in (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(C $\equiv$ CPh)<sub>2</sub> [2.19(3), 2.21(3) Å],<sup>10</sup> which may be attributed to the large steric congestion caused by three alkynyl ligands in **1a**. However, the C $\equiv$ C distances [1.210(12), 1.230(12) and 1.215(12) Å] in **1a** are similar to those in (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(C $\equiv$ CPh)<sub>2</sub> [1.23(4) and 1.24(4) Å]. The THF molecule is coordinated to the Li<sup>+</sup> along the Zr...Li axis (Zr...Li–O angle 175.8°) with a Li–O bond distance of 1.905(8) Å. The Zr...Li distance of 3.071(8) Å shows no direct interaction between two metal centers.



**Fig. 1** Structure of (oep)Zr( $\eta^1$ -C $\equiv$ CPh)<sub>3</sub>Li(THF) **1a**. Selected bond distances (Å) and angles (°): Zr–N(1) 2.254(4), Zr–N(2) 2.257(3), Zr–N(3) 2.272(4), Zr–N(4) 2.253(3), Zr–C(41) 2.334(10), Zr–C(49) 2.329(9), Zr–C(57) 2.305(10), Li–C(41) 2.212(12), Li–C(49) 2.240(12), Li–C(57) 2.227(12), Li–C(42) 2.611(12), Li–C(50) 2.676(12), Li–C(58) 2.590(12), C(41)–C(42) 1.210(12), C(49)–C(50) 1.230(12), C(57)–C(58) 1.215(12), Li–O 1.905(8), Zr...Li 3.071(8), C(41)–Zr–C(49) 77.2(3), C(49)–Zr–C(57) 78.3(3), C(41)–Zr–C(57) 76.8(3), Zr...Li–O 175.8.

Complexes **1a–2b** are highly sensitive to moisture similarly to other alkyl zirconium porphyrin complexes. Upon the addition of water, they are readily hydrolyzed to produce the corresponding acetylene HC≡CR and hydroxo-bridged dimeric zirconium porphyrins.<sup>2b</sup> On the other hand, treatment of **1a** with anhydrous HCl in C<sub>6</sub>D<sub>6</sub> produces quantitatively a C–C bond coupled product H<sub>2</sub>C=CPh(C≡CPh) and HC≡CPh along with (oep)ZrCl<sub>2</sub>. In contrast, under the same conditions **1b** produces mainly the simple alkyne HC≡CSiMe<sub>3</sub> along with (*E*)-Me<sub>3</sub>-SiCH=CHC≡CSiMe<sub>3</sub> as a minor product. The tpp analogs **2a** and **2b** show similar reactivities. It is not surprising that **1b** and **2b** exhibit different reactivity and regioselectivity from **1a** and **2a**. Such differences of the dimerization of terminal alkynes have been found in the literature,<sup>5,6</sup> which is believed to be due to the different electronic effect of the substituent on the alkyne. Negishi and coworkers reported similar reactivities of Li[Cp<sub>2</sub>Zr(C≡CPh)<sub>3</sub>] which is generated *in situ* from the reaction of Cp<sub>2</sub>ZrCl<sub>2</sub> with 3 equiv. of LiC≡CPh.<sup>11</sup> Upon quenching Li[Cp<sub>2</sub>Zr(C≡CPh)<sub>3</sub>] with aqueous HCl, (*Z*)-PhCH=CHC≡CPh was produced as an isomerically pure compound. They proposed that C–C bond formation proceeds *via* a non-dissociative mechanism such as 1,2-migration of an alkynyl group. The mechanism of C–C bond formation in our case is still unclear, but the following observation is informative. Treatment of **1a** or **2a** with anhydrous HCl in the presence of an excess of HC≡CR (R = *p*-Tol, SiMe<sub>3</sub>) produces only H<sub>2</sub>C=CPh(C≡CPh) as a C–C bond coupled product without cross-coupled products such as H<sub>2</sub>C=CPh(C≡CR) or H<sub>2</sub>C=CR(C≡CPh). The result implies that C–C bond formation does not proceed *via* the dissociative pathway involving the reinsertion of free HC≡CPh into the Zr–C≡CPh, followed by protonolysis.

We have also attempted to synthesize the dialkynyl complexes (por)Zr(C≡CR)<sub>2</sub> using 2 equiv. of LiC≡CR, but the reaction afforded (por)Zr(C≡CR)<sub>3</sub>Li(THF) as the major product. This is in sharp contrast to the zirconocene case in which stable dialkynyl complexes are isolated.<sup>12</sup> More electropositive metal centers of the Zr(por) unit compared to the Cp<sub>2</sub>Zr moiety may account for their different reactivities.

In summary, we synthesized the novel trialkynyl zirconium porphyrin complexes (por)Zr(η<sup>1</sup>-C≡CR)<sub>3</sub>Li(THF). The porphyrin complexes show different reactivities compared to the analogous Cp<sub>2</sub> complex. Further studies on the mechanism of the enyne formation upon treatment of the alkynyl complexes with HCl as well as other reactivities of the alkynyl zirconium porphyrin complexes are underway. These complexes may be useful entries to a variety of bimetallic porphyrin complexes by replacing Li<sup>+</sup>. Work along this line is also in progress.

We gratefully acknowledge support from the Korea Research Foundation (Non Directed Research Fund, 1996) and in part from Korea Science and Engineering Foundation through Center for Biofunctional Molecules.

## Notes and references

† (oep)Zr(η<sup>1</sup>-C≡CPh)<sub>3</sub>Li(THF) **1a**: to a suspension of (oep)ZrCl<sub>2</sub> (0.280 g, 0.40 mmol) in toluene (*ca.* 30 mL) was slowly added a THF solution (*ca.* 3 mL) of LiC≡CPh (0.132 g, 1.22 mmol). The reaction mixture was stirred at room temp. for 12 h and then filtered. The solvent was removed under reduced pressure to give **1a** as a dark red solid in 92% yield. Analytically pure material was recrystallized from toluene–pentane. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 10.67 (s, 4H, *meso*-H), 6.78 (m, 9H, *m*-, *p*-Ph), 6.66 (d, 6H, *o*-Ph), 4.07 (m, 16H, CH<sub>2</sub>CH<sub>3</sub>), 2.14 (br s, 4H, α-THF), 1.89 (t, 24H, CH<sub>2</sub>CH<sub>3</sub>),

0.15 (br s, 4H, β-THF). IR (KBr, cm<sup>-1</sup>): ν 2066 (C≡C). UV–VIS (toluene, nm): λ<sub>max</sub> (log ε) 400 (5.24), 532 (4.31), 568 (4.58). MS (FAB): *m/z* 933 ([M – THF]H<sup>+</sup>), 831 ([M – THF – C≡CPh]<sup>+</sup>). Anal. Calc. for C<sub>64</sub>H<sub>67</sub>N<sub>4</sub>O<sub>4</sub>LiZr: C, 76.37; H, 6.72; N, 5.57. Found: C, 76.41; H, 6.36; N, 5.87%.

(oep)Zr(η<sup>1</sup>-C≡CSiMe<sub>3</sub>)<sub>3</sub>Li(THF) **1b**: **1b** was synthesized from (oep)ZrCl<sub>2</sub> and LiC≡CSiMe<sub>3</sub> in 83% yield after recrystallization from pentane by the same procedure as for **1a**. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 10.55 (s, 4H, *meso*-H), 4.24 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 3.98 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 2.70 (br s, 4H, α-THF), 1.86 (t, 24H, CH<sub>2</sub>CH<sub>3</sub>), 0.72 (br s, 4H, β-THF), –0.18 [s, 27H, Si(CH<sub>3</sub>)<sub>3</sub>]. IR (KBr, cm<sup>-1</sup>): ν 2010 (C≡C). UV–VIS (toluene, nm): λ<sub>max</sub> (log ε) 400 (5.32), 532 (4.03), 568 (4.37). MS (FAB): *m/z* 921 ([M – THF]H<sup>+</sup>), 823 ([M – THF – C≡CSiMe<sub>3</sub>]<sup>+</sup>). No satisfactory elemental analysis was obtained due to extreme air/moisture sensitivity.

Using the same procedure as for **1a** (tpp)Zr(η<sup>1</sup>-C≡CPh)<sub>3</sub>Li(THF) **2a** was synthesized from (tpp)ZrCl<sub>2</sub> and LiC≡CPh in 61% yield after recrystallization from toluene–pentane. Likewise, (tpp)Zr(η<sup>1</sup>-C≡CSiMe<sub>3</sub>)<sub>3</sub>Li(THF) **2b** was synthesized from (tpp)ZrCl<sub>2</sub> and LiC≡CSiMe<sub>3</sub> in 72% yield after recrystallization. Full experimental data and descriptions of reactions as well as details of crystal data and structural refinement can be accessed electronically: see <http://www.rsc.org/suppdata/cc/1999/1033>.

‡ *Crystal data*: for **1a**: C<sub>60</sub>H<sub>59</sub>N<sub>4</sub>LiZrC<sub>4</sub>H<sub>8</sub>O, *M* = 1006.38, monoclinic, *C*2/*c* (no. 15), *a* = 19.265(6), *b* = 19.952(3), *c* = 28.991(12) Å, β = 104.88(2)°, *U* = 10769(6) Å<sup>3</sup>, *Z* = 8, μ(Mo-Kα) = 2.5 cm<sup>-1</sup>, *T* = 188 K, Enraf-Nonius CAD4 diffractometer, Mo-Kα (λ = 0.71073 Å), anisotropic refinement for all nonhydrogen atoms (except for phenyl groups), final cycle of full matrix least squares refinement on *F*<sup>2</sup> with 6593 independent reflections and 705 variables (SHELXL-93), *R*1 [*I* > 2σ(*I*)] = 0.0535, *wR*2 (all data) = 0.1331, GOF = 1.039. CCDC 182/1233. See <http://www.rsc.org/suppdata/cc/1999/1033/> for crystallographic files in .cif format.

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Communication 9/01923E