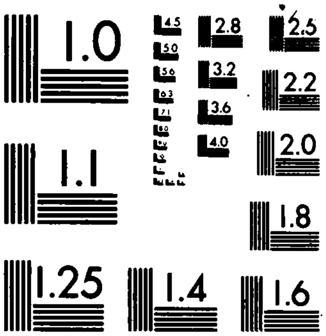
AD-A141 512   SUBSTITUTION AND ADDITION REACTIONS OF A   1/1
(METHYLENE)PHOSPHINE WITH ALKYLL..(U) TEXAS CHRISTIAN
UNIV FORT WORTH DEPT OF CHEMISTRY B L LI ET AL.
UNCLASSIFIED 18 MAY 84 TCU/DC/TR-84-04 N00014-79-C-0632 F/G 7/3 NL



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

12

OFFICE OF NAVAL RESEARCH

Contract No. N00014-79-C-0632

Task No. NR-053-720

TECHNICAL REPORT NO. TCU/DC/TR-84-04

Substitution and Addition Reactions of a (Methylene)phosphine with Alkyllithium Reagents

by

Bi-L. Li and R.H. Neilson

Prepared for Publication

in

Inorganic Chemistry

Texas Christian University
Chemistry Department
Fort Worth, TX 76129

May 18, 1984

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER
TCU/DC/TR-84-04

2. GOVT ACCESSION NO.
AD-A141512

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
Substitution and Addition Reactions of a (methylene)phosphine with Alkyllithium Reagents

5. TYPE OF REPORT & PERIOD COVERED
Technical Report, 1983

6. PERFORMING ORG. REPORT NUMBER
TR-84-04

7. AUTHOR(s)
Bi-L. Li and R.H. Neilson

8. CONTRACT OR GRANT NUMBER(s)
N00014-79-C-0632

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Texas Christian University
Fort Worth, Texas 76129

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
NR 053-720

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research

12. REPORT DATE
May 18, 1984

13. NUMBER OF PAGES
10

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)
Prepared for Publication in Inorganic Chemistry

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
(Methylene)phosphine
diphosphinomethane
trialkylphosphine
[bis(trimethylsilyl)methyl]phosphine

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Treatment of the (methylene)phosphine $(Me_3Si)_2NP{=}CHSiMe_3$ (1) with alkyllithium reagents and Me_3SiCl affords either the diphosphinomethane derivative $R_2P\text{-}CH(SiMe_3)\text{-}P(R)CH(SiMe_3)_2$ (2, R = Me) or the trialkylphosphine $R_2PCH(SiMe_3)_2$ (3, R = t-Bu). A reaction pathway involving both nucleophilic substitution and addition reactions at the P=C moiety is suggested. Compound 2 exhibits hindered rotation about the $P\text{-}CH(SiMe_3)_2$ bond with a measured $\Delta G_c^{\ddagger}$ of 17.7 kcal/mole.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

Substitution and Addition Reactions of a (Methylene)phosphine with Alkyllithium Reagents

Bei-Li Li and Robert H. Neilson*

Department of Chemistry
Texas Christian University
Fort Worth, Texas 76129

Abstract

Treatment of the (methylene)phosphine $(Me_3Si)_2NP{=}CHSiMe_3$ (1) with alkyllithium reagents and Me_3SiCl affords either the diphosphinomethane derivative $R_2P{-}CH(SiMe_3){-}P(R)CH(SiMe_3)_2$ (2, R = Me) or the trialkylphosphine $R_2PCH(SiMe_3)_2$ (3, R = t-Bu). A reaction pathway involving both nucleophilic substitution and addition reactions at the P=C moiety is suggested. Compound 2 exhibits hindered rotation about the $P{-}CH(SiMe_3)_2$ bond with a measured $\Delta G^{\ddagger}_{c}$ of 17.7 kcal/mole.

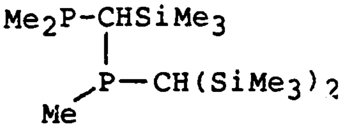
delta G+ sub c

Many recent reports have dealt with the preparative chemistry of (methylene)phosphines $RP{=}CR'_2$ as well as their structural and bonding characteristics.[1] Moreover, some relatively clear and consistent patterns of reactivity of such compounds are now emerging. The types of reactions of (methylene)phosphines reported thus far include: (1) addition of polar electrophilic reagents to the P=C bond[2], (2) oxidation to 3-coordinate P(V) derivatives[3], (3) complexation of transition metals to the phosphorus lone pair or to the P=C π bond[4], and (4) various cycloaddition processes such as Diels-Alder reactions.[5] In another general mode of reactivity, we find that these coordinatively unsaturated phosphorus compounds will also react smoothly with nucleophiles.[6] We report here some novel examples involving both substitution and addition reactions of a bis(trimethylsilyl)amino substituted (methylene)phosphine with alkyllithium reagents.

Treatment of [bis(trimethylsilyl)amino](trimethylsilylmethylene)phosphine[2c] **1** in Et_2O at -78°C with MeLi, followed by quenching with Me_3SiCl, does not yield the expected[7] phosphine $(Me_3Si)_2NP(Me)CH(SiMe_3)_2$. Instead, the reaction takes a much more complicated course, forming the novel diphosphinomethane derivative **2** (eq 1). The product **2** is isolated as a colorless liquid in 88% yield by fractional distillation. The characterization of **2** is based mainly on NMR data (Table I) with the AB pattern in the ^{31}P NMR spectrum being especially diagnostic. A satisfactory elemental analysis and the appropriate mass spectral fragmentation pattern were also obtained for **2**.

$$2\ (Me_3Si)_2NP{=}CHSiMe_3 \ + \ 3\ MeLi \ + \ 3\ Me_3SiCl \longrightarrow$$

1



$$Me_2P{-}CHSiMe_3 \ \big|\ MeP{-}CH(SiMe_3)_2 \ + \ 3\ LiCl \ + \ 2\ (Me_3Si)_3N \qquad (1)$$

2

Under similar conditions, the reaction of **1** with *t*-BuLi occurs in a 1:2 stoichiometry (eq 2) to afford the di(*t*-butyl)-phosphine **3** in 69% yield rather than a P-C-P product analogous to **2**.

$$(Me_3Si)_2NP{=}CHSiMe_3 \ + \ 2\ t\text{-}BuLi \ + \ 2\ Me_3SiCl \longrightarrow$$

1

$$(t\text{-}Bu)_2P{-}CH(SiMe_3)_2 \ + \ 2\ LiCl \ + \ (Me_3Si)_3N \qquad (2)$$

3

These remarkably clean reactions of the (methylene)phosphine **1** with alkyllithium reagents must involve both nucleophilic displacement of the bis(trimethylsilyl)amide group as well as addition across the P=C bond. The reaction pathway proposed in Scheme I is strongly suggested by the following experimental observations: (1) The byproduct $(Me_3Si)_3N$ can be isolated and identified by NMR, indicating that $(Me_3Si)_2NLi$ is indeed formed.[8]

Moreover, the ^{1}H NMR integration of the crude reaction product is consistent with the stoichiometry given by equation 1. (2) The use of 1:1 mole ratios of **1** to RLi yields only unreacted **1** in addition to products **2** or **3**. (3) The formation of **3** in the *t*-BuLi reaction rather than a product similar to **2** is consistent with increased steric hindrance at phosphorus in intermediates **A** and **B** when R = *t*-Bu. (4) When the reaction with MeLi is monitored by low-temperature ^{31}P NMR, the (methylene)phosphine intermediate **A** is not seen but an AB pattern (δ_A -1.8, δ_B -6.8, J_{AB} = 69.3 Hz) assignable to the diphosphorus anion **C** is clearly observed prior to the addition of Me_3SiCl.

A final point of interest concerns the ^{1}H and ^{13}C NMR spectra of the di(*t*-butyl)phosphine **3** which reveal non-equivalence of the *t*-Bu signals at room temperature. A high temperature ^{1}H NMR study shows that the two *t*-butyl doublets coalesce to a single doublet at 65°C (in C_6H_6 solution) indicating a barrier to rotation about the $P\text{-}CH(SiMe_3)_2$ bond of approximately 17.7 kcal/mole. The extreme steric hindrance caused by the bis(trimethylsilyl)methyl group in phosphorus (III) compounds has been previously noted.[9]

Experimental Section

Materials and General Procedures. The (methylene)phosphine **1** was prepared according to the published procedure.[2c] Alkyllithium reagents were used as received from commercial sources. Ether and hexane were distilled from CaH_2 prior to use.

Proton NMR spectra were recorded on a Varian EM-390 spectrometer; ^{13}C and ^{31}P, both with ^{1}H decoupling, were obtained on a JEOL FX-60 instrument. Mass spectral data were obtained on Finnigan OWA 1020 GC-MS system. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The procedures described below are typical of those which gave the best yields of compounds 2 and 3. Preliminary experiments using equimolar quantities of 1 and the alkyllithium reagents afforded the same products together with unreacted (methylene)phosphine.

Reaction of 1 with MeLi. Methyllithium (30 mmol, 21.5 mL, 1.4 M in Et_2O) was added at -78°C to a stirred solution of 1 (20 mmol, 5.6 g) in Et_2O (50 mL) to yield a light yellow precipitate, presumably anion C (Scheme I). After stirring the mixture for 2.5 h at -78°C, Me_3SiCl (30 mmol, 3.8 mL) was added and the mixture was allowed to warm to room temperature. After stirring overnight, Et_2O was removed under vacuum and hexane (20 mL) was added. The mixture was then filtered and the solvent and $(Me_3Si)_3N$ (identified by ^{1}H NMR) were removed under vacuum. Distillation through a short path column afforded compound 2 as a colorless liquid (3.1 g, 87% yield, bp 99-105°C/0.05 mm). Anal. Calcd: C, 47.73; H, 10.80. Found: C, 47.51; H, 10.77. Mass spectrum, m/e (relative intensity): 352 (2), 337 (9), 291 (22), 279 (6), 205 (4), 193 (10), 147 (14), 73 (100).

*Reaction of **1** with t-BuLi.* By means of a similar procedure, **1** (20 mmol) was treated with *t*-BuLi (40 mmol, 22.2 mL, 1.8 M in pentane) at -78°C in Et_2O (50 mL). After quenching with Me_3SiCl (40 mmol) and work-up as described above, distillation gave **3** as a colorless liquid (4.2 g, 69% yield, bp 82-83°C/0.15 mm). Anal. Calcd: C, 59.21; H, 12.17. Found: C, 59.08; H, 12.05. Mass spectrum, m/e (relative intensity): 304 (22), 289 (25), 248 (81), 159 (28), 145 (14), 73 (100).

Acknowledgment. We thank the U.S. Office of Naval Research and the Robert A. Welch Foundation for generous financial support.

References and Notes

(1) For a general review see: Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 731.

(2) (a) Kleback, T.C.; Lourens, R.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1978**, *100*, 4887.

(b) Issleib, K.; Schmidt, H.; Wirkner, Ch. *Z. Anorg. Allg. Chem.* **1981**, *473*, 85.

(c) Neilson, R.H. *Inorg. Chem.* **1981**, *20*, 1679.

(3) (a) Niecke, E.; Wildbredt, D.-A. *J. Chem. Soc., Chem. Commun.* **1981**, 72.

(b) Caira, M.; Neilson, R.H.; Watson, W.H.; Wisian-Neilson, P.; Xie, Z.-M. *J. Chem. Soc., Chem. Commun.*, in press.

(4) (a) Kroto, H.W.; Nixon, J.F.; Taylor, M.J.; Frew, A.A.; Muir, K. *Polyhedron* **1982**, *1*, 89.

(b) van der Knaap, Th. A.; Bickelhaupt, F.; van der Poel, H.; van Koten, G.; Stam, C.H. *J. Am. Chem. Soc.* **1982**, *104*, 1756.

(c) Cowley, A.H.; Jones, R.A.; Stewart, C.A.; Stuart, A.L. *J. Am. Chem. Soc.* **1983**, *105*, 3737.

(d) Al-Resayes, S.I.; Klein, S.I.; Kroto, H.W.; Meidine, M.F.; Nixon, J.F. *J. Chem. Soc., Chem. Commun.* **1983**, 930.

(e) van der Knaap, Th.A.; Jenneskens, L.W.; Meenwissen, H.J.; Bickelhaupt, F.; Walther, D.; Dinjus, E.; Uhlig, E.; Spek, A.L. *J. Organomet. Chem.* **1983**, *254*, C33.

(f) Neilson, R.H.; Thoma, R.J.; Vickovic, I.; Watson, W.H. *Organometallics*, submitted for publication.

(5) (a) Appel, R.; Korte, S.; Halstenberg, M.; Knach, F. *Chem. Ber.* **1982**, *115*, 3610.

(b) Meriem, A.; Majoral, J.-P.; Revel, M.; Navech, J. *Tettrahedron Lett.* **1983**, *24*, 1975.

(c) van der Knaap, Th. A.; Bickelhaupt, F. *Tetrahedron* **1983**, *38*, 3189.

(d) Appel, R.; Zimmermann, R. *Tetrahedron Lett.* **1983**, *24*, 3591.

(6) Nucleophilic displacement of chloride from P-Chloro substituted methylenephosphines is known:

(a) Appel, R.; Kundgen, U. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 219.

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

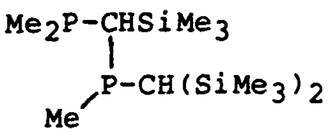
(c) Cowley, A.H.; Kilduff, J.E.; Pakulski, M.; Stewart, C.A. *J. Am. Chem. Soc.* **1983**, *105*, 1655.

(7) Addition of MeLi to the analogous iminophosphine $(Me_3Si)_2NP{=}NSiMe_3$ does yield the simple P-Me derivative: Cowley, A.H.; Kemp, R.A.; *J. Chem. Soc., Chem. Commun.* **1982**, 319.

(8) Displacement of the $(Me_3Si)_2N$ group from the analogous iminophosphine by very bulky organolithium compounds has recently been reported: Romanenko, V.D.; Ruben, A.V.; Markovski, L.N. *J. Chem. Soc., Chem. Commun.* **1983**, 187.

(9) Goldwhite, H.; Power, P.P. *Org. Magn. Res.* **1978**, *11*, 499.

Table I. NMR Spectroscopic Data[a]

compd	Signal	^1H δ	^1H J_{PH}	^{13}C δ	^{13}C J_{PC}	^{31}P δ
 2	Me_3SiC	0.14	1.0	2.56	5.4,	-23.7[b],
					1.8	-37.9
	$(Me_3Si)_2C$[c]	0.10	0.4	1.89	6.7	
				3.49	2.4	
	Me_2P[c]	1.15	4.8	[d]		
		1.16	4.2			
	MeP	1.30	6.0	[d]		
	Si_2CH	1.04	2.4	[d]		
	P_2CH	[e]		22.80	48.0,	
					33.3	
(t-Bu)$_2$P-CH(SiMe$_3$)$_2$ 3	Me_3Si[c]	0.12	0.2	2.48	11.0	47.6
		0.18		5.12		
	CH	1.15	13.5	28.67	55.6	
	Me_3C[c]	1.17	12.3	30.20	14.0	
		1.09	10.8	32.02	16.5	
	Me_3C[c]			30.95	30.5	
				32.42	17.1	

[a] Chemical shifts are downfield from Me_4Si for ^1H and ^{13}C spectra and from H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: ^1H, CH_2Cl_2; ^{13}C and ^{31}P, $CDCl_3$.

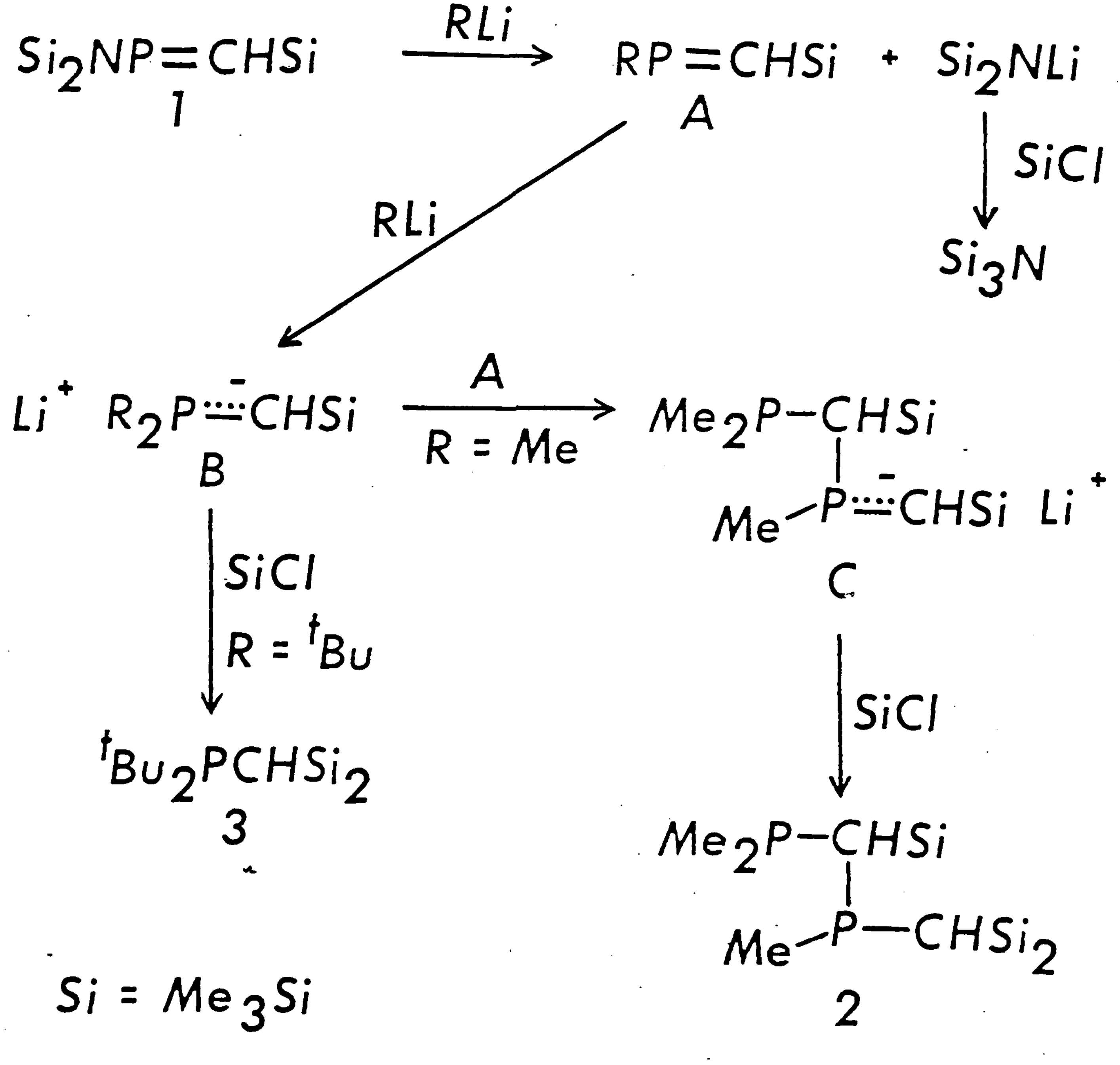
[b] AB pattern with J_{PP} = 95.2 Hz.

[c] Diastereotopic groups observed in ^1H and/or ^{13}C NMR spectra.

[d] Multiplet of ca. 16 overlapping peaks in range δ 9.8 - δ 15.1.

[e] Signals obscured by MeP resonances.

Scheme I


Si2NP=CHSi
1
RLi
RP=CHSi
A
+ Si2NLi
SiCl
Si3N
RLi
Li+ R2P⋯CHSi
B
A
R = Me
Me2P—CHSi
Me—P⋯CHSi Li+
C
SiCl
R = tBu
tBu2PCHSi2
3
SiCl
Me2P—CHSi
Me—P—CHSi2
2
Si = Me3Si

END

FILMED

DTIC