slight excess of $NEt_4Cl(\cdot xH_2O)$[10] (1.2 equiv) **7** transforms at 20 °C within 15 min to **6** without a detectable amount of **5**. However, formation of the nitrilium complex **5** is favored by an increase in chloride concentration. For example, upon addition of a 10-fold excess of $NEt_4Cl(\cdot xH_2O)$ to **7** at room temperature, a 1:2 mixture of **5** and **6** (estimated by IR) forms within 15 min.[10] The transformation of **7b** to **6** can also be induced by addition of $CH_3OH$.[11a] When $CH_3OH$ is used as the solvent, the reaction of **4** with HCl (gas or concentrated aqueous HCl) affords only **6**. From the latter reaction, complex **6** may be isolated in 83% yield after chromatography on silica ($CH_2Cl_2$/hexane, 1:1; -40 °C) and recrystallization from THF/hexane.

These experiments show that the preferred site of protonation of **4** is the alkylidyne carbon (MC $\pi$ bond). The resulting alkylidene ligand is easily deprotonated, but it does not rearrange into an alkylidyne hydride system, nor does it undergo coupling with either the carbonyl or isocyanide ligand. Formation of the nitrilium complex **5** is proposed to involve addition of $Cl^-$ to **7** to give the seven-coordinate alkylidene complex $[W(CHPh)Cl_2(CNCMe_3)(CO)(PMe_3)_2]$ (**8**). The postulation of **8** as an intermediate is based on the observation that an increase of the chloride ion concentration favors formation of **5**. A second protonation of the former alkylidyne carbon in **8**, followed by migration of the generated benzyl ligand to the isocyanide ligand,[12] would generate the nitrilium ligand. Final substitution of trimethylphosphine by choride would then give **5**. An analogous reaction of $[W(CC_6H_4\text{-}4\text{-}CH_3)(\eta^5\text{-}C_5H_5)(CO)_2]$ with HCl, resulting in formation of the $\eta^2$-acyl complex $[WCl_2(\eta^2\text{-}OCCH_2C_6H_4\text{-}4\text{-}CH_3)(\eta^5\text{-}C_5H_5)(CO)]$, was reported by Kreissl.[2a] The formation of the aminoalkyne complex **6** is facilitated by the presence of $H_2O$ or $CH_3OH$. These reagents are believed to play a dual role: to reduce the nucleophilicity of the chloride ions, thus inhibiting formation of **8**, and to act as weak bases for the transfer of the proton from the alkylidyne carbon atom to the isocyanide nitrogen atom, thereby generating the alkylidyne aminocarbyne metal complex $[W(CPh)(CNHCMe_3)Cl(CO)(PMe_3)_2]^+$ (**9**). Whether the actual ligand-coupling step to give the aminoalkyne occurs spontaneously after proton transfer or the chloride ion is actively assisting this step is under current investigation.[11b] The proton-induced coupling of alkylidyne and isocyanide ligands[13] was recently demonstrated by Filippou.[14] Proton and electrophile-induced coupling reactions of carbyne ligands with isocyanide and carbonyl ligands were previously postulated and recently demonstrated by Lippard to be involved as key steps in coupling reactions of isocyanide and carbon monoxide ligands.[15]

According to molecular orbital calculations on low-valent alkylidyne complexes, the HOMO in various systems may be a filled metal d orbital, the MC $\pi$ bond(s), or a ligand-centered orbital.[16] However, the alkylidyne carbon is consistently calculated to carry a net negative charge, thus favoring charge-controlled attack at this atom. This work shows that the preferred site of protonation in the alkylidyne isocyanide complex **4** is the alkylidyne carbon. Protonation at the isocyanide ligand is thermodynamically much less favorable, but given the proper reaction conditions, it can become a step along the major reaction pathway.

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**Supplementary Material Available:** Tables of crystallographic parameters, atomic coordinates, thermal parameters, and bond distances and angles for **5** and **6** (22 pages); tables of observed and calculated structure factors for **5** and **6** (48 pages). Ordering information is given on any current masthead page.

(10) $NEt_4Cl\text{-}xH_2O$ was dried in vacuo at 80 °C for 1 h. This material still contains residual $H_2O$. If $NEt_4Cl$ is dried at 80 °C ($10^{-2}$ Torr) for 6 h, complex **5** is obtained as the main product. However, in this case formation of **6** as the only product is achieved by addition of one drop of water prior to the addition of $NEt_4Cl$. Reactions were reproducible for given batches of $NEt_4Cl$.

(11) (a) Methanol was also found to assist formation of an aminoalkyne ligand in the triflate salt **7a**. Addition of a small amount of methanol to a solution of **7a** in $CH_2Cl_2$ affords $[WCl(CF_3SO_3)(CO)(PhCCNHCMe_3)(CO)(PMe_3)_2]$, **10**: 108-110 °C dec; IR ($cm^{-1}$, ether) $\nu_{CO}$ = 1957, $\nu_{CN}$ = 1651; $^1H$ NMR (ppm, $CDCl_3$) 8.18, (br, 1 H, NH), 6.7-7.4 (m, 5 H, $C_6H_5$), 1.41 (t, 18 H, $P(CH_3)_3$), 1.12 (s, 9 H, $C(CH_3)_3$); $^{13}C$ NMR (ppm, $CDCl_3$) 230.6 ($CNHCMe_3$), 209.1, 206.8 (CPh and CO), 119.1 (q, $CF_3SO_3$). (b) This result shows that a strongly nucleophilic anion does not need to be involved in the proton-induced alkylidyne-isocyanide coupling step.

(12) For isocyanide alkyl migratory insertion reactions, see, for example: Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059.

(13) The proton-induced alkylidyne-isocyanide coupling is related to the previously demonstrated formal coupling of two alkylidyne ligands. McDermott, G. A.; Mayr, A. *J. Am. Chem. Soc.* **1987**, *109*, 580.

(14) (a) Filippou, A. C.; Grünleitner, W. *Z. Naturforsch. B* **1989**, *44*, 1023. (b) Filippou, A. C. *Polyhedron* **1990**, *9*, 727.

(15) (a) Vrtis, R. N.; Rao, C. P.; Warner, S.; Lippard, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 2699. (b) Carnahan, E. M.; Lippard, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 3220.

(16) (a) Kostić, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 489. (b) Ushio, J.; Nakatsuji, H.; Yonezawa, T. *J. Am. Chem. Soc.* **1984**, *106*, 5892. (c) Poblet, J. M.; Strich, A.; Wiest, R.; Bénard, M. *Chem. Phys. Lett.* **1986**, *126*, 169.

## Remote Oxidation of Unactivated C-H Bonds in Steroids via Oxometalloporphinates

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Nature's ability to catalyze the monooxygenation of unactivated C-H bonds in steroids employing enzymatic systems (e.g., cytochrome P-450) has long been recognized.[1] In contrast, chemist's attempts to mimic nature by replacing a hydrogen atom attached to an unactivated carbon of a steroid with a hydroxyl group, while maintaining the integrity of the carbon atom, constitute a formidable challenge.[2] Despite the fact that the use of covalently attached templates to catalyze the remote functionalization of steroids was introduced by Breslow[3] over 20 years ago, the direct remote hydroxylation of steroids with high predictability and specificity has yet to be accomplished.

We report that synthetic metalloporphyrins attached to steroidal substrates catalyze the hydroxylation of unactivated carbons with iodosylbenzene as the source of oxygen (cf. **1** → **3**).[4,5] By manipulation of the length of the tether linking the steroid to the template, the intermediate oxometalloporphinate can be directed to abstract a hydrogen atom at either the C(12), C(14), or C(17) position, thereby leading to hydroxyl incorporation at these sites.

In a preliminary study, the manganese(III) (*m*-((androstanyloxy)carbonyl)phenyl)triphenylporphyrin **1** (R = OMe)[6] was

(1) Ortiz de Montellano, P. R., Ed. *Cytochrome P-450, Structure, Mechanism and Biochemistry*; Plenum Press: New York and London, 1986. Takemori, S.; Kominami, S. *Trends Bio. Sci.* **1984**, *9*, 393.

(2) Mazur, Y. *Pure Appl. Chem.* **1975**, *51*, 145. Also see: Breslow, R.; Baldwin, S. *J. Am. Chem. Soc.* **1970**, *92*, 732. Barton, D. H. R.; Göktürk, A. K.; Morzycki, J. W.; Motherwell, W. B. *J. Chem. Soc., Perkin Trans. 1* **1985**, 853. Rozen, S.; Brand, M.; Kol, M. *J. Am. Chem. Soc.* **1989**, *111*, 8325.

(3) Breslow, R. *Acc. Chem. Res.* **1980**, *13*, 170. Breslow, R. *Chemtracts: Org. Chem.* **1988**, *1*, 333.

(4) For model systems that mimic the hydroxylation of cytochrome P-450 and related systems, see: Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032. Chang, C. K.; Kuo, M.-S. *Ibid.* **1979**, *101*, 3413. Hill, C. L.; Schardt, B. C. *Ibid.* **1980**, *102*, 6375. Groves, J. T.; Kruper, W. J., Jr.; Haushalter, R. C. *Ibid.* **1980**, *102*, 6377. Mansuy, D.; Bartoli, J. F.; Momenteau, M. *Tetrahedron Lett.* **1982**, *23*, 2781. Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 6243. Dolphin, D.; James, B. R.; Leung, T. *Inorg. Chim. Acta* **1983**, *79*, 25. Traylor, P. S.; Dolphin, D.; Traylor, T. G. *J. Chem. Soc., Chem. Commun.* **1984**, 279. Hill, C. L.; Brown, R. B., Jr. *J. Org. Chem.* **1988**, *53*, 5762. Battioni, P.; Renaud, J. P.; Bartoli, J. F.; Reina-Artiles, M.; Fort, M.; Mansuy, D. *J. Am. Chem. Soc.* **1988**, *110*, 8462.

(5) The selective C(25) hydroxylation of cholesterol has been achieved in ca. 2.0% yield (based on cholesterol) by employing a catalytic membrane-spanning manganese(III) porphyrin (Groves, J. T.; Neumann, R. *J. Org. Chem.* **1988**, *53*, 3891).

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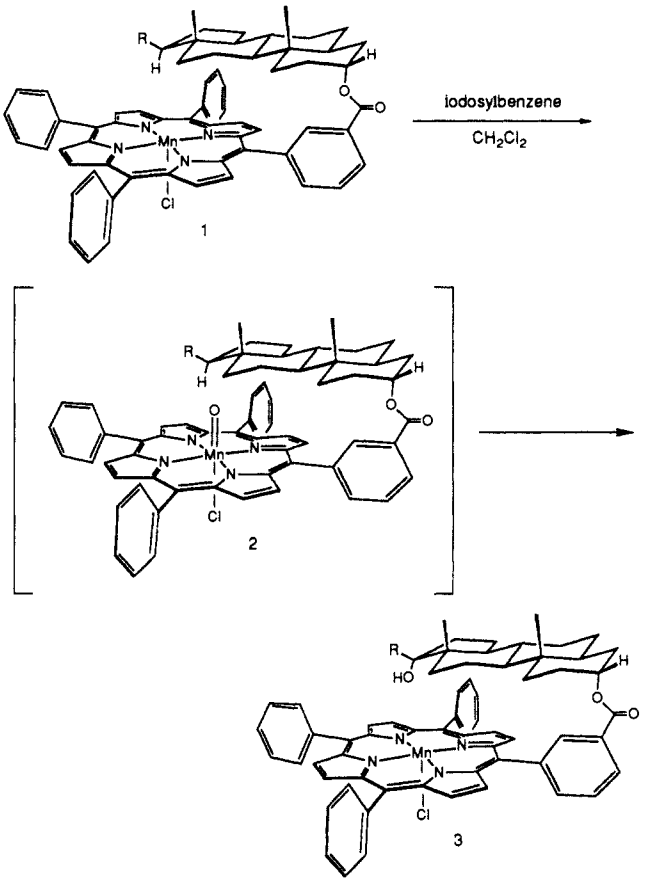
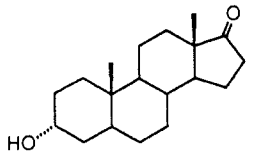



prepared in a straightforward manner from 17β-methoxy-5α-androstan-3α-ol (**4**) and subjected to oxidation with excess iodosylbenzene. A $6 \times 10^{-4}$ M solution (degassed) of **1** (R = OMe) in dry methylene chloride under argon was treated with 10.0 equiv of iodosylbenzene for 2.5 h at ambient temperature. Removal of the solvent in vacuo followed by hydrolysis (MeOH/8% aqueous KOH/THF, 4:1:1, reflux, 6 h) of the ester linkage gave rise to a 47% isolated yield (80% based on recovered **4**) of crystalline androsterone (**5**), mp 185.5–186.0 °C (lit.[7] mp 185.0–185.5 °C).



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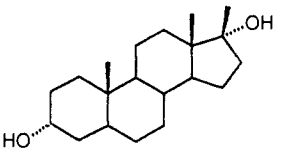
The rigid nature of the steroid framework, which is covalently linked to the reactive oxomanganese(V) species **2** (R = OMe), directs hydrogen atom abstraction exclusively from C(17). In contrast, when a solution ($6 \times 10^{-4}$ M in dry degassed methylene chloride) of the benzoate of 17β-methoxy-5α-androstan-3α-ol was exposed (14 h) to 1 equiv of (tetraphenylporphinato)manganese(III) chloride and 10.0 equiv of iodosylbenzene at ambient temperature under argon, followed by hydrolysis of the benzoate ester, there was obtained an 86% yield of recovered starting 17β-methoxy-5α-androstan-3α-ol (**4**). Androsterone could not be detected.

Attachment of the rigid metalloporphyrin fragment to 17β-methyl-5α-androstan-3α-ol (cf. **1**, R = Me) also leads directly to hydroxylation at C(17) upon exposure to iodosylbenzene. Treatment of **1** (R = Me) ($6 \times 10^{-4}$ M in methylene chloride) under argon with 10.0 equiv of iodosylbenzene for 4 h gave rise after hydrolysis to a 54% isolated yield (90% based on recovered **4**) of 17β-methyl-5α-androstane-3α,17α-diol (**6**), mp 189–189.5 °C (lit.[8] mp 188–189 °C).



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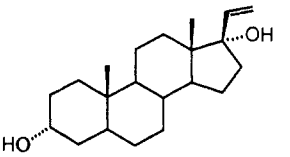

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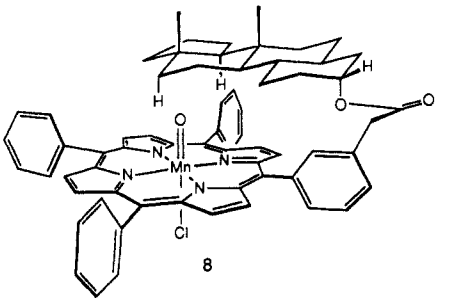
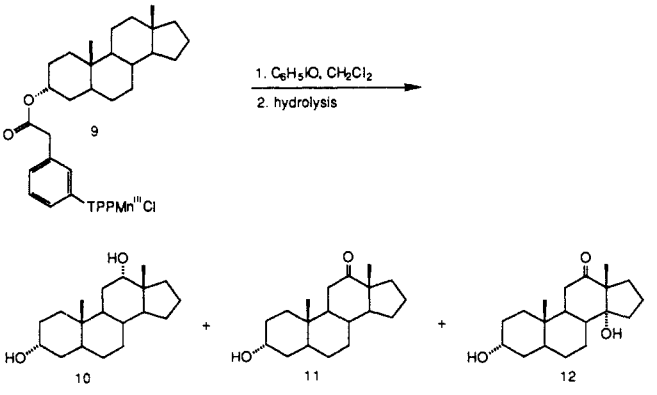
Specific functionalization at C(17) was also observed when 17β-vinyl-5α-androstan-3α-ol was attached to the metalloporphyrin fragment and subjected to oxidation. Under conditions identical with those described above for the formation of **6**, substrate **1** (R = CH=$CH_2$) afforded a 33% isolated yield (76% based on recovered starting material) of crystalline 17β-vinyl-5α-androstane-3α,17α-diol (**7**), mp 199–200 °C.[9]

The remote functionalization of steroids can be directed to both C(12) and C(14) in a single operation by employing the intermediate oxometalloporphinate **8**. The incorporation of a meth-


8

ylene group between the carbonyl group and the phenyl ring (cf. **8**) imparts substantial maneuverability to the rigid "P-450 like template" such that attachment of the porphyrin-derived reagent to the α-side of a steroid leads to hydrogen atom abstraction from both the α- and β-faces of the steroid backbone. Treatment of a $6 \times 10^{-4}$ M solution (degassed) of **9** in methylene chloride with 10.0 equiv of iodosylbenzene for 6 h and subsequent cleavage of the ester linkage under the standard conditions detailed above gave rise to a 23% yield of 5α-androstane-3α,12α-diol (**10**), mp 162–164 °C, a 47% yield of 12-oxo-5α-androstan-3α-ol (**11**), mp 176.0–176.5 °C, and a 16% yield of 12-oxo-5α-androstane-3α,14α-diol (**12**), mp 205.0–206.5 °C.[11] Compounds **11** and **12**




undoubtedly arise from **10** by β-hydrogen atom abstraction at

(6) The preparation of the required porphyrins was achieved by employing a minor modification of the procedure of Lindsey (Lindsey, J. S.; Schreiman, I. C.; Hsu, H.-C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827). Coupling of the steroid substrate and the porphyrin carboxylic acid was realized by employing 1-cyclohexyl-3-(2-morpholinoethyl)carbodiimide metho-*p*-toluenesulfonate (1.5 equiv) in methylene chloride containing DMAP (1.5 equiv). The resulting porphyrin was metalated in straightforward fashion according to the procedure of Basolo (Jones, R. D.; Summerville, D. A.; Basolo, F. *J. Am. Chem. Soc.* **1978**, *100*, 4416).

(7) Ruzicka, L. *Helv. Chim. Acta* **1934**, *17*, 1389.

(8) Templeton, J. F.; Jackson, C. C. *Steroids* **1983**, *41*, 485.

(9) Compound **7** upon reduction ($H_2$, Pd/C, EtOH) gave rise to the known 17β-ethyl-5α-androstane-3α,17α-diol, mp 196.0–197.5 °C (lit.[10] mp 197.0–197.5 °C).

(10) Ryoko, O.; Norio, K.; Itsuo, Y. *Chem. Pharm. Bull.* **1978**, *26*, 2262.

(11) The structures of **10–12** follow from transformations into known androstane derivatives.

C(12). Examination of a space-filling model of **8** reveals that the intermediate manganese(V) oxo species can readily abstract the C(12) $\alpha$- and $\beta$-hydrogens. It is of interest to note that the reagent with the shorter, more rigid tether **2** leads to hydrogen atom abstraction at the site furthest removed from the 3$\alpha$-position on the steroid. Surprisingly, the more flexible reagent **8**, which in principle can hydroxylate at C(12), C(14), and/or C(17), only induces hydrogen atom abstraction at C(12) and C(14), only a few atoms removed from the point of attachment.

In summary, intramolecular hydrogen atom abstraction via reactive oxomanganese(V) species such as **2** and **8** leads to direct hydroxylation of steroids. It should be pointed out that attempts to effect such transformation employing the corresponding iron(III) porphyrin analogues gave rise to significantly lower yields of hydroxylated steroids.[12] The major limitation of steroid hydroxylation via oxometalloporphinates, in particular with the iron(III) porphyrin, is the facile oxidative degradation of the porphyrin. Further studies are underway to (1) determine the scope of this metalloporphyrin-based oxygen transfer process for the hydroxylation of steroids and (2) design porphyrin ligands that are not prone to oxidative degradation.

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(12) Unpublished results of Dr. Randolph Belter, Indiana University.

## Base-Free Silylene Complexes $[(\eta^5\text{-}C_5Me_5)(PMe_3)_2Ru{=}Si(SR)_2]BPh_4$ (R = Et, *p*-$MeC_6H_4$)

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Transition-metal silylene complexes ($L_nM{=}SiR_2$) have attracted attention as intriguing synthetic targets for many years. This interest relates to their proposed roles in various catalytic cycles, but also derives from the rich reaction chemistry associated with closely related carbene complexes ($L_nM{=}CR_2$).[1] Recently the first well-characterized examples of silylene complexes as donor adducts ($L_nMSiR_2{\leftarrow}B$) have been reported by groups in the U.S.,[2] Germany,[3] and Japan.[4] Our route is based on electron-rich transition-metal fragments for stabilization of the silylene silicon, and removal of a group bound to silicon.[2] The complex Cp*-$(PMe_3)_2RuSiPh_2OTf$ (Cp* = $\eta^5$-$C_5Me_5$) possesses a weakly bound triflate group as characterized by its behavior in solution, the molecular structure, and a downfield $^{29}Si$ NMR shift of 112.39 ppm. The triflate group is readily displaced by acetonitrile to give $[Cp^*(PMe_3)_2RuSiPh_2(NCMe)]^+$. Dynamic NMR studies have shown that, in dichloromethane, this complex dissociates acetonitrile to produce the base-free silylene $[Cp^*(PMe_3)_2Ru{=}SiPh_2]^+$.[2b]

Calculations[5] and experimental work by Lambert and coworkers[6] indicate that thiolate groups have a stabilizing influence on silylenium ions ($SiR_3^+$). These results prompted us to investigate the use of thiolate groups in stabilizing cationic silylene complexes, which would also contain a three-coordinate silicon center. Here we report results of these studies, which have allowed isolation of the first base-free silylene complexes.

The tris(thiolato)silyl complexes **1** and **2** were prepared in good yields by an established procedure from $Cp^*(PMe_3)_2RuCH_2SiMe_3$ and the appropriate silane $HSi(SR)_3$.[2b] Starting from these new silyl complexes, triflate derivatives **3–5** have been obtained by exchange reactions with $Me_3SiOTf$ (eq 1).[7] As expected, the

$$Cp^*(PMe_3)_2RuSi(SR)_3 \xrightarrow[-Me_3SiSR]{Me_3SiOTf} Cp^*(PMe_3)_2RuSi(SR)_2OTf \xrightarrow[-Me_3SiSR]{Me_3SiOTf} Cp^*(PMe_3)_2RuSiSR(OTf)_2 \quad (1)$$

1, R = *p*-tol; 2, R = Et — 3, R = *p*-tol; 4, R = Et — 5, R = *p*-tol

X-ray crystal structures of **3** and **5** established the presence of covalent, but long, Si–O(triflate) bonds.[8] Spectroscopic data are also consistent with covalent structures in the solid state and in dichloromethane solution. The $^{29}Si$ NMR shifts for **3–5** ($\delta$ 77.14, 86.05, and 37.10, respectively) are upfield from the shift for $Cp^*(PMe_3)_2RuSiPh_2OTf$, but are not unusual.[1] For **3**, infrared $\nu(SO_3)$ vibrational modes for covalently bound triflate were observed for the solid state (1367 $cm^{-1}$, Nujol mull) and in dichloromethane solution (1362 $cm^{-1}$).[9]

As for $Cp^*(PMe_3)_2RuSiPh_2OTf$, the triflate groups of **3** and **4** are chemically labile. In acetonitrile solution, triflate is displaced to produce $[Cp^*(PMe_3)_2RuSi(SR)_2NCMe]^+OTf^-$ complexes, as indicated by $\nu(SO_3)$ infrared bands that reveal the presence of only ionic triflate (**3**, 1269 $cm^{-1}$; **4**, 1268 $cm^{-1}$). For **4**, the inequivalent methylene protons of the SEt groups exchange rapidly, appearing as a single resonance (q, $\delta$ 2.88) in dichloromethane-$d_2$ down to −70 °C. In the less polar solvent toluene-$d_8$, the process that exchanges these protons is slowed considerably, resulting in an observed coalescence temperature of 21 °C ($\Delta G^*_{294K}$ = 14.9 ± 0.3 kcal $mol^{-1}$). These results are most consistent with an exchange mechanism consisting of dissociation of triflate anion to form $Cp^*(PMe_3)_2Ru{=}Si(SEt)_2^+$, and return of triflate anion to the opposite face of the silylene ligand.[10] Since it then appeared that the base-free silylene complexes $[Cp^*(PMe_3)_2Ru{=}Si(SR)_2]BPh_4$ (**6**, R = *p*-tol; **7**, R = Et) might be reasonably stable, attempts were made to isolate them.

Compounds **3** and **4** react with $NaBPh_4$ in dichloromethane to produce a precipitate of NaOTf. Workup of the solution and crystallization from dichloromethane–diethyl ether allow isolation of compounds **6** and **7** (eq 2). Elemental analyses and NMR

$$Cp^*(PMe_3)_2RuSi(SR)_2OTf \xrightarrow[-NaOTf]{+NaBPh_4} \left[Cp^*(PMe_3)_2Ru{=}Si\begin{matrix}SR\\SR\end{matrix}\right]^+ BPh_4 \quad (2)$$

6, R = *p*-tol; 7, R = Et

spectra show that these yellow, crystalline materials do not contain solvent. Correlations between $^{13}C$ and $^{29}Si$ NMR shift data[11] suggest that a silylene complex would exhibit a low-field $^{29}Si$ NMR shift, since $^{13}C$ NMR shifts for terminal carbene ligands are generally in the range 240–370 ppm.[12] For example, the $^{13}C$

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(1) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24, p 1415 and references therein.

(2) (a) Straus, D. A.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 5872. (b) Straus, D. A.; Zhang, C.; Quimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673.

(3) (a) Zybill, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 669. (b) Zybill, C.; Wilkinson, D. L.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 583. (c) Zybill, C.; Müller, G. *Organometallics* **1988**, *7*, 1368. (d) Zybill, C.; Wilkinson, D. L.; Leis, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 203.

(4) (a) Ueno, K.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1988**, *110*, 4092. (b) Tobita, H.; Ueno, K.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 3415.

(5) Apeloig, Y.; Godleski, S. A.; Heacock, D. J.; McKelvey, J. M. *Tetrahedron Lett.* **1981**, *22*, 3297.

(6) Lambert, J. B.; Schulz, W. J., Jr.; McConnell, J. A.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 2201.

(7) Full characterization data and syntheses for new compounds are provided in the supplementary material.

(8) Grumbine, S. D.; Straus, D. A.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L., manuscript in preparation.

(9) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

(10) A similar process has been identified for $Cp(NO)(Ph_3P)$-$ReGePh_2OTf$: Lee, K. E.; Gladysz, J. A. *Polyhedron* **1988**, *7*, 2209.

(11) Olah, G. A.; Field, L. D. *Organometallics* **1982**, *1*, 1485.

0002-7863/90/1512-7801$02.50/0 