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Silene stereochemistry. 2. Stereochemical induction in the generation of 1-methyl-1-phenyl-2-neopentylsilene. 1

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Silene Stereochemistry. 2. Stereochemical Induction in the Generation of 1-Methyl-1-phenyl-2-neopentylsilene[1]

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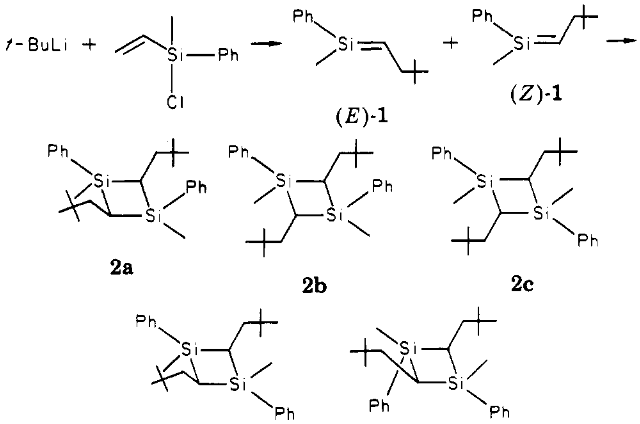
The reaction of *tert*-butyllithium with chloromethylphenylvinylsilane in hydrocarbon solvents at room temperature or below generates the *E* and *Z* isomers of 1-methyl-1-phenyl-2-neopentylsilene which can be trapped as their [4 + 2] cycloadducts by cyclopentadiene, 2,3-dimethyl-1,3-butadiene, or anthracene. A consistent ratio of 70/30 for the (*E*)-silene to (*Z*)-silene trapped by the dienes is interpreted as evidence for stereochemical induction in the silene generation reaction. Evidence is also presented which is consistent with the suggestion that the dimerization of the silenes to give 1,3-disilacyclobutanes occurs by a stepwise rather than a concerted pathway.

Introduction

The reaction of *tert*-butyllithium with vinyldimethylchlorosilane in hydrocarbon solvents at low temperatures gives rise to 1,1-dimethyl-2-neopentylsilene which dimerizes to give the typical 1,3-disilacyclobutanes.[2] Extension of this reaction to chloromethylphenylvinylsilane produces the *E* and *Z* isomers of 1-methyl-1-phenyl-2-neopentylsilene, **1**, which dimerize to give all possible stereoisomers of 1,3-dimethyl-1,3-diphenyl-2,4-dineopentyl-1,3-disilacyclobutane, **2**.[1] Silenes produced from α-lithiochlorosilanes can be trapped by conjugated dienes.[3,4] We wish to report the results for reactions of the (*E*)- and (*Z*)-silene isomers, **1**, with cyclopentadiene, 2,3-dimethyl-1,3-butadiene, and anthracene.

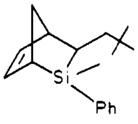


(*E*)-**1** (*Z*)-**1**

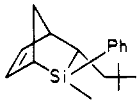
2a **2b** **2c** **2d** **2e**

Results

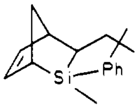
When **1** is generated by the reaction of *tert*-butyllithium with chloromethylphenylvinylsilane in hexane at low temperatures in the presence of cyclopentadiene, in addition to a 5% yield of the isomeric 1,3-disilacyclobutanes, **2**, there is obtained a 77% yield of the four isomeric [4 + 2] cycloadducts of the silene with cyclopentadiene, **3a–d**.



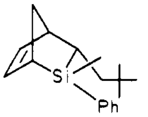
3a



3b



3c



3d

Based on the NMR spectral data given for chromatographically purified isomers given in Tables I and II, we have assigned the stereochemistry as follows: **3a**, 2-methyl-2-*endo*-phenyl-3-*exo*-neopentyl-, 24%; **3b**, 2-methyl-2-*exo*-phenyl-3-*endo*-neopentyl-, 29%; **3c**, 2-methyl-2-*exo*-phenyl-3-*exo*-neopentyl-, 13%; and **3d**, 2-methyl-2-*endo*-phenyl-3-*endo*-neopentyl-2-silabicyclo[2.2.1]-hept-5-ene, 11%.

For both compounds in which the silicon methyl group is endo, the *exo*-Ph-*endo*-nP-, **3b**, and the *exo*-Ph-*exo*-nP-norbornene, **3c** (nP = neopentyl), it is the most shielded, both in the carbon and proton spectra. The γ effect of the endo-neopentyl group[5] in the *exo*-Ph-*endo*-nP-norbornene, **3b**, adds another 2 ppm to this shielding in the carbon spectrum. Similarly the *tert*-butyl group is more shielded when it is endo, as in the *exo*-Ph-*endo*-nP-, **3b**, and the *endo*-Ph-*endo*-nP-norbornene, **3d**. The ipso carbon of the phenyl group is most shielded when it is cis to the neopentyl group, as in **3c,d**, than when it is trans, as in **3a,b**. Ring carbon 3 is most shielded when both the phenyl and neopentyl groups are exo, as in **3c**, and least shielded when the two bulky substituents are endo, as in **3d**. In the reaction mixture the ratio of the *endo*-Ph-*exo*-nP-, **3a**, and the *exo*-Ph-*endo*-nP-silanorbornene, **3b**, in which the phenyl- and neopentylsilene substituents have an *E* stereochemistry, to the *exo*-Ph-*exo*-nP- and *endo*-Ph-*endo*-nP-norbornenes, **3c**, and **d**, in which these bulky substituents have a *Z* relationship, is 69/31.

If 2,3-dimethyl-1,3-butadiene is used as the silene trap, three silene products in addition to a 2% yield of the dimers are obtained: (*E*)-1-phenyl-6-neopentyl-1,3,4-trimethylsilacyclohex-3-ene, (*E*)-**4**, 44%; the *Z* isomer, (*Z*)-**4**, 17%; and the product of the intermolecular "ene" reaction between **1** and 2,3-dimethyl-1,3-butadiene,[3,4] **5**, 20%. The stereochemistry of isomers (*E*)-**4** and (*Z*)-**4** were again assigned on the basis of their carbon-13 NMR spectra. The chemical shifts and assignments are illustrated in Figure 1. As we have observed previously,[1] the silicon methyl carbon is shielded by an additional 2–3 ppm when it is cis

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[1] Paper 1 in this series: Jones, P. R.; Lee, M. E. *J. Organomet. Chem.* **1982**, *232*, 33–39.

[2] Jones, P. R.; Lim, T. F. O. *J. Am. Chem. Soc.* **1977**, *99*, 2013–15, 8447–51.

[3] Jones, P. R.; Lim, T. F. O.; Priece, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 4970–3.

[4] Wiberg, N.; Preiner, G.; Schieda, O. *Chem. Ber.* **1981**, *114*, 3518–32.

[5] Wehrly, F. W.; Wirthlin, T. "Interpretation of ^{13}C-NMR Spectra"; Heyden & Son, Ltd.: London, 1976; pp 37–39.

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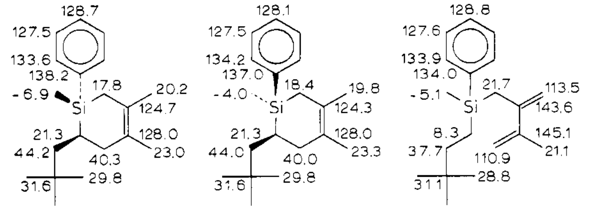
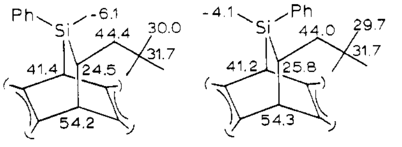


4a 4b 5

Figure 1. ^{13}C Chemical shifts for the products of the (*E*)- and (*Z*)-silene, **1**, with 2,3-dimethyl-1,3-butadiene.



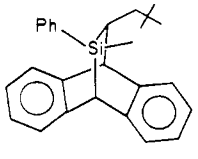
6a 6b

Figure 2. ^{13}C Chemical shifts for the *E*, (*E*)-**6**, and *Z*, (*Z*)-**6**, isomers of 2-methyl-2-phenyl-3-neopentyl-5.6:7.8-dibenzo-2-silabicyclo[2.2.2]octane. The aryl carbons which appeared in the region 125–140 ppm are omitted for clarity.

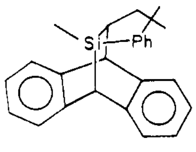
to the neopentyl group, (*E*)-**4**, than when it is trans, (*Z*)-**4**. The shielding is also apparent in the chemical shifts for the silicon methyl protons. The ipso carbons of the phenyl groups show a similar, although smaller effect, being more shielded in (*Z*)-**4** than in (*E*)-**4**.

The ratio of the *E* isomer, (*E*)-**4**, to the *Z* isomer, (*Z*)-**4**, obtained in the reaction is 72/28.

Trapping reactions of **1** with anthracene were carried out at room temperature by using benzene as the solvent due to the low solubility of anthracene in hexane. From the reaction we obtained the [4 + 2] cycloadducts of the (*E*)- and (*Z*)-silene, **1**, (*E*)-**6** and (*Z*)-**6**, in 55% and 22% yields, respectively, along with a 5% yield of dimers. The stereochemical assignments were again based primarily on the carbon-13 chemical shifts for (*E*)-**6** and (*Z*)-**6**, which are given in Figure 2. Again, as with the other dienes, the ratio of *E* to *Z* cycloadduct, (*E*)-**6**/(*Z*)-**6** is 71/29.



6a



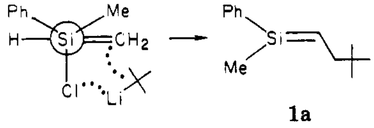
6b

In each of the three trapping reactions small amounts of the silene dimers, **2**, were obtained in similar stereochemical distributions. These are given in Table III.

Discussion

The results indicate that the silene **1** can be efficiently trapped as its [4 + 2] cycloadducts by conjugated dienes. Most striking is the consistent 70/30 ratio of *E* to *Z* cycloadducts which is obtained with each diene. If the reaction of *tert*-butyllithium with chloromethylphenylvinylsilane generated equal amounts of the (*E*)- and (*Z*)-silene, **1**, this ratio would indicate that the (*E*)-silene undergoes [4 + 2] cycloaddition reactions 2.3 times faster than does the (*Z*)-silene. This rate difference would correspond to a remarkably consistent difference in the activation energies for the cycloadditions of the (*Z*)- and (*E*)-silene isomers, *independent* of diene! In a [4 + 2] cycloaddition reaction which, at least for systems to which symmetry considerations apply, is both thermally allowed and concerted,[6,7] this situation seems highly unlikely.

It seems much more likely that the 70/30 ratio of cycloadducts observed in these reactions represents the ratio of (*E*)- to (*Z*)-silene which are formed. This conclusion carries with it the implication that silenes are configurationally stable under our reaction conditions. Brook and co-workers have observed that the two silicons in the trimethylsilyl groups of several 1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-substituted silenes are magnetically nonequivalent at temperatures up to 60 °C, indicating that these silenes are configurationally stable up to (at least) that temperature.[8] It is thus certainly reasonable to expect the (*E*)- and (*Z*)-silenes, **1**, to be configurationally stable at room temperature and below. Therefore it appears that, in the reaction of *tert*-butyllithium with chloromethylphenylvinylsilane which leads to the silene, **1**, stereochemical induction occurs which favors the formation of the *E* isomer. This induction can be rationalized in terms of the mechanism of silene formation. The initial interaction between the lithium reagent and the vinylsilane almost certainly involves some sort of association between the two species.[3,9] A greatly simplified construct for a complex, **7**, in the conformation which would tend to minimize the steric interaction between the phenyl group on silicon and the very bulky alkyllithium aggregate can be drawn. Such a complex could eliminate LiCl leading directly to the (*E*)-silene.



7 **1a**

If we are correct in considering the ratio of (*E*)-silene to (*Z*)-silene in these reactions to be 70/30, then the stereochemical distribution of the dimers **2**, given in Table III, provides some information as to the pathway leading to them. For purposes of comparison we have included in Table III the predicted distribution of dimers for the 70/30 mixture of (*E*/*Z*)-silene reacting in a statistical fashion by either a concerted (perhaps dipolar) [2s + 2s] or a [2s + 2a] pathway. Neither distribution corresponds very well with the experimental results obtained either with or without dienes present. One might argue that the activation energies for concerted pathways leading to the various silene dimers are significantly different. However, on the basis of the reported negligible barrier to silene dimerization[10] and the fact that similar dimer distributions are obtained when the silene **1** is generated in flash vacuum thermolysis experiments at 550 °C,[11] this seems unlikely. It is more probable that, at least in our systems, the dimerization of silenes to give disilacyclobutanes is a stepwise process.

Experimental Section

Hexane was dried by distillation from sodium/potassium alloy prior to use. Benzene was distilled from solid potassium hydroxide. All experiments were carried out in flame-dried glassware

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[6] Woodward, R. B.; Katz, T. J. *Tetrahedron* **1959**, *5*, 70.

[7] Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie, GmbH, Weinheim/Bergstrasse, 1970.

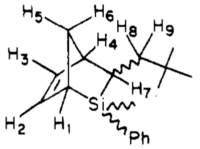
[8] Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Plavac, N. *Organometallics* **1982**, *1*, 994–8.

[9] Jones, P. R.; Cheng, A. H.-B., unpublished results.

[10] Gusel'nikov, L. E.; Konobeevski, V. M.; Vdovin, V. M.; Nametkin, N. S. *Dokl. Akad. Nauk SSSR* **1979**, *235*, 1086. Basu, S.; Davidson, I. M. T.; Laupert, R.; Potzinger, P. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 1282.

[11] Jones, P. R.; Lee, M. E., unpublished observations; 14th Central Regional Meeting of the American Chemical Society, June 16–18, 1982, Midland, MI, Abstract No. 143.

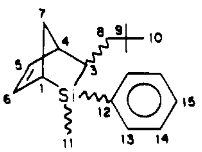
Table I. Proton NMR Data for the 2-Silanorbornenes[a]



	3a	**3b**	**3c**	**3d**
Si-Me (6 H)	−0.04 (s)	−0.26 (s), −0.07 (s)	−0.15 (s), 0.05 (s)	0.15 (s)
t-Bu (9 H)	0.45 (s)	0.41 (s)	0.52 (s)	0.39 (s)
H-8,9	1.52 (m)	0.82 (m)	*b*	*b*
H-5,6	0.95 (m)	1.20 (m)	0.75 (m)	1.40 (m)
H-4	2.25 (m)	2.35 (m)	2.25 (m)	2.47 (m)
H-1	1.88 (m)	1.70 (m)	*c*	*c*

[a] Chemical shifts in ppm relative to Me_4Si using CH_2Cl_2 as a standard. Si-Ph (5 H), 6.4–7.1 (m), H-2,3, 5.3–5.6 ppm (m). [b] 0.65–1.50 ppm (br). [c] 1.5–1.9 ppm (br).

Table II. ^{13}C NMR Data for the 2-Silanorbornenes[a]



C no.	**3a**	**3b**	**3c**	**3d**
12 (s)	136.8	138.1	134.2	132.6
11 (q)	−3.9	−6.0	−4.2	−3.2
7 (t)	43.6	44.6	42.4	48.1
4 (d)	50.3	47.6	50.4	45.4
3 (d)	22.2	23.3	20.8	28.1
1 (d)	30.8	33.4	31.7	30.1
other	*b*	*c*	*d*	*e*

[a] Chemical shifts in ppm downfield from Me_4Si using an external D_2O lock and $CDCl_3$ as the reference. Letters in parentheses indicate the multiplicity for the off-resonance proton-decoupled spectra. [b] C-15, 128.9, C-14, 127.6, C-13, 134.8, C-10, 29.6, C-9, 31.7, C-8, 45.1, and C-5 and -6, 135.0 ppm. [c] C-15, 128.8, C-14, 127.7, C-13, 134.0, C-10, 29.9, C-9, 31.5, C-8, 44.6, and C-5 and -6, 132.5 and 134.5 ppm. [d] C-15, 128.8, C-14, 127.4, C-13, 134.4, C-10, 29.9, C-9, 31.5, C-8, 44.6 ppm, and C-5 and -6, not detected. [e] C-15, 127.8, C-14, 127.3, C-13, 134.4, C-10, 29.9, C-9, 31.6, C-8, 44.3 ppm, and C-5 and -6, not detected.

Table III. Dimer Stereochemistry in the Trapping Reactions

trap	**2a**	**2b**	**2c**	**2d**	**2e**
none[1]	8.6	22.6	29.9	23.1	15.8
cyclopentadiene	12.0	23.9	25.9	24.6	13.6
2,3-dimethyl-1,3-butadiene	10.1	24.5	25.5	22.2	17.7
anthracene	8.0	22.8	24.9	24.4	19.9
average	9.7	23.4	26.6	23.6	16.7
calcd[a]					
[2s + 2s]	7.0	16.3	22.5	16.3	37.9
[2s + 2a]	18.0	23.0	18.0	23.0	18.0

[a] Calculated by assuming a 70/30 ratio of (*E*)-1 to (*Z*)-1 reacting on a statistical basis.

under an atmosphere of dry nitrogen.

Samples for characterization were purified by preparative GLC using a Varian series 1600 gas chromatograph equipped with thermal conductivity detection and a 20 ft by 0.375 in stainless steel column packed with 15% OV-17 on 60–80 mesh Supelcoport. Yields were determined by quantitative GLC analysis using *n*-decane as the internal standard with a Perkin-Elmer Sigma 3 gas chromatograph equipped with flame ionization detection, a 25-m SE-54 capillary column, and a Hewlett Packard 3300A reporting integrator. In this section compounds are reported in the order that they elute under these chromatographic conditions.

Proton and carbon NMR spectra were obtained on neat samples in capillary tubes using Hitachi Perkin-Elmer R24B 60-MHz or JEOL FX-90Q 90-MHz spectrometers. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Mass spectra were obtained by using a Finnegan automated 9500 GC/MS system. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, or Midwest Microlabs, Indianapolis, IN.

Trapping Experiments with Cyclopentadiene. To a solution of 7.5 mL (40 mmol) of chloromethylphenylvinylsilane (Petrarch), 6 mL (60 mmol) of cyclopentadiene, and 180 mL of dry hexane cooled to −78 °C was slowly added 23 mL (40 mmol) of a solution of *tert*-butyllithium (1.8 M in pentane, Aldrich). The mixture was allowed to warm slowly to room temperature and stirred overnight. The white precipitate which had formed dissolved when the reaction was hydrolyzed with 40 mL of a saturated ammonium chloride solution. The organic layer was separated and combined with two hexane extractions of the aqueous layer. The resulting solution was dried with anhydrous sodium sulfate and concentrated by using a rotary evaporator. GLC analysis of the mixture gave in order of elution *endo*-Ph-*exo*-nP-, **3a**, *exo*-Ph-*exo*-nP-, **3c**, *endo*-Ph-*endo*-nP- **3d**, and *exo*-Ph-*endo*-nP-silanorbornene, **3b**, in 24, 13, 11, and 29% yields, respectively, and a 5% yield of a mixture of the dimer isomers, **2**. The mixture of silanorbornenes, **3**, could be distilled as a colorless viscous oil, bp 88–93 °C at 0.25 torr. The compounds, when purified by preparative GLC for characterization, were colorless oils.

Proton and carbon NMR data for the isomers of **3** are given in Tables I and II. The characterization of the dimers, **2**, has been reported.[1]

The mass spectra for all four of the silanorbornene isomers, **3**, were very similar: *m*/*e* (relative intensity) 270 (P (3)), 213 (p − *t*-Bu (5)), 204 ($[PhMeSi{=}CH(t\text{-}Bu)]^+$ (7)), 148 ($[PhMeSi{=}CCH_3]^+$ (17)), 147 ($[PhMeSi{=}CCH_2]^+$ (100)), 121 ($[PhMeSiH]^+$ (53)), 105 (18). Anal. Calcd for $C_{18}H_{26}Si$: C, 79.92; H, 9.69. Found for a mixture of the silanorbornene isomers, **3**: C, 79.89; H, 9.78.

Trapping Reaction Using 2,3-Dimethyl-1,3-butadiene. To a solution of 4.5 mL (20 mmol) of chloromethylphenylvinylsilane and 3 mL (30 mmol) of 2,3-dimethyl-1,3-butadiene (Aldrich) in 100 mL of dry hexane cooled to −78 °C was added slowly 12 mL (20 mmol) of a solution of *tert*-butyllithium in pentane. Workup as described above was followed by GLC analysis which gave **5**, (*Z*)-**4**, (*E*)-**4**, and **2** in 20, 17, 44, and 2% yields, respectively. The reaction products of the silene with dimethylbutadiene, **5**, (*Z*)-**4**, and (*E*)-**4**, could be distilled at ca. 75–80 °C at 0.003 torr. The compounds were isolated by preparative GLC as colorless liquids.

The carbon NMR data for (*E*)-**4** and (*Z*)-**4** and **5** are given in Figure 1. Proton NMR: (*E*)-**4**, δ 0.11 (s, 3 H), 0.65 (s, 9 H), 0.60–1.05 (m, 3 H), 1.25 (m, 2 H), 1.52 (s, 6 H), 1.55–2.15 (m, 2 H), 6.60–7.20 (m, 5 H); (*Z*)-**4**, δ 0.21 (s, 3 H), 0.65 (s, 9 H), 0.60–1.05 (m, 3 H), 1.25 (m, 2 H), 1.50 (s, 6 H), 1.55–2.15 (m, 2 H), 6.60–7.20 (m, 5 H); **5**, δ 0.40 (s, 3 H), 0.49 (m, 2 H), 0.97 (s, 9 H), 1.14 (m, 2 H), 1.95 (s, 3 H), 2.00 (m, 2 H), 4.65–4.91 (m, 2 H), 4.85–5.00 (m, 2 H), 7.01–7.50 (m, 5 H). Mass spectrum (*E*)-**4** and (*Z*)-**4**, *m*/*e* (relative intensity) 286 (P (15)), 229 (P − *t*-Bu (9)), 151 (17), 148 (10), 147 ($[PhMeSi{=}CCH_2]^+$ (61)), 135 (15), 121 ($[PhMeSiH]^+$ (100)), 107 (19), 105 (35), 67 (19), 57 (48); **5**, 286 P (6), 135 (13), 127 (11), 123 (15), 121 (100), 57 (14), 43 (15). Anal. Calcd for $C_{19}H_{30}Si$: C, 79.64; H, 10.55. Found for a mixture of the silacyclohexene isomers: C, 79.85; H, 10.67. Found for the intermolecular ene product, **5**: C, 79.45; H, 10.55.

Trapping Reaction with Anthracene. To a mixture of 8.8 mL (50 mmol) of chloromethylphenylvinylsilane and 26.7 g (150 mmol) of anthracene in 700 mL of dry benzene at room temperature was slowly added 26.3 mL (50 mmol) of a solution of *tert*-butyllithium in pentane. The mixture was allowed to stir overnight and then subjected to the usual workup. Analysis showed the mixture of dimers, **2**, in 5% yield and (*Z*)-**6** and (*E*)-**6** in 22 and 55% yields, respectively. The anthracene adducts, after purification by preparative GLC, were obtained as pale yellow-green extremely viscous oils.

The carbon NMR for (*E*)-**6** and (*Z*)-**6** are reported in Figure 2. Proton NMR: (*E*)-**6**, 0.13 (s, 3 H), 0.91 (s, 9 H), 1.00–1.50 (br, 3 H), 3.88 (s, 1 H), 4.20–4.32 (m, 1 H), 6.60–7.40 (13 H); (*Z*)-**6**, 0.22 (s, 3 H), 0.82 (s, 9 H), 1.00–1.35 (br, 3 H), 3.90 (s, 1 H), 4.25–4.35 (m, 1 H), 6.60–7.40 (13 H). Anal. Calcd for $C_{27}H_{30}Si$: C, 84.75; H, 7.90. Found for a mixture of (*E*)-6 and (*Z*)-6: C, 84.36; H, 8.14.

Acknowledgment. We gratefully acknowledge the National Science Foundation and the North Texas State Univeristy Organized Research Fund for their support of this work. L.T.L. thanks the Robert A. Welch Foundation for a Predoctoral Fellowship.

Registry No. (*E*)-1, 85803-36-7; (*Z*)-1, 85803-37-8; **2a**, 83686-83-3; **2b**, 83709-79-9; **2c**, 83709-80-2; **2d**, 83709-81-3; **2e**, 83709-82-4; **3a**, 85803-35-6; **3b**, 85879-91-0; **3c**, 85880-58-6; **3d**, 85879-92-1; **4a**, 85803-38-9; **4b**, 85803-39-0; **5**, 85827-91-4; **6a**, 85803-40-3; **6b**, 85803-41-4.

Communications

Some Observations on the $RuCl_3/PR_3$ Catalyzed Conversion of Primary Amines to Secondary Amines

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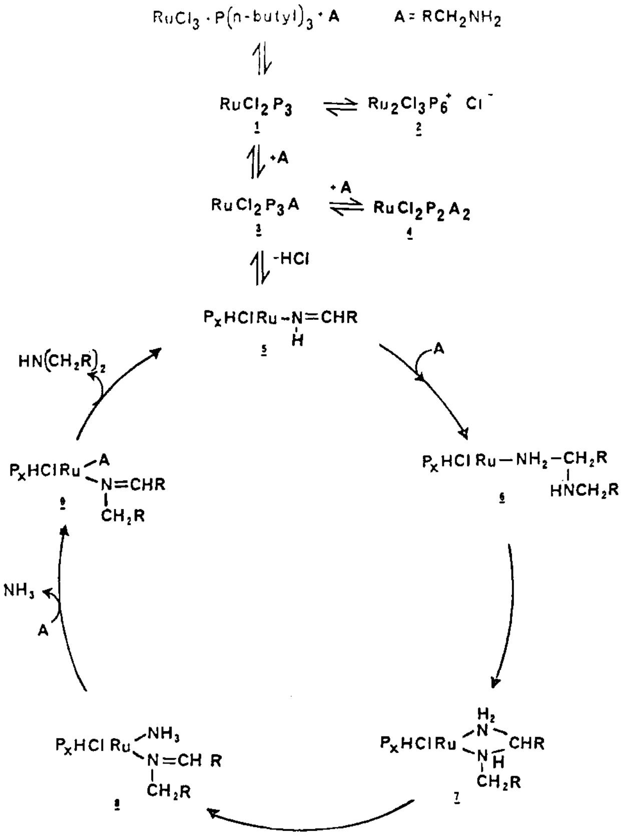
Summary: Close examination of the $RuCl_2(PPh_3)_3$ catalyzed synthesis of secondary amines from primary amines reveals the presence of benzene formed via PPh_3 decomposition during the reaction. $RuCl_3/PBu_3$ generates a much more active and stable system. Rate studies indicate imine hydrogenation occurs ~200 times faster than the overall reaction, indicating amine dehydrogenation is probably the rate-determining step. Reactions under D_2 reveal deuteration of the α-carbon of the alkyl amines. A mechanism consistent with these and other observations is proposed.

There has been much recent interest in the homogeneous[1-5] catalysis of amine redistribution reactions.[6] Porzi et al. have reported that $RuCl_2(PPh_3)_3$ catalyzes alkyl group scrambling,[3] the conversion of primary to secondary amines,[4] and the formation of heterocycles from α,ω-aliphatic diamines.[5] Although the catalyst was not examined during or after the reaction, it was assumed that such reactions proceed via metal-catalyzed dehydrogenation/hydrogenation sequences. Our work on the dehydrogenation of alcohols[7] using homogeneous ruthenium catalysts revealed catalytic activity extremely dependent on the nature of the phosphine ligand. As a continuation of these studies we have examined the effect of PR_3 on the $RuCl_2(PR_3)_3$ catalyzed conversion of primary to secondary amines.

Scheme I



Rate and selectivity data for the conversion of decyl to didecylamine are given in Table I.[8] The reaction rates were determined by GC analysis of reactions run in sealed vessels[9] and by measurement of NH_3 evolution by a gas buret.

Under our conditions the $RuCl_2(PPh_3)_3$ catalyst system reveals an initial first-order dependence on catalyst and amine concentration.[10] As the reaction proceeds, however,

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(1) Shvo, L.; Laine, R. M. *J. Chem. Soc., Chem. Commun.* **1980**, 753.

(2) Laine, R. M.; Thomas, D. W.; Cary, L. W. *J. Am. Chem. Soc.* **1982**, *104*, 1763.

(3) Arcelli, A.; Khai, B. T.; Porzi, G. *J. Organomet. Chem.* **1982**, *231*, C31.

(4) Khai, B. T.; Concilio, C.; Porzi, G. *J. Org. Chem.* **1981**, *46*, 1759.

(5) Khai, B. T.; Concilio, C.; Porzi, G. *J. Organomet. Chem.* **1981**, *208*, 249.

(6) Redistribution is herein meant to imply all amine reactions where net movement of alkyl groups occurs.

(7) Jung, C. W.; Garrou, P. E. *Organometallics* **1982**, *1*, 658.

(8) The decylamine model system was chosen because the high boiling points of the reactants and products allowed acquisition of reliable rate date and because the slower rates of such long chain amines enabled differences in reactivity due to PR_3 substitution to be readily observed. Similar results were obtained with hexyl and other aliphatic amines.

(9) Aliquots of a decane solution of $RuCl_3/4PR_3$ and primary amine were sealed in glass vessels and periodically withdrawn from a constant temperature bath to examine the reaction profile.

(10) Running the reaction in an open vessel connected to a gas buret results in secondary imine becoming the major product (Table I), thus H_2 as well as NH_3 is being evolved complicating the rate data obtained in this manner. When the reaction is conducted in a sealed vessel with 2–4% catalyst as described,[4] secondary amine is the major (>90%) product.