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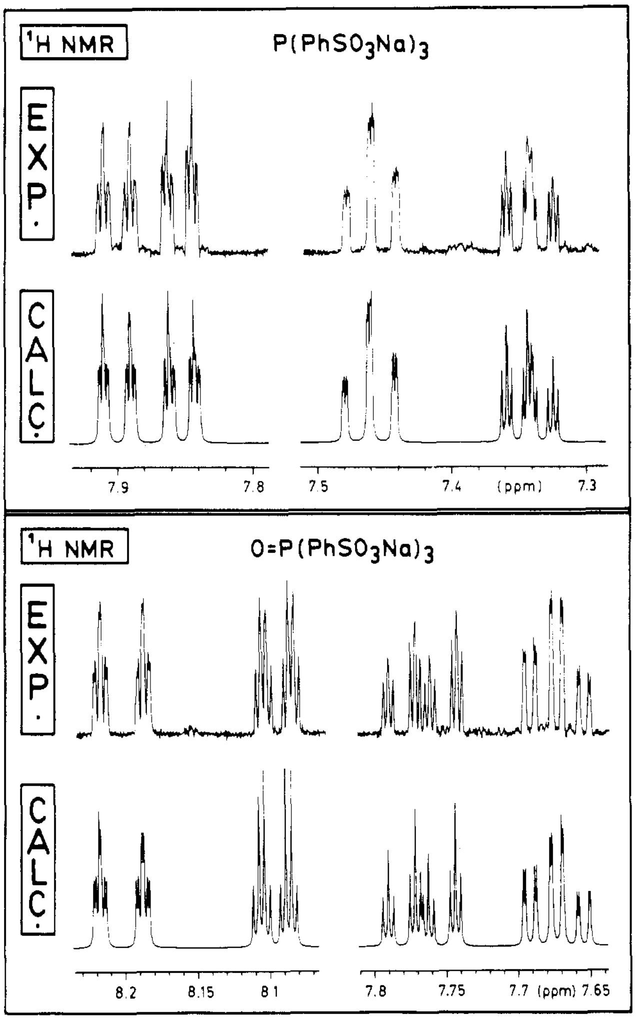

Figure 3. Experimental and calculated 400-MHz ^{1}H NMR spectra for TPPTS and TPPTS oxide.

products have chemical shifts of −4.4, −4.0, and −3.7 ppm for $P(C_6H_5)_2(C_6H_4SO_3Na)$, $P(C_6H_5)(C_6H_4SO_3Na)_2$, and $P(C_6H_4SO_3Na)_3$, respectively.

Direct monitoring of the reaction mixture in fuming sulfuric acid by either ^{1}H or ^{31}P NMR gave insufficient resolution to distinguish the extent of sulfonation. Line widths on the order of 2–3 ppm in the ^{31}P NMR spectrum were observed. This is greater than the expected chemical shift difference between the various sulfonated products; thus, direct observation of the ^{31}P NMR spectrum in oleum cannot reliably predict the extent of sulfonation. Narrow ^{31}P lines are observed for the sulfonated products in the methanol/THF/water solvent system described above. Interestingly all the sulfonated products reproducibly give multiple lines in the high-resolution ^{31}P NMR spectra at 162 MHz (Figure 2). The overall line widths are 8–10 Hz for the sulfonated phosphines as well as for TPP. Although substituted propeller-shaped molecules result in isomers depending on the orientation of the substituent with respect to the propeller,[10] this does not appear to explain the splitting in the ^{31}P NMR since neither the ^{1}H nor the ^{13}C NMR spectra show similar splittings. However, ^{31}P chemical shifts for free phosphines correlate well with Tolman's steric parameter,[11] and it may be argued that different orientations of the metal–sulfonato group will lead to slightly different steric parameters at the phosphorus atom; each isomer may have a different ^{31}P chemical shift.

Remarkably all eight protons in a mixture of TPPTS and TPPTS oxide can be resolved by ^{1}H NMR at 400 MHz. These are assigned as follows: for TPPTS, 7.34, 7.46, 7.85, and 7.90 ppm for D, C, B, and A, respectively, and for TPPTS oxide, 7.67, 7.77, 8.09, and 8.20 ppm for C, D, B, and A, respectively. The peaks and coupling constants are sufficiently well resolved to make reasonable estimates of all the coupling constants in the ABCDX spin system. The experimental and calculated spectra (Figure 3) show good agreement for the assignments made in Tables I and II.

The FAB mass spectra show the molecular ion plus a proton. The principal fragmentation processes give peaks at $+Na^+ - H^+$, $-Na^+ + H^+$, and $-SO_3Na + H^+$. The last of these corresponds to the desulfonation of TPPTS and leads to the formation of triphenylphosphine in the mass spectrometer. The peak in the mass spectrum at *m*/*z* 263 is assigned to protonated TPP formed in this manner. Desulfonation of aryl sulfonates is generally accomplished by thermolysis in strong acid. The cleavage of C–S bonds under FAB conditions has been observed for organic sulfonium salts.[12]

Acknowledgment. We thank the NSF for support of this work (Grant CTS 9101846). Mr. Kim Harich recorded the FAB mass spectra.

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(13) The solubility of Na_2SO_4 was determined to be 190 mg/100 g in hot dry methanol and 350 mg/100 g in hot aqueous (20%) methanol.

(14) It was observed that TPPTS and TPPTS oxide have different solubilities in several complex solvent mixtures. The greatest differences in solubility are observed in 50–80% acetone/20–40% methanol/5–10% water and 70% THF/25% methanol/5% water.

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Unusual Metalloporphycenes. First Syntheses of Carbonyl- and Dioxo-Containing Osmium and Ruthenium Tetrapropylporphycene Complexes

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Introduction

Porphycene, a novel porphine isomer first synthesized by Vogel and co-workers several years ago, promises rich and colorful metalloporphycene chemistry.[1] It is of interest to study metalloporphycene complexes in comparison with their porphyrin analogues.[2] A few transition metals, such as Mn, Fe, Co, Ni, Cu, Zn, Pd, and Pt, have been inserted into the porphycene ligand.[3] Coordination of the relatively large osmium ion with porphycene, however, has so far been unsuccessful. This was considered as evidence for the small cavity of porphycene.[2] In our study on the reaction of triosmium dodecacarbonyl [$Os_3(CO)_{12}$] with 2,7,12,17-tetrapropylporphycene (H_2TPrPC), we found that this reaction readily afforded a carbonylosmium(II) porphycene complex. Similar reaction with $Ru_3(CO)_{12}$ also resulted in the insertion of ruthenium into porphycene. Here we describe the first synthesis and characterization of carbonylosmium and carbonylruthenium porphycene complexes and a dioxoosmium(VI) porphycene complex in which the metal has an unprecedentedly high oxidation state in metalloporphycene complexes.

Experimental Section

Materials. Dodecacarbonyltriosmium and dodecacarbonyltriruthenium were purchased from Strem Chemicals, Inc., and Aldrich

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Table I. ^1H NMR Spectral Data (δ) for Ruthenium and Osmium Porphycene Complexes As Compared with Those of the Octaethylporphyrin Analogues (270 MHz, $CDCl_3$, TMS)

complex	H-9,10,19,20 (s, 4 H)	H-3,6,13,16 (s, 4 H)	α-CH_2 (8 H)	β-CH_2 (sext, 8 H)	CH_3 (t, 12 H)
Ni(TPrPC)[a]	9.40	8.86	3.90 (t)	2.32	1.31
Os(TPrPC)(CO) (**1**)	9.38	8.74	3.97 (m)	2.32	1.36
Ru(TPrPC)(CO) (**2**)	9.51	8.85	4.00 (m)	2.41	1.38
Os(TPrPC)$(O)_2$ (**3**)	10.33	9.47	4.28 (t)	2.57	1.47

complex	H_{meso} (s, 4 H)	CH_2 (q, 16 H)	CH_3 (t, 24 H)
Os(OEP)(CO)(Py)[b]	9.64	3.81[e]	1.81[e]
Ru(OEP)(CO)(Py)[c]	9.75	3.88	1.82
Os(OEP)$(O)_2$[d]	10.75	4.25	2.13

[a] Reference 3a. [b] Reference 10. [c] Reference 11. [d] Reference 6a. [e] Reference 9 (in C_6D_6).

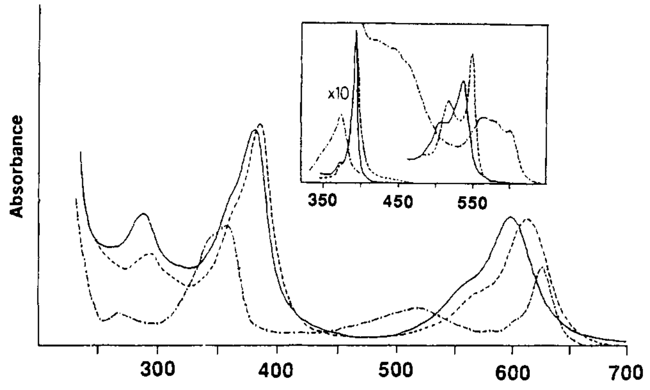

Figure 1. UV-visible spectra of Os(TPrPC)(CO) (—), Ru(TPrPC)(CO) (- - -), and Os(TPrPC)$(O)_2$ (- · ·) (in CH_2Cl_2). Inset: Spectra of Os(OEP)(CO)(Py) (—), Ru(OEP)(CO)(Py) (- - -), and Os(OEP)$(O)_2$ (- · ·) (reproduced from ref 9).

Chemical Co., respectively. 2,7,12,17-Tetrapropylporphycene was prepared by the literature method.[3a]

Preparation of Os(TPrPC)(CO). A mixture of H_2TPrPC (30 mg) and $Os_3(CO)_{12}$ (50 mg) in diethylene glycol monomethyl ether (20 mL) was refluxed under nitrogen for 30 min to give a dark blue solution. The solvent was distilled off under vacuum. The residue was dissolved in *n*-hexane/dichloromethane (1:1), and the solution was then chromatographed on an Al_2O_3 (activity II, BDH) column. The leading band was removed using *n*-hexane as the eluent. The second band (blue) eluted with *n*-hexane/dichloromethane (1:1) was collected and then evaporated to dryness, affording a violet solid (yield 75%). Anal. Calcd for $C_{33}H_{36}N_4OOs$: C, 57.04; H, 5.22; N, 8.06. Found: C, 57.16; H, 5.40; N, 8.14. UV/vis ($CHCl_3$) [λ_{max}/nm (ε)]: 291 (32 800), 359 (29 700) sh, 384 (54 500), 556 (13 100) sh, 600 (32 800).

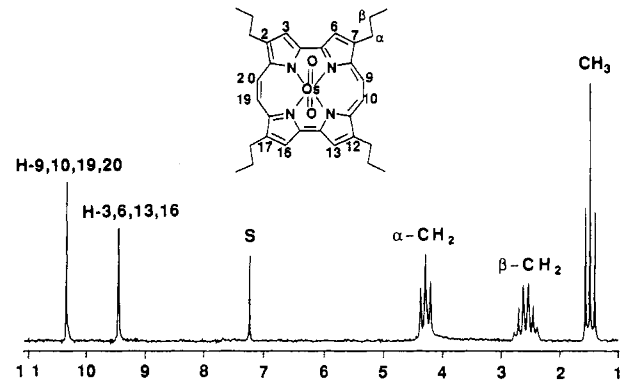

Figure 2. ^1H NMR spectrum of Os(TPrPC)$(O)_2$ (270 MHz, $CDCl_3$, TMS).

Preparation of Ru(TPrPC)(CO). A mixture of H_2TPrPC (30 mg) and $Ru_3(CO)_{12}$ (50 mg) in decalin (20 mL) was refluxed under nitrogen for 1 h. The final blue solution was cooled to room temperature. Decalin was removed either by chromatography on an Al_2O_3 column with *n*-hexane as the eluent or by distillation under vacuum. The residue was dissolved in *n*-hexane/dichloromethane (1:1), and then the solution was chromatographed on an Al_2O_3 column. The same mixed solvent was used to remove the leading band. The second band (blue) was eluted with dichloromethane and collected. Removal of solvents gave a violet solid (yield 71%). Anal. Calcd for $C_{33}H_{36}N_4ORu$: C, 65.43; H, 5.99; N, 9.25. Found: C, 65.01; H, 5.82; N, 9.34. UV/vis ($CHCl_3$) [λ_{max}/nm (ε)]: 294 (21 300), 360 (28 800) sh, 385 (56 900), 566 (11 800) sh, 612 (28 900).

Preparation of Os(TPrPC)$(O)_2$. To a solution of Os(TPrPC)(CO) (30 mg) in dichloromethane (20 mL) was added excess *m*-chloroperoxybenzoic acid (*m*-CPBA). The color of the solution changed from blue to red violet immediately. The mixture was stirred at room temperature for several minutes and then evaporated to dryness to give a dark purple solid. This was collected, washed with methanol/H_2O (1:1), and air-dried. Chromatography on an Al_2O_3 column using dichloromethane/petroleum ether (1:1) as the eluent afforded the product of high purity (yield ≈50%). Anal. Calcd for $C_{32}H_{36}N_4O_2Os$: C, 55.00; H, 5.19; N, 8.02. Found: C, 54.88; H, 5.07; N, 8.12. UV/vis ($CHCl_3$) [λ_{max}/nm (ε)]: 266 (12 800), 344 (51 400) sh, 356 (57 000), 515 (18 600), 602 (12 400) sh, 625 (40 200).

Spectral Measurements. ^1H NMR spectra were measured on a JEOL JNM-GSX 270 FT NMR spectrometer (270 MHz), and the chemical shifts (δ, ppm) were reported relative to tetramethylsilane (TMS). UV-visible spectra were recorded on a Milton Roy Spectronic 3000 array spectrometer. Infrared spectra were obtained using a Nicolet 20 SXC FT-IR spectrometer (KBr pellets).

Results and Discussion

The osmium and ruthenium porphycene complexes M(TPrPC)(CO) (M = Os, Ru) are prepared by reaction of $M_3(CO)_{12}$ (M = Os, Ru) with the free-base porphycene in diethylene glycol monomethyl ether or decalin. This reaction is moderately rapid at elevated temperature. We use $Os_3(CO)_{12}$ as the metal carrier, since it can react with free-base porphyrins to generate carbonylosmium(II) porphyrin complexes containing strong Os → C≡O back-bonding,[4] which is expected to reduce the size of the Os(II) ion.[5] This reduction should facilitate the coordination of osmium with the porphycene dianion having a smaller cavity

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than its porphyrin analogue. The same consideration is also appropriate for ruthenium. Oxidation of Os(TPrPC)(CO) with *m*-CPBA in dichloromethane readily results in the generation of a dioxoosmium(VI) porphycene complex Os(TPrPC)(O)$_2$, which is as stable as its porphyrin analogue.[6] However, attempts to isolate the corresponding dioxoruthenium(VI) porphycene complex by treatment of Ru(TPrPC)(CO) with *m*-CPBA in dichloromethane have failed. Like Os(OEP)(O)$_2$,[7] Os(TPrPC)(O)$_2$ reacted with hydrazine hydrate in tetrahydrofuran under N$_2$ affording a dinitrogenosmium(II) porphycene complex which exhibits ν(N$_2$) band at 2035 cm^{-1}.

For both Os(TPrPC)(CO) and Ru(TPrPC)(CO), there appears only a single, very strong C≡O stretching band in the IR spectrum. The ν(C≡O) band of Os(TPrPC)(CO) found at 1893 cm^{-1} is very similar to that of Os(OEP)(CO)(THF) at 1897 cm^{-1} (OEP = octaethylporphyrin dianion, THF = tetrahydrofuran).[7] Ru(TPrPC)(CO) exhibits a C≡O stretching vibration at 1937 cm^{-1}, also similar to that of its porphyrin analogues.[8] The IR spectrum of Os(TPrPC)(O)$_2$ shows an intense band at 823 cm^{-1} with a shoulder at 837 cm^{-1}. The 823-cm^{-1} band, which is absent in H$_2$TPrPC and Os(TPrPC)(CO), can reasonably be assigned to the ν_{as}(OsO$_2$) stretch. For comparison, the ν_{as}(OsO$_2$) band of Os(OEP)(O)$_2$ appears at 825 cm^{-1}.[6a]

Figure 1 shows the UV–visible absorption spectra of Os(TPrPC)(CO), Ru(TPrPC)(CO), and Os(TPrPC)(O)$_2$ and the spectra of their octaethylporphyrin analogues[9] (inset) for comparison. The spectra of M(TPrPC)(CO) (M = Os, Ru) are typical of those of metalloporphycenes as described in the literature,[3] but the ratios of the oscillator strength of the near-UV bands to that of the visible bands are anomalously low. The spectra of the three new porphycene complexes are like those of their OEP counterparts. In the order from Os(TPrPC)(CO) to Ru(TPrPC)(CO), the bands in the visible region are significantly red shifted just as the case from Os(OEP)(CO)(Py) to Ru(OEP)(CO)(Py) (Py = pyridine). In previous studies, a similar red shift observed from Ni(TPrPC) to Cu(TPrPC) was ascribed to expansion of the porphycene macrocycle.[3f] However, in this work, the red shift of this kind could not be readily understood in this way since the Ru(II) ion should be slightly smaller than the Os(II) ion.[5] It is also evident from Figure 1 that oxidation of Os(TPrPC)(CO) to Os(TPrPC)(O)$_2$ leads to a remarkable blue shift of the near-UV bands, a large red shift of the visible bands, and appearance of a broad extra band in the visible region. This again superficially resembles the corresponding porphyrin system.

All the three new porphycene complexes give well-resolved ^{1}H NMR spectra. The spectral data appear in Table I, in which the data found for the related porphyrin and nickel(II) porphycene complexes are also cited for comparison. For Os(TPrPC)(CO), Ru(TPrPC)(CO), and Ni(TPrPC), the proton resonances of the porphycene ligand appear at similar positions. However, the α-CH$_2$ protons for the carbonyl complexes give a multiplet rather than a triplet as those in Ni(TPrPC), indicating that Os(TPrPC)(CO) and Ru(TPrPC)(CO) have a C_{2v} symmetry. Figure 2 shows the ^{1}H NMR spectrum of Os(TPrPC)(O)$_2$. It is apparent, from a comparison between the data of Os(TPrPC)(O)$_2$ and Os(OEP)(O)$_2$ (Table I), that Os(TPrPC)(O)$_2$ is diamagnetic. Just like the osmium porphyrin complexes, the 9,10,19,20-proton resonances (related to H$_{meso}$ in octaethylporphyrin) and the 3,6,13,16-proton resonances (related to H$_\beta$ in tetraphenylporphyrin) are significantly downfield shifted from that of the divalent metalloporphycene complexes (see Table I). The α-CH$_2$ protons of Os(TPrPC)(O)$_2$ appear as a triplet, consistent with a D_{2h} symmetry resulting from the embedment of a small Os(VI) ion in the center of the porphycene dianion ligand.

Conclusions

Our work demonstrated the following: (i) Porphycene can even coordinate with the relative large osmium as well as ruthenium ion to form stable complexes although it has smaller cavity than that of porphyrin. (ii) The chemistry of ruthenium and osmium porphycene complexes resembles that of their porphyrin analogues.

Acknowledgment. We acknowledge supports from the Hong Kong Research Grants Council and University of Hong Kong. C.-M.C. thanks the National Science Council of Taiwan for a Visiting Professorship.

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Additions and Corrections

1991, Volume 30

Wei Cen, Kenneth J. Haller, and Thomas P. Fehlner*: Transition-Metal Clusters as Substituents. Synthesis, Structure, and Thermal Decomposition of Zn$_4$O[(CO)$_9$Co$_3$(μ_3-CCO$_2$)]$_6$.

Pages 3120–3121. Additional models of higher symmetry for the structure of Zn$_4$O[(CO)$_9$Co$_3$(μ_3-CCO$_2$)]$_6$, including refinement as a $\bar{3}$ disordered/averaged structure in space group $R\bar{3}$, have been explored. ORTEP plots of the $P\bar{1}$ (R_1 = 0.087, R_2 = 0.106) and $R\bar{3}$ (R_1 = 0.085, R_2 = 0.098) models are almost perfect superpositions of each other (including the orientations and magnitudes of the thermal ellipsoids). The diethyl ether of solvation is now modeled as a 9-position disorder, resulting in a more reasonable geometry. The highest residual electron density peaks are of similar heights and locations for the two models.

We thank Professor Richard E. Marsh for his comments and helpful suggestions concerning this problem.

Supplementary Material Available. A complete structure report for the $R\bar{3}$ model, including a textual description of the X-ray experimental procedures and tables of crystal data, fractional coordinates, thermal parameters, and interatomic distances and angles (9 pages); a listing of structure factors (9 pages). Ordering information is given on any current masthead page.—Thomas P. Fehlner