1,3,2-Diazaphosphinines and -Diazaarsinines as Precursors for Polyfunctional Phosphinines and Arsinines

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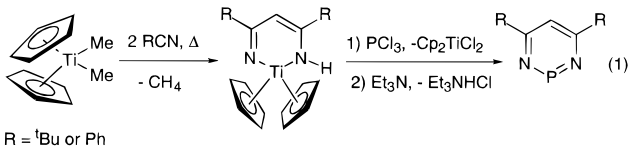
Thermal reactions of 4,6-di-*tert*-butyl-1,3,2-diazaphosphinine **1a**, obtained from the reaction of the corresponding diazatitanacycle with PCl_3 in the presence of NEt_3, with various functional alkynes are dicussed. Phosphinines are produced in good yields (from 55 to 75%) via two [4 + 2] cycloaddition−cycloreversion sequences with extrusion of two molecules of pivalonitrile from **1a**. Two 2-diethoxymethyl-substituted, **3** and **4**, one 3-propynyl-substituted, **6**, and two examples of 3-monosubstituted and 3,5-disubstituted ferrocenylphosphinines, **8** and **9**, have been synthesized. The X-ray structure of the 2,6-bis(trimethylsilyl)-3,5-bis(ferrocenyl)phosphinine **9** has been determined. Due to a strong steric crowding between the silyl and ferrocenyl groups, the ring adopts a twisted geometry with a dihedral angle of 11.65°. Upon reaction of **1a** with bis(diphenylphosphino)acetylene, a 2,3-bis-(diphenylphosphino)-substituted, **11**, and the 2,3,5,6-tetrakis(diphenylphosphino)-substituted, **12**, phosphinines have been obtained. Reactions of **1a** with 1,*n*-diynes ($n > 3$) also provides easy access to Ph−P-, $(CH_2)_3$-, and $SiMe_2$-, linked bis(phosphinines) **14**, **16**, and **18**, respectively. A $SiMe_2$ linked tris(phosphinine) has also been prepared using a two step sequence which involves the preliminary synthesis of a 2,6-bis(phenylethynyl)dimethylsilyl-phosphinine **20**. Reaction of 2 equiv of **1a** with 1 equiv of **20** and then with 2 equiv of (trimethylsilyl)acetylene gave the tris(phosphinine) **22**. This methodology has also been extended to the synthesis of arsinine derivatives. In a similar way, the first example (4,6-di-*tert*-butyl) of a 1,3,2-diazaarsinine **1b** has been prepared (yield 20−25% relative to Cp_2-$TiMe_2$) from the reaction of the corresponding diazatitanacycle with $AsCl_3$ in the presence of Et_3N. Similar to its phosphorus counterpart **1a**, **1b** reacts with alkynes by the same cycloaddition−cycloreversion sequence to give tetrafunctional arsinines (yields from 40 to 50%). The 2,6-bis- and 2,3,5,6-tetrakis(trimethylsilyl), **23** and **24**, respectively, derivatives have been obtained from reaction of **1b** with phenyl(trimethylsilyl)acetylene and bis-(trimethylsilyl)acetylene, respectively. The reaction of **1b** with bis(diphenylphosphino)-acetylene gave a 2,6-bis(diphenylphosphino)arsinine **25**, which has also been characterized by an X-ray diffraction study.

Introduction

As attested by a number of reports, zircona- and titanacycle transfer reactions are an attractive and promising field of investigations in the synthesis of four- and five-membered group 15 heterocycles.[1] In spite of this striking development, the synthesis of six-membered rings has received much less attention so far. As part of a continuing program aimed at developing synthetic methodologies for the synthesis of polyfunctional phosphinines,[2] we recently demonstrated that 1,3,2-diazatitanacyclohexadienes, initially synthesized by Doxsee[3] *et al.* turn out to be very efficient precursors of the previously unknown 1,3,2-diazaphosphinines via N−Ti, N−P bond metathesis (eq 1).[4]



Although no theoretical investigations have been performed so far, it appears that the replacement of two carbon atoms by two nitrogen atoms at the positions adjacent to phosphorus considerably reduces the aro-

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(1) See for example: (a) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (b) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880. (c) Doxsee, K. M.; Mouser, J. K. M.; Farahi, J. B. *Synlett*. **1992**, 13 (review). (d) Petasis, N. A.; Fu, D.-K. *Organometallics* **1993**, *12*, 3776. (e) Doxsee, K. M.; Shen, G. S.; Knobler, C. B. *J. Am. Chem. Soc.* **1989**, *111*, 9129. (f) Doxsee, K. M.; Shen, G. S.; Knobler, C. B. *J. Chem. Soc., Chem. Commun.* **1990**, 1649. (g) Breen, T. L.; Stephan, D. W. *Organometallics* **1997**, *16*, 365. (h) Tumas, W.; Suriano, J. A.; Harlow, R. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 75. (i) Hsu, D. P.; Warner, B. P.; Fisher, R. A.; Davis, W. M.; Buchwald, S. L. *Organometallics* **1994**, *13*, 5160. (j) Boutonnet, F.; Dufour, N.; Straw, T.; Igau, A.; Majoral, J. P. *Organometallics* **1991**, *10*, 3939. (k) Avarvari, N.; Le Floch, P.; Charrier, C.; Mathey, F. *Heteroatom Chem.* **1996**, *7*, 397.

(2) (a) Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1993**, *115*, 10665. (b) Le Floch, P.; Kolb, A.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1994**, 2065. (c) Trauner, H.-G.; Le Floch, P.; Ricard, L.; Mathey, F. *Synthesis* **1995**, 719.

(3) (a) Doxsee, K. M.; Farahi, J. B. *J. Am. Chem. Soc.* **1988**, *110*, 7239. (b) Doxsee, K. M.; Farahi, J. B.; Hope, H. *J. Am. Chem. Soc.* **1988**, *113*, 8889. (c) Doxsee, K. M.; Farahi, J. B. *J. Chem. Soc., Chem. Commun.* **1990**, 1452.

(4) Avarvari, N.; Le Floch, P.; Mathey, F. *J. Am. Chem. Soc.* **1996**, *118*, 11978.

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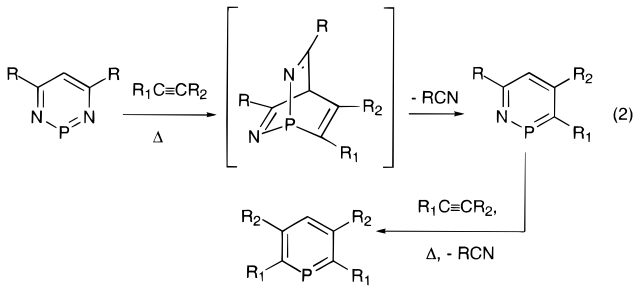
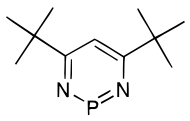
maticity within the ring compared to phosphinines. Indeed, 1,3,2-diazaphosphinines were found to be highly reactive toward protic reagents which readily add to the P═N double bond, thus confirming that they behave more as genuine diazaphosphacyclohexatrienes. However, their reactivity toward alkynes turned out to be the most interesting feature of their chemistry. Hence, we found that they could be efficiently used for the synthesis of 1,2-azaphosphinines and symetrically-substituted tetrafunctional phosphinines via a [4 + 2] cycloaddition−cycloreversion sequence which is depicted in (eq 2).[4]



Although comparable with a sequence previously described by Märkl in the case of 1,3-aza-[5] and 1,3,5-diazaphosphinines,[6] this new approach offers two significant advantages. Firstly, 1,3,2-diazaphosphinines are directly prepared in fair yields (40−45%) in a one-pot reaction from Cp_2TiMe_2 and need not be isolated before reactions with alkynes. This is of importance considering that 1,3,5-diazaphosphinines are only obtained in low yields (5−6%) from the reaction of $P(SiMe)_3$ with 2,4,6-triaryl-3,5-diazapyrilium salts. Secondly, due to the high polarity of the formal 1,4 dipole −P═N−C═C−, these [4 + 2] cycloadditions proceed under mild conditions and, in most cases, with a high regioselectivity. In the present study, we report further developments of this chemistry with the syntheses of various tetrasymmetrically- and unsymmetrically-substituted mono- and polyphosphinines whose preparation could not be achieved using other known synthetic methods. Furthermore, we present preliminary investigations which demonstrate that this approach can also be successfully extended to the synthesis of arsinine derivatives.

Results and Discussion

All of our experiments were conducted with the 4,6-ditertiobutyl-1,3,2-diazaphosphinine **1a**, which was preferred to the 4,6-diphenyl derivative for the following two reasons. Firstly, traces of unreacted pivalonitrile,

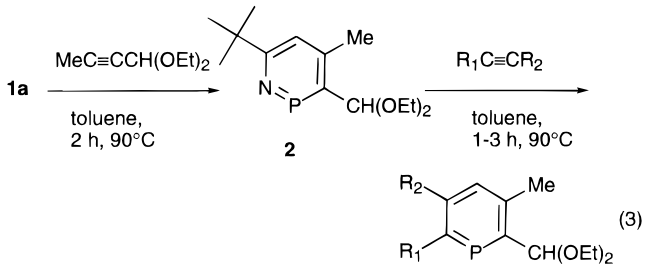


1a

which are always present after the condensation with $Cp_2Ti{=}CH_2$, are more easily removed from the reaction mixture than that of benzonitrile. Secondly, due to the presence of the two ^{t}Bu groups which provide a significant kinetic stabilization, **1a** turns out to be more stable in solution than its diphenyl analogue.

As explained before, diazaphosphinines, which are highly sensitive toward hydrolysis, need not be isolated as pure oils before reactions with alkynes. In routine experiments, a simple titration by ^{31}P NMR using triphenylphosphine as the internal standard allows an exact determination of the molarity of **1a** in toluene solutions (see Experimental Section). In each preparation of **1a**, yields were systematically determined in a range from 40 to 45% starting from Cp_2TiMe_2.

During our previous work, we only focussed on the syntheses of symmetrically-tetrasubstituted phosphinines. In order to demonstrate that our sequence may also be very attractive for the preparation of unsymmetrically-substituted derivatives, we investigated several combinations of alkynes first. Some selected examples are presented in the following schemes and equations. An interesting application of this methodology is given by the reaction of **1a** with 1,1-diethoxy-2-butyne which gives exclusively azaphosphinine **2** after 2 h of heating at 90 °C in toluene. As for 1,3,2-diazaphosphinines, 1,2-azaphosphinines are highly reactive toward protic reagents,[4,7] and during this work, we only limited their characterizations to ^{31}P NMR experiments. Two 1,2-azaphosphinines had been succesfully identified in our previous report.[4] As expected, **2** is still sufficiently reactive to give [4 + 2] cycloadditions with various alkynes. Masked aldehydes **3** and **4** were, thus, readily obtained with a 55% yield from the reaction of **2** with trimethylsilyl- and phenylacetylene, respectively (eq 3).



3, $R_1 = SiMe_3$, $R_2 = H$ (55%)
4, $R_1 = H$, $R_2 = Ph$ (55%)

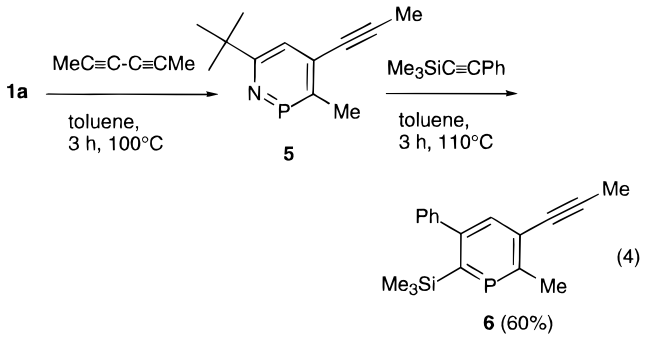
As previously noted, the observed regioselectivities of these [4 + 2] cycloadditions are in good agreement with the polarity of the two partners, the more electronegative carbon atom of the alkyne always reacting at the highly electropositive phosphorus atom of **1a.** Obviously, this rule also applies for 1,2-azaphosphinines which display the same polarity pattern. Thus, the introduction of functionalities onto the ring can be easily predicted by examining the shielding of the sp carbons in the ^{13}C NMR spectra of alkynes. This rule turns out to be general except in the case of 1,3-diynes where the anisotropic cones due to the two π systems cause an important shielding of the signals corresponding to the two central sp carbons. Hence, with 2,4-butadiyne, the most shielded carbon atom was found to attach at the C_5-H position in the synthesis of azaphosphinine **5**. In return, with (trimethylsilyl)phenylacetylene, the rule is

(5) (a) Märkl, G.; Dorfmeister, G. *Tetrahedron Lett.* **1987**, *28*, 1093. (b) Märkl, G.; Dörges, Ch.; Riedl, Th.; Klärner, F.-G.; Lodwig, C. *Tetrahedron Lett.* **1990**, *32*, 4589. (c) Märkl, G.; Dorsch, S. *Tetrahedron Lett.* **1995**, *36*, 3839.

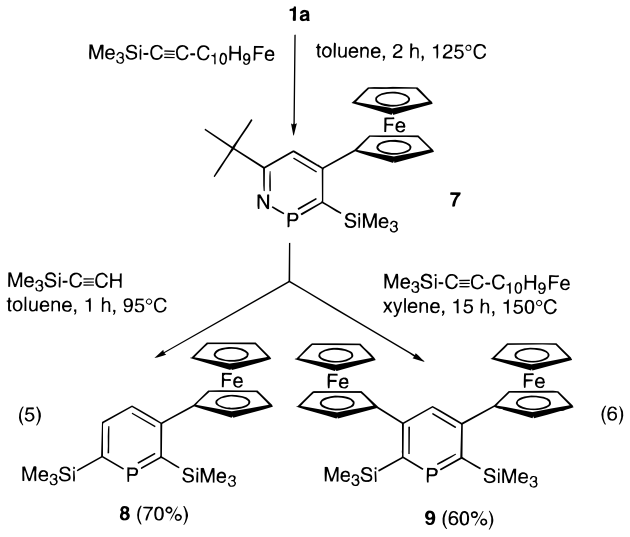
(6) Märkl, G.; Dörges, C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 106.

(7) Bourdieu, C.; Foucaud, A. *Tetrahedron Lett.* **1987**, *28*, 4673.

operative and the most shielded carbon atom reacts at the phosphorus atom of **5** to give phosphinine **6** (eq 4).



Another interesting application of this chemistry concerns the introduction of ferrocenyl groups using (trimethylsilyl)ferrocenylacetylene which reacts with **1a** under more drastic conditions to give azaphosphinine **7**. The presence of the Fc group does not significantly alter the reactivity of **7** toward highly polarized terminal alkynes, as shown by the reaction with trimethysilylacetylene which proceeds under mild conditions, 95 °C in toluene, to give phosphinine **8**. This derivative, which was isolated as an orange solid, is the first example of a ferrocenyl-substituted phosphinine (eq 5). The condensation of **7** with a second equivalent of $Me_3SiC{\equiv}C{-}Fc$ turned out to be more problematic, probably as a result of a strong steric hindrance between the two Fc groups and the *tert*-butyl substituent during the approach of the alkyne. Nevertheless, after 15 h of heating at 150 °C in xylene, phosphinine **9** was isolated as very stable orange needles (eq 6). The synthesis of



9 demonstrates that this method should be sufficiently flexible to accommodate the preparation of phosphinines having various bulky substitution patterns.

The molecular structure of **9** has been determined by an X-ray diffraction study. An ORTEP view of the molecule is presented in Figure 1. Selected bond distances and angles are given in Table 1. On rapid examination of these data, it appears that the proximity of the two bulky trimethylsilyl and ferrocenyl groups has large structural consequences over the geometry of the molecule. To minimize this interaction, the two Fc groups, which lie above and below the plane of the ring, are both directed toward the back of the molecule.

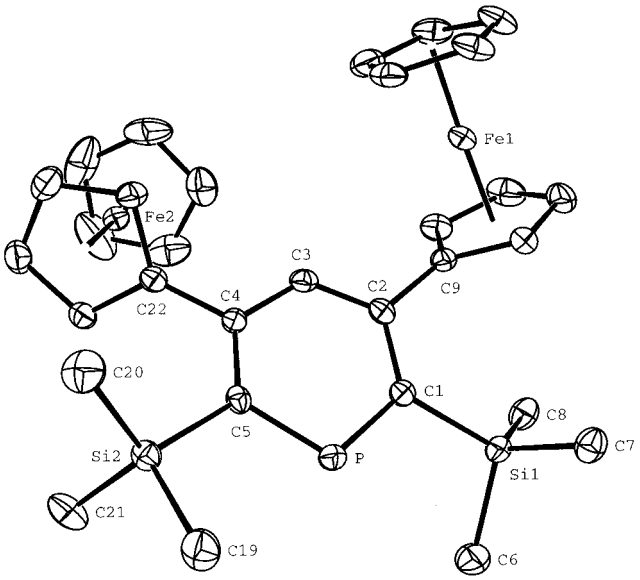


Figure 1. ORTEP drawing of **9**. Ellipsoids are scaled to enclose 50% of the electron density. The crystallographic labeling is arbitrary and different from the numbering used for assignment of the ^{13}C spectra.

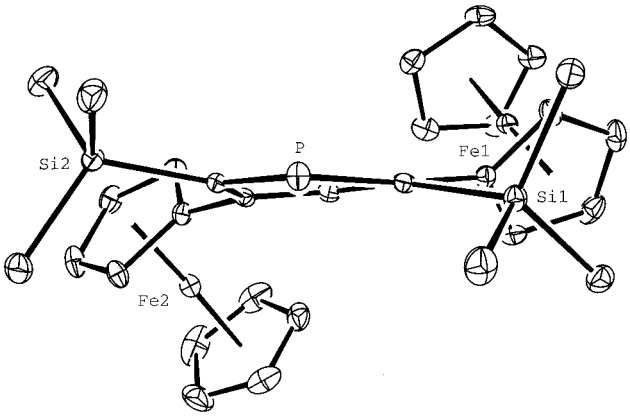


Figure 2. A view of **9** along the $C_1{-}C_2$ axis, showing the twisted geometry of the ring.

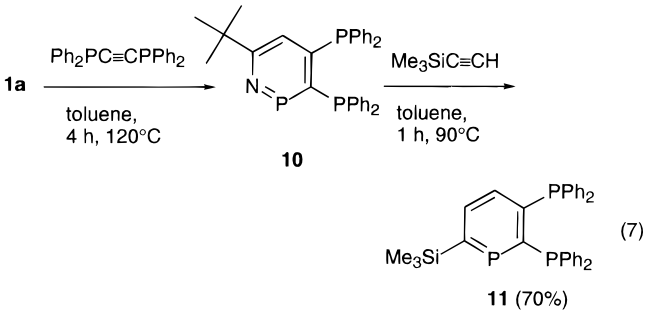
Table 1. Selected Bond Lengths (Å) and Angles (deg) for 9

Bond Lengths			
P−C1	1.727(2)	C4−C5	1.410(3)
P−C5	1.725(2)	C1−Si1	1.888(2)
C1−C2	1.414(3)	C5−Si2	1.891(2)
C2−C3	1.386(3)	C2−C9	1.485(3)
C3−C4	1.401(3)	C4−C22	1.475(3)
Bond Angles			
C1−P−C5	106.1(1)	P−C1−Si1	112.1(1)
P−C1−C2	121.2(2)	Si1−C1−C2	126.6(2)
C1−C2−C3	121.9(2)	C1−C2−C9	119.9(2)
C2−C3−C4	126.4(2)	C9−C2−C3	118.1(2)
C3−C4−C5	122.0(2)		
C4−C5−P	120.9(2)		

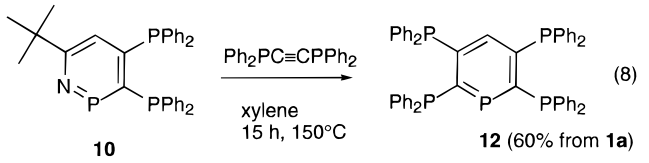
Nevertheless, the most interesting feature of this structure is given by the ring itself, which adopts a twisted geometry with a torsion angle ($C_3{-}C_4{-}C_5{-}P$) of 11.65°. Another view of the molecule, showing this distorsion is presented in Figure 2. As a result, to accomodate this strong deviation from planarity, the two internal angles $C_2{-}C_3{-}C_4$ and $C_5{-}P{-}C_1$ angles open to 126.4(2)° and 106.1(1)°, respectively. To the best of our knowledge, this latter value is the largest recorded to date, standard values for C−P−C angles in free phosphinines usually

falling in a range from 99 to 103°. Paradoxically, if one neglects these deviations, the bond distances and angles within the ring are not notably modified, as shown by the two P=C bond separations which are quite normal at 1.727(2) and 1.725(2) Å. To conclude with the presentation of these data, it must be pointed out that the structural consequences of bulky substitution patterns have already been discussed by Maas and Regitz in the case of the highly distorted 2,4,5,6-tetra-*tert*-butyl-3-(carboxymethyl)phosphinine,[8a] which isomerizes to its Dewar-benzene form upon heating.[8b]

Another synthetic challenge of interest concerns the elaboration of methods allowing the introduction of several phosphino groups onto the phosphinine ring. During our previous studies, we have shown that the reaction of 1,3,2-diazaphosphinines with (diphenylphosphino)phenylacetylene constituted a valuable approach for the synthesis of 2,6-bis(diphenylphosphino)phosphinines. Nevertheless, this result could not be considered as a major advance since these interesting tripodal ligands can be easily prepared in large amounts from the palladium-catalyzed cross-coupling reaction of (trimethylsilyl)diphenylphosphine with 2,6-dibromophosphinines.[2a,c] The synthesis of 2,3-bis(diphenylphosphino) derivatives is by far more difficult, and to date, the only known method to prepare this class of compounds, which was described by Hughes *et al.*, relies on the [4 + 2] cycloaddition of 2*H*-phospholes with bis(diphenylphosphino)acetylene.[9] Despite its bulkiness, the latter cleanly reacts with **1a** to give the corresponding 1,2-azaphosphinine **10**, which was only identified by ^{31}P NMR (toluene). As expected, the spectrum of **10** exhibits three signals, which are unfortunately insufficiently resolved to allow the determination of all of the coupling constants: a strongly deshielded signal, at 291.80 ppm (bs, P_X) which was unambiguously ascribed to the P atom of the ring and two others at −19.32 (bd, P_A) and −6.06 (bd, $^3J(P-P) = 151.68$ Hz, P_B) ppm which were, respectively, assigned to the PPh_2 group located at C_3 (α to the P ring) and to the other PPh_2 group located at C_4. The assignments of the shifts for these two groups were made by comparison with the shift of the PPh_2 group (δ(toluene) = −19.0 ppm) in 3-diphenylphosphino-4-phenyl-6-^{t}Bu-1,2-azaphosphinine which was reported in our previous work. Another interesting feature of this spectrum concerns the magnitude of the $^3J(P-P)$ coupling constant between the two neighboring PPh_2 groups. This value, which reflects a strong through-space interaction between the two nonbonding pairs of orbitals of the two phosphorus atoms, is in good agreement with that reported by Hughes in the case of 2,3-bis(diphenylphosphino)-6-phenylphosphinine ($^3J(P-P)$ = 178.30 Hz).[9] Although sterically crowded, azaphosphinine **10** is still reactive enough to condense with other alkynes, as shown by the two selected examples which are presented in the two following equations. The reaction with trimethylsilylacetylene, which occurred under mild conditions at 90 °C for 1 h, gave phosphinine **11**, which was isolated as a very air stable yellow solid (eq 7).



The structure of **11** could not be easily established simply on the basis of the ^{31}P NMR spectrum which only shows two broad singlets at 255.95 (P_1 ring) and −10.35 ppm (superposition of the signals of P_2 and P_3). Fortunately, the NMR data (^1H and ^{13}C), mass spectrum, and elemental analyses all support the formulation of **11**. The condensation of **10** with another equivalent of bis(diphenylphosphino)acetylene occurred under more drastic conditions to give the phosphorus analogue of 1,2,4,5-tetrakis(diphenylphosphino)benzene,[10a] a molecule which has found interesting applications in the elaboration of various bridged dimetallic complexes and coordination polymers.[10b] After 15 h of heating in xylene, **12** was isolated as a poorly soluble yellow solid with a 60% yield (starting from **1a**) (eq 8).



The formulation of **12** could be unambiguously established simply on the basis of the ^{31}P NMR spectrum which exhibits a simplified AA′BB′X (A_2B_2X) spin pattern ($^4J(A-A') = {}^4J(B-B') = {}^5J(A-B') = 0$ Hz) with 17 bands (9 for P_X, 4 for P_A, and 4 for P_B). Simulation allowed the complete assignments of all coupling constants (see Experimental Section). Additional evidence supporting the proposed structure have also been provided by NMR (^1H, ^{13}C), mass spectrometry, and elemental analyses.

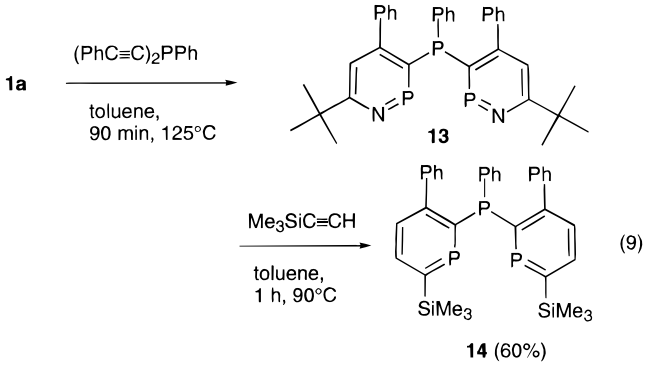
Until now, we have limited our studies to the preparation of monophosphinines having a disymmetrical or a symmetrical substitution pattern. Suspecting that our approach could also provide a powerful entry to the synthesis of more sophisticated species such as P−R-, $SiMe_2$-, and $(CH_2)_n$-linked bis- and tris(phosphinines), we decided to investigate the reactivity of **1a** toward various nonconjugated diynes. To extend the range of 2-phosphinophosphinines, we first studied the condensation of bis(phenylethynyl)phenylphosphine. As previously found in the case of other phosphinoalkynes, the [4 + 2] cycloaddition with **1a** proceeded with complete regioselectivity to give the bis(1,2-azaphosphininyl)-phenylphosphine **13**, which was identified by ^{31}P NMR only. Upon reaction with trimethylsilylacetylene at 90 °C, **13** was easily converted into the Ph−P-linked bis(phosphinine) **14** (eq 9).

Routine NMR analyses (^1H, ^{13}C), the mass spectrum, and elemental analysis are all consistent with the

(8) (a) Maas, G.; Fink, J.; Wingert, H.; Blatter, K.; Regitz, M. *Chem. Ber.* **1987**, *120*, 819. (b) Blatter, K.; Rösch, W.; Vogelbacher, U.-J.; Fink, J.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *25*, 85.

(9) Holah, D. G.; Hughes, A. N.; Knudsen, K. L.; Perrier, R. *J. Heterocyclic Chem.* **1988**, *25*, 155.

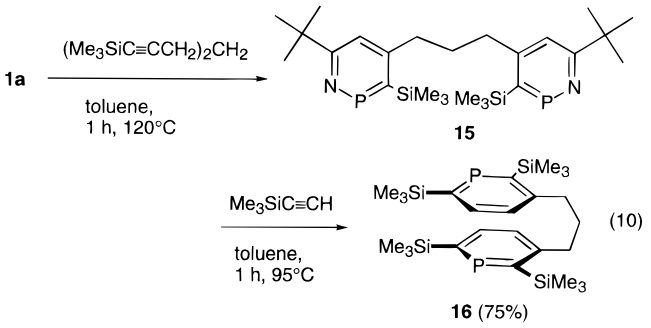
(10) (a) McFarlane, H. C. E.; Mcfarlane, W. *Polyhedron* **1988**, *7*, 1875. (b) Wang, P.-W.; Fox, M. A. *Inorg. Chem.* **1994**, *33*, 2938.



(9)

proposed structure, as is the ^{31}P NMR spectrum. This exhibits a classical AX_2 system with two resonances at 256.25 and −11.30 ppm ($^2J(P_A-P_X) = 15.25$ Hz), which were assigned to the two ring P atoms and to the phenylphosphino group, respectively.

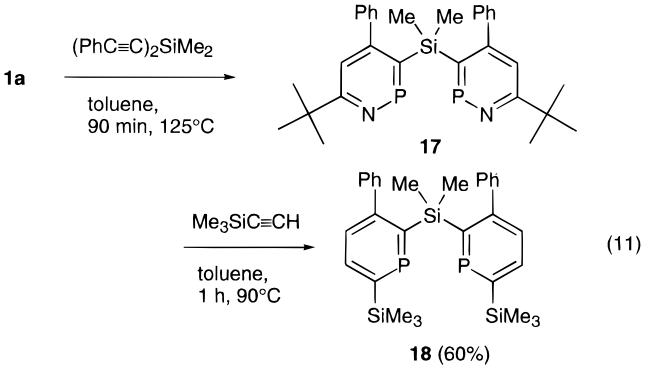
As outlined before, we were also interested in evaluating our approach for the synthesis of $(CH_2)_n$-linked phosphinines. Paradoxically, the attachment of phosphinines by hydrocarbon chains still remains an important synthetic challenge in phosphinine chemistry. If one excludes a brief mention of the reaction of ^{t}BuCP with suitable bis(α-pyrones),[11] no valuable approach has been devised so far for the synthesis of such ligands, which might have some interest in the coordination chemistry for the assembly of sandwich complexes. In order to facilitate the monitoring of the reaction by ^{31}P NMR, we decided to work with the 1,7-disilylated-1,6-heptadiyne, which was preferred to the unsubstituted diyne because of its higher boiling point. Furthermore, as shown before, cycloadditions with silylated alkynes always proceed with complete regioselectivity. After 1 h of heating at 120 °C with 1 equiv of diyne, **1a** was easily converted into the bis(diazaphosphinine) **15**, which, upon reaction with trimethylsilylacetylene, gave the bis(phosphinine) **16** (eq 10).



(10)

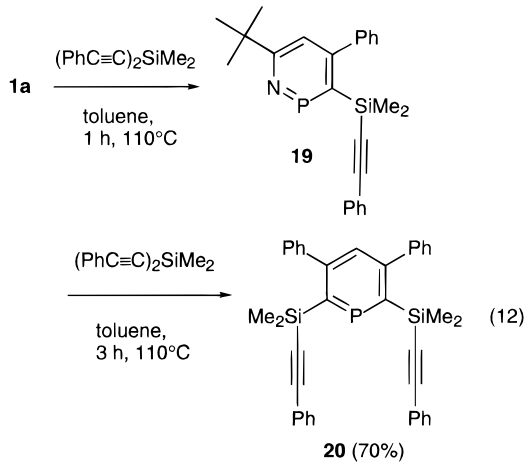
Compound **16** which was recovered as a colorless air-stable oil has been identified by conventional NMR experiments and elemental analysis. The synthesis of $SiMe_2$-linked bis- and tris(phosphinines) was achieved using a similar approach. As depicted in the following equation, bis(phosphinine) **18** was readily obtained with a 60% yield from the reaction of **1a** with bis(phenylethynyl)dimethylsilane and trimethylsilylacetylene (eq 11).

The preparation of such bidentate ligands is not totally unprecedented. A similar dimethyltin derivative



(11)

has already been obtained in low yields by Bickelhaupt *et al.* from the reaction of a 2-organozinc derivative of 4,5-dimethylphosphinine with Me_2SnCl_2.[12] In contrast, molecules such as the tris(phosphinine) **22** are totally unknown and probably unavailable using other conventional approaches. Its preparation could be achieved via a two-step sequence involving the preliminary synthesis of the 2,6-disilyl-substituted phosphinine **20**. This latter compound was easily obtained in a yield of 70% from the reaction of **1a** with 4 equiv of 1,4-diyne (eq 12). Excess of diyne, which was further eliminated



(12)

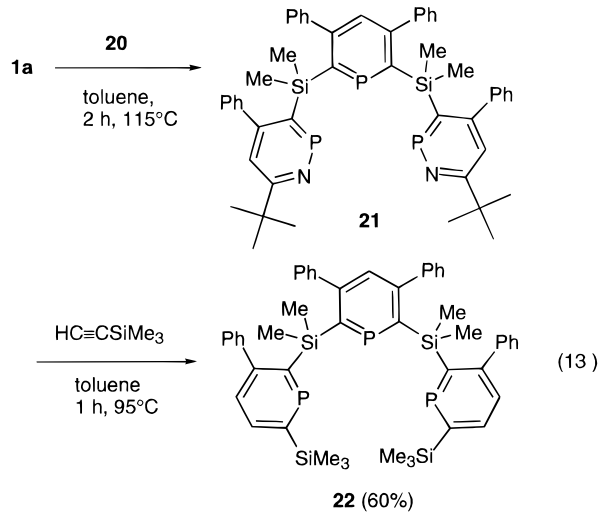
by chromatographic separation, turned out to be necessary to prevent the formation of oligomers.

The formation of intermediate **21** also required strict control of the experimental conditions (stoichiometry and temperature) to avoid the formation of oligomers. After 2 h of heating at 115 °C, no traces of **1a** remained in solution and **21** was identified by ^{31}P NMR (toluene) as a classical AX_2 spin system with two resonances at 275.85 (t) and 304.30 (d, $^4J(P-P) = 11.95$ Hz) ppm, which were assigned to the phosphinine central unit and to the two 1,2-azaphosphinines, respectively. Upon reaction with trimethylsilylacetylene, **21** was rapidly converted to **22** (eq 13).

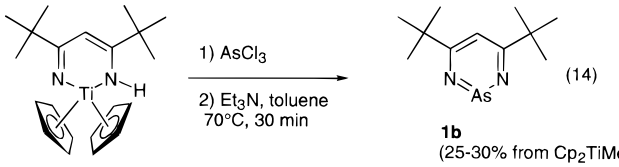
After chromatographic separation, **22** was recovered as a pale yellow air-stable solid. Its formulation was confirmed by a combination of ^1H and ^{13}C NMR experiments, mass spectrometry, and elemental analysis. Additional evidence was provided by the ^{31}P NMR spectrum which exhibits, similar to that of **21**, a characteristic AX_2 spin pattern (see Experimental Section).

(11) Regitz, M.; Annen, U. Unpublished results, Kaiserslautern, 1988 cited in Regitz, M. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: New York, 1990; p 58 (see p 82).

(12) Teunissen, H. T.; Bickelhaupt, F. *Organometallics* **1996**, *15*, 802.



Prompted by these results, we logically attempted to duplicate this approach to arsinine derivatives, and as expected, 1,3,2-diazatitanacyclohexadienes turned out to be convenient precursors for the previously unknown 1,3,2-diazaarsinines[13] upon reaction with $AsCl_3$. We found that the formation of 1,3,2-diazaarsinine **1b** is critically dependent on the experimental conditions, and prolonged heating of diazatitanacycle and $AsCl_3$ with Et_3N (up to 1 h) only led to decomposition (yields below 10%). Reproducible yields of 25−30% (estimated by ^1H NMR integration using 1,2-diphenylethane as an internal standard) were obtained upon heating the reaction mixture at 70 °C for only 30 min (eq 14). After filtration



of the Et_3NHCl salt and Cp_2TiCl_2 and evaporation of toluene, **1b** was recovered as a brownish oil contaminated by some traces of unidentified titanium complexes. Though extremely sensitive toward hydrolysis, **1b** was found to be sufficiently robust to survive NMR experiments and mass spectrometry (CI) (see Experimental Section).

Diazaarsinine **1b** is not the first example of a six-membered aromatic ring containing both nitrogen and arsenic. Indeed, in 1988, Märkl reported the synthesis of 2,4,6-triaryl-1,3-azaarsinines from the reaction of $As(SiMe_3)_3$ with 1,3-azapyrylium salts.[14a] In a subsequent report, he has also shown that these derivatives could be used as precursors for functional arsinines upon reaction with alkynes.[14b]

As its phosphorus counterpart, **1b** cleanly reacts with alkynes to give arsinines via the same cycloaddition−cycloreversion sequence. Until now, we have limited our investigations to the synthesis of symmetrically-substituted derivatives using silyl- and diphenylphosphino-substituted alkynes as partners (eq 15). In all cases,

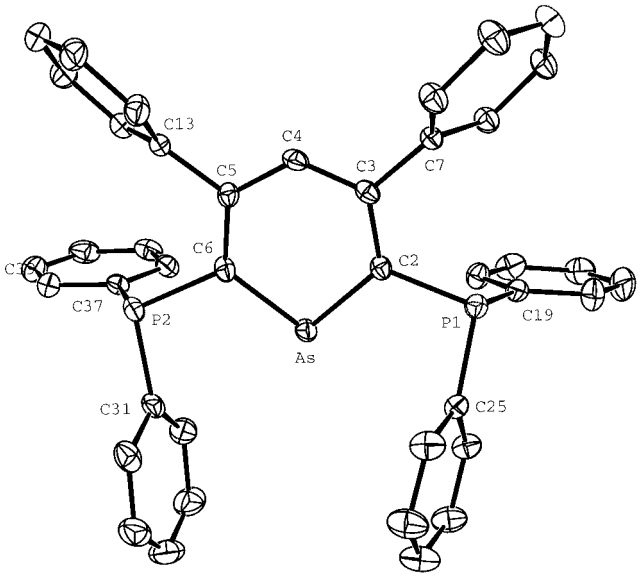
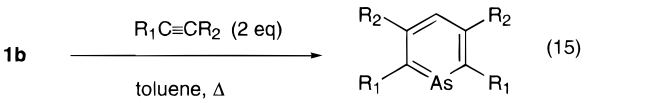


Figure 3. ORTEP drawing of **25**. Ellipsoids are scaled to enclose 50% of the electron density. The crystallographic labeling is arbitrary and different from the numbering used for assignment of the ^{13}C spectra.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 25

	Bond Lengths		
As−C2	1.870(2)	C5−C6	1.408(2)
As−C6	1.867(2)	C2−P1	1.838(2)
C2−C3	1.404(2)	C3−C7	1.498(2)
C3−C4	1.395(2)	C5−C13	1.500(2)
C4−C5	1.397(2)	C6−P2	1.842(2)
	Bond Angles		
C2−As−C6	100.47(7)	As−C2−P1	119.15(9)
Ac−C2−C3	122.3(1)	P1−C2−C3	118.3(1)
C2−C3−C4	123.4(1)	C2−C3−C7	121.6(1)
C3−C4−C5	128.2(2)	C4−C5−C13	113.7(1)
C4−C5−C6	123.0(2)	C13−C5−C6	123.3(1)
C5−C6−As	122.5(1)	C5−C6−P2	118.1(1)



23 : $R_1 = SiMe_3$, $R_2 = H$, 90 min, 95°C (40%)
24 : $R_1 = R_2 = SiMe_3$, 12 h, 125°C (40%)
25 : $R_1 = PPh_2$, $R_2 = Ph$, 12 h, 120°C (50%)

experimental conditions were found to be quite similar to those used for the synthesis of phosphinines although giving arsinines in lower yields, comparatively.

Arsinines **23**−**25** have been successfully identified by a combination of NMR experiments, mass spectrometry, and elemental analysis for **25**. Unfortunately, **23** and **24** turned out to be too sensitive toward oxygen to give reproducible combustion data. Furthermore, the structure of the tridentate ligand **25** was unambiguously established by X-ray crystallography. An ORTEP view of the molecule is presented in Figure 3. Selected bond distances and angles are given in Table 2. The structure of **25** only constitutes the second example of a X-ray structural determination for this type of compound, the first being reported by Daly in 1972 for the 2,5,6-triphenyl-substituted derivative.[15] Our data are consistent with those of Daly concerning both the bond

(13) Märkl, G.; Kreitmeier, P. In *Comprehensive Heterocyclic Chemistry II*, Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: New York, 1996; Vol. 6, p 1073.

(14) (a) Märkl, G.; Dietl, S. *Tetrahedron Lett.* **1988**, *29*, 535. (b) Märkl, G.; Dietl, S. *Tetrahedron Lett.* **1988**, *29*, 539. (c) Märkl, G.; Kreitmeier, P. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: New York, 1996; Vol. 6, p 1019.

(15) (a) Daly, J. J.; Sanz, F. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 630. (b) Daly, J. J.; Sanz, F. *J. Chem. Soc. Dalton Trans.* **1973**, 511.

lengths and angles within the ring. The most interesting feature concerns the opening of the internal angles at As and C_4. Whereas the first value (C_6-As-C_2) is comparable with that currently observed in free phosphinines, the second one ($C_3-C_4-C_5$) is significantly higher as a result of an increase of the heteroatom=C double bonds (average *d*(P=C), 1.73 Å; average *d*(As=C), 1.868(2)). If one excludes this feature, C=C bond separations appear to be quite normal for a 6π aromatic system (between 1.395(2) and 1.408(2) Å) as is the relative disposition of the two diphenylphosphino groups which experience a steric repulsion with the two phenyl groups located at C_3 and C_5.

Though a number of routes to functional phosphinines[16] and arsinines[17] are known, this new synthetic approach should serve as a convenient complement by allowing the direct synthesis of unknown tetrafunctional derivatives. Furthermore, as demonstrated by the preparation of bi- **(18)** and triphosphinine (**22**), it should also provide an entry to the assembly of various phosphinine- and arsinine-based macrocycles. Investigations are currently in progress in this area, and we will report on these studies in due course.

Experimental Section

All reactions were routinely performed under an inert atmosphere of nitrogen by using Schlenk techniques and dry deoxygenated solvents. Dry THF, toluene, xylene, hexane, and pentane were obtained by distillation from Na/benzophenone and dry CH_2Cl_2 by distillation fom P_2O_5. Silica gel (70−230 mesh) was used for chromatographic separations and dry Celite for filtrations. Nuclear magnetic resonance spectra were obtained on a Bruker AC-200 SY spectrometer operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from external TMS (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P), and coupling constants are given in Hertz. Mass spectra were obtained at 70 eV with an HP 5989 B spectrometer coupled with a HP 5890 chromatograph by the direct inlet method. The following abreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. Elemental analyses were performed by the Service d'analyse du CNRS, at Gif sur Yvette, France. Cp_2TiMe_2,[18] $(C_{10}H_8Fe)C{\equiv}CSiMe_3$,[19] $PhC{\equiv}CPPh_2$ and $(PhC{\equiv}C)_2PPh$,[20] $(PhC{\equiv}C)_2SiMe_2$,[21] and $(Me_3SiC{\equiv}CCH_2)_2CH_2$[22] were prepared according to published procedures.

Synthesis of 4,6-Di-*t*-butyl-1,3,2-diazaphosphinine (1a). A solution of Cp_2TiMe_2 (3.40 g, 16.35 mmol) and pivalonitrile (3.0 g, 36 mmol) in toluene (35 mL) was heated at 68−70 °C for 4−5 days under nitrogen in a Schlenk tube wrapped in aluminium foil. The resulting diazatitanacyclohexadiene was utilized without further purification. The solution was cooled to −20 °C, and degassed PCl_3 (2.3 g, 16 mmol) was added via a syringe. After the solution was warmed to room temperature and stirred for 15 min, NEt_3 (25 mL, ca. 10 equiv) was added and the mixture was heated at 70 °C for 1 h. The collected solid which contains titanium and $Et_3N{\cdot}HCl$ salts was filtered on a glass frit under nitrogen and then washed with toluene (2 × 10 mL). Cp_2TiCl_2 was recovered in ca. 40−50% yield by treatment of the green solid with a mixture of acetone and HCl(aq), followed by an extraction with dichloromethane and a chromatography on silica gel using dichloromethane as the solvent. The orange solution of diazaphosphinine was evaporated under vacuum, and crude **1a** was, thus, obtained in 40−45% yield as an orange oil, very sensitive to air and moisture. In routine experiments, the yield of diazaphosphinine was estimated by ^{31}P NMR. The volume of solution was reduced to 30 mL, and 1 mL was transferred into a 5 mm NMR tube. A known amount of triphenylphosphine (usually 55 mg) was added before the recording of the ^{31}P NMR spectrum. In this manner, the molarity of **1a** in solution can be exactly determined by a simple integration of the two respective signals.

See ref 4 for NMR (^{31}P, ^{1}H, ^{13}C) and mass spectroscopic characterizations.

Synthesis of 6-*t*-Butyl-4-methyl-3-(diethoxymethyl)-1,2-azaphosphinine (2) and 2-(Diethoxymethyl)-3-methyl-6-(trimethylsilyl)phosphinine (3). A solution of **1a** (0.25 g, 1.2 mmol) and $MeCCCH(OEt)_2$ (0.2 g, 1.4 mmol) in toluene (5 mL) was heated at 90 °C for 2 h. After this period, trimethylsilylacetylene (0.7 g, 7.1 mmol) was added to the solution of 1,2-azaphosphinine **2** and the reaction mixture was heated at 90 °C for 1 h. After the solution was cooled to room temperature, Celite (1 g) was added and the solvents were removed under vacuum. The brown powder, thus, obtained was deposited onto the top of a silica gel column for chromatography. Elution with a deoxygenated hexane/ether (80:20) mixture and evaporation of the solvents in vacuo yielded phosphinine **3** as an orange oil. Yield: 0.18 g (55%).

2: ^{31}P NMR (toluene) δ 271.94.

3: ^{31}P NMR ($CDCl_3$) δ 228.75; ^{1}H NMR ($CDCl_3$) δ 0.34 (d, 9H, ^4J(H−P) = 0.80, $SiMe_3$), 1.25 (t, 6H, part X of ABX_3 system, ^3J(H−H) = 7.11, 2Me of $CH(OEt)_2$), 2.52 (d, 3H, ^4J(H−P) = 1.71, Me), 3.66 (4H, part AB of ABX_3 system, $^2J(H_A-H_B)$ = 9.50, $^3J(H_A-H_X) = {}^3J(H_B-H_X)$ = 7.11, $2CH_2$ of $CH(OEt)_2$), 5.72 (d, 1H, ^3J(H−P) = 6.71, C*H*$(OEt)_2$), 7.30 (dd, ^4J(H−P) = 2.70, ^3J(H−H) = 8.02, H_4), 7.88 (dd, ^3J(H−H) = 8.02, ^3J(H−P) = 10.31, H_5); ^{13}C NMR ($CDCl_3$) δ 0.61 (d, ^3J(C−P) = 6.12, $SiMe_3$), 15.81 (s, 2Me of $CH(OEt)_2$), 22.29 (s, Me), 62.78 (s, $2CH_2$ of $CH(OEt)_2$), 103.70 (d, ^2J(C−P) = 24.42, *C*$H(OEt)_2$), 132.89 (d, ^3J(C−P) = 19.60, C_4), 138.62 (d, ^2J(C−P) = 11.83, C_5), 143.90 (d, ^2J(C−P) = 12.41, C_3), 166.43 (d, ^2J(C−P) = 61.02, C_2), 167.51 (d, ^2J(C−P) = 74.82, C_6). MS, *m*/*z* (ion, relative intensity): 284 (M, 27), 269 (M − Me, 20), 255 (M − Et, 100).

Synthesis of 2-(Diethoxymethyl)-3-methyl-5-phenylphosphinine (4). A solution of **1a** (0.12 g, 0.6 mmol) and $MeCCCH(OEt)_2$ (0.1 g, 0.7 mmol) in toluene (5 mL) was heated at 90 °C for 2 h in a Schlenk tube. Complete formation of 1,2-azaphosphinine **2** was observed by ^{31}P NMR spectroscopy. Phenylacetylene (0.2 g, 2 mmol) was then added to the solution, and the reaction mixture was heated further at 90 °C for 3 h. Purification by chromatography on a silica gel column using a deoxyenated hexane/diethyl ether (80:20) mixture and removal of the solvents in vacuo yielded phosphinine **4** as an orange oil. Yield: 0.09 g (55%).

^{31}P NMR ($CDCl_3$): δ 204.80 (^2J(P−H) = 38.81); ^{1}H NMR ($CDCl_3$) δ 1.29 (t, 6H, part X of ABX_3 system, ^3J(H−H) = 6.90, 2Me of $CH(OEt)_2$), 2.59 (d, 3H, ^4J(H−P) = 1.51, Me), 3.70 (4H, part AB of ABX_3 system, $^2J(H_A-H_B)$ = 9.00, $^3J(H_A-H_X) = {}^3J(H_B-H_X)$ = 6.91, $2CH_2$ of $CH(OEt)_2$), 5.75 (d, 1H, ^3J(H−P) = 6.60, C*H*$(OEt)_2$), 7.36−7.74 (m, 6H, Ph, H_4), 8.74 (dd, ^4J(H−H) = 1.10, ^2J(H−P) = 39.12, H_6); ^{13}C NMR ($CDCl_3$) δ 15.91 (s, 2Me of $CH(OEt)_2$), 22.80 (s, Me), 62.78 (s, $2CH_2$ of $CH(OEt)_2$), 103.21 (d, ^2J(C−P) = 22.41, *C*$H(OEt)_2$), 128.22−131.56 (m, CH of Ph), 133.90 (d, ^3J(C−P) = 15.12, C_4), 143.02 (d, ^3J(C−P) = 3.13, $C_{5'}$), 144.52 (d, ^2J(C−P) = 13.70, C_3), 147.03 (d, ^2J(C−P) = 13.71, C_5), 150.58 (d, ^1J(C−P) = 50.30, C_6), 165.11 (d, ^1J(C−P) = 52.02, C_2). MS, *m*/*z* (ion, relative intensity): 288 (M,

(16) (a) Märkl, G. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: New York, 1990; p 220. (b) Hewitt, D. G. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: New York, 1996; Vol. 5, p 639.

(17) Ashe, A. J., III In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: New York, 1996; Vol. 5, p 669.

(18) Clauss, V. K.; Bestian, H. *Justus Liebigs Ann. Chem.* **1962**, 8.

(19) (a) Buchmeiser, M.; Schottenberger, H. *J. Organomet. Chem.* **1992**, *436*, 223. (b) Doisneau, G.; Balavoine, G.; Fillebeen-Khan, T. *J. Organomet. Chem* **1992**, *425*, 113.

(20) Hengefeld, A.; Nast, R. *Chem. Ber.* **1983**, *116*, 2035.

(21) Freeburger, M. E.; Spialter, L. *J. Org. Chem.* **1970**, *35*, 652.

(22) Auderset, P. C.; Dreiding, A. S.; Gesing, E. R. F. *Synth. Commun.* **1983**, *13*, 881.

35), 259 (M − Et, 100). Anal. Calcd for $C_{17}H_{21}O_2P$: C, 70.82; H, 7.34. Found: C, 70.95; H, 7.32.

Synthesis of 6-*t*-Butyl-3-methyl-4-propynyl-1,2-azaphosphinine (5) and 2-(Trimethylsilyl)-3-phenyl-5-propynyl-6-methylphosphinine (6). A solution of **1a** (0.25 g, 1.20 mmol) and 1,4-dimethylbutadiyne (0.10 g, 1.30 mmol) in toluene (5 mL) was stirred at 100 °C for 3 h in a Schlenk tube. After complete formation of 1,2-azaphosphinine **5,** phenyl-(trimethylsilyl)acetylene (0.40 g, 2.40 mmol) was then added and the reaction mixture was heated for 3 h at 110 °C. Purification by chromatography with deoxygenated hexane as the eluent and evaporation of the solvent in vacuo yielded phosphinine **6** as a yellow pale solid. Yield: 0.21 g (60%).

5: ^{31}P NMR (toluene) δ 268.53.

6: ^{31}P NMR (C_6D_6) δ 233.19; ^{1}H NMR (C_6D_6) δ 0.18 (d, 9H, ^4J(H−P) = 1.70, $SiMe_3$), 1.67 (s, 3H, Me of propynyl), 2.87 (d, 3H, ^3J(H−P) = 14.83, Me), 7.08−7.50 (m, 5H, Ph), 7.58 (d, ^4J(H−P) = 2.33, H_4); ^{13}C NMR (C_6D_6) δ 2.81 (d, ^3J(C−P) = 10.61, $SiMe_3$), 4.78 (s, Me of propynyl), 24.14 (d, ^2J(C−P) = 37.50, Me), 80.11 (d, ^3J(C−P) = 3.02, *C*≡CMe), 93.34 (s, C≡*C*Me), 128.22−132.91 (m, CH of Ph, C_5), 136.35 (d, ^3J(C−P) = 16.88, C_4), 146.20 (d, ^3J(C−P) = 3.00, $C_{3'}$), 152.78 (d, ^2J(C−P) = 13.69, C_3), 167.40 (d, ^1J(C−P) = 61.00, C_6), 168.11 (d, ^1J(C−P) = 80.91, C_2). MS, *m*/*z* (ion, relative intensity): 296 (M, 16), 281 (M − Me, 100).

Synthesis of 3-(Trimethylsilyl)-4-ferrocenyl-6-*t*-butyl-1,2-azaphosphinine (7) and 2,6-Bis(trimethylsilyl)-3-ferrocenylphosphinine (8). A solution of **1a** (0.25 g, 1.2 mmol) and ferrocenyl(trimethylsilyl)acetylene (0.34 g, 1.2 mmol) in toluene (5 mL) was heated at 125 °C for 2 h. After this period, the formation of 1,2-azaphosphinine **7** was completed and trimethylsilylacetylene (0.7 g, 7 mmol) was then added. The mixture was heated further at 95 °C for 1 h. After removal of the solvents and excess trimethylsilylacetylene under vacuum, the resulting phosphinine was purified by chromatography on a silica gel column using deoxygenated hexane as the eluent. After evaporation of the hexane, phosphinine **8** was recovered as a red-brown solid. Yield: 0.35 g (70%).

7: ^{31}P NMR (toluene) δ 300.30.

8: ^{31}P NMR (C_6D_6) δ 258.10; ^{1}H NMR (C_6D_6) δ 0.33 (d, 9H, ^4J(H−P) = 1.76, $SiMe_3$), 0.44 (d, 9H, ^4J(H−P) = 0.65, $SiMe_3$), 4.00 (s, 5H, Cp), 4.02−4.04 (pseudo t, 2H, ΣJ(H−H) = 3.63, part B of AA′BB′ system), 4.37−4.39 (pseudo t, 2H, ΣJ(H−H) = 3.63, part A of AA′BB′ system), 8.03 (dd, ^3J(H−H) = 8.40, ^3J(H−P) = 9.32, H_5), 8.17 (dd, ^4J(H−P) = 0.71, ^3J(H−H) = 8.41, H_4); ^{13}C NMR (C_6D_6) δ 0.80 (d, ^3J(C−P) = 6.08, $SiMe_3$), 3.50 (d, ^3J(C−P) = 11.35, $SiMe_3$), 68.74 (s, $2C_{3''}$ or $2C_{3'''}$), 70.60 (s, CH of Cp), 72.06 (s, $2C_{3''}$ or $2C_{3'''}$), 96.64 (d, ^3J(C−P) = 2.46, $C_{3'}$), 133.25 (d, ^3J(C−P) = 24.11, C_4), 138.57 (d, ^2J(C−P) = 11.25, C_5), 151.03 (d, ^2J(C−P) = 12.14, C_3), 168.20 (d, ^1J(C−P) = 82.10, C_2 or C_6), 169.51 (d, ^1J(C−P) = 90.32, C_6 or C_2). MS, *m*/*z* (ion, relative intensity): 424 (M, 100), 351 (M − $SiMe_3$, 70). Anal. Calcd for $C_{21}H_{29}FePSi_2$: C, 59.42; H, 6.89. Found: C, 59.33; H, 6.84.

Synthesis of 2,6-Bis(trimethylsilyl)-3,5-bis(ferrocenyl)-phosphinine (9). A solution of **1a** (0.25 g, 1.2 mmol) and ferrocenyl(trimethylsilyl)acetylene (0.67 g, 2.4 mmol) in toluene (5 mL) was heated in xylene (5 mL) at 150 °C for 15 h. After the reaction mixture was cooled to room temperature, Celite (1 g) was added and the solvent removed under vacuum. Phosphinine **9** was purified by chromatography on silica gel using deoxygenated hexane as the eluent. Evaporation of the solvents and recrystallization from methanol yielded phosphinine **9** as a red-brown solid. Yield: 0.435 g (60%). Suitable crystals for X-ray analysis were grown from a hexane solution.

9: ^{31}P NMR (C_6D_6) δ 264.09; ^{1}H NMR (C_6D_6) δ 0.38 (d, 18H, ^4J(H−P) = 1.29, $2SiMe_3$), 4.07−4.09 (pseudo t, 4H, ΣJ(H−H) = 3.47, part B of AA′BB′ system), 4.14 (s, 10H, Cp), 4.58−4.60 (pseudo t, 4H, ΣJ(H−H) = 3.51, part A of AA′BB′ system), 9.04 (s, H_4); ^{13}C NMR (C_6D_6) δ 3.56 (d, ^3J(C−P) = 9.70, $2SiMe_3$), 69.15 (s, $4C_{3'''}$ or $4C_{3''}$), 70.74 (s, CH of Cp), 71.91 (s, $4C_{3''}$ or $4C_{3'''}$), 96.38 (d, ^3J(C−P) = 2.58, $2C_{3'}$), 137.71 (d, ^3J(C−P) = 20.74, C_4), 150.49 (d, ^2J(C−P) = 10.94, C_3, C_5), 166.40 (d, ^1J(C−P) = 87.08, C_2, C_6). MS, *m*/*z* (ion, relative intensity): 608 (M, 100), 593 (M − Me, 10), 535 (M − $SiMe_3$, 25). Anal. Calcd for $C_{31}H_{37}Fe_2PSi_2$: C, 61.19; H, 6.13. Found: C, 61.41; H, 6.07.

Synthesis of 3,4-Bis(diphenylphosphino)-6-*t*-butyl-1,2-azaphosphinine (10) and 2,3-Bis(diphenylphosphino)-6-(trimethylsilyl)phosphinine (11). A solution of **1a** (0.25 g 1.2 mmol) and bis(diphenylphosphino)acetylene (0.47 g, 1.2 mmol) in toluene (5 mL) was heated at 120 °C for 4 h in a Schlenk tube. The reaction was monitored by ^{31}P NMR spectroscopy. After the solution was cooled to room temperature, trimethylsilylacetylene (0.49 g, 4.8 mmol) was added and the reaction mixture was heated further at 90 °C for 1 h. At the end of the reaction, Celite (1 g) was then added and the solvent was removed in vacuo. Phosphinine **11** was purified by chromatography using a deoxygenated mixture of hexane/toluene (70:30) as the eluent. After evaporation of the solvents, phosphinine **11** was obtained as a yellow solid. Yield: 0.45 g (70%).

10: ^{31}P NMR (toluene) δ −19.32 (bd, ^3J(P−P) = 151.68, P_2), −6.06 (bd, ^3J(P−P) = 151.68, P_3), 291.80 (bs, P_1).

11: ^{31}P NMR ($CDCl_3$) δ −10.32 (bs, P_2 and P_3), 255.94 (bs, P_1); ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 9H, $SiMe_3$), 7.26−7.46 (m, 21H, 4Ph, H_4), 7.93 (dd, ^3J(H−H) = 8.41, ^3J(H−P) = 9.27, H_5); ^{13}C NMR ($CDCl_3$) δ 0.47 (d, ^3J(C−P) = 6.10, $SiMe_3$), 128.68−129.18 (m, CH of Ph), 133.41 (dt, J(C−P) = 3.40, J(C−P) = 21.09, C_4), 134.49−135.14 (m, CH (*ortho*) of Ph), 137.71 (d, ^2J(C−P) = 9.94, C_5), 137.52−138.17 (m, $4C_{ipso}$ of PPh_2), 151.34−151.83 (m, C_3), 173.00 (d, ^1J(C−P) = 82.71, C_6), 175.34 (dt, ^1J(C−P) = 93.10, J(C−P) = 7.65, C_2). MS, *m*/*z* (ion, relative intensity): 536 (M, 70), 459 (M − Ph, 85), 351 (M − PPh_2, 40), 73 ($SiMe_3$, 100). Anal. Calcd for $C_{32}H_{31}P_3Si$: C, 71.63; H, 5.82. Found: C, 71.71; H, 5.87.

Synthesis of 2,3,5,6-Tetrakis(diphenylphosphino)phosphinine (12). A solution of **1a** (0.25 g, 1.2 mmol) and bis-(diphenylphosphino)acetylene (0.94 g, 2.4 mmol) in xylene (5 mL) was heated at 150 °C for 15 h. After the solution was cooled to room temperature, Celite (1 g) was added and the solvent was removed under vacuum, yielding a brown powder. Phosphinine **12** was purified by chromatography using a deoxygenated mixture of toluene/hexane (80:20). Evaporation of the solvents in vacuo yielded **12** as a yellow solid. Yield: 0.59 g (60%).

12: ^{31}P NMR (CD_2Cl_2:THF) δ −10.44 (dd, $^3J(P_3-P_1)$ = 8.20, $^3J(P_3-P_2)$ = 167.92, $2P_3$), −5.91 (dd, $^2J(P_2-P_1)$ = 22.40, $^3J(P_2-P_3)$ = 167.92, $2P_2$), 247.30 (tt, $^3J(P_1-P_3)$ = 8.20, $^2J(P_1-P_2)$ = 22.40, P_1); ^{1}H NMR ($CDCl_3$) δ 6.72−7.21 (m, 41H, 8Ph, H_4); ^{13}C NMR (CD_2Cl_2:THF) δ 128.73−129.24 (m, CH of Ph), 134.23 (d, ^2J(C−P) = 18.62, CH (*ortho*) of Ph), 135.12 (d, ^2J(C−P) = 19.45, CH (*ortho*) of Ph), 137.43 (dd, ^4J(C−P) = 4.58, ^1J(C−P) = 13.73, $2C_{3'}$, $2C_{5'}$), 137.85 (ddd, $^4J(C-P_3)$ = 6.10, $^3J(C-P_1)$ = 9.15, $^1J(C-P_2)$ = 10.68, $2C_{2'}$, $2C_{6'}$), 142.34−142.83 (m, C_4), 149.24 (ddd, ^2J(C−P) = 10.68, ^2J(C−P) = 19.83, $^1J(C-P_3)$ = 25.94, C_3 and C_5), 178.67 (dd, $^1J(C-P_2)$ = 22.89, $^1J(C-P_1)$ = 93.08, C_2, C_6). MS, *m*/*z* (ion, relative intensity): 832 (M, 100), 755 (M − Ph, 90). Anal. Calcd for $C_{53}H_{41}P_5$: C, 76.44; H, 4.96. Found: C, 76.21; H, 5.07.

Synthesis of Bis(4-phenyl-6-*t*-butyl-1,2-azaphosphinine-3-yl)phenylphosphine (13) and Bis(3-phenyl-6-(trimethylsilyl)phosphinine-2-yl)phenylphosphine (14). To a solution of **1a** (0.4 g, 1.9 mmol) in toluene (10 mL), bis(phenylethynyl)phenylphosphine (0.3 g, 0.95 mmol) was added and the resulting mixture was heated at 125 °C for 1.5 h. In the solution of bis(1,2-azaphosphinine) **13** thus prepared, trimethylsilylacetylene (0.7 g, 7.1 mmol) was added and the reaction mixture was heated further at 90 °C for 1 h. Bis-(phosphinine) **14** was purified by chromatography on a silica gel column eluted with a deoxygenated hexane/toluene (70:30) mixture. After evaporation of the solvents, phosphinine **14** was obtained as a yellow solid. Yield: 0.340 g (60%).

13: ^{31}P NMR (toluene) δ −28.66 (bs, P_2), 289.88 (bs, $2P_1$).

14: ^{31}P NMR ($CDCl_3$) δ −11.30 (t, ^2J(P−P) = 15.25, P_2),

256.23 (d, ^2J(P−P) = 15.25, 2P$_1$); ^{1}H NMR ($CDCl_3$) δ 0.32 (s, 18H, 2SiMe$_3$), 6.92−7.26 (m, 17H, 3Ph, 2H$_4$), 7.90−7.98 (m, 2H$_5$); ^{13}C NMR ($CDCl_3$) δ 0.60 (s, SiMe$_3$), 127.61−136.13 (m, CH of Ph, 2C$_4$), 137.35−137.55 (pseudo t, part X of ABMX system, Σ^2J(C−P) = 10.06, 2C$_5$), 137.70−138.11 (m, C$_{ipso}$ of PPh), 143.59 (d, ^3J(C−P) = 7.63, 2C$_{3'}$), 153.21−153.96 (pseudo dt, part X of ABMX system, ΣJ(C−P) = 37.72, 2C$_3$), 166.00−170.26 (m, 2C$_2$, 2C$_6$). MS, *m*/*z* (ion, relative intensity): 594 (M, 40), 521 (M − SiMe$_3$, 100). Anal. Calcd for $C_{34}H_{37}P_3Si_2$: C, 68.66; H, 6.27. Found: C, 68.52; H, 6.37.

Synthesis of 1,3-Bis(3-(trimethylsilyl)-6-*t*-butyl-1,2-azaphosphinine-4-yl)propane (15) and 1,3-Bis(2,6-bis(trimethylsilyl)phosphinine-3-yl)propane (16). A solution of **1a** (0.25 g, 1.2 mmol) and $Me_3SiCC(CH_2)_3CCSiMe_3$ (0.14 g, 0.6 mmol) in toluene (5 mL) was heated at 120 °C for 1 h. The reaction was monitored by ^{31}P NMR spectroscopy. When the formation of bis(1,2-azaphosphinine) **15** was completed, trimethylsilylacetylene (0.35 g, 3.5 mmol) was then added and the reaction mixture was heated further at 95 °C for 1 h. Purification by chromatography with deoxygenated hexane as the eluent and evaporation of the solvent in vacuo yielded bis(phosphinine) **16** as a colorless oil. Yield: 0.23 g (75%).

15: ^{31}P NMR (toluene) δ 304.70.

16: ^{31}P NMR ($CDCl_3$) δ 261.06; ^{1}H NMR ($CDCl_3$) δ 0.42 (s, 18H, 2SiMe$_3$), 0.50 (d, 18H, ^4J(H−P) = 1.61, 2SiMe$_3$), 2.04−2.09 (m, 2H, $CH_2CH_2CH_2$), 3.02 (t, 4H, ^3J(H−H) = 7.91, CH_2-CH_2CH_2), 7.38 (d, 2H, ^3J(H−H) = 8.35, 2H$_4$), 8.08 (dd, 2H, ^3J(H−H) = 8.35, ^3J(H−P) = 9.04, 2H$_5$); ^{13}C NMR ($CDCl_3$) δ 0.69 (d, ^3J(C−P) = 5.85, 2SiMe$_3$), 2.55 (d, ^3J(C−P) = 10.80, 2SiMe$_3$), 35.70 (s, $CH_2CH_2CH_2$), 40.00 (s, $CH_2CH_2CH_2$), 129.36 (d, ^3J(C−P) = 25.02, 2C$_4$), 139.51 (d, ^2J(C−P) = 11.00, 2C$_5$), 153.58 (d, ^2J(C−P) = 12.45, 2C$_3$), 167.70 (d, ^1J(C−P) = 82.40, 2C$_2$ or 2C$_6$), 167.72 (d, ^1J(C−P) = 88.50, 2C$_6$ or 2C$_2$). MS, *m*/*z* (ion, relative intensity): 520 (M, 30), 447 (M − SiMe$_3$, 35), 417 (M − SiMe$_3$ − 2Me, 35), 359 (M − 2SiMe$_3$ − Me, 25), 73 (SiMe$_3$, 100). Anal. Calcd for $C_{25}H_{46}P_2Si_4$: C, 57.64; H, 8.90. Found: C, 57.48; H, 8.92.

Synthesis of Bis(4-phenyl-6-*t*-butyl-1,2-azaphosphinine-3-yl)dimethylsilane (17) and Bis(3-phenyl-6-(trimethylsilyl)phosphinine-2-yl)dimethylsilane (18). To a solution of **1a** (0.52 g, 2.5 mmol) in toluene (12 mL), bis(phenylethynyl)dimethylsilane (0.32 g, 1.25 mmol) was added and the reaction mixture was stirred at 110 °C. The reaction was monitored by ^{31}P NMR spectroscopy. Formation of bis(1,2-azaphosphinine) **17** was completed after 1.5 h, and trimethylsilylacetylene (1.00 g, 10.60 mmol) was then added. The reaction mixture was heated further at 90 °C for 1 h. After the solution was at room temperature, Celite (1.5 g) was added and the solvent was removed under vacuum. Phosphinine **18** was purified by chromatography using deoxygenated hexane as the eluent. After evaporation of the solvents, **18** was recovered as a yellow pale solid. Yield: 0.40 g (60%).

17: ^{31}P NMR (toluene) δ 304.22.

18: ^{31}P NMR ($CDCl_3$) δ 264.05; ^{1}H NMR ($CDCl_3$) δ 0.28 (t, 6H, ^4J(H−P) = 2.10, SiMe$_2$), 0.34 (bs, 18H, 2SiMe$_3$), 6.81−7.30 (m, 12H, 2Ph, 2H$_4$), 7.89−7.98 (m, part X of AA′XY system, 2H$_5$); ^{13}C NMR ($CDCl_3$) δ 0.66−0.77 (pseudo t, part X of ABX system, Σ^3J(C−P) = 5.32, 2SiMe$_3$), 4.40 (t, ^3J(C−P) = 12.85, SiMe$_2$), 127.78−130.13 (m, CH of Ph, 2C$_4$), 138.11−138.31 (pseudo t, part X of ABX system, Σ^2J(C−P) = 10.46, 2C$_5$), 146.00 (s, 2C$_{3'}$), 153.56−153.79 (pseudo t, part X of ABX system, Σ^2J(C−P) = 11.55, 2C$_3$), 166.36−168.29 (m, 2C$_2$, 2C$_6$). MS, *m*/*z* (ion, relative intensity): 544 (M, 100), 471 (M − SiMe$_3$, 40), 441 (M − SiMe$_3$ − 2Me, 15). Anal. Calcd for $C_{30}H_{38}P_2Si_3$: C, 66.14; H, 7.03. Found: C, 65.84; H, 7.11.

Synthesis of 3-((Phenylethynyl)dimethylsilyl)-4-phenyl-6-*t*-butyl-1,2-azaphosphinine (19) and 2,6-Bis((phenylethynyl)dimethylsilyl)-3,5-diphenylphosphinine (20). A solution of **1a** (0.52 g, 2.5 mmol) and bis(phenylethynyl)-dimethylsilane (2.60 g, 10 mmol) in toluene (16 mL) was stirred at 110 °C. Formation of 1,2-azaphosphinine **19** was completed after 1 h. The reaction mixture was heated further at 110 °C for 3 h. After the solution was at room temperature, Celite (1 g) was added and the solvent was removed in vacuo. Phosphinine **20** was purified by chromatography using a deoxygenated hexane/toluene (80:20) mixture as the eluent. After evaporation of the solvents, phosphinine **20** was recovered as a white solid. Yield: 0.97 g (70%).

19: ^{31}P NMR (toluene) δ 304.14.

20: ^{31}P NMR ($CDCl_3$) δ 273.27; ^{1}H NMR ($CDCl_3$) δ 0.32 (d, 12H, ^4J(H−P) = 1.50, 2SiMe$_2$), 7.28−7.53 (m, 21H, 4Ph, H$_4$); ^{13}C NMR ($CDCl_3$) δ 2.34 (d, ^3J(C−P) = 10.46, 2SiMe$_2$), 95.21 (d, ^3J(C−P) = 7.34, 2C≡C−Ph), 107.71 (s, 2C≡C−Ph), 123.97 (s, 2C$_{ipso}$ of C≡C−*Ph*), 128.38−132.56 (m, CH of Ph), 133.47 (d, ^3J(C−P) = 19.86, C$_4$), 145.55 (s, C$_{3'}$, C$_{5'}$), 155.21 (d, ^2J(C−P) = 10.69, C$_3$, C$_5$), 162.08 (d, ^1J(C−P) = 88.50, C$_2$, C$_6$). MS, *m*/*z* (ion, relative intensity): 564 (M, 100), 491 (M − SiMe$_3$, 10). Anal. Calcd for $C_{37}H_{33}PSi_2$: C, 78.68; H, 5.89. Found: C, 78.61; H, 6.02.

Synthesis of 2,6-Bis[(4′-phenyl-6′-*tert*-butyl-1′,2′-azaphosphinine-3′-yl)dimethylsilyl]-3,5-diphenylphosphinine (21) and 2,6-Bis[(3′-phenyl-6′(trimethylsilyl)phosphinine-2′-yl)dimethylsilyl]-3,5-diphenylphosphinine (22). A solution of **1a** (0.22 g, 1.05 mmol) and **20** (0.30 g 0.52 mmol) in toluene (6 mL) was heated at 115 °C for 2 h. After this period the formation of bis(1,2-azaphosphininyl)phosphinine **21** was complete. Trimethylsilylacetylene (1.00 g, 10.2 mmol) was added, and the resulting solution was heated further at 95 °C for 1 h. Tris(phosphinine) **22** was purified by chromatographic separation using a deoxygenated hexane/toluene (85:15) mixture as the eluent. After evaporation of the solvents, **22** was recovered as a yellow pale solid. Yield: 0.265 g (60%).

21: ^{31}P NMR (toluene) δ 275.86 (t, ^4J(P−P) = 11.96, P$_1$), 304.30 (d, ^4J(P−P) = 11.96, 2P$_{1'}$).

22: ^{31}P NMR ($CDCl_3$) δ 263.83 (d, ^4J(P−P) = 11.69, 2P$_{1'}$), 274.37 (t, ^4J(P−P) = 11.69, P$_1$); ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 12H, 2SiMe$_2$), 0.33 (s, 18H, 2SiMe$_3$), 6.81−7.16 (m, 23H, 4Ph, 2H$_{4'}$, H$_4$), 7.92 (dd, ^3J(H$_{5'}$−H$_{4'}$) = 8.22, ^3J(H$_{5'}$−P$_{1'}$) = 9.38, 2H$_{5'}$); ^{13}C NMR ($CDCl_3$) δ 0.75 (d, ^3J(C−P) = 5.99, 2SiMe$_3$), 4.45 (t, ^3J(C−P) = 12.20, 2SiMe$_2$), 127.74−130.15 (m, CH of Ph), 132.62 (d, ^3J(C−P) = 20.27, 2C$_{4'}$), 132.67 (d, ^3J(C−P) = 15.68, C$_4$), 138.19 (d, ^2J(C−P) = 11.27, 2C$_{5'}$), 145.95 (s, 2C$_{ipso}$ of Ph), 146.05 (s, 2C$_{ipso}$ of Ph), 153.10 (d, ^2J(C−P) = 10.68, 2C$_{3'}$ or C$_3$, C$_5$), 153.69 (d, ^2J(C−P) = 12.13, C$_3$, C$_5$ or 2C$_{3'}$), 163.98 (dd, ^3J(C−P) = 3.39, ^1J(C−P) = 90.01, 2C$_{2'}$ or C$_2$, C$_6$), 167.44 (d, ^1J(C−P) = 83.82, 2C$_{6'}$), 167.69 (dd, ^3J(C−P) = 4.24, ^1J(C−P) = 91.14, C$_2$, C$_6$ or 2C$_{2'}$). MS, *m*/*z* (ion, relative intensity): 848 (M, 47), 775 (M − SiMe$_3$, 5), 604 (M − $C_{14}H_{17}PSi$, 76), 73 (SiMe$_3$, 100). Anal. Calcd for $C_{49}H_{55}P_3Si_4$: C, 69.30; H, 6.53. Found: C, 69.03; H, 6.61.

Synthesis of 4,6-Di-*tert*-butyl-1,3,2-diazaarsinine (1b). The experimental procedure is identical with that used for **1a**. $AsCl_3$ (3.01 g, 16.35 mmol) was added to a solution of diazatitanacyclohexadiene prepared from Cp_2TiMe_2 (3.40 g, 16.35 mmol) and pivalonitrile (3.0 g, 36 mmol) in toluene (35 mL). The resulting reaction mixture, also containing NEt_3 (25 mL, ca. 10 equiv), was heated at 70 °C for 30−35 min. After filtration and evaporation of the solvents in vacuo, crude **1b** was recovered as a brownish oil, which is extremely sensitive to air and moisture, in 25−30% yield. Accurate yields can be estimated by ^{1}H NMR spectroscopy using the following procedure. The toluene solution of **1b** was evaporated to 25 mL. A sample of this solution (1 mL) was evaporated separately and then dissolved in $CDCl_3$ in a NMR tube containing a known amount of 1,2-diphenylethane. Integration of the signal of H$_5$ with the CH_2 signal of 1,2-diphenylethane gave the exact molarity of **1b**.

^{1}H NMR ($CDCl_3$): δ 1.24 (s, 18H, 2*tert*-butyl), 6.71 (s, H$_5$). ^{13}C NMR ($CDCl_3$): δ 29.70 (s, 6Me of *tert*-butyl), 39.28 (s, 2C of *tert*-butyl), 121.36 (s, C$_5$), 178.00 (s, C$_4$, C$_6$). MS (CI, NH_3), *m*/*z* (ion, relative intensity): 255 (M + 1, 100).

Synthesis of 2,6-Bis(trimethylsilyl)arsinine (23). A solution of **1b** (0.25 g, 1mmol) and trimethylsilylacetylene (0.6 g, 6.1 mmol) in toluene (5 mL) was heated at 95 °C for 90 min.

Arsinine **23** was purified by rapid chromatography on silica gel using deoxygenated hexane. After evaporation of the solvent in vacuo, **23** was recovered as a yellow highly oxygen sensitive oil. Yield: 0.110 g (40%).

^{1}H NMR ($CDCl_3$): δ 0.41 (s, 18H, $2SiMe_3$), 7.56 (pseudo dd, 1H, part A of AB_2 system, $^3J(H_A-H_B) = 8.29$, H_4), 8.19 (d, 2H, part B of AB_2 system, $^3J(H_B-H_A) = 8.29$, H_3, H_5). ^{13}C NMR ($CDCl_3$): δ 0.80 (s, $2SiMe_3$), 126.06 (s, C_4), 137.68 (s, C_3, C_5), 187.50 (s, C_2, C_6). MS, *m*/*z* (ion, relative intensity): 284 (M, 31), 269 (M − Me, 100).

Synthesis of 2,3,5,6-Tetrakis(trimethylsilyl)arsinine (24). A solution of **1b** (0.25 g, 1 mmol) and bis(trimethylsilyl)-acetylene (0.34 g, 2 mmol) in toluene (5 mL) was heated at 125 °C for 12 h. Arsinine **24** was purified by chromatographic separation on a silica gel column using dry deoxygenated pentane as the eluent. Evaporation of the solvent in vacuo yielded **24** as a yellow pale very sensitive to air and moisture solid. Yield: 0.17 g (40%).

^{1}H NMR ($CDCl_3$) δ 0.43 (s, 18H, $2SiMe_3$), 0.52 (s, 18H, $2SiMe_3$), 8.20 (s, 1H, H_4). ^{13}C NMR ($CDCl_3$): δ 3.02 (s, $2SiMe_3$), 4.44 (s, $2SiMe_3$), 139.07 (s, C_4), 148.75 (s, C_3, C_5), 195.72 (s, C_2, C_6). MS, *m*/*z* (ion, relative intensity): 428 (M, 40), 413 (M − Me, 30), 355 (M − $SiMe_3$, 30), 325 (M − $SiMe_3$ − 2Me, 100).

Synthesis of 2,6-Bis(diphenylphosphino)-3,5-diphenylarsinine (25). A solution of **1b** (0.25 g, 1 mmol) and $PhCCPPh_2$ (0.56 g, 2 mmol) in toluene (5 mL) was heated at 120 °C for 12 h. The reaction was monitored by ^{31}P NMR spectroscopy. Chromatographic separation on a silica gel column using a deoxygenated hexane/toluene (60:40) mixture and evaporation of the solvents under vacuum yielded arsinine **25** as a stable yellow solid. Yield: 0.320 g (50%).

^{31}P NMR ($CDCl_3$): δ −9.32. ^{1}H NMR ($CDCl_3$) δ 7.11−7.30 (m, 6Ph, H_4). ^{13}C NMR ($CDCl_3$): δ 127.88−135.17 (m, CH of Ph, C_4), 138.14 (d, $^1J(C-P) = 11.14$, $4C_{ipso}$ of PPh_2), 143.59 (d, $^3J(C-P) = 8.35$, $C_{3'}$, $C_{5'}$), 152.53 (d, $^2J(C-P) = 24.34$, C_3, C_5), 183.20 (d, $^1J(C-P) = 31.66$, C_2, C_6). MS, *m*/*z* (ion, relative intensity): 660 (M, 100), 475 (M − PPh_2, 13). Anal. Calcd for $C_{41}H_{31}AsP_2$: C, 74.55; H, 4.73. Found: C, 74.21; H, 4.84.

X-ray Structure Determinations. All data sets were collected on an Enraf-Nonius CAD4 diffractometer using Mo Kα (λ = 0.710 73 Å) and a graphite monochromator. The crystal structures were solved by direct methods using SIR92 and refined with the Enraf-Nonius MOLEN package using reflections having $F^2 < 3.0\sigma(F^2)$. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. Crystal data are assembled in Table 3.

Table 3. Crystal Data for Compounds 9 and 25

compound	**9**	**25**
formula	$C_{31}H_{37}Fe_2Si_2P$	$C_{41}H_{31}AsP_2$
space group	$P2_1/n$ (No. 14)	P-1 (2)
data collection temperature (K)	123	123
a (Å)	15.841(3)	9.828(2)
b (Å)	11.441(2)	13.659(3)
c (Å)	16.522(4)	14.128(3)
α (deg)		112.06(2)
β (deg)	105.83(1)	95.22(2)
γ (deg)		108.83(2)
V (Å^3)	2881(2)	1614(1)
Z	4	2
d_{calc}(g/cm^3)	1.406	1.358
μ (cm^{-1})	11.6	11.7
max 2θ	60.0	60.0
no. of reflns measd	9032	9742
no. of reflns included	5170	7085
no. of params refined	325	397
unweighted agreement factor	0.035	0.029
weighted agreement factor	0.045	0.044
GOF	1.03	1.02
convergence, largest shift/error	0.00	0.00

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Supporting Information Available: Tables of the X-ray structure determination for **9** and **25**, including positional parameters, bond distances and angles for non-hydrogen atoms, least-squares planes, and β_{ij} values (20 pages). Ordering information is given on any current masthead page.

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