Tantalum Porphyrin Chemistry. Synthesis and Reactivity of Organometallic Derivatives and the X-ray Crystal Structure of the Sandwich Compound $[Ta(OEP)_2][TaCl_6]$

Denisha Y. Dawson, Holger Brand, and John Arnold*

Department of Chemistry
University of California
Berkeley, California 94720

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Porphyrin chemistry of the early transition metals is considerably less developed than that of late transition metal derivatives.[1-3] Our interest in exploring the former relates to the unusual *cis*, out-of-plane coordination geometries found in these complexes, a feature that can be ascribed to large size of the metal atom. Recent studies have shown that the octaethylporphyrin ligand (OEP) provides a stable coordination environment for a wide range of scandium and zirconium compounds, including chlorides, alkoxides, and σ- and π-bonded organometallic derivatives.[4-12] In contrast to the wealth of tantalocene chemistry developed in recent years, predominantly by Bercaw and Schrock,[13-15] tantalum porphyrinates are extremely rare.[16-18] Here we describe the synthesis of several Ta(V) porphyrin derivatives, including the sandwich compound $[Ta(OEP)_2][TaCl_6]$, the first organometallic tantalum metalloporphyrins, the monoalkyl $[Ta(OEP)Me(Ot\text{-}Bu)][BPh_4]$, the dialkyl $[Ta(OEP)Me_2][BPh_4]$, and the novel trialkyl $Ta(OEP)Me_3$, which represents an unprecedented structural type in metalloporphyrin chemistry. We also present a preliminary examination of the reactivity of these compounds.

Our synthetic route to porphyrin derivatives of Sc and Zr made use of dilithium porphyrin reagents in simple metathesis reactions (eq 1):[5-7,12]

$$MCl_n + Li_2OEP(THF)_2 \rightarrow M(OEP)Cl_{(n-2)} + 2LiCl \quad (1)$$

Surprisingly, however, all attempts to synthesize $Ta(OEP)Cl_3$ from $TaCl_5$ in the above reaction resulted instead in the formation of the sandwich compound $[Ta(OEP)_2][TaCl_6]$, which was isolated as air-stable black crystals from dichloromethane/ether.[19] An X-ray structure determination (Figure 1) shows that each $Ta(OEP)_2^+$ moiety has crystallographic 4-fold symmetry, with one unique pyrrole ring per OEP, and that each cation is surrounded by four $TaCl_6^-$ anions. The two porphyrins are staggered with respect to each other, and the ethyl groups are all pointed away from the tantalum. The separation between the N_4 planes (2.40 Å) is the shortest of any reported sandwich compound,[8,20,21] with the closest being 2.53 Å in $Zr(OEP)_2$. In the latter, the porphyrin rings are more domed than those in the tantalum compound, with dihedral angles between the pyrrole rings and the 24-atom core mean plane of the porphyrin of between 12.3° and 19.9° (av 16°), as compared to 13.6° and 13.7° in $[Ta(OEP)_2][TaCl_6]$. In addition, the porphyrin rings in $Zr(OEP)_2$ are ruffled, a feature that is absent in the tantalum complex due to its 4-fold symmetry. The longer M–N and N_4 plane–N_4 plane distances in $Zr(OEP)_2$ reflect the larger size of the metal ion.

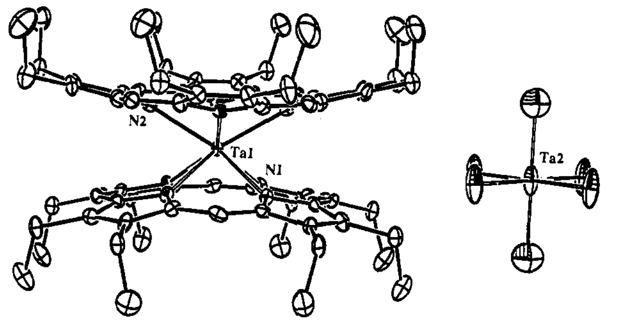

Figure 1. ORTEP view of the structure of $[Ta(OEP)_2][TaCl_6]\cdot 2CH_2Cl_2$. Thermal ellipsoids are scaled to represent the 50% probability level. Selected distances (angstroms) and angles (degrees): Ta–N(1) 2.299(4), Ta–N(2) 2.303(4), N(1)–Ta–N(1) 116.8(2), N(1)–Ta–N(2) 141.5(1), N(2)–Ta–N(2) 117.5(2).

Because of their short porphyrin–porphyrin separations, porphyrin sandwich compounds are of interest as models for the "special pair" in the reaction center in photosynthesis and have been the subject of studies investigating the electronic and photophysical effects that derive from π–π interactions.[8,20-23] The electronic spectra of Hf and Zr OEP sandwich compounds show red-shifted Q bands and blue-shifted Soret bands (with respect to the monoporphyrinates), along with a characteristic broad, low-energy (>650 nm) absorption (Table 1). The electronic spectrum of $[Ta(OEP)_2][TaCl_6]$ shows similar features, with the Q-bands and the low-energy absorption being further red-shifted than those of the Zr or Hf sandwich compounds, suggesting a stronger interaction of the porphyrin rings in the Ta complex.

A novel entry into the "half-sandwich" chemistry shown in Scheme 1 involves reaction of a slight excess of $TaMe_3Cl_2$ with dilithium octaethylporphyrin in dichloromethane at room temperature. Crystallization from toluene gave $Ta(OEP)Me_3$ as bright red crystals in 65% yield.[24] A single methyl resonance at δ -4.0 ppm in the ^1H NMR of $Ta(OEP)Me_3$ may be compared to shifts of -4.5 and -6.0 ppm for methyls in $Zr(OEP)Me_2$ and Sc(OEP)Me, respectively. This trend is ascribed to two effects: (i) the decrease in electronegativity from Ta to Sc and (ii) the increased ring anisotropy as ligands move closer to the center of the porphyrin.[25] As in all the compounds reported here, the

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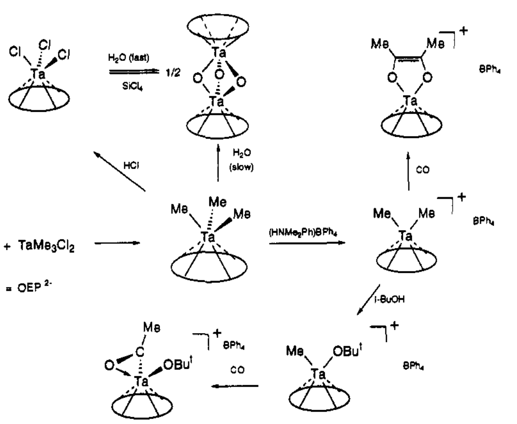
Table 1. Comparison of UV–Vis Spectra of $[Ta(OEP)_2][TaCl_6]$ and $Zr(OEP)_2$[a]

	Soret			Q-bands			
$[Ta(OEP)_2][TaCl_6]$	318	374	448	486	598	614	820
	(4.99)	(4.87)	(4.10)	(4.14)	(4.27)	(4.27)	(2.64)
$Zr(OEP)_2$[21]		382		490	550	592	750
		(5.22)		(4.10)	(3.78)	(4.39)	(2.72)
$Zr(OEP)_2$[8]	355(sh)	381		483	547	589	

[a] λ_{max} [nm], log ϵ in parentheses.

Scheme 1



methylene protons on the ethyl groups of the porphyrin are diastereotopic, indicating a lack of mirror symmetry in the plane of the porphyrin. The dimethyl is stable indefinitely as a solid when stored under N_2 in the dark but is moderately light sensitive, especially in solution. On exposure to ambient light, it decomposes to give a green solution which, according to ^1H NMR data, contains a complex mixture of unidentified products.

$Ta(OEP)Cl_3$ was generated from the trimethyl by reaction with HCl in diethyl ether. The trichloride is a useful synthon and reacts with dimethylmagnesium in CH_2Cl_2 to regenerate the trimethyl. In contrast with the Sc and Zr OEP chlorides,[6,12] $Ta(OEP)Cl_3$ is *very* sensitive toward hydrolysis, which in this case cleanly generates the tris-μ-oxo binuclear complex $[Ta(OEP)]_2O_3$.[17] Refluxing the latter complex in toluene with an excess of silicon tetrachloride is a cleaner, high-yield route to the trichloride. The oxo species can also be generated from the trimethyl derivative, but this reaction is very slow (days), in marked contrast to the very water-sensitive $Zr(OEP)Me_2$ and $Sc(OEP)Me$. Similarly, whereas both zirconium and scandium OEP methyls rapidly and quantitatively insert acetone and CO_2 into the metal carbon bond to give *tert*-butoxide and acetate derivatives, respectively, and rapidly react with H_2, the tantalum trimethyl does not react with these reagents under similar conditions. All three compounds react rapidly with CO, although a complex mixture is formed in each case.

One methyl group of $Ta(OEP)Me_3$ was removed by protonation with 1 equiv of $[HMe_2NPh]BPh_4$ in dichloromethane to yield $[Ta(OEP)Me_2]BPh_4$, a porphyrin analogue to Schrock's dimethyltantalocene cation.[15,26] Insoluble in toluene or ether, this compound dissolves in dichloromethane to give deep burgundy, light-sensitive solutions. Though not as light sensitive as the trimethyl, it is much more sensitive to hydrolysis. Reaction with H_2 is rapid, but we have been unable to isolate any pure compounds to date. A major problem is the insolubility of the dimethyl cation in nonchlorinated solvents. We are currently preparing more soluble tetraarylporphyrin derivatives in the hope that this reactivity may be elucidated. Like the trimethyl derivative, $[Ta(OEP)Me_2]BPh_4$ does not react with ethylene, acetone, or CO_2, but reaction with CO is clean. Spectroscopic data of the product are in accord with the enediolate structure shown in Scheme 1. The ^{13}C NMR spectrum of the ^{13}C-labeled product, obtained by reaction of $[Ta(OEP)Me_2]BPh_4$ with ^{13}CO, shows a singlet at δ 140 ppm, and, in the ^1H NMR spectrum, the methyl resonance appears as a doublet at δ −1.62 ppm ($^2J_{CH}$ = 5.7 Hz). There is ample precedent for this type of coupling chemistry in zirconocene and tantalocene systems.[27,28]

Although the putative η^2-acyl intermediate in this reaction was not detected, evidence for such a species was obtained by studying the corresponding reactions of mono-alkyl derivatives. Addition of excess *tert*-butyl alcohol to $[Ta(OEP)Me_2]BPh_4$ quantitatively yields $[Ta(OEP)Me(OtBu)]BPh_4$, which, upon addition of CO, gave a product in which the four meso protons and eight ethyl groups are inequivalent by ^1H NMR spectroscopy. The CH_3 group resonance shifts from δ −4.08 ppm to δ −0.34 ppm upon carbonylation, indicating that it is no longer bound directly to the metal. The ^{13}C-labeled carbon of the ^{13}CO insertion product shows a ^{13}C NMR resonance at δ 289 ppm, which is diagnostic for η^2-acyl ligands on early metal centers.[28–32] These data are consistent with the structure shown in Scheme 1 in which there is no plane of symmetry. A more symmetrical arrangement, in which the η^2-acyl and *tert*-butoxide ligand are all in the same plane, is unlikely, both sterically and electronically. We have been unable to isolate either the enediolate or the η^2-acyl as analytically pure solids due to apparent decomposition as the reaction solutions are concentrated, although efforts are continuing.

Forthcoming papers will give details of this and the related tetraarylporphyrin chemistry and will include a full account of the $Ta(Por)_2^+$ system.

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Supplementary Material Available: Characterization data for all new compounds and details of the structure determination of $[Ta(OEP)_2]TaCl_6$ including tables of crystal and data collection parameters, temperature factor expressions, positional parameters, intramolecular distances and angles, and least-squares planes (16 pages); listing of observed and calculated structure factors (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(24) Selected characterization data for new compounds. $Ta(OEP)Me_3$: ^1H NMR (300 MHz, C_6D_6) δ −4.00 (s, 9), 1.90 (t, 24, J = 7.5 Hz), 4.18 (m, 16), 10.50 (s, 4). $[Ta(OEP)Me_2]BPh_4$: ^1H NMR (300 MHz, $CDCl_3$) δ −3.54 (s, 6), 1.98 (t, 24, J = 7.6 Hz), 4.27 (m, 16), 6.76 (m, 4), 6.96 (m, 8), 7.43 (br, 8), 10.73 (s, 4). $[Ta(OEP)]_2O_3$: ^1H NMR (300 MHz, $CHCl_3$) δ 1.66 (t, 24, J = 7.6 Hz), 4.04 (m, 16), 9.67 (s, 4). $Ta(OEP)Cl_3$: ^1H NMR (300 MHz, $CDCl_3$) δ 1.88 (t, 24, J = 7.5Hz), 4.28 (q, 8, J = 7.5 Hz), 4.13 (q, 8, J = 7.5 Hz), 10.54 (s, 4). $[Ta(OEP)(O_2C_2Me_2)]BPh_4$: ^1H NMR (300 MHz, $CDCl_3$) δ −1.61 (s, 6), 2.00 (t, 24, J = 7.6 Hz), 4.30 (m, 16), 6.77 (m, 4), 6.97 (m, 8), 7.43 (br, 8), 10.81 (s, 4). $[Ta(OEP)Me(OtBu)]BPh_4$: ^1H NMR (300 MHz, $CDCl_3$) δ −4.08 (s, 3), −0.84 (s, 9), 1.97 (t, 24, J = 7.4 Hz), 4.25 (m, 16), 6.78 (m, 4), 6.97 (m, 8), 7.43 (br, 8), 10.69 (s, 4). $[Ta(OEP)(\eta^2\text{-}COMe)(OtBu)]BPh$: ^1H NMR (300 MHz, CD_2Cl_2) δ −1.28 (s, 9), 0.34 (d, 3, J = 6.1 Hz), 1.78 (m, 6), 1.95 (m, 6), 2.04 (m, 12), 4.32 (m, 8), 4.20 (m, 4), 4.04 (m, 4), 6.85 (m, 4), 7.03 (m, 8), 7.42 (br, 8), 10.53 (s, 1), 10.59 (s, 1), 10.60 (s, 1), 10.69 (s, 1). Full details are provided as supplementary material.

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