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Investigations of a Highly Crowded Phosphino-Substituted Biphenyl: A Precursor for a λ^3,λ^5-Diphosphaphenanthrene

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ABSTRACT

*The synthesis of 2,2'-bis(bis(dimethylamino)-phosphino)-3,3',5,5'-tetra-*tert*-butylbiphenyl* (**5**) *is described. It was extensively studied by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Furthermore, the X-ray analysis of* **5** *is reported. Crystals of* **5** *are tetragonal, space group $P\bar{4}2_1c$, a = b = 24.770 (3) Å, c = 12.658 (4) Å, Z = 8. The surprising reaction of* **5** *with proton acids leading to the formation of various phosphorus containing five- and six-membered ring compounds is discussed. On reaction of one of the six-membered ring compounds* (**9**) *with magnesium in THF, a λ^3,λ^5-diphosphaphenanthrene* (**19**) *was obtained.*

INTRODUCTION

One of the challenging problems in chemistry has been connected with the preparation of compounds containing double bonds of the $p\pi$-$p\pi$ type involving atoms of the second or higher rows of the periodic table. In general, higher row elements prefer to form σ-bonds, and their compounds containing π-bonds tend to dimerize or polymerize for thermodynamic reasons. Phosphorus is an example of a second row element, reluctant to form double bonds. However, bulky substituents can prevent the formation of dimers or oligomers in which phosphorus has the usual coordination number three. Alternatively, the dicoordinated state can be made thermodynamically more stable by including phosphorus into a delocalized π-system.

Since 1966, aromatic heterocycles with dicoordinated phosphorus have been known in the literature. Monocyclic [1], bicyclic [2], and tricyclic [3] derivatives have been synthesized in several ways. Though many examples of (stable) phosphaaromatic compounds are known to date, there are very few with more than one phosphorus atom in the aromatic system. With the exception of two nitrogen-containing five-membered ring systems reported quite recently [4a,b], they either do not contain two phosphorus atoms bonded to each other [4c,d] or have only been obtained as transition metal π-complexes [4d,e].

Inspired by the well known Yoshifuji reaction, which leads to a diphosphene with a localized P=P double bond [5], we decided to investigate the approach outlined in Scheme 1 to prepare the λ^3,λ^3-diphosphaphenanthrene **2** from **1**. In fact, **2** is a tied-back analogue of the *Z*-isomer of the Yoshifuji diphosphene. We were aware of the probability that this tricyclic compound would display less stabilization than a corresponding monocyclic 1,2-diphosphabenzene, but we preferred **2** for reasons of

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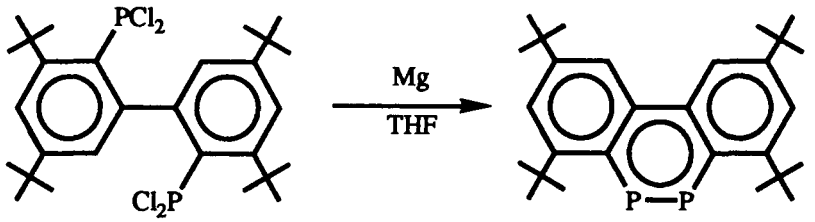


1 2

SCHEME 1

preparative accessibility; moreover, it was anticipated that **2** derives its stability, if not from resonance, from steric protection by the bulky *tert*-butyl groups.

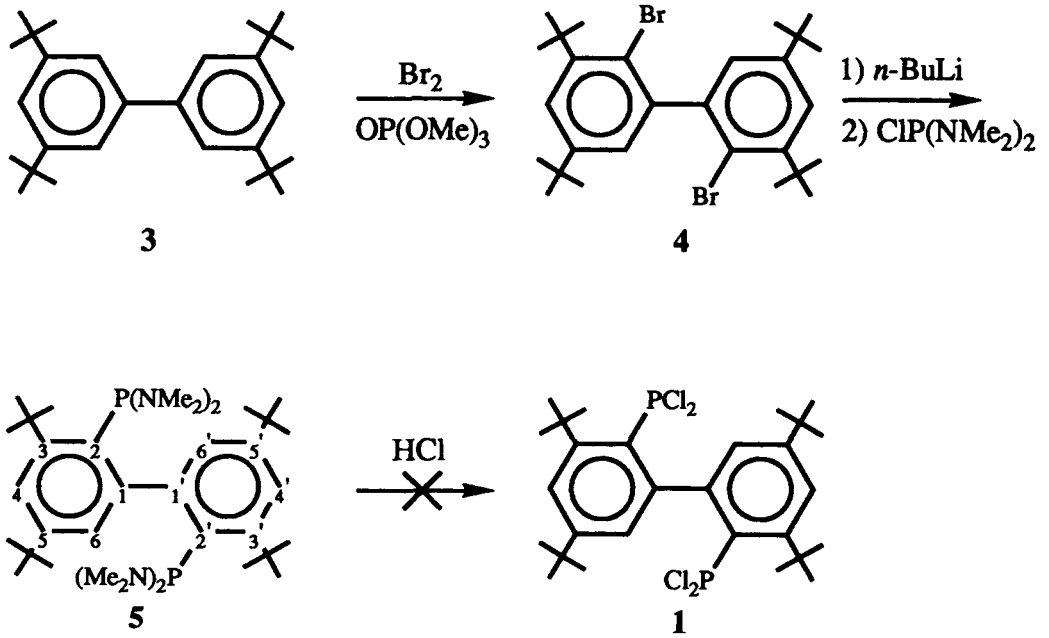
In this paper, we are concerned with chemistry encountered en route to **2**. We report on the preparation of some new, highly congested, phosphorus substituted biphenyls. The NMR spectroscopy and X-ray analysis of 2,2′-bis(bis(dimethylamino)-phosphino)-3,3′,5,5′-tetra-*tert*-butyl biphenyl (**5**) is discussed. The reactivity of **5** was investigated in some detail; in particular, the formation of the λ^3,λ^5-diphosphaphenanthrene **17** and of some other phosphorus containing ring compounds will be discussed.

RESULTS AND DISCUSSION

Synthesis and Reactions of **5**

For the synthesis of the precursor of the desired λ^3,λ^3-diphosphaphenanthrene **2**, we followed the approach outlined in Scheme 2. Biphenyl **3** [6] was treated with two equivalents of bromine at 140°C in trimethyl phosphate to give the dibromo derivative **4** in 63% yield (after crystallization from ethanol). Compound **4** was converted to its dilithio derivative with *n*-butyllithium in diethyl ether. It was anticipated that its reaction with trichlorophosphine would not yield the desired **1**, but would instead result in the formation of a five-membered ring compound (vide infra). Therefore, we first prepared the protected compound **5** in 40% yield by treatment of the dilithio intermediate with chlorobis(dimethylamino)phosphine, with the intention of converting **5** to **1** with hydrogen chloride, a reaction that, under normal circumstances, works quite reliably.

However, instead of **1**, an unexpected new compound with a bond between the two phosphorus atoms (^{31}P NMR ($CDCl_3$): δ 66.9 (d, ^1J(PP) = 268 Hz) and 37.6 (d, ^1J(PP) = 268 Hz)) was formed when **5** was treated with an excess of hydrogen chloride in chloroform. Therefore, we decided to investigate this reaction more carefully. The results of the re-



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SCHEME 2

TABLE 1 ^{31}P NMR Data of Products Obtained from **5**

Reaction Conditions	δ	^1J(PP)[Hz]	*Relative Intensity*	*Assignment*
1 or 2 eq HCl	61.8 (s)[a]	—	1	**12**
	57.3 (d)	340	6	**8**
	25.9 (d)	340	6	**8**
≥4 eq HCl	82.3 (s)[a]	—	1	**13**
	66.9 (d)	268	6	**9**
	37.6 (d)	268	6	**9**
MeOH	174.2 (s)[b]	—	—	—
	142.7 (s)	—	—	—
	109.4 (s)	—	—	—
	63.0 (s)	—	—	**12**
	59.0 (d)	340	—	**8'**
	26.6 (d)	340	—	**8'**
H_2O/THF	113.1 (s)[a]	—	18	—
	61.9 (s)	—	2	—
	58.8 (s)	—	3	—
	55.4 (s)	—	1.5	—
	38.1 (d)	208	9	**15**
	29.1 (s)	—	1	—
	27.3 (s)	—	2	—
	23.9 (s)	—	1.3	—
	−8.9 (d)	208	8	**15**

[a] In $CDCl_3$.
[b] In MeOH.

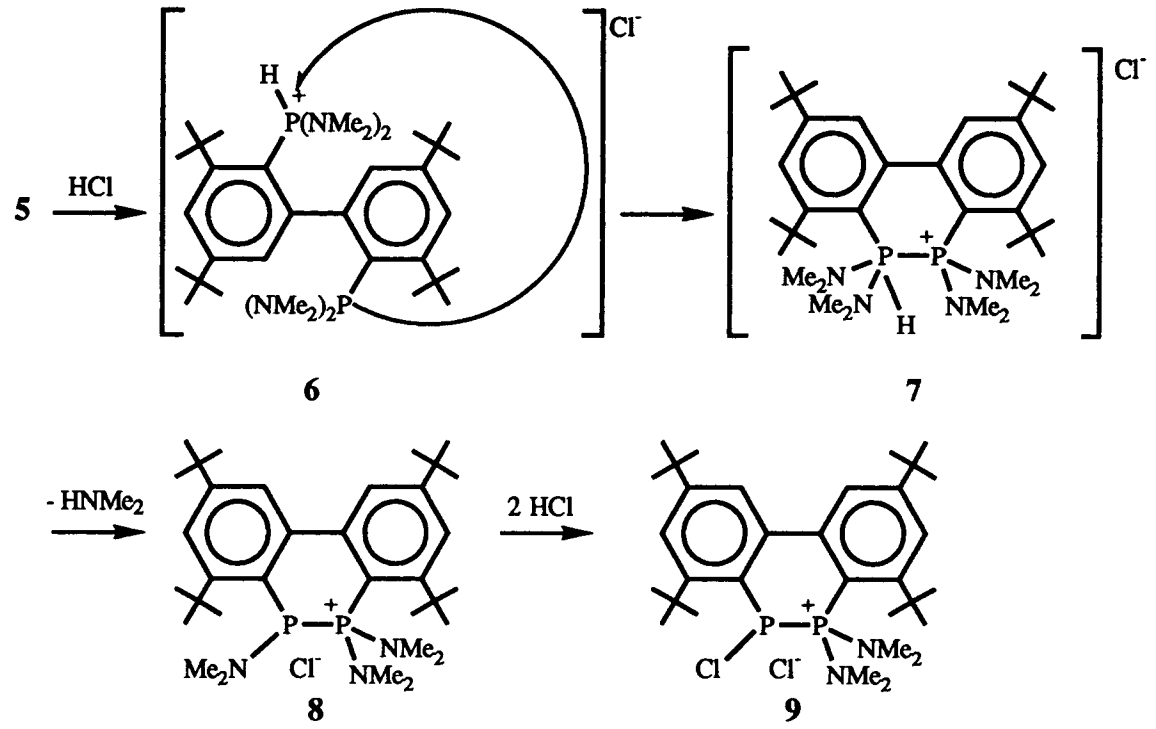
action of **5** with 1, 2, 4, and 20 equivalents of hydrogen chloride are summarized in Table 1.

According to ^{31}P NMR spectroscopy, two sets of products were obtained in all reactions: one set obtained with 1 or 2 equivalents of hydrogen chloride and another one with 4 or more equivalents. Of each set, one product (**8** or **9**) showed a strong coupling between two phosphorus atoms (^1J(PP) = 340 Hz or 268 Hz, respectively), which implies a ring closure reaction. The other signal of each set stems from five-membered ring compounds (**12** or **13**), as was proven by independent synthesis.

To rationalize this unexpected outcome, we propose a mechanism as outlined in Scheme 3. Essential in this mechanism is protonation of a phosphorus atom of **5** to furnish the phosphonium cation **6**. Such a protonation has, in certain cases, been invoked as the first step in the exchange of amino groups by chlorine [7]. The usual subsequent step is addition of chlorine to phosphorus. In the case of **6**, this is apparently impossible because it would further increase the considerable strain already present in the highly crowded molecule; again, there is precedent for such behavior [7]. Instead, the strain is reduced by attack of the cationic phosphorus on the tertiary, basic phosphorus, leading to the formation of a P—P bond in **7**. Elimination of dimethylamine gives the phosphonium cation **8**. It should be pointed out that, up to this point, only one molecule of hydrogen chloride has been used, and in line with this proposal, the transformation **5** → **8** is indeed complete with one equivalent of hydrogen chloride; under these conditions, dimethylamine formation has been detected by smell and by ^1H NMR spectroscopy. The second equivalent of hydrogen chloride is used to neutralize the dimethylamine; it leaves **8** unchanged. Further reaction is observed only on addition of four or more equivalents of hydrogen chloride; it involves the conventional substitution of the dimethylamino group at the tertiary phosphorus by chlorine to furnish **9**. This is accompanied by the expected deshielding of both phosphorus nuclei (Table 1). The two remaining amino substituents of the phosphonium groups are protected against chloro substitution by the positive charge.

Due to the presence of about 15% of the side products **12** and **13**, respectively, **8** and **9** could not be obtained in pure form. Nevertheless, their structures can be assigned with great confidence because of the typical ^{31}P chemical shifts and the large ^1J(PP) couplings; furthermore, their insolubility in apolar solvents testifies to their salt-like character.

The structure of the minor components **12** and **13** as 9-phosphafluorenes was established by independent synthesis: the dilithio derivative formed from **4** and *n*-butyllithium reacted with trichlorophosphine to give **13** (not **1**! vide supra), which was converted to **12** by an excess of dimethylamine. Their formation from **5** is explained in Scheme 4. We propose that the electrophilic phosphorus of **6** can relieve the steric congestion by attack not only on the



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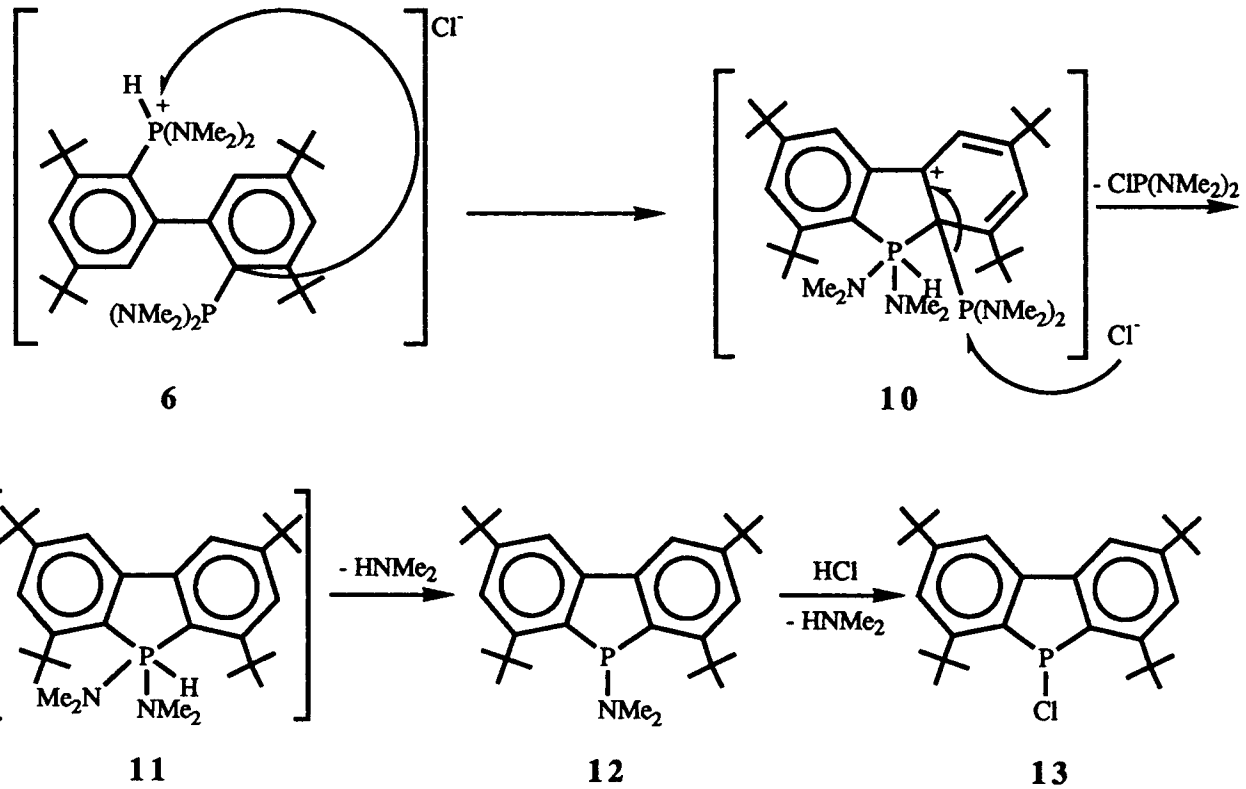


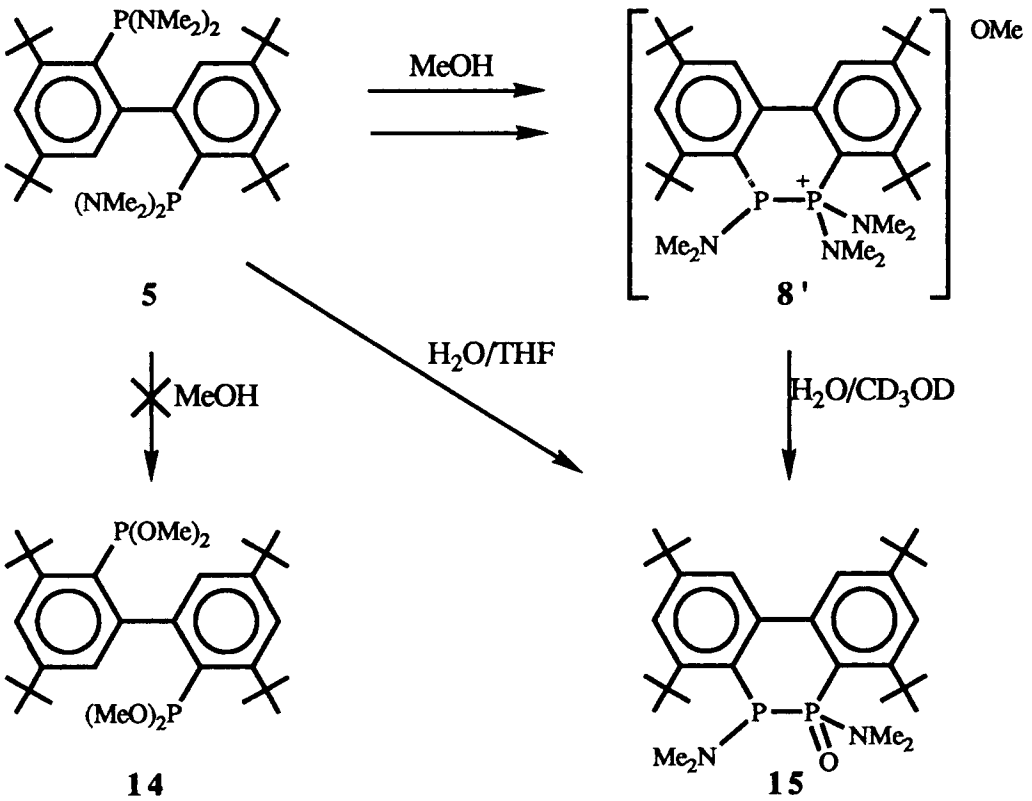
SCHEME 4

second phosphorus to give **7**, but also on the *ipso*-carbon of the other aromatic ring to give **10**. The preference for the *ipso*-carbon above the other *ortho*-carbon probably entails both electronic and steric reasons; the *ipso*-carbon is more nucleophilic due to its electron-rich phosphine substituent, and the release of strain is larger, because the bulky phosphino substituent is bending out of the crowded plane of the heavily substituted benzene ring. The S_E2 substitution is completed by cleavage of the phosphino substituent from **10** to give **11**, which releases dimethylamine to form **12**. With excess hydrogen chloride, **12** is converted in a conventional way to **13**. Trichlorophosphine converted **5** to a mixture of **8** and **9** without formation of **12** and **13**.

The direct conversion of **5** to **1** with hydrogen chloride having unexpectedly failed, we next attempted to achieve this transformation stepwise via **14**. Again, and to our surprise, even under the mild conditions of dissolving **5** in pure methanol, ring closure to a compound very similar to **8** occurred (Table 1); we assign to this compound, with some reservation, structure **8'**. It differs from **8** only by the counter anion methoxide instead of chloride. Again, the formation of **8'** must be initiated by even the low protic activity of methanol; the unexpected fact that methoxide does not add to phosphorus must be explained by steric congestion (Scheme 5).

The structure assignment of **8'** is based on its ^{31}P NMR spectrum (Table 1; cf. also **8**) and on the reaction with water that converts **8'** to **15**, a compound that can be obtained directly from **5** (together with other products (Table 1)) with water in tetrahydrofuran. Again, the weakly acidic properties of this medium are apparently sufficient to induce phosphorus–phosphorus bond formation. We assume that water or, more likely, the hydroxide ion is able to penetrate the crowded surroundings of the phosphonium phosphorus of intermediate **7** (Scheme 3), where the methoxide ion of **8'** does not; this results in the formation of the phosphinamide **15**. Remarkably, **8** with chloride as the counterion is not attacked by water; we take this as evidence that it is the hydroxide ion that triggers the formation of **15**, because with water, **8'** can form OH^- whereas **8** can not.

As a model for **5**, we also prepared and investigated its monofunctional analogue **16** (Scheme 6). The synthesis of **16** and **17** was analogous to that of **5**. Reaction of **16** with a small excess of hydrogen chloride gave **12** and **13** together with the "normal" substitution product **18** (ratio 1:1:1). The formation of **18** signals less strain in the monofunctional series and thus confirms the importance of strain for the unusual behavior of **5** and **6**. The formation of the phosphafluorenes **12** and **13** proves that ring closure



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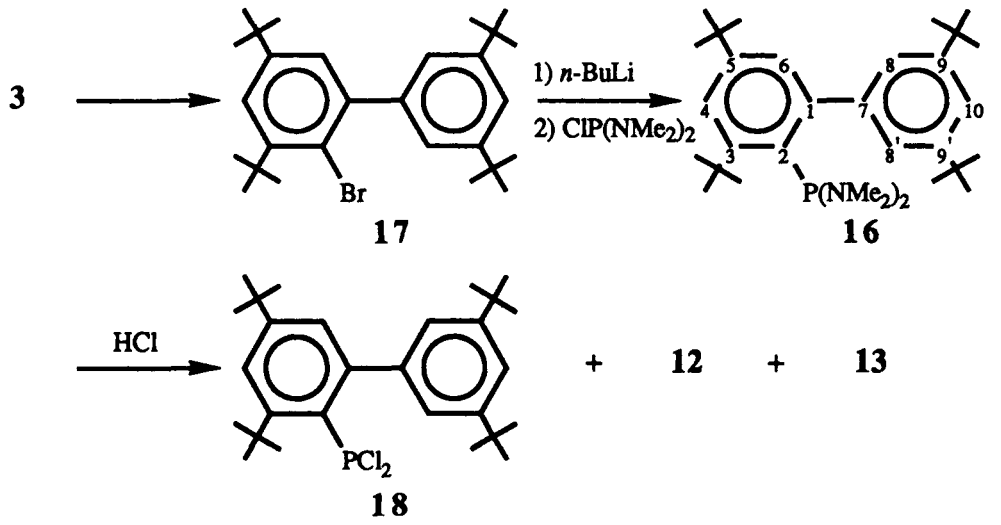


SCHEME 6

is also possible from monofunctional precursors. This raises the question whether from **5**, too, **12** and **13** are formed via **16**, i.e. by dephosphinylation prior to ring closure. However, we do not consider this alternative likely because from **5**, the formation of **18** was never observed (^{31}P NMR spectroscopy).

NMR Spectroscopy of **5**, **12**, *and* **16**

The phosphorus chemical shifts of **5** find some analogy in the literature [8]. The interpretation of the ^{1}H and ^{13}C spectra was initially complicated because **5**, although being a symmetrical compound, has magnetically nonequivalent phosphorus nuclei [9]. This results in AA'X-systems in both the ^{1}H (see Experimental) and the ^{13}C NMR spectra (see Table 2, with data of **16** for comparison). In these spectra A = A' = ^{31}P and X = ^{13}C or ^{1}H, respectively. Proper simulation of the ^{13}C NMR spectrum turned out to be impossible for two reasons. Firstly, in order to check the accuracy of the coupling constants determined from the ^{13}C NMR spectra, it would have been necessary to observe the ^{13}C satellites; this was not possible due to the inherently broad linewidth of the phosphorus signal. For the same reason, it was not possible to see the contribution of the different phosphorus atoms to the phosphorus–carbon coupling. Therefore, only the sum of the coupling constants is given in Table 2. The coupling constant between the two phosphorus atoms is estimated to be 22 Hz. Secondly, in one multiplet the linewidth of the various signals differs too much; therefore we could not determine the relative intensities.

Compound **12** raised our interest by not showing any signals of the dimethylamino group in the ^{1}H NMR spectrum at room temperature. Cooling to −50°C resulted in decoalescence to two signals at δ = 1.69 (s) and 2.74 (d, ^{3}J(PH) = 3.8 Hz). This unforeseen nonequivalence must be due to hindered rotation around the phosphorus–nitrogen single bond, which is another indication for the rather crowded character of these tetra-*tert*-butylbiphenyl derivatives. The large difference in chemical shift and phosphorus coupling can be explained as follows. Due to the pyramidal configuration of phosphorus, the dimethylamino group sticks out from the phosphafluorene plane at a certain angle. Due to steric hindrance, the $PNMe_2$ plane stands more or less perpendicular to the tricyclic aryl plane. This brings one methyl group (δ = 2.74) close to this aryl plane, where it is deshielded relative to the other one. In this conformation, the deshielded methyl group is oriented cis to the phosphorus lone pair, while the other one is trans. According to the well known angular dependence of ^{2}J(PX) coupling [9, 10], this leads to the observed coupling pattern.

X-ray Crystal Structure of **5**

In the context of the interesting NMR phenomena of **5** (see previous section), and to clarify its crowded stereochemistry, an X-ray crystal structure was determined. Figure 1 shows the molecule with adopted numbering. Both benzene rings are significantly puckered with maximum deviation of 0.050 (6) Å at C6 and C12; a similar degree of nonplanarity has earlier been observed in bis(2,4,6-tri-*tert*-butylphenyl)phosphinic chloride [11]. The highly crowded nature of **5** is revealed by 21 contacts (1–4 or greater) that are considerably shorter (by 0.20 to 0.65 Å) than the van der Waals contact distances; no less than 17 of these involve the two bis(dimethylamino)phosphino substituents. This strongly supports our claim that the crowded situation, especially

TABLE 2 ^{13}C NMR Data (C_6D_6) of **5** and **16**

5				16			
Atom[a]	δ	*J*(CP)(Hz)[b]	*J*(CH)(Hz)	*Atom*[a]	δ	*J*(CP)(Hz)	*J*(CH)(Hz)
1	148.787	5.80	—	1	148.755	6.63	—[c]
2	138.751	48.05	—[d]	2	139.293	32.85	—[e]
3	152.224	21.00	multiplet[f]	3	156.826	11.43	multiplet[f]
4	128.324	—	155.13[g]	4	125.258	—	151.32[h]
5	147.847	—	multiplet[f]	5	148.946	1.68	multiplet[f]
6	123.654	3.59	153.40	6	125.886	1.66	156.96[i]
NCH_3	41.731	15.25	133.70	7	146.292	—	—[j]
NCH_3	41.108	25.82	133.96	8,8′	123.606	2.62	154.72[k]
$C(CH_3)_3^{(3)}$	39.537	—	—	9,9′	149.650	—	multiplet[f]
$C(CH_3)_3^{(3)}$	34.155	13.88	125.63	10	119.789	—	151.82[l]
$C(CH_3)_3^{(5)}$	34.611	—	—	NCH_3	41.714	17.07	133.91
$C(CH_3)_3^{(5)}$	31.480	—	125.44	$C(CH_3)_3^{(3)}$	40.095	3.63	—
				$C(CH_3)_3^{(3)}$	33.662	9.33	125.63
				$C(CH_3)_3^{(5)}$	34.964	—	—
				$C(CH_3)_3^{(5)}$	31.480	—	125.46
				$C(CH_3)_3^{(9)}$	34.964	—	—
				$C(CH_3)_3^{(9)}$	31.707	—	125.44

[a] The numbers are indicated in Schemes 2 (**5**) and 6 (**16**).
[b] This is the sum of both $J(CP^1)$ and $J(CP^2)$.
[c] $^3J(CH)$ = 3.90 Hz, with H^8.
[d] $^3J(CH)$ = 6.1 Hz, with H^4 and H^6.
[e] $^3J(CH)$ = 5.82 Hz, with H^4 and H^6.
[f] $^3J(CH)$ = 3.4 Hz, with $C(CH_3)_3$.
[g] $^3J(CH)$ = 6.91 Hz, with H^6.
[h] With H^4 and $^3J(CH)$ = 6.83 Hz with H^6.
[i] With H^4 and $^3J(CH)$ = 6.98 Hz, with H^4.
[j] $^3J(CH)$ = 4.25 Hz, with H^6.
[k] With H^8 and $^3J(CH)$ = 6.59 Hz, with H^8 and H^{10}.
[l] With H^{10} and $^3J(CH)$ = 6.67 Hz, with H^8.

around phosphorus, is the cause of the unusual chemical behavior of **5**.

A λ^3,λ^5-diphosphaphenanthrene (**19**)

In a final attempt to introduce a double bond between the two phosphorus atoms, we investigated the behavior of **8** and **9** toward magnesium. Not surprisingly, the all-amino substituted **8** showed only decomposition and no identifiable products in a slow reaction. In contrast, **9** has a P–Cl functionality that is more susceptible to reduction; within five hours, stirring **9** with magnesium in THF produced an orange-colored solution from which, after workup, the λ^3,λ^5-diphosphaphenanthrene **19** was identified as the major product by its characteristic ^{31}P NMR data; unfortunately, purification was not possible as **13**, present as an impurity in **9**, was simultaneously reduced to **20** (Scheme 7). The structure of **20** was confirmed by its independent synthesis from **13** with lithium aluminum hydride.

The ^{31}P NMR data of **19** (δ = 94.5 (d) and −129.0 (d) $^1J(PP)$ = 469 Hz), in particular the large phosphorus–phosphorus coupling, confirm the structure of **19**, but at the same time show no unusual spectroscopic properties as compared to those of normal λ^3,λ^5-diphosphenes, which are known to be ylids rather than π-bonded species [12].

CONCLUSIONS

The highly crowded biphenyl **5** could be prepared. Due to its strained character, which manifests itself in the crystal structure, attempts to convert it to **1** (and further to the λ^3,λ^3-diphosphaphenanthrene **2**) were not successful, but they furnished interesting examples of unusual reactivity of phosphorus compounds. However, the λ^3,λ^5-diphosphaphenanthrene **19** could be obtained from **9** and magnesium; its spectroscopic properties identify **19** as a normal ylid without special aromatic properties of the (formal) diphosphabenzene ring system.

EXPERIMENTAL

The reactions and subsequent manipulations of air sensitive compounds were carried out in a high vacuum system. The reported melting points are uncorrected. Elemental analyses were performed by the Mikroanalytisches Labor Pascher, Remagen-Bandorf, Germany. The NMR spectra were measured on a Bruker WM 250 NMR spectrometer at 250 MHz (^1H), 62.89 MHz (^{13}C), or 101.2 MHz (^{31}P)

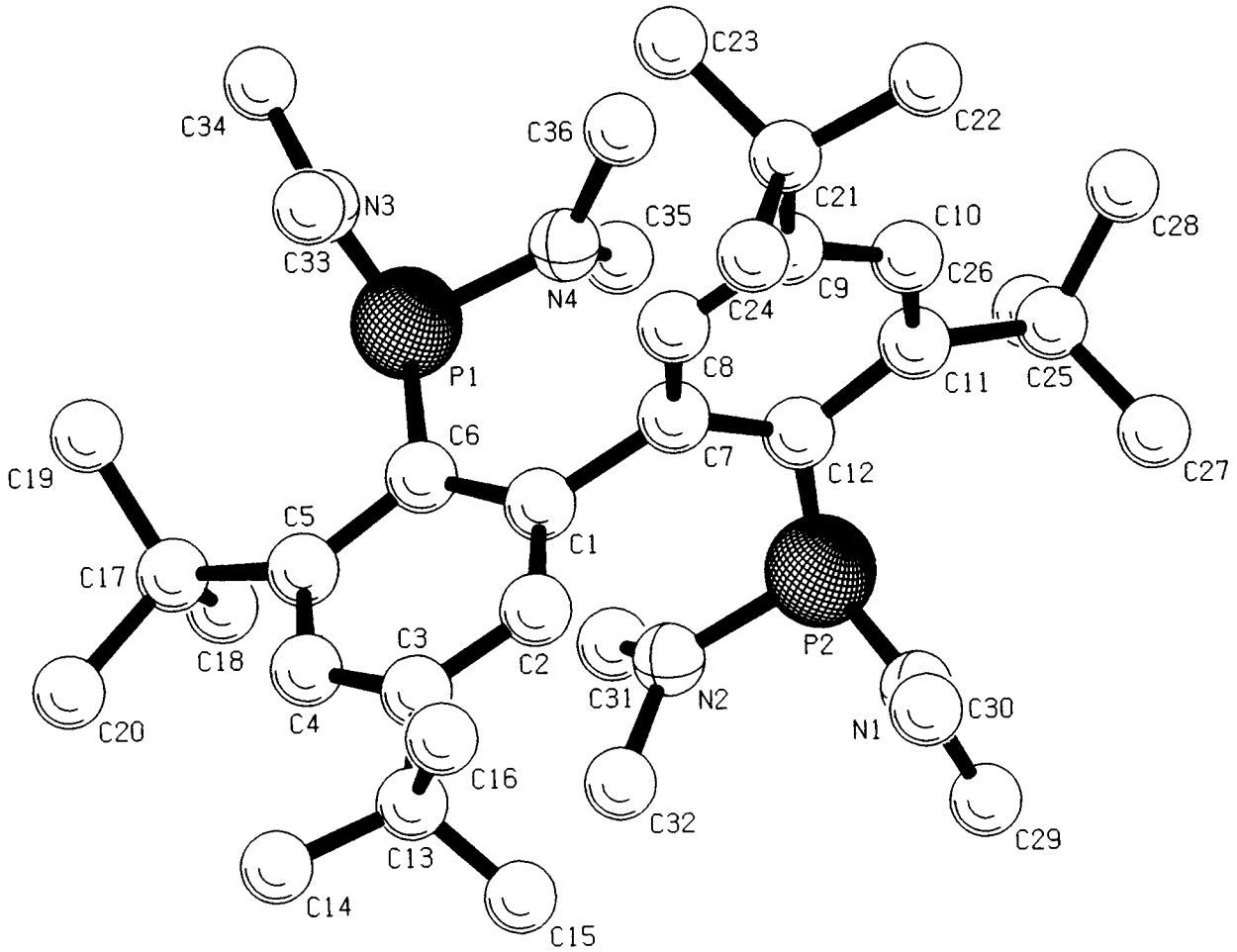
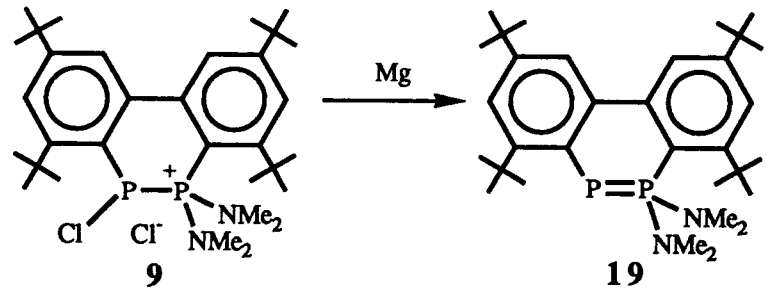
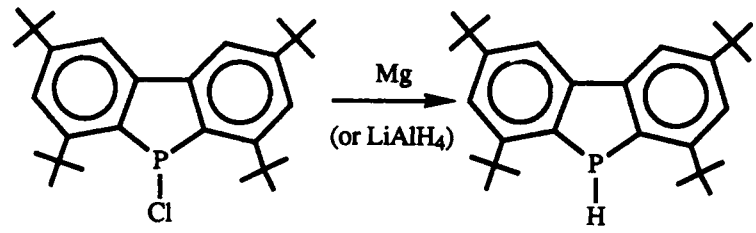


FIGURE 1 PLUTON drawing of **5** with adopted numbering. H-atoms were left out for clarity.





SCHEME 7

and a Bruker MSL 400 NMR spectrometer at 400 MHz (^{1}H) or 100.63 MHz (^{13}C). Chemical shifts were measured relative to external $(CH_3)_4Si$ or 85% H_3PO_4. GCMS was performed on a 5070 Hewlett-Packard Mass Selective Detector connected to a HP 5890 gas chromatograph equipped with a 25 m CP sil 5 CB capillary column and using a column head pressure of 12 psi. HR mass spectra were obtained on a Finnigan MAT 90 (Finnigan MAT, San José, USA); the exact masses were checked by peak-matching against an appropriate reference signal.

2,2'-Dibromo-3,3'5,5'-tetra-tert-*butylbiphenyl* (**4**)

A solution of bromine (10 g, 62.5 mmol) in trimethyl phosphate (200 mL) was added within half an hour to a solution of **3** [6] (5.9 g, 15.6 mmol) in trimethyl phosphate (50 mL) at 140°C. After having been stirred for 120 min at this temperature, the reaction mixture was poured onto ice. The water layer was extracted several times with pentane. The combined organic layers were washed with water till neutral, and subsequently with an aqueous solution of $Na_2S_2O_3$ (10%) and dried over $MgSO_4$. After filtration and evaporation of the filtrate, the residue was recrystallized from ethanol, yielding **4** as colorless crystals (5 g, 60% yield), mp 193°C. ^{1}H NMR ($CDCl_3$) δ 1.36 (s, 18H, *t*-Bu *p* to Br), 1.60 (s, 18H, *t*-Bu *o* to Br), 7.13 (d, ^4J(HH) = 2.6 Hz, 2H, ArH), 7.52 (d, ^4J(HH) = 2.5 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ 149.1 (s), 147.3 (s), 146.4 (s), 126.2 (d, ^1J(CH) = 157 Hz), 124.0 (d, ^1J(CH) = 143 Hz), 121.2 (s), 37.5 (s), 34.9 (s), 31.4 (q, ^1J(CH) = 125 Hz), 30.3 (q, ^1J(CH) = 125 Hz). MS (70 eV) *m/z* (%): 538 (5), 536 (7), 534 (3), 457 (50), 455 (52), 57 (100). Anal. Calcd. for $C_{28}H_{40}Br_2$ (536.4): C, 62.69; H, 7.52; Br, 29.79. Found: C, 62.76; H, 7.48; Br, 30.0.

2,2'-Bis(bis(dimethylamino)phosphino)-3,3'5,5'-tetra-tert-*butylbiphenyl* (**5**)

A solution of *n*-butyllithium (11.2 mmol) in *n*-hexane (7.5 mL) was added to a solution of **4** (3 g, 5.6 mmol) in diethyl ether (50 mL) at 0°C. The reaction mixture was allowed to warm to room temperature within one hour. Then, a solution of chlorobis(dimethylamino)phosphine (11.2 mmol) in *n*-hexane was added at −70°C. The reaction mixture was warmed to room temperature in 30 min and stirred for another 90 min. The solvent was evaporated and *n*-hexane (30 mL) was added. After filtration from the lithium salts, the residue was recrystallized at −20°C, yielding **5** as colorless crystals (2.29 g, 37%), mp 214°C. ^{1}H NMR (C_6D_6) δ 1.34 (s, 18H, *t*-Bu), 1.80 (s, 18H, *t*-Bu), 2.13 (AA'X-system, J(PH) = 8.45 Hz, 6H, —$N(CH_3)_2$), 2.41 (AA'X-system, J(PH) = 8.2 Hz, 6H, —$N(CH_3)_2$), 7.21 (d, ^4J(HH) = 2.1 Hz, 2H, ArH$^{(6)}$), 7.59 (dd, ^4J(HH) = 2.1 Hz, ^4J(PH) = 1.9 Hz, 2H, ArH$^{(4)}$). ^{13}C NMR (C_6D_6) see Table 2. ^{31}P NMR (C_6D_6): δ 114.1 (s). Anal. Calcd. for HRMS $C_{36}H_{64}N_4P_2$: 614.461. Found: 614.463. Anal. Calcd. for $C_{36}H_{64}N_4P_2$ (614.5): C, 70.12; H, 10.46. Found: C, 70.07; H, 10.55. To obtain suitable crystals for X-ray analysis, **5** was recrystallized twice from hexane at −20°C. To avoid oxidation, the crystals were sampled under a nitrogen atmosphere in a glovebox.

Reaction of **5** *with Hydrogen Chloride*

In a typical run, gaseous hydrogen chloride (0.26, 0.52, 1.04, or 5.20 mmol, respectively) was added to a solution of **5** (0.26 mmol) in HCl-free chloroform (10 mL) at room temperature. After 4 h, the ^{31}P NMR spectrum was recorded from the crude reaction mixture (see Table 1). Then the chloroform was removed by evaporation and the residue was "washed" with *n*-pentane to remove the side products (mainly phosphafluorenes). The remaining traces of *n*-pentane were pumped off carefully and the resulting colorless solid material was dissolved in DCl-free $CDCl_3$. The product analysis was performed by ^{31}P NMR spectroscopy (see Table 1). **8** ^{1}H NMR ($CDCl_3$) δ 1.24 (s, 9H, *t*-Bu), 1.25 (s, 9H, *t*-Bu), 1.35 (s, 9H, *t*-Bu), 1.50 (s, 9H, *t*-Bu), 2.24 (d, ^3J(PH) = 8.2 Hz, 6H, NMe_2), 2.28 (d, ^3J(PH) = 8.8 Hz, 6H, NMe_2), 2.81 (d, ^3J(PH) = 9.1 Hz, 6H, NMe_2), 7.08 (d, ^4J(HH) = 1.4 Hz, 1H, ArH), 7.11 (dd, ^4J(HH) = 3.2 Hz, ^4J(PH) = 1.6 Hz, 1H, ArH), 7.57 (d, ^4J(HH) = 5.7 Hz, 1H, ArH), 7.65 (dd, ^4J(HH) = 1.8 Hz, ^4J(PH) = 1.5 Hz, 1H, ArH). **9** ^{1}H NMR ($CDCl_3$) δ 1.263 (s, 9H, *t*-Bu), 1.275 (s, 9H, *t*-Bu), 1.37 (s, 9H, *t*-Bu), 1.56 (s, 9H, *t*-Bu), 2.42 (d, ^3J(PH) = 9.82 Hz, 6H, NMe_2), 2.95 (d, ^3J(PH) = 10.3 Hz, 6H, NMe_2), 7.07 (d, ^4J(HH) = 1.3 Hz, 1H, ArH), 7.13 (dd, ^4J(HH) = 3.9 Hz, ^4J(PH) = 1.4 Hz, 1H, ArH), 7.55 (d, ^4J(HH) = 5.8 Hz, 1H, ArH), 7.65 (dd, ^4J(HH) = 3.3 Hz, ^4J(PH) = 1.53 Hz, 1H, ArH). Compounds **8** and **9** are air sensitive and decompose above 300°C without melting.

9-Chloro-1,3,6,7-tetra-tert-*butyl-9-phosphafluorene* (**13**)

A solution of *n*-butyllithium (1.0 mmol) in *n*-pentane (2.0 mL) was added to a solution of **4** (0.268 g, 0.50 mmol) in diethyl ether (10 mL) at room temperature. After stirring for 15 min, the reaction mixture was cooled to −20°C and a solution of trichlorophosphine (0.50 mmol) in *n*-pentane (2.0 mL) was added slowly. The reaction mixture was allowed to warm to room temperature slowly. Then, the solvent was evaporated and *n*-pentane (10 mL) was added. After filtration from the lithium salts, the residue was recrystallized at −20°C, yielding **13** as colorless crystals, mp 110°C. ^{1}H NMR (C_6D_6) δ 1.30 (s, 18H, *t*-Bu), 1.67 (s, 18H, *t*-Bu) 7.57 (dd, 2H, ^4J(PH) = 4.8, ^4J(HH) = 2 Hz, ArH), 7.88 (d, 2H, 2H, J = 2 Hz). ^{31}P NMR (C_6D_6) δ 81.3 (s). Anal. Calcd. for HRMS $C_{28}H_{40}PCl$: 442.2556. Found: 442.2565.

Anal. Calcd. for $C_{28}H_{40}PCl$ (442.3): C, 75.91; H, 9.10. Found: C, 77.41; H, 9.70.

9-Dimethylamino-1,3,6,7-tetra-tert-*butyl-9-phosphafluorene* (**12**)

An excess of dimethylamine (about 1 mL) was added to a solution of **13** (0.25 mmol) in diethyl ether (3.0 mL) at 0°C. After 30 min, the solvents were evaporated and *n*-pentane (10 mL) was added. After filtration from the ammonium salts, it was not possible to crystallize **12** properly. Therefore analyses were performed on the oily compound. ^{1}H NMR ($CDCl_3$) (−50°C) δ 1.23 (s), 1.37 (s), 1.69 (s), 2.74 (d, ^3J(PH) = 3.8 Hz), 6.95 (d, ^1J(HH) = 1.6 Hz), 7.32 (d, ^1J(HH) = 1.6 Hz). ^{31}P($CDCl_3$) δ 61.8 (s). Anal. Calcd. for HRMS $C_{32}H_{46}NP$: 451.681. Found: 451.337.

Reaction of **5** *with Methanol*

A solution of **5** (0.08 mmol) in *n*-pentane (2 mL) was evaporated to dryness and methanol (10 mL) was added. The suspension was stirred for several hours. A ^{31}P NMR spectrum was measured from the crude reaction mixture (see Table 1).

Reaction of **5** *with Water*

A solution of **5** (0.08 mmol) in *n*-pentane (2 mL) was mixed with a solution of water (0.5 mL) in THF (10 mL). After the mixture had been stirred for several hours, the solvents were evaporated, the dry residue was dissolved in DCl-free $CDCl_3$, and a ^{31}P NMR spectrum was recorded (see Table 1).

Reaction of **5** *with Trichlorophosphine*

To a solution of **5** (0.08 mmol) in *n*-pentane (2 mL), a solution of trichlorophosphine (0.5 mmol) in *n*-pentane was added at room temperature. After having been stirred for 6 h and filtered from the salts, the solvents were evaporated and the residue dissolved in $CDCl_3$ (0.5 mL). ^{31}P NMR spectroscopy showed that a mixture of **8** and **9** (ratio 4:1) had been formed.

Reaction of **8** *with Magnesium*

A solution of **8** (0.26 mmol) in THF (10 mL) was stirred for several days on twice sublimed magnesium (100 mg). No identifiable products could be detected.

Reaction of **8** *with Hydrogen Chloride*

Gaseous hydrogen chloride (2.6 mmol) was added to a solution of **8** (0.26 mmol) in $CHCl_3$ (10 mL) at room temperature. After the mixture had been stirred for 6 h, ^{31}P NMR spectroscopy of the crude reaction mixture showed almost clean formation of **9**.

Reaction of **9** *with Magnesium*

A solution of **9** (0.26 mmol) in THF (10 mL) was stirred for 5 h at room temperature on twice sublimed magnesium (100 mg). The reaction mixture turned slowly orange. After evaporation of the solvents, *n*-pentane was added and the salts were filtered off. Then the *n*-pentane was removed by pumping carefully and the oily residue (**19**) was dissolved in C_6D_6 (0.5 mL). ^{31}P NMR δ 94.5 (d, ^1J(PP) = 469 Hz), −129.0 (d, ^1J(PP) = 469 Hz). The coupling was confirmed by ^{31}P-COSY-NMR. Mass spectroscopy under EI conditions was not possible because **19** decomposes upon heating. **19** was mainly contaminated by **20**, ^{31}P NMR δ −60.1 (d, ^1J(PH) = 207 Hz).

1,3,6,7-Tetra-tert-*butyl-9-phosphafluorene* (**20**)

A suspension of $LiAlH_4$ (1 mmol) was added to a solution of **13** (0.25 mmol) in diethyl ether (10 mL) at −20°C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. Then, the solvent was evaporated and *n*-pentane (10 mL) was added. After filtration from the salts, the residue was recrystallized from *n*-pentane at −20°C, yielding **20** as colorless crystals, mp 254–256°C. ^{1}H NMR (C_6D_6) δ 1.40 (s), 1.60 (s), 5.66 (d, ^1J(PH) = 207 Hz), 7.63 (dd, ^4J(PH) = 4.2 Hz, ^4J(HH) = 1.6 Hz), 8.17 (d, ^1J(HH) = 1.6 Hz). ^{31}P NMR (C_6D_6): vide supra. Anal. Calc. for HRMS $C_{28}H_{41}P$: 408.2946. Found: 408.2941. Anal. Calcd. for $C_{28}H_{41}P$ (408.3): C, 82.13; H, 10.11. Found: C, 79.90; H, 9.90.

2-Bromo-3,3',5,5'-tetra-tert-*butyl biphenyl* (**17**)

A solution of bromine (0.8 g, 5 mmol) in trimethyl phosphate (5 mL) was slowly added to a solution of **3** (0.75 g, 2 mmol) in trimethyl phosphate (40 mL) at 100°C. After having been stirred for 75 min at this temperature, the reaction mixture was poured into an aqueous solution of $Na_2S_2O_3$ (10%). A formed precipitate was filtered off and washed several times with water. The crude compound was recrystallized from ethanol, yielding **17** as colorless crystals (0.65 g, 70%), mp 171°C. ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 9H, *t*-Bu), 1.38 (s, 18H, *t*-Bu), 1.61 (s, 9H, *t*-Bu), 7.25 (d, ^4J(HH) = 2.5 Hz, 2H, ArH), 7.29 (d, ^4J(HH) = 2.5 Hz, 1H, ArH), 7.49 (t, ^4J(HH) = 2.5 Hz, 1H, ArH), 7.57 (d, ^4J(HH) = 2.5 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) 149.78 (s), 149.12 (s), 147.54 (s), 145.88 (s), 142.91 (s), 126.45 (d, ^1J(CH) = 155.4 Hz), 124.29 (d, ^1J(CH) = 156.6 Hz), 124.19 (d, ^1J(CH) = 153.2 Hz), 120.62 (d, ^1J(CH) = 152.7 Hz), 120.51 (s), 37.69 (s), 34.98 (s), 34.85 (s), 31.62 (q, ^1J(CH) = 125.6 Hz), 31.43 (q, ^1J(CH) = 126.1 Hz), 30.38 (q, ^1J(CH) = 125.9 Hz). MS (70 eV) *m/z* (%): 458 (100), 456 (100), 443 (83), 442 (23), 441 (84), 253 (4), 214 (13), 57 (43). Anal. Calcd. for $C_{28}H_{41}Br$ (457.5): C, 73.50; H, 9.03; Br, 17.46. Found: C, 73.68; H, 9.03; Br, 17.7.

2-Bis(dimethylamino)phosphino-3,3'5,5'-tetra-tert-*butylbiphenyl* (**16**)

This compound was prepared in the same manner as compound **5**, using **17** instead of **4** as starting material. After filteration from the lithium salts, the residue was recrystallized from *n*-pentane at −20°C, yielding **16** as colorless crystals, mp 150–153°C. ^{1}H NMR (C_6D_6) δ 1.33 (s, 9H, *t*-Bu$^{(5)}$), 1.38 (s, 18H, *t*-Bu$^{(9)}$), 1.69 (s, 9H, *t*-Bu$^{(3)}$), 2.25 (AA'X-system, J(PH) = 8.9 Hz, 6H, —N(CH_3)$_2$), 7.32 (dd, ^4J(HH) = 2.2 Hz, ^4J(PH) = 2.0 Hz, 1H, ArH$^{(6)}$), 7.37 (d, ^4J(HH) = 1.9 Hz, 1H, ArH$^{(10)}$), 7.59 (d, ^4J(HH) = 1.9 Hz, 2H, ArH$^{(8)}$), 7.68 (dd, ^4J(HH) = 2.16 Hz, ^4J(PH) = 2.0 Hz, 1H, ArH$^{(4)}$). ^{13}C NMR (C_6D_6) see Table 2. ^{31}P NMR (C_6D_6) δ 108.1 (s). Anal. Calcd. for $C_{32}H_{53}N_2P$ (443.1): C, 77.30; H, 10.75; N, 5.64; P, 6.24. Found: C, 77.44; H, 10.86; N, 5.54; P, 6.27.

Reaction of **16** *with Hydrogen Chloride*

Gaseous hydrogen chloride (0.7 mmol) was added to a solution of **15** (~0.4 mmol) in C_6D_6 (0.5 mL) at room temperature. After the mixture had been stirred for 5 h, the ^{31}P NMR spectrum was measured: δ 161.9 (s)(**18**), 81.3 (s)(**13**), 61.9 (s)(**12**) (ratio: 1:1:1).

2-Dichlorophosphino-3,3'5,5'-tetra-tert-*butylbiphenyl* (**18**)

This compound was prepared from **17** in the same manner as compound **16**, using trichlorophosphine instead of chlorobis(dimethylamino)phosphine. After filtration from the lithium salts, it turned out to be impossible to crystallize **18** properly. Therefore, the analyses were performed on the crude oily residue. ^{31}P NMR (C_6D_6) δ 161.9 (s).

X-ray Crystal Structure Determination of **5**

Crystal Data. $C_{36}H_{64}N_4P_2$, Mr = 614.87, tetragonal, $P\bar{4}2_1c$, $a = b = 24.770$ (3) Å, $c = 12.658$ (4) Å, $V = 7766$ (3) Å^3, $Z = 8$, $D_x = 1.052$ gcm^{-3}, λ (MoKα) = 0.71073 Å, $\mu = 1.3$ cm^{-1}, F (000) = 2704, $T = 295$ K.

Structure Determination. Data were collected on an Enraf-Nonius CAD4-F diffractometer for a colorless transparent crystal (0.25 × 0.28 × 1.30 mm) mounted in a Lindemann glass capillary. Unit cell parameters and their e.s.d's were derived from a least-squares treatment of 25 SET4 reflections ($9 < \theta < 11°$). Intensity data for 8183 reflections (h 0:23, k 0:31, l − 15:0; $\theta < 26.5°$; Zr-filtered MoKα radiation) were collected in the $\omega/2\theta$ scan mode with $\Delta\omega = 0.60 + 0.35 \tan\theta°$. Three reference reflections (−3 0 −1, 0 −3 −1, and 4 −4 0) indicated no decay. The space group was derived from the observed systematic absences. The intensity data were corrected for Lp but not for absorption and averaged (R_{int} = 0.02) into a unique set of 4197 reflections. The structure was solved by direct methods (SHELXS-86 [13]) and refined on F by full-matrix least-squares with SHELX-76 [14]. H atoms were introduced on calculated positions (C–H = 0.98 Å) and refined with fixed geometry with respect to the atoms they are attached to and with two common isotropic thermal parameters. Refinement with weights, $w^{-1} = \sigma^2(F) + 0.0024 F^2$, converged at $R = 0.058$ ($wR = 0.075$; $S = 1.78$; 420 parameters; 2613 reflections with $I > 2.5\,\sigma(I)$, $(\Delta/\sigma)_{max} = 0.5$). A final difference Fourier map did not show residual peaks outside −0.24 and 0.43 eA^{-3}. Six methyl groups (C14, C15, C16, C26, C27, C28) show significant librational motion. The reflection 1 1 0 was omitted from the final refinement cycles. Scattering factors of Cromer and Mann [15] and anomalous-dispersion terms from Cromer and Liberman [16] were used. Refinement of the inverted structure resulted in slightly higher R-values. The programs PLATON and PLUTON (Spek, 1982) [17] were used for the calculation of geometrical data and the plot respectively. All calculations were done on a micro VAX-II cluster.

SUPPLEMENTARY MATERIAL

Tables with positional parameters for all atoms, bond distances, and angles have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW England.

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REFERENCES

[1] See for a comprehensive review: G. Märkl, *Phosphorus and Sulfur, 3,* 1977, 77.

[2] (a) G. Märkl, K.-H. Heier, *Angew. Chem., 84,* 1972, 1066. (b) H. G. de Graaf, J. Dubbeldam, H. Vermeer, F. Bickelhaupt, *Tetrahedron Lett., 85,* 1973, 2397. (c) G. Märkl, K.-H. Heier, *Tetrahedron Lett., 15,* 1974, 4501. (d) H. G. de Graaf, Ph. D. Thesis, Vrije Universiteit, Amsterdam, 1974. (e) H. G. de Graaf, F. Bickelhaupt, *Tetrahedron, 31,* 1975, 1097.

[3] (a) P. de Koe, F. Bickelhaupt, *Angew. Chem., 79,* 1967, 468. (b) P. de Koe, R. van Veen, F. Bickelhaupt, *Angew. Chem., 80,* 1968, 486. (c) P. de Koe, F. Bickelhaupt, *Angew. Chem., 80,* 1968, 912. P. de Koe, Ph. D. Thesis, Vrije Universiteit, Amsterdam, 1969. (d) C. Jongsma, R. Lourens, F. Bickelhaupt, *Tetrahedron,*

32, 1976, 121. (e) F. Nief, C. Charrier, F. Mathey, M. Simalty, *Tetrahedron Lett., 21*, 1980, 1441.
[4] (a) W. Güth, T. Busch, W. W. Schoeller, E. Niecke, B. Krebs, M. Dartmann, P. Rademacher, *New J. Chem., 13*, 1989, 309. (b) K. Rauzy, M. R. Mazières, P. Page, M. Sanchez, J. Bellan, *Tetrahedron. Lett., 31*, 1990, 4463. (c) J. Kobayashi, H. Hamana, Sh. Fujino, A. Ohsawa, I. Kumadaki, *J. Am. Chem. Soc., 102*, 1980, 252. And complexed to Mo: (d) A. R. Barron, A. H. Cowley, *Angew. Chem., 99*, 1987, 956. (e) O. J. Scherer, H. Sitzmann, G. Wolmershäuser, *Angew. Chem., 97*, 1985, 358.
[5] M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc., 103*, 1981, 4587.
[6] (a) K. Ishizu, M. Ohnishi, H. Shikata, *Bull. Chem. Soc. Jpn., 50*, 1977, 76. (b) R. Edler, J. Voss, *Chem. Ber., 122*, 1989, 122.
[7] Th. A. van der Knaap, F. Bickelhaupt, *Phosphorus and Sulfur, 21*, 1984, 227, and references cited.
[8] L. Ernst, P. G. Jones, P. Hook-Herber, R. Schmutzler, *Chem. Ber., 123*, 1990, 35, and references cited.
[9] Compare 1,6-Diphosphatriptycene, S. Sørensen, H. J. Jakobsen, *Org. Magn. Res., 9*, 1977, 101.
[10] J. P. Allbrand, D. Gagnaire, J. Martin, J. B. Robert, *Bul. Soc. Chim. Fr.*, 1969, 40.
[11] M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *Angew. Chem., 92*, 1980, 405.
[12] (a) A. B. Burg, *J. Inorg. Nucl. Chem., 33*, 1971, 1575. (b) J. Emsley, D. Hall: *The Chemistry of Phosphorus*, Harper & Row, London, 1976. (c) S. Lochsmidt, A. Schmidpeter, *Phosphorus and Sulfur, 29*, 1986, 73, and references cited. (d) F. Zurmühlen, M. Regitz, *Angew. Chem., 99*, 1987, 65.
[13] G. M. Sheldrick: *SHELXS-86. A program for Crystal Structure Determination*, University of Göttingen, Germany, 1986.
[14] G. M. Sheldrick: *SHELX-76. A program for Crystal Structure Determination*, University of Cambridge, England, 1976.
[15] D. T. Cromer, J. B. Mann, *Acta Cryst., A24*, 1968, 321.
[16] D. T. Cromer, D. Liberman, *J. Chem. Phys., 53*, 1970, 1891.
[17] A. L. Spek: The EUCLID package, in D. Sayre (ed): *Computational Crystallography*, Oxford, Clarendon Press, p. 528 (1982).