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Alkali-metal-catalyzed addition of primary and secondary phosphines to carbodiimides. A general and efficient route to substituted phosphaguanidines†

Wen-Xiong Zhang, Masayoshi Nishiura and Zhaomin Hou*

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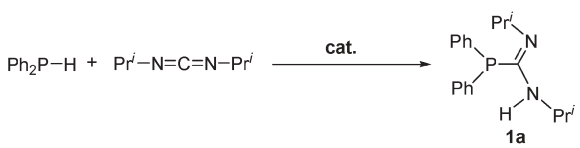
Organo alkali metal compounds such as ^{n}BuLi and $(Me_3Si)_2NK$ act as excellent catalyst precursors for the addition of phosphine P–H bonds to carbodiimides, offering a general and atom-economical route to substituted phosphaguanidines, with excellent tolerability to aromatic C–Br and C–Cl bonds.

Metal-catalyzed C–P bond formation reactions by P–H bond activation are among the most important transformations in synthetic organic chemistry.[1,2] Catalytic addition of phosphine R_2P–H bonds across the C–N double bond of carbodiimides (R′N=C=NR′) could be, in principle, a straightforward and atom-economical route to substituted phosphaguanidines R′N=C(PR_2)(NHR′), a class of heteroatom-containing compounds which may be used as building blocks for organic synthesis and as unique ligands for various metal complexes.[3] However, such catalytic process has been hardly explored. The synthesis of neutral phosphaguanidines was first reported in 1980.[4,5] Addition of diphenylphosphine to an *N*,*N*′-diaryl substituted carbodiimide such as *p*-MeC_6H_4N=C=NC_6H_4Me-*p* was reported to occur at elevated temperatures to afford the corresponding *N*,*N*′-diaryl substituted phosphaguanidine *p*-MeC_6H_4N=C(PPh_2)(NHC_6H_4Me-*p*).[4] However, *N*,*N*′-dialkyl or *N*-alky-*N*′-aryl substituted phosphaguanidines could not be obtained in this way because the less electrophilic *N*,*N*′-dialkyl or *N*-alky-*N*′-aryl carbodiimides could not accept nucleophilic attack of a phosphine. Silylated phosphaguanidines R′N=C{PR($SiMe_3$)}{N($SiMe_3$)R′} could be obtained by insertion of a carbodiimide into one of the P–Si bonds of bis-silylated phosphines, but depending on the nitrogen substituents, silyl-migration could occur to give the phosphaalkene derivatives RP=C{N($SiMe_3$)R′}$_2$.[5] Very recently, Coles and coworkers reported the synthesis of *N*,*N*′-dialkyl substituted phosphaguanidines R′N=C(PPh_2)(NHR′) (R′ = Cy, *i*-Pr) by nucleophilic addition of $LiPPh_2$ (generated *in-situ* from Ph_2PH and *n*-BuLi) to a stoichiometric amount of R′N=C=NR′, followed by protonolysis of the resultant lithium phosphaguanidinates [$Ph_2PC(NR'_2)$Li] with [$HNEt_3$][Cl].[3a] We report here a novel catalytic synthesis of phosphaguanidines by alkali-metal-catalyzed addition of phosphines to carbodiimides.[6–8] The commercially readily available alkali metal compounds such as $(Me_3Si)_2NM$ (M = Li, Na, K) and RLi (R = *n*-Bu, CH_2SiMe_3) can be used as excellent catalyst precursors. Aromatic C–Br and C–Cl bonds survived the reaction conditions. The alkali metal phosphaguanidinate species has been confirmed to be a true catalyst species.

As a control experiment, *N*,*N*′-diisopropylcarbodiimide was heated with diphenylphosphine in C_6D_5Cl at 140 °C, but no reaction was observed in 12 h (Table 1, entry 1). In contrast, addition of a small amount of an organo alkali metal compound such as $(Me_3Si)_2NM$ (M = Li, Na, K) or RLi (R = *n*-Bu, CH_2SiMe_3) resulted in rapid reaction to give the corresponding phosphaguanidine **1a** at room temperature (Table 1).‡ THF seemed to be a better solvent than benzene or toluene (Table 1, entries 2–4). Among $(Me_3Si)_2NM$ (M = Li, Na, K), the activity increased as the metal size becomes larger (K > Na > Li) (Table 1, entries 2, 7, 8). Thus, in the presence of 1 mol% of $(Me_3Si)_2NK$, the reaction of Ph_2PH with ^iPrN=C=N^iPr yield **1a** quantitatively at room temperature in less than 5 min (Table 1, entries 9–11).

Table 2 summarizes some representative results of the $(Me_3Si)_2NM$-catalyzed reactions between phosphines and carbodiimides having various substituents. In the presence of 1 mol% of $(Me_3Si)_2NK$, the reaction of Ph_2PH with carbodiimides having *N*,*N*′-diaryl, *N*-aryl-*N*′-alkyl, and *N*,*N*′-dialkyl substituents was completed at room temperature within 5 min to yield the

Table 1 Alkali-metal-catalyzed addition of diphenylphosphine to *N*,*N*′-diisopropylcarbodiimide[a]



Entry	**Cat.** (mol%)	Solvent	Temp (°C)	Time (min)	Conv[b] (%)
1	—	C_6D_5Cl	140	720	**1a** (0)
2	$(Me_3Si)_2NLi$ (3)	C_6D_6	r.t.	40	**1a** (>99)
3	$(Me_3Si)_2NLi$ (3)	THF-d_8	r.t.	15	**1a** (>99)
4	$(Me_3Si)_2NLi$ (3)	toluene-d_8	r.t.	45	**1a** (>99)
5	*n*-BuLi (3)	C_6D_6	r.t.	40	**1a** (>99)
6	$(Me_3Si)CH_2Li$ (3)	C_6D_6	r.t.	40	**1a** (>99)
7	$(Me_3Si)_2NNa$ (3)	C_6D_6	r.t.	10	**1a** (>99)
8	$(Me_3Si)_2NK$ (3)	C_6D_6	r.t.	<5	**1a** (>99)
9	$(Me_3Si)_2NK$ (1)	C_6D_6	r.t.	<5	**1a** (>99)
10	$(Me_3Si)_2NK$ (1)	THF-d_8	r.t.	<5	**1a** (>99)
11	$(Me_3Si)_2NK$ (1)	toluene-d_8	r.t.	<5	**1a** (>99)

[a] Conditions: diphenylphosphine, 0.60 mmol; diisopropylcarbodiimide, 0.60 mmol. [b] Conversion determined by ^{31}P NMR.

Organometallic Chemistry Laboratory, RIKEN (The Institute of Physical and Chemical Research), Hirosawa 2-1, Wako, Saitama 351-0198, Japan. E-mail: houz@riken.jp; Fax: 81 48 462 4665; Tel: 81 48 467 9393

† Electronic supplementary information (ESI) available: experimental details, X-ray data for **2**, and scanned NMR spectra of all new products. See DOI: 10.1039/b609198a

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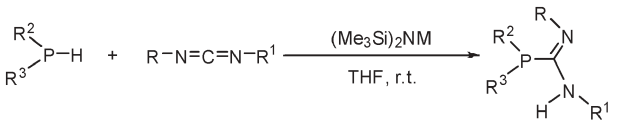
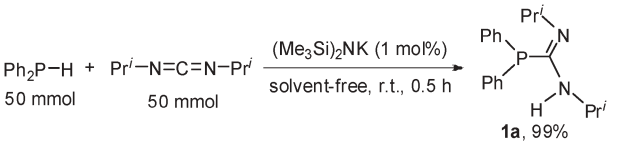
Table 2 Catalytic addition of phosphines to carbodiimides[a]



Entry	R^2R^3PH	R, R^1	M (mol%)	Time	Yield[b] (%)
1	Ph_2PH	*i*-Pr	K (1)	5 min	**1a** (99)
2	Ph_2PH	Cy	K (1)	5 min	**1b** (99)
3	Ph_2PH	*t*-Bu, Et	K (1)	5 min	**1c** (98)
4	Ph_2PH	Ph, Cy	K (1)	5 min	**1d** (99)
5	Ph_2PH	*p*-tolyl	K (1)	5 min	**1e** (99)
6	$(2\text{-}MeC_6H_4)_2PH$	*i*-Pr	K (1)	5 min	**1f** (99)
7	$(3\text{-}MeC_6H_4)_2PH$	*i*-Pr	K (1)	5 min	**1g** (99)
8	$(4\text{-}MeC_6H_4)_2PH$	*i*-Pr	K (1)	5 min	**1h** (99)
9	$(3,5\text{-}Me_2C_6H_3)_2PH$	*i*-Pr	K (1)	5 min	**1i** (98)
10	$(4\text{-}MeOC_6H_4)_2PH$	*i*-Pr	K (1)	5 min	**1j** (99)
11	$(4\text{-}ClC_6H_4)_2PH$	*i*-Pr	K (1)	5 min	**1k** (98)
12	$(3,5\text{-}Cl_2C_6H_3)_2PH$	*i*-Pr	K (1)	5 min	**1l** (98)
13	$(4\text{-}BrC_6H_4)_2PH$	*i*-Pr	K (1)	5 min	**1m** (97)
14	PhEtPH	*i*-Pr	K (3)	4 h	**1n** (96)
15	PhEtPH	*i*-Pr	Li (3)	24 h	**1n** (0)
16	PhEtPH	*i*-Pr	Li (3)	8 h	**1n** (90)[c]
17	$(i\text{-}Bu)_2PH$	*i*-Pr	K (3)	12 h	**1o** (95)
18	$(i\text{-}Bu)_2PH$	*i*-Pr	Li (3)	24 h	**1o** (0)
19	$(i\text{-}Bu)_2PH$	*i*-Pr	Li (3)	48 h	**1o** (25)[d]
20	$PhPH_2$	*i*-Pr	K (1)	1 h	**1p** (97)
21	$CyPH_2$	*i*-Pr	K (1)	1 h	**1q** (80)[e]

[a] Conditions: phosphine, 2.02 mmol; carbodiimide, 2.00 mmol; catalyst, 0.02 mmol; solvent, 5 mL, unless otherwise noted. [b] Isolated yield. [c] Toluene, 110 °C. [d] THF, 110 °C; conversion determined by ^{31}P NMR. [e] $(^iPrN{=}CNH^iPr)_2(PCy)$ (15%, determined by ^{31}P NMR) was also observed.

corresponding substituted phosphaguanidines quantitatively (Table 2, entries 1–5). A wide range of diarylphosphines could be used as the nucleophiles. The reaction was not affected by either electron-withdrawing or -donating substituents or their positions at the phenyl ring of the phosphines (Table 2, entries 6–13). Aromatic C–Cl (entries 11 and 12) and C–Br (entry 13) bonds survived the catalytic conditions to yield selectively the corresponding halogen-substituted phosphaguanidines **1k–m**, a new class of phosphaguanidine building blocks that could be useful for construction of further larger phosphaguanidine derivatives. It is also noteworthy that such halogen-tolerance was also observed even when *n*-BuLi was used as a catalyst. This is in sharp contrast with the stoichiometric reactions between $(4\text{-}XC_6H_4)_2PH$/*n*-BuLi and $^iPrN{=}C{=}N^iPr$, which yielded a mixture of the X-containing phosphaguanidines and the X-free phosphaguanidines (X = Cl, Br) after protonolysis with $[HNEt_3][Cl]$. The reaction of an alkyl/aryl phosphine such as ethylphenylphosphine (entry 14) or a dialkyl phosphine such as diisobutylphosphine (entry 17) with $^iPrN{=}C{=}N^iPr$ required a longer time for completion, probably owing to the weaker acidity of these phosphines compared to that of diaryl phosphines. The reaction of $PhPH_2$ with $^iPrN{=}C{=}N^iPr$ afforded selectively the mono-addition product $^iPrN{=}C(PHPh)(NH^iPr)$ (**1p**) (entry 20), while in the case of $CyPH_2$, the bis-addition product $(^iPrN{=}CNH^iPr)_2(PCy)$ was also obtained as a minor product (15%) in addition to the mono-addition product $^iPrN{=}C(PHCy)(NH^iPr)$ (**1q**, 80%) (entry 21). In most of the above reactions, the resulting phosphaguanidine



Scheme 1 Catalytic addition of diphenylphosphine to *N,N′*-diisopropylcarbodiimide under a solvent-free condition.

products could be isolated in excellent yields by a single recrystallization.

The present catalytic reaction could also be carried out under a solvent-free condition on a larger preparative scale, demonstrating well its practical usefulness. For example, addition of 1 mol% of $(Me_3Si)_2NK$ to Ph_2PH (50 mmol) and $^iPrN{=}C{=}N^iPr$ (50 mmol) at room temperature yielded $^iPrN{=}C(PPh_2)(NH^iPr)$ (**1a**) quantitatively in 30 min (Scheme 1).

In a 1 : 1 : 1 reaction of $(Me_3Si)_2NK$, Ph_2PH, and CyN=C=NCy, the potassium phosphaguanidinate complex $[Ph_2PC(NCy)_2K(OEt_2)]_2$ (**2**) was isolated quantitatively from a diethyl ether solution and confirmed by an X-ray diffraction analysis.§ There is a crystallographic inversion centre in **2**. Complex **2** adopts an "inverse sandwich" dimeric structure, in which the two K atoms are bridged by two coplanar guanidinate units in a $\mu\text{-}\eta^2,\eta^2$-fashion through the nitrogen atoms (Fig. 1). This coordination mode is in contrast with that observed in a lithium analogue,[3b] and as far as we are aware, has not been reported previously for a phosphaguanidinate unit.[9] Addition of 2 molar equiv. of Ph_2PH to a THF solution of **2** yielded **1b** and $KPPh_2$ quantitatively.

A possible mechanism for the present catalytic reaction could be proposed as shown in Scheme 2. The acid–base reaction between $(Me_3Si)_2NK$ and a phosphine P–H bond should yield straightforwardly a phosphide species such as **A**. Nucleophilic addition of the phosphide species to a carbodiimide would afford the phosphaguanidinate species **B**, which on abstraction of a proton from another molecule of phosphine would yield the phosphaguanidine product **1** and regenerate the phosphide **A**. The isolation of **2** and its reaction with Ph_2PH to give **1b** and $KPPh_2$ strongly support this mechanism.

In summary, we have demonstrated that alkali metal compounds such as $(Me_3Si)_2NK$ can act as an excellent catalyst precursor for the addition of various phosphine P–H bonds to carbodiimides, which offers the first general and atom-economical

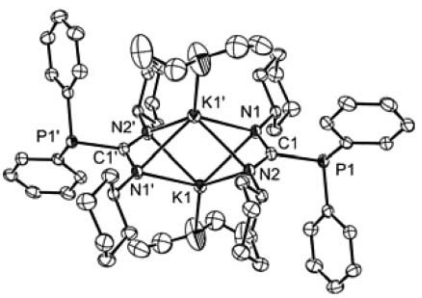


Fig. 1 ORTEP drawing of **2** (ellipsoids drawn at the 50% probability level; hydrogen atoms omitted for clarity). Selected bond length (Å): K(1)–N(1) 2.891(2), K(1)–N(2) 2.759(2), K(1)–N(1′) 2.857(2), K(1)–N(2′) 2.788(2), N(1)–C(1) 1.331(3), N(2)–C(1) 1.319(3). $' = -x, -y, -z$.

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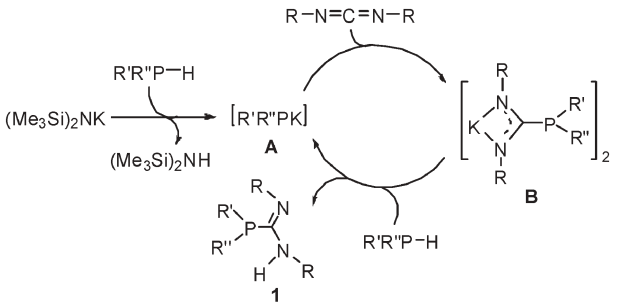

Scheme 2 A possible mechanism of catalytic addition of phosphines to carbodiimides.

route to substituted phosphaguanidines, with excellent tolerability to aromatic carbon–halogen bonds. In addition, this catalytic process is very clean and can also be carried out under solvent-free conditions, showing high potential of practical use.

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Notes and references

‡ **A typical procedure for the preparation of phosphaguanidines 1 by use of $(Me_3Si)_2NK$ as a catalyst**. Under a dry and oxygen-free argon atmosphere, a THF solution (3 mL) of diphenylphosphine (376 mg, 2.02 mmol) was added to a THF solution (2 mL) of $(Me_3Si)_2NK$ (4 mg, 0.02 mmol) in a Schlenk tube. Then *N*,*N*′-diisopropylcarbodiimide (252 mg, 2.00 mmol) was added to the above reaction mixture. After 5 min of stirring, the solvent was removed under reduced pressure. The residue was extracted with hexane and filtered to give a clean solution. After removal of the solvent under vacuum, the residue was recrystallized in hexane to provide a colorless solid **1a**. It should be noted that this type of phosphaguanidine is very sensitive to oxygen, and must be stored under an inert atmosphere. IR (Nujol): ν = 3431 (N–H), 1599 (C=N), 1462, 1377, 1173, 1026, 743, 696 cm^{-1}; ^1H NMR (300 MHz, C_6D_6): δ = 0.94 (d, J = 6.6 Hz, 6H, $CH(CH_3)_2$), 1.23 (d, J = 6.3 Hz, 6H, $CH(CH_3)_2$), 3.63 (d, ^3J = 6.3 Hz, 1H, NH), 4.28–4.43 (m, 2H, CH), 7.03–7.05 (m, 6H, C_6H_5), 7.42–7.47 (m, 4H, C_6H_5); ^{13}C NMR (75 MHz, C_6D_6): δ = 22.5, 25.3, 42.9, 52.2 (d, $^3J_{PC}$ = 35.3 Hz), 129.0 (d, $^3J_{PC}$ = 6.8 Hz), 129.3, 134.3 (d, $^2J_{PC}$ = 19.8 Hz), 135.5 (d, $^1J_{PC}$ = 13.7 Hz), 152.4 (d, $^1J_{PC}$ = 31.6 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, C_6D_6): δ = −18.5; HRMS Calcd for $[M + H]^+$ $C_{19}H_{26}N_2P$ 313.1834; Found 313.1853.

Isolation of the potassium phosphaguanidinate $[Ph_2PC(NCy)_2K(OEt_2)]_2$ (2). Under a dry and oxygen-free argon atmosphere, a THF solution (3 mL) of diphenylphosphine (372 mg, 2.00 mmol) was added to a THF solution (5 mL) of $(Me_3Si)_2NK$ (399 mg, 2.00 mmol) in a Schlenk tube. Then *N*,*N*′-dicyclohexylcarbodiimide (413 mg, 2.00 mmol) was added to the above reaction mixture. After 1 h of stirring, the solvent was removed under reduced pressure. The residue was extracted with ether and filtered to give a clean solution. The solution volume was reduced under vacuum to precipitate **2** as light yellow crystalline powder (969 mg, 0.96 mmol, 96% yield). Single crystals of **2** suitable for X-ray analysis were grown in ether at room temperature overnight. IR (Nujol): ν = 2122, 1582, 1471, 1377, 1339, 1076, 979, 740 cm^{-1}; ^1H NMR (400 MHz, C_6D_6): δ = 1.01 (t, J = 7.2 Hz, 12H, $(CH_3CH_2)_2O$), 1.21–1.86 (br, 40H, CH_2(Cy)), 3.11–3.16 (m, 4H, CH(Cy)), 3.28 (q, J = 7.2 Hz, 8H, $(CH_3CH_2)_2O$), 6.76–6.80 (m, 4H, C_6H_5), 7.03–7.09 (m, 8H, C_6H_5), 7.65 (br, 8H, C_6H_5); ^{13}C NMR (100 MHz, C_6D_6): δ = 15.8, 25.0, 26.0, 35.5, 55.8, 66.0, 129.0 (d, $^3J_{PC}$ = 6.6 Hz), 129.3, 134.3 (d, $^1J_{PC}$ = 18.9 Hz), 135.9 (d, $^2J_{PC}$ = 16.5 Hz), 139.8 (d, $^1J_{PC}$ = 34.6 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, C_6D_6): δ = −14.8, −18.0, −20.6; Anal. Calcd for $C_{58}H_{84}K_2N_4O_2P_2$: C, 69.01; H, 8.39; N, 5.55; Found: C, 68.96; H, 8.18; N, 5.38%.

§ Cryatal data for **2**: $C_{58}H_{84}K_2N_4O_2P_2$, M_w = 1009.43 g mol^{-1}, T = 173(1) K, Monoclinic, space group $P2(1)/c$, a = 11.1009(12), b = 19.529(2), c = 14.3917(15) Å, α = 90, β = 112.539(2), γ = 90°, V = 2881.6(5) $Å^3$, Z = 2, ρ_{calcd} = 1.163 Mg m^{-3}, μ = 0.263 mm^{-1}, reflections collected: 14823, independent reflections: 5091 (R_{int} = 0.0259), Final R indices [$I > 2\sigma I$]: R_1 = 0.0539, wR_2 = 0.1626, R indices (all data): R_1 = 0.0689, wR_2 = 0.1716. The unique coordinated ether molecule has its CH_2 groups disordered equally over two sites (only one of which is shown in Fig. 1). No allowance was made for the ether H atoms. CCDC 606651. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b609198a

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