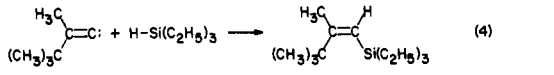
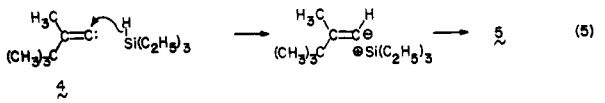
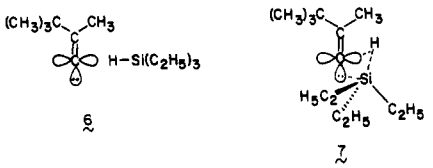
reaction trajectory of the reaction of a carbene with a silicon–hydrogen bond, our experimental results are consistent with the most recent theoretical efforts involving attack of carbenes on the carbon–hydrogen bond.[10]

Both Newman[6,7] and Stang[8] have reported that 2,3,3-trimethyl-1-butenylidene (4) reacts with triethylsilane to afford predominantly the *Z* isomer 5, the thermodynamically less stable product of Si–H insertion (eq 4). Newman[6] rationalized this result by proposing that the reaction proceeded by way of initial hydride abstraction on the sterically less hindered face of the carbene, followed by trapping of the vinyl anion, which is presumed to retain its initial conformation, by the triethylsilylenium ion (eq 5).[6] In the context of the present work, such a mechanism is rendered unlikely since, in our opinion, a colinear arrangement of the Si–H bond and the carbenic carbon atom might be expected, as shown by 6, and such a geometry at the rate-determining transition state for the reaction should produce a temperature-dependent isotope effect, according to Kwart's hypothesis.[2]





A more conventional mechanism for the insertion that accounts for the stereochemical outcome of eq 4 and for the temperature independence of the isotope effect involves a nonlinear transition state such as 7, in which the



substituents on the α-carbon atom of the carbene are oriented so as to minimize steric interactions. The plane defined by the carbon skeleton of the alkylidenecarbene can be at various angles relative to that defined by Et, Si, and H (the plane of the paper as shown for 7), but electronic considerations suggest an orientation that allows development of interaction between the electropositive silicon atom and the filled "sp"-hybrid orbital of the carbene at the transition state of the reaction. This same type of transition state has previously been proposed for the insertion of dichlorocarbene in the silicon–hydrogen bond.[11]

It is to be noted that the magnitude of the isotope effect measured in this work is in line with the values of 1.23 and 1.26 associated with the insertion of dichlorocarbene into the silicon-hydrogen bond of tri-*n*-butylsilane[12a] and methylphenylsilane,[12b] respectively. As reported earlier,[3] similarity in magnitudes also exists between the kinetic deuterium isotope effects for insertion of dichlorocarbene and of alkylidenecarbenes into carbon–hydrogen bonds.

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Experimental Section

IR spectra were recorded on a Beckman AccuLab 8 spectrophotometer, and the polystrene absorption at 1601 cm^{-1} was used as reference. Samples were run as liquid films between salt plates. ^1H NMR spectra were measured with a Varian Associates EM-390 spectrometer; chloroform-*d* was used as the solvent and Me_4Si served as the internal standard. GC–MS data were obtained with a Finnegan 4023 instrument having an INCOS data system; the ionizing voltage was 60 eV.

Triethylsilane-d_1 (3b). Chlorotriethylsilane was reduced in 62% yield by $LiAlD_4$, using a procedure modeled after that of Finholt et al.[13] The IR and ^1H NMR spectra were identical with those of a commercial sample of triethylsilane[14] except that the deuterated silane had a ^1H NMR spectrum devoid of the peak at the chemical shift for the proton bound to silicon and gave an IR spectrum containing an Si–D stretching band at 1120 cm^{-1} in lieu of the corresponding absorption at 2100 cm^{-1} in protio material: MS, *m/e* (relative intensity) 119 (M + 2, 3.3%), 118 (m + 1, 8.7%), 117 (M^+, 60.8%), 88 (M – C_2H_5, 99.5%); 60 (M – C_4H_{10}, 100%).

Reaction between Triethylsilane-d_x and 2-Methyl-1-propenylidene (2). Potassium *tert*-butoxide (0.273 g, 2.44 mmol) and anhydrous THF (2.5 mL) were combined in a round-bottomed flask equipped for magnetic stirring. The flask was purged with dry nitrogen and sealed with a rubber septum, and a solution of **3a** and **3b** (1.1 mL, 0.82 g, 6.9 mmol) was added. After the flask was placed in a bath held at either −78 or 21 °C, a solution of acetone (0.10 g, 1.7 mmol), dimethyl (diazomethyl)phosphonate (0.28 g, 1.9 mmol), and THF (1.0 mL) was added dropwise over 2 min. The resulting mixture was stirred for 3 h, with venting as needed to relieve pressure. Pentane (3 mL) was added, and the solution was washed with water (3 × 5 mL) and dried (Na_2SO_4). After concentration by rotary evaporation, the residue (ca. 1 mL) was analyzed by GC–MS.

The IR and ^1H NMR spectra of **3a**, prepared from triethylsilane by the above procedure and purified by gas chromatography (Varian A-90-P, 3 m × 0.25 in. column packed with 10% SE-30 on 30/60 mesh Chromosorb W, 110 °C, 55 mL/min helium), were identical with those reported.[7]

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Registry No. 1, 27491-70-9; 2, 26265-75-8; 3a, 18081-24-8; 3b, 96617-49-1; CH_3COCH_3, 67-64-1; Et_3SiH, 617-86-7; Et_3SiD, 1631-33-0; D_2, 7782-39-0; chlorotriethylsilane, 994-30-9.

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A Convenient Preparation of Dicarbonyl(η^5-cycloheptadienyl)(triphenyl phosphite)iron Tetrafluoroborate, a Potential Macrolide Antibiotic Precursor

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(Dienyl)$Fe(CO)_3$ cations occupy a prominent place as emerging synthetic intermediates,[2] largely due to their ready availability, low cost, and reactivity toward nucleo-

(1) Undergraduate research participant 1983.

(2) Reviews: Pearson, A. J. *Acc. Chem. Res.* **1980**, *13*, 463; Comprehensive Organometallic Chemistry; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Elmstord New York, 1982; Chapter 58; *Transition Met. Chem. (Weinheim, Ger.)* **1981**, *6*, 67; *Chem. Ind. (London)* **1982**, 741; *Pure Appl. Chem.* **1983**, *55*, 1767; *Science (Washington, DC)* **1984**, *223*, 895.

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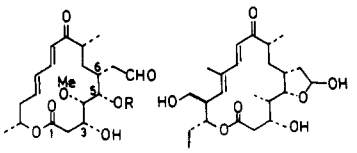
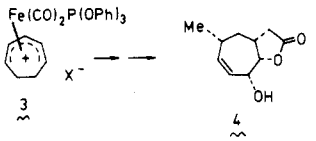
philes which allows the preparation of substituted dienes which can be further transformed into a variety of natural products. To date, most applications have involved the cyclohexadienyl derivatives. We are currently examining the application of (cycloheptadienyl)$Fe(CO)_2L$ cations to the stereocontrolled construction of acyclic fragments of the macrolide antibiotics magnamycin B (1) and aglycone tylonolide (2), and we recently showed that the triphenyl



1 R = Sugar 2

phosphite complex 3 can be converted in eight steps to the hydroxy lactone 4.[3] This compound has correct relative stereochemistry for C(5), C(6), and C(8) of magnamycin B, but opposite stereochemistry at C(4), and we fully anticipate that it can be efficiently converted to the right-hand segment of the macrolide.



3 4

Our original work utilized cycloheptadiene as a starting material for complex 3. While this is commercially available, its high cost precludes large-scale synthetic work, so we set out to utilize the inexpensive cycloheptatriene, readily converted to the tricarbonyliron derivative 5 by literature methods.[4] Pauson has previously reported low yields (27%) in converting 5 to the triphenylphosphine complexes (L = PPh_3) and, moreover, reported a failure to convert the product to the dienyl complexes by protonation.[5] Furthermore, a number of difficulties have been reported in the displacement of CO from 5 using trialkyl phosphites.[6] We reinvestigated this sequence using triphenylphosphite ligand, paying careful attention to reaction conditions.

Reaction of triene complex 5 with triphenyl phosphite in refluxing di-*n*-butyl ether was found to be highly dependent on dilution. At normal concentrations (ca. 10% w/v of 5) thermal ligand displacement occurred to give 6, which required extensive purification and was obtained in only 21% yield. Higher dilution of the reaction mixture led to better yields: 5% w/v of 5 gave 68% yield of 6, while 2% w/v of 5 gave 75% yield. These reactions were all reproducible. In contrast to the literature report[5] protonation of complex 6 proceeded smoothly to give the desired dienyl complex 3.

The effect of dilution on the ligand exchange reaction is most likely due to competing dimer formation owing to the presence of the uncomplexed double bond in 5, also reported[7] to be a side reaction during the preparation of 5. This is expected to be more important at high concentrations of 5, although we have not rigorously investigated this aspect.

5 L = CO
6 L = $P(OPh)_3$

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 1420 instrument and NMR spectra on a Varian XL 200. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Di-*n*-butyl ether was filtered through basic alumina to remove peroxides and degassed with a stream of nitrogen prior to use, and tetrahydrofuran was used as supplied. Combustion analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Preparation of Dicarbonyl(η^4-cycloheptatriene)(triphenyl phosphite)iron (6) (a) High Dilution. Triphenyl phosphite (2.94 g, 9.48 mmol) was dissolved in di-*n*-butyl ether (100 mL), and the stirred solution was heated under nitrogen at reflux temperature while a solution of tricarbonyl(cycloheptatriene)iron (5) (2.003 g, 8.63 mmol) in di-*n*-butyl ether (10 mL) was added dropwise. The solution was refluxed for 27 h (using oil bath at 145–150 °C as heat source) or until the reaction was complete by infrared analysis. The cooled mixture was filtered through Celite, and the pad was washed with di-*n*-butyl ether. Removal of solvent in vacuo followed by chromatography (neutral alumina, 40% diethyl ether in hexane) afforded pure complex 6 (3.332 g, 75%) as a yellow crystalline solid: mp 111.5–113.5 °C; IR (CCl_4) ν_{max} 2010, 1947, 1594 cm^{-1}; NMR ($CDCl_3$) δ 7.4–7.1 (15 H, Ar-H), 5.66 (1 H, br t, J = 7 Hz, 5-H), 5.03 (1 H, m, 6-H), 4.66 (2 H, m, 2-H and 3-H), 3.1 (1 H, m, 4-H), 2.8 (1 H, m, 1-H), 2.25 and 2.05 (1 H each, AB_q, J_{AB} = 20 Hz, 7-CH_2). Anal. Calcd for $C_{27}H_{23}FeO_5P$: C, 63.04; H, 4.47. Found: C, 63.3; H, 4.70.

(b) Intermediate Dilution. The procedure was as above but using triphenyl phosphite (0.735 g) and tricarbonyl(cycloheptatriene)iron (0.500 g) in di-*n*-butyl ether (10 mL). Workup and chromatography gave complex 6 (0.75 g, 68%).

(c) Low Dilution. Triphenyl phosphite (1.47 g) and complex 5 (1.00 g) were refluxed in di-*n*-butyl ether (10 mL) as above. Purification afforded 6 (0.46 g, 21%).

Conversion of 6 to Dicarbonyl(η^5-cycloheptadienyl)(triphenyl phosphite)iron Tetrafluoroborate (3). A solution of complex 6 (2.00 g, 3.89 mmol) in THF (ca. 4 mL) was added to degassed acetic anhydride (20 mL). The stirred solution was cooled to 0 °C, and aqueous tetrafluoroboric acid (48% w/v, 0.78 g, 4.26 mmol HBF_4) was added dropwise. After 30 min the solution was poured into stirred diethyl ether (300 mL) and the resulting precipitate was removed by filtration, washed with ether (3 × 50 mL), and dried in air to give complex 3 as a pale yellow solid, mp 152–154 °C (2.24 g, 95%). This complex was spectroscopically identical with that previously reported[3] and was produced in analytically pure form. Anal. Calcd for $C_{27}H_{24}FeO_5PBF_4$: C, 53.84; H, 3.99. Found: C, 54.10; H, 4.29.

Acknowledgment. We are grateful to the National Institutes of Health (GM 32114) for financial support of this research and to the National Science Foundation (CHE 80-24633) and National Institutes of Health (RR-01689) for grants toward the purchase of high-field NMR equipment.

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