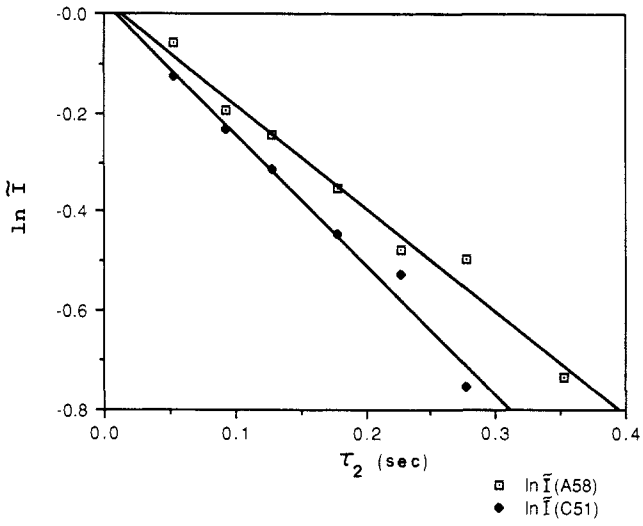

Figure 3. Linear least-squares fit of ln I versus τ_2 for the residues Cys 51 and Ala 58 where $I = [(I(\tau_2) - I(\infty))/(I(0) - I(\infty))]$. The value of T_1 obtained from the fit was 378 ± 6 ms for Cys 51 and 477 ± 30 ms for Ala 58. The average error in the measurement of T_1 was found to be 5.4%.

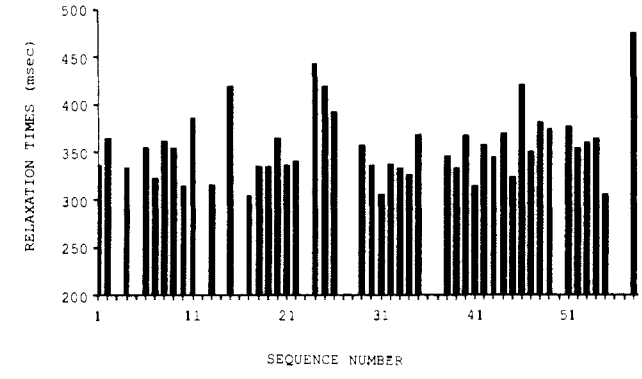

Figure 4. Relaxation times of the α-carbon signals of BPTI vs amino acid sequence. T_1 values of glycyl residues were not measured (see text). Asp 3, Asp 50, Ala 16, and Ala 27 could not be analyzed because of resonance overlap (Figure 2), and Cys 14 and Tyr 23 could not be analyzed due to strong line broadening at 36 °C.

B factors obtained from the crystal structure of BPTI.[6] This is reasonable since the main contribution to relaxation times originates from the overall rotational motions of the protein whereas B factors measure mainly internal mobility. It is more surprising, however, that the residues expected to have greater mobility (when comparing crystallographic B factors or when considering their location at the protein surface) have longer T_1 values. These residues are the C-terminal Ala 58, the residues at the β-turn (Asn 24 to Lys 26), or the residue in the reactive site (Lys 15). This observation is consistent with the results of Richarz et al.[5] where longer T_1's have been measured for the methyl groups in the same regions. This may indicate that for these surface regions of the molecule we have conditions of $\omega\tau_c < 1$, and there is a larger variation of effective correlation times in BPTI than indicated from the relatively small variations of T_1 values in Figure 4. On the other hand, the lack of dramatic variations of T_1 values assures us that measurements of nuclear Overhauser effects for determination of protein structures in solution are not significantly biased by internal motions, at least as far as the backbone is concerned.

Acknowledgment. This research was supported by NSF (Projects DMB-8616059 and BBS-8615223) and NIH (Project GM 38608-01A1).

(6) Deisenhofer, J., private communication.

Preparation, Isolation, and Characterization of Transition-Metal η^2-Silene Complexes. X-ray Crystal Structure of $(\eta^5\text{-}C_5Me_5)[P(i\text{-}Pr)_3]Ru(H)(\eta^2\text{-}CH_2SiPh_2)$

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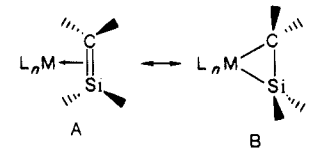
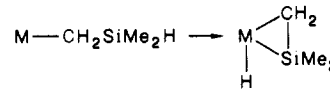
Silenes ($R_2C{=}SiR'_2$) are usually reactive organosilicon intermediates whose formation can be established indirectly with trapping reactions.[1,2] Recent interest in silenes has been stimulated by syntheses of isolable examples that are stabilized by steric protection of the Si=C double bond.[3,4] Given the well-known ability of transition metals to stabilize reactive species (e.g., carbenes, carbynes, cyclobutadienes, ketenes, and thiocarbonyl) by ligation, it seemed reasonable to assume that stable transition-metal silene complexes $L_nM(\eta^2\text{-}R_2CSiR'_2)$ (A,B) could be



isolated and studied. Silene complexes have been proposed as intermediates in a number of metal-mediated rearrangements of organosilicon ligands.[5] Intermediates generated by the β-hydrogen-transfer reaction shown in eq 1 were originally proposed by Pannell[5a] and have recently been observed spectroscopically



(1)

at low temperature by Wrighton.[6] Near-UV photolysis of $Cp^*(CO)_2FeCH_2SiMe_2H$ ($Cp^* = \eta^5\text{-}C_5Me_5$) in the presence of a ligand L (CO or PPh_3) was shown to result in formation of $Cp^*(CO)(L)FeSiMe_3$ via the intermediate $Cp^*(CO)Fe(H)(\eta^2\text{-}CH_2SiMe_2)$, which was stable to 225 K.[6b]

We have an interest in studying reactive organosilicon intermediates in the coordination sphere of transition metals[7] and have attempted syntheses of stable silene complexes that can be isolated and subjected to structural and chemical studies. The approach reported here involves use of the hydrogen-transfer process of eq 1 and stabilization of the formally more oxidized metal center with a noble metal (ruthenium) and electron-donating ligands (Cp* and trialkylphosphines). Additionally, since the hydrogen

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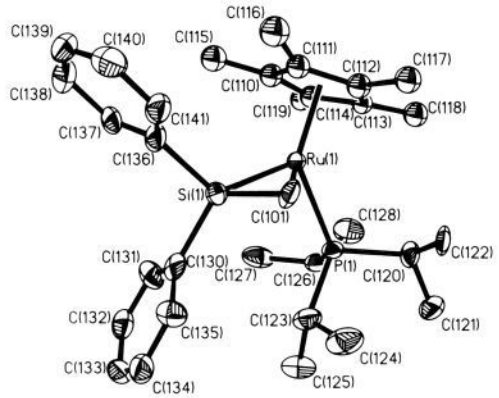
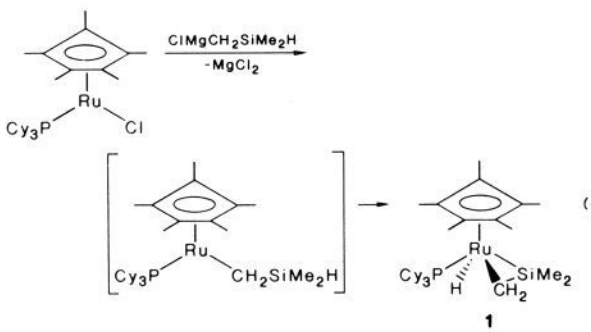


Figure 1. ORTEP view of **3** with atom-labeling scheme. Selected bond distances (Å) and angles (deg), with values for the second enantiomer in brackets: Ru(1)–Si(1) 2.382 (4) [2.365 (5)], Ru(1)–C(101) 2.25 (2) [2.26 (1)], Ru(1)–P(1) 2.365 (4) [2.345 (5)], Si(1)–Ru(1)–P(1) 100.0 (2) [99.3 (2)], C(101)–Ru(1)–P(1) 90.9 (4) [91.3 (4)], Si(1)–Ru(1)–C(101) 45.2 (5) [45.4 (4)], Si(1)–C(101)–Ru(1) 71.3 (7) [70.2 (5)], Ru(1)–Si(1)–C(101) 63.5 (5) [64.3 (5)], Ru(1)–Si(1)–C(130) 124.3 (5) [127.9 (5)], Ru(1)–Si(1)–C(136) 120.8 (6) [119.1 (6)].

transfer requires an open coordination site, our efforts have concentrated on the preparation of 16-electron MCH_2SiR_2H complexes. Here we report syntheses of the first isolated η^2-silene complexes $Cp^*(PCy_3)Ru(H)(\eta^2\text{-}CH_2SiMe_2)$ (**1**, Cy = cyclohexyl) and $Cp^*(PR_3)Ru(H)(\eta^2\text{-}CH_2SiPh_2)$ (**3**, R = *i*-Pr; **4**, R = Cy) and the X-ray crystal structure of **3**.

The 16-electron complex $Cp^*Ru(PCy_3)Cl$[8] reacts with $ClMgCH_2SiMe_2H$ in cold (−78 °C) diethyl ether to provide yellow microcrystals from pentane after rapid workup. The ^1H NMR spectrum (benzene-d_6, 25 °C) of this product, which contains peaks assigned to the inequivalent hydrogens (at −0.28 and −0.10 ppm) and methyl groups (at 0.54 and 0.56 ppm) of the η^2-silene, allows formulation of the product as **1** (eq 2). Compound **1** is thermally



(2)

1

unstable and decomposes in solution (benzene-d_6, 25 °C, $t_{1/2}$ = 30 min) and in the solid state (complete decomposition within 1 week at 25 °C). In diethyl ether solution this decomposition cleanly produces $HSiMe_3$ and a new ruthenium hydride that gives spectroscopic and combustion analysis data consistent with a complex containing a dimetalated PCy_3 ligand, $Cp^*Ru(PC_{18}H_{31})H$ (**2**).[9]

More stable silene complexes are derived from the diphenylsilylmethyl group, $-CH_2SiPh_2H$. Diethyl ether solutions of $ClMgCH_2SiPh_2H$ and $Cp^*Ru(PR_3)Cl$ (R = *i*-Pr or Cy) were combined at −78 °C and then warmed to room temperature. In each case, a yellow crystalline product was isolated by crystallization from diethyl ether. Both thermally stable η^2-silene complexes, $Cp^*(PR_3)Ru(H)(\eta^2\text{-}CH_2SiPh_2)$ (**3**, R = *i*-Pr, 73%; **4**, R = Cy, 75%), were characterized by NMR and infrared spectroscopy.[10] Apparently these reactions proceed via intermediate 16-electron ruthenium alkyls $Cp^*Ru(PR_3)(CH_2SiPh_2H)$, which undergo β-elimination to give the observed silene complexes. However, monitoring these reactions by variable-temperature ^{31}P NMR (toluene-d_8, −70 °C → 25 °C) provided no evidence for the postulated alkyl intermediate. Compared to **1**, complex **4** exhibits increased thermal stability, decomposing in solution at room temperature over several days to produce $HSiMePh_2$ and **2**. The deuteride $Cp^*(PCy_3)Ru(D)(\eta^2\text{-}CH_2SiPh_2)$ (**4**-*d*), prepared from $Cp^*Ru(PCy_3)Cl$ and $ClMgCH_2SiPh_2D$, decomposed over 3 h at 90 °C (benzene-d_6) to cleanly give complex **2** and $HSi(CDH_2)Ph_2$, as determined by ^1H and ^2H NMR. The thermal decomposition of **4** therefore appears to involve initial migration of hydride to the methylene carbon of the $\eta^2\text{-}CH_2SiPh_2$ ligand, producing the 16-electron silyl complex $Cp^*Ru(PCy_3)Si(CDH_2)Ph_2$. Further aspects of the chemistry of these silene complexes will be reported shortly.

The crystal structure of **3**[11] shows that the asymmetric unit contains both enantiomers, one of which is shown in Figure 1. Bond angles about Ru indicate that the hydride ligand is cis to the ligated silicon atom. Of particular interest are the Si–CH_2 distances in the silene ligand, 1.78 (2) and 1.79 (2) Å, which seem to reflect partial double bond character since Si–C single bond distances normally range from 1.87 to 1.91 Å.[12] As expected, these distances are somewhat longer than Si=C double bond distances observed for isolated silenes. The heteroatom-substituted silene $(Me_3Si)_2Si{=}C(OSiMe_3)$(1-adamantyl) has a Si=C double bond distance of 1.764 (3) Å,[13] which is longer than values observed for both $Me_2Si{=}C(SiMe_3)(SiMe^tBu_2)$ (1.702 (5) Å)[14] and its tetrahydrofuran complex $(THF)Me_2Si{=}C(SiMe_3)(SiMe^tBu_2)$ (1.747 (5) Å).[15]

Acknowledgment is made to the National Science Foundation for their generous support and to the DoD University Research Instrumentation Program (Grant DAAL03-87-G-0071) for funds to purchase an X-ray diffractometer. T.D.T. thanks the Alfred P. Sloan Foundation for a research fellowship (1988–90). We thank Prof. A. L. Rheingold for useful suggestions regarding the structure.

Supplementary Material Available: A listing of crystal, data collection, and refinement parameters and tables of positional and

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(9) For **2**: ^1H NMR (benzene-d_6, 25 °C, 300 MHz) δ −12.57 (d, $^2J_{PH}$ = 39 Hz, 1 H, RuH); $^{31}P\{^1H\}$ NMR (benzene-d_6, 25 °C, 121.5 MHz) δ −71.08; IR (Nujol, CsI, cm^{-1}), ν(RuH) = 2000 cm^{-1}.

(10) For **3**: ^1H NMR (benzene-d_6, 25 °C, 300 MHz) δ −11.64 (d, $^2J_{PH}$ = 18 Hz, 1 H, RuH), 0.23 (m, 1 H, $SiCH_2$), 0.42 (m, 1 H, $SiCH_2$) (these two multiplets were computer simulated to give the coupling constants J_{HH} = −9.81 Hz, J_{HP} = −0.08, 9.93); $^{13}C\{^1H\}$ NMR (benzene-d_6, 25 °C, 75.5 MHz) δ −29.04 (d, $^2J_{PC}$ = 5.4 Hz, $SiCH_2$); $^{31}P\{^1H\}$ NMR (benzene-d_6, 25 °C, 121.5 MHz) δ 63.58; $^{29}Si\{^1H\}$ NMR (toluene-d_8, −20 °C, 59.6 MHz, INEPT) δ 6.14. Anal. ($C_{32}H_{49}PSiRu$): C, H, P. For **4**: ^1H NMR (benzene-d_6, 25 °C, 300 MHz) δ −11.69 (d, $^2J_{PH}$ = 19 Hz, 1 H, RuH), 0.29 (m, 1 H, $SiCH_2$), 0.41 (m, 1 H, $SiCH_2$); $^{13}C\{^1H\}$ NMR (benzene-d_6, 25 °C, 75.5 MHz) δ −29.68 (d, $^2J_{PC}$ = 4.4 Hz, $SiCH_2$); $^{31}P\{^1H\}$ NMR (benzene-d_6, 25 °C, 121.5 MHz) δ 50.00.

(11) $C_{32}H_{49}PSiRu$, monoclinic, $P2_1/c$, a = 10.298 (5) Å, b = 41.51 (2) Å, c = 14.90 (1) Å, β = 108.29 (5) °, V = 6047 (6) Å^3, Z = 8, μ = 6.17 cm^{-1}, Mo Kα radiation (λ = 0.71073 Å), 173 K (−100 °C), Nicolet R3m/V diffractometer with graphite monochromator. 10825 reflections were collected ($3° \le 2\theta \le 50°$) using ω scans and were corrected for absorption. Of these, 9815 reflections were unique (R_{int} = 11.13%) and 5086 were considered observed ($F \ge 6.0\sigma(F)$). The large R_{int} is due to slight crystal twinning. Solution by direct methods, refinement by full-matrix least-squares methods (SHELXTL PLUS computer programs, Nicolet Instrument Corp., Madison, WI). All non-hydrogen atoms (except the carbon atoms of the C_5Me_5 rings) were refined anisotropically, and hydrogen atoms (except those of $SiCH_2Ru$) were refined isotropically in fixed and idealized positions. Neither the $SiCH_2Ru$ hydrogens nor the ruthenium hydride ligand were located. R_F = 9.79%, R_{wF} = 12.2%, data/parameter = 9.6, GOF = 2.45, largest Δ/σ = 0.042, highest peak = 1.74 e$^-$/Å^3 (0.92 Å from Ru (2)).

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thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates for **3** (11 pages); tables of observed and calculated structure factors for **3** (36 pages). Ordering information is given on any current masthead page.

Facile Stereoselective Allylic Hydroxylation by Dopamine β-Monooxygenase

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The copper protein, dopamine β-monooxygenase (DBM, E. C.1.14.17.1) catalyzes hydroxylation at the pro-R hydrogen of dopamine to form norepinephrine in a variety of mammalian tissues.[1-4] We and others have shown that DBM also readily catalyzes benzylic oxygenation of functionalities such as carbon (saturated or unsaturated), carbinol, sulfur, selenium, or nitrogen in a variety of substrate analogues,[5-17] and the mechanism of DBM catalysis has been the subject of much recent interest.[9,12,18-22] We now report the first example of allylic oxygenation by DBM, and we demonstrate that this reaction is highly facile and stereoselective, with the absolute configuration of the product corresponding to that previously established for benzylic hydroxylation[3] and sulfoxidation[5] by DBM.

In view of the well-known physico-chemical similarities of allylic and benzylic systems,[23] 2-(1-cyclohexenyl)ethylamine (CyHEA) was chosen as the prototypical substrate for allylic hydroxylation, since it shares a number of structural similarities with 2-phenethylamine. DBM was isolated from bovine adrenal medullae and purified as described previously.[9,24] Kinetic parameters for CyHEA turnover were found to be k_{cat} = 90 s^{-1} and K_M = 6.1 mM under standard turnover conditions. These values represent highly facile turnover, comparable to those for the most highly active DBM substrates known to date.[25]

Preparative scale enzymatic reaction allowed product isolation by preparative TLC after derivatizing enzymatic reaction mixtures with succinimidyl-4-nitrophenylacetate (SNPA),[9] and the product was identified as 1-(1-cyclohexenyl)-2-[(4-nitrophenyl)acetamido]ethanol on the basis of FT NMR and mass spectrometry [^{1}H NMR (δ, $CDCl_3$) 7.83 (dd, 4 H), 5.8 (br s, 1 H), 5.65 (m, 1 H), 4.04 (br s, 1 H), 3.45 (s, 2 H), 3.2-3.6 (m, 2 H), 1.4-2.1 (m, 8 H); mass spectrum (EI) M^+ 304]. An oxygen/ascorbate/product stoichiometry of 1:1.2:1.1 was determined for CyHEA oxygenation by quantitative comparison of oxygen con-

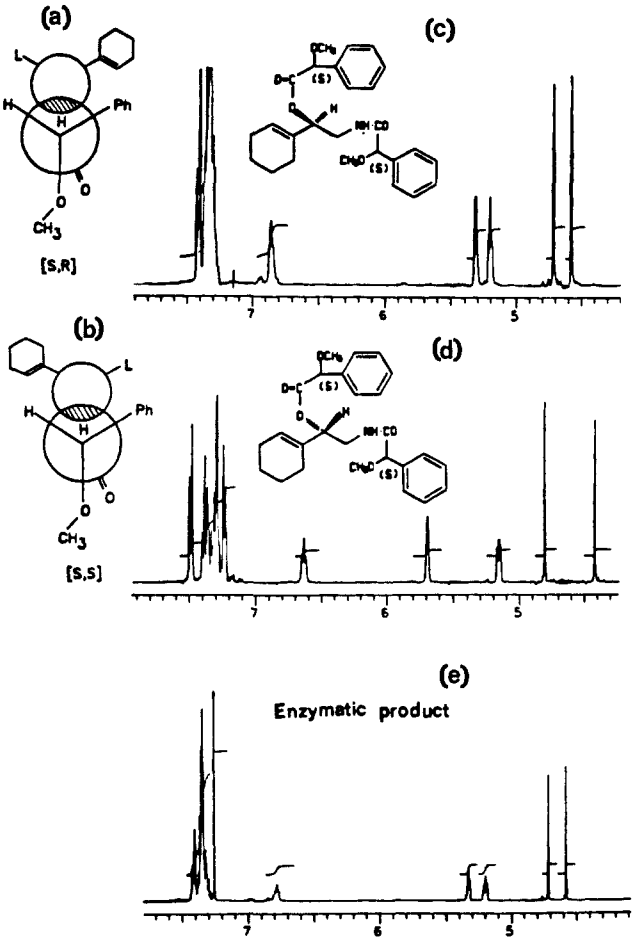

Figure 1. Configuration correlation models and FT NMR spectra of (*S*)-*O*-methylmandelic acid esters of (*R*)- and (*S*)-1-(1-cyclohexenyl)-2-aminoethanols. The proton resonance for the vinyl proton was identified by NMR decoupling. (a) The extended Newman projection for diacylated (*R*)-1-(1-cyclohexenyl)-2-aminoethanol. (b) The extended Newman projection for diacylated (*S*)-1-(1-cyclohexenyl)-2-aminoethanol. (c) FT NMR spectrum of *N*-[(*S*)-α-methoxyphenylacetyl]-*O*-[(*S*)-α-methoxyphenylacetyl]-1-(1-cyclohexenyl)-2-aminoethanol (slow eluting diastereomer). (d) FT NMR spectrum of *N*-[(*S*)-α-methoxyphenylacetyl]-*O*-[(*S*)-α-methoxyphenylacetyl]-1-(1-cyclohexenyl)-2-aminoethanol (fast eluting diastereomer). (e) FT NMR spectrum of *N*-[(*S*)-α-methoxyphenylacetyl]-*O*-[(*S*)-α-methoxyphenylacetyl]-1-(1-cyclohexenyl)-2-aminoethanol (enzymatic product).

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