Table I. Hydrolysis of Selected Amine–Boranes in 50% Aqueous Dioxane at 25.0 °C and $I = 0.50$ M

amine–borane	10^8k_1 (s^{-1})[a]	10^3k_2 (M^{-1} s^{-1})[a]
benzyl–	2.2	8.27
N-methylbenzyl–	3.5	0.328
N,*N*-dimethylbenzyl–	13	0.00224
2-methoxybenzyl–	8.6	11.3
3-methoxybenzyl–	4.9	9.13
4-methoxybenzyl–	15	
4-methylbenzyl–		10.7
4-chlorobenzyl–		7.82
aniline–[b]	1.9×10^4[c]	1.74
4-methylaniline–[b]	8.3×10^3[c]	2.71
4-methoxyaniline–[b]	4.7×10^3[c]	3.02
quinoline–[d]	5.4×10^2[c]	0.26
4-methylquinoline–[d]	2.8×10^2[c]	0.74
isoquinoline–[d]	4.6×10^1[c]	1.56

[a] $-d[AB]/dt = [AB](k_1 + k_2[H^+])$, AB = amine–borane. [b] Reference 1. [c] $I \simeq 0$. [d] Reference 7.

Table II. Temperature Dependence of Rate of Hydrolysis of Benzylamine–Borane in 50% Aqueous Dioxane

t (°C)	[HCl] (M)	10^3k_{obs}[a] (s^{-1})	10^3k_2[b] (M^{-1} s^{-1})
11.50	0.126	0.198	1.57
15.00	0.151	0.361	2.39
25.05	0.108	1.03	9.57
30.10	0.101	1.68	16.6
32.70	0.102	1.88	18.4

$\Delta H^* = 20.6$ kcal/mol; $\Delta S^* = 0.912$ cal/(mol K)

[a] From eq 1 where $k_{obs} = k_1 + k_2[H^+]$. [b] $k_2[H^+] \gg k_1$; thus $k_2 \simeq k_{obs}/[H^+]$.

being conducted. This is prompted, in part, by the fact that amine structure has been shown to influence the stoichiometry of reaction of amine–boranes with HOCl leading in some instances to hydride oxidation and in others to B-chlorination.[16,17]

Acknowledgment. We thank the TCU Research Fund and the Welch Foundation (Grant P-0162) for financial support and Dr. David E. Minter for obtaining NMR spectra.

Supplementary Material Available: Details of preparative yields, analyses, and NMR spectral data (5 pages). Ordering information is given on any current masthead page.

---

(16) Wilson, I.; Kelly, H. C. *Inorg. Chem.* **1982**, *21*, 1622.
(17) Kelly, H. C.; Yasui, S. C.; Twiss-Brooks, A. B. *Inorg. Chem.* **1984**, *23*, 2220.

Contribution from the Department of Chemistry,
Virginia Polytechnic Institute and State University,
Blacksburg, Virginia 24061-0212

Comments on the Synthesis of Trisulfonated Triphenylphosphine: Reaction Monitoring by NMR Spectroscopy

Tamâs Bartik,† Berit Bartik,‡ Brian E. Hanson,* Tom Glass, and William Bebout

Received December 27, 1991

Introduction

There is widespread interest in the coordination chemistry of trisulfonated triphenylphosphine, TPPTS, owing to its utility in the hydroformylation reaction.[1-4] While the synthesis of TPPTS is straightforward, the reported workup procedures are cumbersome. Recently it has been shown that a complex mixture from a synthesis that contains 30% TPPTS and as many as four additional components can be separated by gel permeation chromatography.[5] As further noted by Herrmann et al.[5] analytical data not only for TPPTS itself but for complexes of TPPTS are remarkably sketchy; it appears to be the case that many compounds reported to be TPPTS derivatives most likely contain a mixture of mono-, di-, and trisulfonated triphenylphosphine. Sinou and Bakos et al.[6] have also shown that chromatography can be used to separate mono-, di-, tri-, and tetrasulfonated chiral diphosphines.[3] Kuntz reports that the synthesis of TPPTS yields a crude mixture that contains approximately 80% TPPTS and 20% TPPTS oxide after 20 h at 30 °C.[1] (We find that the reaction mixture contains significant disulfonated product after 30 h at 22 °C, vide infra.) Kuntz showed further that workup with butyl phosphate eliminates sodium sulfate and that formation of the barium salt yielded TPPTS in greater than 95% purity.[1] Although ^{1}H NMR data, in addition to ^{13}C and ^{31}P NMR data, are mentioned in several cases in the literature for TPPTS, nowhere does a detailed list of chemical shift data appear. Extensive ^{31}P NMR data are available for rhodium complexes of TPPTS,[7] and a reproduction of the ^{1}H NMR spectrum of TPPTS is reported in a dissertation; however, chemical shifts and coupling constants are not given.[8]

The ^{1}H NMR spectrum, in fact, is very sensitive to the extent of the sulfonation. Here we report the ^{1}H, ^{13}C, and ^{31}P NMR spectra of TPPTS and TPPTS oxide and give a detailed procedure for their use to monitor the extent of sulfonation of triphenylphosphine. Additionally the mass spectra for TPPTS and TPPTS oxide, recorded using fast atom bombardment, are reported.

Experimental Section

All manipulations were performed under nitrogen by standard Schlenk techniques. Fuming sulfuric acid was obtained from Aldrich. Triphenylphosphine was purchased from either Aldrich or Strem Chemical Co. and used without further purification. NMR solvents, methanol-d_4, THF-d_8, and D_2O were obtained from Aldrich.

Routine NMR measurements were done on a Bruker 200-MHz spectrometer, at an observation frequency of 200.133 MHz for ^{1}H and 81.015 MHz for ^{31}P. High-field ^{1}H, ^{13}C, and ^{31}P NMR data were obtained on a Varian RU400 NMR spectrometer at 399.052, 100.577, and 161.903 MHz, respectively. The FAB mass spectra[9] were recorded on a VG 7070E-HF spectrometer. The samples were vaporized and ionized with 8-kV Ar atoms from a glycerol matrix. The accelerating voltage was 4 kV, and the spectrum was scanned from 50 to 750 amu. Summaries of the fragmentation patterns for TPPTS and TPPTS oxide are given in Tables I and II.

Sufonation of Triphenylphosphine (TPP). With minor changes the procedure reported by Kuntz was followed for the sulfonation of TPP.[1] A 10-g sample of TPP was added slowly to 100 mL of 20% fuming sulfuric acid at 0 °C.; efficient cooling is necessary to prevent local overheating. The mixture was allowed to reach room temperature (22 °C) and the reaction continued for up to ca. 150 h to give complete sulfonation.

---

* To whom correspondence should be addressed.

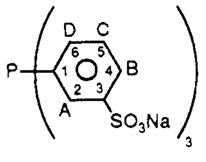
† Research Group for Petrolchemistry of the Hungarian Academy of Sciences (Veszprêm).

‡ FRG Research Fellow (Deutsche Forschungsgemeinschaft-Bonn), 1991–1992.

(1) (a) Kuntz, E. German Patent 2627354, 1976. (b) Kuntz, E. U.S. Patent 4,248,802, 1981. (c) Kuntz, E. French Patent 2,314,910, 1975.
(2) Borowski, A. F.; Cole-Hamilton, D. J.; Wilkinson, G. *Nouv. J. Chem.* **1978**, *2*, 145.
(3) (a) Arhancet, J. P.; Davis, M. E.; Merola, J. S.; Hanson, B. E. *Nature*, **1989**, *339*, 454. (b) Arhancet, J. P.; Davis, M. E.; Merola, J. S.; Hanson, B. E. *J. Catal.* **1990**, *121*, 327.
(4) Horvath, I. T.; Kastrup, R. V.; Ostwald, A. A.; Mozeleski, E. J. *Catal. Lett.* **1989**, *2*, 85.
(5) (a) Herrmann, W. A.; Kellnar, J.; Riepl, H. *J. Organomet. Chem.* **1990**, *389*, 103. (b) Herrmann, W. A.; Kulpe, J. A.; Konkol, W.; Bahrmann, H. *J. Organomet. Chem.* **1990**, *389*, 85. (c) Herrmann, W. A.; Kulpe, J. A.; Kellnar, J.; Riepl, H.; Bahrmann, H.; Konkol, W. *Angew. Chem.* **1990**, *102*, 408.
(6) (a) Amrani, Y.; Lecomte, L.; Sinou, D.; Bakos, J.; Toth, I.; Heil, B. *Organometallics* **1989**, *8*, 542. (b) Lecomte, L.; Triolet, J.; Sinou, D.; Bakos, J.; Toth, I.; Heil, B. *J. Chromatogr.* **1987**, *408*, 416.
(7) (a) Larpent, C.; Dabard, R.; Patin, H. *New J. Chem.* **1988**, *12*, 907. (b) Larpent, C.; Dabard, R.; Patin, H. *Inorg. Chem.* **1987**, *26*, 2922.
(8) Arhancet, J. P. Ph.D. Dissertation, Virginia Polytechnic Institute and State University, 1989.

0020-1669/92/1331-2667$03.00/0

Table I. NMR and Mass Spectrometry Data for TPPTS



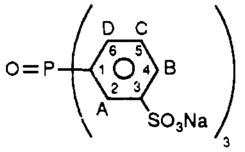
TPPTS

NMR[a]			
	frequency (MHz)	solvent	δ (ppm) (*J* (Hz))
^{1}H	200.133	MTW[b]	7.34 (t,[c] 1 H, *J*(PH) = 7.16); 7.47 (t,[c] 1 H, *J*(PH) = 7.46); 7.87 (t,[c] 2 H, *J*(PH) = 8.15)
	200.133	D_2O	7.54 (quin,[c] 2 H, *J*(PH) = 9.04); 7.86 (m, 2 H)
	399.952	MTW[b]	7.34 (t′, H^D, $^{3}J(PH^D)$ = 6.68, $^{4}J(H^DH^A)$ = 1.45, $^{4}J(H^DH^B)$ = 1.55, $^{3}J(H^DH^C)$ = 7.72); 7.46 (tdd, H^C, $^{4}J(PH^C)$ = 1.00, $^{5}J(H^CH^A)$ = 0.43, $^{3}J(H^CH^B)$ = 7.80); 7.85 (dt″, H^B, $^{5}J(PH^B)$ = 0.40, $^{4}J(H^BH^A)$ = 1.20); 7.90 (dt″, H^A, $^{3}J(PH^A)$ = 8.34)
^{13}C	100.577	D_2O	129.39 (s, C^4); 132.49 (d, C^5, $^{3}J(PC)$ = 6.13); 133.10 (d, C^6, $^{3}J(PC)$ = 23.64); 139.21 (d, C^2, $^{2}J(PC)$ = 16.00); 139.36 (d, C^1, $^{1}J(PC)$ = 8.45); 145.82 (d, C^3, $^{3}J(PC)$ = 10.60)
^{31}P	81.015	MTW[b]	−3.76
	81.015	D_2O	−5.14
	161.903	MTW[b]	−3.72

MS	
	m/z
FAB (glycerol matrix)	$(M + H)^+$ = 569; 547, 525, 502, 483, 467, 445, 343, 321, 263, 245, 229, 208, 137

[a] Abbreviations used for NMR: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet; dt, doublet of triplets; tdd, triplet of doublets of doublets; t′ approximated by t + q + t; t″ approximated by q + t + q. [b] MTW = solvent mixture (methanol-d_4:THF-d_8:D_2O = 5:3:2). [c] Pseudotriplets.

Table II. NMR and Mass Spectrometry Data for TPPTS Oxide



TPPTS oxide

NMR[a]			
	frequency (MHz)	solvent	δ(ppm) (*J* (Hz))
^{1}H	200.133	MTW[b]	7.62–7.78 (m, 2 H); 8.07–8.23 (m, 2 H)
	200.133	D_2O	7.65–7.92 (m, 2 H); 8.02–8.27 (m, 2 H)
	399.952	MTW[b]	7.67 (tdd, H^C, $^{4}J(PH^C)$ = 3.15, $^{5}J(H^CH^A)$ = 0.58, $^{3}J(H^CH^B)$ = 7.78, $^{3}J(H^CH^D)$ = 7.78); 7.77 (ddt H^D, $^{3}J(PH^D)$ = 11.70, $^{4}J(H^DH^A)$ = 1.50, $^{4}J(H^DH^B)$ = 1.50); 8.09 (dq, H^B, $^{5}J(PH^B)$ = 1.60, $^{4}J(H^BH^A)$ = 1.60); 8.20 (dtd, H^A, $^{3}J(PH^A)$ = 12.30)
^{13}C	100.577	D_2O	128.78 (d, C^5, $^{3}J(PC)$ = 12.27); 130.31 (d, C^6, $^{2}J(PC)$ = 12.97); 130.58 (d, C^4, $^{4}J(PC)$ = 2.30); 134.97 (d, C^2, $^{2}J(PC)$ = 10.66); 143.71 (d, C^1, $^{1}J(PC)$ = 12.97); 143.75 (d, C^3, $^{3}J(PC)$ = 12.97)
^{31}P	81.015	MTW[b]	30.34
	81.015	D_2O	35.15
	161.903	MTW[b]	30.59

MS	
	m/z
FAB (glycerol matrix)	$(M + H)^+$ = 585; 563, 541, 525, 505, 483, 461, 351, 337, 321, 259, 245, 229, 137, 123, 107

[a] Abbreviations used for NMR: d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets; dq, doublet of quartets; dtd, doublet of triplets of doublets; tdd, triplet of doublets of doublets; ddt, doublet of doublets of triplets. [b] MTW = solvent mixture (methanol-d_4:THF-d_8:D_2O = 5:3:2).

(a) Reaction Sampling for Monitoring the Extent of Sulfonation. Periodically a 3-mL aliquot of the reaction mixture was removed and neutralized with 20% aqueous NaOH as indicated by phenolphthalein. The water was vacuum distilled, and the resulting white solid was refluxed with 30 mL of hot methanol for approximately 20 min and filtered hot.[13] The methanol was removed under vacuum to yield a white solid which was then analyzed by NMR as described below.

(b) Product Workup. The reaction is complete after ca. 150 h at 22 °C as determined by NMR spectroscopy (vide infra). The reaction mixture was carefully neutralized at 0 °C with 20% aqueous NaOH, and the volume was reduced to 200 mL by distillation. The residue was heated to reflux with 1 L of methanol and filtered hot. The solid was further extracted with 500 mL of hot methanol, and the combined extracts were reduced to 200 mL in volume. The sulfonated products were precipitated by the addition of 800 mL of acetone. Typically the product is a mixture of 75–85% **TPPTS** and 25–15% **TPPTS** oxide. The oxide content can be further reduced by extraction with 300 mL of acetone/methanol/water (10:5:1)[14] and repeated dissolution, reprecipitation, and extraction as described above. When this procedure is done twice, the oxide content can be reliably reduced to less than 5%. From a 10-g sample of **TPP** as described above 11.9 g (55.5% yield) of **TPPTS** was recovered after extraction; the purity, as determined by NMR, was ca. 97%.

---

(9) Barber, M.; Bordoli, R. S.; Sedgwick, R. D.; Tyler, A. N. *J. Chem. Soc., Chem. Commun.* **1981**, 325.

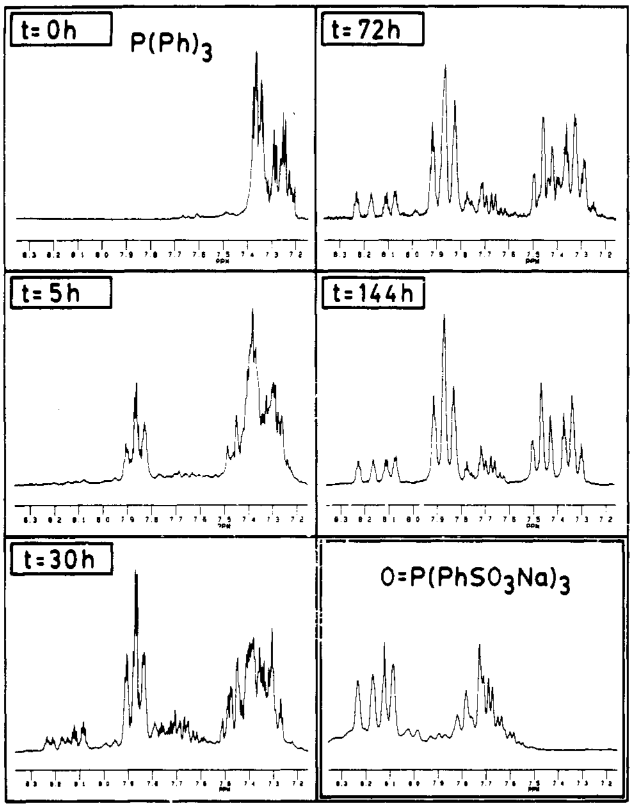


Figure 1. ^{1}H NMR (200 MHz) spectra of quenched aliquots of the sulfonation reaction mixture in the aromatic region. The solvent is a mixture of methanol, THF, and water as described in the Experimental Section. The lower right panel gives the spectrum of TPPTS oxide alone obtained by oxidation with aqueous H_2O_2.

Results

The sulfonation of triphenylphosphine was monitored by both ^{1}H and ^{31}P NMR spectroscopy. To do this 3-mL aliquots were removed from the reaction mixture, neutralized, and extracted with hot methanol as described in the Experimental Section. It was found that a mixture of methanol, THF, and water (5:3:2) dissolved all components of the reaction mixture, including unreacted triphenylphosphine and its sulfonated derivatives. This solvent mixture (see MTW in Tables I and II) was used to record all NMR spectra; fortuitously the solvent mixture gave a better dispersion of chemical shifts than water alone as a solvent. Chemical shift data for TPPTS in the solvent mixture described above and in water are given in Table I. Also included are the FAB mass spectrometry results. The corresponding information for the oxide is presented in Table II. The ^{1}H NMR spectra of the quenched aliquots are shown in Figure 1. Integration of the signals in the spectrum recorded at 144 h shows that the sample contains 76% TPPTS and 24% TPPTS oxide at this point in time. Figure 2 shows some of the corresponding high-field ^{31}P NMR spectra of the aliquots; the mono-, di-, and trisulfonated products can all be distinguished. Attempts to directly observe the ^{31}P NMR spectra in the sulfuric acid reaction medium in all instances gave a broad asymmetric signal which was not very sensitive to the reaction mixture composition.

Generally the final reaction mixtures were found to contain 75–85% TPPTS and 15–25% TPPTS oxide. This is similar to the crude reaction composition reported by Kuntz.[1] The TPPTS could be further purified by extraction with the methanol/acetone/water mixture as described in the Experimental Section. In this manner an acceptable level of purity of TPPTS (>97%) for most purposes in organometallic chemistry can be achieved.

The experimental and calculated 400-MHz ^{1}H NMR spectra for TPPTS and TPPTS oxide are shown in Figure 3. The peak assignments and coupling constants are listed in Tables I and II.

Discussion

As seen from the spectra in Figure 1 the extent of sulfonation of triphenylphosphine as well as oxidation can be determined in a straightforward fashion from the proton NMR spectrum of the crude reaction product. Upon complete sulfonation the peaks in the 7.3–7.5 ppm region simplify, at 200 MHz, to two triplets. Protons due to unsulfonated phenyl groups overlap with this region; thus, the appearance of the this region of the spectrum is sensitive to the extent of sulfonation.

Sulfonation also has an influence on the position of the ^{31}P NMR signal of the phosphine; triphenylphosphine has a chemical shift of −5.0 ppm in methanol/THF/water while the sulfonated

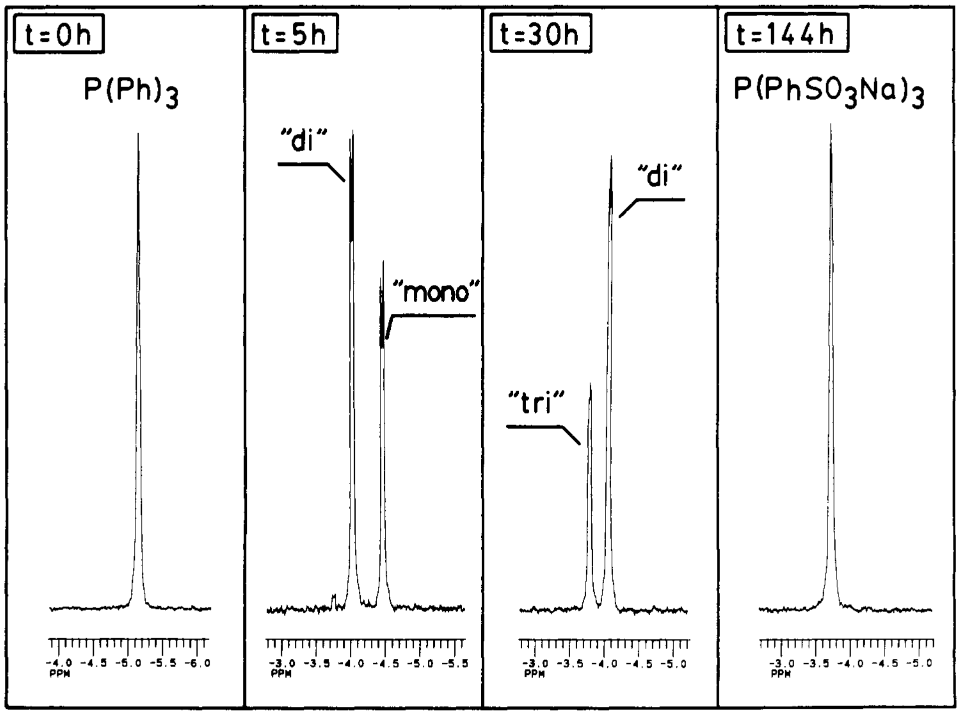


Figure 2. Proton-decoupled 162-MHz ^{31}P NMR spectra in methanol/THF/water showing the relative chemical shifts for mono-, di-, and trisulfonated triphenylphosphine.

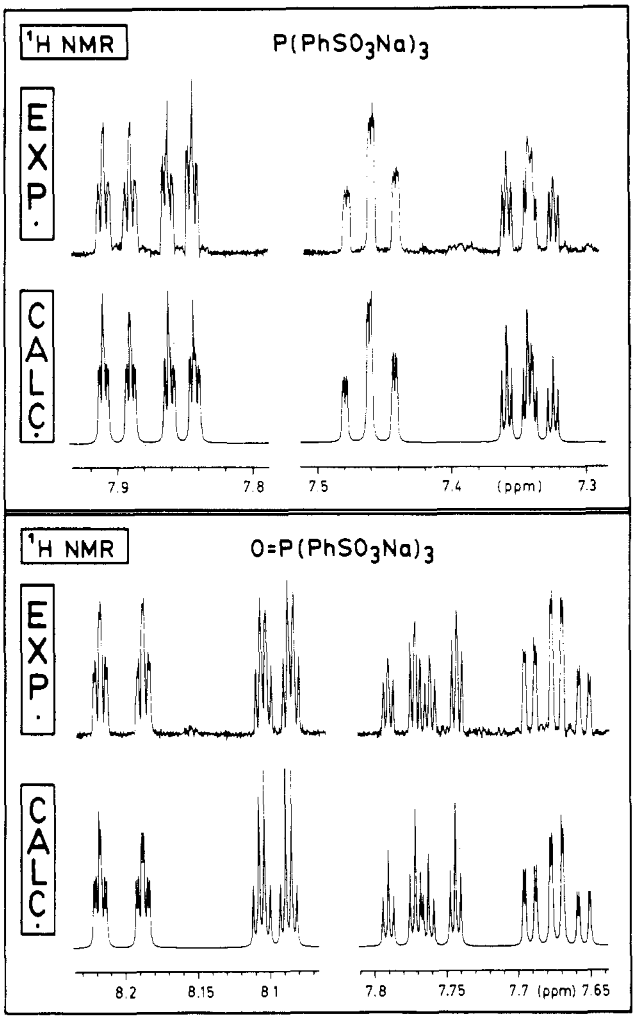


Figure 3. Experimental and calculated 400-MHz ^{1}H NMR spectra for TPPTS and TPPTS oxide.

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.

---

(10) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26.
(11) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(12) Yin, J.; Schurz, H. H.; Busch, K. L. ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, TN, May 19–24, 1991.
(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.

Contribution from the Departments of Chemistry,
University of Hong Kong, Pokfulam Road, Hong Kong,
and Michigan State University, East Lansing, Michigan 48824

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

Zao-Ying Li,[†] Jie-Sheng Huang,[†] Chi-Ming Che,*[,†]
and C. K. Chang[‡]

Received December 26, 1991

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

---

[†] University of Hong Kong.
[‡] Michigan State University.