Diels-Alder Reactions of *tert*-Butylphosphaethyne with 1,3,2-Diaza- and 1,2-Azaphosphinines

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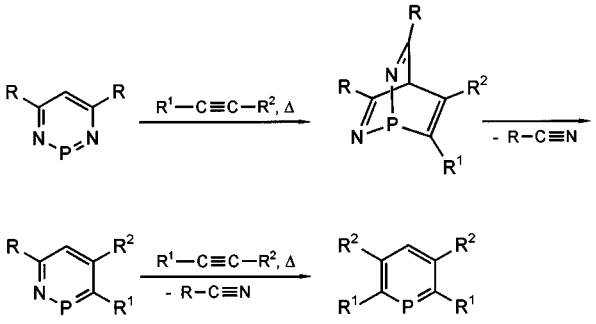
tert-Butylphosphaethyne (**2**) undergoes a Diels-Alder reaction with the 1,3,2-diazaphosphinine **1** at room temperature to furnish the diazadiphosphabarrelene **3**. In the presence of an excess of **2** in toluene under reflux compound **3** experiences elimination of a molecule of pivalonitrile to afford the 1-aza-2,4-diphosphinine **5** which, in turn, reacts with a further equivalent of **2** to form the transient azatriphosphabarrelene **6**. Formation of the final product, the stable tetraphosphatetracyclic compound **4**, is the result of a homo Diels-Alder reaction between **6** and yet another equivalent of **2**. The structure of **4** has been confirmed by an X-ray crystallographic analysis of its pentacarbonyltungsten complex **7**. As a consequence of the high steric overcrowding in **4**, complexation occurs exclusively at its phosphaalkene phosphorus atom. The reactivity of **2** towards the four functionally substituted 1,2-azaphosphinines **8a–d** has also been examined. At room temperature smooth [4 + 2] cycloaddition reactions proceed to yield the azadiphosphabarrelenes **9a–d**. While thermolyses of the barrelenes **9a–c** in toluene under reflux lead exclusively to the starting compounds **8a–c** by a [4 + 2] cycloreversion process with concomitant elimination of **2**, pyrolysis of **9d** under the same conditions furnishes the 1,3-diphosphinine **10**, also unambiguously identified by analysis of its tpentacarbonyltungsten complex **11**.

Introduction

It is now well established that replacement of a CH unit in a phosphinine ring by a nitrogen atom has a pronounced effect on the reactivity of the system. Although no theoretical calculations have as yet been performed it is clear that such a substitution considerably reduces the aromaticity of the heterocyclic ring system. Thus, while phosphinines hardly undergo Diels-Alder reactions with alkynes[1], 1,3-aza- and 1,3,5-diazaphosphinines react with various alkynes at high temperatures to furnish azaphosphabarrelenes which are thermally unstable under the reaction conditions and decompose by [4 + 2] cycloreversion reactions with concomitant elimination of one equivalent of the respective nitrile to furnish phosphinines or 1,3-azaphosphinines, respectively[2]. This reactivity is even more pronounced for 1,3,2-diazaphosphinines, prepared for the first time in our laboratory in 1996[3], on account of the presence of two nitrogen atoms directly adjacent to the phosphorus atom which strongly enhances the polarity within the ring. Recently, we have found that, like the 1,3-azaphosphinines and the 1,3,5-diazaphosphinines, these 1,3,2-diazaphosphinines are versatile precursors for the syntheses of various polyfunctional 1,2-azaphosphinines, phosphinines, and polyphosphinines under mild conditions as shown in Scheme 1[4].

Scheme 1



As part of our program on the exploitation of 1,3,2-diazaphosphinines for the synthesis of heterocyclic phosphorus compounds we have consequently examined their reactions with *tert*-butylphosphaethyne (**2**)[5], a compound with an enormous potential for participating in Diels-Alder and homo Diels-Alder reactions[6] with various unsaturated systems and now present the first results of this work.

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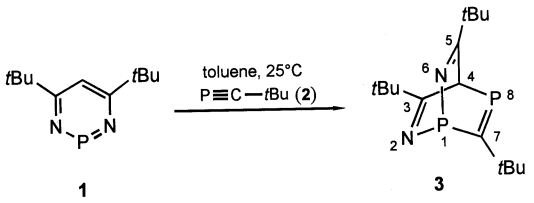
Results and Discussion

For these experiments we used the readily available 4,6-di-*tert*-butyl-1,3,2-diazaphosphinine (**1**), prepared from Cp_2TiMe_2, pivalonitrile, and PCl_3 in an one-step process[3][4a]. The reaction of **1** with one equivalent of *tert*-butylphosphaethyne (**2**) in toluene at room temperature proceeded cleanly to furnish the diphosphadiazabarrelene **3**, isolated as an orange oil after extraction with dry hexane (Scheme 2).

Scheme 2

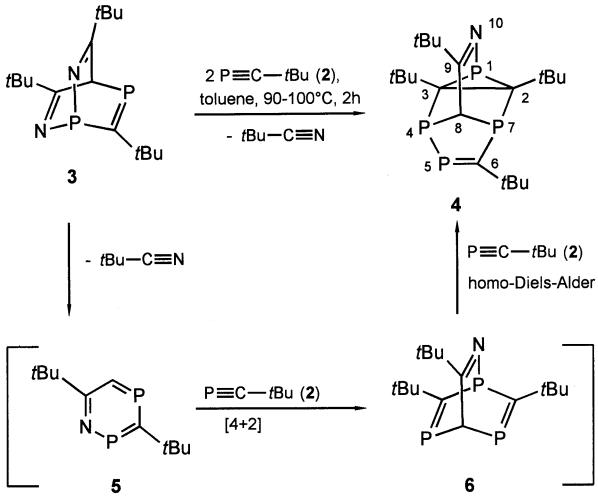


The proposed structure for **3** is supported above all by its NMR-spectroscopic data. The ^{31}P-NMR spectrum confirms the presence of two magnetically non-equivalent phosphorus atoms (P-1 and P-8) and the lack of any coupling between them. The strongly deshielded signal at δ = 185.27 can be unambiguously assigned to the phosphaalkene atom P-8 whereas the bridgehead phosphorus atom P-1 gives rise to a signal at δ = 15.28. In the ^{13}C-NMR spectrum the signal for C-7 appears as a doublet of doublets; both the chemical shift (δ = 231.70) and the size of the ^1J couplings with P-1 and P-8 (J = 69.40 and 60.65 Hz, respectively) are indicative for a P=*C*−P unit. In addition, these values are in good agreement with those reported by Binger et al. for the sp^2 carbon atom of 1,3,5,7-tetraphosphabarrelene (δ = 229.60, $^1J_{C,P}$ = 55.80 and 45.80 Hz)[7]. Finally, the carbon atoms C-3 and C-5 give rise to a single pseudo-triplet signal at δ = 188.0 ($^2J_{C,P}$ = 5.50 Hz) in the region typical for related imines.

The formation of **3** is interesting from two points of view. Firstly, it confirms that the 1,3,2-diazaphosphinines possess more 1,4-dipolar character than the corresponding 1,3-azaphosphinines. Indeed, it has been shown that reactions of the latter species with **2** do not furnish azabarrelenes but rather afford intermediate heterosemibullvalene derivatives by way of a complex mechanism involving initial attack of the sp carbon atom of **2** at the phosphorus atom of the phosphinine[8]. Secondly, the regioselectivity of the cycloaddition is in good agreement with the polarities of the reaction partners since the phosphaalkyne also bears a substantial positive partial charge at the phosphorus atom[5b].

On the basis of the chemistry developed with alkynes, we then turned our attention to the thermal decomposition of **3** and the question of whether a 1,2,4-azadiphosphinine **5** would be formed by loss of one molecule of pivalonitrile. The pyrolysis reaction of **3** was performed in toluene at 90°C. As already observed in the mass spectrum of **3**, the elimination of **2** also proved to be the favored process under pyrolysis conditions. After heating of **3** in toluene for 1 hour, a ^{31}P-NMR spectrum of the reaction mixture revealed formation of the diazaphosphinine **1** (80%) and a complicated tetraphosphorus compound (**4**; 20%) giving rise to an AMNX signal pattern. Suspecting that this product may have arisen from the addition of two equivalents of the liberated **2** with the expected 1,2,4-azadiphosphinine **5**, we repeated the thermolysis reaction in the presence of an excess (3 equivalents) of the phosphaalkyne **2**. Under these conditions the equilibrium was apparently shifted towards the formation of **4** which was isolated as the only phosphorus-containing product in 70% yield after purification (Scheme 3).

Scheme 3



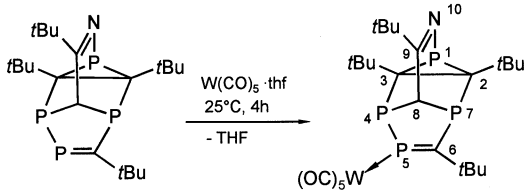
The structure of **4** is easily deduced from the four distinct multiplets in its ^{31}P-NMR spectrum. The highly deshielded signal at δ = 381.15 and that at δ = −91.92 are clearly attributable to the phosphaalkene phosphorus atom P-5 and the phosphirane phosphorus atom P-1, respectively. The assignments of the two central multiplets at δ = 89.28 and δ = 80.88 are somewhat more difficult. However, these two values are very close to those reported by Binger et al. for the 1,2-dihydro-1,3-diphosphole moiety in an adduct obtained from the reaction of a 1,3,5-triphospha Dewar benzene with methyl propynoate (δ = 87 and 89)[6g]. Further support for the structure **4** is provided by the large size of the coupling constant between P-5 and P-4 (^1J = 273.94 Hz) which indicates that the phosphaalkene unit is connected to P-4 by its phosphorus atom. Finally, the presence of the imino bridge is apparent from the ^{13}C-NMR signal at δ = 198.65 (C-9) and that of the bridgehead CH unit from the ^{1}H-NMR signal at δ = 2.35 which appears as an ABCX spin system (see Experimental Section).

From the mechanistic point of view, the formation of **4** cannot be explained without the intermediate occurrence of a 1,2,4-azadiphosphinine and thus we suggest the following sequence. In the presence of excess **2** the thermal decomposition of **1** is directed exclusively to the formation of the 1,2,4-azadiphosphinine **5** with elimination of one equivalent of pivalonitrile. For formation of the azabarrelene intermediate **6** it must be assumed that **5** undergoes a [4 + 2] cycloaddition with one equivalent of **2**. The regioselectivity

of this addition is in good agreement with the polarity of **5** which probably carries an appreciable positive partial charge at the phosphorus atom adjacent to the nitrogen atom. The last step in the sequence is then a classical homo Diels-Alder reaction between a second equivalent of **2** and the two P=C double bonds of **6**. Although without precedent in the chemistry of diphosphabarrelenes, [2 + 2 + 2] cycloadditions of **2** with related structures such as 2-phosphabicyclo[2.2.*n*]alka-2,5-dienes[6a][6b][6c] and triphospha Dewar benzene[6d][6e][6f] have been described previously.

The cycloadduct **4** was also characterized as its pentacarbonyltungsten complex **7** (Scheme 4). Presumably because of a strong steric repulsion between the metal fragment and the *tert*-butyl groups complexation occurs exclusively at the phosphorus atom of the phosphaalkene moiety. This coordination of the $W(CO)_5$ fragment is demonstrated in the ^{31}P-NMR spectrum by a strong shielding of the P-5 signal (δ = 305.84 in **7** compared with 381.15 in **4**) and the presence of $^1J_{P,W}$ couplings (see Experimental Section).

Scheme 4



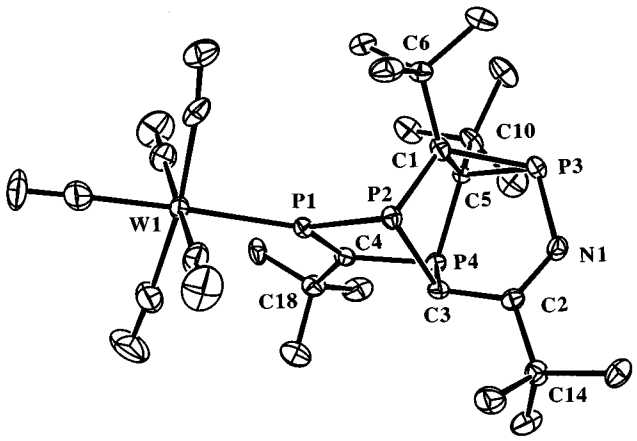
4 **7**

Slow concentration of an *n*-pentane solution of **7** furnished crystals suitable for X-ray analysis. An ORTEP drawing of the structure is shown in Figure 1. The crystallographic labelling used is arbitrary and differs from the numbering used for NMR spectral assignments. The structure does not exhibit any unusual features and bond lengths and angles are in the expected ranges. With the exception of the P1=C4 double bond [1.676(8) Å], all P−C bond lengths are between 1.848(9) Å (P2−C3) and 1.902(8) Å (P3−C1).

Encouraged by these promising results, we next turned our attention to the reactivity of 1,2-azaphosphinines with **2** and selected a series of functional derivatives with differing substitution patterns. As described in a previous paper[4a], the compounds **8a−d** are easily accessible by reactions of **1** with one equivalent (**8a**, **b**) or, when the alkyne is volatile, an excess (**8c**, **d**) of an alkyne in toluene at 90−100°C. The substitution pattern apparently does not have a significant effect on the reactivity of the ring of **8** towards **2** and all reactions were complete within 15 minutes at room temperature. Similar to compound **1**, compounds **8a−d** undergo [4 + 2] cycloadditions with one equivalent of **2** to afford the azadiphosphabarrelenes **9a−d** in fair to good yields (55−75%) (Scheme 5).

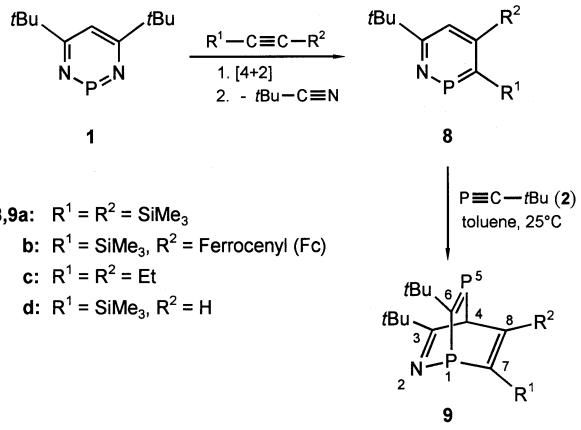
The structures of the products **9** were elucidated by conventional NMR spectroscopy and mass spectrometry. Unequivocal evidence for the structures is provided by the ^{31}P-NMR spectra which each contain a classical set of two doublets; the ones at lower field (δ = 219.50 to 233.69) being

Figure 1. ORTEP drawing of **7** as determined by a single-crystal X-ray diffraction analysis; ellipsoids are drawn to enclose 50% of the electron density; hydrogen atoms are omitted for clarity[a]



[a] Selected bond lengths [Å] and angles [°]: W1−P1 2.502(2), P1−P2 2.211(3), P1−C4 1.676(8), P2−C1 1.851(8), P2−C3 1.848(9), C3−P4 1.858(6), P4−C4 1.851(8), P4−C5 1.887(9), C1−C5 1.56(1), C1−P3 1.902(8), C5−P3 1.896(7), P3−N1 1.714(7), N1−C2 1.29(1), C2−C3 1.49(1); W1−P1−C2 119.31(9), W1−P1−C4 139.7(3), P1−C4−C18 125.6(6), C4−P1−P2 100.3(3), P4−C4−P1 115.4(4), C3−P2−C1 94.8(4), P2−C1−P3 112.6(4), P2−C3−P4 103.7(4), C1−P3−N1 110.1(3), P3−N1−C2 124.8(5), N1−C2−C3 120.7(7), P3−C1−C5 65.6(4), C1−C5−P3 66.0(4), C5−P3−C1 48.4(3), P3−C5−P4 111.1(3).

Scheme 5

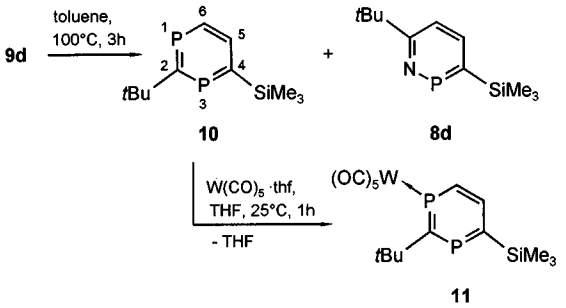


assignable to P-5 while the others characterize the bridgehead phosphorus atoms P-1 (δ = −3.49 to −14.64). It is understandable that the latter signals appear at higher field than the corresponding P-1 signal for **3** (δ = 15.28) since the phosphorus atoms in **9a−d** are bonded to only one nitrogen atom each. Furthermore, the ^{13}C-NMR spectra confirm the presence of the C=N and P−C=P units as well as the bridgehead carbon atom C-4; the latter giving a doublet of doublets signal at almost the same chemical shift as that of the corresponding carbon atom in **3**. Finally, the ^1H-NMR spectra each reveal the presence of two different *tert*-butyl groups together with a characteristic doublet of doublets signal at low field (δ = 6.12−7.19) assigned to 4-H.

The thermal decomposition of these barrelenes is also of interest: as also evidenced by mass-spectrometric experi-

ments, loss of the phosphaalkene bridge in a retro Diels-Alder reaction proves to be the main process in the thermolysis of **9a−c** in refluxing toluene and furnishes the corresponding 1,2-azaphosphinines **8a−c**. The phosphaalkyne **2** was detected in traces by ^{31}P-NMR spectroscopy. The barrelene **9d**, however, undergoes decomposition by a different pathway to afford **8d** as the major product together with the 1,3-diphosphinine **10** which is formed by loss of pivalonitrile. After purification by chromatography, product **10** was obtained as a yellow, oxygen-sensitive oil in 20% yield (Scheme 6).

Scheme 6



As expected, the ^{31}P-NMR spectrum of **10** contains two characteristic resonances at low field (δ = 256.95 and 233.05), assigned to P-3 and P-1, respectively, on the basis of a ^{1}H,^{31}P-coupled spectrum ($^{2}J_{H,P-1}$ = 42.75 Hz). The magnitude of the $^{2}J_{P,P}$ coupling constant (18.0 Hz) further supports the proposed structure since it is similar to values previously reported for other functionalized 1,3-diphosphinines by Zenneck et al.[9]. In the ^{13}C-NMR spectrum, the doublet of doublets signal for C-2 ($^{1}J_{C,P}$ = 73.05 and 85.70 Hz) confirms its linkage to two heteroatoms. The diphosphinine **10** was also characterized as its pentacarbonyltungsten complex **11**, obtained as a yellow oil after chromatographic work-up.

Complexation occurs exclusively at the less hindered phosphorus atom P-1, the ^{31}P-NMR signal of which (δ = 192.00, Δδ = −41) appears at higher field than that of P-3 which is not so strongly shifted by the complex formation (δ = 271.80, Δδ = 15). Elemental analysis, ^{1}H-, ^{13}C-NMR, and mass-spectrometric data are in full accordance with the proposed structure of **11**.

Formation of the diphosphinine **10** is difficult to explain on the basis of the results obtained from the thermolyses of the barrelenes **9a−c**. The electronic nature of the substituents at the C=C double bond of the barrelenes apparently has no influence on the reaction course since formation of the 1,2-azaphosphinine occurs in the presence of both non-polarizing (Et) and polarizing ($SiMe_3$) groups. On the other hand the only structural difference between **9a−c** and **9d** involves the substitution at C-8 (H in **9d**). With this difference in mind it can be argued that the extrusion of the phosphaalkyne **2** is less favored when steric repulsion is released in the starting barrelene or in the formed 1,3-diphosphinine. In the case of monophosphinines, the presence of bulky substituents usually gives rise to twisted geometries. An impressive example of this phenomenon is given by the synthesis of the highly distorted methyl 2,4,5,6-tetra-*tert*-butylphosphinine-3-carboxylate[10] which isomerizes to the corresponding Dewar benzene isomer on heating[11]. Further investigations to identify the factors controlling the thermal decompositions of these azadiphosphabarrelenes are currently in progress.

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Experimental Section

General: All reactions were performed under an inert gas (nitrogen) using Schlenk techniques and dry, oxygen-free solvents. Dry THF, toluene, hexane, and *n*-pentane were obtained by distillation from sodium/benzophenone. Dry Celite was used for filtration. − NMR: Bruker AC-200 SY operating at 200.12 MHz for ^{1}H, 50.32 MHz for ^{13}C, and 81.91 MHz for ^{31}P; chemical shifts (ppm) are relative to TMS (^{1}H and ^{13}C) or 85% H_3PO_4 (^{31}P). − MS: HP 5989 B (70 eV) coupled with an HP 5890 gas chromatograph by the direct inlet method. − Elemental analyses: "Service d'analyse du CNRS", Gif-sur-Yvette, France. Diazaphosphinine **1**[4a], *tert*-butylphosphaethyne (**2**)[12], and $(C_{10}H_8Fe)C{\equiv}CSiMe_3$[13] were prepared by published methods.

3,5,7-Tri-tert-butyl-2,6-diaza-1,8-diphosphabicyclo[2.2.2]octa-2,5,7-triene (**3**): To a solution of **1** (0.25 g, 1.2 mmol) in toluene (5 ml) was added *tert*-butylphosphaethyne (**2**; 0.12 g, 1.2 mmol) and the mixture stirred at room temperature. The reaction was complete after 15 min, and the toluene was evaporated under vacuum. Extraction of the residue with dry *n*-hexane (10 ml) and evaporation of the solvent yielded **3** (0.30 g, 80%) as an orange, very air- and moisture-sensitive oil. − ^{1}H NMR ($CDCl_3$): δ = 1.11 (s, 18 H, 3- and 5-*t*Bu), 1.32 (d, $^{4}J_{H,P}$ = 2.00 Hz, 9 H, 7-*t*Bu), 6.96 (dd, $^{4}J_{H,P-1}$ = 6.55 Hz, $^{2}J_{H,P-8}$ = 19.50 Hz, 1 H, 4-H). − ^{13}C NMR ($CDCl_3$): δ = 27.60 [s, 3- and 5-C(CH_3)$_3$], 31.50 [dd, $^{3}J_{C,P}$ = 8.95 and 12.15 Hz, 7-C(CH_3)$_3$], 40.85 [d, $^{3}J_{C,P}$ = 5.10 Hz, 3- and 5-*C*(CH_3)$_3$], 41.70 [dd, $^{2}J_{C,P}$ = 15.75 and 22.15 Hz, 7-*C*(CH_3)$_3$], 66.60 (dd, $^{3}J_{C,P}$ = 28.90 Hz, $^{1}J_{C,P}$ = 51.90 Hz, C-4), 188.00 (t, $^{2}J_{C,P-1}$ = $^{2}J_{C,P-8}$ = 5.50 Hz, C-3 and C-5), 231.70 (dd, $^{1}J_{C,P}$ = 60.65 and 69.40 Hz, C-7). ^{31}P NMR ($CDCl_3$). δ = 15.28 (s, P-1), 185.27 (s, P-8). − MS; *m/z* (%): 267 [M − 43] (100), 227 [M − *t*BuCN] (5), 211 [M − *t*BuCP + 1] (32). − Elemental analyses could not be performed on account of the extreme oxygen sensitivity of compound **3**.

2,3,6,9-Tetra-tert-butyl-10-aza-1,4,5,7-tetraphosphatetracyclo[5.3.0^{1,3}.0^{2,7}.0^{4,8}]deca-5,9-diene (**4**): To a solution of **1** (0.25 g, 1.2 mmol) in toluene (5 ml) was added *tert*-butylphosphaethyne (**2**; 0.12 g, 1.2 mmol) and the mixture was stirred at room temperature for about 15 min. Then further **2** (0.36 g, 3.60 mmol) was added and the mixture heated at 90°C for 1 h with magnetic stirring. After cooling to room temperature, the solvent was evaporated under vacuum and dry *n*-hexane (10 ml) added to the residue. After filtration and evaporation of the solvent **4** was obtained as an orange, oxygen-sensitive oil (0.35 g, 70%). − ^{1}H NMR ($CDCl_3$): δ = 1.09 (s, 9 H, *t*Bu), 1.32 (t, $^{4}J_{H,P}$ = 2.00 Hz, 9 H, *t*Bu), 1.35 (s, 9 H, *t*Bu), 1.53 (d, $^{4}J_{H,P}$ = 1.63 Hz, 9 H, *t*Bu), 2.36 (ddd, $J_{H,P}$ = 5.04, 10.20, and 11.93 Hz, 1 H, 8-H). − ^{13}C NMR ($CDCl_3$): δ = 28.05 [s, C(CH_3)$_3$], 34.65 [dd, $^{3}J_{C,P}$ = 6.75 and 13.00 Hz, C(CH_3)$_3$], 35.85 [dd, $^{3}J_{C,P}$ = 9.90 and 11.60 Hz, C(CH_3)$_3$], 37.45−37.75 [m,

$C(CH_3)_3$], 34.45−37.75 (m, C-2 and C-3), 40.00−40.85 [m, $C(CH_3)_3$], 43.50 [d, $^2J_{C,P}$ = 7.55 Hz, $C(CH_3)_3$], 46.65 [dd, $^2J_{C,P}$ = 12.20 and 22.80 Hz, $C(CH_3)_3$], 49.15 (dddd, $^3J_{C,P-1}$ = 2.75 Hz, $^2J_{C,P-5}$ = 10.75 Hz, $^1J_{C,P}$ = 16.70 and 27.45 Hz, C-8), 198.65 (ddd, $^2J_{C,P}$ = 4.55, 6.10 and 18.30 Hz, C-9), 221.80 (dd, $^1J_{C,P}$ = 65.30 and 82.15 Hz, C-6). − ^{31}P NMR ($CDCl_3$): δ = −91.92 (d, $^2J_{P-1,P-7}$ = 3.38 Hz, P-1), 80.88 (ddd, $^2J_{P-7,P-1}$ = 3.38 Hz, $^2J_{P-7,P-4}$ = 8.15 Hz, $^2J_{P-7,P-5}$ = 19.46 Hz, P-7), 89.28 (dd, $^2J_{P-4,P-7}$ = 8.15 Hz, $^1J_{P-4,P-5}$ = 273.94 Hz, P-4), 381.13 (dd, $^2J_{P-5,P-7}$ = 19.46 Hz, $^1J_{P-5,P-4}$ = 273.94 Hz, P-5). − MS (CI, NH_3); *m/z* (%): 428 [M + 1] (100). − Elemental analyses could not be performed on account of the extreme oxygen sensitivity of compound **4**.

2,3,6,9-Tetra-tert-butyl-10-aza-1,4,5,7-tetraphosphatetracyclo-[5.3.0^{1,3}.0^{2,7}.0^{4,8}]deca-5,9-diene-5-pentacarbonyltungsten (**7**): A solution of **4** (0.10 g, 0.24 mmol) and $W(CO)_5$(THF) (0.10 g, 0.25 mmol) in THF (8 ml) was stirred at room temperature for 4 h. The reaction was monitored by ^{31}P-NMR spectroscopy. After this time, Celite (0.5 g) was added to the reaction mixture and the solvent evaporated under vacuum. The residue was placed on top of a short silica gel column and eluted with oxygen-free *n*-hexane/toluene (80:20). Concentration of the eluate under vacuum furnished the complex **7** (0.14 g, 80%) as a yellow solid with m.p. 100−112°C. − ^{1}H NMR ($CDCl_3$): δ = 1.10 (s, 9 H, *t*Bu), 1.38 (t, $^4J_{H,P}$ = 1.43 Hz, 9 H, *t*Bu), 1.44 (bs, 9 H, *t*Bu), 1.67 (s, 9 H, *t*Bu), 2.65 (dddd, $^4J_{H,P-1}$ = 0.88 Hz, $^3J_{H,P-5}$ = 4.11 Hz, $^2J_{H,P}$ = 9.10 and 14.08 Hz, 8-H). − ^{13}C NMR ($CDCl_3$): δ = 28.00 [s, $C(CH_3)_3$], 30.40 [s, $C(CH_3)_3$], 35.30−36.25 [m, $C(CH_3)_3$], 35.30−38.10 [m, $C(CH_3)_3$ and C-2, C-3], 37.55 [dd, $^3J_{C,P}$ = 7.45 and 12.15 Hz, $C(CH_3)_3$], 43.90 [d, $^2J_{C,P}$ = 6.95 Hz, $C(CH_3)_3$], 45.25 [d, $^2J_{C,P}$ = 23.30 Hz, $C(CH_3)_3$], 50.40−51.55 (m, C-8), 196.65 (dd, $^3J_{C,P-4}$ = 2.95 Hz, $^2J_{C,P-5}$ = 7.65 Hz, 4 CO_{eq}), 198.20−198.35 (m, C-9), 200.55 (dd, $^3J_{C,P-4}$ = 3.05 Hz, $^2J_{C,P-5}$ = 30.55 Hz, CO_{ax}), 234.60 (ddd, $^2J_{C,P-4}$ = 4.60 Hz, $^1J_{C,P}$ = 25.95 and 74.75 Hz, C-6). − ^{31}P NMR ($CDCl_3$): δ = −91.35 (br. s, P-1), 84.77 (ddd, $^2J_{P-7,P-1}$ = 2.03 Hz, $^2J_{P-7,P-4}$ = 4.88, $^2J_{P-7,P-5}$ = 26.98 Hz, P-7), 110.25 (dd, $^2J_{P-4,P-7}$ = 4.88, $^1J_{P-7,P-5}$ = 314.45 Hz, P-4), 305.84 (ddd, $^3J_{P-5,P-1}$ = 3.56 Hz, $^2J_{P-5,P-7}$ = 26.98 Hz, $^1J_{P-5,P-4}$ = 314.45 Hz, $^1J_{P-5,W}$ = 232.10 Hz, P-5). − MS: *m/z* (%): 751 [M] (6), 723 [M − CO] (6), 695 [M − 2 CO] (7), 667 [M − 3 CO] (6), 639 [M − 4 CO] (11), 611 [M − 5 CO] (30), 528 [M − 5 CO − *t*BuCN] (25), 427 [M − $W(CO)_5$] (32), 169 [$C_{10}H_{18}P$] (100). − $C_{26}H_{37}NO_5P_4W$ (751.3): calcd. C 41.57, H 4.96; found C 41.61, H 5.13.

3,6-Di-tert-butyl-7,8-bis(trimethylsilyl)-2-aza-1,5-diphosphabicyclo[2.2.2]octa-2,5,7-triene (**9a**): A solution of **1** (0.25 g, 1.2 mmol) and bis(trimethylsilyl)acetylene (0.21 g, 1.2 mmol) in toluene (6 ml) was heated at 100°C for 12 h. The reaction was monitored by ^{31}P-NMR spectroscopy. To the thus obtained solution of 1,2-azaphosphinine **8a** was added **2** (0.12 g, 1.2 mmol) and the mixture stirred at room temperature for 15 min. After evaporation of the toluene, extraction of the residue with dry *n*-hexane (10 ml), and evaporation, **9a** was obtained as an orange, very air- and moisture-sensitive powder (0.25 g, 53%) with m.p. 90−92°C. − ^{1}H NMR ($CDCl_3$): δ = 0.14 (s, 9 H, $SiMe_3$), 0.27 (d, $^4J_{H,P}$ = 1.97 Hz, 9 H, $SiMe_3$), 1.14 (s, 9 H, *t*Bu), 1.30 (d, $^4J_{H,P}$ = 1.94 Hz, 9 H, *t*Bu), 7.19 (dd, $^4J_{H,P-1}$ = 2.45 Hz, $^2J_{H,P-5}$ = 18.18 Hz, 1 H 4-H). − ^{13}C NMR ($CDCl_3$): δ = 0.55, 1.60 [$Si(CH_3)_3$], 27.75 [s, 3-$C(CH_3)_3$], 32.10 [dd, $^3J_{C,P}$ = 9.00 and 12.40 Hz, 6-$C(CH_3)_3$], 41.05 [d, $^3J_{C,P}$ = 6.05 Hz, 3-$C(CH_3)_3$], 42.00 [dd, $^2J_{C,P}$ = 16.50 and 23.20 Hz, 6-$C(CH_3)_3$], 71.70 (dd, $^3J_{C,P}$ = 18.30 Hz, $^1J_{C,P}$ = 50.35 Hz, C-4), 159.20 (dd, $^3J_{C,P}$ = 10.65 Hz, $^1J_{C,P}$ = 65.60 Hz, C-7), 159.90 (d, $^2J_{C,P}$ = 6.85 Hz, C-8), 195.05 (dd, $^2J_{C,P}$ = 4.95 and 7.30 Hz, C-3), 232.80 (dd, $^1J_{C,P}$ = 58.00 and 65.55 Hz, C-6). − ^{31}P NMR ($CDCl_3$): δ = −8.64 (d, $^2J_{P,P}$ = 6.58 Hz, P-1), 220.97 (d, $^2J_{P,P}$ = 6.58 Hz, P-5). − MS (CI, NH_3); *m/z* (%): 398 [M + 1] (24), 298 [M − *t*BuCP + 1] (100).− Elemental analyses could not be performed on account of the extreme oxygen sensitivity of compound **9a**.

3,6-Di-tert-butyl-8-ferrocenyl-7-trimethylsilyl-2-aza-1,5-diphosphabicyclo-[2.2.2]octa-2,5,7-triene (**9b**): A solution of **1** (0.4 g, 1.9 mmol) and ferrocenyl(trimethylsilyl)acetylene (0.54 g, 1.9 mmol) in toluene (10 ml) was heated at 100°C for 4 h in a Schlenk tube. After cooling to room temperature, the thus formed 1,2-azaphosphinine **8b** was treated with **2** (0.2 g, 2.0 mmol) and the mixture stirred at room temperature for 15 min. The solvent was evaporated under vacuum, the residue extracted with dry *n*-hexane (10 ml), filtered, and concentrated to leave **9b** as an orange, very air- and moisture-sensitive powder (0.65 g, 67%) with m.p. 100−112°C. − ^{1}H NMR ($CDCl_3$). δ = 0.27 (d, $^4J_{H,P}$ = 1.70 Hz, 9 H, $SiMe_3$), 1.25 (s, 9 H, 3-*t*Bu), 1.38 (d, $^4J_{H,P}$ = 1.86 Hz, 9 H, 6-*t*Bu), 4.00−4.41 (m, 4 H, C_5H_4 of Fc), 4.42 (s, 5 H, C_5H_5 of Fc), 7.12 (dd, $^4J_{H,P-1}$ = 3.44 Hz, $^2J_{H,P-5}$ = 17.52 Hz, 1 H, 4-H). − ^{13}C NMR ($CDCl_3$): δ = 2.20 [d, $^3J_{C,P}$ = 10.25 Hz, $Si(CH_3)_3$], 27.90 [s, 3-$C(CH_3)_3$], 31.90 [dd, $^3J_{C,P}$ = 9.25 and 13.20 Hz, 6-$C(CH_3)_3$], 41.30 [d, $^3J_{C,P}$ = 6.05 Hz, 3-$C(CH_3)_3$], 42.20 [dd, $^2J_{C,P}$ = 15.70 and 22.70 Hz, 6-$C(CH_3)_3$], 68.00 (s, 2 CH of Fc), 69.00 (s, 5 CH of Fc), 69.85 (s, 2 CH of Fc), 72.65 (dd, $^3J_{C,P}$ = 16.35 Hz, $^1J_{C,P}$ = 48.20 Hz, C-4), 92.20 (d, $^3J_{C,P}$ = 3.20 Hz, C of Fc), 139.35 (dd, $^3J_{C,P}$ = 9.90 Hz, $^1J_{C,P}$ = 60.25 Hz, C-7), 159.20 (d, $^2J_{C,P}$ = 7.65 Hz, C-8), 195.90 (dd, $^2J_{C,P}$ = 4.50 and 9.15 Hz, C-3), 229.35 (dd, $^1J_{C,P}$ = 56.45 and 62.55 Hz, C-6). − ^{31}P NMR ($CDCl_3$): δ = −5.24 (d, $^2J_{P,P}$ = 7.97 Hz, P-1), 230.88 (d, $^2J_{P,P}$ = 7.97 Hz, P-5). − MS; *m/z* (%): 509 [M] (8), 426 [M − *t*BuCN] (11), 409 [M − *t*BuCP] (100). − Elemental analyses could not be performed on account of the extreme oxygen sensitivity of compound **9b**.

3,6-Di-tert-butyl-7,8-diethyl-2-aza-1,5-diphosphabicyclo[2.2.2]octa-2,5,7-triene (**9c**): A solution of **1** (0.25 g, 1.2 mmol) and 3-hexyne (1.0 g, 12.2 mmol) in toluene (6 ml) was stirred at 100°C for 1 h after which time the formation of the 1,2-azaphosphinine **8c** was complete and **2** (0.12 g, 1.2 mmol) was added after evaporation of excess hexyne. The mixture was stirred at room temperature for 15 min. After evaporation of the solvent under vacuum, extraction of the residues with dry *n*-hexane (10 ml), and concentration the adduct **9c** was obtained as an orange, air- and moisture-sensitive oil (0.28 g, 75%). − ^{1}H NMR ($CDCl_3$): δ = 0.87−0.99 (m, 6 H, CH_2CH_3), 1.11 (s, 9 H, *t*Bu), 1.30 (d, $^4J_{H,P}$ = 2.00 Hz, 9 H, 6-*t*Bu), 2.07−2.31 (m, 4 H, CH_2CH_3), 6.12 (dd, $^4J_{H,P-1}$ = 1.40 Hz, $^2J_{H,P-5}$ = 19.59 Hz, 1 H, 4-H). − ^{13}C NMR ($CDCl_3$): δ = 12.00 (s, 5-CH_2CH_3), 15.70 (d, $^3J_{C,P}$ = 6.15 Hz, 7-CH_2CH_3), 24.55 (d, $^2J_{C,P}$ = 35.20 Hz, 7-CH_2CH_3), 26.05 (d, $^3J_{C,P}$ = 2.60 Hz, 8-CH_2CH_3), 27.40 [s, 3-$C(CH_3)_3$], 31.90 (dd, $^3J_{C,P}$ = 8.80 and 12.80 Hz, 6-$C(CH_3)_3$], 41.25 [d, $^3J_{C,P}$ = 6.15 Hz, 3-$C(CH_3)_3$], 42.20 [dd, $^2J_{C,P}$ = 16.00 and 22.15 Hz, 6-$C(CH_3)_3$], 66.80 (dd, $^3J_{C,P}$ = 13.30 Hz, $^1J_{C,P}$ = 47.75 Hz, C-4), 142.65 (dd, $^3J_{C,P}$ = 10.70 Hz, $^1J_{C,P}$ = 30.55 Hz, C-7), 144.95 (dd, $^2J_{C,P}$ = 2.60 and 5.30 Hz, C-8), 197.65 (dd, $^2J_{C,P}$ = 4.55 and 9.20 Hz, C-3), 234.65 (t, $^1J_{C,P}$ = 57.20 Hz, C-6). − ^{31}P NMR ($CDCl_3$): δ = −3.49 (d, $^2J_{P,P}$ = 8.05 Hz, P-1), 233.69 (d, $^2J_{P,P}$ = 8.05 Hz, P-5). − MS (CI, NH_3); *m/z* (%): 310 [M + 1] (2), 210 [M − *t*BuCP + 1] (100). − $C_{17}H_{29}NP_2$ (309.4): calcd. C 66.00, H 9.45; found C 66.35, H 9.29.

3,6-Di-tert-butyl-7-trimethylsilyl-2-aza-1,5-diphosphabicyclo[2.2.2]octa-2,5,7-triene (**9d**): A solution of **1** (0.25 g, 1.2 mmol) and trimethylsilylacetylene (0.7 g, 7 mmol) in toluene (6 ml) was heated at 90°C for 10 min. After cooling to room temperature,

excess trimethylsilylacetylene was evaporated under vacuum and the thus formed 1,2-azaphosphinine **8d** was treated with **2** (0.12 g, 1.2 mmol). Formation of **9d** was complete after 15 min stirring at room temperature. The mixture was extracted with dry *n*-hexane (10 ml), the extract filtered, and the filtrate concentrated under vacuum to leave **9d** as an orange, very air- and moisture-sensitive oil (0.3 g, 75%). – ^{1}H NMR ($CDCl_3$): δ = 0.08 (s, 9 H, $SiMe_3$), 1.06 (s, 9 H, 3-*t*Bu), 1.25 (d, $^4J_{H,P}$ = 1.88 Hz, 9 H, 6-*t*Bu), 6.60 (ddd, $^4J_{4\text{-H,P-1}}$ = 2.84 Hz, $^3J_{4\text{-H,8-H}}$ = 6.51 Hz, $^2J_{4\text{-H,P-5}}$ = 19.98 Hz, 1 H, 4-H), 6.69 (ddd, $^3J_{8\text{-H,P}}$ = 1.8 Hz, $^3J_{8\text{-H,4-H}}$ = 6.51 Hz, $^3J_{8\text{-H,P}}$ = 9.67 Hz, 1 H, 8-H). – ^{13}C NMR ($CDCl_3$). δ = −0.30 [d, $^3J_{C,P}$ = 4.45 Hz, Si(*C*H_3)$_3$], 27.10 [s, 3-C(*C*H_3)$_3$], 31.80 [dd, $^3J_{C,P}$ = 9.15 and 12.45 Hz, 6-C(*C*H_3)$_3$], 40.85 [d, $^3J_{C,P}$ = 5.14 Hz, 3-*C*(CH$_3$)$_3$], 42.05 [dd, $^2J_{C,P}$ = 16.35 and 22.45 Hz, 6-*C*(CH$_3$)$_3$], 65.50 (dd, $^3J_{C,P}$ = 18.30 Hz, $^1J_{C,P}$ = 48.85 Hz, C-4), 147.95 (d, $^2J_{C,P}$ = 6.70 Hz, C-8), 148.50 (d, $^3J_{C,P}$ = 9.15 Hz, $^1J_{C,P}$ = 55.90 Hz, C-7), 195.40 (dd, $^2J_{C,P}$ = 4.55 and 9.05 Hz, C-3), 230.15 (dd, $^1J_{C,P}$ = 59.10 and 61.55 Hz, C-6). – ^{31}P NMR ($CDCl_3$): δ = −14.64 (d, $^2J_{P,P}$ = 6.50 Hz, P-1), 219.50 (d, $^2J_{P,P}$ = 6.50 Hz, P-5). – MS; *m/z* (%): 242 [M − *t*BuCN] (18), 226 [M − *t*BuCP + 1] (100). – $C_{16}H_{29}NP_2Si$ (325.4). calcd. C 59.05, H 8.98; found C 59.50, H 8.90.

2-tert-Butyl-4-trimethylsilyl-1,3-diphosphinine (**10**): A solution of **9d** (0.26 g, 0.8 mmol) in toluene (10 ml) was stirred at 100°C for 3 h. After cooling to room temperature, dry Celite (0.5 g) was added and the solvent evaporated under vacuum to leave a brownish powder. The product was quickly purified by chromatography using oxygen-free *n*-hexane as eluent. Concentration of the eluate under vacuum afforded **10** as a yellow, oxygen-sensitive oil (0.04 g, 20%). – ^{1}H NMR ($CDCl_3$): δ = 0.45 (d, $^4J_{H,P\text{-}3}$ = 0.75 Hz, 9 H, $SiMe_3$), 1.70 (t, $^4J_{H,P}$ = 1.35 Hz, 9 H, *t*Bu), 8.15 (ddd, $^3J_{5\text{-H,6-H}}$ = 10.05 Hz, $^3J_{5\text{-H,P}}$ = 10.70 and 12.15 Hz, 1 H, 5-H), 8.80 (ddd, $^4J_{6\text{-H,P-3}}$ = 3.15 Hz, $^3J_{6\text{-H,5-H}}$ = 10.05 Hz, $^2J_{6\text{-H,P-1}}$ = 42.75 Hz, 1 H 6-H). – ^{13}C NMR ($CDCl_3$): δ = 0.75 [d, $^3J_{C,P\text{-}3}$ = 7.50 Hz, Si(CH_3)$_3$], 35.90 [t, $^3J_{C,P}$ = 12.80 Hz, C(*C*H_3)$_3$], 43.55 [t, $^2J_{C,P}$ = 19.85 Hz, *C*(CH$_3$)$_3$], 135.65 (t, $^2J_{C,P}$ = 11.25 Hz, C-5), 149.70 (dd, $^3J_{C,P\text{-}3}$ = 21.55 Hz, $^1J_{C,P\text{-}1}$ = 53.75 Hz, C-6), 167.20 (dd, $^3J_{C,P\text{-}1}$ = 17.06 Hz, $^1J_{C,P\text{-}3}$ = 81.45 Hz, C-4), 217.50 (dd, $^1J_{C,P}$ = 73.05 and 85.70 Hz, C-2). – ^{31}P NMR ($CDCl_3$): δ = 233.05 (d, $^2J_{P,P}$ = 18.00 Hz, P-1), 256.95 (d, $^2J_{P,P}$ = 18.00 Hz, P-3). – MS; *m/z* (%): 242 [M] (59), 227 [M − Me] (42), 73 [$SiMe_3$] (100). – $C_{11}H_{20}P_2Si$ (242.3): calcd. C 54.52, H 8.32; found C 54.20, H 8.41.

(2-tert-Butyl-4-trimethylsilyl-1,3-diphosphinine-P^1)pentacarbonyltungsten (**11**). A solution of **10** (0.04 g, 0.16 mmol) and $W(CO)_5$(THF) (0.07 g, 0.16 mmol) in THF (5 ml) was stirred at room temperature for 1 h. Then dry Celite (0.3 g) was added and the solvent evaporated under vacuum. The resultant powder was placed on the top of a short silica gel column and eluted with dry, oxygen-free *n*-hexane. Concentration of the eluate under vacuum afforded the complex **11** as a yellow oil (0.08 g, 85%). – ^{1}H NMR ($CDCl_3$). δ = 0.40 (d, $^4J_{H,P\text{-}3}$ = 0.98 Hz, 9 H, $SiMe_3$), 1.76 [dd, $^4J_{H,P}$ = 0.39 and 2.45 Hz, 9 H, *t*Bu), 7.97 (ddd, $^3J_{5\text{-H,6-H}}$ = 10.00 Hz, $^3J_{5\text{-H,P}}$ = 11.95 Hz and 22.05 Hz, 1 H, 5-H), 8.57 (ddd, $^4J_{6\text{-H,P-3}}$ = 2.85 Hz, $^3J_{6\text{-H,5-H}}$ = 10.00 Hz, $^2J_{6\text{-H,P-1}}$ = 30.45 Hz, 1 H, 6-H). – ^{13}C NMR ($CDCl_3$): δ = 0.60 [d, $^3J_{C,P\text{-}3}$ = 5.50 Hz, Si(*C*H_3)$_3$], 35.25 [dd, $^3J_{C,P}$ = 9.30 Hz and 15.35 Hz, C(*C*H_3)$_3$], 43.60 [dd, $^2J_{C,P}$ = 9.50 and 20.15 Hz, *C*(CH$_3$)$_3$], 139.45 (dd, $^2J_{C,P}$ = 10.05 and 15.30 Hz, C-5), 153.45 (dd, $^3J_{C,P\text{-}3}$ = 18.30 Hz, $^1J_{C,P\text{-}1}$ = 21.35 Hz, C-6), 164.50 (dd, $^3J_{C,P\text{-}1}$ = 30.50 Hz, $^1J_{C,P\text{-}3}$ = 82.40 Hz, C-4), 196.90 (d, $^2J_{C,P\text{-}1}$ = 8.75 Hz, CO_{cis}), 199.80 (d, $^2J_{C,P\text{-}1}$ = 30.10 Hz, CO_{trans}), 204.05 (dd, $^1J_{C,P}$ = 16.80 and 94.50 Hz, C-2). – ^{31}P NMR ($CDCl_3$): δ = 192.00 (d, $^2J_{P,P}$ = 38.80 Hz, $^1J_{P,W}$ = 253.40 Hz, P-1], 271.80 (d, $J_{P,P}$ = 38.80 Hz, P-3]. – MS; *m/z* (%): 566 [M] (12), 510 [M − 2 CO] (17), 482 [M − 3 CO] (34), 454 [M − 4 CO] (8), 426 [M − 5 CO] (58), 242 [M − $W(CO)_5$] (30), 73 [$SiMe_3$] (100). – $C_{16}H_{20}O_5P_2SiW$ (566.2): calcd. C 33.94, H 3.56; found C 33.60, H 3.53.

X-ray Structural Analysis of **7**[14]: Crystals of **7**, $C_{26}H_{37}NO_5P_4W$, were grown from an *n*-pentane solution of the compound. Data were collected at 123 ± 0.5 K with an Enraf Nonius CAD 4 diffractometer using Mo-K_α (λ = 0.71073 Å) radiation and a graphite monochromator. The crystal structure was solved using the Enraf Nonius MOLEN package. The compound crystallizes in space group $P\bar{1}$ (no. 2; *a* = 11.854(1), *b* = 17.066(2), *c* = 17.102(2) Å, α = 105.27(1), β = 90.08(1), γ = 109.36(1)°; *V* = 3133.74(1.4) Å^3; *Z* = 4, $d_{calcd.}$ = 1.592 g/cm^3; μ = 40.0 cm^{-1}; *F*(000) = 1496. A total of 18493 unique reflections were recorded in the range 2° ≤ 2θ ≤ 56.1° of which 9278 were considered as unobserved [$F^2 < 3.0\sigma(F^2)$], leaving 9215 for solution and refinement. Direct methods (SIR92) yielded a solution for all atoms. 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. A non-Poisson weighting scheme was applied with a *p* factor equal to 0.08. The final agreement factors were R = 0.047, R_w = 0.066, *G.O.F.* = 1.31.

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