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1°); the scan rate varied as a function of maximum peak intensity from 0.5 to 29.3°/min. A total of 4694 independent reflections were collected ($2\theta_{max} = 55°$) of which 4679 with $F > 3\sigma(F)$ were used for the refinement. The structure was solved by the Patterson method and refined by anisotropic full-matrix least squares. The hydrogen positions were calculated and considered isotropically. Final $R = 0.035$ and $R_w = 0.036$. The final atomic positional parameters of the non-hydrogen atoms are given in Table II. The compound crystallizes with one molecule of benzene in the asymmetric unit. The carbon atoms C24 and C27 lie on a 2-fold axis that generate atoms C24a and C25a.

**Acknowledgment.** We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Ind. for financial support. We also gratefully acknowledge support by Dr. G. Lange and F. Dadrich (mass spectra), U. Neumann, R. Schedl, and C. P. Kneis (elemental analyses), and Degussa AG (chemicals).

**Registry No.** **1**, 97477-25-3; **2**, 107135-81-9; **3**, 136475-81-5; **4**, 101307-50-0; **5**, 136371-68-1; **6**, 136371-69-2; **7**, 136371-70-5; **8**, 136371-50-1; **9**, 136371-51-2; **10**, 136444-43-4; **11**, 101307-51-1; **11**-$d_3$, 136444-44-5; **12**, 136444-45-6; **13**, 136444-46-7; **14**, 136444-47-8; **15**, 136444-48-9; **16**, 136444-49-0; **17**, 136444-50-3; **18**, 136444-51-4; **19**, 101307-52-2; **20**, 136444-52-5; **21**, 101307-53-3; **22**, 136444-53-6; **23**, 136444-54-7; (*E*)-**24**, 136475-82-6; (*Z*)-**24**, 136444-55-8; **25**, 136444-56-9; **26**, 136444-57-0; **27**, 136444-58-1; **28**, 97477-26-4; **29**, 136444-59-2; **30**, 101307-54-4; **31**, 136444-60-5; **32**, 136444-61-6; **33**, 136444-62-7; **34**, 136444-63-8; **35**, 136444-64-9; **36**, 136444-65-0; **37**, 136444-66-1; **38**, 136444-67-2; **39**, 101307-55-5; **40**, 101307-56-6; **41**, 136444-68-3; **42**, 136444-69-4; **43**, 136444-70-7; **44**, 101307-57-7; **45**, 136444-71-8; **46**, 136444-72-9; **47**, 136444-73-0; **48**, 136444-74-1; **49**, 136444-75-2; (*E*)-**50**, 104067-71-2; (*Z*)-**50**, 104112-52-9; $MeC{\equiv}CH$, 74-99-7; $PhC{\equiv}CH$, 536-74-3; $AgC{\equiv}CPh$, 33440-88-9; $CH_2I_2$, 75-11-6; $CHBr_3$, 75-25-2; $CF_3CO_2Ag$, 2966-50-9; $BrMgCH{=}CHPh$, 30094-01-0; CuCl, 7758-89-6; $NaC_5H_5$, 4984-82-1; $LiC_5Me_5$, 51905-34-1; sulfur, 7704-34-9; selenium, 7782-49-2; benzoyl azide, 582-61-6.

**Supplementary Material Available:** A table of structure factors for **21** (28 pages). Ordering information is given on any current masthead page.

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# Synthesis, Reactivity, and Characterization of the First Donor-Stabilized Silylene Complexes of Osmium *meso*-Tetra-*p*-tolylporphyrin (TTP)Os=SiR$_2$·THF (R = Me, Et, $^i$Pr) and the Molecular Structure of (TTP)Os=SiEt$_2$·2THF

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*Received March 22, 1991*

The preparation and characterization of the first donor-stabilized silylene complexes of osmium *meso*-tetra-*p*-tolylporphyrin are described. The silylene complex $(TTP)Os{=}SiMe_2{\cdot}THF$ (**1**·THF) is prepared by the reaction of $[Os(TTP)]_2$ with hexamethylsilacyclopropane. Treating $K_2[Os(TTP)]$ with $Cl_2SiR_2$ also generates the silylene complexes $(TTP)Os{=}SiR_2{\cdot}THF$ [R = Me (**1**·THF), Et (**2**·THF), $^i$Pr (**3**·THF)]. $^1$H NMR spectroscopy indicates that, in solution, one molecule of THF is coordinated to the silicon in all of these complexes. This has been verified by 2D-NOESY experiments. In **2**·THF, the methylene protons are diastereotopic, indicating that the silicon is pyramidalized. Addition of 1 equiv of pyridine to **1**·THF or **2**·THF replaces the THF on silicon with pyridine. Coordination of pyridine to silicon was also confirmed by a 2D-NOESY experiment. The structure of **2**·THF was determined by a single-crystal X-ray diffraction experiment. The diethyl complex **2**·2THF crystallizes with two additional THF molecules as solvates in the monoclinic space group $P2_1/c$ with $a = 21.649$ (5) Å, $b = 13.829$ (3) Å, $c = 19.526$ (3) Å, $\beta = 98.08$ (2)°, $V = 5788$ (4) Å$^3$, $Z = 4$, $R = 5.0\%$, and $R_w = 5.7\%$. The Os–Si distance (2.325 (8) Å) is the shortest observed to date. Other metrical parameters of this complex are discussed.

## Introduction

In contrast to the well-established chemistry of terminal transition-metal carbene complexes,[2] much less is known for the heavier group 14 analogues, terminal silylene complexes. In the latter case, preparation and investigation of this type of compound has been achieved solely with the use of organometallic complexes. For example, one of the first reported syntheses employed Collman's reagent, $Na_2Fe(CO)_4$, as a metal source in reaction with $(^tBuO)_2SiCl_2$ to yield $(CO)_4Fe{=}Si(O^tBu)_2{\cdot}L$ (L = HMPT, THF).[3] Subsequently, Tilley demonstrated that electrophilic abstraction of a silicon-based group from a ruthenium silyl complex can produce cationic base-stabilized complexes such as $[Cp^*(PMe_3)_2Ru{=}SiPh_2{\cdot}NCCH_3]^+$.[4] More recently, Ogino has obtained a donor-stabilized bis(silylene) complex by photolysis of $Cp^*(CO)_2FeSiMe_2SiMe(OMe)_2$.[5] Only nine examples of silylene complexes have been structurally characterized by X-ray diffraction, and in all cases, coordination of a donor molecule to silicon is observed.[3-5,6,7] Thus, a particularly significant development is Tilley's report of the first iso-

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0276-7333/91/2310-3977$02.50/0

lated example of a "base-free" complex in which a truly two-coordinate silylene ligand is bonded to ruthenium in $[Cp^*(PMe_3)_2Ru{=}Si(SR)_2]BPh_4$ (R = *p*-tolyl, ethyl).[8] This base-free complex has not yet been crystallographically characterized. Jutzi and Möhrke have also reported the synthesis of a novel base-free silylene complex of gold, $(\eta^1\text{-}Me_5C_5)(\eta^5\text{-}Me_5C_5)SiAuCl$.[9]

To date, no coordination complex, consisting primarily of classical ligands (e.g. amines, cyanides, etc.), is known to stabilize silylene ligands. This is not surprising, since classical coordination compounds have not shown any propensity to form stable carbene complexes, despite recent studies which demonstrate that strong $\pi$ bonds with $\eta^2$-arenes and alkynes are possible.[10] Thus, it is clear that distinct boundaries still divide organometallic and classical coordination chemistry. However, metalloporphyrin compounds serve an important role in unifying these two traditional areas of chemistry.[11] Although metalloporphyrins have been of long-standing interest in classical coordination chemistry, they have recently been found to bind organic $\pi$-acid ligands.[12,13]

As an extension of the utility of metalloporphyrins, we describe here the synthesis and characterization of donor-stabilized metalloporphyrin silylene complexes. Previous attempts at preparing terminal silylene complexes have utilized bulky substituents on silicon to increase kinetic stability. Our approach was to employ large, planar porphyrin ligands as a means of providing steric bulk at the metal for similar reasoning. In addition, an electron-rich, late transition metal was chosen in hopes that further stabilization of the adjacent electron-deficient three-coordinate silicon atom would be realized. Furthermore, hexamethylsilacyclopropane serves as a useful reagent for producing transient dimethylsilylene under mild conditions.[14] Using this rationale, we report a new method for the preparation of silylene complexes which involves silylene transfer as well as a method which uses dichlorosilanes as the silylene source.

## Experimental Section

**General Methods.** All manipulations of reagents and products were carried out under a nitrogen atmosphere using a Vacuum Atmospheres glovebox equipped with a Model MO40H Dri-Train gas purification system or on a vacuum line using standard Schlenk techniques. All solvents were dried and distilled from purple solutions of sodium/benzophenone. $^1$H NMR spectra were recorded on a Nicolet 300-MHz or Varian VXR 300-MHz spectrometer. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN, or Oneida Research Services, Whitesboro, NY. Dichlorodialkylsilanes were purchased from commercial sources, distilled from $K_2CO_3$ or $CaH_2$, and degassed by three freeze–pump–thaw cycles prior to use. $[Os(TTP)]_2$[15] was prepared by the literature procedure.[16] Hexamethylsilacyclopropane, HMS, was prepared from $(CH_3)_2Si(CH(CH_3)_2)_2$.[17]

**$(CH_3)_2Si(CH(CH_3)_2)_2$.** A 1.5 M solution of LiMe in $Et_2O$ (72.0 mL, 108 mmol) was added dropwise over 1.75 h to $Cl_2Si(^iPr)_2$ (9.962 g, 53.85 mmol) while the solution was cooled at −78 °C under $N_2$. The reaction mixture was allowed to warm slowly to ambient temperature and subsequently heated at reflux for 18 h. The solution was cooled to ambient temperature and hydrolyzed with 1 M HCl (~100 mL) until evolution of methane stopped. After the aqueous layer was washed with $Et_2O$ (3 × 50 mL), the combined organic fractions were concentrated to 100 mL under reduced pressure and dried over $MgSO_4$. Distillation and collection of the 137–140 °C fraction produced 3.651 g (47%) of product. $^1$H NMR ($CDCl_3$): 0.92 (br m, 14 H, $^i$pr), 0.14 ppm (s, 6 H, Si–$CH_3$).

**$(TTP)Os{=}Si(CH_3)_2{\cdot}OC_4H_8$ (1·THF). Method 1.** $[Os(TTP)]_2$ (15.0 mg, 8.72 $\mu$mol) was stirred in 3 mL of THF with potassium (approximately 20 mg) until the brown solution became emerald green. After filtration of the solution through a plug of glass wool to remove the potassium, 2.2 $\mu$L (18 $\mu$mol) of $Cl_2SiMe_2$ dissolved in 3 mL of THF was added dropwise to the stirred solution of $K_2[Os(TTP)]$ at ambient temperature to form an orange-brown solution. After the solution was stirred for 1 h, THF and excess silane were removed under reduced pressure. The residues were redissolved in $C_6H_6$, and the mixture was filtered on a medium glass frit to remove all salts. Removal of the solvent from the filtrate under reduced pressure afforded 17.0 mg of brown solid (98.5% yield). $^1$H NMR ($C_6D_6$): 8.25 (s, 8 H, $\beta$-H), 8.07 (d, 4 H, aryl), 7.95 (d, 4 H, aryl), 7.36 (d, 4 H, aryl), 7.30 (d, 4 H, aryl), 2.39 (s, 12 H, tolyl $CH_3$), −2.10 (s, 6 H, $SiCH_3$), 1.36 (m, 4 H, $\alpha$-THF), 0.55 ppm (m, 4 H, $\beta$-THF). UV–vis ($C_6H_6$): 408 (Soret), 504 nm. Anal. Calcd for $C_{54}H_{50}N_4OOsSi$: C, 65.56; H, 5.09; N, 5.66. Found: C, 66.29; H, 4.79; N, 5.45.

**Method 2.** Approximately 3 mL of benzene containing 10.4 $\mu$L (73.2 $\mu$mol) of HMS and 7.0 $\mu$L (86 $\mu$mol) of THF was added to $[Os(TTP)]_2$ (12.2 mg, 7.09 $\mu$mol) dissolved in 2 mL of dry benzene. The solution was stirred at 24 °C for 1 h before the solvent was removed under reduced pressure. The resulting orange-brown solid was dispersed in hexane (2 mL), cooled to −20 °C for 20 min, and filtered on a medium-porosity glass frit. The solid was washed from the frit with 5 mL of benzene containing 5 drops of THF. Removal of the solvent under reduced pressure produced 7.3 mg of 1·THF (52% yield). MS ($M^+$ − THF): found, *m/e* 918.2802; calcd *m/e* 918.2793.

**$(TTP)Os{=}SiMe_2{\cdot}NC_5H_5$ (1·py).** To 3.8 mg (3.8 $\mu$mol) of $(TTP)Os{=}SiMe_2{\cdot}THF$ in 0.5 mL of $C_6D_6$ was added 0.6 $\mu$L (7.4 $\mu$mol) of pyridine (py) to produce 1·py quantitatively by $^1$H NMR spectroscopy. Removal of the solvent under reduced pressure produces 3.8 mg of brown solid which is found by $^1$H NMR spectroscopy to consist of a 65:35 1·py:Os(TTP)(py)$_2$ ratio. $^1$H NMR ($C_6D36$): 8.16 (s, 8 H, $\beta$-H), 7.97 (d, 8 H, aryl), 7.36 (d, 4 H, aryl), 7.23 (d, 4 H, aryl), 2.39 (s, 12 H, tolyl $CH_3$), −1.84 (s, 6 H, $SiCH_3$), 6.50 (t, 1 H, py $H_p$), 6.00 (t, 2 H, py $H_m$), 5.70 ppm (d, 2 H, py $H_o$). UV–vis ($C_6D_6$): 414 (Soret), 498 nm.

**$(TTP)Os{=}SiEt_2{\cdot}OC_4H_8$ (2·THF).** Using method 1, 2·THF was prepared in 95% yield from $Cl_2SiEt_2$ (3.0 $\mu$L, 20 $\mu$mol) and $K_2Os(TTP)$ prepared in situ using 17.4 mg (10.1 $\mu$mol) of $[Os(TTP)]_2$. $^1$H NMR ($C_6D_6$): 8.24 (s, 8 H, $\beta$-H), 8.03 (dd, 8 H, aryl), 7.37 (d, 4 H, aryl), 7.30 (d, 4 H, aryl), 2.39 (s, 12 H, tolyl $CH_3$), −0.48 (t, 6 H, $SiCH_2CH_3$), −1.50 (m, 4 H, $SiCH_2CH_3$), 1.60 (m, 4 H, $\alpha$-THF), 0.65 ppm (m, 4 H, $\beta$-THF). $^{29}Si\{^1H\}$ NMR ($C_6D_6$): 24.53 ppm (s). UV–vis ($C_6H_6$): 408 (Soret), 502 nm. Anal. Calcd for $C_{56}H_{54}N_4OOsSi$: C, 66.11; H, 5.35, N, 5.51. Found: C, 67.01; H, 5.53; N, 4.56.

**$(TTP)Os{=}SiEt_2{\cdot}NC_5H_5$ (2·py).** $(TTP)Os{=}SiEt_2{\cdot}THF$ (6.0 mg, 6.0 $\mu$mol) was dissolved in $C_6D_6$, and the mixture was treated with 1.6 $\mu$L (20 $\mu$mol) of pyridine. The $^1$H NMR spectrum of this sample showed quantitative formation of 2·py. Removal of the solvent under reduced pressure yielded 4.4 mg of brown solid consisting of a 7:3 mixture as determined by $^1$H NMR spectroscopy of 2·py/Os(TTP)(py)$_2$. NMR ($C_6D_6$): 8.15 (s, 8 H, $\beta$-H), 8.02 (d, 4 H, aryl), 7.96 (d, 4 H, aryl), 7.37 (d, 4 H, aryl), 7.23 (d, 4 H, aryl),

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[15] Abbreviations: TTP is the dianion of *meso*-tetra-*p*-tolylporphyrin; py is pyridine.

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**Table I. Crystal Data**

| | |
|---|---|
| formula | $OsSiO_2N_4C_{60}H_{62}\cdot 2OC_4H_8$ |
| fw | 1227.67 |
| space group | $P2_1/c$ |
| $a$, Å | 21.649 (5) |
| $b$, Å | 13.829 (3) |
| $c$, Å | 19.526 (3) |
| $\alpha$, deg | 90.0 |
| $\beta$, deg | 98.08 (2) |
| $\gamma$, deg | 90.0 |
| $V$, Å | 5788 (4) |
| $Z$ | 4 |
| $d_{calc}$, g/cm$^3$ | 1.416 |
| cryst size, mm | 0.32 × 0.15 × 0.25 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 22.6 |
| data collcn instrument | Enraf-Nonius CAD4 |
| radiation (monochromated in incident beam) | Mo K$\alpha$ ($\lambda$ = 0.71073 Å) |
| orientation reflns: no.; range ($2\theta$), deg | 25; $10.0 < \theta < 22.0$ |
| temp, °C | −62 (1) |
| scan method | $\theta$–$2\theta$ |
| data collcn range ($2\theta$), deg | 4.0–45.0 |
| no. of data collcd | 13644 |
| no. of unique data, tot. with $F_o^2 > 3\sigma(F_o^2)$ | 5134<br>2406 |
| no. of params refined | 283 |
| transm factors, max and min ($\psi$ scans) | 0.999, 0.972 |
| $R^a$ | 0.050 |
| $R_w{}^b$ | 0.057 |
| quality-of-fit indicator$^c$ | 1.13 |
| largest shift/esd, final cycle | 0.01 |
| largest peak, e/Å | 1.3 (1) |

$^a R = \sum||F_o| - |F_c|/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2|F_o|)$. $^c$Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

2.37 (s, 12 H, tolyl $CH_3$), −0.36 (t, 6 H, $SiCH_2CH_3$), −1.25 (m, 4 H, $SiCH_2CH_3$), 6.56 (t, 1 H, py $H_p$), 6.05 (t, 2 H, py $H_m$), 5.86 ppm (d, 2 H, py $H_o$). UV–vis ($C_6H_6$): 390 (sh), 410 (Soret), 498 nm.

**(TTP)Os=Si($^i$Pr)$_2$·THF (3·THF).** Using method 1, **3**·THF was prepared from $[Os(TTP)]_2$ (3.9 mg, 2.3 $\mu$mol) and $Cl_2Si^iPr$ (0.8 $\mu$L, 4.4 $\mu$mol) in 63% yield. $^1$H NMR ($C_6D_6$): 8.25 (s, 8 H, $\beta$-H), 8.08 (d, 4 H, aryl), 8.01 (d, 4 H, aryl), 7.36 (d, 4 H, aryl), 7.28 (d, 4 H, aryl), 2.38 (s, 12 H, tolyl $CH_3$), −0.43 (d, 12 H, $SiCH(CH_3)_2$), −0.94 (m, 2 H, $SiCH(CH_3)_2$), 1.38 (m, 4 H, $\alpha$-THF), 0.53 ppm (m, 4 H, $\beta$-THF). UV–vis ($C_6H_6$): 408 (Soret), 502 nm.

**X-ray Structure Determination of 2·2THF.** A single crystal of (TTP)Os=SiEt$_2$(THF)$_2$·2THF suitable for X-ray structure analysis was grown from a THF solution layered with octane. A brown crystal having approximate dimensions of 0.32 × 0.15 × 0.25 mm was attached to a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) for data collection at −62 ± 1 °C. The cell constants for data collection were determined from a list of reflections found by an automated search routine. Pertinent data collection and reduction information is given in Table I. Lorentz and polarization corrections were applied. A correction based on a decay in the standard reflections of 1.4% was applied to the data. An absorption correction based on a series of $\psi$ scans was applied. The agreement factor for the averaging of observed reflections was 3.5% (based on $F$).

The space group $P2_1/c$ was unambiguously determined by systematic absences prior to the solution. The positions of the osmium and silicon atoms were determined by direct methods.[18] The remaining non-hydrogen positions were determined by successive difference Fourier maps. Two solvent molecules of tetrahydrofuran were located in the asymmetric unit. Only four atoms of one THF could be found by difference Fourier maps. The THF molecules appear to be caged by the porphyrin substituent groups. The closest nonbonded contact distance is 3.62 Å for a carbon of the THF group bound to the silicon and a THF of solvation.

Only the osmium and silicon atoms were refined anisotropically[19] because of a lack of $3\sigma$ data. As is common in structure determinations involving THF,[20] the THF molecules of solvation of **2**·THF exhibit a high degree of thermal motion. Consequently, these solvate molecules were not refined positionally or isotropically in the final cycle of least squares. All hydrogens were placed in the porphyrin group at distances of 0.95 Å with isotropic temperature factors 1.3 times the respective carbon atoms.

X-ray data collection and structure solution were carried out at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Corp. Micro VAX II computer using the CAD4-SDP programs.[21]

## Results

**Synthesis.** When a dark brown solution of the paramagnetic dimer $[Os(TTP)]_2$ is treated with a 10-fold excess of hexamethylsilacyclopropane (HMS) containing THF, a rapid color change to orange is observed at ambient temperature. The $^1$H NMR spectrum for the material isolated from this reaction is consistent with a new diamagnetic metalloporphyrin complex which can be formulated as the dimethylsilylene complex (TTP)Os=SiMe$_2$·THF (**1**·THF) (eq 1). In $C_6D_6$, the dimethylsilylene complex **1**·THF maintains a time-averaged 4-fold porphyrin symmetry, as indicated by the single $\beta$-pyrrole signal at 8.25 ppm and the single $p$-tolyl methyl peak at 2.39 ppm. The appearance of distinct resonances for the $o$-, $o'$-, $m$-, and $m'$-tolyl protons at 8.07, 7.95, 7.36, and 7.30 ppm indicate that mirror symmetry in the porphyrin plane is absent. The coordinated dimethylsilylene ligand gives rise to a new six-proton singlet at −2.10 ppm. The far-upfield position of this signal is characteristic of protons held above a porphyrin ring current. Resonances for a single THF molecule are also observed at 1.36 (m, 4 H) and 0.55 (m, 4 H) ppm. The upfield shift of these signals also indicates that THF is bound above the porphyrin. Coordination of the THF molecule directly to silicon and not to osmium was established by 2D-NOESY NMR spectroscopy. A cross peak between the THF resonance at 1.36 ppm and the SiMe$_2$ resonance at −2.10 ppm indicates that the THF and silylene methyl groups are indeed proximal to each other. Further support for the composition of the silylene complex is provided by mass spectral analysis. Electron-impact ionization of a sample of **1**·THF allowed observation of an ion fragment having an exact mass of 918.2802 amu. This corresponds to a daughter ion formed by loss of THF (calculated mass: 918.2793 amu).

(1)

A more versatile method for preparing silylene complexes involves a simple metathetical reaction between the dianionic complex $[Os(TTP)]^{2-}$ and dichlorosilanes. Venburg and Collman have independently reported a similar procedure.[22] Thus, when a dark green THF so-

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[19] An alternative model was used in an attempt to improve the structure. This model refined osmium, silicon, C49, C50, C51, C52, O1, and O2 anisotopically and refined the solvent molecules positionally and isotropically. The refinement did not converge after 10 cycles of least-squares refinement and showed no significant improvement with the addition of these 66 parameters.

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[21] *Enraf-Nonius Structure Determination Package*: Enraf-Nonius: Delft, Holland. Neutral-atom scattering factors and anomalous scattering corrections were taken from: *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.

lution of $K_2[Os(TTP)]$[23] is treated with 1 equiv of dichlorodimethylsilane, formation of **1**·THF occurs within minutes (eq 2). The $^1H$ NMR and 2D-NOESY spectra of **1**·THF prepared from $[Os(TTP)]^{2-}$ are identical to those of material prepared from the HMS method.

$$K_2[Os(TTP)] + Cl_2SiR_2 \xrightarrow{THF} (TTP)Os{=}SiR_2{\cdot}THF + 2KCl \quad (2)$$
$$\mathbf{1},\ R = Me \qquad \mathbf{2},\ R = Et \qquad \mathbf{3},\ R = {}^{i}Pr$$

As indicated by eq 2, the diethyl- and diisopropylsilylene complexes can also be prepared. However the more sterically hindered silanes $Cl_2Si^tBu_2$ and $Cl_2SiPh_2$ undergo no reaction with $[Os(TTP)]^{2-}$ at 22 °C. At higher temperatures, destruction of both $[Os(TTP)]^{2-}$ and the dichlorosilanes occurs. In both **2**·THF and **3**·THF, a single coordinated THF molecule is present, as indicated by significant upfield shifts for the $\alpha$- and $\beta$-protons in the $^1H$ NMR spectrum. Particularly noteworthy in the NMR spectrum of **2**·THF are the ethyl $CH_2$ resonances. These appear as a diastereotopic multiplet at −1.50 ppm, indicating that the silicon must be pyramidalized. Irradiation of the ethyl triplet at −0.48 ppm collapses the methylene signal into an AB quartet. The 2D-NOESY spectrum for **3**·THF indicates that THF is coordinated to silicon in this case also. The proton-decoupled silicon NMR spectrum of **2**·THF has a single resonance at 24.53 ppm.

Simple displacement reactions at the silylene silicon are possible. When 1 equiv of pyridine is added to $(TTP)Os{=}SiMe_2{\cdot}THF$ (**1**·THF) in $C_6D_6$, a new complex $(TTP)Os{=}SiMe_2{\cdot}py$ (**1**·py) is produced, quantitatively as determined by $^1H$ NMR spectroscopy. One equivalent of free THF is observed in the proton NMR spectrum at 3.57 and 1.40 ppm, and new resonances for bound pyridine appear at 6.50 (t, 1 H), 6.00 (t, 2 H), and 5.70 ppm (d, 2 H). Coordination of the pyridine to silicon was also established by a 2D-NOESY experiment. The new silylene methyl resonance appears at −1.84 ppm, and the corresponding porphyrin signals are observed at 8.16 (s, 8 H, $\beta$-H), 7.97 (d, 8 H, aryl), 7.36 (d, 4 H, aryl), 7.23 (d, 4 H, aryl), and 2.39 ppm (s, 12 H, $CH_3$). Removal of the solvent under reduced pressure results in partial decomposition of the pyridine adduct, **1**·py, to $Os(TTP)py_2$ (**4**). The resulting solid contains a 7:3 mixture of **1**·py and **4**. Similarly, addition of pyridine to $(TTP)Os{=}SiEt_2{\cdot}THF$ produces $(TTP)Os{=}SiEt_2{\cdot}py$ (**2**·py). The methylene protons in this complex are also diastereotopic, indicating that pyridine is coordinated to silicon.

**X-ray Structure of 2·2THF.** The molecular structure of the diethylsilylene complex, **2**·2THF, was determined by single-crystal X-ray diffraction. Because of the small size and weak diffraction of the crystal, only a relatively small number of observed reflections could be collected. Consequently, in order to preserve a reasonable data-to-parameter ratio, the majority of atoms were refined with isotropic temperature factors. As a result of these limitations, small differences between bond lengths are probably not experimentally significant. Nonetheless, the structure of **2**·THF was clearly established as a base-stabilized silylene complex as shown in Figure 1. Crystallographic data for the structure determination and fractional coordinates for non-hydrogen atoms are listed in Tables I and II. Table III gives selected bond distances and angles.

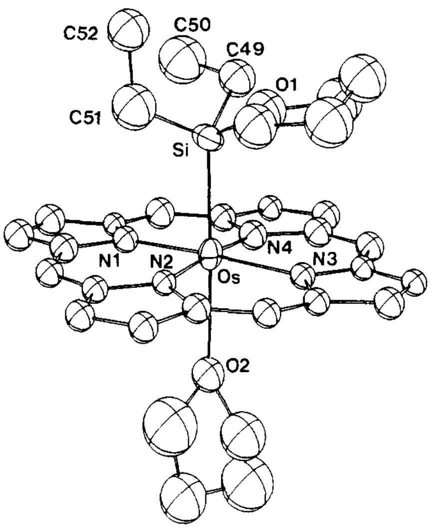

**Figure 1.** Molecular structure with 50% probability thermal ellipsoids and partial atom numbering scheme for $(TTP)Os{=}SiEt_2{\cdot}2THF$.

The diethylsilylene complex **2**·2THF crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. As expected for a six-coordinate complex, the porphyrin ligand in this molecule is nearly planar. The largest deviation from planarity occurs at N1, which is 0.085 (15) Å out of the mean porphyrin plane. The coordination sphere of the osmium atom approaches an ideal octahedral geometry with bond angles between cis-related ligands ranging from 85.4 to 95.1°. The osmium atom is slightly drawn out of the mean porphyrin plane 0.116 (2) Å toward the silylene ligand. The Os–O2 distance of 2.40 (s) Å[24] suggests that the silylene ligand has a strong trans effect. This is supported by reactivity studies (vide infra).

The Os–Si bond length in **2**·2THF (2.325 (8) Å) is the shortest Os–Si distance reported to date.[25] This bond distance is comparable to the shortest known Ru–Si distance, 2.328 (2) Å, in the base-stabilized silylene complex reported by Tilley in $[Cp^*(PMe_3)_2Ru{=}SiPh_2{\cdot}N{\equiv}CCH_3]BPh_4$.[6] The Si–O1 distance (1.82 (2) Å) is longer than typical Si–O bond distances (1.63–1.66 Å) in four-coordinate silicon compounds.[26] Of the nine previously reported silylene complexes containing a coordinated oxygen donor, $Cp^*(PMe_3)_2Ru{=}SiPh_2(OTF)$ has the longest Si–O distance (1.853 (5) Å).[6] Other metal–silylene complexes stabilized by neutral oxygen bases have Si–O distances of 1.73–1.74 Å.[2-7]

The coordination geometry about silicon in **2**·2THF is similar to that for previously reported base-stabilized silylene complexes. The Os–Si–C bond angles of 121 (1) and 117 (1)° are near the values expected for an $sp^2$-hybridized silicon. Consistent with the partial double-bond character in the Os–Si interaction is the C–Si–C bond angle of 111.0 (2)°. This is more typical of the C–Si–C bond angles of 115–118° in disilenes, $R_2Si{=}SiR_2$, and may reflect some $sp^2$ character.[27] Note that in other base-stabilized transition-metal silylene complexes, the R–Si–R angles range from 102 to 104°.

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[24] The closest comparison for this distance is the Ru–O bond length (2.21 (2) Å) in Ru(OEP)(CO)(EtOH): Bonnet, J. J.; Eaton, S. S.; Eaton, G. R.; Holm, R. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 2141.

[25] The shortest Os–Si distance previously reported is 2.367 (13) Å: Einstein F. W. B.; Pomeroy, R. K.; Willis, A. C. *J. Organomet. Chem.* **1986**, *311*, 257.

[26] Wieberg, N.; Wagner, G.; Müller, G.; Riede, J. *J. Organomet. Chem.* **1984**, *271*, 381.

[27] (a) Cowley, A. H. *Acc. Chem. Res.* **1984**, *17*, 386. (b) Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1.

Table II. Positional Parameters and Their Estimated Standard Deviations

| atom | $x$ | $y$ | $z$ | $B$,[a] Å$^2$ |
|---|---|---|---|---|
| Os | 0.75180 (8) | 0.21829 (7) | 0.49835 (9) | 2.52 (1) |
| N1 | 0.6846 (7) | 0.265 (1) | 0.5534 (7) | 2.2 (3)* |
| N2 | 0.7566 (7) | 0.349 (1) | 0.4553 (7) | 1.9 (3)* |
| N3 | 0.8241 (7) | 0.169 (1) | 0.4496 (7) | 2.1 (3)* |
| N4 | 0.7508 (8) | 0.090 (1) | 0.5486 (8) | 2.9 (4)* |
| C1 | 0.6557 (7) | 0.218 (2) | 0.6031 (8) | 1.7 (3)* |
| C2 | 0.6126 (9) | 0.280 (2) | 0.628 (1) | 3.6 (4)* |
| C3 | 0.615 (1) | 0.365 (2) | 0.598 (1) | 3.6 (5)* |
| C4 | 0.6600 (9) | 0.360 (2) | 0.550 (1) | 2.8 (5)* |
| C5 | 0.6797 (9) | 0.437 (2) | 0.513 (1) | 2.6 (4)* |
| C6 | 0.7240 (9) | 0.435 (1) | 0.467 (1) | 2.2 (4)* |
| C7 | 0.7430 (9) | 0.513 (1) | 0.429 (1) | 2.6 (5)* |
| C8 | 0.789 (1) | 0.478 (2) | 0.392 (1) | 3.0 (5)* |
| C9 | 0.7989 (9) | 0.377 (1) | 0.411 (1) | 2.6 (4)* |
| C10 | 0.8410 (9) | 0.319 (1) | 0.385 (1) | 2.6 (5)* |
| C11 | 0.8556 (9) | 0.222 (2) | 0.407 (1) | 2.7 (4)* |
| C12 | 0.8969 (9) | 0.160 (2) | 0.378 (1) | 2.5 (4)* |
| C13 | 0.8926 (8) | 0.072 (1) | 0.408 (1) | 2.0 (4)* |
| C14 | 0.8495 (8) | 0.077 (1) | 0.4535 (9) | 1.9 (4)* |
| C15 | 0.8324 (9) | −0.001 (1) | 0.494 (1) | 2.7 (5)* |
| C16 | 0.786 (1) | 0.007 (2) | 0.539 (1) | 3.0 (5)* |
| C17 | 0.771 (1) | −0.070 (2) | 0.582 (1) | 3.1 (5)* |
| C18 | 0.7271 (9) | −0.034 (1) | 0.618 (1) | 2.4 (4)* |
| C19 | 0.7118 (9) | 0.062 (1) | 0.599 (1) | 2.5 (4)* |
| C20 | 0.669 (1) | 0.124 (2) | 0.621 (1) | 3.1 (5)* |
| C21 | 0.6513 (8) | 0.535 (1) | 0.5215 (9) | 1.8 (4)* |
| C22 | 0.589 (1) | 0.551 (2) | 0.497 (1) | 4.4 (6)* |
| C23 | 0.561 (1) | 0.637 (2) | 0.507 (1) | 5.1 (6)* |
| C24 | 0.598 (1) | 0.712 (2) | 0.540 (1) | 6.0 (6)* |
| C25 | 0.658 (1) | 0.704 (2) | 0.558 (1) | 4.4 (5)* |
| C26 | 0.687 (1) | 0.611 (2) | 0.555 (1) | 5.0 (6)* |
| C27 | 0.567 (2) | 0.811 (2) | 0.551 (2) | 8.7 (9)* |
| C28 | 0.878 (1) | 0.366 (2) | 0.333 (1) | 3.5 (5)* |
| C29 | 0.850 (1) | 0.396 (2) | 0.270 (1) | 3.9 (5)* |
| C30 | 0.883 (1) | 0.440 (2) | 0.223 (1) | 4.1 (6)* |
| C31 | 0.946 (1) | 0.454 (2) | 0.241 (1) | 4.2 (6)* |
| C32 | 0.976 (1) | 0.423 (2) | 0.299 (1) | 3.9 (5)* |
| C33 | 0.941 (1) | 0.379 (2) | 0.348 (1) | 3.8 (5)* |
| C34 | 0.983 (1) | 0.498 (2) | 0.187 (1) | 6.4 (7)* |
| C35 | 0.8641 (9) | −0.095 (1) | 0.488 (1) | 2.3 (4)* |
| C36 | 0.9240 (9) | −0.110 (1) | 0.506 (1) | 2.0 (4)* |
| C37 | 0.9494 (9) | −0.200 (2) | 0.499 (1) | 3.3 (5)* |
| C38 | 0.9157 (9) | −0.279 (2) | 0.476 (1) | 3.1 (4)* |
| C39 | 0.856 (1) | −0.265 (2) | 0.457 (1) | 7.0 (8)* |
| C40 | 0.826 (1) | −0.172 (2) | 0.461 (1) | 3.3 (5)* |
| C41 | 0.943 (1) | −0.373 (2) | 0.466 (1) | 7.0 (8)* |
| C42 | 0.6260 (9) | 0.082 (1) | 0.671 (1) | 2.1 (4)* |
| C43 | 0.650 (1) | 0.056 (2) | 0.735 (1) | 3.2 (5)* |
| C44 | 0.614 (1) | 0.025 (2) | 0.786 (1) | 5.2 (7)* |
| C45 | 0.552 (1) | 0.013 (2) | 0.762 (1) | 3.2 (5)* |
| C46 | 0.527 (1) | 0.034 (2) | 0.696 (1) | 3.3 (5)* |
| C47 | 0.5641 (9) | 0.067 (2) | 0.648 (1) | 3.0 (5)* |
| C48 | 0.507 (1) | −0.019 (2) | 0.817 (2) | 6.7 (8)* |
| Si | 0.6734 (3) | 0.1653 (5) | 0.4129 (3) | 3.4 (2) |
| C49 | 0.637 (1) | 0.045 (2) | 0.418 (1) | 5.3 (6)* |
| C50 | 0.581 (1) | 0.049 (2) | 0.464 (2) | 8.0 (9)* |
| C51 | 0.615 (1) | 0.251 (2) | 0.380 (2) | 6.9 (8)* |
| C52 | 0.564 (1) | 0.228 (2) | 0.323 (1) | 6.5 (7)* |
| O1 | 0.6982 (8) | 0.140 (1) | 0.3295 (8) | 5.6 (4)* |
| C53 | 0.732 (1) | 0.046 (2) | 0.314 (2) | 7.4 (8)* |
| C54 | 0.740 (1) | 0.068 (2) | 0.240 (2) | 7.3 (8)* |
| C55 | 0.758 (1) | 0.171 (2) | 0.236 (2) | 7.6 (9)* |
| C56 | 0.714 (1) | 0.219 (2) | 0.284 (1) | 5.9 (6)* |
| O2 | 0.8296 (6) | 0.279 (1) | 0.5879 (6) | 3.3 (3)* |
| C57 | 0.891 (1) | 0.239 (2) | 0.596 (1) | 5.7 (7)* |
| C58 | 0.926 (2) | 0.292 (3) | 0.653 (2) | 10. (1)* |
| C59 | 0.899 (1) | 0.391 (2) | 0.650 (2) | 7.3 (8)* |
| C60 | 0.846 (1) | 0.375 (2) | 0.596 (2) | 8.5 (9)* |
| O3 | 0.149 | 0.376 | 0.285 | 13.5* |
| C61 | 0.146 | 0.313 | 0.344 | 9.2* |
| C62 | 0.098 | 0.235 | 0.315 | 10.0* |
| C63 | 0.115 | 0.223 | 0.234 | 13.2* |
| C64 | 0.135 | 0.324 | 0.223 | 10.7* |
| C65 | 0.610 | 0.798 | 0.279 | 10.0* |
| C66 | 0.638 | 0.776 | 0.360 | 10.0* |
| C67 | 0.690 | 0.758 | 0.323 | 10.0* |
| C68 | 0.659 | 0.779 | 0.246 | 10.0* |

[a] Starred $B$ values are for atoms that were refined isotropically. $B$ values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Selected Intramolecular Bond Distances and Angles[a]

| | | | |
|---|---|---|---|
| Bond Distances (Å) | | | |
| Os–N1 | 2.03 (2) | Os–O2 | 2.40 (2) |
| Os–N2 | 2.01 (2) | Si–C49 | 1.85 (3) |
| Os–N3 | 2.06 (2) | Si–C51 | 1.79 (4) |
| Os–N4 | 2.03 (2) | Si–O1 | 1.82 (2) |
| Os–Si | 2.325 (8) | | |
| Bond Angles (deg) | | | |
| N1–Os–Si | 88.7 (5) | Os–Si–C49 | 121 (1) |
| N1–Os–O2 | 89.1 (6) | Os–Si–C51 | 117 (1) |
| N2–Os–Si | 93.5 (6) | Os–Si–O1 | 115.2 (6) |
| N2–Os–O2 | 85.3 (7) | C49–Si–C51 | 110 (1) |
| N3–Os–Si | 95.2 (4) | C49–Si–O1 | 93 (1) |
| N3–Os–O2 | 87.1 (5) | C51–Si–O1 | 95 (1) |
| N4–Os–Si | 90.9 (6) | Si–C49–C50 | 111 (2) |
| N4–Os–O2 | 90.3 (7) | Si–C51–C52 | 122 (2) |
| Si–Os–O2 | 177.4 (5) | | |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

## Discussion

The reaction of $[Os(TTP)]_2$ with HMS represents a new method for the preparation of base-stabilized silylene complexes. The formation of 1·THF from this reaction occurs rapidly at 22 °C. Since the generation of the free silylene ($Me_2Si$:) from HMS has a half-life of greater than 9 days at ambient temperature, formation of 1·THF is unlikely to arise from thermal extrusion of $Me_2Si$: from HMS. The formation of the dimethylsilylene complex 1·THF may involve a prior electron-transfer step between $[Os(TTP)]_2$ and HMS leading to a chain radical process.[28]

Unoptimized yields of 1·THF from the HMS method are typically on the order of 50%. For a significant reaction to take place, an excess of HMS (HMS:Os > 3) is required. As a result, a major byproduct (presumably oligomeric and polymeric dimethylsilanes) arises from the decomposition of HMS. The majority of these silicon contaminants can be removed by washing with hexanes, but traces of impurities still remain. However, we have found that 1·THF can be prepared independently from $K_2[Os(TTP)]$ and $Cl_2SiMe_2$ using a method similar to that reported by Zybill and Müller.[3] This reaction proceeds rapidly at 22 °C and produces high yields of much cleaner 1·THF. In an analogous manner, the diethyl, 2·THF, and diisopropyl, 3·THF, derivatives can be prepared. These compounds are all thermally and air-sensitive materials and slowly decompose to uncharacterized materials over a few days at 23 °C. Qualitatively, the stability toward decomposition appears to decrease with the size of the alkyl substituent on Si. For example, we have found that 3·THF completely decomposes in less than 48 h.

In all three complexes, one molecule of coordinated THF is present, as demonstrated by $^1H$ NMR integrations. All isolated silylene complexes have a donor molecule coordinated to the silylene ligand, with one exception, [Cp*-

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(28) Berry, D. H.; Mitstifer, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 3777.

(PMe$_3$)$_2$Ru=Si(SR)$_2$]BPh$_4$, where R is *p*-tolyl or ethyl.[8] This latter example can be considered to be base stabilized by an internal donation of a lone pair from sulfur to silicon. In any event, all of these examples involve 18-electron metal complexes. The base-free complex (TTP)Os=SiR$_2$ is formally a 16-electron complex. Thus, THF could coordinate to either the osmium or silicon. In fact, both sites can bind THF, as indicated by the X-ray crystal structure of **2**·2THF. However, it is apparent that under normal workup conditions, one of the THF molecules is easily removed. The question of which site binds the donor molecule when only one THF is present was answered by $^1$H 2D-NOESY. The appearance of a cross peak between the THF signal at 1.34 ppm and the SiMe$_2$ signal in **1**·THF indicates that THF is coordinated to silicon. This is further supported by the diastereotopic nature of the CH$_2$ ethyl signals of the mono-THF adduct **2**·THF. Pyramidalization of the silicon of the diethylsilylene group is likely to be due to coordination of THF to Si.

Further evidence for the coordination of a donor molecule to the silylene ligand in **2**·THF is provided by $^{29}$Si NMR spectroscopy. The $^{29}$Si chemical shift for **2**·THF appears at 24.53 ppm in C$_6$D$_6$. Other base-stabilized silylene complexes exhibit $^{29}$Si resonances in the range −9 to +127 ppm.[3,5,6] In contrast the base-free silylene complexes [Cp*(PMe$_3$)$_2$Ru=Si(SR)$_2$]BPh$_4$ have characteristic $^{29}$Si signals that appear at very low field (250–264 ppm).[8]

The 16-electron valence configuration for the five-coordinate (TTP)Os=SiR$_2$·THF complexes suggested that a sixth ligand could bind to osmium to produce 18-electron complexes. Surprisingly, when 1 equiv of pyridine was added to the dimethylsilylene complex **1**·THF, loss of THF from the complex was observed by $^1$H NMR spectroscopy and a new species, **1**·py, appeared. The fact that free THF was observed indicates that simple substitution at silicon had occurred. Verification that pyridine was bound to silicon and not to osmium in **1**·py was established by 2D-NOESY $^1$H NMR spectroscopy. In a similar manner, when the diethyl analogue **2**·THF was treated with 1 equiv of pyridine, formation of the new base-stabilized complex **2**·py was observed. The diastereotopic methylene protons of the SiEt$_2$ ligand indicate that pyridine is bound to silicon. It is remarkable that the osmium center prefers to remain five-coordinate in the base-stabilized silylene complexes (TTP)Os=SiR$_2$·L. This suggests that the silylene ligand has a stronger trans effect than carbon monoxide in osmium porphyrin complexes.[16] Despite the presence of a neutral, electron-rich, d$^6$, third-row transition-metal $\pi$-donor fragment, the silylene complexes prepared here still have a strong tendency to form base-stabilized, four-coordinate silicon. In an attempt to prevent coordination of donor molecules to Si, use of bulky alkyl substituents to hinder four-coordination at Si was examined. Unfortunately, $^t$Bu$_2$SiCl$_2$ and Ph$_2$SiCl$_2$ do not react with K$_2$[Os(TTP)] in THF at 22 °C. No appearance of the desired silylene complex is observed, and destruction of the dianion and the dichlorosilane occurs after several hours at higher temperatures.

## Concluding Remarks

The preparation and structural characterization of the first base-stabilized osmium silylene complexes have been accomplished. Despite the use of an electron-rich metal system, the strong $\pi$-donor ability of osmium in these systems is still insufficient to allow isolation of a true base-free silylene complex. The fact that these complexes are also the first 16-electron species known to contain the silylene ligand may account for this observation. These novel complexes also show little tendency to achieve an 18-electron valence configuration at osmium. Substitution of the neutral base bonded to silicon is the preferred reaction on treatment with additional ligands. This illustrates a strong trans effect of the silylene ligand.

**Acknowledgment.** We thank Dr. Dave Scott for assistance with the 2D-NOESY experiments and Ms. Jan Beane for performing the mass spectral characterization. Funding for this work was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the NSF.

**Registry No.** **1**·THF, 136804-99-4; **1**·py, 136805-03-3; **2**·THF, 136805-00-0; **2**·2THF, 136805-02-2; **2**·py, 136805-04-4; **3**·THF, 136805-01-1; HMS, 55644-09-2; py, 110-86-1; K$_2$[Os(TTP)], 136805-05-5; [Os(TTP)]$_2$, 89184-07-6; Cl$_2$Si$^i$Pr$_2$, 7751-38-4; (CH$_3$)$_2$Si(CH(CH$_3$)$_2$)$_2$, 3429-53-6; LiMe, 917-54-4; Cl$_2$SiMe$_2$, 75-78-5; Cl$_2$SiEt$_2$, 1719-53-5.

**Supplementary Material Available:** For **2**·2THF, a listing of hydrogen atom coordinates (3 pages); a table of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.