DOI: 10.1002/ejic.200700082

Preferred Phosphorus Ylide Formation Upon Alkylation of Lithiobis(diphenylphosphanyl)acetonitrile

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Dedicated to Professor Rolf Gleiter on the occasion of his 70th birthday

Keywords: Chelates / Phosphane ligands / Carbanions / Ylides / Alkylation

Deprotonation of the readily available chelate phosphane bis(diphenylphosphanyl)acetonitrile (**6**) leads to stabilized carbanion system **7**. Lithiobis(diphenylphosphanyl)acetonitrile (**7**) features a unique thf-stabilized monomeric structure in the crystal form with a short cyanonitrogen–Li contact. Alkylation of **7** with *n*-alkyl bromides (R–Br, R = ethyl, *n*-propyl, *n*-butyl, *n*-hexyl) takes place selectively at one phosphorus atom to yield stabilized ylides **8a**–**d** (two examples characterized by X-ray diffraction). Treatment of **7** with the more reactive alkylation agents methyl iodide or benzyl bromide results in alkylation at both phosphorus atoms to give delocalized bis(phosphonium)ylides **9a**,**b** (both characterized by X-ray diffraction). Similarly, the reaction of **7** with 1,3-dibromopropane or 1,4-dibromobutane yields six- and seven-membered heterocyclic bis(phosphonium)ylides **10a**,**b**, respectively. The spectroscopic characterization and X-ray crystal structure analysis again indicate the presence of delocalized $Ph_2RP–C(CN)–PRPh_2$ substructures.

Introduction

A variety of structural alternatives has been discussed for α-lithiated acetonitrile derivatives.[1] From a number of experimental studies complemented by spectroscopic and theoretical investigations it seemed clear that the majority of $RCHCN^-$ systems favored dimeric structures of type **1** in the solid state, which are characterized by the presence of a central N_2Li_2 four-membered heterocyclic arrangement (Figure 1).[2–6]

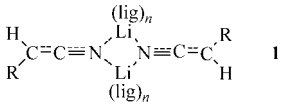

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Figure 1. Preferred dimeric structures of lithiated acetonitrile derivatives.

We recently observed a monomeric structure of a lithiated acetonitrile example, namely lithiobis(diphenylphosphanyl)acetonitrile (**7**, see below).[7a] Phosphorus substituted ylides such as **2** or **3** are very interesting multifunctionalized organophosphorus compounds. Their structural and chemical features have attracted considerable interest.[7–10] Investigations in this field have led to the discovery of extended systems such as **4** or **5** (Figure 2).[8c,11–12]

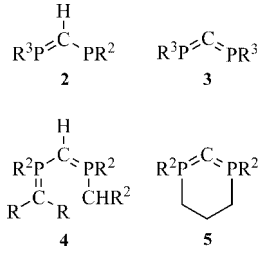

Figure 2. Examples of *P*-substituted phosphorus ylides.

We have now combined the chemistry of the $Li[(Ph_2P)_2CCN]$ system (**7**) with that of the P-stabilized ylides. This followed from a very typical reaction mode that is characteristic of **7**, namely its preferred alkylation at phosphorus upon treatment with a variety of alkyl halide electrophiles with the formation of new cyano-functionalized phosphorus ylides derived from the framework of **7**. A detailed description of some of this work is presented in this account.

Results and Discussion

We previously showed that bis(diphenylphosphanyl)acetonitrile (**6**, dppmCN)[13] was readily obtained from the reaction of acetonitrile with chlorodiphenylphosphane in the

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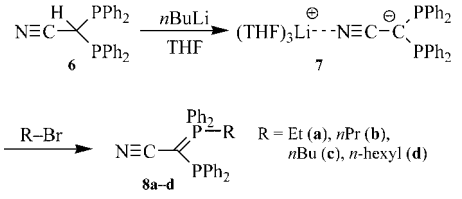
presence of a strong base. System **6** has served as a chelate ligand for metal complex formation. The in situ generated Pd(dppmCN) catalyst was shown to give very high activities in a Suzuki–Miyaura carbon–carbon coupling reaction.[14]

The deprotonation of dppmCN (**6**) was cleanly effected by treatment with *n*-butyllithium (Scheme 1).[7a] The resulting lithiobis(diphenylphosphanyl)acetonitrile product (**7**) was characterized by X-ray diffraction.[15–17] System **7** features a shortened C1–C2 [1.386(3) Å] bond and the C2–N linkage [1.162(3) Å] is lengthened relative to that reported for **6**[6] [cf. C1–C2 1.462(3) Å, C2–N 1.148(3) Å]. In **7**, the C1–P bonds are markedly shortened [1.784(2) Å, 1.775(2) Å] relative to the P1–C(Ar) bonds in **7** [1.835(2)–1.845(2) Å] and those reported in the literature for **6**[6] [1.874(2) Å, 1.895(2) Å]. These characteristic data indicate some electronic delocalization in **7**, including the pair of phosphorus groups. Most remarkably, system **7** is monomeric in the solid state – quite different from the preferred dimeric structures of its congeners **1** – with a N–Li contact of 1.957(4) Å. Figure 3 shows a view of the molecular structure of **7**.



Scheme 1.

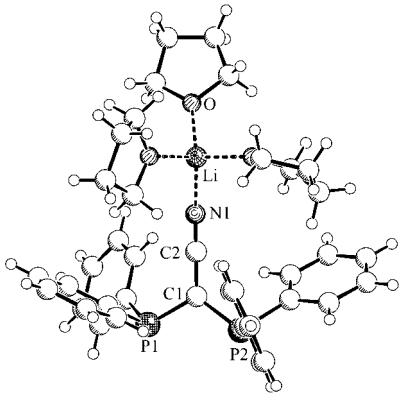


Figure 3. A view of the molecular structure of **7**.

Compound **7** is attacked by primary *n*-alkyl bromide electrophiles exclusively at one of the phosphorus atoms with clean formation of the respective ylide products (**8a**–**d**, R = ethyl, *n*-propyl, *n*-butyl, *n*-hexyl). Spectroscopically, the products are characterized by the observation of two very different ^{31}P NMR spectroscopic phosphorus resonances. The ylidic phosphorus signal is shifted substantially to positive δ values relative to its neutral precursor **6** or its anionic precursor **7** (for details see Table 1). The central carbon atom C1 consequently features two very different $^{1}J_{P,C}$ coupling constants (e.g. **8a**: δ = 6.92 ppm, $^{1}J_{P,C}$ = 128.0, 28.9 Hz).

Table 1. Selected spectroscopic data of ylide products **8a**–**d**.[a]

	8a (C_2H_5)	**8b** (nC_3H_7)	**8c** (nC_4H_9)	**8d** (nC_6H_{13})
δ(3-H)	2.71	2.65	2.68	2.66
δ(4-H)	1.23	1.64	1.58	1.59
$\delta(^{13}C1)$	6.9	7.4	7.4	7.3
$^{1}J_{P,C}$	128.0, 28.9	128.2, 29.3	128.0, 28.5	128.1, 28.8
$\delta(^{13}C{\equiv}N)$	125.0	125.0	125.0	125.1
$^{2}J_{P,C}$	13.1, 0.8	13.0, 1.0	13.0, 1.1	12.9, 1.1
$\delta(^{13}C3)$	19.1	27.6	25.3	25.6
$^{1}J_{P,C}$	62.5, 9.9	60.7, 9.3	60.8, 9.2	60.9, 9.8
$\delta(^{31}P1)$	29.3	27.0	26.9	26.9
$\delta(^{31}P2)$	–19.2	–19.0	–19.5	–19.5
$^{2}J_{P,P}$	140.8	141.2	140.8	142.0
$\tilde{\nu}$(C≡N)	2137	2148	2133	2151

[a] NMR spectra in CD_2Cl_2, δ [ppm], J [Hz]; IR spectra in KBr, $\tilde{\nu}$ [cm^{-1}].

Compounds **8a**,**c** both exhibit very similar structures (Table 2). Therefore, only example **8c** (R = *n*-butyl) is described here in detail (Figure 4 and Table 2). Single crystals suitable for X-ray crystal structure analysis were obtained by the slow evaporation of solvent from a toluene/dichloromethane solution of functionalized ylide **8c**.

Table 2. Selected structural parameters of ylide products **8a**,**c**.[a]

	8a (ethyl)	**8c** (*n*-butyl)
C2–N1	1.155(3)	1.151(3)
C1–C2	1.409(3)	1.412(3)
C1–P1	1.793(2)	1.790(2)
C1–P2	1.728(2)	1.721(2)
P1–C1–P2	121.0(1)	118.8(1)
P1–C3	1.816(2)	1.809(2)

[a] Bond lengths [Å]; angles [°].

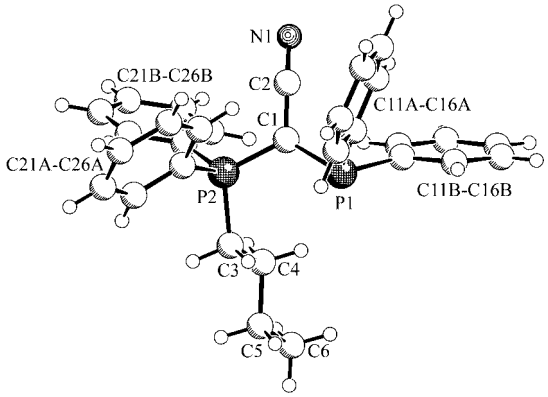
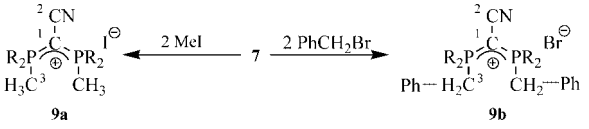


Figure 4. Molecular geometry of **8c**.

Compound **8c** features a central sp^2 hybridized planar tricoordinate ylidic carbon center (C1) to which a cyano substituent and a pair of differently substituted phosphorus atoms are bonded (Figure 4). The C1–C≡N unit is linear [angle C1–C2–N1 178.6(2)°]. Relative to the reference molecule bis(diphenylphosphanyl)acetonitrile (**6**), the C≡N bond in **8c** is slightly longer at 1.151(3) Å [cf. **6**: 1.148(2) Å] and the adjacent C1–C2 linkage is shorter [**8c**: 1.412(3) Å, cf. **6**: 1.462(2) Å], which indicates some conjugative stabilization of the adjacent ylide moiety [P2–C1: 1.721(2) Å]. Consequently, the remaining C1–P1 bond [1.790(2) Å] is

markedly longer. The bond angles at C1 amount to 118.8(1)° (P1–C1–P2), 117.4(1)° (P2–C1–C2), and 121.5(1)° (P1–C1–C2) and the *n*-butyl substituent angle at P2 is 112.5(1)° [C1–P2–C3; P2–C3: 1.809(2) Å]. The remaining P–C aryl bond lengths at the tetracoordinate phosphorus atom P2 [P2–C21A: 1.812(2) Å, P2–21B: 1.810(2) Å] are slightly shorter relative to the P–C(aryl) bonds of its tricoordinate congener P1 [P1–C11A: 1.837(2) Å, P1–C11B: 1.835(2) Å].

The reaction of anion **7** takes a slightly different course when more reactive alkyl halide electrophiles are employed. Thus, treatment of **7** with methyl iodide results in the formation of a bisalkylated product (**9a**) (Scheme 2). In this case, a methyl group becomes attached at each phosphorus atom.[8c,11] Formally, the product may be regarded as a cyano-stabilized phosphorus ylide that is further stabilized by a newly formed phosphonium cation substituent. In reality, it appears that a delocalized bis(phosphonium)ylide is formed. In solution, this led to the observation of a single ^{31}P NMR spectroscopic resonance at δ = 21.7 ppm and there is a single [P]–CH_3 ^{1}H NMR spectroscopic signal at δ = 2.40 ppm.



Scheme 2.

The ^{13}C NMR spectrum of **9a** features a binominal triplet resonance of the central carbon atom C1 at δ = 5.6 ppm with a $^1J_{P,C}$ = 117.1 Hz. The corresponding C≡N ^{13}C NMR spectroscopic signal was located at δ = 119.4 ppm. Both the P–CH_3 and the P–C_{ipso}(aryl) ^{13}C NMR spectroscopic signals (δ = 14.6 and 122.6 ppm) have a more complicated appearance due to nonfirst-order splitting of the respective ^{13}C/^{31}P NMR spin systems (for further details see Table 3 and the Experimental Section).

Table 3. Selected spectroscopic data of compounds **9** and **10**.[a].

	9a (CH_3)	**9b** (CH_2Ph)	**10a** $(CH_2)_3$	**10b** $(CH_2)_4$
δ(^{31}P1/ ^{31}P2)	21.7	23.9	18.3	28.8
δ(^{13}C1)	5.6	3.2	3.2	4.7
$^1J_{PC}$	117.1	117.3	103.8	108.9
δ(^{13}C2)	119.4	120.4	119.1	119.8
$^2J_{PC}$	3.9	4.8	[c]	2.3
δ(^{13}C3)	14.6	36.6	21.5	24.7
δ(*i*-Ph^P)[b]	122.6	119.4	123.4	123.6
δ(*o*-Ph^P)[b]	132.8	134.0	133.1	132.9
δ(*m*-Ph^P)[b]	130.4	129.9	130.2	130.3
δ(*p*-Ph^P)[b]	134.8	134.6	134.6	134.6
$\tilde{\nu}$(C≡N)	2160	2159	2166	2157

[a] NMR spectra in CD_2Cl_2, δ [ppm], *J* [Hz]; IR in KBr, $\tilde{\nu}$ [cm^{-1}]. [b] Tentative absolute assignment. [c] Singlet structure with $\nu_{1/2}$ ca. 2 Hz.

The reaction of **6** with benzyl bromide takes a similar course. We isolated doubly benzylated bis(phosphonium)ylide product **9b** from the reaction mixture in close to quantitative yield. Product **9b** exhibits similar spectroscopic features (Table 3). Both products **9a**,**b** were characterized by X-ray diffraction. Single crystals of **9a** were obtained by the slow evaporation of a saturated toluene/dichloromethane solution. Single crystals of **9b** were similarly obtained from dichloromethane.

Compound **9a** exhibits a delocalized bis(phosphonium)ylide-type structure with well separated cations and anions (Figure 5). In the crystal form, a chiral conformation is adopted. Nevertheless, the pair of C1–P1 and C1–P2 bonds is almost equal in length [1.734(4) Å, 1.751(4) Å]. The system features a distorted U-shaped conformation ranging from the aryl *ipso*-carbon C11B through P1, C1, and P2 to the methyl carbon atom C4 (Figure 5). The C1–C2(N) bond of **9a** is short [1.413(6) Å], which is a structural indication of CN stabilization of the central ylidic moiety. The conformation of the central section of the molecule is characterized by dihedral angles 104.3(3)° (C3–P1–C1–P2), –34.6(4)° (P1–C1–P2–C4), –80.2° (C3–P1–C1–C2), and 149.9° (C2–C1–P2–C4). The C1–C2–N1 unit is close to linear [178.7(5)°].

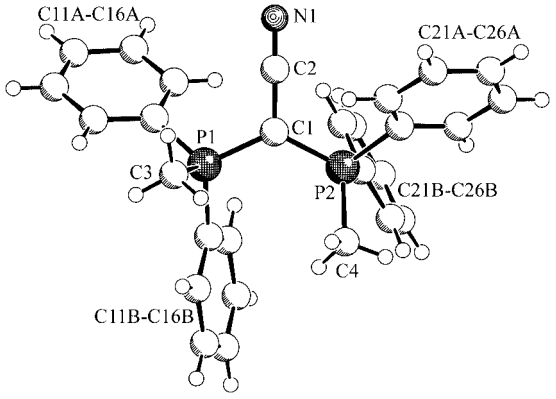


Figure 5. Molecular structure of **9a** (only the cation is depicted).

Compound **9b** features an overall structure that is similar to **9a**. Again, the P–C(sp^2) bond lengths are similar to each other (Table 4) and both the C1–C2 and the adjacent C2–N1 bonds are rather short. Compound **9b** exhibits a slightly different conformation. The trio of aryl and alkyl substituents at the phosphorus atoms are arranged such that they are oriented close to the staggered position along the hypothetical P1···P2 axis. Both benzyl groups are pointing away from the core of molecule **9b** in this geometrical arrangement (Figure 6).

The reaction of anionic reagent **7** with 1,3-dibromopropane takes a similar course. Alkylation at both phosphorus atoms yields ylidic product **10a** (87%, isolated) (Scheme 3). The NMR spectra of **10a** point to a similar delocalized bis(phosphonium)ylide structure as it was found for **9a**,**b**. Compound **10a** features a single ^{31}P NMR spectroscopic resonance at δ = 18.3 ppm and a single set of ^{1}H/^{13}C NMR phenyl spectroscopic resonances (Table 3 and the Experimental Section). The bridging trimethylene unit appears to be symmetrical in solution, and in the ^{1}H NMR spectrum it resonates as a 4 H multiplet at δ = 3.50 ppm ([P]–CH_2) and a 2 H signal at δ = 2.45 ppm (–CH_2–).

Table 4. Selected structural parameters of compounds **9a**,**b** and **10a**,**b**.[a]

	9a (CH_3)	**9b** (CH_2Ph)	**10a** $(CH_2)_3$	**10b** $(CH_2)_4$
C2–N1	1.151(6)	1.148(3)	1.157(4)	1.150(4)
C1–C2	1.413(6)	1.410(3)	1.410(4)	1.410(4)
C1–C2–N1	178.7(5)	179.0(3)	179.5(4)	179.1(3)
P1–C1	1.734(4)	1.751(2)	1.744(3)	1.748(2)
P2–C1	1.751(4)	1.747(2)	1.731(3)	1.745(2)
P1–C3	1.787(5)	1.820(2)[b]	1.800(3)	1.786(3)
P2–C4	1.793(4)	1.823(2)[c]	1.803(3)[d]	1.801(3)[e]
P1–C1–P2	126.9(2)	126.4(1)	121.9(2)	128.3(2)
P1–C1–C2	115.7(3)	117.1(2)	118.5(2)	116.4(2)
P2–C1–C2	117.2(3)	115.7(1)	118.3(2)	115.3(2)

[a] Bond lengths [Å]; angles [°]. [b] P1–C11. [c] P2–C41 (Figure 6). [d] P2–C5 (Figure 7). [e] P2–C6 (see Figure 6).

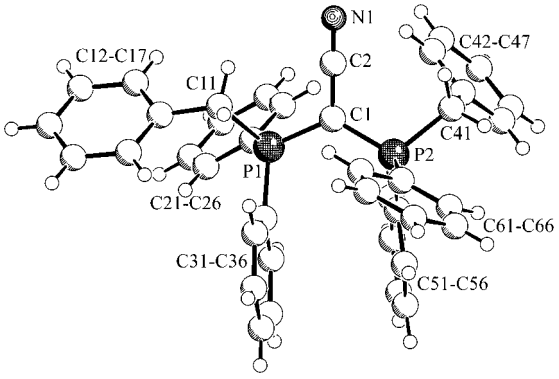
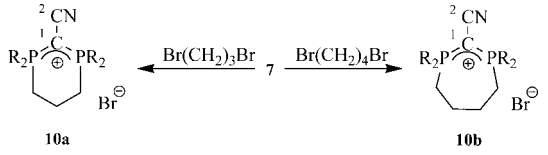


Figure 6. A projection of the molecular geometry of compound **9b** in the crystal form (only the cation is shown).



Scheme 3.

The corresponding ^{13}C NMR spectroscopic signals were observed at δ = 21.5 ppm (C3/C5) and δ = 17.0 ppm (t, $^3J_{P,C}$ = 6.0 Hz, C-4). As expected, the central ylidic carbon atom resonance shows up as a binominal triplet due to coupling with a pair of symmetry-equivalent phosphorus neighbors (δ = 3.2 ppm, $^1J_{P,C}$ = 103.8 Hz), and the adjacent nitrile carbon atom resonance appears at δ = 119.1 ppm (s, $\nu_{1/2}$ ca. 2 Hz).

The reaction of **7** with 1,4-dibromobutane proceeds analogously to yield product **10b** (73% isolated). Compound **10b** also seems to be a delocalized stabilized ylide. It features spectroscopic data similar to **10a** (Table 3).

Single crystals for X-ray crystal structure analyses of compounds **10a**,**b** were obtained by slow evaporation of the solvent from toluene/dichloromethane solutions. The structure of **10a** features a six-membered heterocycle (Figure 7). It contains a delocalized P1–C2–P2 unit with a pair of close-to-equal P–C bond lengths (Table 4). The corresponding C1–C2 bond length is in the typical range [1.410(4) Å] as is the adjacent C2–N1 linkage [1.157(4) Å]. The coordination geometry around the central ylidic carbon atom C1 is trigonal planar (for bond angles, see Table 4). The endocyclic saturated trimethylene unit of **10a** exhibits a typical staggered conformation.

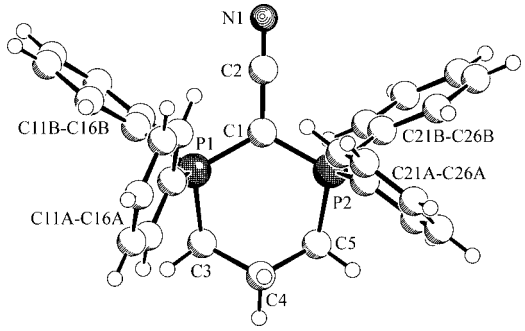


Figure 7. Molecular structure of **10a** (cation only).

The bonding parameters of the P1–C(CN)–P2 unit of seven-membered heterocyclic compound **10b** are similar to those of **10a**. In this case, the P1–C1 [1.748(2) Å] and P–C2 [1.745(2) Å] bonds are in fact almost identical in length as it is expected for a delocalized stabilized bis(phosphonium)-ylide structure. Again, the P–C(aryl) vectors are oriented close to the eclipsed conformation along the hypothetical P1···P2 connection and the P1–C3 [1.786(3) Å] and P2–C6 [1.801(3) Å] vectors are arranged close to parallel to each other. The remaining connecting tetramethylene unit of compound **10b** adopts an all-staggered conformation (Figure 8).

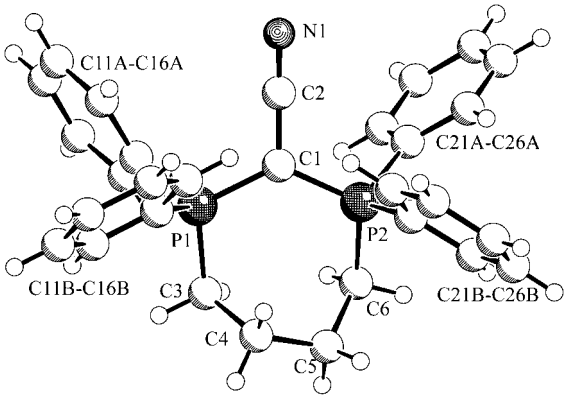


Figure 8. A view of the molecular structure of compound **10b** (cation only).

Conclusions

We have shown that the chelate phosphane bis(diphenylphosphanyl)acetonitrile (dppmCN, **6**) is readily deprotonated by treatment with, for example, *n*-butyllithium to selectively yield monoanionic system **7**. Lithiobis(diphenylphosphanyl)acetonitrile (**7**) features a unique monomeric thf-stabilized structure in the crystal form that contains a delocalized P–C(CN)–P moiety and a short contact of the lithium cation to the nitrile nitrogen at the opposite end of the system. Nevertheless, the alkylation with a variety of alkyl ha-

lide electrophiles very selectively takes place only at phosphorus. In each of the examples studied and described here, the –CN nitrogen atom as well as the "carbanionic" P_2C1 carbon center was left untouched by these reagents under the applied reaction conditions.[18] In some cases, selective alkylation at one of the two phosphorus centers was observed, which resulted in the formation of phosphorus ylides that are stabilized by the cyano substituent and the $–PR_2$ group at the ylidic carbon atom. Upon treatment with more strongly electrophilic reagents such as methyl iodide or benzyl bromide, twofold alkylation at phosphorus was observed, which led to the formation of apparently delocalized bis(phosphonium)ylide structures. Treatment of **7** with difunctional α,ω-dibromoalkanes led to analogous cyclic bis(phosphonium)ylide products. We assume that the subsequent P–C bond-forming step was favored because it took place intramolecularly. Now that such highly stabilized ylidic systems have become so easily available and their structure and spectroscopic features investigated and characterized, it will be interesting to learn their specific chemical properties and their potential synthetic use.

Experimental Section

General Information: Most reactions were carried out under an inert atmosphere (argon) in Schlenk-type glassware or in a glove box. Solvents were dried and distilled under an atmosphere of argon prior to use. NMR spectra were recorded with Bruker AC 200 FT (^{1}H: 200 MHz, ^{13}C: 50.3 MHz, ^{31}P: 81 MHz), Varian Inova 500 (^{1}H: 499.8 MHz, ^{13}C: 126 MHz), or Unity Plus 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{31}P: 242.5 MHz) spectrometers. Most NMR assignments were supported by additional 2D experiments. The assignment of $J_{P,H}$ or $J_{P,C}$ was made by ^{1}H{^{31}P} or ^{13}C{^{1}H,^{31}P} NMR decoupling experiments. Melting points were determined with a DSC 2010 (TA-Instruments) apparatus. IR spectra were obtained with a Varian 3100 FT-IR (ECALIBUR Serie) spectrometer. MS (ESI) spectra were measured with a Micromass QuatroLC-Z mass spectrometer. GC was performed with a Hewlett Packard HP 6890 Series GC System. X-ray crystal structure data sets were collected with a Nonius KappaCCD diffractometer with Mo-radiation and equipped with a rotating anode generator. The following programs were used for data analysis: data collection, COLLECT;[19] data reduction, Denzo-SMN;[20] absorption correction, SORTAV[21] and Denzo;[22] structure solution, SHELXS-97;[23] structure refinement, SHELXL-97;[24] graphics, SCHAKAL.[25] CCDC-629968, -629969, and -631598 to -631602 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparation of Lithiobis(diphenylphosphanyl)acetonitrile (7): Bis(diphenylphosphanyl)acetonitrile (3.26 g, 7.96 mmol) was dissolved in dry tetrahydrofuran (50 mL) and cooled to –78 °C. After the addition of *n*-butyllithium (1.6 M in hexane, 5.47 mL, 8.76 mmol), the reaction mixture was warmed to room temperature and stirred overnight. The solvent was removed in vacuo, and the residue was suspended in pentane (40 mL). The product was collected by filtration, washed with pentane (3 × 40 mL), and dried in vacuo (white solid, yield: 3.68 g, 73%). M.p. 144 °C (DSC). ^{1}H NMR (600 MHz, C_6D_6/tdf, 298 K): δ = 7.40 (m, 8 H, *o*-Ph), 7.06 (m, 8 H, *m*-Ph), 6.99 (m, 4 H, *p*-Ph), 3.54 (br. s, 12 H, thf), 1.68 (br. s, 12 H, thf) ppm. ^{13}C{^{1}H} NMR (151 MHz, C_6D_6/TDF, 298 K): δ = 147.2 (m, *i*-Ph), 133.1 (m, *o*-Ph), 129.4 (t, $^2J_{P,C}$ = 3.3 Hz, CN), 127.6 (m, *m*-Ph), 126.3 (s, *p*-Ph), 68.1 (m, thf), 26.3 (m, thf), 15.5 (t, $^2J_{P,C}$ = 13.5 Hz, C-1) ppm. ^{31}P{^{1}H} NMR (81 MHz, C_6D_6/tdf, 298 K): δ = 2.7 (s) ppm. FTIR (KBr): $\tilde{\nu}$ = 3043, 2968, 2878, 2107, 2066, 1478, 1429, 1040, 744, 695, 560, 508 cm^{-1}. $C_{26}H_{20}LiNP_2$·3thf (631.66): calcd. C 72.26, H 7.02, N 2.22; found C 71.53, H 6.85, N 2.11. X-ray crystal structure analysis of **7**: formula $C_{26}H_{20}NP_2Li$·$(C_4H_8O)_3$, M = 631.62, light yellow crystal 0.25 × 0.25 × 0.20 mm, a = 9.658(1), b = 18.516(1), c = 19.627(1) Å, β = 96.27(1)°, V = 3488.9(4) Å^3, $\rho_{calcd.}$ = 1.202 g cm^{-3}, μ = 0.161 mm^{-1}, empirical absorption correction ($0.961 \le T \le 0.969$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 198 K, ω and ϕ scans, 23326 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.66 Å^{-1}, 8344 independent (R_{int} = 0.059) and 5029 observed reflections [$I \ge 2\sigma(I)$], 410 refined parameters, R = 0.057, wR_2 = 0.147, max. residual electron density 0.41 (–0.30) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

General Procedure for the Reaction of 7 with Alkyl Bromides: Lithium cyanobis(diphenylphosphanyl)methanide·$(thf)_3$ (**7**, 1 equiv.) was dissolved in dry tetrahydrofuran (50 mL). After the addition of the respective alkyl halide (4 or 6 equiv.) the solution was stirred at room temperature overnight. The solvent was removed in vacuo, and the residue was suspended in dichloromethane (50 mL). The precipitate was filtered off and washed with dichloromethane (3 × 20 mL). The organic phases were combined, and the volatilities were removed in vacuo. The obtained crude product was suspended in pentane (40 mL), collected by filtration, washed with pentane, and then dried in vacuo.

8a: The reaction of **7** (0.50 g, 0.79 mmol) with bromoethane (0.35 g, 0.24 mL, 3.21 mmol) yielded **8a** as a white solid (0.24 g, 69%). M.p. 129 °C (DSC). ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 7.67 (m, $^3J_{P-1,H}$ = 12.1 Hz, 4 H, *o*-Ph^1), 7.63 (m, $^5J_{P-1,H}$ = 1.8 Hz, 2 H, *p*-Ph^1), 7.52 (m, $^4J_{P-1,H}$ = 2.9 Hz, 4 H, *m*-Ph^1), 7.45 (m, $^3J_{P-2,H}$ = 7.8 Hz, 4 H, *o*-Ph^2), 7.32 (m, $^4J_{P-2,H}$ = 1.5 Hz, 4 H, *m*-Ph^2), 7.30 (m, 2 H, *p*-Ph^2), 2.71 (dq, $^2J_{P-1,H}$ = 12.2 Hz, $^3J_{H,H}$ = 7.4 Hz, PCH_2), 1.23 (td, $^3J_{P-1,H}$ = 18.4 Hz, $^3J_{H,H}$ = 7.4 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ = 141.1 (dd, $^1J_{P-2,C}$ = 8.5 Hz, $^3J_{P-1,C}$ = 7.2 Hz, *i*-Ph^2), 133.04 (dd, $^2J_{P-1,C}$ = 9.2 Hz, $^4J_{P-2,C}$ = 1.5 Hz, *o*-Ph^1), 133.03 (d, $^4J_{P-1,C}$ = 2.9 Hz, *p*-Ph^1), 132.7 (d, $^2J_{P-2,C}$ = 19.6 Hz, *o*-Ph^2), 129.4 (d, $^3J_{P-1,C}$ = 12.0 Hz, *m*-Ph^1), 128.5 (d, $^3J_{C,P-2}$ = 6.8 Hz, *m*-Ph^2), 128.2 (s, *p*-Ph^2), 127.0 (dd, $^1J_{P-1,C}$ = 86.7 Hz, $^2J_{P-1,C}$ = 2.6 Hz, *i*-Ph^1), 125.0 (dd, $^2J_{P-1,C}$ = 13.1 Hz, $^2J_{P-2,C}$ = 0.8 Hz, C≡N), 19.1 (dd, $^1J_{P-1,C}$ = 62.5 Hz, $^3J_{P-2,C}$ = 9.9 Hz, CH_2), 6.96 (dd, $^2J_{P-1,C}$ = 4.9 Hz, $^4J_{P-2,C}$ = 2.9 Hz, CH_3), 6.92 (dd, $^1J_{P-1,C}$ = 128.0 Hz, $^1J_{P-2,C}$ = 28.9 Hz, P=C) ppm. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 298 K): δ = 29.3 (d, $^2J_{P-1,P-2}$ = 140.8 Hz, P-1), –19.2 (d, $^2J_{P-2,P-1}$ = 140.8 Hz, P-2) ppm. FTIR (KBr): $\tilde{\nu}$ = 3058, 2957, 2137, 1429, 1261, 1100, 1025, 800, 695, 564 cm^{-1}. MS (EI, 70 eV): m/z (%) = 437.2 (72) $[M]^+$, 408.1 (100) $[M - CH_2CH_3]^+$, 360 (17) $[M - C_6H_5]^+$, 262.1 (16), 185.1 (23) $[M - C_{12}H_{10}P]^+$, 183.0 (29) $[C_{12}H_8P]^+$. $C_{28}H_{25}NP_2$ (437.46): calcd. C 76.88, H 5.76, N 3.20; found C 76.43, H 5.71, N 3.11. X-ray crystal structure analysis of **8a**: formula $C_{28}H_{25}NP_2$, M = 437.43, colorless crystal 0.30 × 0.30 × 0.20 mm, a = 9.602(1), b = 15.189(1), c = 15.789(1) Å, β = 100.05(1)°, V = 2267.4(3) Å^3, $\rho_{calcd.}$ = 1.281 g cm^{-3}, μ = 0.208 mm^{-1}, empirical absorption correction ($0.941 \le T \le 0.960$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 198 K, ω and ϕ scans, 15000 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.67 Å^{-1}, 5441 independent (R_{int} = 0.043) and 4049 observed reflections [$I \ge 2\sigma(I)$], 281 refined parameters, R = 0.045, wR_2 = 0.112, max. residual electron density

0.33 (–0.38) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

8b: The reaction of **7** (1.00 g, 1.58 mmol) with 1-bromopropane (0.78 g, 0.58 mL, 6.34 mmol) yielded **8b** as a white solid (0.66 g, 93%). M.p. 122 °C (DSC). ^{1}H NMR (499.8 MHz, CD_2Cl_2, 298 K): δ = 7.67 (m, $^3J_{P-1,H}$ = 12.1 Hz, 4 H, *o*-Ph^1), 7.62 (m, $^5J_{P-1,H}$ = 1.8 Hz, 2 H, *p*-Ph^1), 7.52 (m, $^4J_{P-1,H}$ = 2.9 Hz, 4 H, *m*-Ph^1), 7.45 (m, $^3J_{P-2,H}$ = 7.7 Hz, 4 H, *o*-Ph^2), 7.32 (m, $^4J_{P-2,H}$ = 1.7 Hz, 4 H, *m*-Ph^2), 7.30 (m, $^5J_{P-2,C}$ = 0.5 Hz, 2 H, *p*-Ph^2), 2.65 (m, $^2J_{P-1,H}$ = 12.1 Hz, PCH_2), 1.64 (m, $^3J_{P-1,H}$ = 16.6 Hz, 2 H, CH_2), 1.03 (td, $^3J_{H,H}$ = 7.4 Hz, $^4J_{P-1,H}$ = 1.6 Hz, 3 H, CH_3) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ = 141.1 (dd, $^1J_{P-2,C}$ = 8.5 Hz, $^3J_{P-1,C}$ = 7.2 Hz, *i*-Ph^2), 133.00 (d, $^4J_{P-1,C}$ = 2.9 Hz, *p*-Ph^1), 132.99 (dd, $^2J_{P-1,C}$ = 9.4 Hz, $^4J_{P-2,C}$ = 1.6 Hz, *o*-Ph^1), 132.7 (d, $^2J_{P-2,C}$ = 19.7 Hz, *o*-Ph^2), 129.4 (d, $^3J_{P-1,C}$ = 12.0 Hz, *m*-Ph^1), 128.4 (d, $^3J_{C,P-2}$ = 6.8 Hz, *m*-Ph^2), 128.2 (s, *p*-Ph^2), 127.3 (dd, $^1J_{P-1,C}$ = 86.7 Hz, $^2J_{P-1,C}$ = 2.4 Hz, *i*-Ph^1), 125.0 (dd, $^2J_{P-1,C}$ = 13.0 Hz, $^2J_{P-2,C}$ = 1.0 Hz, C≡N), 27.6 (dd, $^1J_{P-1,C}$ = 60.7 Hz, $^3J_{P-2,C}$ = 9.3 Hz, PCH_2), 16.7 (dd, $^2J_{P-1,C}$ = 3.8 Hz, $^4J_{P-2,C}$ = 3.2 Hz, CH_2), 15.6 (d, $^3J_{P-1,C}$ = 17.1 Hz, CH_3), 7.4 (dd, $^1J_{P-1,C}$ = 128.2 Hz, $^1J_{P-2,C}$ = 29.3 Hz, P=C) ppm. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 298 K): δ = 27.0 (d, $^2J_{P-1,P-2}$ = 141.2 Hz, P-1), –19.0 (d, $^2J_{P-1,P-2}$ = 141.2 Hz, P-2) ppm. ^{1}H,^{31}P ghmbc (499.8/202 MHz, CD_2Cl_2, 298 K): ^{31}P/^{1}H, δ = 27.0/7.67, 7.62, 7.52, 2.65, 1.64, 1.03 (P-1/*o*, *p*, *m*-Ph^1, PCH_2, CH_2, CH_3); –19.0/7.45 (P-2/*o*-Ph^2) ppm. FTIR (KBr): $\tilde{\nu}$ = 3055, 2963, 2873, 2148, 1436, 1172, 1118, 1070, 955, 803, 69 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 451.2 (30) $[M]^+$, 408.1 (68) $[M - C_3H_7]^+$, 374.2 (6) $[M - C_6H_5]^+$, 262.1 (32), 185.1 (39) $[M - C_{12}H_{10}P]^+$, 183.0 (100) $[C_{12}H_8P]^+$.

8c: The reaction of **7** (1.00 g, 1.58 mmol) with 1-bromobutane (0.87 g, 0.68 mL, 6.33 mmol) yielded **8c** as a white solid (0.55 g, 75%). M.p. 134 °C (DSC). ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 7.68 (m, 4 H, *o*-Ph^1), 7.63 (m, 2 H, *p*-Ph^1), 7.52 (m, 4 H, *m*-Ph^1), 7.46 (m, 4 H, *o*-Ph^2), 7.33 (m, 4 H, *m*-Ph^2), 7.31 (m, 2 H, *p*-Ph^2), 2.68 (m, PCH_2), 1.58 (m, 2 H, PCH_2CH_2), 1.43 (m, 2 H, CH_2CH_3), 0.87 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3) ppm. ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ = 141.1 (dd, $^1J_{P-2,C}$ = 8.6 Hz, $^3J_{P-1,C}$ = 7.4 Hz, *i*-Ph^2), 132.96 (d, $^4J_{P-1,C}$ = 3.2 Hz, *p*-Ph^1), 132.95 (dd, $^2J_{P-1,C}$ = 9.2 Hz, $^4J_{P-2,C}$ = 1.6 Hz, *o*-Ph^1), 132.7 (d, $^2J_{P-2,C}$ = 19.7 Hz, *o*-Ph^2), 129.4 (d, $^3J_{P-1,C}$ = 11.9 Hz, *m*-Ph^1), 128.4 (d, $^3J_{C,P-2}$ = 6.8 Hz, *m*-Ph^2), 128.2 (s, *p*-Ph^2), 127.3 (dd, $^1J_{P-1,C}$ = 86.8 Hz, $^2J_{P-1,C}$ = 2.4 Hz, *i*-Ph^1), 125.0 (dd, $^2J_{P-1,C}$ = 13.0 Hz, $^2J_{P-2,C}$ = 1.1 Hz, C≡N), 25.3 (dd, $^1J_{P-1,C}$ = 60.8 Hz, $^3J_{P-2,C}$ = 9.2 Hz, PCH_2), 24.8 (t, $^2J_{P-1,C}$ = $^4J_{P-2,C}$ = 3.5 Hz, PCH_2CH_2), 24.3 (d, $^3J_{P-1,C}$ = 15.9 Hz, CH_2CH_3), 13.6 (CH_3), 7.4 (dd, $^1J_{P-1,C}$ = 128.0 Hz, $^1J_{P-2,C}$ = 28.5 Hz, P=C) ppm (assignment made by comparison with the NMR spectroscopic data of **8a**,**b**). ^{31}P{^{1}H} NMR (81 MHz, CD_2Cl_2, 298 K): δ = 26.9 (d, $^2J_{P-1,P-2}$ = 140.8 Hz, P-1), –19.5 (d, $^2J_{P-1,P-2}$ = 140.8 Hz, P-2) ppm. FTIR (KBr): $\tilde{\nu}$ = 3050, 2957, 2923, 2867, 2133, 1628, 1433, 1261, 1103, 976, 800, 748, 688 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 465.2 (66) $[M]^+$, 408.1 (100) $[M - C_3H_7]^+$, 388.0 (15) $[M - C_6H_5]^+$, 262.1 (54) $[P(C_6H_5)_3]^+$, 185.1 (39) $[M - C_{12}H_{10}P]^+$, 183.0 (100) $[C_{12}H_8P]^+$, 108.0 (25) $[PC_6H_5]^+$. X-ray crystal structure analysis of **8c**: formula $C_{30}H_{29}NP_2$, M = 465.48, light yellow crystal 0.50 × 0.30 × 0.15 mm, a = 10.493(1), b = 14.584(1), c = 17.167(1) Å, β = 97.95(1)°, V = 2601.8(3) Å^3, $\rho_{calcd.}$ = 1.188 g cm^{-3}, μ = 0.185 mm^{-1}, empirical absorption correction (0.913 ≤ T ≤ 0.973), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 198 K, ω and ϕ scans, 18706 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.67 Å^{-1}, 6292 independent (R_{int} = 0.038) and 5226 observed reflections [$I \geq 2\sigma(I)$], 299 refined parameters, R = 0.049, wR_2 = 0.142, max. residual electron density 1.01 (–0.33) e·Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

8d: The reaction of **7** (0.50 g, 0.79 mmol) with 1-bromohexane (0.52 g, 0.44 mL, 3.14 mmol) yielded **8d** as a white solid (0.33 g, 85%). M.p. 155 °C (DSC). ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 7.68 (m, 4 H, *o*-Ph^1), 7.63 (m, 2 H, *p*-Ph^1), 7.52 (m, 4 H, *m*-Ph^1), 7.45 (m, 4 H, *o*-Ph^2), 7.32 (m, 4 H, *m*-Ph^2), 7.31 (m, 2 H, *p*-Ph^2), 2.66 (m, PCH_2), 1.59 (m, 2 H, PCH_2CH_2), 1.39 (m, 2 H, $PCH_2CH_2CH_2$), 1.22 (m, 4 H, $CH_2CH_2CH_3$), 0.84 (m, 3 H, CH_3) ppm. ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ = 141.1 (dd, $^1J_{P-2,C}$ = 8.5 Hz, $^3J_{P-1,C}$ = 7.3 Hz, *i*-Ph^2), 132.97 (d, $^4J_{P-1,C}$ = 2.9 Hz, *p*-Ph^1), 132.96 (dd, $^2J_{P-1,C}$ = 9.3 Hz, $^4J_{P-2,C}$ = 1.5 Hz, *o*-Ph^1), 132.7 (d, $^2J_{P-2,C}$ = 19.9 Hz, *o*-Ph^2), 129.4 (d, $^3J_{P-1,C}$ = 12.0 Hz, *m*-Ph^1), 128.4 (d, $^3J_{C,P-2}$ = 6.8 Hz, *m*-Ph^2), 128.2 (s, *p*-Ph^2), 127.3 (dd, $^1J_{P-1,C}$ = 86.7 Hz, $^2J_{P-1,C}$ = 2.6 Hz, *i*-Ph^1), 125.1 (dd, $^2J_{P-1,C}$ = 12.9 Hz, $^2J_{P-2,C}$ = 1.1 Hz, C≡N), 31.4 (d, $^4J_{P-1,C}$ = 0.8 Hz, $CH_2CH_2CH_3$), 30.8 (d, $^3J_{P-1,C}$ = 15.6 Hz, $PCH_2CH_2CH_2$), 25.6 (dd, $^1J_{P-1,C}$ = 60.9 Hz, $^3J_{P-2,C}$ = 9.8 Hz, PCH_2), 22.70 (CH_2CH_3), 22.66 (dd, $^2J_{P-1,C}$ = 4.0 Hz, $^4J_{P-2,C}$ = 3.1 Hz, PCH_2CH_2), 14.1 (CH_3), 7.3 (dd, $^1J_{P-1,C}$ = 128.1 Hz, $^1J_{P-2,C}$ = 28.8 Hz, P=C) ppm (assignment made by comparison with the NMR spectroscopic data of **8a**,**b**). ^{31}P{^{1}H} NMR (81 MHz, CD_2Cl_2, 298 K): δ = 26.9 (d, $^2J_{P-1,P-2}$ = 142.0 Hz, P-1), –19.5 (d, $^2J_{P-2,P-1}$ = 142.0 Hz, P-2) ppm. FTIR (KBr): $\tilde{\nu}$ = 3057, 2961, 2931, 2859, 2151, 1436, 1260, 1184, 1100, 1017, 804, 744, 718, 691, 549 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 493.2 (63) $[M]^+$, 408.1 (100) $[M - C_6H_{13}]^+$, 262.1 (67) $[P(C_6H_5)_3]^+$, 186.1 (53) [M(408) – $C_{12}H_{10}P]^+$, 108.0 (26) $[PC_6H_5]^+$.

9a: The reaction of **7** (0.70 g, 1.11 mmol) with methyl iodide (0.95 g, 0.41 mL, 6.69 mmol) yielded **9a** as a white solid (0.48 g, 76%). M.p. 221 °C (DSC). ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 7.72 (m, 4 H, *p*-Ph), 7.67 (m, 8 H, *o*-Ph), 7.58 (m, 8 H, *m*-Ph), 2.40 (m, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ = 134.8 (*p*-Ph), 132.8 (m, *o*-Ph), 130.4 (m, *m*-Ph), 122.6 (m, *i*-Ph), 119.4 (t, $^2J_{P,C}$ = 3.9 Hz, C≡N), 14.6 (m, CH_3), 5.6 (t, $^1J_{P,C}$ = 117.1 Hz, P=C) ppm. ^{31}P{^{1}H} NMR (81 MHz, CD_2Cl_2, 298 K): δ = 21.7 ppm. FTIR (KBr): $\tilde{\nu}$ = 3050, 2957, 2885, 2160, 1435, 1105, 1049, 886, 747, 689 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 438 (9) $[M]^+$, 423 (47) $[M - CH_3]^+$, 408.1 (32) $[M - 2CH_3]^+$, 360 (17) $[M - C_6H_5]^+$, 262.1 (14), 185.1 (46) $[M - C_{12}H_{10}P]^+$, 183.0 (42) $[C_{12}H_8P]^+$. $C_{28}H_{26}INP_2$ (565.37): calcd. C 59.48, H 4.64, N 2.48; found C 59.31, H 4.68, N 2.34. X-ray crystal structure analysis of **9a**: formula $C_{28}H_{26}INP_2$, M = 565.34, colorless crystal 0.25 × 0.25 × 0.10 mm, a = 9.596(1), b = 9.803(1), c = 13.891(1) Å, α = 88.18(1), β = 77.69(1), γ = 84.98(1)°, V = 1271.7(2) Å^3, $\rho_{calcd.}$ = 1.476 g cm^{-3}, μ = 11.193 mm^{-1}, empirical absorption correction (0.166 ≤ T ≤ 0.401), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223 K, ω and ϕ scans, 15740 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 4481 independent (R_{int} = 0.040) and 4413 observed reflections [$I \geq 2\sigma(I)$], 291 refined parameters, R = 0.047, wR_2 = 0.139, max. residual electron density 1.93 (–0.91) e·Å^{-3} close to I, hydrogen atoms calculated and refined as riding atoms.

9b: The reaction of **7** (0.30 g, 0.47 mmol) with benzyl bromide (0.50 g, 0.34 mL, 2.92 mmol) yielded **9b** as a white solid (0.23 g, 73%). M.p. 182 °C (DSC). ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 7.60 (m, 4 H, *p*-Ph^P), 7.35 (m, 2 H, *p*-Ph), 7.33 (m, 8 H, *m*-Ph^P), 7.27 (m, 8 H, *o*-Ph^P), 7.24 (m, 4 H, *m*-Ph), 7.03 (m, 4 H, *o*-Ph), 4.34 (m, 4 H, CH_2) ppm. ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ = 134.6 (m, *p*-Ph^P), 134.0 (m, *o*-Ph^P), 131.6 (m, *o*-Ph), 129.9 (m, *m*-Ph^P), 129.2 (*m*-Ph), 129.0 (*p*-Ph), 128.6 (*i*-Ph, assigned by ^{1}H,^{13}C ghmbc experiment), 120.4 (t, $^2J_{P,C}$ = 4.8 Hz, C≡N),

119.4 (m, *i*-Ph^P), 36.6 (m, CH_2), 3.2 (t, $^1J_{P,C}$ = 117.3 Hz, P=C) ppm. $^{31}P\{^1H\}$ NMR (81 MHz, CD_2Cl_2, 298 K): δ = 23.9 ppm. FTIR (KBr): $\tilde{\nu}$ = 3050, 3009, 2854, 2781, 2159, 1434, 1149, 1104, 1047, 833, 782, 743, 691, 582 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 589 (1) $[M]^+$, 499 (12) $[M - CH_2(C_6H_5)]^+$, 408.1 (32) $[M - 2CH_2(C_6H_5)]^+$, 360 (17) $[M - C_6H_5]^+$, 262.1 (14), 183.0 (77) $[C_{12}H_8P]^+$, 91 (100) $[CH_2(C_6H_5)]^+$. $C_{40}H_{34}BrNP_2$ (670.57): calcd. C 71.65, H 5.11, N 2.09; found C 70.91, H 5.07, N 1.87. X-ray crystal structure analysis of **9b**: formula $C_{40}H_{34}BrNP_2 \cdot CH_2Cl_2$, M = 755.46, colorless crystal 0.50 × 0.35 × 0.25 mm, a = 10.323(1), b = 18.641(1), c = 19.633(1) Å, β = 104.19(1)°, V = 3662.7(4) $Å^3$, $\rho_{calcd.}$ = 1.370 $g\,cm^{-3}$, μ = 3.923 mm^{-1}, empirical absorption correction ($0.244 \le T \le 0.441$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223 K, ω and ϕ scans, 28553 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.58 $Å^{-1}$, 5911 independent (R_{int} = 0.041) and 5588 observed reflections [$I \ge 2\,s(I)$], 424 refined parameters, R = 0.037, wR_2 = 0.100, max. residual electron density 0.58 (–0.51) e·$Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

10a: The reaction of **7** (0.30 g, 0.47 mmol) with 1,3-dibromopropane (0.39 g, 0.20 mL, 1.93 mmol) yielded **10a** as a white solid (0.22 g, 88%). M.p. 128 °C (DSC). ^1H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 7.88 (m, 8 H, *o*-Ph), 7.72 (m, 4 H, *p*-Ph), 7.61 (m, 8 H, *m*-Ph), 3.50 (m, 4 H, PCH_2), 2.45 (m, 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 298 K): δ = 134.6 (m, *p*-Ph), 133.1 (m, *o*-Ph), 130.2 (m, *m*-Ph), 123.4 (m, *i*-Ph), 119.1 (C≡N), 21.5 (m, PCH_2), 17.0 (t, $^3J_{P,C}$ = 6.0 Hz, CH_2), 3.2 (t, $^1J_{P,C}$ = 103.8 Hz, P=C) ppm. $^{31}P\{^1H\}$ NMR (81 MHz, CD_2Cl_2, 298 K): δ = 18.3 (s) ppm. FTIR (KBr): $\tilde{\nu}$ = 3054, 3014, 2884, 2166, 1435, 1156, 1108, 1041, 995, 849, 722, 688 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 450 (100) $[M]^+$, 408 (22) $[M - C_3H_6]^+$, 262.1 (27), 183.0 (86) $[C_{12}H_8P]^+$, 108 (34) $[C_6H_5P]^+$. $C_{29}H_{26}BrNP_2$ (530.38): calcd. C 65.67, H 4.94, N 2.64; found C 65.70, H 5.40, N 2.30. X-ray crystal structure analysis of **10a**: formula $C_{29}H_{26}NP_2Br \cdot 1/2\ C_7H_8$, M = 576.43, colorless crystal 0.40 × 0.35 × 0.07 mm, a = 9.714(1), b = 16.270(1), c = 10.062(1) Å, α = 107.84(1), β = 92.61(1), γ = 101.18(1)°, V = 1475.7(2) $Å^3$, $\rho_{calcd.}$ = 1.297 $g\,cm^{-3}$, μ = 1.522 mm^{-1}, empirical absorption correction ($0.581 \le T \le 0.901$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 198 K, ω and ϕ scans, 15825 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.67 $Å^{-1}$, 7092 independent (R_{int} = 0.053) and 5386 observed reflections [$I \ge 2\sigma(I)$], 337 refined parameters, R = 0.071, wR_2 = 0.218, max. residual electron density 1.72 (–0.69) e·$Å^{-3}$ close to Br, bromine atom and the toluene solvent molecule are disordered and refined with split positions, hydrogen atoms calculated and refined as riding atoms.

10b: The reaction of **7** (0.50 g, 0.79 mmol) with 1,4-dibromobutane (0.68 g, 0.38 mL, 3.15 mmol) yielded **10b** as a white solid (0.27 g, 63%). M.p. 146 °C (DSC). ^1H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 7.83 (m, 8 H, *o*-Ph), 7.76 (m, 4 H, *p*-Ph), 7.66 (m, 8 H, *m*-Ph), 3.34 (m, 4 H, PCH_2), 2.02 (m, 4 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 298 K): δ = 134.6 (*p*-Ph), 132.9 (m, *o*-Ph), 130.3 (m, *m*-Ph), 123.6 (m, *i*-Ph), 119.8 (t, $^2J_{P,C}$ = 2.3 Hz, C≡N), 24.7 (m, PCH_2), 21.5 (m, CH_2), 4.7 (t, $^1J_{P,C}$ = 108.9 Hz, P=C) ppm. $^{31}P\{^1H\}$ NMR (81 MHz, CD_2Cl_2, 298 K): δ = 28.8 (s) ppm. FTIR (KBr): $\tilde{\nu}$ = 2911, 2875, 2852, 2835, 2799, 2157, 1479, 1433, 1400, 1163, 1150, 1107, 1051, 992, 821, 748, 719, 689, 554, 525, 508 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 464 (54) $[M]^+$, 408 (7) $[M - C_4H_8]^+$, 262.1 (28), 183.0 (100) $[C_{12}H_8P]^+$, 108 (55) $[C_6H_5P]^+$. $C_{30}H_{28}BrNP_2$ (544.41): calcd. C 66.19, H 5.18, N 2.57; found C 66.14, H 4.95, N 2.42. X-ray crystal structure analysis of **10b**: formula $C_{30}H_{28}NP_2Br$, M = 544.38, colorless crystal 0.40 × 0.30 × 0.20 mm, a = 10.659(1), b = 11.425(1), c = 12.583(1) Å, α = 115.27(1), β = 99.22(1), γ = 99.03(1)°, V = 1323.5(2) $Å^3$, $\rho_{calcd.}$ = 1.366 $g\,cm^{-3}$, μ = 3.392 mm^{-1}, empirical absorption correction ($0.344 \le T \le 0.550$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223 K, ω and ϕ scans, 18436 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.59 $Å^{-1}$, 4515 independent (R_{int} = 0.027) and 4483 observed reflections [$I \ge 2\sigma(I)$], 307 refined parameters, R = 0.040, wR_2 = 0.118, max. residual electron density 0.43 (–0.88) e·$Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

Acknowledgments

Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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Received: January 23, 2007
Published Online: May 11, 2007

