Phosphorus-Containing *N*-Methyleneamine Type Compounds: Synthesis, Structure, and Reactivity

Christophe Galliot,† Anne-Marie Caminade,† Françoise Dahan,† Jean-Pierre Majoral,*,† and Wolfgang Schoeller‡

Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne, 31077 Toulouse Cedex, France, and Fakultät für Chemie, Universität Bielefeld, W-7800 Bielefeld, Germany

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Addition of paraformaldehyde to phosphonodihydrazides $PhP(X)(NCH_3NH_2)_2$, **1a** (X = S) or **1b** (X = O), led to 1,2,4,5,3-perhydrotetrazaphosphorines **4a** or **4b** and then to stable phosphonodihydrazones $PhP(X)(N(CH_3)N{=}CH_2)_2$, **6a** (X = S) or **6b** (X = O). Similarly, addition of paraformaldehyde to the hexahydrazino cyclotriphosphazene $N_3P_3(NCH_3NH_2)_6$ afforded a tris(1,2,4,5,3-perhydrotetrazaphosphorine)cyclotriphosphazene, **12**, which in turn is transformed to the stable hexakis(*N*-methyleneamine)cyclotriphosphazene **13** by addition of paraformaldehyde. The crystal and molecular structure of **13** was examined by single crystal X-ray diffraction. Treatment of **6a** or **6b** with the phosphanylium ion $(iPr_2N)_2P^+CF_3SO_3^-$, **15**, gave a mixture of bicyclic phosphonium salts **17** and **18** or **19** and **20** respectively. A pyridinium salt **21** was prepared by reacting **6a** with trifluoro acetic anhydride in the presence of pyridine. Interaction of the borenium salt $(C_5H_9)_2B^+CF_3SO_3^-$, **22**, with **6a** led to the salt **23** [**6a**·$2B(C_5H_9)_2{\cdot}CF_3SO_3$].

It is now well documented that phosphonodihydrazides $RP(X)(N(CH_3)NH_2)_2$ (X = O or S) or phosphonotrihydrazides $XP(N(CH_3)NH_2)_3$ (X = O or S) are useful reagents for the preparation of a variety of heterocycles,[1] macrocycles,[2] and more elaborated systems such as cryptands, spherands,[3] and even dendrimers.[4] Phosphono di or trihydrazones $RP(X)(N(CH_3)N{=}C<)_2$ (R = $N(CH_3){-}N{=}C<$, alkyl, aryl etc. ...) are also easily accessible and present a high stability in comparison with the corresponding imines (for example, the hydrolysis of imines is much more faster than the hydrolysis of phosphonohydrazones).

Similar *N*-methyleneamine type compounds $H_2C{=}N{-}R$ (R = CR'_3, NR'_2, OR') are also used in a lot of reactions but most of these derivatives are unstable even at low temperature and quickly dimerize,[5] trimerize[6] or polymerize. Because of this instability only X-ray structures of some related salts or complexes have been reported.

Taking into account all these observations it appeared interesting to try to prepare unknown C unsubstituted phosphonodihydrazones $RP(X)(N(CH_3)N{=}CH_2)_2$ or related species $N_3P_3(N(CH_3)N{=}CH_2)_6$ and to study their reactivity; the presence of a phosphorus substituent in β position relative to the unsaturation was expected to modify the stability and the reactivity in comparison with those of classical *N*-methyleneamine type compounds.

In a preliminary communication[7] we described the synthesis of new bis- or hexakis(*N*-methylenehydrazones), the X-ray structure of one of these compounds, and some examples of the reactivity of these species. We report here full details concerning these investigations as well as (i) the first X-ray structure determination of an hexakis(*N*-methylenehydrazone), (ii) all information concerning the mechanism of formation of these compounds, and (iii) additional examples of the reactivity of these species and some theoretical calculations explaining

† Laboratoire de Chimie de Coordination du CNRS.
‡ Universität Bielefeld.
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(1) (a) Majoral, J.-P.; Kraemer, R.; Navech, J.; Mathis, F. *Tetrahedron Lett.* **1975**, 1481. (b) Majoral, J.-P.; Kraemer, R.; Navech, J.; Mathis, F. *Tetrahedron* **1976**, *32*, 2633. (c) Majoral, J.-P.; Kraemer, R.; Navech, J. *J. Chem. Soc. Perkin Trans. 1.* **1976**, 2093. (d) Majoral, J.-P.; Kraemer, R.; Navech, J.; Germa, H.; Revel, M. *J. Heterocycl. Chem.* **1977**, *14*, 749. (e) Majoral, J.-P. *Synthesis* **1978**, *8*, 557. (f) Navech, J.; Kraemer, R.; Majoral, J.-P. *Tetrahedron Lett.* **1980**, 1449. (g) Engelhardt, U.; Bünger, T.; Viertel, H.; Stromburg, B.; Giersdorf, K. *Phosphorus Sulfur* **1987**, *30*, 768.

(2) (a) Majoral, J.-P.; Badri, M.; Caminade, A.-M.; Delmas, M.; Gaset, A. *Inorg. Chem.* **1988**, *27*, 3873. (b) Majoral, J.-P.; Badri, M.; Caminade, A.-M.; Gorgues, A.; Delmas, M.; Gaset, A. *Phosphorus Sulfur Silicon* **1990**, *49–50*, 413. (c) Badri, M.; Majoral, J.-P.; Caminade, A.-M.; Delmas, M.; Gaset, A.; Gorgues, A.; Jaud, J. *J. Am. Chem. Soc.* **1990**, *112*, 5618. (d) Badri, M.; Majoral, J.-P.; Gonce, F.; Caminade, A.-M.; Sallé, M.; Gorgues, A. *Tetrahedron Lett.* **1990**, *31*, 6343. (e) Majoral, J.-P.; Badri, M.; Caminade, A.-M.; Delmas, M.; Gaset, A. *Inorg. Chem.* **1991**, *30*, 344. (f) Majoral, J.-P.; Badri, M.; Caminade, A.-M. *Heteroatom Chem.* **1991**, *2*, 45. (g) Gonce, F.; Caminade, A.-M.; Majoral, J.-P. *Tetrahedron Lett.* **1991**, *32*, 203. (h) Colombo, D.; Caminade, A.-M.; Majoral, J.-P. *Inorg. Chem.* **1991**, *30*, 3367. (i) Gonce, F.; Caminade, A.-M.; Boutonnet, F.; Majoral, J.-P. *J. Org. Chem.* **1992**, *57*, 970. (j) Gonce, F.; Caminade, A.-M.; Majoral, J.-P.; Jaud, J.; Vignaux, J. *Bull. Soc. Chim. Fr.* **1992**, *129*, 237. (k) Delavaux-Nicot, B.; Mathieu, R.; Lungan, N.; Majoral, J.-P. *Inorg. Chem.* **1992**, *31*, 334. (l) Colombo-Khater, D.; Caminade, A.-M.; Delavaux-Nicot, B.; Majoral, J.-P. *Organometallics* **1993**, *12*, 2861. (m) Oussaid, B.; Garrigues, B.; Jaud, J.; Caminade, A.-M.; Majoral, J.-P. *J. Org. Chem.* **1993**, *58*, 4500. (n) Caminade, A.-M.; Majoral, J.-P. *Chem. Rev.* **1994**, *94*, 1183.

(3) Mitjaville, J.; Caminade, A.-M.; Mathieu, R.; Majoral, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 5007.

(4) Launay, N.; Caminade, A.-M.; Lahana, R.; Majoral, J.-P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1589.

(5) (a) Riddell, F. G.; Murray-Rust, P. *J. Chem. Soc. Chem. Commun.* **1970**, 1075. (b) Hocker, J.; Wendisch, D. *J. Chem. Res. Synop.* **1977**, 236.

(6) See for example: Sprung, M. M. *Chem. Rev.* **1940**, *26*, 297.

(7) Galliot, C.; Caminade, A.-M.; Dahan, F.; Majoral, J.-P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1477.

(8) (a) Braillon, B.; Lasne, M. C.; Ripoll, J. L.; Denis, J. M. *New J. Chem.* **1982**, *6*, 121. (b) Barluenga, J.; Bayon, A. M.; Asensio, G. *J. Chem. Soc., Chem. Commun.* **1983**, 1109. (c) *ibid* **1984**, 427. (d) Overman, L. E.; Burk, R. M. *Tetrahedron Lett.* **1984**, *25*, 1635.

(9) (a) Harff, G. A.; Sinnema, A.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 71. (b) Möhrle, H.; Scharf, U.; Rühmann, E.; Schmid, R. *Arch. Pharm. (Weinheim, Ger.)* **1983**, *316*, 222. (c) Kamitori, Y.; Hojo, M.; Masuda, R.; Fujitani, T.; Ohara, S.; Yokoyama, T. *J. Org. Chem.* **1988**, *53*, 129.

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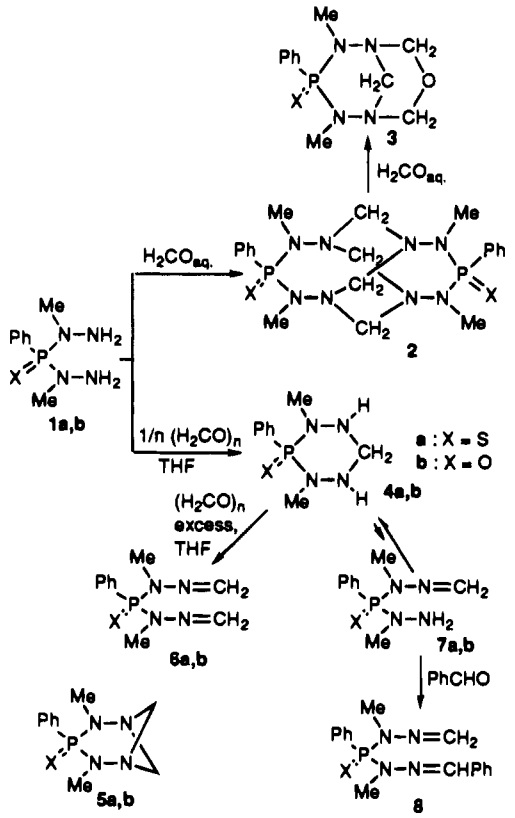
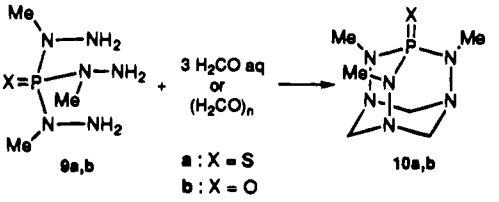
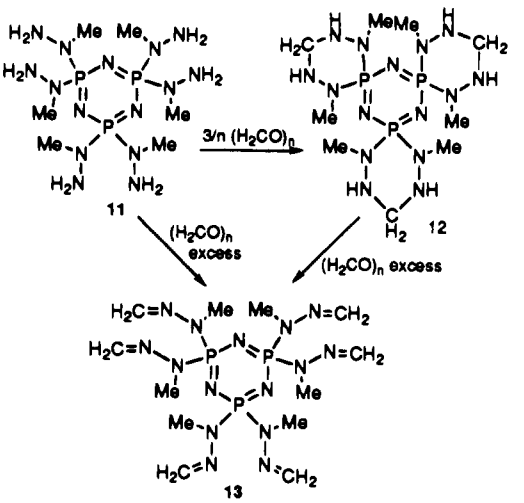
Scheme 1



Scheme 2



Scheme 3



their unusual reactivity. This work presents another facet of the usefulness of species possessing P−N−N linkage[1−4] which easily allow the preparation of so far unique linear or cyclic salts. Moreover, it demonstrates that these new stable C-unsubstituted phosphonohydrazones react unexpectedly as imines and not as hydrazones.

Results and Discussion

Numerous reactions were undertaken to generate compounds with $H_2C{=}N$ units.[8] The most common involves the use of formaldehyde.[9] Nevertheless, the addition of aqueous formaldehyde to the phosphonodihydrazides **1a** or **1b** leads initially to the dimer **2** and then to the bicycle **3**.[10,11] A different reaction takes place when **1a** or **1b** (1 equiv) in THF is added to paraformaldehyde $(CH_2O)_n$ (2 equiv) in THF solution and in the presence of molecular sieve. In these cases, bis(*N*-methylhydrazone) derivatives **6a** or **6b** are isolated in nearly quantitative yield (Scheme 1). If the same reaction is performed with 1 equiv of paraformaldehyde and not 2 equiv, 1,2,4,5,3-perhydrotetrazaphosphorines **4a** or **4b** are formed. Further addition of an excess of paraformaldehyde to **4a** or **4b** gives **6a** or **6b** which were fully characterized by NMR and in the case of **6a** also by X-ray diffraction studies. One can postulate that the transformation **4a** → **6a** or **4b** → **6b** might involve the transient generation of the bicyclic adduct **5a** or **5b**. Nevertheless, no evidence for the formation of this compound has been found in ^{31}P NMR. The existence of an equilibrium between the cyclic form **4a** (or **4b**) and the phosphonomonohydrazone **7a** (or **7b**) can also be evoked, this equilibrium being shifted toward the thermodynamically more favored cyclic structure **4a** (or **4b**), but formaldehyde would react much more easily with **7a** (or **7b**) than with **4a** or (**4b**). Indeed, addition of benzaldehyde (1 equiv) to **4b** results in the formation of the phosphonodihydrazone **8**, nevertheless obtained in poor yield.[11]

Note that phosphonotrihydrazide **9a** and **9b** in the presence of 3 equiv of aqueous formaldehyde or paraformaldehyde gave exclusively phosphoradamantanes **10a** or **10b** (Scheme 2).[1b]

Analogous results to those obtained with **1a** or **1b** can be observed from the addition of paraformaldehyde to hexahydrazinocyclotriphosphazene **11**: the tetracyclic compound **12** is formed when 3 equiv of paraformaldehyde are used, while the derivative **13** possessing six $H_2C{=}N$ units is isolated from the reaction of 6 equiv of paraformaldehyde with 1 equiv of **11** (Scheme 3). Moreover, addition of an excess of $(CH_2O)_n$ to **12** allows to form **13** in quantitative yield. The generation of **12** and **13** can be detected by ^{31}P NMR (**11**, δ 29.5; **12**, δ 24.7; **13**, δ 14.9 ppm). These two new species were characterized by spectral data. Indeed, the ^1H NMR spectrum of **12** shows the presence of a multiplet at 3.64 ppm, characteristic for $N{-}CH_2{-}N$ groups while a multiplet in ^{13}C NMR is also observed for the same groups at 60.2 ppm. Mass spectrometry corroborates the formation of **12** (*m/e* 442 $[M + 1]^+$). The ^1H NMR spectrum of **13** is fully consistent with the presence of $H_2C{=}N$ groups (δ: 6.27 and 6.38 ppm, AB system $^2J_{HAHB}$ = 11.2 Hz) as well as ^{13}C NMR spectrum ($H_2C{=}N$ δ: 124.8 (m) ppm). Fast atom bombardment mass spectrometry confirms the structure of **13** (*m/e* 478 $[M + 1]^+$) which was fully corroborated by an X-ray diffraction study.[7] The ORTEP drawing showing the atomic numbering scheme is illustrated in Figure 1. Bond lengths and angles of the phosphonodihydrazono moieties compare well with that of derivative **6a**.[7] Therefore, these experiments offer an easy access to unexpected stable compounds which contain two or six methylene amine units; in marked contrast to classical *N*-methyleneamine type derivatives, compounds **6a**, **6b**, **13** can be stored several days in air or several months under H_2O free argon without any decomposition. Furthermore, their reactivity appears to be quite different from that of the corresponding C-substituted compounds like PhP(S)[N(Me)N=CRR′]$_2$ (R = Ph, R′ = H; R = R′ = Ph) **14** or

(10) Jaud, J.; Galy, J.; Kraemer, R.; Majoral, J.-P. *Nevech, J. Acta Crystallogr. Sect. B* **1980**, *36*, 869.
(11) Majoral, J.-P.; Revel, M.; Navech, J. *J. Chem. Res. Synop.* **1980**, *129*; *J. Chem. Res. Miniprint* **1980**, 2001.

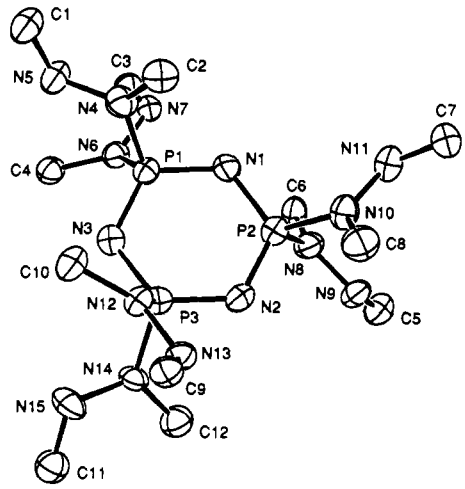
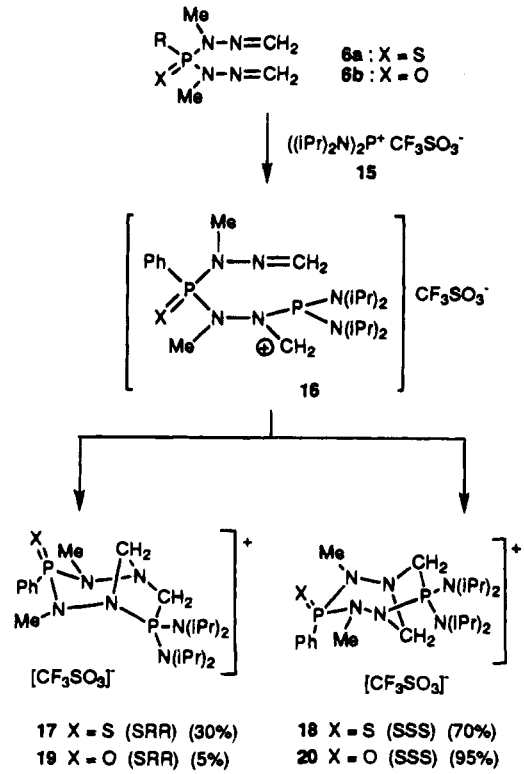


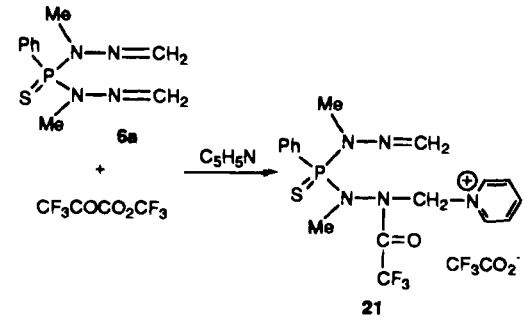
Figure 1. Structure of **13**. Selected bond lengths (Å) and bond angles (deg): P(1)–N(4) 1.687(4), P(1)–N(6) 1.663(4), P(2)–N(8) 1.651-(4), P(2)–N(10) 1.665(4), P(3)–N(12) 1.669(4), P(3)–N(14) 1.668-(4), C(1)–N(5) 1.259(6), C(3)–N(7) 1.268(6), C(5)–N(9) 1.244(6), C(7)–N(11) 1.268(6), C(9)–N(13) 1.274(6), C(11)–N(15) 1.253(6); N(3)–P(1)–N(4) 112.9(2), N(1)–P(1)–N(6) 111.5(2), N(1)–P(1)–N(4) 104.0(2), N(4)–P(1)–N(6) 104.1(2).

Scheme 4

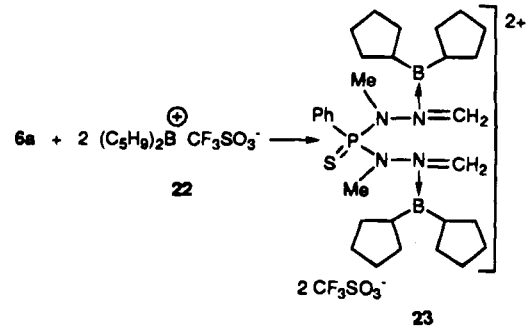


from that of classical hydrazones. While **14** does not react with the phosphanylium ion **15** $(iPr_2N)_2P^+CF_3SO_3^-$, **6a** does, quantitatively (Scheme 4), giving rise to a mixture of the cations **17** and **18** which were isolated and fully characterized by NMR and X-ray diffraction studies.[7] Electrophilic attack of the phosphanylium ion **15** also occurs when a dichloromethane solution of **15** is slowly added to **6b** in solution in dichloromethane at −80 °C. One cyclic cation **20** was isolated in high yield (90%), the other one **19** being formed in very poor yield (5%). Attempts to obtain suitable crystals for an X-ray structure determination failed until now. Nevertheless, the structure of **20** is clearly established by NMR, mass spectra, and elemental analysis. The ^{31}P NMR spectra reveals the presence of two singlets at 8.9 (Ph–P=O) and 76.8 (>P^+<)

Scheme 5



Scheme 6



ppm while ^1H and ^{13}C NMR spectra show characteristic signals for CH_2 groups. The mass spectrum (FAB^+) confirms that the compound arises from the addition of one phosphanylium ion to bis(*N*-methylenehydrazone), **6b**. Derivative **19** was only characterized by ^{31}P NMR [**19** δ = 18.7 (d), 80.4 (d) $^3J_{PP}$ = 6 Hz]. As in the case of species **17** and **18** no thermal equilibrium between **19** and **20** was detected by variable temperature NMR experiments. The structure of **19** and **20** might be attributed by analogy with that of **17** and **18** taking into account that the ^{31}P NMR spectra of **17** and **19** present two doublets with $^3J_{PP}$ coupling constants of 8.5 and 6 Hz respectively while the ^{31}P NMR spectra of **18** and **20** consist of two singlets ($^3J_{PP}$ = 0 Hz). One can postulate that the first step of all these reactions leading to **17**, **18** or **19**, **20** is the electrophilic attack of the phosphanylium ion on an imino-nitrogen atom with the transient generation of the carbocation **16** (X = S or O) which intramolecularly rearranges to the two isomers **17** and **18** or **19** and **20**. If it is true, the formation of these unusual cyclic phosphonium salts implies that **6a** reacts as an imine[12] and not as an hydrazone in which the azomethine carbon atom is negatively charged because of the conjugation of the C=N bond with the adjacent nitrogen atom. To check this assumption the phosphonodihydrazone **6a** was reacted with trifluoroacetic anhydride in the presence of pyridine: under these conditions the pyridinium salt **21** was isolated in 80% yield (Scheme 5). Electrophilic attack of CF_3CO^+ on one of the imino nitrogen atoms and subsequent trapping of the resulting carbocation with pyridine can be reasonably postulated. This is in marked contrast with the reaction of hydrazones $R_2N–N=CHR'$ (R = Me, R' = Et, Ph) with trifluoroacetic anhydride in the same experimental conditions; in this case, electrophilic substitution reaction at the azomethine carbon atom takes place with the formation of $R_2N–N=C(R')COCF_3$.

Interaction of the borenium salt $(C_5H_9)_2B^+CF_3SO_3^-$, **22**, with **6a** provides another example for the reactivity of these phospho-

(12) It has been demonstrated that the phosphanylium salt **15** reacts with imines. See for example: Mazières, M. R.; Roques, C.; Kim, T.; Majoral, J.-P.; Wolf, R.; Sanchez, M. *Phosphorus, Sulfur Silicon* **1990**, 49–50, 309. Kim, T.; Mazières, M. R.; Wolf, R.; Sanchez, M. *Tetrahedron Lett.* **1990**, *31*, 4459.

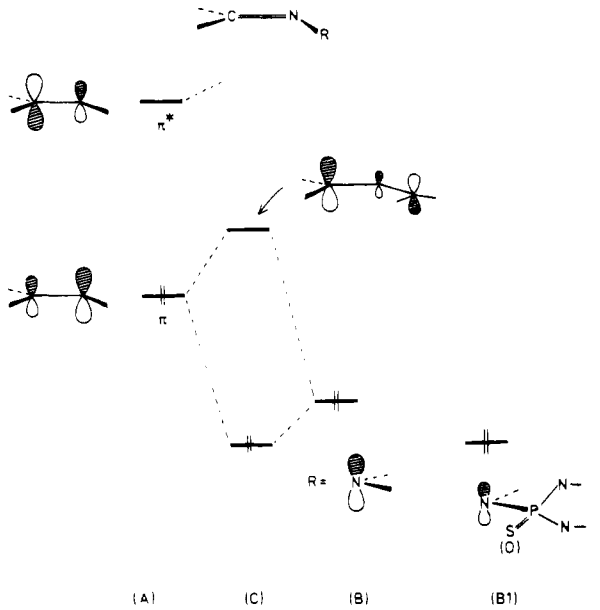


Figure 2. Interaction diagram for the composition of a substituted methyleneimine (C = A−B) from orbital overlap of a methyleneimine (A) with an amino group (B) or (B1).

nodihydrazones. Such a reaction leads quantitatively to the salt **23** when 1 equiv of **6a** is treated with 2 equiv of **22** (Scheme 6). An expected deshielding effect is observed in ^{1}H NMR for the imino proton [6.37, 6.48 ppm (AB system) for **6a**; 7.7 ppm (hidden by C_6H_5 signals) for **23**] and in ^{13}C NMR for the imino carbon [126.9−132.6 ppm (hidden by C_6H_5 signals) for **6a**; 151 (s) ppm for **23**]. The structure of **23** was confirmed by mass spectrometry (FAB$^+$) and elemental analysis. Note that the addition of 1 equiv of **22** to 1 equiv of **6a** gives an unstable compound which quickly decomposes even at low temperature.

The higher stability of **6a**, **6b** in comparison with amino−iminomethylene type compounds can be quantitatively understood on the basis of an orbital interaction diagram (Figure 2). Methylene imine (A) possesses a π and π^* orbital. The former orbital bears the larger coefficient at the nitrogen atom, due to its larger electronegativity compared with its neighboring carbon atom. Conjugation of an amino group (B) causes interaction of the p-orbital (at (B)) with the π, π^* orbitals (at (A)) under formation of an amino−iminomethylene (C). As a consequence, the π-orbital is lowered in its ionization potential with concomitant inverse polarization of the resulting π-system. Thus, the larger coefficient in the highest occupied molecular orbital results at the carbon rather than at the nitrogen atom. This view is in accord with the bonding situation in enamines.[13]

In the case of phosphonodihydrazones, the bonding situation is different. The p-orbital at (B1) donates electron density simultaneously into the π-bond (at (A)) and the neighboring phosphorus atom. Hence (B_1) refers to a much weaker donor than (B). In other words, the donation of electron density into the π-system of (A) is in competition with the π-acceptor properties of the neighboring hypervalent phosphorus atom. Accordingly, a reactive π-system results, intermediate between methylenimine and aminoiminomethylene.

In order to corroborate these qualitative arguments we performed ab initio calculations[14] on (a) methylenimine, (b) aminoiminomethylene and (c) a model substituted derivative of (b), $H_2C{=}N{-}NHP(S)(CH_3)_2$ (Cs symmetry imposed, all trans conformations) utilizing the G-31g (d, p) basis set.[15] The resulting HOMO energies (in eV) are (in consecutive order for a, b, and c as follows: −12.3; −9.1; −10.5. It corroborates the qualitative assertion that the modified amino group (in c) is a weak π-donor for the electron enrichment of the nitrogen−carbon double bond.

In conclusion stable poly *N*-methyleneamine type compounds of general formula $RP(X)[N(CH_3)N{=}CH_2]_2$ or $P_3N_3[N(CH_3)N{=}CH_2]_6$ easily prepared in high yield, appear to be useful reagents for the preparation of a variety of acyclic or cyclic salts, when they are reacted with electrophiles. Additional studies concerning the imine-like reactivity of these new reagents are underway.

Experimental Section

All manipulations were carried out with standard high vacuum or dry argon atmosphere techniques. ^{1}H, ^{11}B, ^{31}P and ^{13}C NMR spectra were recorded on Bruker AC 80 and AC 200 spectrometers. ^{31}P NMR chemical shifts are reported in ppm relative to 85% H_3PO_4. Mass spectra were obtained by methane desorption or fast atom bombardment. The literature procedures were employed for the synthesis of the known phosphonodihydrazides **1a**, **1b**.[1a,b]

Synthesis of 1,2,4,5,3-Perhydrotetraphosphorines, 4a and 4b. A solution of phosphodihydrazide **1a** (0.280 g, 1.22 mmol) or **1b** (0.260 g, 1.22 mmol) in 30 mL of THF is added to paraformaldehyde (0.037 g, 1.22 mmol) in the presence of molecular sieves (4 Å) at room temperature. After this is stirred for 4 days[16] the solution is filtered and then the solvent is evaporated to give quantitatively **4a** or **4b** as white powders.[1a,b]

Synthesis of Phosphonobis(*N*-methylenehydrazones), 6a, 6b. A mixture of **1a** (0.280 g, 1.22 mmol) or **1b** (0.260 g, 1.22 mmol) in 30 mL of THF and paraformaldehyde (0.260 g, 8.66 mmol) is stirred for 10 h in the presence of molecular sieves (4 Å). Filtration of the solution, followed by evaporation to dryness gave **6a** or **6b** as white powders, which were recrystallized in acetone or toluene.

6a: mp 94−96 °C; 98% yield. ^{31}P{^{1}H}NMR ($CDCl_3$): δ 77.4 (s). ^{1}H NMR ($CDCl_3$): δ 3.01 (d, $^3J_{HP}$ = 9.4 Hz, 6H, N−CH_3), 6.37 and 6.48 (AB system, $^2J_{HAHB}$ = 9.3 Hz, 4H, $H_2C{=}N$), 7.24−8.09 (m, 5H, C_6H_5−P). ^{13}C NMR ($CDCl_3$): δ 29.6 (qd, $^1J_{CH}$ = 138.8 Hz, $^2J_{CP}$ = 9.5 Hz, CH_3), 126.9−132.6 (m, N=CH_2 and P−C_6H_5). MS (DCI/CH_4): $[M + 1]^+$ = 255. Anal. Calcd for $C_{10}H_{15}N_4PS$: C, 47.23; H, 5.95; N, 22.03. Found C, 47.18; H, 5.90; N, 21.90.

6b: 98% yield. ^{31}P{^{1}H}NMR ($CDCl_3$): δ 21.4 (s). ^{1}H NMR ($CDCl_3$): δ 2.90 (d, $^3J_{HP}$ = 7.2 Hz, 6H, N−CH_3), 6.25 and 6.41 (AB system, $^2J_{HAHB}$ = 10.8 Hz, 4H, $H_2C{=}N$), 7.29−7.77 (m, 5H, C_6H_5−P). ^{13}C NMR ($CDCl_3$): δ 29.6 (qd, $^1J_{CH}$ = 138.5 Hz, $^2J_{CP}$ = 9.4 Hz, CH_3), 126.9−132.5 (m, N=CH_2 and P−C_6H_5). MS: 239 $[M + 1]^+$. Anal. Calcd for $C_{10}H_{15}N_4OP$: C, 50.42; H, 6.35; N, 23.52. Found: C, 50.24; H, 6.27; N, 23.42.

Synthesis of the Phosphono(*N*-methylenehydrazone)(*N*-phenylmethylenehydrazone) 8. To a solution of **4a** (0.242 g, 1 mmol) in 10 mL of CH_2Cl_2 at room temperature was added benzaldehyde (0.106 g, 1 mmol) in 10 mL of CH_2Cl_2. The resulting mixture was heated for 6 h at 40 °C. After evaporation of the solvent the residue is crystallized in a 1/1 hexane/chloroform solution to give **8**[11] in 52% yield.

Synthesis of the Tris(1,2,4,5,3-perhydrotetrazaphosphorine)-cyclotriphosphazene 12. A solution of hexamethylhydrazinocyclotriphosphazene, **11** (0.500 g, 1.23 mmol), in 30 mL of THF is added to paraformaldehyde (0.111 g, 3.69 mmol) at room temperature in the

(13) Schoeller, W. W.; Wiemann, J.; Rademacher, P. *J. Chem. Soc., Perkin Trans 2* **1988**, 369.
(14) Gaussian 92, Revision, A.; Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Hill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Guassian Inc., Pittsburgh, PA, 1992.
(15) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(16) Solutions were stirred at ambient temperature for long periods, and not at slightly elevated temperatures (for shorter periods) in order to avoid degradation of compounds **4a**, **4b**, **12**, or **13** and therefore in order to increase their yields.

Table 1. Crystallographic Data at 20 °C for **13**

chem formula: $C_{12}H_{30}N_{15}P_3$	$\lambda = 0.71073$ Å
fw: 477.4	$Z = 8$
cryst. syst: orthorhombic	$F(000) = 2016$
space group: *Pbca* (No.61)	$D_{calc} = 1.362$ g.cm^{-3}
$a = 8.349(1)$ Å	$\mu = 0.28$ mm^{-1}
$b = 16.316(2)$ Å	transm coeff = 0.955−0.999
$c = 34.191(3)$ Å	$R = 0.037$
$V = 4658(1)$ Å^3	$R_w = 0.045$

presence of molecular sieve (4 Å). After this is stirred for 5 days[16] the solvent is evaporated to give **12** as a white powder.

12: mp 86−88 °C, 98% yield. $^{31}P\{^1H\}$ ($CDCl_3$): δ 24.7. ^1H NMR ($CDCl_3$): δ 2.59 (m, 18H, CH_3), 3.64 (m, 6H, CH_2), 4.36 (m, 6H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 35.3 (br s, CH_3), 60.2 (m, CH_2) ppm. IR (KBr): 3247 (ν_{NH}) cm^{-1}. MS (FAB$^+$): 442 [M+1]$^+$. Anal. Calcd for $C_9H_{30}N_{15}P_3$: C, 24.49; H, 6.85; N, 47.60. Found: C, 24.32; H, 6.68; N, 47.48.

Synthesis of Hexabis(*N*-methylenehydrazono)cyclotriphosphazene, 13. A solution of **11** (0.500 g, 1.23 mmol) in solution in 30 mL of THF is added to paraformaldehyde (0.333 g, 11.1 mmol) in the presence of molecular sieves (4 Å) at room temperature. After this is stirred for 3 days,[16] the solution is filtered and the solvent is evaporated to give **13** as a white powder.

13: mp 179−180 °C, 99% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 14.9; ^1H NMR ($CDCl_3$): δ 2.99 (m, 18H, CH_3), 6.27, 6.38 (AB system, $^2J_{HA-HB}$ = 11.2 Hz, 12H, N=CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 29.7 (m, CH_3), 124.8 (m, H_2C=N). MS (FAB$^+$): 478 [M + 1]$^+$. Anal. Calcd for $C_{12}H_{30}N_{15}P_3$: C, 30.19; H, 6.33; N, 44.01. Found C, 30.06; H, 6.31; N, 43.87. Main crystallographic data for **13** are given in Table 1.

Synthesis of Phosphonium Salts 17 and **18.** A solution of the phosphanylium salt **15** (0.483 g, 1.27 mmol) in 10 mL of CH_2Cl_2 was added by canula at −80 °C to a solution of **6a** (0.323 g, 1.27 mmol) in 10 mL of CH_2Cl_2. The mixture was stirred overnight, and then the solvent was evaporated to give a residue which was washed with CH_2Cl_2/pentane (1:3) to give an oil. Treatment of this oil with 10 mL of Et_2O then 10 mL of THF gave a white powder **18** and a solution which was evaporated to give an oil. After several treatments of this oil with Et_2O and then THF as above, **17** was obtained as a white powder.

17: 25% yield. $^{31}P\{^1H\}$NMR ($CDCl_3$): δ 69.2 (d, $^3J_{PP}$ = 8.5 Hz, P=S), 81.0 (d, $^3J_{PP}$ = 8.5 Hz, P$^+$). ^1H NMR ($CDCl_3$): δ 1.35 (br d, $^3J_{HH}$ = 6.3 Hz, 24H, CH−CH_3), 2.88 (d, $^3J_{HP}$ = 14.3 Hz, 3H, N−CH_3), 2.91 (d, $^3J_{HP}$ = 14.4 Hz, 3 H, N−CH_3), 3.62−4.37 (m, 8H, N−CH and CH_2), 7.32−7.95 (m, 5H, C_6H_5). MS (FAB$^+$): [M − CF_3SO_3]$^+$ = 485. Anal. Calcd for $C_{23}H_{43}F_3N_6O_3P_2S_2$: C, 43.52; H, 6.83; N, 13.24. Found: C, 43.36; H, 6.71; N, 13.14.

18: mp 75 °C dec, 70% yield. $^{31}P\{^1H\}$NMR ($CDCl_3$): δ 64.4 (s, P=S), 77.5 (s, P$^+$); ^1H NMR ($CDCl_3$): δ 1.34 (d, $^3J_{HH}$ = 6.4 Hz, 6H, CH−CH_3), 1.37 (d, $^3J_{HH}$ = 6.3 Hz, 6H, CH−CH_3), 1.53 (d, $^3J_{HH}$ = 6.9 Hz, 12H, N−(CH−CH_3)$_2$), 2.98 (d, $^3J_{HP}$ = 10.6 Hz, 3 H, N−CH_3), 3.15 (d, $^3J_{HP}$ = 9.2 Hz, 3H, N−CH_3), 3.27−3.85 (m, 4H, N−CH), 3.91−4.28 (m, 4H, CH_2), 7.50−7.72 (m, 5H, C_6H_5). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 21.8 (d, $^3J_{CP}$ = 1.2 Hz, N−CH−CH_3), 22.5 (d, $^3J_{CP}$ = 2.4 Hz, N−CH−CH_3), 23.1 (d, $^3J_{CP}$ = 4.5 Hz, N−CH−CH_3), 23.7 (d, $^3J_{CP}$ = 1.6 Hz, N−CH−CH_3), 34.9 (d, $^2J_{CP}$ = 8.7 Hz, N−CH_3), 38.4 (dd, $^2J_{CP}$ = 10.1 Hz, $^3J_{CP}$ = 6.2 Hz, N−CH_3), 49.5 (d, $^2J_{CP}$ = 13.9 Hz, N−CH−CH_3), 49.6 (d, $^2J_{CP}$ = 14.4 Hz, N−CH−CH_3), 56.6 (d, $^1J_{CP}$ = 64.3 Hz, CH_2P), 71.2 (dd, J_{CP} = 26.1 Hz, J_{CP} = 25.0 Hz, N−CH_2−N) 128.2−130.2 (m, C_6H_5); MS (FAB$^+$): [M − CF_3SO_3]$^+$ = 485. Anal. Calcd for $C_{23}H_{43}F_3N_6O_3P_2S_2$: C, 43.52; H, 6.83; N, 13.24. Found: C, 43.32; H, 6.74; N, 13.12.

Synthesis of the Phosphonium Salt 20. The same procedure employed to prepare **18** is used.

20: 90% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 8.7 (s, Ph−P=O), 76.8 (s, >P$^+$<) ppm. ^1H NMR ($CDCl_3$): δ 1.22 (m, 28 H, N−CH−CH_3), 2.67 (m, 6H, N−CH_3), 3.50−4.21 (m, 8H, N−CH, CH_2), 7.22−7.78 (m, 5H, C_6H_5). MS (FAB$^+$): 469 [M − CF_3SO_3]$^+$. Anal. Calcd for $C_{23}H_{43}F_3N_6O_4P_2S$: C, 44.65; H, 7.01; N, 13.58. Found: C, 44.41; H, 6.87; N, 13.40.

Synthesis of the Pyridinium Salt 21. To a solution of **6a** (0.4 g, 1.575 mmol) and pyridine (127 μL, 1.575 mmol) in 3 mL of $CHCl_3$ was added dropwise trifluoroacetic anhydride (222 μL, 1.575 mmol) at 0 °C. Then 15 mL of CH_2Cl_2 were added after 5 min of stirring. The resulting solution was stirred for 2 h at room temperature then evaporated to dryness. The residue was washed with 20 mL of pentane, giving a yellow oil. Addition of 10 mL of ether allows **21** to precipitate as white powder.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2 × 100) for **13**

	x	*y*	*z*	*Ueq*[a]
P(1)	0.5980(1)	0.18461(7)	0.33397(3)	4.06(6)
N(1)	0.4655(5)	0.2535(2)	0.33660(9)	4.8(2)
P(2)	0.4186(1)	0.29671(7)	0.37631(4)	4.49(6)
N(2)	0.4849(5)	0.2575(2)	0.4151(1)	4.8(2)
P(3)	0.5947(2)	0.17809(7)	0.41445(3)	4.55(7)
N(3)	0.6752(5)	0.1539(2)	0.3740(1)	5.2(2)
N(4)	0.5082(5)	0.1086(2)	0.3087(1)	5.2(2)
N(5)	0.6097(5)	0.0572(2)	0.2898(1)	5.2(2)
C(1)	0.5547(6)	−0.0059(3)	0.2734(1)	5.8(3)
C(2)	0.3412(6)	0.0878(3)	0.3141(1)	5.9(3)
N(6)	0.7496(5)	0.2132(2)	0.30551(9)	4.5(2)
N(7)	0.6978(4)	0.2559(2)	0.2731(1)	4.5(2)
C(3)	0.7960(6)	0.2727(3)	0.2460(1)	5.6(3)
C(4)	0.9070(6)	0.1734(3)	0.3059(1)	5.3(3)
N(8)	0.4712(5)	0.3938(2)	0.3718(1)	5.1(2)
N(9)	0.4241(5)	0.4415(2)	0.4025(1)	5.1(2)
C(5)	0.4646(6)	0.5148(3)	0.4039(1)	6.1(3)
C(6)	0.5527(6)	0.4287(3)	0.3395(1)	5.4(3)
N(10)	0.2205(4)	0.2989(2)	0.3819(1)	5.0(2)
N(11)	0.1424(5)	0.3452(2)	0.3541(1)	5.1(3)
C(7)	−0.0093(6)	0.3483(3)	0.3544(1)	5.7(3)
C(8)	0.1342(6)	0.2558(3)	0.4114(1)	5.9(3)
N(12)	0.4921(5)	0.0956(2)	0.4289(1)	4.8(2)
N(13)	0.4127(5)	0.1078(2)	0.4630(1)	5.0(2)
C(9)	0.3431(6)	0.0471(3)	0.4791(1)	5.9(3)
C(10)	0.5159(6)	0.0153(3)	0.4134(1)	5.8(3)
N(14)	0.7287(5)	0.1955(2)	0.44965(9)	5.2(2)
N(15)	0.7986(5)	0.1253(2)	0.4636(1)	5.5(3)
C(11)	0.8843(6)	0.1312(3)	0.4935(1)	5.6(3)
C(12)	0.7519(7)	0.2719(3)	0.4693(1)	5.9(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

21: 80% yield. $^{31}P\{^1H\}$NMR (CD_3CN): δ 8.15 ppm (s); ^1H NMR(CD_3CN): δ 2.78 (d, $^3J_{HP}$ = 10.5 Hz, 3H, H_2C=N−N−CH_3), 3.22 (d, $^3J_{HP}$ = 6.5 Hz, 3 H, H_2C−N−N−CH_3), 6.44 and 6.56 (AB system, $^2J_{HA-HB}$ = 14.1 Hz, 2H, N=CH_2), 6.92 (s, 2H, N−CH_2−N), 7.50−8.01 (m, 5H, C_6H_5), 8.12−9.06 (m, 5H, C_5H_5N). $^{13}C\{^1H\}$NMR(CD_3CN): δ 32.4 (d, $^2J_{CP}$ = 8.75 Hz, H_2C=N−N−CH_3), 40.6 (s, H_2C−N−N−CH_3), 73.2 (s, N−CH_2−NC_5H_5), 116.5 (q, $^1J_{CF}$ = 288.0 Hz, CF_3), 117.9 (q, $^1J_{CF}$ = 289.0 Hz, CF_3), 129.3, 146.6, 148.9 (NC_5H_5), 130.0 (d, J_{CP} = 14.3 Hz), 133.3 (d, J_{CP} = 12.1 Hz), 134.0 (d, J_{CP} = 13.0 Hz), 134.4 (s, C_6H_5), 154.2 (d, $^2J_{CF}$ = 37.4 Hz, CO), 157.3 (d, $^2J_{CF}$ = 44.2 Hz, OCO). ^{19}F NMR (CD_3CN): δ 2.60 and 9.05 (br s, N−$COCF_3$ and $CF_3CO_2^-$). FAB$^+$-MS: *m/z* 429 [M − CF_3CO_2]$^+$. Anal. Calcd for $C_{19}H_{20}F_6N_5O_3PS$: C, 41.99; H, 3.71; N, 12.89. Found: C, 41.64; H, 3.54; N, 12.70.

Synthesis of the Diboronium Salt 23. To a solution of **6a** (0.100 g, 0.39 mmol) in 5 mL of CH_2Cl_2 was added 1.575 mL (0.79 mmol) of a solution of dicyclopentylborontriflate in CH_2Cl_2 (0.5 M) at −80 °C. The resulting mixture was stirred for 1 h and then evaporated to dryness. The residue was dissolved in a minimum amount of CH_2Cl_2 and precipitated with 15 mL of pentane. **23** was then obtained as a brown powder.

23: 90% yield. $^{31}P\{^1H\}$NMR ($CDCl_3$): δ 79.2. ^1H NMR ($CDCl_3$): δ 0.88 (m, 4H, CH), 1.16−1.70 (m, 32H, CH_2), 2.94 (d, $^3J_{HP}$ = 11.2 Hz, 6H, CH_3), 7.60−7.87 (m, 9H, C_6H_5, CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 27.0 (s, CH_2), 28.5 (s, CH_2), 32.5 (br s, CH), 34.1 (d, $^2J_{CP}$ = 6 Hz, CH_3), 119.3 (q, $^1J_{CF}$ = 320 Hz, CF_3), 130.0 (d, J_{CP} = 14.4 Hz, *o*-C_6H_5), 132.0 (d, J_{CP} = 12.3 Hz, *m*-C_6H_5), 135.3 (s, *p*-C_6H_5), 151.8 (s, N=CH_2), (i-C_6H_5 not detected). $^{11}B\{^1H\}$NMR ($CDCl_3$): δ 54 (br s). Anal. Calcd for $C_{32}H_{51}B_2F_6N_4O_6PS_3$: C, 45.19; H, 6.04; N, 6.59. Found: C, 45.28; H, 6.12; N, 6.49.

Crystallographic Data Collection and Refinement of Structure 13. Suitable single crystals for **13** were obtained from recrystallization

in CH_2Cl_2/hexane (1/1). A translucid parallelepiped of 0.45 × 0.40 × 0.15 mm dimensions was glued on a glass fiber. The accurate unit cell parameters were obtained by means of least-squares fit of 25 centered reflections. The data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A summary of the crystallographic data and data collection and refinement parameters is given in Table 1. Three standard reflections were monitored every 2 h and showed no significant variation over the data collection. Data were reduced in the usual way with the MolEN package.[17] An empirical absorption correction[18] was applied on the basis of y scans. The structure was solved by direct methods[19] and refined by the full-matrix least-squares technique,[20] using anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were introduced in calculations with fixed isotropic displacements parameters, using a riding model. Atomic scattering factors were taken from a standard source.[21] The fractional coordinates are given in Table 2.

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Supplementary Material Available: Hydrogen atom parameters (Table S1), anisotropic thermal parameters (Table S2), and bond lengths and angles for **13** (Table S3) (3 pages). Ordering information is given on any current masthead pages.

(17) Fair, C. K. *MolEN. Structure Solution Procedures*; Enraf-Nonius: Delft, Holland, 1990.
(18) North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *A21*, 351.
(19) Sheldrick, G. M. *SHELXS-86. Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Federal Republic of Germany, 1986.
(20) Sheldrick, G. M. *SHELX76. Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.
(21) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.