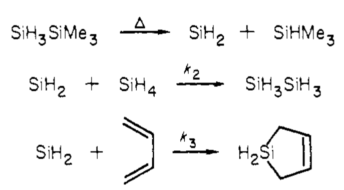
Scheme III



converter", does not significantly affect the reactivity ratio when present at mole fractions of 0.93 and 0.96. Nitric oxide, an efficient free radical scavenger, also has little effect, either in the presence or absence of argon moderator. Hence it is unlikely that intermediate X is reacting in an excited electronic state or in any triplet state. (4) The reactivity ratio also remains unaltered in the presence of trimethylamine, whose ionization potential is lower than that of atomic silicon.[13] Therefore X is probably not cationic.

That X of Scheme I is indeed $^{31}SiH_2$ has been established beyond doubt by reinvestigating the competition for thermally generated silylene. When the static pyrolysis carried out by Paquin and Ring (Scheme II)[10] was instead carried out in a single-pass flow system over a 75-deg temperature range from 385 to 460 °C, no variation in the ratio, k_1:k_2 was found, and the values observed,[14] 1.38 ± 0.05, 1.35 ± 0.05, and 1.40 ± 0.05, agreed well with the reactivity ratio 1.32 ± 0.04 found in the recoil experiments. Thus the product-forming intermediates in the recoil reactions display the same temperature-independent relative reactivity toward silane–methylsilane mixtures as thermally generated singlet SiH_2.[15]

Evidence has also been found indicating that nucleogenic SiH_2 is relaxed to the ambient temperature. In a second series of flow pyrolysis experiments silane and butadiene were allowed to compete for thermally generated SiH_2.[16]

A small but systematic and reproducible variation in the reactivity ratio k_2:k_3 from 1.37 ± 0.05 to 1.05 ± 0.05 over the temperature range 377–470 °C was observed.[17,18] An Arrhenius plot (Figure 2) is reasonably linear, with correlation coefficient 0.984, $E_a^2 - E_a^3 = -2.6 \pm 0.3$ kcal/mol[19] and $A_1/A_2 = 0.18 \pm 0.03$, and leads to an extrapolated value at room temperature of k_2:k_3 = 13 ± 4, which is similar to the reactivity ratio 9 ± 1 obtained in a recoil experiment.[9]

Thus at long last quantitative agreement has been found between the relative reactivity of an important product-forming intermediate formed from high-energy silicon atoms in mixtures containing labile hydrogen and ground-state singlet silylene. On the basis of this agreement the one can be identified with the other.

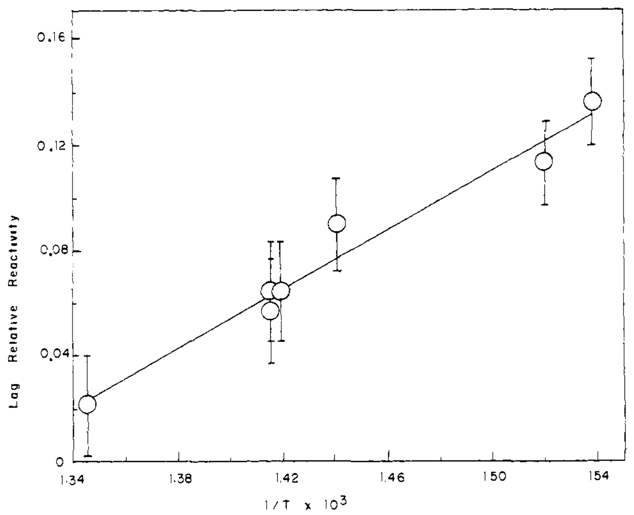


Figure 2. Temperature dependence of the relative reactivity of silane and butadiene toward thermally generated SiH_2, k_2:k_3, for the formation of SiH_3SiH_3 and 1-silacyclopent-3-ene in copyrolysis of mixtures of SiH_3SiMe_3, SiH_4, and butadiene.

It has furthermore been possible to measure, for the first time, the temperature of a polyatomic intermediate in a recoil reaction, and it was found that nucleogenic silylene reacts at its ambient temperature. Finally one must reject an earlier suggestion, based on a reduction of product yields in the presence of free radical scavenger, that nucleogenic silylene reacts principally in a triplet electronic state.[7] In the present experiments the *relative* reactivity is unaltered as product yields are decreased, and thus the effect of scavengers is on a species that appears earlier in the reaction sequence initiated by silicon atoms than the ultimate silylene intermediates.

Acknowledgment. This work received financial support from the United States Department of Energy. This is Technical Report COO-1713-111.

Registry No. ^{31}Si, 14276-49-4; $^{31}SiH_2$, 53971-28-1; SiH_4, 7803-62-5; SiH_3Me, 992-94-9; butadiene, 106-99-0.

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[12] The absolute yields of disilane and methyldisilane are reduced by 40–50% in these moderator experiments.

[13] Ionization potentials: Si, 8.151 eV, (Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K.; Field, F. H. "Ionization Potentials, Appearance Potentials, and Heats of Formation of Positive Ions" *NSRDS-NBS* **1969**, *26*, 162); Me_3N, 7.95 ± 0.10 eV (Rosenstock, H. M.; Sims, D.; Schroyer, S. S.; Webb, W. J. "Ion Energetics Measurements" *NSRDS-NBS* **1980**, *66* (Part I), 86).

[14] The flow pyrolyses were carried out at pressures of 15–25 torr and contact times of ca. 0.1 s. Reaction mixtures contained 0.65 mmol of SiH_3SiMe_3 and 23.5 mmol of SiH_4 + SiH_3Me, varying in ratio from 4:5 to 5:4, with 26–58% decomposition of SiH_3SiMe_3.

[15] There was already an indication in the photochemical experiments of Davidson that the selectivity of dimethylsilylene (:$SiMe_2$) toward Si–H insertion does not vary with temperature: Davidson, I. M. T.; Lawrence, F. T.; Ostah, N A. *J. Chem. Soc., Chem. Commun.* **1980**, 859.

[16] The reaction conditions were the same as those of ref 14, with reaction mixtures containing 0.65 mmol of SiH_3SiMe_3 and 26 mmol of SiH_4 + C_4H_6 in ratios from 3:5 to 3:2, with conversion of SiH_3SiMe_3 from 14% to 80%.

[17] It should be noted that this directly determined relative reactivity of silane and butadiene is in excellent agreement with a previous estimate based on an indirect comparison, footnote 42, ref 9.

[18] From results of shock tube experiments, a relative reactivity for butadiene and trimethylsilane of 1.0 ± 0.3 at 930 K has been estimated: Dzarnoski, J.; Rickborn, S. F.; O'Neal, H. E.; Ring, M. A. *Organometallics* **1982**, *1*, 1217.

[19] The higher activation energy for silacyclopentene formation is likely to be due to the rearrangement of an initial adduct, a vinylsilacyclopropane: Hwang, R.-J.; Conlin, R. T.; Gaspar, P. P. *J. Organomet. Chem.* **1975**, *94*, C38. The present results with SiH_3Me–SiH_4 mixtures suggest that the energy barrier for SiH_2 insertion into an Si–H bond is small; this has already been suggested for $SiMe_2$.[15]

Nickel-Promoted Thermal Dimerization of 1-Phenyl-3,4-dimethylphosphole: The First Synthesis of a Diphospholene

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Pursuing our interest[1-3] in the novel reactions of phospholes, we have investigated the thermolysis of 1-phenyl-3,4-dimethylphosphole in the presence of nickel(II) chloride. We have previously shown[3] that 1-phenylphospholes rearrange at high tem-

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[1] Santini, C. C.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 5809.

[2] Mathey, F.; Mercier, F.; Nief, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1982**, *104*, 2077.

[3] Mathey, F.; Mercier, F.; Charrier, C.; Fischer, J.; and Mitschler, A. *J. Am. Chem. Soc.* **1981**, *103*, 4595.

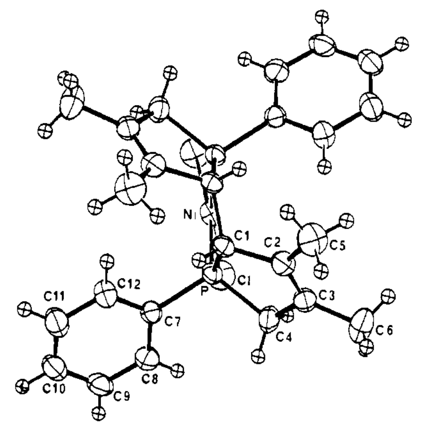
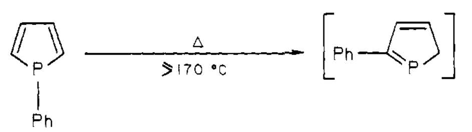
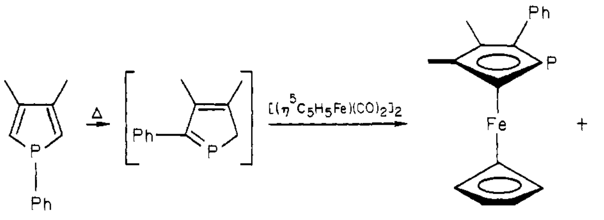


Figure 1. Structure of dichloro-2,2′-bis[1-phenyl-3,4-dimethylphosphol-3-ene]nickel(II) showing the 50% probability elipsoids. Selected bond distances (in Å): Ni–Cl, 2.201; Ni–P, 2.126; P–C_1, 1.852; P–C_4, 1.825; C_1–C_2, 1.528; C_2–C_3, 1.338; C_3–C_4, 1.517; C_1–C_1', 1.527.

perature through 1,5-phenyl migrations to give 2*H*-phospholes (reaction 1), and it has been possible to trap[3] one such 2*H*-phosphole by reaction with $[(\eta^5\text{-}C_5H_5Fe)(CO)_2]_2$ (reaction 2).

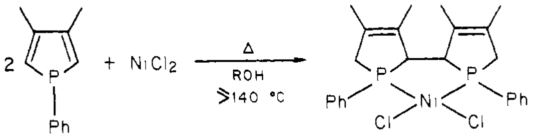


(1)



other products (2)

Thus, we hoped that at high temperatures the reaction of 1-phenylphospholes with metal halides would lead to new types of complexes instead of the classical[4] complexes obtained under standard conditions. We observed that thermolysis of 1-phenyl-3,4-dimethylphosphole with nickel(II) chloride in an alcohol solvent at temperatures between 140 and 170 °C produced an entirely new ligand complex, **1**, according to reaction 3. Heating a mixture of 20.46 g (0.1088 mol) of 1-phenyl-3,4-dimethylphosphole, 7 g (0.054 mol) of anhydrous nickel(II) chloride and 100 mL of cyclohexanol at 140 °C under nitrogen for 24 h afforded 8.03 g (29.3%) of $NiLCl_2$(l) as red crystals (dp 306–308 °C) after removal of the solvent under vacuum and recrystalization of the residue from $CHCl_3/CH_3OH$. This new complex was characterized by elemental analysis, ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^1H\{^{31}P\}$ NMR spectroscopy, infrared spectroscopy, mass spectrometry, and X-ray crystallography. The data follows. Anal. Calcd for $C_{24}H_{28}Cl_2NiP_2$: C, 56.74 H, 5.51; Ni, 11.56; Cl, 13.96; P, 12.20. Found: C, 55.84; H, 5.65; Ni, 10.58; Cl, 14.89; P, 11.52. ^1H NMR (100 MHz, $CDCl_3$, internal Me_4Si) δ 1.28 (s, 6, CH_3), 1.92 (s, 6, CH_3), 3.06, 3.67 ($^1H\{^{31}P\}$ AB quartet, 4, J_{HH} = 18 Hz, CH_2), 3.12 ($^1H\{^{31}P\}$ s, 2, CH), 7.45–7.90 (m, 10, Ph). $^{13}C\{^1H\}$ NMR (25 MHz, $CDCl_3$, internal Me_4Si) δ 14.1 (AA′X triplet, $|^3J_{PC} + {}^5J_{PC}|$ = 6.1 Hz, CH_3), 17.1 (AA′X triplet $|^3J_{PC} + {}^4J_{PC}|$ = 11 Hz, CH_3), 37.9 (AA′X triplet $|^1J_{PC} + {}^3J_{PC}|$ = 32.9 Hz, CH_2), 57.9 (AA′X triplet, $|^1J_{PC} + {}^2J_{PC}|$ = 51.3 Hz, CH), 128.7 (AA′X triplet, $|^3J_{PC} + {}^5J_{PC}|$ = 9.8 Hz, meta Ph), 129.2 (s, C_2), 129.6 (AA′X triplet $|^1J_{PC} + {}^3J_{PC}|$ = 43.8 Hz, PhC_1), 131.3 (s, C_3), 131.5 (s para Ph, 132.8 (AA′X triplet $|^2J_{PC} + {}^4J_{PC}|$ = 8.5 Hz ortho Ph). $^{31}P\{^1H\}$ NMR (40.26 MHz, $CDCl_3$, 85% H_3PO_4 external) δ 80.04. Mass spectrum (70 eV), *m/e* (relative intensity) 508 (2.5) M^+, 378(12), 266 (57), 189 (100) $L/2^+$. IR (polythene) 317, 341 cm^{-1} (ν_{NiCl}), 386, 404 cm^{-1} (ν_{NiP}); (KBr) 1660 cm^{-1} ($\nu_{C=C}$). Crystal data: space group $C_{2/C}$, a = 14.127 (5) Å, b = 9.611 (3) Å, c = 17.777 (6) Å, β = 106.81 (2)°, d_{calcd} = 1.455 g cm^{-3}, d_{obsd} = 1.43 ± 0.02 g cm^{-3}, Z = 4; 1486 unique reflections with $I > 3\sigma(I)$ were collected with a Phillips PW 1100/16 difractometer with use of Cu K$\bar{\alpha}$ (1.5418 Å) radiation. The structure was solved by heavy-atom methods (with anisotropic thermal parameters for all non-hydrogen atoms). At the present state of refinement,[5,6] R_F = 0.041 and R_{wF} = 0.078.



(3)

1

There are several notable features of the structure of **1** (Figure 1). The nickel atom deviates from square planarity only slightly with the dihedral angle between the ClNiCl and PNiP planes being 13.6°. This tetrahedral distortion is less than that observed[7] for *cis*-dichlorobis(1-benzyl-Δ^3-phospholene)nickel(II) (**2**) where the equivalent dihedral angle is 20.4°. Similarly, both the NiCl bond (2.201 Å) and the NiP bond (2.126 Å) are shorter in 1 than those found[7] for **2** NiCl (2.216 Å), NiP (2.155 Å).

Most interesting, however, is the fact that **1** is isolated exclusively as a racemic mixture of the *R,R* and *S,S* forms of the ligand with none of the *R,S* (meso) isomer being detected. This suggests that this thermal dimerization is surprisingly stereoselective.[8]

Diphospholenes have not been previously reported, and their directed synthesis would be expected to be difficult to achieve. Hence, reaction 3 is noteworthy on several counts. It proceeds in reasonable yield and gives a stereochemically pure compound from readily available starting materials.[9] The conformation of the chelate ring is rigid and contains four asymmetric centers. The phenyl rings are disposed so as to create a cleft approximately normal to a line joining the two phenyl rings. Hence, resolved[10] complexes of this ligand should coordinate to an olefin in a highly stereospecific manner. This type of substrate selectivity forms the basis[11] for presently successful asymmetric hydrogenations. We are at present investigating the synthesis of other metal complexes of this ligand and their optical resolution. This work along with details regarding the mechanism of this novel reaction (eq 3) will be reported elsewhere.

Acknowledgment. J.H.N. is grateful to UNR, the Fulbright Foundation, and CNRS for providing sabbatical leave funding for the period June 1981–July 1982 during which time some of this work was accomplished.

Registry No. 1, 88288-44-2; $NiCl_2$, 7718-54-9; 1-phenyl-3,4-dimethylphosphole, 30540-36-4.

Supplementary Material Available: Listings of atomic positional and thermal parameters, of interatomic distances and angles, and of observed and calculated structure factors (×10) (9 pages). Ordering information is given on any current masthead page.

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(4) Mathey, F.; Fischer, J.; Nelson, J. H. *Struct. Bonding* (*Berlin*) **1983**, 55, 153.

(5) $R = \sum(||F_o| - |F_c||)/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$, and $w = 1/\sigma^2F + 0.08F^2$.

(6) Tables of positional and thermal parameters are available as supplementary material.

(7) McPhail, A. T.; Komson, R. C.; Engel, J. F.; Quin, L. D. *J. Chem. Soc. Dalton Trans.* **1972**, 874.

(8) In a similar dimerization of 1-*tert*-butyl-3,4-dimethylphosphole, we detected a minor amount of the meso diastereomer in the crude product by $^{31}P\{^1H\}$ NMR spectroscopy. Thus, the stereoselectivity of this reaction is generally high but not complete.

(9) Breque, A; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983.

(10) We have attempted to achieve asymmetric induction in this synthesis by performing the reaction in *l*-menthol. However, racemic product was obtained. Thus, this reaction may not be very susceptible to asymmetric induction.

(11) Vineyard, B. D.; Knowles, W. S.; Sebacky, M. J.; Backman, G. L.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5946.