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Remarkable Product Diversity in the "Self-Organized" Reaction of Deprotonated Acetonitrile with Chlorophosphines

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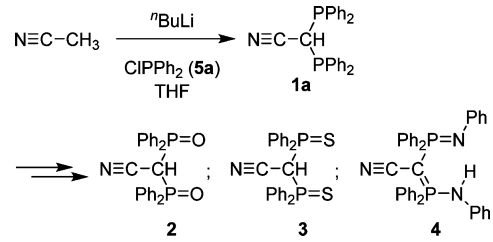
Abstract: This study examined the reaction of *in situ* deprotonated acetonitrile with different chlorophosphines $ClPR_2$ (**5a**−**d**) to find new nitrile functionalized bis(diphenylphosphino)methane (dppm) ligands. Depending on the steric and electronic demand of the phosphines, very different and unexpected products (**1b**, **6**, **9b** and **11**) were found. In the case of aryl-substituted phosphines ($ClPPh_2$ (**5a**) and $ClPMes_2$ (**5b**)), bis(diarylphosphino)acetonitrile compounds (**1a** and **1b**) were found. Introduction of alkyl substituents at the $ClPR_2$ fragment ($R =$ ^{t}butyl (**5c**) and cyclohexyl (**5d**)) changes the overall reaction behavior drastically. A new heteropentafulvene type structure (**6**), a P/N-disubstituted acetylene (**9**), and a P-substituted 3-amidocrotononitrile species (**11**) were found. Considering the experimental simplicity of these three-component reactions, these products are complex and their formations are highly organized. Most compounds were characterized by X-ray diffraction, NMR spectroscopy, and elemental analysis.

Introduction

Bis(diphenylphosphino)methane (dppm) is a very important chelate ligand system in coordination chemistry and catalysis.[1] We have recently described the closely related cyano-substituted analogue (**1a**, dppm-CN).[2] In addition to bearing the additional functional group, this system shows the advantageous feature of being markedly more acidic. Its bis-P-oxides, -sulfides and -imines (**2**−**4**) were prepared; the bis(phosphinimine) **4** is exclusively found in the favored NH tautomeric form (see Scheme 1).[3] These systems form interesting coordination compounds, mostly in their monoanionic state.[4] The phosphorus-based chelate ligands[5] show interesting properties when compared to their related carbon centered analogues, for example, the ubiquitous acac[6] or nacnac[7] metal complex systems.

Scheme 1



The parent dppm-CN chelate system (**1a**) is easily prepared by a remarkably simple one-pot reaction. Treatment of acetonitrile with *n*-butyl lithium followed by chlorodiphenylphosphine (**5a**) in a 1:1:1 ratio in tetrahydrofuran directly gave the product $NC-CH(PPh_2)_2$ (**1a**) in a reasonable yield (66%, relative to the base equivalents used) after conventional workup. Although using an apparently "wrong" stoichiometric ratio of reagents, this simple procedure gave the interesting product dppm-CN (**1a**) in an easy way and acceptable yield under these carefully optimized reaction conditions. We assume that the initially formed Ph_2P-CH_2-CN intermediate was rapidly deprotonated and the corresponding anion trapped by the $ClPPh_2$ reagent to yield **1a**. The possible third deprotonation/phosphination was apparently not favored under the applied reaction conditions. This observation made us aware of the great synthetic potential that such a system might specifically have, namely, to allow the selective preferred formation of a single compound out of a complicated manifold of possible products by the choice of one specific reagent under otherwise standard conditions. In other words, it needed to be tested whether various possible phosphination products of our substrate example acetonitrile could selectively be obtained under just the same simple (or similar) reaction conditions, as they were schematically outlined above for the formation of **1**, just by changing the substituents of the chlorophosphine reagent $ClPR_2$ (**5**) used. Actually, this

(1) See, for example: (a) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432–2439. (b) Appleton, T. G.; Bennett, M. A.; Tomkins, I. B. *J. Chem. Soc., Dalton Trans.* **1976**, 439–446. (c) Puddephatt, R. J. *J. Chem. Soc. Rev.* **1983**, *12*, 99–127. (d) Minahan, D. M. A.; Hill, W. E. *Coord. Chem. Rev.* **1984**, *55*, 31–54. (e) Lee, C.-L.; Yang, Y.-P.; Rettig, S. J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Organometallics* **1986**, *5*, 2220–2228. (f) Schmidbaur, H.; Reber, G.; Schier, A.; Wagner, F. E.; Müller, G. *Inorg. Chim. Acta* **1988**, *147*, 143–150. (g) Oliver, D. L.; Anderson, G. K. *Polyhedron* **1992**, *11*, 2415–2420. (h) Luo, L.; Zhu, N.; Zhu, N.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1994**, *13*, 669–675. (i) Li, C.; Cucullu, M. E.; McIntyre, R. A.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1994**, *13*, 3621–3627. (j) Reid, S. M.; Mague, J. T.; Fink, M. J. *J. Am. Chem. Soc.* **2001**, *123*, 4081–4082. (k) Dossett, S. J.; Gillon, A.; Orpen, A. G.; Fleming, J. S.; Pringle, P. G.; Wass, D. F.; Jones, M. D. *Chem. Commun.* **2001**, 699–700. (l) Bruce, M. I.; Ellis, B. G.; Low, P. J.; Skelton, B. W.; White, A. H. *Organometallics* **2003**, *22*, 3184–3198, and references cited in these articles.

(2) Braun, L.; Liptau, P.; Kehr, G.; Ugolotti, J.; Fröhlich, R.; Erker, G. *Dalton Trans.* **2007**, 1409–1415.

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(4) Spannhoff, K.; Kehr, G.; Kehr, S.; Fröhlich, R.; Erker, G. *Dalton Trans.* **2008**, 3339–3344.

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turned out to be true for this overall reaction scheme: we observed the selective formation of a remarkable variation of phosphination products of acetonitrile under our simple standard reaction conditions (or conditions related to them) by just changing the substituents of the $ClPR_2$ reagent (**5**). Several remarkable examples of such a "self-organized" reaction type are described in this article.

Results and Discussion

We first changed the steric bulk of the aryl substituents at the reagent **5** by employing the considerably more bulky chlorodimesitylphosphine reagent (**5b**) under otherwise unchanged reaction conditions, that is, by employing the reagents CH_3CN, *n*-butyl lithium and $ClP(mesityl)_2$ in a 1:1:1 ratio. This did not change the favored reaction pathway: we isolated the bis(dimesitylphosphino)acetonitrile product (**1b**, see Figure 1) as a white solid in 50% yield, calculated on the basis of the molar equivalents of base used, which, of course, corresponds only to a yield of 25% based on the cheap acetonitrile starting material. Repeating the reaction with the "correct" 1:2:2 stoichiometry of acetonitrile, *n*-butyl lithium base and chlorodimesitylphosphine gave product **1b** in 53% yield (see Scheme 2). As this yield corresponds equally to any reagent employed in the "correct" 1:2:2 stoichiometry, this practically means that the yield was doubled relative to our previous "standard" (i.e., 1:1:1) conditions.

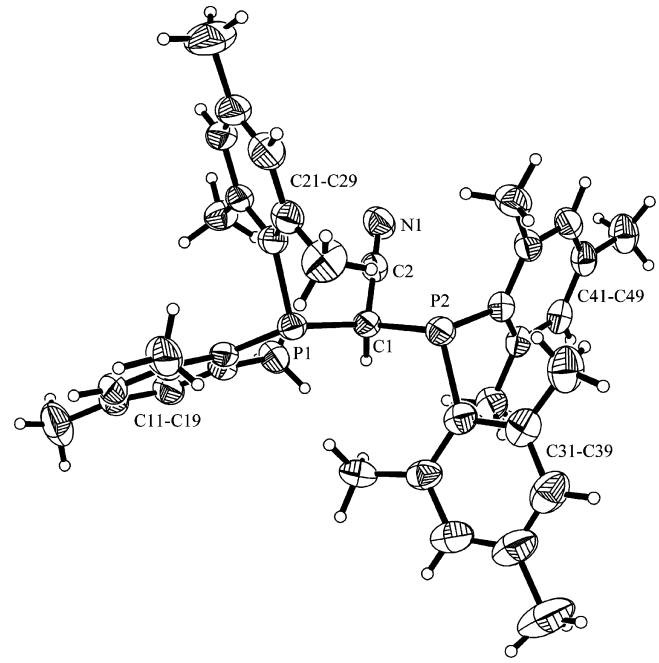
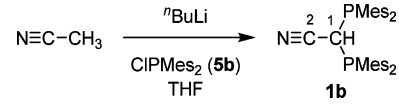


Figure 1. Molecular structure of compound **1b**.

Scheme 2



Compound **1b** was characterized by C,H,N elemental analysis, spectroscopically and by X-ray diffraction. It features a strong $\tilde{\nu}$(C≡N) IR band at 2223 cm^{-1}. The ^{31}P NMR signal is found at δ −19.3 (in d_6-benzene). The ^{13}C NMR features of the $[P]_2CHCN$ moiety are observed at δ 118.4 (t, $^2J_{PC}$ = 5.9 Hz, *C*≡N) and δ 27.6 [t, $^1J_{PC}$ = 38.1 Hz, *C*H, corresponding ^1H NMR signal at δ 5.66 (t, $^2J_{PH}$ = 7.6 Hz, 1H)]. The product **1b** is prochiral and it features a pair of nonplanar tricoordinated phosphorus atoms attached to the central methine carbon C1; therefore, we observe the NMR signals of pairwise diastereotopic mesityl groups at the phosphorus atoms [e.g., δ 2.52 (s, 12H)/2.41 (s, 12H), mesityl *o*-CH_3].

Single crystals of **1b** suited for the X-ray crystal structure analysis were obtained from a benzene/pentane mixture at room temperature. In the crystal compound **1b** features a structure in which the central carbon atom C1 is pseudotetrahedrally coordinated by the -C≡N substituent (C1−C2: 1.456(3) Å, C2−N1: 1.149(2) Å, angle C1−C2−N1: 178.6(2)°), the single remaining hydrogen and a pair of -P(mesityl)$_2$ substituents (C1−P1: 1.885(2) Å, C1−P2: 1.902(2) Å, angle P1−C1−P2: 106.6(1)°). Each P atom features a nonplanar coordination geometry (e.g., angles C1−P1−C11: 110.5(1)°, C1−P1−C21: 105.7(1)°, C11−P1−C21 105.2(1)°/C1−P2−C31: 110.6(1)°, C1−P2−C41: 98.6(1)°, C31−P2−C41: 103.1(1)°). We note that both the structures of **1a** (see above) and **1b** are very similar as

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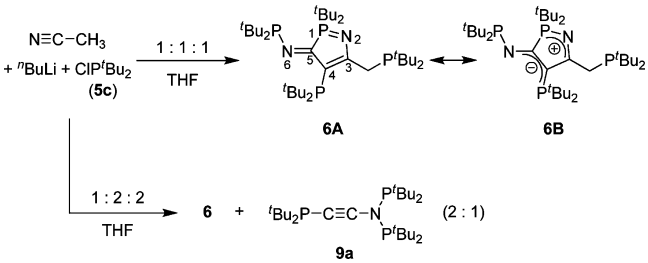
Scheme 3



are their modes of formation. The actually observed reaction pathway did not respond to changing the bulk of the aryl groups at the $ClPAr_2$ reagents even when going from phenyl groups to the much more bulky mesityl substituents.

The overall reaction behavior changed drastically by the introduction of bulky alkyl substituents at the $ClPR_2$ reagent. The reaction between acetonitrile, *n*-butyl lithium and di-*tert*-butylchlorophosphine (**5c**) in a 1:1:1 molar ratio was carried out under our standard conditions. After conventional workup we isolated the heterocyclic product **6** (see Scheme 3) in ca. 19% yield as a yellow solid. The product **6** was identified by X-ray crystal structure analysis, and the compound was then further characterized spectroscopically and by C,H,N elemental analysis.

Compound **6** features a distorted heteropentafulvene type core structure in the crystal (see Figure 2). The central five-membered ring contains a long, probably strongly polarized C═C double bond (C3−C4: 1.432(3) Å) which is in conjugation with an electron-donating R_3P = N- unit (P4−N6: 1.651(2) Å, C4−N6: 1.328(3) Å, angles P4−N6−C4: 108.7(1)°, N6−C4−C3: 121.7(2)°) and an electron-withdrawing phosphinimine functional group at the sp^2-carbon center C2 (C2−P4: 1.964(2) Å, C2−C3: 1.430(3) Å, angles P4−C2−C3: 100.6(1)°, N6−P4−C2: 96.0(1)°, C71−P4−C81: 115.9(1)°, C2−C3−C4: 113.0(2)°; $^tBu_2$−P-N═[C]: N1−C2: 1.294(3) Å, P1−N1: 1.717(2) Å, angles P1−N1−C2: 123.1(2)°, N1−C2−P4: 129.7(2)°, N1−C2−C3: 129.7(2)°). The core of the compound seems to contain a conjugated π-system ranging from the exocyclic N═C bond through the internal C═C and N═P double bonds, but excluding the endocyclic C2−P4 linkage. The system is completed by the attached substituents [$^tBu_2$P- at C3 (P2−C3: 1.835(2) Å) and $^tBu_2$P−CH_2− at C4 (C4−C5: 1.501(3) Å, C5−P3: 1.843(3) Å, angle C4−C5−P3: 118.0(2)°)].

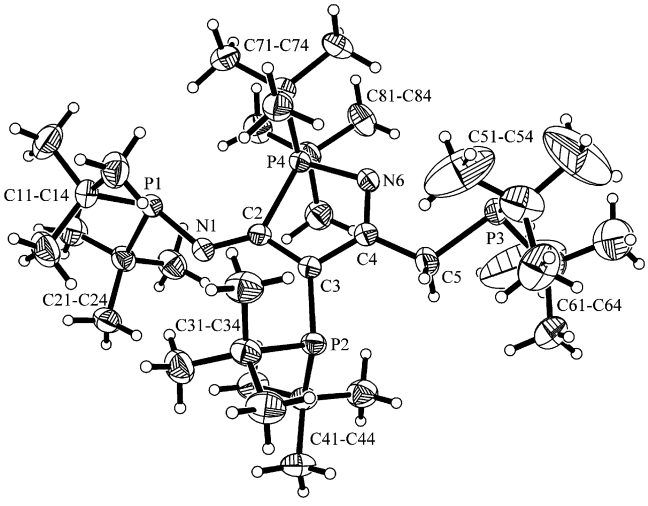
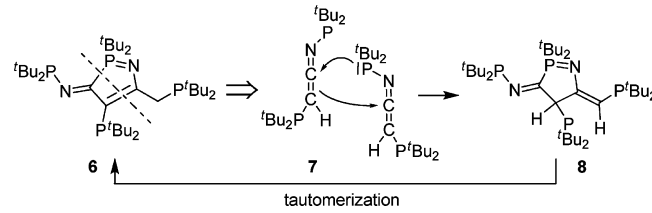


Figure 2. View of the molecular geometry of compound **6**.

Scheme 4



These structural data indicate that the heterocyclic core of compound **6** is markedly polarized. It is probably best schematically represented by a resonance hybrid description between the canonical mesomeric formulas **6A** and **6B** (see Scheme 3). This is supported by some of the characteristic spectroscopic parameters of **6**. The ^1H NMR spectrum features a 2H intensity signal of the exocyclic methylene group at δ 3.64. We monitor the $^{31}P/^1H$ NMR signal pairs of a total of four different P^tBu_2 moieties [P6: δ 128.8/1.33 ($^3J_{PH}$ = 10.9 Hz), P3: δ 36.9 ($^3J_{PP}$ = 3.7 Hz)/1.36 ($^3J_{PH}$ = 10.6 Hz), P1: δ 82.1/1.39 ($^3J_{PH}$ = 14.7 Hz), P4: δ 30.4/1.55 ($^3J_{PH}$ = 12.0 Hz)]. The carbon NMR resonances of the heterocyclic core of **6** occur at δ 204.6 (tentatively assigned to C3), δ 106.9 (C4) and δ 179.8 (C5). The ^{13}C NMR signal of the methylene group was found at δ 32.8 (for coupling constants and further details see the Experimental Section and the Supporting Information).

Apparently in the base-induced reaction with the ClP^tBu_2 reagent (**5c**) acetonitrile was overall twice deprotonated and, consequently, twice phosphorylated, similar as in the reaction with the aromatic $ClPAr_2$ reagents **5a** and **5b**. However, the obtained product (**6**) indicates that here a sequence of P−C/P-N (or *vice versa*) bond formations has occurred. We assume that this has led to the formation of the doubly phosphorylated ketenimine intermediate (**7**), which was, however, not observed directly.[8] Under the applied reaction conditions the ketenimine is not stable but undergoes a specific dimerization reaction (possibly involving intermediate deprotonation) to eventually yield the final observed product **6** (see Scheme 4).[9] The formulated tautomerization step seems to take place prior to the workup; we obtained the product (6-D_2) with a pendant -$CD_2P^tBu_2$ group >75% deuterated from the analogous treatment of CD_3CN with the *n*-butyl lithium base and ClP^tBu_2 (**5c**) (for details see the Supporting Information).

The observed reaction path would again require a "correct" acetonitrile/base/chlorophosphine ratio of 1:2:2. Therefore, we performed this reaction by treatment of CH_3CN with *n*-butyl lithium and ClP^tBu_2 (**5c**) in the 1:2:2 ratio. In this case we obtained a mixture of the expected product **6** with the new product **9a** in a 2:1 ration in a combined yield of ca. 35% (see Scheme 3). The composition of the minor product **9a** was tentatively assigned from its characteristic spectroscopic data,

(8) Sung, K. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1169–1173.
(9) See for a comparison: (a) Schmidpeter, A.; Zeiss, W. *Angew. Chem.* **1971**, *11*, 397–398. *Angew. Chem., Int. Ed.*, **1971** *10*, 396−397. (b) Schmidpeter, A.; Zeiss, W.; Eckert, H. *Z. Naturforsch.* **1972**, *27B*, 769–771. (c) Zeiss, W.; Schmidpeter, A. *Tetrahedron Lett.* **1972**, *13*, 4229–4232. (d) Bestmann, H. J.; Schmid, G.; Böhme, R.; Wilhelm, E.; Burzlaff, H. *Chem. Ber.* **1980**, *113*, 3937–3941. (e) Bestmann, H. J.; Schmid, G. *Tetrahedron Lett.* **1981**, *22*, 1679–1680. (f) Lukashev, N. V.; Zhichkin, P. E.; Tarasenko, E. A.; Luzikov, Yu. N.; Kazankova, M. A. *Russ. J. Gen. Chem.* **1993**, *63*, 1234–1239. *Zh. Obshch. Khim.*, **1993** *63*, 1767−1775. (g) Veneziani, G.; Réau, R.; Dahan, F.; Bertrand, G. *J. Org. Chem.* **1994**, *59*, 5927–5929. (h) Amsallem, D.; Mazières, S.; Piquet-Fauré, V.; Gornitzka, H.; Baceiredo, A.; Bertrand, G. *Chem.—Eur. J.* **2002**, *8*, 5305–5311.

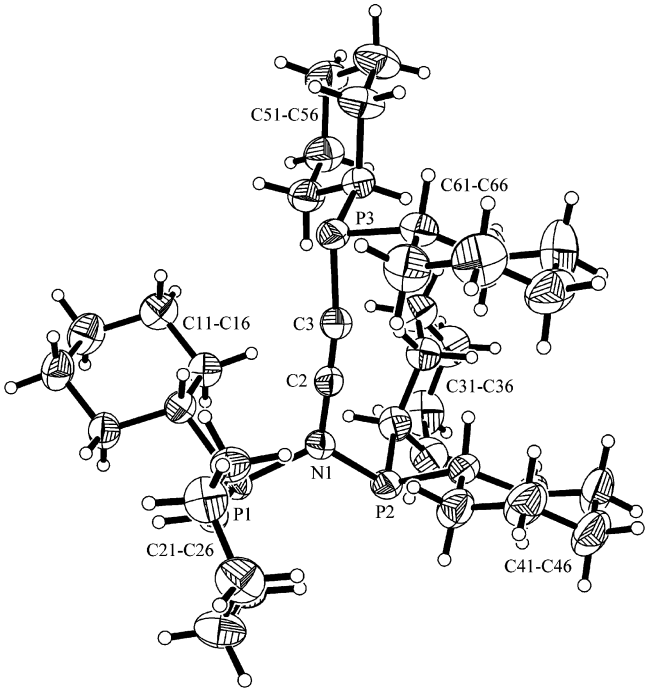


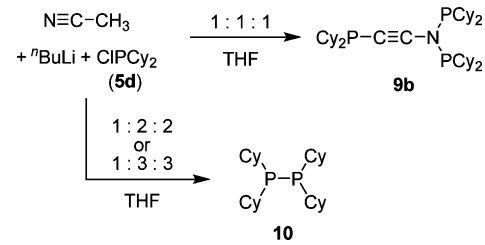
Figure 3. Projection of the molecular geometry of the acetylene **9b**.

obtained from the mixture, in comparison with the isolated and fully characterized analogue **9b** (see below). Typical spectroscopic features of compound **9a** include an IR(C≡C) band at $\tilde{\nu}$ = 2113 cm^{-1}, an ESI-MS-EM feature at m/z = 474.3547 [M + H]$^+$, and ^{31}P NMR resonances at δ 122.4 (2P) and δ 23.8 (t, $^4J_{PP}$ = 2.5 Hz, 1P).

In addition to the observed competing formation of **9a**, we have obtained some evidence for the proposed N/C phosphorylation pathway from the related reaction of acetonitrile/*n*-butyl lithium with chlorodi(cyclohexyl)phosphine (**5d**). The reaction was again first carried out under our standard reaction conditions employing a 1:1:1 ratio of the reagents. Conventional workup gave the *N,N,C*-tris-phosphorylated product **9b** (13% yield) as a slightly air and moisture sensitive pale yellow solid.[10,11] Single crystals suited for X-ray crystal structure analysis of the P/N-disubstituted acetylene **9b** were obtained from toluene at ambient temperature.

The crystal compound **9b** features a linear central [N]−C≡C−[P] core with a C2−C3 (1.201(2) Å) carbon carbon triple bond (bond angles P3−C3−C2: 171.4(2)°, C3−C2−N1: 179.2(2)°) (see Figure 3). The C(sp)−P bond is rather short (C3−P3: 1.757(2) Å) compared to the adjacent C(sp^3)−P linkages (P3−C51/C61: 1.861(2)/1.860(2) Å). The phosphorus center P3 is pyramidalized (sum of the CPC angles: 306.7°). The other end of the C3−C2 triple bond bears the -N(PCy_2)$_2$ substituent. The C2−N1 bond length amounts to 1.352(2) Å. The nitrogen

Scheme 5



coordination geometry is close to trigonal planar (sum of the bonding angles at N1: 359.4°). The N−P bond lengths were found at 1.760(1) Å (N1−P1) and 1.756(1) Å (N1−P2), respectively, which is shorter than the adjacent P−C(sp^3) linkages (e.g., P1−C11: 1.851(2) Å, P1−C21: 1.854(2) Å). Both the phosphorus atoms P1 and P2 exhibit nonplanar coordination geometries (sum of bond angles at P1: 308.4°, at P2: 307.5°).

Compound **9b** shows ^{13}C NMR features of the [N]−C≡C−[P] unit at δ 106.2 (t, $^2J_{PC}$ = 10.1 Hz, [N]−*C*≡) and δ 55.6 (d, $^1J_{PC}$ = 13.7 Hz, ≡*C*−[P]). The ^{31}P NMR [≡C]−*P* resonance was found at δ −20.1, whereas the both phosphorus nuclei bonded to the nitrogen atom give rise to a signal at δ 89.7.

The formation of the tris-phosphorylated compound **9b** eventually required 3-fold deprotonation of the acetonitrile starting material. Therefore, the use of the three reagents acetonitrile, *n*-butyl lithium and chlorodi(cyclohexyl)phosphine in a 1:1:1 ratio, as used here, is counterintuitive. However, our experiments employing these reagents in a 1:2:2 ratio (alternatively 1:3:3) opened a favorable competitive pathway that resulted in the formation of the known compound Cy_2P-PCy_2 (**10**) (Scheme 5).[12] Apparently, halogen/lithium exchange followed by nucleophilic P−P bond formation takes over in this case. Compound **10** was isolated from the reaction mixture and characterized, including X-ray diffraction (for details see the Supporting Information).

We briefly examined how the overall reaction scheme described in this account might change if an excess of acetonitrile was used. To that purpose we treated acetonitrile with *n*-butyl lithium and chlorodi(*tert*-butyl)phosphine (**5c**) in THF in a 2:1:1 ratio. From the reaction mixture we isolated the product **11** in 52% yield. Compound **11** was characterized by an X-ray crystal structure analysis (see Figure 4). It features the newly formed P1−N1 linkage (1.727(2) Å) and the newly formed N−C(2)═C(4) carbon carbon bond (C2−C4: 1.353(3) Å, C2−N1: 1.365(3) Å, angles P1−N1−C2: 126.4(2)°, N1−C2−C4: 120.3(2)°, C2−C4−C5: 123.6(2)°). Carbon atom C2 bears the methyl substituent, carbon atom C4 the cyano functional group (C4−C5: 1.399(4) Å, C5−N6: 1.146(4) Å, angle C4−C5−N6: 178.4(3)°).

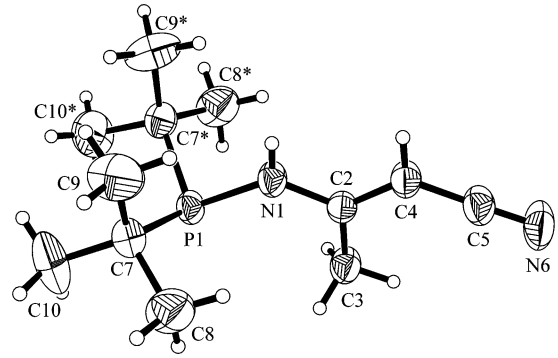


Figure 4. Molecular structure of compound **11**.

(10) (a) Himbert, G.; Regitz, M. *Chem. Ber.* **1974**, *107*, 2513–2536. (b) Bestmann, H. J.; Schmid, G. *Chem. Ber.* **1980**, *113*, 3369–3372. (c) Bestmann, H. J.; Schade, G.; Lütke, H.; Mönius, T. *Chem. Ber.* **1985**, *118*, 2640–1658. (d) Witulski, B.; Alayrac, C. *Sci. Synth.* **2006**, *4*, 883–904.

(11) For organic reactions of α-metallated nitrile substrates see, for example: (a) Fleming, F. F.; Liu, W. *Eur. J. Org. Chem.* **2009**, *69*, 9–708. (b) Fleming, F. F.; Shook, B. C *Tetrahedron* **2002**, *58*, 1–23.

(12) (a) Richter, R.; Kaiser, J.; Sieler, J.; Hartung, H.; Peter, C. *Acta Crystallogr.* **1977**, *B33*, 1887–1892. (b) Dodds, D. L.; Haddow, M. F.; Orpen, A. G.; Pringle, P. G.; Woodward, G. *Organometallics* **2006**, *25*, 5937–5945.

Scheme 6

Compound **11** features characteristic NMR data [^{1}H: δ 4.71 (br., 1 H, C*H*CN), δ 4.46 (N*H*); ^{13}C: δ 165.0 (d, $^2J_{PC}$ = 16.5 Hz, N−*C*═), δ 68.6 (d, $^3J_{PC}$ = 20.7 Hz, ═*C*(CN)), δ 121.3 (d, $^4J_{PC}$ = 2.1 Hz, *C*N); ^{31}P: δ 61.2]. It shows a strong IR(C≡N) band at $\tilde{\nu}$ = 2199 cm^{-1}. Apparently, under these reaction conditions the carbanion generated from acetonitrile added to a second CH_3CN molecule, followed by phosphine trapping/tautomerization to yield **11** (Scheme 6). Related product formation had previously been observed in base-induced metalation reactions of acetonitrile with group 14 main group metal reagents.[13−15]

Conclusions

The base induced three-component reactions of acetonitrile with the diaryl- or dialkylchlorophosphines (**5**) show a remarkable variability in the favored reaction courses taken. All these reactions presumably take place *via* the respective monoanion intermediates, generated *in situ* in cascades that depend critically on the specific reaction conditions and phosphorus reagents chosen.

Generating the acetonitrile monoanion in an excess of the acetonitrile starting material resulted in a rapid trapping reaction toward the formation of the C−C coupling product **11**. The alternative scenario was met when the acetonitrile anion was generated in the presence of both two molar equivalents of base and the $ClPMes_2$ reagent. In this case we must assume the formation of a Mes_2P-CH_2CN intermediate that undergoes subsequent deprotonation and phosphorylation to give the "DArPM-CN" chelate phosphine derivative **1b** in a fair yield.

It is interesting to note that the base induced reactions of acetonitrile follow different pathways in the case of treatment with the dialkylphosphines (**5c**, **5d**). At the same time these reactions seem to be critically dependent on the specific reaction conditions chosen. Both these systems feature *N*,*C*-bis-phosphorylation pathways. In the case of ClP^tBu_2 the resulting alleged $^tBu_2P-N{=}C{=}CH-P^tBu_2$ intermediate (**7**) apparently undergoes dimerization to eventually yield **6**. At higher base concentrations eventually further deprotonation/phosphorylation is observed to give **9** [($^tBu_2P$-): **a**; (Cy_2P-): **b**], but this reaction pathway is lost with increasing base concentrations toward the pathway eventually leading to the competing R_2P-PR_2 product.

We see that an interesting array of products is arising from the base induced phosphorylation reaction of acetonitrile. The outcome of the specific three-component-reaction is critically dependent in detail on the reaction conditions and the diorganylchlorophosphine reagent used. However, we have found that the described compounds, such as the doubly P,N-donor-substituted acetylenes (**9**) or the remarkable "heteropentafulvenoide" compound **6**, of quite different composition can be obtained rather selectively by simple one-pot-procedures, albeit in low yields, by applying our standard reaction and workup conditions. This seems to indicate a remarkable potential of "self-organization" of these reactions under rather simple practical experimental conditions.

Experimental Section

All reactions were carried out under an inert gas atmosphere (argon) in Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior use. The following instruments were used for the physical characterization of the compounds. NMR: *Bruker AC*200 P-FT (^{31}P: 81.0 MHz), *Bruker* AV400 (^{1}H: 400 MHz, ^{13}C: 101 MHz), *Varian Inova* 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{31}P: 202 MHz), *Bruker Unity Plus* 600 (^{1}H: 600 MHz, ^{31}C: 151 MHz, ^{31}P: 243 MHz). Most NMR assignments were supported by additional 1D and 2D experiments. Melting points and decomposition points: *Ta-Instruments* "Differential-Scanning-Calorimeter Q20" (heating-up rate: 10 °C/min). IR: *Varian 3100 FT-IR* spectrometer (KBr pellet or ATR). MS: *Bruker Daltronics* MicroTof (calibration directly before the sample is measured with potassium formiate cluster). Elemental analyses: *Elementar* Vario El III. X-ray structure analysis: Data sets were collected with *Nonius* KappaCCD diffractometers, in case of Mo-radiation equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Otwinowski, Z.; Minor, W. Methods Enzymol. 1997, 276, 307−326), absorption correction SORTAV (Blessing, R. H. Acta Crystallogr. 1995, A51, 33−37; Blessing, R. H. J. Appl. Crystallogr. 1997, 30, 421−426) and Denzo (Otwinowski, Z.; Borek, D.Majewski, W.; Minor, W. Acta Crystallogr. 2003, A59, 228−234), structure solution SHELXS-97 (Sheldrick, G. M. Acta Crystallogr. 1990, A46, 467−473), structure refinement SHELXL-97 (Sheldrick, G. M. Acta Crystallogr. 2008, A64, 112−122), graphics XP (BrukerAXS, 2000).

General Procedure. All compounds were synthesized according to the procedure published for the literature known compound dppm-CN **1a**: Under stirring *n*-butyl lithium (1.6 M in hexane) was added to acetonitrile (dried over CaH_2 and distilled prior use) in tetrahydrofuran (20 mL) at −78 °C. After stirring for 30 min at −78 °C and another 2.5 h at room temperature the solution was again cooled to −78 °C and chlorodiarylphosphine **5b** or chlorodialkylphosphine **5c** or **5d**, respectively, was added drop by drop. The reaction mixture was allowed to warm slowly to room temperature overnight. Then the solvent was removed *in vacuo* and the residue was suspended in dichloromethane (25 mL) in order to remove the lithium chloride by filtration over *Celite*. Once more the solvent was removed *in vacuo* and this time the residue was dissolved in a small amount of ethanol (dried over Mg and distilled prior use, 3−5 mL). After the product precipitated from solution while stirring, it was collected by filtration and dried *in vacuo*.

Compound 1b. 1b was synthesized according to the general procedure using two different stoichiometries A (1:1:1) and B (1:2:2) of CH_3CN, *n*-butyl lithium, and chlorodimesitylphosphine. *Stoichiometry A:* The reaction starting from 2.29 g chlorodimesitylphosphine[16] (7.50 mmol,[17] 1.50 equiv) in 10 mL tetrahydrofuran yielded 719 mg (1.24 mmol, 50%) of compound **1b** as a white air stable solid. *Stoichiometry B:* The reaction of acetonitrile (125 μL, 2.38 mmol, 1.0 equiv), *n*-butyl lithium (3.00 mL, 4.76 mmol, 2.0 equiv), chlorodimesitylphosphine (1.45 g, 4.76 mmol, 2.0 equiv) in 10 mL tetrahydrofuran gave **1b** (724 mg, 1.25 mmol, 53%). Single crystals suitable for X-ray structure analysis were obtained from a benzene/pentane mixture at room temperature. ^{1}H NMR ([D$_6$]-benzene, 400 MHz, 298 K): δ 6.72 (s, 4H, *m*-Mes′), 6.59 (s, 4H, *m*-Mes), 5.66 (t, $^2J_{PH}$ = 7.6 Hz, 1H, C*H*), 2.52 (s, 12H, *o*-$CH_3^{Mes'}$), 2.41 (s, 12H, *o*-CH_3^{Mes}), 2.01 (s, 6H, *p*-$CH_3^{Mes'}$), 2.00

(13) For silyl acetonitriles, see: Krempner, C.; Martens, K.; Reinke, H. *J. Organomet. Chem.* **2007**, *692*, 5799–5803, and references cited therein.
(14) For germyl acetonitriles, see: (a) Wiberg, N.; Kim, C.-K. *Chem. Ber.* **1986**, *119*, 2966–2979. (b) Subashi, E.; Rheingold, A. L.; Weinert, C. S. *Organometallics* **2006**, *25*, 3211–3219.
(15) For the 3-amidocrotononitrile species tBu$_3$Ge[NHC(CH$_3$)CHCN], see: Amadoruge, M. L.; DiPasquale, A. G.; Rheingold, A. L.; Weinert, C. S. *J. Organomet. Chem.* **2008**, *693*, 1771–1778.
(16) Goldwhite, H.; Kaminski, J.; Millhauser, G.; Ortiz, J.; Vargas, M.; Vertal, L. *J. Organomet. Chem.* **1986**, *310*, 21–25.
(17) Due to a 33% impurity, the initial amount of the starting material was higher to achieve 1.0 equiv of chlorodimesitylphosphine.

(s, 6H, *p*-CH_3^{Mes}). $^{13}C\{^1H\}$ NMR ([D$_6$]-benzene, 101 MHz, 298 K): δ 144.6 (t, $^2J_{PC}$ = 8.2 Hz, *o*-Mes′), 141.8 (t, $^2J_{PC}$ = 8.2 Hz, *o*-Mes), 139.6 (*p*-Mes′), 138.2 (*p*-Mes), 131.7 (t, $^1J_{PC}$ = 11.7 Hz, *i*-Mes), 130.9 (t, $^3J_{PC}$ = 1.6 Hz, *m*-Mes), 130.7 (t, $^3J_{PC}$ = 1.9 Hz, *m*-Mes′), 129.2 (t, $^1J_{PC}$ = 7.4 Hz, *i*-Mes′), 118.4 (t, $^2J_{PC}$ = 5.9 Hz, *C*N), 27.6 (t, $^1J_{PC}$ = 38.1 Hz, *C*H), 23.7 (t, $^3J_{PC}$ = 9.7 Hz, *o*-C$H_3^{Mes'}$), 23.4 (t, $^3J_{PC}$ = 9.1 Hz, *o*-CH_3^{Mes}), 20.9 (*p*-C$H_3^{Mes'}$), 20.7 (*p*-CH_3^{Mes}). $^{31}P\{^1H\}$ NMR ([D$_6$]-benzene, 81 MHz, 298 K): δ −19.3 (s, $\nu_{1/2}$ = 2.3 Hz). Anal. calcd for $C_{38}H_{45}NP_2$: C, 79.00; H, 7.85; N, 2.42. Found: C, 78.58; H, 7.79; N, 2.33. IR (ATR): $\tilde{\nu}$ 2223 (ν(C≡N)). Melting Point (DSC): 167 °C.

X-Ray Crystal Structure Analysis of 1b. Formula $C_{38}H_{45}NP_2$, M = 577.69, colorless crystal 0.40 × 0.40 × 0.20 mm^3, a = 30.2865(2), c = 14.7582(2) Å, V = 13537.3(2) Å^3, ρ_{calc} = 1.134 g cm^{-3}, μ= 0.154 mm^{-1}, empirical absorption correction (0.941 ≤ T ≤ 0.970), Z = 16, tetragonal, space group $I4_1/a$ (No. 88), λ= 0.71073 Å, T = 223(2) K, ω and φ scans, 59657 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.66 Å^{-1}, 8075 independent (R_{int} = 0.084) and 4984 observed reflections [$I \geq 2\,\sigma(I)$], 382 refined parameters, R = 0.049, wR^2 = 0.136, max. residual electron density 0.21 (−0.26) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Compound 6. 6 was synthesized according to the general procedure using CH_3CN, *n*-butyl lithium and di-*tert*-butylchlorophosphine in a 1:1:1 ratio. The reaction of CH_3CN (250 μL, 4.76 mmol, 1.0 equiv) and *n*-butyl lithium (3.00 mL, 4.76 mmol, 1.0 equiv) with di-*tert*-butylchlorophosphine (860 mg, 4.76 mmol, 1.0 equiv) gave compound **6** as a yellow air stable solid (150 mg, 0.23 mmol, 19%). Single crystals were obtained from a benzene solution at room temperature. ^1H NMR ([D$_6$]-benzene, 600 MHz, 298 K): δ 3.64 (m, 2H, CH_2), 1.55 (d, $^3J_{PH}$ = 12.0 Hz, 18H, 4-^{t}Bu), 1.39 (d, $^3J_{PH}$ = 14.7 Hz, 18H, 1-^{t}Bu), 1.36 (d, $^3J_{PH}$ = 10.6 Hz, 18H, 3-^{t}Bu), 1.33 (d, $^3J_{PH}$ = 10.9 Hz, 18H, 6-^{t}Bu). $^{13}C\{^1H\}$ NMR ([D$_6$]-benzene, 126 MHz, 298 K): δ 204.6 (dddd, J_{PC} = 40.7 Hz, J_{PC} = 15.6 Hz, J_{PC} = 2.7 Hz, J_{PC} = 0.9 Hz, C3), 179.8 (dddd, J_{PC} = 43.5 Hz, J_{PC} = 39.5 Hz, J_{PC} = 13.0 Hz, J_{PC} = 2.4 Hz, C5), 106.9 (dddd, J_{PC} = 64.9 Hz, J_{PC} = 36.8 Hz, J_{PC} = 13.3 Hz, J_{PC} = 1.8 Hz, C4), 37.1 (d, $^1J_{PC}$ = 26.0 Hz, 1-^{t}Bu^q), 36.7 (d, $^1J_{PC}$ = 22.0 Hz, 6-tBu^q), 34.0 (d, $^1J_{PC}$ = 21.5 Hz, 4-^{t}Bu^q), 32.8 (ddd, J_{PC} = 31.1 Hz, J_{PC} = 24.3 Hz, J_{PC} = 19.9 Hz, *C*H$_2$), 32.5 (d, $^1J_{PC}$ = 26.5 Hz, 3-^{t}Bu^q), 32.1 (d, $^2J_{PC}$ = 15.5 Hz, 4-^{t}Bu^{Me}), 31.0 (d, $^2J_{PC}$ = 12.6 Hz, 6-^{t}Bu^{Me}), 30.6 (dd, $^2J_{PC}$ = 15.0 Hz, J_{PC} = 1.9 Hz, 3-^{t}Bu^{Me}), 28.6 (dd, $^2J_{PC}$ = 7.5 Hz, J_{PC} = 1.9 Hz, 1-^{t}Bu^{Me}). $^{31}P\{^1H\}$ NMR ([D$_6$]-benzene, 243 MHz, 298 K): δ 128.8 (s, $\nu_{1/2}$ = 6.5 Hz, P6), 82.1 (d, J_{PP} = 2.3 Hz, $\nu_{1/2}$ = 3.2 Hz, P1), 36.9 (d, J_{PP} = 3.7 Hz, $\nu_{1/2}$ = 2.3 Hz, P3), 30.4 (d, J_{PP2} = 3.7 Hz, $\nu_{1/2}$ = 2.4 Hz, P4). Anal. Calcd. for $C_{36}H_{74}N_2P_4$: C, 65.62; H, 11.32; N, 4.25. Found: C, 65.01; H, 11.32; N, 4.31. MS-ESI-EM Calcd for ($C_{36}H_{74}N_2P_4$)H: 659.4875. Found: 659.4872. Melting Point (DSC): 240.8 °C.

X-Ray Crystal Structure Analysis for 6. Formula $C_{36}H_{74}N_2P_4$, M = 658.85, yellow crystal 0.50 × 0.25 × 0.15 mm^3, a = 8.7518(4), b = 15.1375(5), c = 15.6376(7) Å, α = 97.622(2), β = 91.057(2), γ = 97.509(2)°, V = 2034.4(2) Å^3, ρ_{calc} = 1.076 g cm^{-3}, μ = 1.883 mm^{-1}, empirical absorption correction (0.453 ≤ T ≤ 0.765), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ= 1.54178 Å, T = 223(2) K, ω and φ scans, 23091 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 7027 independent (R_{int} = 0.038) and 6747 observed reflections [$I \geq 2\,\sigma(I)$], 403 refined parameters, R = 0.051, wR^2 = 0.137, max. residual electron density 0.71(−0.56) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Compound 9b. 9b was synthesized according to the general procedure using CH_3CN, *n*-butyl lithium and chlorodicyclohexylphosphine) in a 1:1:1 ratio. The reaction of acetonitrile (250 μL, 4.76 mmol, 1.0 equiv), *n*-butyl lithium (3.00 mL, 4.76 mmol, 1.0 equiv) and chlorodicyclohexylphosphine (1.11 g, 4.76 mmol, 1.0 equiv) gave the pale yellow air sensitive solid **9b** (125 mg, 0.20 mmol, 13%). Single crystals suitable for X-ray analysis were obtained from a toluene solution at room temperature. ^1H NMR ([D$_6$]-benzene, 500 MHz, 298 K): δ 2.25, 1.64 (*o*-Cy^{PN}), 2.14 (*i*-Cy^{PN}), 2.12, 1.57 (*o*′-Cy^{PC}), 1.92, 1.52 (*o*′-Cy^{PN}), 1.87, 1.41 (*o*-Cy^{PC}), 1.87, 1.36 (*m*-Cy^{PN}), 1.84, 1.28 (*m*-Cy^{PC}), 1.76, 1.27 (*m*-Cy^{PN}, *m*-Cy^{PC}), 1.74 (*i*-Cy^{PC}), 1.67, 1.27 (*p*-Cy^{PC}), 1.65, 1.24 (*p*-Cy^{PN}) [chemical shift values extracted from ghsqc NMR experiments]. $^{13}C\{^1H\}$ NMR ([D$_6$]-benzene, 126 MHz, 298 K): δ 106.2 (t, $^2J_{PC}$ = 10.1 Hz, ≡C−N); 55.6 (d, $^1J_{PC}$ = 13.7 Hz, P−C≡), 37.7 (AXX′, $^1J_{PC}$ + $^3J_{P'C}$ = 16.6 Hz, *i*-Cy^{PN}), 33.8 (d, $^1J_{PC}$ = 8.4 Hz, *i*-Cy^{PC}), 30.6 (d, $^2J_{PC}$ = 18.4 Hz, *o*-Cy^{PC}), 30.1 (d, $^2J_{PC}$ = 5.4 Hz, *o*′-Cy^{PC}), 29.6 (AXX′, $^2J_{PC}$ + $^4J_{P'C}$ = 9.9 Hz, *o*-Cy^{PN}), 28.9 (AXX′, $^2J_{PC}$ + $^4J_{P'C}$ = 17.7 Hz, *o*′-Cy^{PN}), 27.5 (d, $^3J_{PC}$ = 6.6 Hz, *m*-Cy^{PC}), 27.5 (d, $^3J_{PC}$ = 13.8 Hz, *m*′-Cy^{PC}), 27.5 (AXX′, $^3J_{PC}$ + $^5J_{PC}$ = 7.9 Hz, *m*-Cy^{PN}), 27.4 (AXX', $^3J_{PC}$ + $^5J_{PC}$ = 11.8 Hz, *m*′-Cy^{PN}), 27.0 (d, $^4J_{PC}$ = 1.0 Hz, *p*-Cy^{PC}), 26.9 (br, *p*-Cy^{PN}). $^{31}P\{^1H\}$ NMR ([D$_6$]-benzene, 202 MHz, 298 K): δ 89.7 ([N]−*P*), −20.1 (s, [C]−*P*). Anal. calcd for $C_{38}H_{66}NP_3$: C, 72.46; H, 10.56; N, 2.22. Found: C, 72.45; H, 10.51; N, 2.24. IR (ATR): $\tilde{\nu}$ 2128 (C≡C). Melting Point (DSC): 133.6 °C. Decomposition Point (DSC): 234.5 °C.

X-Ray Crystal Structure Analysis of 9b. Formula $C_{38}H_{66}NP_3$, M = 629.83, colorless crystal 0.35 × 0.25 × 0.15 mm^3, a = 18.0863(5), b = 9.8117(3), c = 21.5144(7) Å, β = 95.016(2)°, V = 3803.3(2) Å^3, ρ_{calc} = 1.100 g cm^{-3}, μ = 1.606 mm^{-1}, empirical absorption correction (0.603 ≤ T ≤ 0.795), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ= 1.54178 Å, T = 223(2) K, ω and φ scans, 30001 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 6721 independent (R_{int} = 0.042) and 6241 observed reflections [$I \geq 2\,\sigma(I)$], 379 refined parameters, R = 0.043, wR^2 = 0.120, max. residual electron density 0.39(−0.19) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Compound 11. 11 was synthesized according to the general procedure using CH_3CN, *n*-butyl lithium and di-*tert*-butylchlorophosphine in a 2:1:1 ratio. Acetonitrile (500 μL, 9.52 mmol, 1.0 equiv) reacted with *n*-butyl lithium (3.00 mL, 4.76 mmol, 0.5 equiv) and chlorodi-*tert*-butylphosphine (860 mg, 4.76 mmol, 0.5 equiv) to form **11** (556 mg, 2.46 mmol, 52%), which was obtained as a white air stable solid. Single crystals suitable for the X-ray crystal structure analysis were obtained from a saturated benzene solution at 5 °C. ^1H NMR ([D$_2$]-dichloromethane, 500 MHz, 298 K): δ 4.71 (br, 1H, C*H*CN), 4.46 (br, 1H, N*H*), 2.19 (d, $^4J_{PH}$ = 0.8 Hz, 3H, *C*≡CCH_3), 1.10 (d, $^3J_{PH}$ = 12.2 Hz, 18H, C(CH_3)$_3$). $^{13}C\{^1H\}$ NMR ([D$_2$]-dichloromethane, 126 MHz, 298 K): δ 165.0 (d, $^2J_{PC}$ = 16.5 Hz, N−*C*≡), 121.3 (d, $^4J_{PC}$ = 2.1 Hz, *C*N), 68.6 (d, $^3J_{PC}$ = 20.7 Hz, ≡*C*(CN)), 34.2 (d, $^1J_{PC}$ = 20.7 Hz, *C*(CH$_3$)$_3$), 28.0 (d, $^2J_{PC}$ = 15.4 Hz, C(*C*H$_3$)$_3$), 21.4 (br, C≡*C*CH$_3$). $^{31}P\{^1H\}$ NMR ([D$_2$]-dichloromethane, 81 MHz, 298 K): δ 61.2 (s, $\nu_{1/2}$ = 19 Hz). Anal. calcd for $C_{12}H_{23}N_2P$: C, 63.69; H, 10.24; N, 12.38. Found: C, 63.72; H, 10.24; N, 12.39. IR (ATR): $\tilde{\nu}$ 2199 (ν(C≡N)). Melting Point (DSC): 158.4 °C.

X-Ray Crystal Structure Analysis of 11. Formula $C_{12}H_{23}N_2P$, M = 226.29, colorless crystal 0.35 × 0.20 × 0.15 mm^3, a = 10.9903(2), b = 12.2569(3), c = 10.5191(2) Å, V = 1417.00(5) Å^3, ρ_{calc} = 1.061 g cm^{-3}, μ= 1.502 mm^{-1}, empirical absorption correction (0.622 ≤ T ≤ 0.806), Z = 4, orthorhombic, space group $Cmc2_1$ (No. 36), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 7625 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å−1, 1221 independent (R_{int} = 0.047) and 1203 observed reflections [$I \geq 2\,\sigma(I)$], 92 refined parameters, R = 0.030, $wR2$ = 0.077, max. (min.) residual electron density 0.12 (−0.14) e Å^{-3}, hydrogen atoms at N1, C3, and C4 from difference Fourier calculations, others calculated and refined as riding atoms.

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Supporting Information Available: 1D NMR spectra, 2D NMR experiments, IR data, mass spectroscopic data and

crystallographic data (CIF) of the compounds **1b**, **6**, **9b** and **11**. Experimental procedure of the formation of [D_2]-**6**, its 1D and 2D NMR analysis and its analysis by mass spectrometry. Experimental procedure of the stoichiometric reaction for the preparation of **6**: formation of the mixture of **6** and **9a** and some characteristic analytic parameters of **9a**. Experimental procedure of the formation of **10** and its 1D NMR data and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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