

Inefficient kinetic competition between carbon–carbon bond cleavage (k_{cc}) and nonradiative decay (k_{nr}) accounts for the relatively low quantum yields observed for the photochemical degradation process. The next step involves loss of acetone and bimolecular electron transfer to a second Co(III) complex by **9**, which produces 1 equiv of **2** and Co(II), and **10**. Formation of **11** could occur via a migratory insertion reaction in which the amide nitrogen attacks the isocyanate carbon followed by loss of Co(II). Finally, solvolysis of **11** generates products **3** and **4**.²⁶

The unique aspect of the photochemical reaction of **1** is clearly the migratory insertion reaction that leads to cyclic urea **3**. The following line of reasoning leads to the notion that the cyclization occurs within the metal complex. If the ligand becomes uncoordinated before cyclization, the amide nitrogen would become protonated under the pH conditions present in solution.²³ A protonated amide nitrogen is a very poor nucleophile and would not be competitive with the solvent for nucleophilic attack at the isocyanate carbon. Under these conditions, solvolysis of the isocyanate group would lead to formation of product **8**—however, this product is not observed in the reaction mixture.

As noted above, the cyclization reaction leading to formation of cyclic urea **3** bears a remarkable similarity to the reaction leading to hydantoin formation in the Cu(III)–peptide complexes. In addition, several studies reveal that ureas are typically formed in bimolecular reactions between metal-coordinated amides and isocyanates.²⁸ Apparently the similar course of the reactions for the Co(III) complex **1** and the Cu(III)–peptide complexes is due to the fact that in each case LMCT excitation leads to intraligand carbon–carbon bond cleavage and formation of an isocyanate functional group.

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- (26) Solvolysis of imide **11** may be slow at neutral pH (see ref 27); however, HPLC analysis shows unequivocally that **1** is decomposed stoichiometrically to 50% **2** and 50% **3** and that **11** is not observed. We are forced to conclude that, under the conditions of the photolysis, **11** is unstable. The decomposition of **11** may be catalyzed by Co(II).
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Structure and Reactivity of a (Triphenylsilyl)rhodium(I) Compound

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Interest in transition-metal catalysis of hydrosilylation¹ and silane oligomerization² has prompted structural studies of many silyl–transition-metal compounds,^{3a} but only one structurally charac-

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- (2) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059–4066.

Scheme I

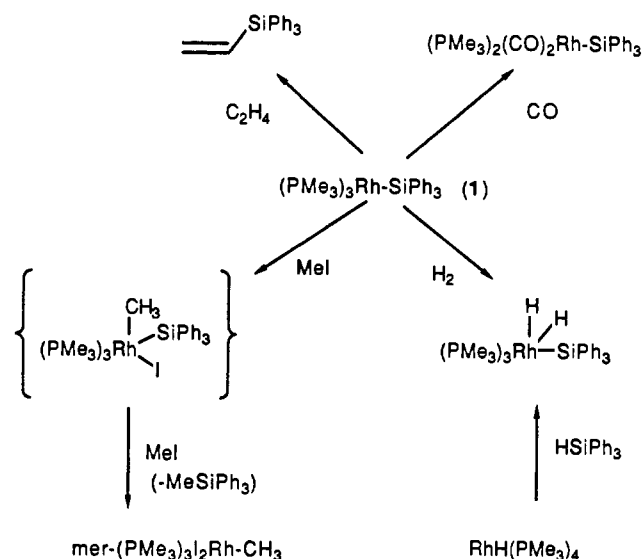
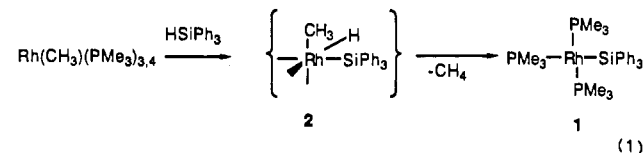


Table I. Selected Interatomic Distances (Å)

Rh(1)–P(1)	2.266 (1)	P(2)–C(5)	1.834 (3)
Rh(1)–P(2)	2.332 (1)	P(2)–C(6)	1.828 (3)
Rh(1)–P(3)	2.271 (1)	P(3)–C(7)	1.822 (3)
Rh(1)–Si(1)	2.317 (1)	P(3)–C(8)	1.831 (3)
P(1)–C(1)	1.823 (3)	P(3)–C(9)	1.820 (3)
P(1)–C(2)	1.828 (3)	Si(1)–C(11)	1.920 (2)
P(1)–C(3)	1.833 (3)	Si(1)–C(21)	1.917 (2)
P(2)–C(4)	1.827 (3)	Si(1)–C(31)	1.913 (2)

terized nonbridging rhodium(I)–silyl compound has been reported.^{3b} The authors of this report note the paucity of Rh(I)–Si structural studies; thus, when we had occasion to prepare the Rh–Si compound (triphenylsilyl)tris(trimethylphosphine)rhodium(I) (**1**), we thought it useful to determine its structure by X-ray diffraction.

Compound **1** is obtained in good yield from the methane elimination reaction of eq 1.⁴ The reaction is complete within



minutes at room temperature. The probable intermediate, the hydrido(methyl)(triphenylsilyl)rhodium(III) compound **2**, has not been observed, but we have characterized the iridium analogue of this putative intermediate (compound **2-Ir**) from the related reaction of $\text{IrMe}(\text{PMe}_3)_4$ with triphenylsilane. Thus compound **2**, assuming it is indeed an intermediate in the synthesis of **1**, must eliminate methane (forming the $\text{H}_3\text{C-H}$ bond) much more rapidly than it eliminates methyltriphenylsilane (forming the $\text{H}_3\text{C-SiPh}_3$ bond). (An interesting contrast is provided by the triethylsilyl analogue of intermediate compound **2**, which eliminates methyltriethylsilane at a rate comparable to that of methane elim-

- (3) (a) See: Mackay, K. M.; Micholson, B. K. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 6, Chapter 43, pp 1043–1114. See also, for example: Wang, W.-D.; Hommeltoft, S. I.; Eisenberg, R. *Organometallics* **1988**, *7*, 2417–2419. (b) Joslin, F. L.; Stobart, S. R. *J. Chem. Soc., Chem. Commun.* **1989**, 504–505. The same compound has been reported in a different space group: Oswald, A. A.; Hendriksen, D. E.; Ansell, G. B.; Zentz, S. Program and Abstracts, Combined Meeting of the 32nd Annual Denver X-ray Conference and American Crystallographic Society, Snowmass, CO, Summer 1983; p 47.
- (4) Other examples of methane elimination from $\text{MeRh}(\text{PMe}_3)_3$ and reactive-hydrogen compounds have been described: Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *J. Am. Chem. Soc.* **1987**, *109*, 6563–6565. In addition, see: Schubert, U.; Müller, C. *J. Organomet. Chem.* **1989**, *373*, 165–172. Schubert, U.; Müller, J. *J. Organomet. Chem.* **1988**, *340*, 101–109.

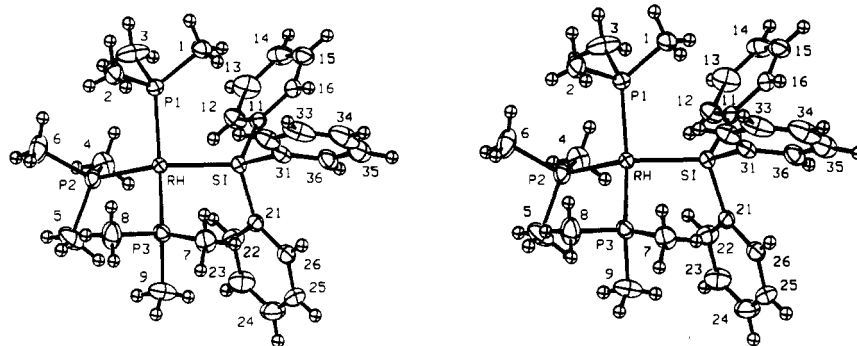


Figure 1. Stereopair drawing of (triphenylsilyl)tris(trimethylphosphine)rhodium(I) (**1**). Thermal ellipsoids are drawn at the 50% probability level.

Table II. Selected Intramolecular Bond Angles (deg)

P(1)–Rh(1)–P(2)	96.18 (3)	C(1)–P(1)–C(2)	99.1 (2)
P(1)–Rh(1)–P(3)	148.21 (3)	C(1)–P(1)–C(3)	98.2 (2)
P(2)–Rh(1)–P(3)	98.70 (3)	C(2)–P(1)–C(3)	101.0 (2)
P(1)–Rh(1)–Si(1)	93.10 (3)	C(4)–P(2)–C(5)	97.8 (2)
P(2)–Rh(1)–Si(1)	143.24 (3)	C(4)–P(2)–C(6)	101.4 (2)
P(3)–Rh(1)–Si(1)	91.56 (2)	C(5)–P(2)–C(6)	99.3 (2)
Rh(1)–P(1)–C(1)	124.4 (1)	C(7)–P(3)–C(8)	98.9 (2)
Rh(1)–P(1)–C(2)	105.4 (1)	C(7)–P(3)–C(9)	98.3 (2)
Rh(1)–P(1)–C(3)	124.0 (1)	C(8)–P(3)–C(9)	102.3 (2)
Rh(1)–P(2)–C(4)	107.5 (1)	Rh(1)–Si(1)–C(11)	110.87 (7)
Rh(1)–P(2)–C(5)	120.9 (1)	Rh(1)–Si(1)–C(21)	106.18 (7)
Rh(1)–P(2)–C(6)	125.3 (1)	Rh(1)–Si(1)–C(31)	126.23 (8)
Rh(1)–P(3)–C(7)	119.6 (1)	C(11)–Si(1)–C(21)	103.1 (1)
Rh(1)–P(3)–C(8)	108.0 (1)	C(11)–Si(1)–C(31)	103.0 (1)
Rh(1)–P(3)–C(9)	125.6 (1)	C(21)–Si(1)–C(31)	105.2 (1)

ination.) Formation of a carbon–triphenylsilyl bond does occur at an appreciable rate, however, in the reaction of **1** with excess methyl iodide to form methyltriphenylsilane and diiodo(methyl)tris(trimethylphosphine)rhodium(III) (Scheme I).

Carbon–silicon bond formation also occurs readily when solutions of compound **1** are exposed to ethylene (Scheme I), forming triphenylvinylsilane in >80% yield. This is ostensibly an example of “olefin insertion” into a metal–silicon bond, a known reaction but one not usually considered important in hydrosilation systems.^{1,5} The rhodium compounds resulting from the reaction of compound **1** with ethylene have not been identified, but they do efficiently catalyze the reaction of ethylene with excess triphenylsilane. The major organic products of the catalytic reaction are triphenylvinylsilane,⁶ triphenylethylsilane, and ethane; $\text{H}_2\text{Rh}(\text{SiPh}_3)(\text{PMe}_3)_3$ is the major Rh-containing component that we have identified. Additional reactions undergone by compound **1** are outlined in Scheme I. Under comparable conditions compound **1** does not react detectably with free triphenylsilane or triethylsilane but does partially undergo silyl exchange with diphenylmethylsilane.

The molecular structure of compound **1** confirms the expected “square” tetracoordinate rhodium center but reveals large distortions from planarity. Angles between trans ligands are quite small compared to those of other mononuclear tetracoordinate rhodium compounds, allowing compound **1** to assume a quasi-tetrahedral structure (see Figure 1). (Interatomic distances and angles for compound **1** are reported in Tables I and II, and angles for other selected Rh(I) compounds in Table III.) In this respect, compound **1** closely resembles $[\text{Rh}(\text{PMe}_3)_4][\text{Cl}]$,^{7,8} which is not

Table III. Interligand Angles (deg) in Selected $\text{RhX}(\text{PR}_3)_3$ Compounds

X	PR ₃	X–Rh–PR ₃ (trans)	R ₃ P–Rh–PR ₃ (trans)	ref
mesityl	P(OMe) ₃	179.5	169.1	<i>a</i>
Cl	PMe ₃ , PPh ₃	175.7	165.9	<i>b</i>
mesityl	P(OMe) ₃ , PPh ₃	174.1	169.6	<i>a</i>
phenyl	PMe ₃	170.0	166.6	<i>c</i>
Cl	PMe ₃	163.2	164.0	7
PMe ₃	PMe ₃	151.5	148.3	7
SiPh ₃	PMe ₃	143.2	148.2	this work

^aDahlenberg, L.; Yardmicioglu, A.; Hoeck, N. *Inorg. Chim. Acta* **1984**, *89*, 213–217. ^bJones, R. A.; Mayor Real, F.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 126–131. ^cDarensbourg, D. J.; Groetsch, G.; Wiegrefe, P.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3827–3830.

surprising since the triphenylsilyl anion is isoelectronic with a phosphine ligand. This leaves unanswered the broader question of why certain mononuclear four-coordinate rhodium compounds, or second- or third-row d⁸ compounds in general, are essentially planar while others are not. “Steric crowding” has been invoked.⁷ But, there are at least two instances where reports of near-tetrahedral second- or third-row d⁸ compounds⁹ are suspect, one as the result of an incorrect determination^{10a} and the other an unverifiable isomorph.^{10b}

As mentioned above, compound **1** is only the second compound to be structurally characterized that contains silicon bonded to univalent rhodium; it is the first that has four-coordinate rhodium and an unconstrained Rh–Si entity. Thus the Rh(I)–Si bond length of 2.317 (1) Å in compound **1** should not be expected to compare well with the value 2.379 (5) Å for the constrained, pentacoordinate Rh–Si bond in the earlier report.^{3b} As would be expected if the compound were fully tetrahedral at Rh, the phenyl groups and phosphine ligands assume a “staggered” conformation about the Si–Rh bond (see Figure 1).

While facile ethylene insertion into metal–silicon bonds is known⁵ and vinylsilanes can be formed in hydrosilation reactions catalyzed by compounds of several metals, including rhodium,⁶ we are not aware that ethylene insertion into Rh(I)–Si bonds has been mentioned previously. Such reactions may be general or perhaps compound **1** is unique in this respect owing to reactivity associated with its “quasitetrahedral” structure.^{11,12}

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- (6) Other examples of vinylsilanes resulting from rhodium catalysis of silanes + ethylene are known. See, for example: Ruiz, J.; Bentz, P. O.; Spencer, C. M.; Taylor, B. F.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1987**, 2709–2713. Kanner, B.; Herdle, W. B.; Quirk, J. M. In *Silicon Chemistry*; Corey, E. R., Corey, J. Y., Gaspar, P. P., Eds.; Ellis Horwood, Ltd. and J. Wiley and Sons: Chichester, U.K. and New York, 1989; pp 123–132 (published for IUPAC).

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- (11) Nonplanar four-coordinate d⁸ compounds are isolobal with methylene and may share similar reactivity trends. See, e.g.: Silvestre, J.; Calhorda, M. J.; Hoffmann, R.; Stoutland, P. O.; Bergman, R. G. *Organometallics* **1986**, *5*, 1841–1851 and references therein.

Table IV. IR and NMR Data

compd	IR ^a	NMR ^b		
		P(CH ₃) ₃	Ph-Si	other
(PMe ₃) ₃ Rh(SiPh ₃) (1)		0.88 (s)	7.1 (m), 7.21 (t, 7), 8.12 (d, 7)	
(PMe ₃) ₂ H ₂ Rh(SiPh ₃)	1958 (br)	0.78 (d, 6.0), 1.13 (d, 6.0)	7.1 (m), 7.23 (t, 7), 8.01 (d, 7)	Rh-H, -10.1 (d, 117, of pseudo t, 16)
(PMe ₃) ₃ (CH ₃)(H)(SiPh ₃)Ir (2-Ir)		0.69 (d, 7.0), 1.08 (d, 7.5), 1.15 (d, 7.0)	7.1 (m), 7.24 (t, 7), 8.10 (d, 7)	Ir-H -11.8 (d, 123, of t, 14.5), Ir-CH ₃ 0.14 (ddd, 12.7, 9.4, 3.6)
(PMe ₃) ₂ (CO) ₂ Rh(SiPh ₃)	1980 (s), 1930 (vs) ^c	0.86 (t, 3.5)	7.1 (m), 7.2 (m), 7.9 (m)	
(PMe ₃) ₃ I ₂ Rh(CH ₃) ^d		1.57 (d, 9.6), 1.85 (t, 3.4)		Rh-CH ₃ 1.00 (q, 5.0, of d, 2.0)
CH ₃ SiPh ₃			7.1 (m), 7.5 (m)	0.69 (s)
CH ₃ CH ₂ SiPh ₃			7.1 (m), 7.5 (m)	1.08 (pseudo t, 8), 1.24 (pseudo q, 8)
CH ₂ =CHSiPh ₃			7.1 (m), 7.6 (m)	5.77 (dd, 20.2, 3.7), 6.11 (dd, 14.5, 3.7), 6.60 (dd, 20.2, 14.5)

^aNujol mull. Frequencies in cm⁻¹. ^bC₆D₆ solutions unless otherwise noted. Chemical shifts in ppm downfield from external Me₄Si; coupling constants in Hz given in parentheses. ^cTransparent; 1480–1900 cm⁻¹. ^dTetrahydrofuran-d₆ solution.

Table V. Crystallographic Data for Rh(SiPh₃)(PMe₃)₃ (1)

formula C ₂₇ H ₄₂ P ₃ RhSi	space group P2 ₁ /n (no. 14)
fw 590.55	T = -70 °C
a = 9.433 (3) Å	λ = 0.710 69 Å (MoKα)
b = 17.692 (2) Å	ρ _{calcd} = 1.337 g cm ⁻³
c = 17.673 (5) Å	μ = 7.87 cm ⁻¹
β = 96.03 (1)°	transm coeff = 0.70–0.75
V = 2933.1 Å ³	R(F _o) = 0.027
Z = 4	R _w (F _o) = 0.027

Experimental Section

All reagents and compounds are air-sensitive, and manipulations were carried out at room temperature under an inert atmosphere (typically in a nitrogen-filled drybox) and with the use of dried, degassed solvents. RhMe(PMe₃)_x (x = 3, 4)^{7,13} and IrMe(PMe₃)₄¹³ were prepared as previously described; other reagents were obtained commercially. C, H analyses were performed by Galbraith Laboratories. ¹H NMR spectra of all compounds were recorded at ambient probe temperature by using GE QE-300 spectrometers. These data are presented in Table IV together with selected IR data.

(Triphenylsilyl)tris(trimethylphosphine)rhodium(I) (1). A toluene solution (15 mL) containing 0.84 g of RhMe(PMe₃)_x was treated with 0.52 g of HSiPh₃. The solution immediately turned red; after being stirred 1 h at room temperature, the solution was concentrated to 2 mL, pentane (15 mL) was added, and a red microcrystalline precipitate formed; this was isolated after 30 min; yield 0.79 g (67%). Anal. Calcd for C₂₇H₄₂P₃RhSi: C, 54.92; H, 7.17. Found: C, 54.94; H, 7.21. In a separate experiment, RhMe(PMe₃)_x (0.042 g) and HSiPh₃ (0.026 g) were combined in 1 mL of deuteriobenzene, and the formation of compound 1 and methane was confirmed by NMR spectroscopy. Irregular blocks of crystalline compound 1 grew from the solution after 1 day at room temperature.

Reactions of compound 1 with carbon monoxide or dihydrogen were observed by bubbling the respective gas through deuteriobenzene solutions of compound 1; in each case the red color bleached rapidly and the respective product was detected in >80% yield by ¹H NMR spectroscopy (see Scheme 1 and Table IV). Analytically pure compounds were obtained by recrystallization from benzene/hexane. Anal. Calcd for H₂Rh(SiPh₃)(PMe₃)₃: C, 54.73; H, 7.48. Found: C, 54.69; H, 7.47. Calcd for Rh(CO)₂(SiPh₃)(PMe₃)₂: C, 54.74; H, 5.83. Found: C, 54.75; H, 5.89. In the reaction of compound 1 with ethylene, an uncharacterized mixture of rhodium compounds was formed, and only vinyltriphenylsilane could be identified among the products. Stirring an ether suspension of compound 1 with 2 equiv of methyl iodide for several hours resulted in its conversion to (PMe₃)₃I₂Rh(CH₃). Anal. Calcd for C₁₀H₃₀I₂P₃Rh: C, 20.02; H, 5.04. Found: C, 19.87, 20.26; H, 5.11, 5.03.

X-ray Data Collection and Structure Solution. A single crystal of compound 1, obtained as above, was sealed in a capillary under N₂, mounted on a Enraf-Nonius CAD4 diffractometer, and cooled to -70 °C under a N₂ stream. Crystal and refinement data are provided in Table V. The structure was solved and refined without difficulty; all non-

Table VI. Fractional Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters

atom	x	y	z	B _{equiv} , Å ²
Rh(1)	3542.3 (2)	3534.7 (1)	2412.6 (1)	1.6 (1)
P(1)	3422.8 (7)	3909.5 (4)	3630.6 (3)	2.1 (1)
P(2)	1807.4 (7)	4364.1 (4)	1864.6 (4)	2.2 (1)
P(3)	3265.6 (7)	2595.2 (4)	1533.8 (4)	2.2 (1)
Si(1)	5980.4 (7)	3331.0 (3)	2604.5 (3)	1.7 (1)
C(1)	4707 (3)	3643 (2)	4429 (2)	3.5 (1)
C(2)	1840 (3)	3446 (2)	3927 (2)	3.4 (1)
C(3)	3122 (6)	4889 (2)	3912 (2)	4.7 (1)
C(4)	2607 (4)	5305 (2)	1865 (2)	3.3 (1)
C(5)	1188 (4)	4312 (2)	847 (2)	4.1 (1)
C(6)	109 (4)	4566 (2)	2235 (2)	4.2 (1)
C(7)	4253 (3)	1715 (2)	1703 (2)	3.2 (1)
C(8)	1453 (3)	2223 (2)	1525 (2)	3.9 (1)
C(9)	3452 (5)	2696 (2)	524 (2)	4.0 (1)
C(11)	6926 (2)	4159 (1)	3150 (1)	1.9 (1)
C(12)	6557 (3)	4901 (1)	2951 (2)	2.9 (1)
C(13)	7172 (4)	5520 (2)	3344 (2)	3.8 (1)
C(14)	8161 (3)	5408 (2)	3963 (2)	3.7 (1)
C(15)	8538 (3)	4684 (2)	4180 (2)	3.2 (1)
C(16)	7947 (3)	4070 (2)	3776 (1)	2.4 (1)
C(21)	6659 (2)	3397 (1)	1621 (1)	1.9 (1)
C(22)	6282 (3)	4023 (2)	1161 (1)	2.8 (1)
C(23)	6674 (4)	4095 (2)	426 (2)	3.6 (1)
C(24)	7439 (3)	3527 (2)	124 (2)	3.8 (1)
C(25)	7823 (3)	2901 (2)	556 (2)	3.4 (1)
C(26)	7437 (3)	2840 (2)	1294 (2)	2.6 (1)
C(31)	6910 (3)	2465 (1)	3076 (1)	2.2 (1)
C(32)	6158 (4)	1927 (2)	3447 (2)	3.1 (1)
C(33)	6847 (5)	1301 (2)	3801 (2)	4.3 (1)
C(34)	8285 (5)	1209 (2)	3796 (2)	4.9 (1)
C(35)	9063 (4)	1729 (2)	3442 (2)	4.3 (1)
C(36)	8378 (3)	2348 (2)	3087 (2)	2.9 (1)

hydrogen atoms were refined anisotropically, and their positional and equivalent isotropic thermal parameters are listed in Table VI.

Supplementary Material Available: Tables of full anisotropic thermal parameters, positional and isotropic parameters for hydrogen atoms, all interatomic distances and intramolecular angles, and a summary of crystallographic data (5 pages); a listing of F_o vs F_c (13 pages). Ordering information is given on any current masthead page.

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Epoxidation of Alkenes by Oxo(5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphyrinato)chromium(V) in Aqueous Solution

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Of continuing interest is alkene epoxidation by hypervalent metalloporphyrins.¹ We recently employed chromium(V)-oxo

- (12) It is conceivable that compound 1 reacts with ethylene such that actual insertion of ethylene into the Rh-Si bond never occurs. One possibility is oxidative addition of the vinyl C-H bond followed by reductive elimination of triphenylvinylsilane. See ref 6 and: Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732–5744 and references therein for examples of vinyl C-H oxidative addition.
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