J. Am. Chem. Soc. 1992, 114, 2266-2267

Early Transition Metal Porphyrins. Synthesis and Reactivity of Some Novel Zirconium Derivatives and the X-ray Crystal Structure of the First Metalloporphyrin *cis*-Dialkyl: (OEP)Zr$(CH_2SiMe_3)_2$

Holger Brand and John Arnold*

Department of Chemistry, University of California
Berkeley, California 94720

Received November 22, 1991

Porphyrin ligation is ubiquitous in late transition metal chemistry, where a wide range of coordination environments has been studied.[1,2] In comparison, porphyrin chemistry of the early transition metals remains relatively undeveloped. We are interested in exploring porphyrin derivatives of heavier second and third row elements, where the metal is constrained to lie out of the porphyrin plane as a result of its large radius.[3] For zirconium and hafnium, few derivatives are known apart from oxo-ligated derivatives originally developed by Buchler and co-workers.[4,5] Drawing an analogy from the metallocene chemistry of zirconium, where Cp_2ZrCl_2 is the starting material for a wide range of compounds, we sought to prepare the porphyrin analogue.[6] Here we describe the preparation of (OEP)$ZrCl_2$ (OEP = dianion of octaethylporphyrin) and its use as a reagent for the preparation of several unprecedented metalloporphyrin derivatives; these include the first examples of metalloporphyrin *cis*-alkoxide and η^8-cyclooctatetraene derivatives. We also report the synthesis and X-ray structure of a novel *cis*-dialkyl complex and preliminary studies indicating that this complex promotes the catalytic hydrogenation of terminal olefins.

Multigram quantities of the *cis*-dichloride complex (OEP)$ZrCl_2$ (**1**) are easily obtained by reaction of $(THF)_4Li_2(OEP)$[7,8] with $ZrCl_4(THT)_2$ (THT = tetrahydrothiophene) in refluxing 1,2-dimethoxyethane (Scheme I). Dark red, air-stable crystals of the hemi-toluene solvate of **1** were obtained in 60% yield from hot toluene.[9] The dichloride is insoluble in hexane and diethyl ether, moderately soluble in THF and toluene, and very soluble in methylene chloride and chloroform in which it forms dark red, air-sensitive solutions. As expected for an out-of-plane structure, the diastereotopic methylene protons of the OEP ligand give rise to a complex multiplet in the ^1H NMR spectrum. The compound sublimes without decomposition, and a strong parent ion is seen in the EI mass spectrum.

As shown in Scheme I, the dichloride is an excellent precursor to new metalloporphyrin derivatives. For example, reaction with 2 equiv of $LiOBu^t$ affords the *cis*-alkoxide derivative **2**. Dark red, moisture-sensitive crystals were isolated in 70% yield from toluene/hexane.[9] The compound is stable to heat and light and has been fully characterized. The *tert*-butoxide protons show a high-field signal at δ −0.38 ppm in the ^1H NMR spectrum due to shielding by the aromatic porphyrin ligand; once again, the appearance of diastereotopic methylenes indicates formation of the cis isomer.

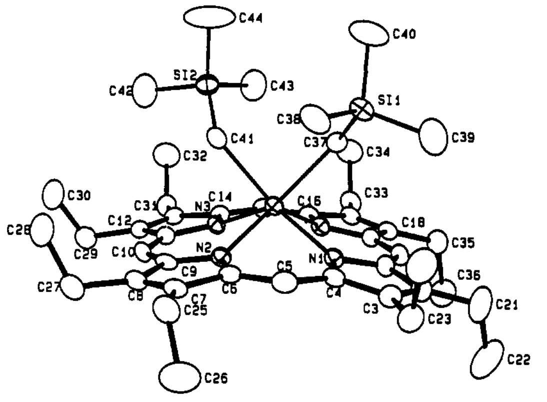
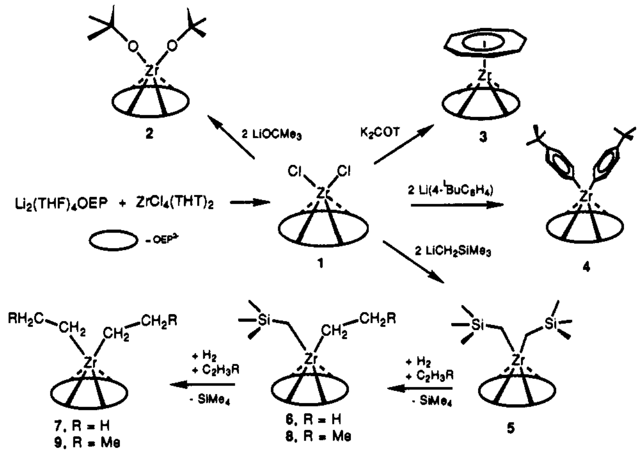


Figure 1. Molecular structure of (OEP)$Zr(CH_2SiMe_3)_2$ (**5**). Thermal ellipsoids were scaled to represent the 50% probability level. Selected distances (angstroms) and angles (degrees): Zr–N(1) 2.236 (3), Zr–N(2) 2.232 (3), Zr–N(3) 2.250 (3), Zr–N(4) 2.248 (3), Zr–C(37) 2.285 (4), Zr–C(41) 2.289 (4), Si(1)–C(37) 1.862 (4), Si(2)–C(41) 1.845 (4); C(41)–Zr–C(37) 82.7 (1), Zr–C(41)–Si(2) 123.2 (2), Zr–C(37)–Si(1) 127.8 (2).

Scheme I



Metalloporphyrin π-complexes are rare; until recently, only a few alkene and alkyne species were known.[10] Our synthesis of η^5-cyclopentadienyl derivatives (OEP)Sc(η^5-C_5R_5)[3] suggested that for Zr the related η^8-$C_8H_8^{2-}$ species might be accessible. Treatment of **1** with K_2COT in THF gave a dark red solution from which the air-sensitive, 18-electron compound (OEP)Zr(η^8-C_8H_8) (**3**) was isolated as red needles in 20% yield.[9]

Organometallic σ-complexes[10,13] are formed quantitatively on addition of 2 equiv of an aryl- or alkyllithium to toluene suspensions of the dichloride. The diaryl species **4** is assigned a cis structure on the basis of ^1H NMR data.[9] The heavily shielded aryl ortho and meta protons appear as doublets at δ 5.83 and 3.44 ppm, respectively.[14] Solutions of **4** are thermally and photo sensitive (even to normal room lighting), and decomposition

---

[1] Dolphin, D. *The Porphyrins*; Academic: New York, 1978; Vols. 1–4.

[2] *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: New York, 1975.

[3] Arnold, J.; Hoffman, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 8620.

[4] Buchler, J. W. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. 1, p 390.

[5] Buchler, J. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: New York, 1975; p 159. Hoard, J. L. *Idem*; p 317.

[6] Berezin, B. D.; Lomova, T. N. *Russ. J. Inorg. Chem.* **1981**, *26*, 203.

[7] Arnold, J. *J. Chem. Soc., Chem. Commun.* **1990**, 976.

[8] Buchler, J. W.; De Cian, A.; Fischer, J.; Hammerschmitt, P.; Weiss, R. *Chem. Ber.* **1991**, *124*, 1051.

[9] Selected characterization data for new compounds. **1**: ^1H NMR (400 MHz, $CDCl_3$) δ 10.61 (s, 4 H), 4.21 (m, 16 H), 1.90 (t, 24 H). **2**: ^1H NMR (400 MHz, C_6D_6) δ 10.41 (s, 4 H), 3.98 (m, 16 H), 1.87 (t, 24 H), −0.38 (s, 18 H). **3**: ^1H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 4 H), 4.16 (m, 16 H), 2.04 (s, 8 H), 1.96 (t, 24 H). **4**: ^1H NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 4 H), 5.82 (d, 4 H), 3.95 (m, 16 H), 3.44 (d, 4 H), 1.81 (t, 24 H), 0.61 (s, 18 H). **5**: ^1H NMR (400 MHz, C_6D_6) δ 10.59 (s, 4 H), 3.94 (m, 16 H), 1.86 (t, 24 H), −1.16 (s, 18 H), −3.82 (s, 4 H). **6**: ^1H NMR (400 MHz, C_6D_6) δ −1.31 (s, 9 H), −2.29 (t, J = 7.6 Hz, 3 H), −3.45 (q, J = 7.6 Hz, 2 H), −4.18 (s, 2 H). **7**: ^1H NMR (400 MHz, C_6D_6) δ −2.65 (t, J = 7.6 Hz, 6 H), −3.79 (q, J = 7.6 Hz, 4 H). **8**: ^1H NMR δ −0.46 (t, J = 7.0 Hz, 3 H), −1.29 (s, 9 H), −2.44 (sext, J = 7.1 Hz, 2 H), −3.44 (t, J = 7.1 Hz, 2 H), −4.16 (s, 2 H). **9**: δ −0.54 (t, J = 6.9 Hz, 6 H), −2.73 (sext, J = 6.9 Hz, 4 H), −3.69 (t, J = 7.2 Hz, 4 H). All compounds isolated gave satisfactory elemental analyses.

[10] Brothers, P. J.; Collman, J. P. *Acc. Chem. Res.* **1986**, *19*, 209.

[11] Westerhof, A.; De Liefde Meijer, H. J. *J. Organomet. Chem.* **1976**, *116*, 319.

[12] Stella, S.; Chiang, M.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1987**, 161.

[13] Guilard, R.; Lecomte, C.; Kadish, K. M. *Struct. Bonding* **1987**, *64*, 207. Guilard, R.; Kadish, K. M. *Chem. Rev.* **1988**, *88*, 1121.

[14] The higher upfield shifts seen in *trans*-diphenyl species such as (OEP)$RuPh_2$ presumably result from the closer proximity of the phenyl ligands to the porphyrin in the latter. See for example: Shista, C.; Ke, M.; James, B. R.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1986**, 787.

0002-7863/92/1514-2266$03.00/0

products have thus far prevented isolation of the material as a pure solid. Addition of acetic acid generates the known diacetate[15] and 2 equiv of arene.

A more tractable organo derivative was prepared by reaction of the dichloride with $LiCH_2SiMe_3$; the resulting *cis*-dialkyl **5** was isolated in quantitative yield and has been fully characterized.[9] Although crystalline **5** is very air-sensitive, it can be stored at room temperature in a fluorescent-lit, nitrogen-filled drybox for many months. Benzene solutions exposed to fluorescent room lighting for several hours decompose to a myriad of products, as indicated by proton NMR spectroscopy. Once again, ligands coordinated to the (OEP)Zr moiety are heavily shielded in the proton NMR spectrum. Singlets at δ -4.18 (4 H) and δ -1.80 (18 H) correspond to the methylene and trimethylsilyl groups, respectively. The cis structure indicated by the appearance of diastereotopic methylenes for the OEP ligand has been confirmed in the solid state by X-ray crystallography (Figure 1).[16]

The Zr–C bond distances (2.285 (4), 2.289 (4) Å) are identical, within experimental error, to those in $Cp_2Zr(CH_2SiMe_3)_2$,[17] and C–Si distances and Zr–C–Si angles are unexceptional. Evidence for the increased steric demand of the OEP ligand versus the Cp_2 moiety may be inferred from the C(37)–Zr–C(41) angle, which is significantly more acute than the corresponding parameter in $Cp_2Zr(CH_2SiMe_3)_2$ [82.7 (1)° and 97.8 (1)°, respectively]. The plane defined by the four nitrogens is exact, although the porphyrin ligand as a whole is both domed and ruffled. The Zr lies 0.93 Å above the N_4 plane and appears to sit closer to one side of the ring, such that Zr–N distances range from 2.236 (3) and 2.232 (3) Å on one side to 2.250 (3) and 2.248 (3) Å on the other. Note, however, that these differences are small and may not be significant given the esd's involved.

Treatment of benzene solutions of **5** with excess carbon monoxide or 2,6-xylyl isocyanide led to rapid, complex reactions from which no pure products have yet been isolated. Protonolysis with acetic acid rapidly forms the diacetate and tetramethylsilane in high yield. Reaction of **5** with hydrogen (1 atm, 20 °C) produces 2 equiv of tetramethylsilane and a dark green paramagnetic solution, the nature of which is still under investigation.[18] Compound **5** was unreactive toward ethylene (2 atm) over 24 h at room temperature; however, when hydrogen (2 atm) was added to these solutions, a smooth hydrogenation occurred over several hours to produce 8–10 equiv of ethane per mole of Zr. NMR spectra taken during this period were highly informative, revealing the formation of two ethyl-containing metalloporphyrins **6** and **7**.[9] Proton chemical shifts for the zirconium-bound ethyl groups are similar to those found in related *trans*-diethyl metalloporphyrins.[10,19,20] NMR spectra of the deuterated analogues **6**-*d* and **7**-d_2 are similar except that the $ZrCH_2CH_2D$ groups each give rise to two sets of triplets. Monitoring the course of the hydrogenation showed that all three compounds (**5**–**7**) were present at an early stage, but that the concentration of the diethyl **7** grew as **5** and **6** were consumed. Over the course of several hours at room temperature, the diethyl complex **7** decomposed and ethane production ceased.

Hydrogenation of propene under similar conditions proceeds via the *n*-propyl derivatives **8** and **9**.[9] We found no spectroscopic evidence for the participation of species resulting from Markownikov addition. The presumed hydride intermediates in these hydrogenation reactions were not detected spectroscopically; presumably, the rate of olefin insertion was rapid compared to that for Zr–C bond hydrogenolysis.[21,22]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society and the Exxon Education Foundation for funding.

Supplementary Material Available: Characterization data for all new compounds and details of the structure determination of **5**, including tables of crystal and data collection parameters, temperature factor expressions, positional parameters, intramolecular distances and angles, and least-squares planes (15 pages); listing of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

---

(15) Buchler, J. W.; Eikelmann, G.; Puppe, L.; Rohbock, K.; Schneehage, H. H.; Weck, D. *Liebigs Ann. Chem.* **1971**, *745*, 135.

(16) Crystal data for **5**: $ZrSi_2N_4C_{44}H_{66}$, space group $P2_1/n$ with a = 13.011 (1), b = 18.052 (2), c = 19.163 (2) Å, β = 98.68 (1)°, V = 4449 (2) $Å^3$, d_{calcd} = 1.19 g cm^{-3}, and Z = 4. Data were collected on a Enraf-Nonius CAD-4 at -88 °C with Mo Kα (λ = 0.71073 Å). A 2θ range from 3 to 45° gave 5784 unique data. The structure was solved by Patterson methods and refined by least squares and Fourier techniques using 461 variables against 4246 data, for which $F^2 > 3\ \sigma(F^2)$, to give R = 3.36%, R_w = 3.74%, and GOF = 1.366. For all 5784 data, R = 5.61%. The crystal structure was determined by Dr. F. J. Hollander, staff crystallographer at the U. C. Berkeley Crystallographic Facility (CHEXRAY).

(17) Jeffrey, J.; Lappert, M. F.; Luong-Thi, N. T.; Webb, M.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1593.

(18) A broad singlet centered around g = 2.00 was observed by ESR at 293 K; this signal was not resolved further on cooling to 77 K.

(19) Balch, A. L.; Cornman, C. R.; Olmstead, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 2963.

(20) Guilard, R.; Kadish, K. M. *Chem. Rev.* **1988**, *88*, 1121.

(21) Schwartz, J. *Pure Appl. Chem.* **1980**, *52*, 733.

(22) For examples of hydrogenolysis of highly polarized M–C bonds, see: Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97. Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558. Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5515 and references therein.

Alkyne–Alkyne Coupling with $W(PhC{\equiv}CPh)_3(CO)$. Crystal Structure of $W(\eta^4\text{-}C_4Ph_4)(PhC{\equiv}CPh)_2(CO)$

Wen-Yann Yeh*

Department of Chemistry
National Sun Yat-Sen University
Kaohsiung, Taiwan 80424, Republic of China

Ling-Kang Liu[†]

Institute of Chemistry
Academia Sinica, Nankang
Taipei, Taiwan 11529, Republic of China

Received October 9, 1991

Reactions of metal carbonyls with alkyne derivatives are known to give a wide variety of organometallic and organic products.[1-4] It has been shown that $Mo(CO)_6$ or (diglyme)$Mo(CO)_3$ reacts with diphenylacetylene to yield hexaphenylbenzene and several molybdenum tetraphenylcyclobutadiene complexes.[5] In contrast, the analogous reaction with either $W(CO)_6$ or $W(CO)_3(NCCH_3)_3$ only leads to the formation of tris(alkyne) complexes of the type $W(RC{\equiv}CR')_3(CO)$.[6] It appears that the $W(RC{\equiv}CR')_3(CO)$ stoichiometry is particularly stable, as suggested by theoretical analyses.[7,8] Thus, further reaction with alkynes is likely to be retarded. We wish to report that under harsh conditions, however, $W(PhC{\equiv}CPh)_3(CO)$ will couple with diphenylacetylene, forming a cyclobutadiene complex.

$W(PhC{\equiv}CPh)_3(CO)$[6a] (200 mg, 0.26 mmol) and diphenylacetylene (135 mg, 0.76 mmol) were mixed and sealed in a glass

---

[†] Author to whom inquiries concerning the X-ray crystallographic work should be addressed.

(1) Bowden, F. L.; Lever, A. B. P. *Organomet. Chem. Rev.* **1968**, *3*, 227.

(2) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203.

(3) Greene, R. L.; Street, G. B. *Science* **1984**, *226*, 651.

(4) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245.

(5) (a) Hübel, W.; Merényi, R. *J. Organomet. Chem.* **1964**, *2*, 213. (b) Potenza, J. A.; Johnson, R. J.; Chirico, R.; Efraty, A. *Inorg. Chem.* **1977**, *16*, 2354. (c) Efraty, A.; Potenza, J.; Zyontz, L.; Daily, J.; Huang, M. H. A.; Toby, B. *J. Organomet. Chem.* **1978**, *145*, 315. (d) Holtzapple, G. M.; Woon, P. S.; Farona, M. F. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 623.

(6) (a) Tate, D. P.; Augl, J. M. *J. Am. Chem. Soc.* **1963**, *85*, 2174. (b) Tate, D. P.; Augl, J. M.; Ritchey, W. M.; Rose, B. L.; Grasselli, J. G. *J. Am. Chem. Soc.* **1964**, *86*, 3261. (c) King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1968**, *7*, 1837. (d) Maher, J. M.; Fox, J. R.; Foxman, B. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 2347. (e) Okuda, J.; Zimmermann, K. H. *J. Organomet. Chem.* **1990**, *384*, C21. (f) Rosenthal, U.; Oehme, G.; Burlakev, V. V.; Petrovskii, P. V.; Sur, V. B.; Vol'pin, M. E. *J. Organomet. Chem.* **1990**, *391*, 119. (g) Wink, D. J.; Cooper, N. J. *Organometallics* **1991**, *10*, 494.

(7) King, R. B. *Inorg. Chem.* **1968**, *7*, 1044.

(8) Wink, D. J.; Greagan, T. *Organometallics* **1990**, *9*, 328.

0002-7863/92/1514-2267$03.00/0