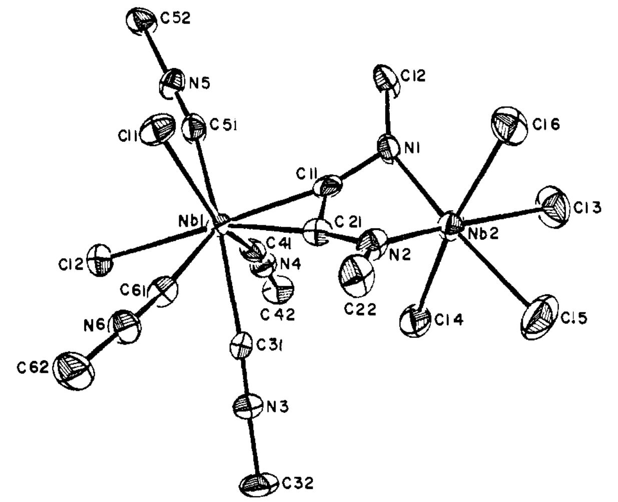

Figure 2. $Nb_2Cl_6(t\text{-}BuNC)_4(\mu\text{-}t\text{-}BuNCCN\text{-}t\text{-}Bu)$ molecule.

We think a reasonable hypothesis, beginning with $t\text{-}Bu—^{+}N{\equiv}C^{-}$: is that the two pairs of π electrons are used to form donor bonds to Nb(1) and Nb(2), in much the same way as alkynes form such RC≡CR to M-M bridging arrangements, while C(11) forms a strong donor bond to Nb(3). It is difficult to assign oxidation numbers unambiguously, and this problem is still under investigation. The compound in solution gives a well-resolved EPR spectrum (9.075 MHz) at room temperature consisting of a symmetrical decet $\langle g \rangle \approx 1.95$ and $\langle A \rangle \approx 130$ G. This is consistent with a spin doublet ground state with the unpaired electron localized on one niobium atom, Nb(3).

The structure and the proposed bonding scheme for **1** are analogous to those recently reported[14] in $Fe_3(CO)_9(CN\text{-}t\text{-}Bu)$, although in this carbonyl compound all metal atoms have 18-electron configurations, whereas in our compound they do not. Formally similar stereoelectronic character is found with a CO ligand in $(\eta^5\text{-}C_5H_5)_3Nb_3(CO)_7$[15] and with a CH_3CN ligand in $Fe_3(CO)_9(CH_3CN)$,[16] and compounds with $\mu^2\text{-}\eta^2$-RNC ligands are also relevant.[17]

Compound **2** contains molecules of the type shown in Figure 2. Again there is an approximate plane of symmetry, containing Cl(1), Cl(2), Nb(1), Nb(2), Cl(4), and Cl(6). In this case, there is a unique bridging ligand that has arisen by the coupling of two isocyanide molecules to form a new carbon-carbon bond; there is at least one prior example of such a coupling.[18] Nb(1) has a coordination number of 8, or 7 if the C(11)-C(21) unit is taken as a single ligand. In the latter case the coordination polyhedron is effectively a pentagonal bipyramid. At Nb(2) the coordination is effectively octahedral.

The bonding in the bridging ligand is uncertain: the average C-N distance, 1.35 [2] Å, and the C-C distance, 1.42 (2) Å, as well as planarity at the nitrogen atoms, suggest a delocalized π system with C-C and C-N bond orders exceeding 1.0. If this bridging ligand is regarded as forming two Nb(1)-C single bonds and two Nb(2)←N donor bonds, the niobium atoms would each be in oxidation state IV. Since the NMR spectrum shows that the molecule is diamagnetic,[19] this picture then needs to be supplemented by some means of pairing the two electrons thus left on the metal atoms. We assume that this occurs through the π system of the BuNCCNBu ligand that connects the two metal atoms. It cannot, of course, be ruled out that the oxidation states of the metal atoms should be assigned as III and V, whereby the diamagnetism could also be accounted for.

Acknowledgment. This work was supported by a grant from the Robert A. Welch Foundation.

Registry No. 1, 85552-55-2; **2**, 85533-79-5; $Nb_2Cl_6(Me_2S)_3$, 75038-66-3.

Supplementary Material Available: Tables of atomic positional and thermal parameters for both structures (8 pages). Ordering information is given on any current masthead page.

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[14] Bruce, M. I.; Hambley, T. W.; Nicholson, B. K. *J. Chem. Soc., Chem. Commun.* **1982**, 353.

[15] Herrmann, W. A.; Bierzack, H.; Ziegler, M. L.; Weidenhammer, K.; Siegel, R.; Rehder, D. *J. Am. Chem. Soc.* **1981**, *103*, 1692.

[16] Andrews, M. A.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7260.

[17] For an example, see: Adams, R. D.; Katahira, D. A.; Yang, L. *Organometallics* **1982**, *1*, 231.

[18] Giandomenico, C. M.; Lam, C. T.; Lippard, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 1263. In this case the coupling was explicitly reductive (Zn) and led to an η^2-RHNCCNHR unit bonded to Mo via the carbon atoms. In our case, the coupling may have been implicitly reductive since the product contains two Nb^{IV} while the starting material contained two Nb^{III}.

[19] The ^1H NMR also shows fluxionality, which is still under study.

A Nondegenerate Mirror-Image Rearrangement: Semibullvalene in the Solid State

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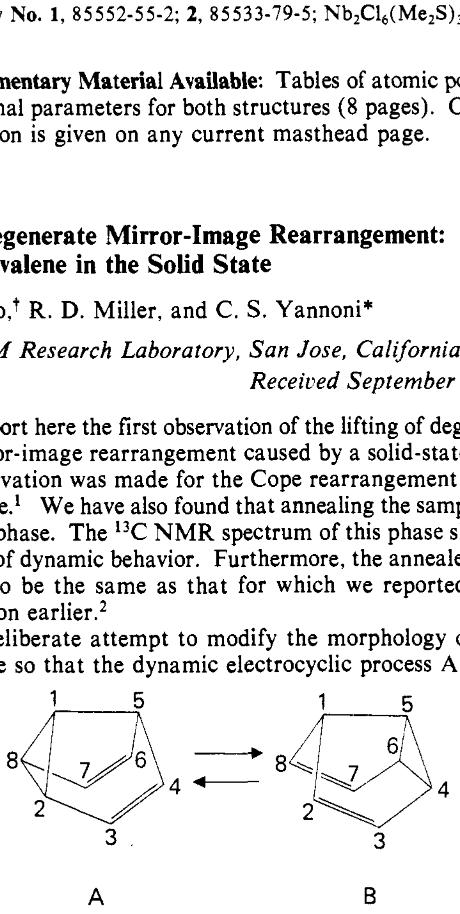
Received September 9, 1982

We report here the first observation of the lifting of degeneracy in a mirror-image rearrangement caused by a solid-state effect; this observation was made for the Cope rearrangement of semibullvalene.[1] We have also found that annealing the sample leads to a new phase. The ^{13}C NMR spectrum of this phase shows no evidence of dynamic behavior. Furthermore, the annealed phase appears to be the same as that for which we reported a rate suppression earlier.[2]

In a deliberate attempt to modify the morphology of semibullvalene so that the dynamic electrocyclic process A ⇌ B is observable in the solid state by ^{13}C NMR, we experimented with a number of rapid cooling techniques.[3,4] Spectra obtained from samples prepared by any of these methods are identical and are shown in Figure 1a as a function of temperature. At −185 °C, the classic five-line pattern characteristic of a nonrearranging semibullvalene (A or B) is observed.[1,2] Increase in temperature causes a broadening of the outer lines accompanied by a slight change in the corresponding chemical shifts. At −95 °C, the appearance of the spectrum has changed dramatically, and the individual aliphatic and vinylic carbon resonances have almost merged into two signals, one upfield and one downfield, respectively. This behavior is completely reversible with temperature. It is important to note that the solution-averaged spectrum (see arrows in Figure 1a) was never observed in the accessible temperature range.[5] This interesting spectral behavior can be ra-



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[1] Cheng, A. K.; Anet, F. A. L.; Mioduski, J.; Meinwald, J. *J. Am. Chem. Soc.* **1974**, *96*, 2887-2891.

[2] Miller, R. D.; Yannoni, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 7396-7397.

[3] Samples were prepared either by quenching a rotor containing ~250 mg of liquid semibullvalene (produced by photolysis of cyclooctatetraene: Turro, N. J.; Liu, J-M.; Zimmerman, H. E.; Factor, R. E. *J. Org. Chem.* **1980**, *45*, 3511-3512), in liquid nitrogen, or by gas-phase deposition under vacuum onto a liquid-nitrogen-cooled surface. In the latter method, the semibullvalene thus deposited was scraped from the cold surface and packed into a rotor at temperatures near 100 K by using previously described techniques.[4]

[4] (a) Myhre, P. C.; Yannoni, C. S. *J. Am. Chem. Soc.* **1981**, *103*, 230-232. (b) Yannoni, C. S.; Macho, V.; Myhre, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 907-909.

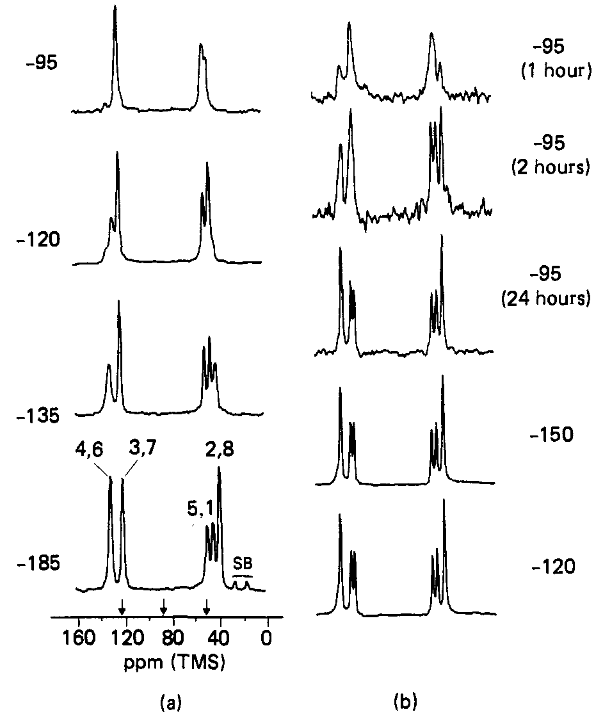

Figure 1. (a) ^{13}C CPMAS spectra of semibullvalene cooled into the solid state showing reversible dynamical behavior. The arrows show the position of the three resonances for the average spectrum obtained in solution.[1] The peaks marked SB are the upfield spinning side bands of the vinylic carbon resonances. (b) Spectra of the same sample during annealing at -95 °C. After annealing for several hours, the spectra no longer change with temperature cycling.

tionalized by considering a rapid Cope rearrangement that is no longer degenerate.[6] In this case, the lifting of degeneracy must be due to subtle perturbations caused by the nature of the solid sample. The resulting energy difference between the rearranging species then leads to a significant population imbalance. The dynamics of exchange between two sites with grossly unequal populations has been treated theoretically[6] and corresponds exactly to the behavior exhibited by the spectra in Figure 1a. In particular, significant spectral changes are expected to be readily observable only for those nuclei with large chemical shift differences. Thus, the chemical shift between the exchanging carbons 1 and 5 is too small to observe even initial line broadening. To obtain the kinetic parameters, a complete dynamic line-shape analysis[7] was performed as follows: both the ratio of the forward and backward reaction rates (k_1/k_{-1}) and the total rate ($k = k_1 + k_{-1}$) were varied independently for a spectrum at a sensitive temperature (-127 °C) until optimum agreement was achieved. The free-energy difference (ΔG°) between the potential minima of each species was then calculated according to the relationship

$$\Delta G^\circ = -RT \ln (k_1/k_{-1}) = -RT \ln (p_B/p_A) \qquad (1)$$

With use of this value, spectra obtained at other temperatures were simulated with k as the only free parameter, the relative populations being calculated according to (1). This entire procedure was then repeated for different values of ΔG° until all the spectra were fit satisfactorily (fits available as supplementary material), and the rate constants thus obtained showed the expected Arrhenius behavior. The values for k and k_{-1} at -132 °C are 486 and 8514 s^{-1}, respectively, and $\Delta G^\ddagger$ for the slow process at this temperature is 6.3 kcal mol^{-1}. The free-energy profile is shown in Figure 2. The rates corresponding to the higher barrier are approximately 10–20 times slower than those found in solution. Nonetheless, a simple Marcus treatment[8] of the above data using the solution value of $\Delta G^\ddagger$ = 5.5 kcal mol^{-1} (-133 °C) for the degenerate rearrangement of semibullvalene[1] suggests that the intrinsic barrier for the rearrangement in the solid state is remarkably close to the solution value.

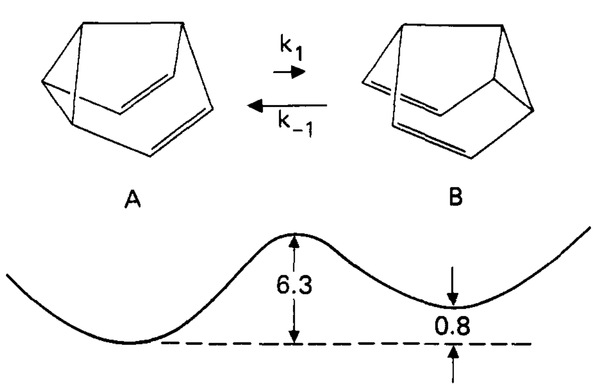

Figure 2. Free-energy profile (kilocalories per mole) for the nondegenerate Cope rearrangement of semibullvalene obtained from line-shape analysis of the ^{13}C CPMAS spectra shown in Figure 1a.

We have also observed that samples prepared by rapid cooling could be thermally annealed to produce a solid phase that shows no temperature dependence in the NMR spectra. After several hours at -95 °C, significant irreversible changes occurred in the sample as demonstrated by transformation of the spectrum (see Figure 1b). We believe that the annealed phase produced in this manner is the same as that for which we previously reported spectra.[2,9] The lack of spectral temperature dependence could mean either that (1) the free-energy difference between isomers in the annealed phase is increased significantly compared with the dynamic phase or (2) that the barrier has increased so much that the rearrangement is slow on the NMR time scale at all temperatures. The small splitting of the olefinic carbon peaks (C_3 and C_7) indicates that the molecular symmetry is broken in the annealed phase and furthermore suggests that the same forces that alter the potential surface for the Cope rearrangement are also responsible for this subtle perturbation of molecular electron distribution.[10] We hope to learn more about this from a low-temperature crystal structure.

In summary, we have demonstrated that solid-state morphology can have a significant influence on intramolecular rearrangements. In the case of semibullvalene, this effect is manifested as a perturbation of the equilibrium that results in a rate retardation without, however, a significant effect on the intrinsic barrier. Although it is not justifiable to assume on the basis of rigidity alone that the solid state will always retard the rate of intramolecular rearrangements,[11] the rate at a given temperature will probably be slower than in solution and a sensitive function of the physical nature of the sample (crystalline, amorphous).[2,12] Furthermore, as we have shown here, it may be possible to deliberately alter this behavior by manipulation of the sample morphology.

Acknowledgment. We acknowledge illuminating discussions with F. A. L. Anet concerning interpretation of the spectra in terms of nonsymmetric exchange dynamics. The skillful technical as-

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(5) Since the melting point of semibullvalene is ~-80 °C, the temperature was always kept below -95 °C to prevent the loss of partially melted material from the spinning rotor.

(6) Anet, F. A. L.; Basus, V. J. *J. Magn. Reson.* **1978**, *32*, 339–343. Akazawa, N.; Sorensen, T. S. *Can. J. Chem.* **1978**, *56*, 2737–2742.

(7) Saunders, M. In "Magnetic Resonance in Biological Systems"; Ehrenberg, A., Ed.; Pergamon Press: Oxford, 1967; p 85.

(8) (a) Marcus, R. A. *J. Phys. Chem.* **1963**, *67* 853; (b) *J. Chem. Phys.* **1963**, *38* 1858.

(9) The small sample size (~25 mg) used in our original experiments[2] required very long data acquisition times (42 h) at -110 °C, conditions that are conducive to annealing.

(10) Failure to observe this splitting in our original spectra was due to line broadening, probably caused by less-than-optimal adjustment of the magic angle spinning axis.

(11) In fact, for rearrangements with specific geometric requirements, where the reactive geometries are favored by crystal packing forces, rates could be considerably faster in the solid state than in solution.

(12) Shiau, W.-H.; Duesler, E. N.; Paul, I. C.; Curtin, D. Y.; Blann, W. G.; Fyfe, C. A. *J. Am. Chem. Soc.* **1980**, *102*, 4546–4547.

sistance of R. D. Kendrick was very helpful. The support of IBM Instruments, Inc., for a postdoctoral fellowship (V.M.) is gratefully acknowledged.

Registry No. Semibulvalene, 6909-37-1.

Supplementary Material Available: Comparison of experimental and simulated spectra (2 pages). Ordering information is given on any current masthead page.

Synthesis and Structure of an η^2-Phosphaalkene Nickel Complex

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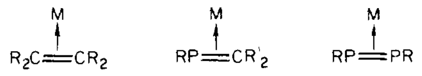
In principle, phosphaalkenes, $RP{=}CR'_2$, can function as η^1 (P donor) or η^2 (P=C π-donor) ligands toward transition metals. However, to date only η^1 behavior has been demonstrated, both for phosphaalkenes[1,2] and also for the isoelectronic molecules $RP{=}NR'$ and $RP{=}O$.[3,4] We now report the synthesis and structure and the first example of an η^2-bonded phosphaalkene complex (**2**), thus completing the series of complexes **1**-**3**.



$$\begin{array}{ccc} M & M & M \\ \uparrow & \uparrow & \uparrow \\ R_2C{=}CR_2 & RP{=}CR'_2 & RP{=}PR \end{array}$$

1[5] 2 3[6]

In a typical reaction, 0.314 g (1.1 mmol) of $(Me_3P)_2NiCl_2$[7] in 50 mL of *n*-hexane was treated with 16.5 mL of a 0.14 M ethereal solution of $\{[(Me_3Si)_2CH]_2P\}Na$.[8] Evacuation of the solvent from the resulting cobalt blue solution produced an oil of the same color. ^{31}P NMR assay of the crude product revealed the presence of $[(Me_3Si)_2CH]_2PH$ (s, δ 72.2)[10] together with a complex set of peaks between +23 and −19 ppm. The blue oil was dissolved in 5 mL of *n*-hexane, and the resulting solution was allowed to stand for 2 days at −20 °C. During this time the color of the solution changed gradually from blue to dark brown, and red-brown crystals were deposited. Two recrystallizations from *n*-hexane afforded pure $(Me_3P)_2Ni[(Me_3Si)_2CPC(H)(SiMe_3)_2]$ (**4**) as orange-red crystals suitable for X-ray diffraction studies.

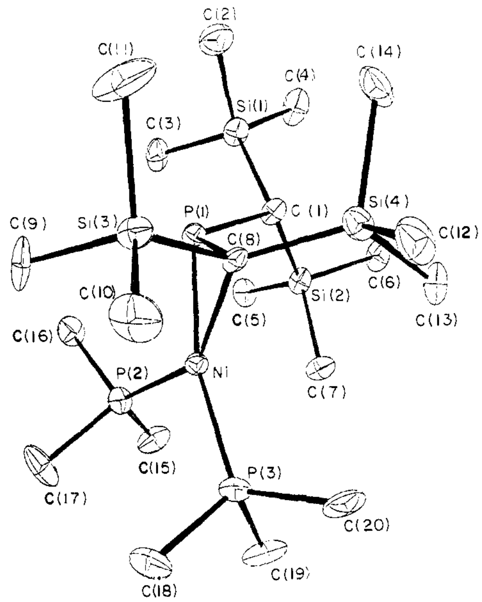


Figure 1. ORTEP view of $(Me_3P)_2Ni[(Me_3Si)_2CPC(H)(SiMe_3)_2]$ (**4**) showing the atom numbering scheme.

Table 1. Pertinent Bond Lengths (Å) and Bond Angles (deg) for $(Me_3P)_2Ni[(Me_3Si)_2CPC(H)(SiMe_3)_2]$ (4)

	Bond Lengths		
Ni-P(1)	2.239 (2)	P(1)-C(8)	1.773 (8)
Ni-P(2)	2.195 (3)	P(1)-C(1)	1.912 (8)
Ni-P(3)	2.202 (3)	C(8)-Si(3)	1.894 (8)
Ni-C(8)	2.020 (8)	C(8)-Si(4)	1.879 (8)
	Bond Angles		
P(1)-Ni-P(2)	99.9 (1)	C(1)-P(1)-C(8)	110.3 (4)
P(2)-Ni-P(3)	102.1 (1)	Ni-P(1)-C(8)	59.1 (3)
P(1)-Ni-C(8)	48.9 (2)	Ni-C(8)-P(1)	72.0 (3)
P(3)-Ni-C(8)	109.9 (2)	Si(3)-C(8)-Si(4)	113.8 (4)

The structure of **1** has been solved by single-crystal X-ray methods[11] and is illustrated in Figure 1 along with the atom numbering protocol. A summary of pertinent metric parameters appears in Table I. The solid state of **4** consists of isolated neutral molecules with no short intermolecular contacts. The geometry at nickel is square planar, deviation (angstroms) from planarity

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(1) (a) Hosseini, H. E.; Kroto, H. W.; Nixon, J. F.; Maah, M. J.; Taylor, M. J. *J. Chem. Soc., Chem. Commun.* **1981**, 199. (b) Kroto, H. W.; Nixon, J. F.; Taylor, M. J.; Frew, A. A.; Muir, K. W. *Polyhedron* **1982**, *1*, 89. (c) Kleback, T. C.; Lourens, R.; Bickelhaupt, F.; Stam, C. H.; Van Herk, A. *J. Organomet. Chem.* **1982**, *210*, 211.

(2) Side-on bonding is, however, known for phosphaalkynes. See: (a) Seyferth, D.; Henderson, R. S. *J. Organomet. Chem.* **1978**, *162*, C35. (b) Burckett-St. Laurent, J. C. T. R.; Hitchcock, P. B.; Kroto, H. W.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1141. (c) Burckett-St. Laurent, J. C. T. R.; Hitchcock, P. B.; Kroto, H. W.; Meidine, M. F.; Nixon, J. F. *J. Organomet. Chem.* **1982**, *238*, C82.

(3) Niecke, E.; Engelmann, M.; Zorn, H.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 710.

(4) Scherer, O. J.; Kuhn, N.; Jungmann, H. *Z. Naturforsch., B.* **1978**, *B33*, 1321.

(5) For a review of η^2-alkene complexes of nickel, see: Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel. Organonickel Complexes"; Academic Press: New York, 1974; Vol. I, Chapter 5, p 244.

(6) For η^2-diphosphene complexes, see: (a) Elmes, P. S.; Scudder, M. L.; West, B. O. *J. Organomet. Chem.* **1976**, *122*, 281. (b) Camillo, E.; Coda, A.; Prout, K.; Daran, J. C. *Acta Crystallogr. Sect. B.* **1977**, *B33*, 2608. (c) Deppisch, B.; Schäfer, H. *Ibid.* **1982**, *38*, 748. (d) Chatt, J.; Hitchcock, P. B.; Pidcock, A.; Warrens, P. W.; Dixon, K. R. *J. Chem. Soc., Chem. Commun.* **1982**, 932.

(7) Dahl, O. *Acta Chem. Scand.* **1969**, *23*, 2342.

(8) This solution can be made by treatment of a mixture of the phosphinyl radical $\{[(Me_3Si)_2CH]_2P\}\cdot$ and the corresponding dimer $[(Me_3Si)_2CH]_4P_2$ with an equimolar quantity of Na in *n*-hexane at 65 °C for 14 h.[9] However, recently we have learned from Professor Philip P. Power (personal communication) that the phosphide anion $\{[(Me_3Si)_2CH]_2P\}^-$ can be prepared more readily by treatment of $[(Me_3Si)_2CH]_2PCl$ with Li powder in Et_2O at 25 °C for 24 h. It is not possible to prepare the phosphide anion by deprotonation of $[(Me_3Si)_2CH]_2PH$, presumably because of steric effects.[10]

(9) Cowley, A. H.; Ebsworth, E. A. V.; Kemp, R. A.; Rankin, D. W. H.; Stewart, C. A. *Organometallics* **1982**, *1*, 1720.

(10) Cowley, A. H.; Kemp, R. A. *Inorg. Chem.* **1983**, *22*, 547.

(11) A single crystal of **4** with dimensions 0.35 × 0.35 × 0.10 mm was grown from *n*-hexane solution at −20 °C and sealed under dry nitrogen in a Lindemann capillary. Some crystal data for **4** are as follows: $C_{20}H_{55}NiP_3Si_4$, monoclinic, space group $P2_1/c$, $a = 8.742$ (6) Å, $b = 19.225$ (6) Å, $c = 20.111$ (8) Å, $\beta = 99.21$ (9)°, $U = 3336.5$ Å^3, $Z = 4$, and $D_c = 1.11$ g cm^{-3}. The final lattice parameters were determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta > 38°$) accurately centered on an Enraf-Nonius CAD-4 diffractometer. A total of 3523 symmetry-independent reflections was recorded (ω–2θ scans) to $2\theta_{max} = 40°$ by using graphite-monochromated Mo K$\bar{\alpha}$ X-radiation with $\bar{\lambda}$ 0.71069 Å. Standard reflections fluctuated within a range ±2% during data collection. The structure was solved by using direct methods (Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368). Full-matrix least-squares refinement using the SHELX system (Sheldrick, G. M. SHELX76) and 1492 reflections with $F_o \geq 2.0\sigma(F_o)$ led to a final $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.031$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.030$. For further details of the diffraction experiment, see: Holton, E.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, *45*.

(12) For example, the P–C bond length in Me_2PH is 1.848 Å. Nelson, R. *J. Chem. Phys.* **1963**, *39*, 2382.

0002-7863/83/1505-3737$01.50/0