Acknowledgment. We wish to thank Professor Henry J. Shine (Texas Tech University) and Professor Björn Åkermark and Dr. Tobias Rein (Royal Institute of Technology, Stockholm, Sweden) for very helpful discussions. We are very grateful to the National Institutes of Health and the National Science Foundation for generous support of this work. We also wish to thank Johnson Matthey Inc. for a loan of palladium reagents.

Registry No. (2*E*,4*E*)-**1**, 93039-04-4; (2*E*,4*Z*)-**1**, 126457-65-6; (2*Z*,4*E*)-**1**, 93039-05-5; **2**, 30361-29-6; **3**, 71570-78-0; **4**, 42817-44-7; **5**, 126457-66-7; **6**, 126457-67-8; **7**, 126457-68-9; **8**, 126457-69-0; **9**, 14371-10-9; **10**, 58045-88-8; *n*-heptanal, 111-71-7; diethyl [(*E*)-4-(*N*,*N*-dimethylamino)-2-buten-1-yl]phosphonate, 93039-18-0; cinnamyl acetate, 103-54-8; benzylmethylamine, 103-67-3; iodine, 7553-56-2.

Selective Nucleophilic Addition Reactions of Alkyllithium Reagents with *N*-(Trimethylsilyl)lactams. Synthesis of Cyclic Ketimines

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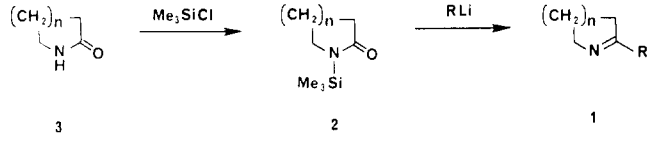
In our studies of the enantioselective synthesis of alkaloids via chiral α-sulfinyl ketimines,[1,2] cyclic ketimines of various ring size and containing diverse substituents, e.g. **1a–h**, were required. Four methods have been reported for the synthesis of cyclic ketimines: (1) additions of organolithium reagents to *N*-vinyllactams,[3] (2) acid-catalyzed rearrangement of tertiary azides,[4] (3) palladium-catalyzed oxidation of amino alkenes,[5] and (4) additions of organolithium[6] or Grignard reagents[7] with lactim ethers. Method 1 requires *N*-vinyllactams of which, however, only *N*-vinylpyrrolidinone is commercially available. Bayer and Geckeler[8] have noted the difficulty of obtaining *N*-vinyllactams in their report on the transvinylation of imides and ϵ-caprolactam with vinyl acetate in the presence of sodium tetrachloropalladate. We found that under these conditions δ-valerolactam (**3d**) was converted into *N*-vinylvalerolactam in only a 20% yield (60% recovery of δ-valerolactam). Method 2 requires a sequence of three steps, two of which utilize HN_3–BF_3·ether and H_2SO_4, respectively. Acid-labile systems like *tert*-butyldimethylsilyl ethers are incompatible with the reagents. Method 3 leads to a mixture of 2-ethyl-1-pyrroline and 2-methyl-1-piperidine (**1d**) in a ratio of 1:2. And, method 4 fails to provide **1d** and 1-aza-2-methyl-1-cycloheptene (**1e**). Herein, we describe a convenient method to prepare cyclic ketimines **1** in high yield from readily available *N*-(trimethylsilyl)lactams **2**.

Silylation of lactams **3** with trimethylsilyl chloride/triethylamine in toluene[9] gave excellent yields of *N*-silyllactams **2**. Nucleophilic additions of organolithium and organomagnesium reagents to **2** provided cyclic ketimines **1** (Scheme I). The results are summarized in Table I. Ethylmagnesium bromide afforded only a 25% yield of ketimine **1c** (entry 3) and 45% of lactam **3a**. Possibly, ethylmagnesium bromide attacks the silicon atom to generate the amide anion. However, high yields of these ketimines were obtained when alkyllithiums were employed.

Scheme I



3 2 1

The general procedure for these reactions consists of treating silyllactams **2** with 1.1 equiv of an alkyllithium at −20 °C for 30 min and then 25 °C for 1 h, or with 1.1 equiv of ethylmagnesium bromide in ether at 0 °C for 15 min and then 40 °C for 3 h.[10] Thus, organolithium reagents attack the carbonyl group of silyllactams; elimination of trimethylsilanol then leads to the products.

Lactams **3a–g** are commercially available. Lactam **3h** was obtained from the reaction of *N*-(trimethylsilyl)lactam **2a** with lithium diisopropylamide (LDA) in THF at −78 °C followed by reaction with bis(trimethylsilyl)peroxide.[11] The crude product was hydrolyzed with acetic acid–H_2O in $CHCl_3$ at 25 °C to give 3-hydroxy-2-pyrrolidinone (**4**) in 43% yield. N,O-Disilylation of **4** with a solution of 2.2 equiv of *tert*-butyldimethylsilyl chloride, 4 equiv of Et_3N, and 0.1 equiv of 4-(dimethylamino)pyridine (DMAP) in CH_2Cl_2 followed by selective N-desilylation with 0.5 equiv of *n*-Bu_4NF in THF at 0 °C for 2 h provided a 91% yield of lactam **3h**.

In summary, nucleophilic additions of alkyllithium reagents to *N*-(trimethylsilyl)lactams selectively provide cyclic ketimines in good to excellent yields. However, the only Grignard reagent used (EtMgBr) apparently attacks the silyllactam mainly at silicon, since the amide anion is generated. Continued utilization of cyclic ketimines in the construction of complex cyclic alkaloids[1,2] is underway.

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were obtained at 400 and 100 MHz, respectively. Infrared spectral data are reported in wavenumbers (cm^{-1}). Satisfactory elemental analyses were obtained for all compounds, except for ketimines **1f** and **1g**. These two compounds were rapidly hydrolyzed with traces of water into acylic keto amines. Davisil silica gel, grade 643 (200–425 mesh) was used for the flash chromatographic separation. Compounds **1b,c,h** are stable. Cyclic ketimines **1a** and **1d** trimerize upon heating, and the trimerization process is reversible. Compounds **1e–g** are unstable in acid medium or under heat (about 80 °C), leading to polymers. Hence, distillations of these three compounds are carried out under reduced pressure and low temperature. All cyclic ketimines should be stored in the refrigerator.

The following experiment serves to illustrate the general procedure for silylation reactions of lactams **3**.

† Fellow of the Alfred P. Sloan Foundation, 1989–1991.

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(8) Bayer, E.; Geckeler, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 533. Various imides and only one lactam (ϵ-caprolactam) were reported in the transvinylation reaction.
(9) Yamamoto, Y.; Kimura, H. *Chem. Pharm. Bull.* **1976**, *24*, 1236.
(10) When the reaction was carried out at 25 °C for 24 h, 15% of ketimine **1c** and 30% of lactam **3a** were obtained along with 35% of recovered *N*-silyllactam **2a**.
(11) Pohmakotr, M.; Winotai, C. *Synth. Commun.* **1988**, *18*, 2141.

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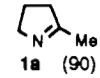
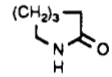
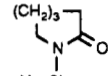
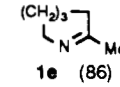
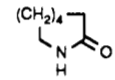
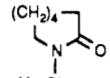
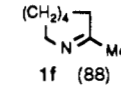
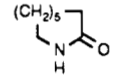
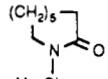
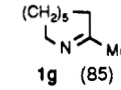
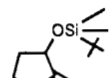
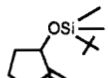
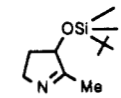
Table I. Preparation of *N*-(Trimethylsilyl)lactams 2 and Cyclic Ketimines 1

entry	lactam 3	*N*-(trimethylsilyl)lactam 2 (% yield)	RLi[a]	cyclic ketimine 1 (% yield)
1	 **3a**	 **2a** (95)	MeLi	 **1a** (90)
2	**3a**	**2a**	*n*-BuLi	 **1b** (74)
3	**3a**	**2a**	EtMgBr	 **1c** (25)[b]
4	**3a**	**2a**	EtLi	**1c** (90)
5	 **3d**	 **2d** (86)	MeLi	 **1d** (92)
6	 **3e**	 **2e** (80)	MeLi	 **1e** (86)
7	 **3f**	 **2f** (95)	MeLi	 **1f** (88)
8	 **3g**	 **2g** (94)	MeLi	 **1g** (85)
9	 **3h**	 **2h** (91)	MeLi	 **1h** (90)

[a] Except Entry 3. [b] 45% of lactam **3a** was recovered.

1-(Trimethylsilyl)-2-pyrrolidinone (2a). To a solution of 17 g (0.2 mol) of 2-pyrrolidinone (**3a**) and 25 g (0.25 mol) of triethylamine in 200 mL of toluene under argon at 25 °C was added 23.9 g (0.22 mol) of trimethylsilyl chloride. The mixture was stirred at 40 °C for 4 h. The ^{1}H NMR spectrum of an aliquot of the mixture indicated the absence of **3a**. The mixture was cooled to 0 °C, diluted with 200 mL of hexane–ether (1:1), and filtered through Celite. The filtrate was concentrated on rotary evaporator, and the residue was distilled under reduced pressure to give 30 g (95% yield) of a colorless oil: bp 90 °C (20 mmHg); IR (neat) 2950, 2845, 1640, 1410 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.34 (t, J = 7 Hz, 2 H, CH_2N), 2.30 (t, J = 7 Hz, 2 H, CH_2CO), 2.01 (quintet, J = 7 Hz, 2 H, CH_2), 0.25 (s, 9 H, Me_3Si); ^{13}C NMR ($CDCl_3$) δ 183.0 (s, C=O), 46.23 (t), 32.45 (t), 21.36 (t), −1.47 (q); MS m/e EI 157 (M^+).

The following experiment serves to illustrate the general procedure for the preparation of ketimines 1.

3,4-Dihydro-5-methyl-2*H*-pyrrole (1a). To a cold (−20 °C) solution of 38.2 mL (0.057 mol) of methyllithium (1.5 M solution in ether) under argon was added a solution of 8.17 g (0.052 mol) of **2a** in 60 mL of ether. The solution was stirred at −20 °C for 30 min and at 25 °C for 1 h and then diluted with a solution of 2.7 g of NH_4Cl in 100 mL of H_2O. The mixture was stirred at 25 °C for 30 min, the ether layer was separated, and the water layer was extracted with CH_2Cl_2 three times (100 mL each). The combined extracts were washed with brine, dried ($MgSO_4$), and distilled under normal pressure to remove ether and CH_2Cl_2. The residue was distilled to give 3.9 g (90% yield) of **1a** as an oil: bp 105 °C (lit.[3] bp 105 °C); IR (neat) 2940, 2850, 1630 (s, C=N), 1420, 1360, 1305, 1030, 1005, 930 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.8 (m, 2 H, CH_2N), 2.46 (t, J = 8 Hz, 2 H, CH_2), 2.03 (s, 3 H, CH_3), 1.87 (quintet, J = 7.4 Hz, 2 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 174.91 (s, C=N), 60.65 (t), 38.49 (t), 22.63 (t), 19.33 (q); MS m/e EI 83 (M^+).

5-*n*-Butyl-3,4-dihydro-2*H*-pyrrole (1b): bp 72 °C (25 mmHg); IR (neat) 2930, 2850, 1627 (C=N), 1450, 1420, 1240, 905, 832, 730; ^{1}H NMR ($CDCl_3$) δ 3.73 (t, J = 7 Hz, 2 H, CH_2N), 2.40 (t, J = 8 Hz, 2 H, CH_2C=), 2.28 (t, J = 7 Hz, 2 H, CH_2C=), 1.79 (quintet, J = 7 Hz, 2 H), 1.52 (quintet, J = 8 Hz, 2 H), 1.29 (setet, J = 8 Hz, 2 H), 0.87 (t, J = 8 Hz, 3 H, Me); ^{13}C NMR ($CDCl_3$) δ 178.6 (s, CN), 60.56 (t, CH_2N), 37.02 (t), 32.4 (t), 28.49 (t), 22.54 (t), 22.46 (t), 13.78 (q); MS m/e EI 125.

3,4-Dihydro-5-ethyl-2*H*-pyrrole (1c): bp 50 °C (45 mmHg); IR (neat) 2940, 2860, 1630, 1450, 1360, 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.76 (t, J = 7 Hz, 2 H, CH_2N), 2.42 (t, J = 7 Hz, 2 H, CH_2C=), 2.30 (q, J = 7 Hz, 2 H, CH_2CH_3), 1.82 (quintet, J = 7 Hz, 2 H, CH_2), 1.11 (t, J = 7 Hz, 3 H, Me); ^{13}C NMR ($CDCl_3$) δ 179.13 (s, C=N), 60.59 (t, CN), 36.76 (t), 26.67 (t), 22.4 (t), 15.06 (q, Me); MS m/e EI 97 (M^+).

1-(Trimethylsilyl)-2-piperidinone (2d): bp 63 °C (3 mmHg); IR (neat) 2940, 2860, 1620, 1400, 1290, 1240, 1015, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.13 (t, J = 6 Hz, 2 H, CH_2N), 2.28 (t, J = 7 Hz, 2 H, CH_2CO), 1.71 (m, 2 H), 1.62 (m, 2 H), 0.20 (s, 9 H, Me_3Si); ^{13}C NMR ($CDCl_3$) δ 177.05 (s, CO), 44.01 (t), 32.48 (t), 23.23 (t), 20.75 (t), −0.34 (q); MS m/e EI 171 (M^+).

2-Methyl-3,4,5,6-tetrahydropyridine (1d): bp 125 °C; IR (neat) 2900, 1640 (C=N), 1430, 1350, 1260 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.54 (m, 2 H, CH_2N), 2.12 (m, 2 H, CH_2C=), 1.91 (s, 3 H, Me), 1.67 (m, 2 H), 1.56 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 167.95 (s, CN), 49.0 (t, CN), 30.08 (t), 27.32 (q, Me), 21.47 (t), 19.45 (t); MS m/e EI 97 (M^+).

2-(Trimethylsilyl)-2-azacycloheptanone (2e): bp 85 °C (1.5 mmHg); IR (neat) 2920, 2850, 1630, 1430, 1390, 1240, 910, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.14 (t, J = 5 Hz, 2 H, CH_2N), 2.45 (t, J = 6 Hz, 2 H, CH_2CO), 1.64 (m, 4 H), 1.48 (m, 2 H), 0.18 (s, 9

H, Me_3Si); ^{13}C NMR ($CDCl_3$) δ 183.29 (s, C=O), 44.50 (t, CN), 37.83 (t), 30.37 (t), 29.82 (t), 23.48 (t), 0.06 (q); MS *m/e* EI 185 (M^+).

1-Aza-2-methyl-1-cycloheptene (1e): bp 65 °C (35 mmHg); IR (neat) 2920, 2840, 1645, 1425, 1360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.55 (t, *J* = 5 Hz, 2 H, CH_2N), 2.37 (t, *J* = 5 Hz, CH_2C=), 2.04 (s, 3 H, Me), 1.78 (quintet, *J* = 7 Hz, 2 H, CH_2), 1.52 (m, 2 H), 1.45 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 176.19 (s, CN), 51.59 (t, CH_2N), 34.0 (t), 31.37 (t), 29.22 (t), 26.24 (q), 22.95 (t); MS *m/e* EI 111 (M^+).

2-(Trimethylsilyl)-2-azacyclooctanone (2f): bp 87 °C (2.5 mmHg); IR (neat) 2910, 2845, 1645, 1615, 1440, 1385, 1240, 1050, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.24 (m, 2 H, CH_2N), 2.38 (m, 2 H, CH_2CO), 1.70 (m, 2 H), 1.47 (m, 6 H), 0.19 (s, 9 H, Me_3Si); ^{13}C NMR ($CDCl_3$) 182.33 (s, C=O), 43.57 (t, CN), 34.06 (t), 32.51 (t), 28.38 (t), 26.3 (t), 23.95 (t), 0.03 (q, Me_3Si); MS *m/e* EI 199 (M^+).

1-Aza-2-methyl-1-cyclooctene (1f): bp 45 °C (15 mmHg); IR (neat) 2900, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.44 (m, 2 H, CH_2N), 2.25 (m, 2 H, CH_2C=), 1.93 (s, 3 H, Me), 1.62 (m, 2 H), 1.49 (m, 2 H), 1.37 (m, 2 H), 1.28 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 172.15 (s, C=N), 48.80 (t, CN), 29.67 (2 C, t), 27.28 (t), 27.04 (q), 25.84 (t), 24.48 (t); MS *m/e* EI 125 (M^+).

2-(Trimethylsilyl)-2-azacyclononanone (2g): bp 70 °C (0.5 mmHg); IR (neat) 2950, 2880, 1630, 1430 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.28 (m, 2 H, CH_2N), 2.39 (m, 2 H, CH_2CO), 1.73 (m, 2 H), 1.50 (m, 4 H), 1.44 (m, 4 H), 0.19 (s, 9 H, Me_3Si); ^{13}C NMR ($CDCl_3$) δ 182.54 (s, CO), 45.39 (t, CN), 34.84 (t), 30.42 (t), 28.38 (t), 25.43 (t), 24.6 (t), 22.02 (t), 0.04 (q); MS *m/e* EI 213 (M^+).

1-Aza-2-methyl-1-cyclononene (1g): bp 70 °C (0.5 mmHg); IR (neat) 2910, 2840, 1640, 1450, 1350 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.67 (t, *J* = 7 Hz, 2 H, CH_2N), 2.42 (t, *J* = 7 Hz, 2 H, CH_2C=), 2.13 (s, 3 H, Me), 1.79 (m, 2 H), 1.58 (m, 2 H), 1.43 (m, 2 H), 1.31 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 174.59 (s, C=N), 43.64 (t, CN), 42.04 (t), 33.58 (t), 29.74 (t), 29.13 (t), 29.02 (t), 26.59 (q), 23.67 (t); MS *m/e* EI 139 (M^+).

3-Hydroxy-2-pyrrolidinone (4). To a cold (−20 °C) solution of 3.5 mL (0.025 mol) of diisopropylamine in 50 mL of THF under argon was added 15.6 mL (0.025 mol) of *n*-BuLi (1.6 M solution in THF). After being stirred at −20 °C for 30 min, the solution was cooled to −40 °C, and a solution of 3.228 g (0.021 mol) of **2a** in 10 mL of THF was added via cannula. The resulting green solution was warmed to −20 °C and stirred at this temperature for 1.5 h, after which 4.75 g (0.027 mol) of bis(trimethylsilyl)-peroxide was added, and the yellow solution was warmed to 25 °C. After 12 h, the solution was diluted with 1.62 g (0.027 mol) of acetic acid and 2 mL of brine, and the solvent was removed on a rotary evaporator. The residue was diluted with 50 mL of CH_2Cl_2, filtered through Celite, and concentrated to give 2.973 g of an oil, to which was added 3.6 g (0.06 mol) of acetic acid, 5 mL of MeOH, and 30 mL of $CHCl_3$. After being stirred at 25 °C for 5 h, the solution was concentrated to dryness and flash chromatographed on silica gel column using a mixture of ethyl acetate and methanol as eluant to give 0.912 g (43% yield) of 3-hydroxy-2-pyrrolidinone: mp 95–96 °C (lit.[12] 102–103 °C); IR (Nujol) 3300 (broad s), 2920, 2850, 1650 (s), 1450, 1280, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.87 (broad s, 1 H, NH), 4.34 (t, *J* = 8 Hz, 1 H, CHO), 4.25 (broad s, 1 H, OH), 3.44 (m, 1 H, CHN), 3.32 (m, 1 H, CHN), 2.52 (m, 1 H), 2.09 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 179.11 (s, C=O), 69.05 (d, CO), 38.78 (t, CN), 29.91 (t); MS, *m/e* EI 101 (M^+).

3-[(*tert*-Butyldimethylsilyl)oxy]-2-pyrrolidinone (3h). A mixture of 1.34 g (0.0134 mol) of 3-hydroxy-2-pyrrolidinone (**4**), 4.44 g (0.0295 mol) of *tert*-butyldimethylsilyl chloride, 5.41 g (0.0536 mol) of triethylamine, and 0.164 g (0.0013 mol) of 4-(dimethylamino)pyridine in 30 mL of CH_2Cl_2 under argon was stirred at 25 °C for 3 h. The mixture was diluted with 250 mL of ether, washed with 50 mL of H_2O, 30 mL of 1 N HCl, 30 mL of aqueous $NaHCO_3$ solution, and 30 mL of brine, dried ($MgSO_4$), and concentrated to give 4.45 g of *N*-(*tert*-butyldimethylsilyl)-3-[(*tert*-butyldimethylsilyl)oxy]-2-pyrrolidinone. This product was dissolved in 80 mL of THF, the solution was cooled to 0 °C, and 6.7 mL (6.7 mmol) of *n*-Bu_4NF (1.0 M in THF) was added. After being stirred for 2 h at 0 °C, the solution was diluted with 300 mL of ether, washed with 50 mL of H_2O and 30 mL of brine, dried ($MgSO_4$), concentrated, and flash chromatographed on a silica gel column with a mixture of ether and methanol as eluant to give 2.62 g (91% yield) of **3h**: mp 77–78 °C; IR (neat) 3300, 2930, 2860, 1680 (s, C=O), 1275, 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.33 (broad s, 1 H, NH), 4.26 (t, *J* = 8 Hz, 1 H, CHO), 3.38 (td, *J* = 9 Hz, 3 Hz, 1 H, CHN), 3.25 (td, *J* = 9, 8 Hz, 1 H, CHN), 2.37 (m, 1 H), 2.04 (m, 1 H), 0.92 (s, 9 H, *t*-Bu), 0.16 (s, 3 H, MeSi), 0.15 (s, 3 H, MeSi); ^{13}C NMR ($CDCl_3$) δ 177.08 (s, C=O), 70.68 (d, CHO), 38.46 (t, CN), 31.47 (t), 25.74 (q, 3 C, *t*-Bu), 18.24 (s, CSi), −4.58 (q, MeSi), −5.14 (q, MeSi); MS *m/e* EI 215 (M^+).

3-[(*tert*-Butyldimethylsilyl)oxy]-1-(trimethylsilyl)-2-pyrrolidinone (2h): an oil; IR (neat) 2950, 2845, 1680 (s, C=O), 1450, 1370, 1360, 1250, 1128, 1075 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.24 (t, *J* = 8 Hz, 1 H, CHO), 3.30 (td, *J* = 8, 3 Hz, 1 H, CHN), 3.17 (td, *J* = 8, 6 Hz, 1 H, CHN), 2.29 (m, 1 H), 1.94 (dq, *J* = 12, 8 Hz, 1 H), 0.91 (s, 9 H, *t*-Bu), 0.27 (s, 9 H, Me_3Si), 0.15 (s, 3 H, MeSi), 0.13 (s, 3 H, MeSi); ^{13}C NMR ($CDCl_3$) δ 181.0 (s, C=O), 72.09 (d, CO), 41.58 (d, CN), 31.87 (t, CH_2), 25.78 (q, 3 C, *t*-Bu), 18.29 (s, *t*-Bu), −1.38 (q, 3 C, Me_3Si), −4.55 (q, MeSi), −5.16 (q, MeSi); MS *m/e* CI 288 (M + 1).

4-[(*tert*-Butyldimethylsilyl)oxy]-3,4-dihydro-5-methyl-2*H*-pyrrole (1h): an oil; IR (neat) 2940, 2840, 1640, 1455, 1350, 1248, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.60 (t, *J* = 7.5 Hz, 1 H, CHO), 3.88 (m, 1 H, CH_2N), 3.57 (m, 1 H, CH_2N), 2.21 (m, 1 H), 2.02 (s, 3 H, Me), 1.7 (m, 1 H), 0.91 (s, 9 H, *t*-Bu), 0.15 (s, 3 H, MeSi), 0.12 (s, 3 H, MeSi); ^{13}C NMR ($CDCl_3$) δ 176.53 (s, C=N), 79.72 (d, CO), 57.38 (t, CN), 33.55 (t), 25.71 (q, 3 C, *t*-Bu), 18.03 (s, *t*-Bu), 16.59 (q, CH_3), −4.64 (q, MeSi), −5.04 (q, MeSi); MS *m/e* EI 213 (M^+).

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Registry No. **1a**, 872-32-2; **1b**, 64319-86-4; **1c**, 1192-29-6; **1d**, 1462-92-6; **1e**, 3338-03-2; **1f**, 126645-91-8; **1g**, 126645-92-9; **1h**, 126645-93-0; **2a**, 14468-90-7; **2d**, 3553-93-3; **2e**, 3553-94-4; **2f**, 57012-52-9; **2g**, 14468-91-8; **2h**, 126645-94-1; **3a**, 616-45-5; **3d**, 675-20-7; **3e**, 105-60-2; **3f**, 673-66-5; **3g**, 935-30-8; **3h**, 126645-95-2; **4**, 15166-68-4; $H_2N(CH_2)_3CH$=$CHCH_3$, 60168-05-0; *N*-(*tert*-butyldimethylsilyl)-3-[(*tert*-butyldimethylsilyl)oxy]-2-pyrrolidinone, 126645-96-3; *N*-vinylvalerolactam, 4370-23-4.

Supplementary Material Available: Elemental analyses for compounds **1a–e**, **2f–h**, and **1h** and ^{13}C NMR spectra of compounds **1f** and **1g** (3 pages). Ordering information is given on any current masthead page.

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Chiral Bismetallocenes with C_2 Symmetry

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The development of methods for positioning metal centers within defined chiral environments continues to be an objective of considerable interest, in large part because of the potential applications such metal centers have to asymmetric synthesis.[1] A recurring theme, attractive

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