Heteroatom Chemistry
Volume 00, Number 0, 2012

Control of Reactivity of Phosphine Imides by Intramolecular Coordination with an Organoboryl Group

Naokazu Kano, Kazuhide Yanaizumi, Xiangtai Meng, and Takayuki Kawashima

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Received 29 March 2012; revised 11 May 2012

ABSTRACT: *Phosphine imides with a boryl substituent* **3–5** *were synthesized. Their structures were revealed to have a tetracoordinated boron and a phosphorus atom, featuring the N–B coordination by X-ray crystallographic analysis and NMR spectroscopy. The phosphine imide moiety was persistent to hydrolysis, methylation, and the aza-Wittig reaction. The N–B coordination remained intact upon treating with pyridine or fluoride ion.* © 2012 Wiley Periodicals, Inc. Heteroatom Chem 00:1–6, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21033

INTRODUCTION

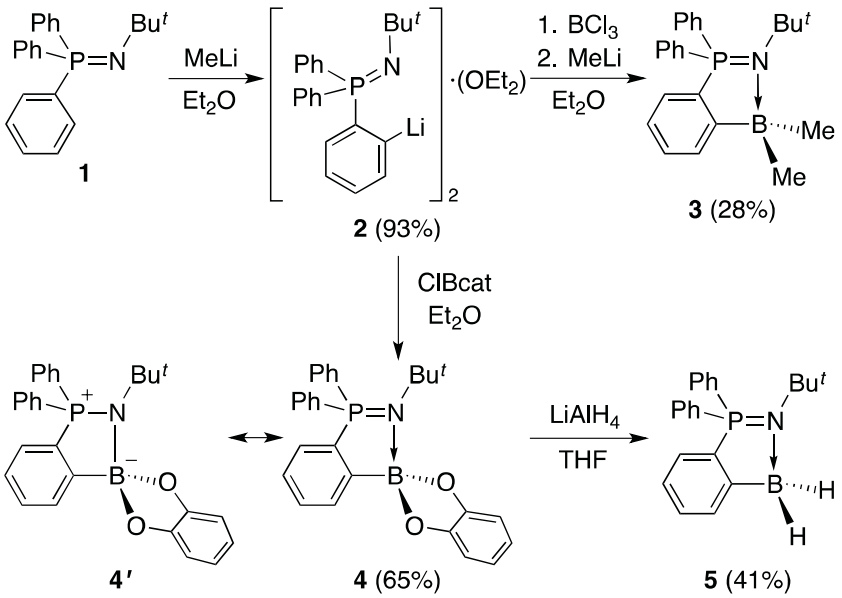
A phosphine imide, a nitrogen analogue of a phosphorus ylide, is important as a reagent for the aza-Wittig reaction [1] and as an intermediate of the Staudinger reaction [2] and the Staudinger ligation [3]. Reactivity of the phosphine imide heavily depends on the degree of polarization of the P^+–N^- bond, which sometimes causes instability against hydrolysis [4]. Stabilization of the phosphine imide is necessary for its utilization for the reactions under various conditions. One stabilization method to avoid undesired reactions is to use bulky substituents or electronically perturbing substituents on the phosphorus and/or the nitrogen atoms, and another method is to lower reactivities by coordination of the lone pair of the nitrogen atom to another atom such as a transition metal [5]. Considering that some reactions such as the hydrolysis of the phosphine imide are triggered by an interaction of the nitrogen atom with a reagent, strong N–B coordination of the nitrogen to a Lewis acid such as an organoborane, which shows high Lewis acidity due to its vacant 2p-orbital, would inhibit both interactions with a reagent and subsequent undesired reactions such as hydrolysis. Although there have been only a few examples of phosphine imides with the N–B coordination [6], perturbation of their stability and reactivity caused by the coordination has not been revealed in detail. We previously reported that boryl-substituted azobenzenes formed an intramolecular N–B coordination [7], which is strong enough to inhibit photoisomerization in some cases. Triphenylphosphine imides, $Ph_3P{=}NR$, which also have a potentially coordinating NR moiety like azobenzenes, are expected to form N–B coordination, which will somewhat change reactivities, if a boryl group is introduced into the ortho position of the phenyl group. As there have been several examples of reactions

Correspondence to: Naokazu Kano; e-mail: kano@chem.s.u-tokyo.ac.jp. Takayuki Kawashima; e-mail: Takayuki.Kawashima@gakushuin.ac.jp.

Present address of Takayuki Kawashima: Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan.

Contract grant sponsor: Grants-in-Aid for the Global COE Program for Chemistry Innovation and for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Contract grant number: 21350025 and 22108508.



SCHEME 1

of ortholithiated triphenylphosphine imides with transition metal complexes and main group element compounds to introduce the elements [8], this method is useful to introduce a boryl group to the phosphine imide moiety. In this paper, we report the synthesis of triphenylphosphine *N-tert*-butylimides bearing a boryl substituent with an intramolecular N–B coordination and perturbation of reactivities.

RESULTS AND DISCUSSION

Phosphine imide, $Ph_3P{=}NBu^t$ (**1**) [9] was lithiated with an Et_2O solution of methyllithium in Et_2O at room temperature to give a dimeric-lithiated derivative **2** solvated with an Et_2O molecule in 93% yield (Scheme 1) [10]. The reaction of the lithiated derivative **2** with trichloroborane and successive addition of methyllithium gave dimethylborane **3** in 28% yield. The reaction of **2** with chlorocatecholborane gave the corresponding catecholborane **4** in 65% yield. Reduction of **4** with $LiAlH_4$ gave dihydroborane **5** in 41% yield. Although the almost quantitative conversion of **4** to **5** was confirmed by the ^{31}P NMR spectrum of the crude product, low crystallinity of **5** in recrystallization resulted in the low yield. The broad ^{11}B NMR signals of **3** and **4** at δ_B 2.2 and 13.7 ppm, respectively, in $CDCl_3$ were shifted fairly upfield from those of dimethylphenylborane (δ_B 77.6 ppm) [11] and phenylcatecholborane (δ_B 31.9 ppm) [7b]. The N–B interaction in **3** and **4** is indicated by the ^{11}B NMR spectroscopy. The ^{31}P NMR spectra of **3–5** (**3**: δ_P 35.2, **4**: δ_P 34.1, **5**: δ_P 37.1 ppm), similar to that of $[Ph_3PNHBu^t]^+Br^-$ (δ_P 32.0) [12], showed downfield shifts from that of **1** (δ_P −8.1 ppm), suggesting strong coordination of nitrogen to boron in the solution state and contribution of phosphonium-borate structure in **3–5** to some extent as represented by **4′**.

The crystal structures of **3–5** were characterized by the X-ray crystallographic analysis (Fig. 1). The N1 atom is directed to the B1 atom to form the N–B coordination in all **3–5**. The N–B distances (**3**: 1.666(3) Å, **4**: 1.584(4), **5**: 1.613(2) Å) are considerably shorter than the sum of the van der Waals radii (3.35 Å) [13], showing intramolecular N–B coordination. As a result, in all cases, the B1 atom has a tetracoordinated tetrahedral geometry. The N–B distances of **3–5** differ, and they reflect the Lewis acidity of each boryl group. This distance of **4** is a little shorter than observed in *o*-[(pyrrolidinylmethyl)phenyl]catecholborane (1.69 Å (average of two isomers)), suggesting a better donor property of the phosphine imide moiety [14]. The P–N bond lengths (**3**: 1.6090(18) Å, **4**: 1.622(2), **5**: 1.6100(14) Å) are similar to those of the *N-tert*-butylaminotriphenylphosphonium bromide (1.621(3) Å) [12] and a gold complex bearing the same phosphine imide moiety (1.6145(14) Å) [15] rather than that of **1** (1.543(2) Å), although they are much shorter than the sum of the covalent radii (1.78 Å) [16], supporting the contribution of the betaine structures such as **4′**.

Compounds **3–5** are thermally stable at room temperature, and they can be handled in the air. Phosphine imide **1** is known to react with some

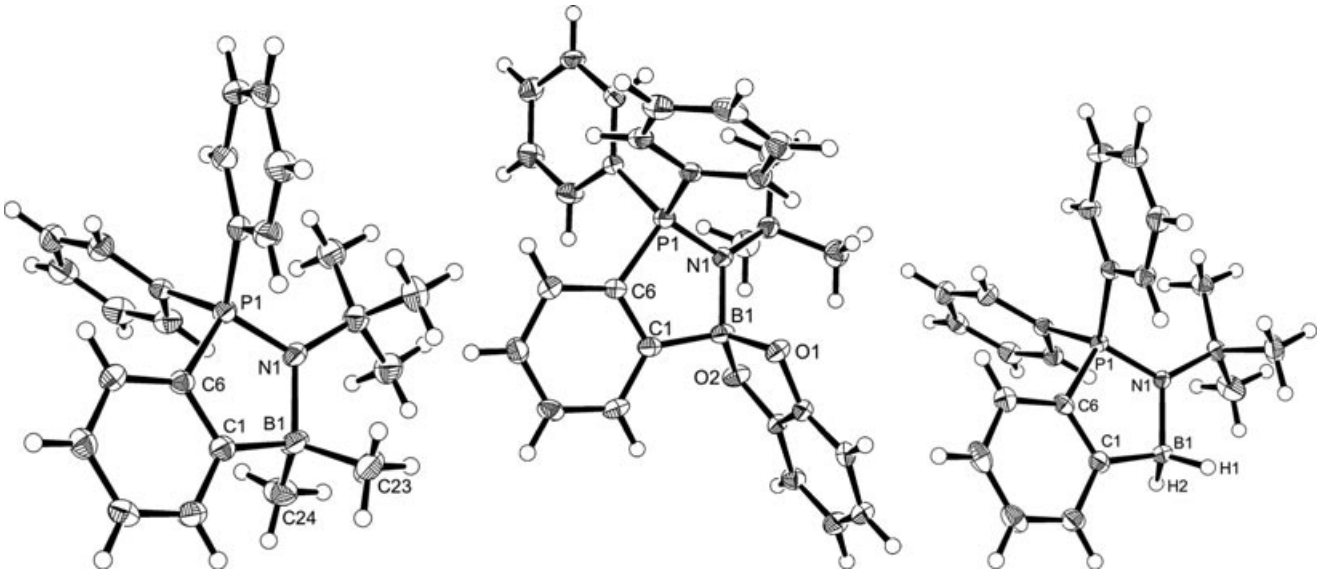
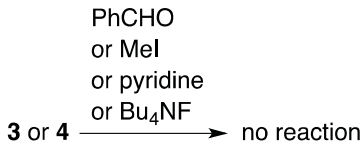


FIGURE 1 ORTEP drawings of **3** (left), **4** (center), and **5** (right) with thermal ellipsoid plot (50% probability). Selected bond lengths (Å) and bond angles (°) of **3**: N1–B1 1.666(3), N1–P1 1.6090(18), B1–C1 1.617(3), B1–C23 1.630(3), B1–C24 1.624(3), C1–B1–C23 109.15(19), C1–B1–C24 108.38(18), C1–B1–N1 101.53(16), C23–B1–C24 113.11(19), N1–B1–C23 111.60(18), N1–B1–C24 112.35(18). **4**: N1–B1 1.584(4), N1–P1 1.622(2), B1–C1 1.601(4), B1–O1 1.519(4), B1–O2 1.499(4), C1–B1–O1 111.1(2), C1–B1–O2 113.1(2), C1–B1–N1 104.2(2), O1–B1–O2 103.7(2), N1–B1–O1 110.4(2), N1–B1–O2 114.5(2). **5**: N1–B1 1.613(2), N1–P1 1.6100(14), B1–C1 1.604(2), B1–H1 1.131(17), B1–H2 1.167(19), C1–B1–H1 111.0(9), C1–B1–H2 110.2(9), C1–B1–N1 103.23(11), H1–B1–H2 112.1(12), N1–B1–H1 109.9(9), N1–B1–H2 110.1(9).



SCHEME 2

carbonyl compounds [17], and the aza-Wittig reaction readily proceeded by treatment of **1** with benzaldehyde to give *N*-benzylidene-*tert*-butylamine and triphenylphosphine oxide. However, borylated phosphine imides **3–5** were unreactive to benzaldehyde. For example, heating a toluene solution of **4** with 6 equiv of benzaldehyde at 120°C for 36 h resulted in no reaction and quantitative recovery of **4** (Scheme 2). Treatment of **4** with methyl iodide also resulted in the recovery of **4**. The depressed reactivity of the iminophosphorane moiety is ascribed to the steric congestion around the nitrogen atom and/or decreased nucleophilicity due to the intramolecular N–B coordination. In these cases, only the boron moiety in the molecule can be converted by a reagent that can react with both boron and iminophosphorane moieties. In the preparation reaction of **3** from the in situ generated dichloroborane derivative, the substitution reaction with methyllithium occurred at the boron center. In addition, treatment of **4** with excess lithium aluminum hydride gave the corresponding dihydroborane **5** with the iminophosphorane moiety intact. In contrast, treatment of **3** with neither excess tetrabutylammonium fluoride in $CDCl_3$ nor pyridine as the solvent at room temperature caused any change in NMR spectra after 12 h, although formation of a fluoroborate or a pyridine–borane complex was anticipated. Similar attempts using **4** instead of **3** also failed. These results can be reasonably understood taking into consideration that the reactions with lithium aluminum hydride can keep the N–B bond, whereas the reaction with pyridine or tetrabutylammonium fluoride must accompany with the cleavage of the bond. It is good contrast with the reactivity of [2-(phenylazo)phenyl]catecholborane, which is in equilibrium between an intramolecularly azo-coordinated form and a pyridine-coordinated complex form in the presence of pyridine [7a]. These results indicate the intramolecular coordination of the iminophosphorane moiety is stronger than that of the azobenzene moiety.

In summary, we synthesized and elucidated the crystal structure of the boron-substituted iminophosphoranes. The boron atom was revealed to be tetracoordinated by the intramolecular coordination from the nitrogen atom. The N–B

coordination remained intact upon treating with pyridine or fluoride ion. The intramolecular N–B coordination is suggested to be stronger than that of the 2-borylazobenzene derivatives. The coordination deactivated the reactivity of the iminophosphorane moiety very much, and the iminophosphorane moiety is persistent to hydrolysis, methylation, the aza-Wittig reaction, and lithium aluminum hydride reduction, whereas dichloro- and catecholborane moieties can be replaced by dimethyl- and dihydroborane moieties, respectively. The reactivity perturbation will be useful to stabilize some reactive species.

EXPERIMENTAL

Formation of {o-C_6H_4[PPh_2N(tert-Bu)]Li}$_2$ · (Et_2O)

A 1.09 M diethyl ether solution of methyllithium (21.0 mL, 22.9 mmol) was added to a diethyl ether solution (20 mL) of iminophosphorane **1** (3.87 g, 11.6 mmol) at room temperature and stirred for 2 h. After evaporation of the solvent, crude solids were washed with dry hexane under argon atmosphere and dried under reduced pressure to give [*o*-C_6H_4{PPh_2N(*tert*-Bu)}Li]$_2$·(Et_2O) (**2**) (3.51 g, 93%) as pale yellow powder. The powder was used as such for the following reaction without further purification.

2: pale yellow powder, mp 152.6–153.4°C. ^{1}H NMR (C_6D_6, 400 MHz) δ 0.80–1.00 (m, 6H), 1.14 (s, 18H), 3.03–3.19 (m, 4H), 7.04 (dd, J = 13.5, 8.0 Hz, 2H), 7.07–7.13 (m, 12H), 7.29 (dd, J = 11.8, 7.8 Hz, 4H), 7.89–8.00 (m, 8H), 8.25 (d, J = 4.8 Hz, 2H). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz) δ 15.17 (s), 35.51 (d, J = 13.0 Hz), 52.54 (d, J = 7.3 Hz), 65.71 (s), 124.52 (d, J = 15.8 Hz), 129.71 (d, J = 27.6 Hz), 130.40 (d, J = 1.4 Hz), 132.90 (d, J = 9.4 Hz), 133.92 (d, J = 8.8 Hz), 136.51 (d, J = 72.0 Hz), 140.11 (d, J = 26.3 Hz), 146.38 (d, J = 141.9 Hz), 190.37 (s). One signal overlapped with a peak of deuterated benzene. ^{31}P NMR (C_6D_6, 202 MHz) δ 14.3.

*Synthesis of o-C_6H_4[PPh_2N(tert-Bu)]BMe_2 (**3**)*

To a diethyl ether solution (10 mL) of **2** (535 mg, 0.75 mmol), a 1.0 M hexane solution of trichloroborane (1.50 mL, 3.05 mmol) was added dropwise at −78°C. The reaction mixture was stirred overnight, whereas the temperature was raised to room temperature. A 1.09 M diethyl ether solution of methyllithium (2.8 mL, 3.05 mmol) was added to the reaction mixture at room temperature and was further stirred overnight. Evaporation of the solvent, extraction of the resulting white solid with dichloromethane, filtration through Celite, and evaporation and recrystallization from ethanol gave **3** (148 mg, 28%) as colorless crystals.

3: colorless crystals, mp 184.8–185.3°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.20 (s, 6H), 1.24 (s, 9H), 6.96–7.03 (m, 2H), 7.31–7.35 (m, 1H), 7.43–7.57 (m, 7H), 7.81–7.86 (m, 4H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 2.2. ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.46 (br. s), 33.18 (d, $^3J_{PC}$ = 5.8 Hz), 55.08 (s), 125.11 (d, J_{PC} = 13.9 Hz), 125.98 (d, J_{PC} = 19.3 Hz), 128.41 (d, $^1J_{PC}$ = 123.6 Hz), 128.69 (d, J_{PC} = 12.0 Hz), 128.93 (d, J_{PC} = 14.6 Hz), 130.54 (d, $^1J_{PC}$ = 85.7 Hz), 130.76 (d, J_{PC} = 2.8 Hz), 132.12 (d, J_{PC} = 2.6 Hz), 133.24 (d, J_{PC} = 10.7 Hz). One ^{13}C signal could not be detected. ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.2. Anal. Calcd for $C_{24}H_{29}BNP$: C, 77.22; H, 7.83; N, 3.75. Found: C, 77.05; H, 7.92; N, 3.62.

*Synthesis of o-C_6H_4[PPh_2N(tert-Bu)] B(1,2-benzenendiolato) (**4**)*

To a diethyl ether solution (20 ml) of **2** (896 mg, 1.19 mmol) was added dropwise a diethyl ether solution (10 ml) of chlorocatecholborane (0.404 g, 2.62 mmol) at room temperature. The reaction mixture was stirred at room temperature for 17 h. After evaporation of the solvent, the residue was separated by column chromatography (Al_2O_3, ethyl acetate/hexane = 1:3) to give **4** (680 mg, 65%) as colorless solids. Recrystallization from ethanol gave analytically pure crystals.

4: colorless crystals, mp 231–231.5°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 9H), 6.66–6.69 (m, 2H), 6.78–6.81 (m, 2H), 7.06–7.11 (m, 1H), 7.15–7.19 (m, 1H), 7.37–7.42 (m, 1H), 7.54–7.67 (m, 7H), 7.93–7.99 (m, 4H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 13.7. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 32.33 (d, J_{PC} = 4.9 Hz), 55.24 (s), 108.96 (s), 117.93 (s), 125.83 (d, J_{PC} = 15.7 Hz), 127.08 (d, J_{PC} = 91.5 Hz), 128.28 (d, J_{PC} = 14.0 Hz), 128.36 (d, J_{PC} = 113.0 Hz), 129.17 (d, J_{PC} = 12.4 Hz), 129.54 (d, J_{PC} = 14.8 Hz), 129.67 (d, J_{PC} = 13.2 Hz), 132.68 (d, J_{PC} = 3.3 Hz), 133.17 (d, J_{PC} = 2.5 Hz), 133.42 (d, J_{PC} = 10.7 Hz), 153.21 (s). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 34.1. GC-MS m/z = 451. Anal. Calcd for $C_{28}H_{27}BNO_2P$: C, 74.52; H, 6.03; N, 3.10. Found: C, 74.41; H, 6.15; N, 3.10.

*Synthesis of o-C_6H_4[PPh_2N(tert-Bu)]BH_2 (**5**)*

To a THF solution (15 mL) of lithium aluminum hydride (150 mg, 3.95 mmol), a THF solution (5 mL) of **4** (160 mg, 0.355 mmol) was added dropwise at room temperature and stirred for 3 h. After quenching with ethyl acetate, evaporation of the solvent, extraction of the resulting solids with chloroform,

TABLE 1 Crystal Data for the Phosphine Imides **3–5**.

	3	*4*	*5*
Empirical formula	$C_{24}H_{29}BNP$	$C_{28}H_{27}BNO_2P$	$C_{22}H_{25}BNP$
Formula weight	373.26	451.29	345.21
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	8.834(5)	9.364(5)	9.137(5)
b (Å)	14.353(7)	13.892(8)	12.526(6)
c (Å)	17.793(9)	18.024(10)	16.541(9)
β(deg)	103.1815(18)	99.189(3)	98.320(3)
V (Å^3)	2197(2)	2315(2)	1873.2(17)
Z	4	4	4
D_{calc} (g/cm^3)	1.129	1.295	1.224
$R1$ ($I > 2\sigma(I)$)	0.0468	0.0427	0.0383
$wR2$ (all data)	0.1394	0.0859	0.1107
GOF	1.095	0.879	1.048

drying with anhydrous magnesium sulfate, and further evaporation gave white solids. The residue was purified by column chromatography (Al_2O_3, ethyl acetate/hexane = 1:4) to give **5** (50.1 mg, 41%) as colorless solids. Recrystallization from ethanol gave analytically pure colorless crystals.

5: colorless crystals, mp 179.0–180.0°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 9H), 3.26 (br, 2H), 7.03–7.06 (m, 2H), 7.32–7.35 (m, 1H), 7.48–7.52 (m, 4H), 7.55–7.58 (m, 2H), 7.64–7.67 (m, 1H), 7.78–7.84 (m, 4H). ^{11}B NMR (128 MHz, $CDCl_3$) δ −9.0. ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.73 (d, $^3J_{PC}$ = 4.9 Hz), 53.81 (s), 125.08 (d, J = 13.5 Hz, CH), 126.51 (d, J = 19.5 Hz, CH), 128.84 (d, J = 12.0 Hz, CH), 129.70 (d, J = 87.0 Hz, quaternary C), 129.91 (d, J = 13.5 Hz, CH), 129.92 (d, J = 123.8 Hz, quaternary C), 130.57 (d, J = 3.0 Hz, CH), 132.50 (d, J = 3.0 Hz, CH), 133.14 (d, J = 11.3 Hz, CH). One ^{13}C signal could not be detected. ^{31}P NMR (162 MHz, $CDCl_3$) δ 37.1. ESI-HRMS Calcd for $C_{22}H_{24}BNP$ ([M – H]$^+$), 344.1739. Found. m/z 344.1752. Anal. Calcd for $C_{22}H_{25}BNP+0.25H_2O$: C, 75.55; H, 7.35; N, 4.01. Found: C, 75.75; H, 7.35; N, 3.85. The water content was confirmed by the ^{1}H NMR spectrum.

X-Ray Crystallographic Analysis

Intensity data for **2–4** were collected at 120 K on the Rigaku Mercury CCD diffractometer and used graphite monochrometric Mo Kα radiation (λ = 0.71070 Å). The structures were solved by direct methods and full-matrix least-squares method based on F^2 using SHELX-97 program package [18]. Nonhydrogen atoms were subjected to anisotropic refinement. The crystal data for **3–5** are summarized in Table 1. All crystallographic data for **3–5** were deposited with the Cambridge Crystallographic Data Centre (CCDC), U.K. with CCDC-698641 (**3**), CCDC-698642 (**4**), and CCDC-698643 (**5**).

REFERENCES

[1] (a) Fresneda, P. M.; Molina, P. Synlett 2004, 1–17; (b) Kano, N.; Xing, J.-H.; Kawa, S.; Kawashima, T. Polyhedron 2002, 21, 657–665.

[2] (a) Staudinger, H.; Meyer, J. Helv Chim Acta 1919, 2, 635–646; (b) Gololobov, Y. G.; Zhmurova, I. N.; Kasukhin, L. F. Tetrahedron 1981, 37, 437–472.

[3] Saxon, E.; Bertozzi, C. R. Science 2000, 287, 2007–2010.

[4] (a) Vaultier, M.; Knouzi, N.; Carrié, R. Tetrahedron Lett 1983, 24, 763–764; (b) Kano, N.; Hua, X. J.; Kawa, S.; Kawashima, T. Tetrahedron Lett 2000, 41, 5237–5241.

[5] (a) Wingerter, S.; Gornitzka, H.; Bertrand, G.; Stalke, D. Eur J Inorg Chem 1999, 173–178; (b) Vicente, J.; Abad, J.-A.; Clemente, R.; López-Serrano, J.; Ramírez de Arellano, M. C.; Jones, P. G.; Bautista, D. Organometallics 2003, 22, 4248–4259; (c) Bielsa, R.; Larrea, A.; Navarro, R.; Soler, T.; Urriolabeitia, E. P. Eur J Inorg Chem 2005, 1724–1736; (d) Aguilar, D.; Contel, M.; Navarro, R.; Urriolabeitia, E. P. Organometallics 2007, 26, 4604–4611; (e) Bielsa, R.; Navarro, R.; Urriolabeitia, E. P.; Lledós, A. Inorg Chem 2007, 46, 10133–10142.

[6] (a) Holley, W. K.; Ryschkewitsch, G. E. Phosphorus Sulfur Silicon Relat Elem 1990, 53, 271–284; (b) Möhlen, M.; Neumüller, B.; Dashti-Mommertz, A.; Müller, C.; Massa, W.; Dehnicke, K. Z Anorg Allg Chem 1999, 625, 1631–1637; (c) Wei, P.; Chan, K. T. K.; Stephan, D. W. Dalton Trans 2003, 3804–3810; (d) Bebbington, M. W. P.; Bontemps, S.; Bouhadir, G.; Bourissou, D. Angew Chem, Int Ed 2007, 46, 3333–3336.

[7] (a) Kano, N.; Yoshino, J.; Kawashima, T. Org Lett 2005, 7, 3909–3911; (b) Yoshino, J.; Kano, N.; Kawashima, T. Tetrahedron 2008, 64, 7774–7781; (c) Yoshino, J.; Kano, N.; Kawashima, T. Chem Commun

2007, 559–561; (d) Yoshino, J.; Furuta, A.; Kambe, T.; Itoi, H.; Kano, N.; Kawashima, T.; Ito, Y.; Asashima, M. Chem Eur J 2010, 16, 5026–5035; (e) Itoi, H.; Kambe, T.; Kano, N.; Kawashima, T. Inorg Chim Acta 2012, 381, 117–123.

[8] (a) Wingerter, S.; Pfeiffer, M.; Stey, T.; Bolboacá, M.; Kiefer, W.; Chandrasekhar, V.; Stalke, D. Organometallics 2001, 20, 2730–2735; (b) Boubekeur, L.; Ricard, L.; Mézailles, N.; Demange, M.; Auffrant, A.; Le Floch, P. Organometallics 2006, 25, 3091–3094; (c) Brown, S. D. J.; Henderson, W.; Kilpin, K. J.; Nicholson, B. K. Inorg Chim Acta 2007, 360, 1310–1315.

[9] Zimmer, H.; Singh, G. J Org Chem 1963, 28, 483–486.

[10] (a) Stuckwisch, C. G. J Org Chem 1976, 41, 1173–1176; (b) Steiner, A.; Stalke, D. Angew Chem, Int Ed 1995, 34, 1752–1755.

[11] Nöth, H; Wrackmeyer, B. Chem Ber 1974, 107, 3089–3103.

[12] Imrie, C.; Modro, T. A.; Van Rooyen, P. H.; Wagener, C. C. P.; Wallace, K.; Hudson, H. R.; McPartlin, M.; Nasirun, J. B.; Powroznyk, L. J Phys Org Chem 1995, 8, 41–46.

[13] Bondi, A. *J Phys Chem* 1964, 68, 441–451.

[14] Zhu, L.; Shabbir, S. H.; Gray, M.; Lynch, V. M.; Sorey, S.; Anslyn, E. V. J Am Chem Soc 2006, 128, 1222–1232.

[15] Kilpin, K. J.; Henderson, W.; Nicholson, B. K. Inorg Chim Acta 2009, 362, 3669–3676.

[16] Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. Dalton Trans 2008, 2832–2838.

[17] (a) Fetyukhin, V. N.; Voek, M. V. J Gen Chem USSR 1983, 53, 1586–1589; (b) Gorbatenko, V. I.; Matveev, Yu. I.; Gertsyuk, M. N.; Samarai, L. I. J Org Chem USSR 1984, 20, 2314–2318.

[18] Sheldrick, G. M. Acta Crystallogr D 2008, 64, 112–122.