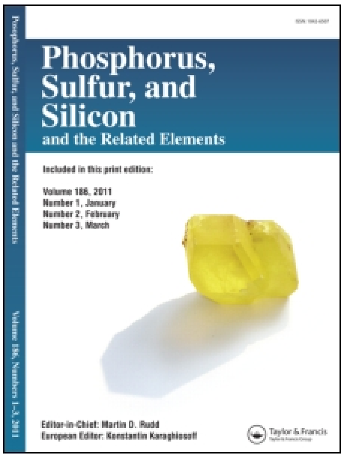

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SYNTHESIS, STRUCTURE AND REACTIVITY OF BIS(N-ARYL-IMINOPHOSPHORANYL)METHANES. X-RAY CRYSTAL STRUCTURES OF $(4\text{-}CH_3\text{-}C_6H_4\text{-}N{=}PPh_2)_2CH_2$ AND $(4\text{-}NO_2\text{-}C_6H_4\text{-}N{=}PPh_2)_2CH_2$

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SYNTHESIS, STRUCTURE AND REACTIVITY OF BIS(N-ARYL-IMINOPHOSPHORANYL)METHANES. X-RAY CRYSTAL STRUCTURES OF $(4\text{-}CH_3{-}C_6H_4{-}N{=}PPh_2)_2CH_2$ AND $(4\text{-}NO_2{-}C_6H_4{-}N{=}PMe_2)_2CH_2$

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The synthesis of novel bis(N-aryl-imino-phosphoranyl)methanes of the type $CH_2(PR_2{=}N{-}Ar)_2$ has been accomplished by reaction of methylene-bisphosphines with arylazides. These compounds have been fully characterized by ^1H, ^{31}P and ^{13}C NMR, IR spectroscopy, Field Desorption Mass Spectroscopy (= FDMS) and elemental analysis. Variable temperature NMR experiments and single crystal X-ray structure determinations of $CH_2(PPh_2{=}N{-}C_6H_4{-}CH_3\text{-}4)_2$ (**1a**) and $CH_2(PMe_2{=}N{-}C_6H_4\text{-}NO_2\text{-}4)_2$ (**1f**) reveal that bis(N-aryl-imino-phosphoranyl)methane occurs as tautomer **1**. Crystals of **1a** are orthorhombic, space group Pcab, with $a = 26.602(2)$, $b = 20.521(1)$, $c = 11.8859(7)$ Å and $V = 6488.5(7)$ Å^3 ($Z = 8$, $R = 0.045$ and $R_w = 0.066$). The crystals of **1f** are monoclinic, space group C/2c, with $a = 20.153(4)$, $b = 5.952(1)$, $c = 16.930(5)$ Å, $\beta = 106.24(3)°$ and $V = 1949.6(6)$ Å^3 ($Z = 4$, molecular symmetry C_2, $R = 0.051$ and $R_w = 0.079$). Both molecules consist of 2 iminophosphoranyl units bridged by a methylene group. The P=N bond distances of 1.568(2) and 1.566(2) Å for **1a** and 1.580(4) Å for **1f** represent normal values for iminophosphoranyl compounds. The N-C bond lengths of 1.386(2) and 1.390(2) Å (**1a**) or 1.372(5) Å for **1f** indicate that some electron delocalisation over the N-aryl moiety takes place. In **1a** the electron delocalisation takes place separately in each iminophosphoranyl entity, while in **1f** electron delocalisation occurs only in the N-aryl-NO_2 moiety.

Compound **1a** is easily deprotonated using lithium-diisopropylamide or NaH and shows typical iminophosphoranyl chemistry, since with CO_2 an aza-Wittig reaction has been found and with HX (X=Cl, Br) protonation of both imide nitrogen atoms has been observed.

Key words: Iminophosphorane; bis(iminophosphoranyl)methane; X-ray crystal structure; aminophosphonium; iminophosphoranylmethanide; organophosphorus.

INTRODUCTION

The synthesis, structure and chemistry of iminophosphoranes have been thoroughly explored and reported in reviews (e.g. ref. 1). Despite the fact that several bis(iminophosphoranyl)methane (= bipm) compounds (**1**), in which two iminophosphoranyl units are bridged by a methylene group, are known and their synthesis is straightforward,[2–4] little attention has so far been focussed on their chemistry and structural characterization, for instance not one crystallographic

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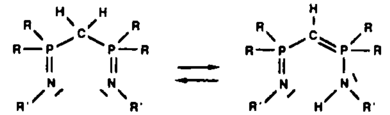
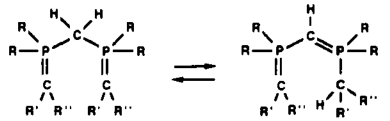
study has been reported to date. This lack of data is surprising, the more because interesting chemistry of such polyfunctional molecules can be expected a priori. In particular, the presence of two strongly polarized P═N moieties bridged by a methylene group may give rise to novel structural and chemical features. Our particular interest lies in the possible coordination and C–H activation of this virtually unexplored ligand toward electron rich transition metal centres, as can be inferred from a recently published preliminary account on the coordination and organometallic chemistry of bipm with Rh(I) compounds.[5] In order to be able to draw comparisons between structural and spectroscopic features of the free ligands on the one hand and their organometallic derivatives on the other hand, we have first turned our attention to the synthesis and structural investigation of several members of this group of potentially versatile ligands.



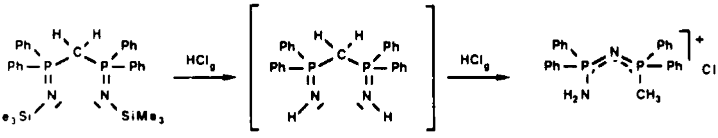
1 1'



2 2'

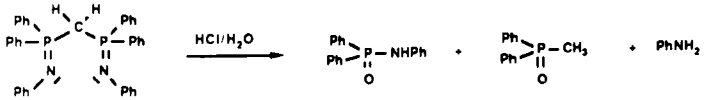
Concerning the molecular structure of bipm (**1**) one may anticipate tautomeric behaviour in solution as has been found for the isoelectronic bis(methylenephosphoranyl)methanes (**2**). Appel *et al.*[6] could establish a tautomeric equilibrium for **2** (R = Ph, R′ = R″ = $SiMe_3$): a hydrogen migrates from the central carbon atom in **2** to the terminal ylid carbon atom to give **2′**. However Schmidbaur *et al.*[7] showed that bis(phenyl-methylene-diphenylphosphoranyl)-methane (**2**; R = Ph, R′ = H, R″ = Ph) exists as tautomer **2′** both in solution and in the solid state.

As expected, the reactivity of bipm is strongly influenced by the polar character of the P═N bond. The methylene bridge, however, has a substantial impact on the final product formation. Appel *et al.*[3] found that reaction of N-silyl substituted bipm (**1**; R = Ph, R = $SiMe_3$) with HCl-gas leads to an amino-[phosphoranylidenamino]-phosphonium chloride (equation 1). The first step in this reaction is probably the formation of bipm (**1**) with R = Ph and R′ = H via substitution of both trimethylsilyl groups by hydrogen (Equation 1). After protonation of one of the iminophosphoranyl groups by HCl, nucleophilic attack of the imide nitrogen on the electrophilic phosphorus atom of the protonated iminophosphoranyl entity takes place. The final product is formed in a rearrangement reaction in which the P–C bond, involving the methylene group, is broken



(1)

and a P–N bond as well as a methyl group is formed. When N-phenyl substituted bipm (**1**, R = R′ = Ph) is reacted with aqueous hydrochloric acid, hydrolysis occurs instead due to nucleophilic attack of water on the aminophosphonium entity with the formation of monomeric phosphinoxides and aniline as the sole products (Equation 2).[4,8]



(2)

In this paper the synthesis and structure of several novel bis(iminophosphoranyl)methanes (bipm) are reported. The structure of bipm in solution was studied by variable temperature ^{1}H and ^{31}P NMR and in the solid state by IR spectroscopy and single crystal X-Ray structure determinations of bis(p-tolyl-imino-diphenylphosphoranyl)methane (**1a**) and bis(p-nitro-phenyl-imino-dimethylphosphoranyl)methane (**1f**). In addition, reactions of **1a** towards CO_2, some bases and HX (X = Cl, Br) have been carried out and will be discussed to illustrate the basic chemistry of bis(iminophosphoranyl)methanes. It will be shown that, in contrast with the aforementioned results obtained by Appel *et al.*[3] and Aguiar *et al.*[4,8] the reaction of **1a** with HX leads to the exclusive formation of the doubly protonated amino(aminophosphoniummethyl)phosphonium dihalide **4**.

RESULTS AND DISCUSSION

Synthesis of Bis(iminophosphoranyl)methanes (1)

Several methods for the synthesis of iminophosphoranes are known, of which the Staudinger[9] and the Kirsanov[10] reactions are the most widely applicable. Gilyarov *et al.*[2] showed that bis(N-aryl-imino-diphenylphosphoranyl)methanes, containing two P═N moieties bridged by a methylene group, can only be synthesized using the Staudinger reaction (Equation 3). We used this method to synthesize the bis(N-aryl-imino-diphenylphosphoranyl)methanes **1a**, **c** and **e**. The new bis(N-aryl-imino-dimethylphosphoranyl)methanes **1b**, **d** and **f**, with methyl substituents on both phosphorus atoms, were synthesized from bis(dimethylphosphino)methane (= dmpm) and arylazides in a similar way (Equation 3).

$$CH_2(PR_2)_2 + 4\text{-}R'\text{-}C_6H_4\text{-}N_3 \longrightarrow CH_2(PR_2{=}N\text{-}C_6H_4\text{-}R'\text{-}4)_2 \tag{3}$$

a: R = Ph, R′ = Me; d: R = Me, R′ = MeO
b: R = Me, R′ = Me; e: R = Ph, R′ = NO_2
c: R = Ph, R′ = MeO; f: R = Me, R′ = NO_2

All compounds were obtained in good yield and no other reaction products were found. The bis(iminophosphoranyl)methanes are not soluble in apolar solvents such as pentane and diethylether. Compounds **1a–d** are quite soluble in benzene, halogenated solvents, THF, nitromethane and acetonitrile, in which compounds **1e** and **1f** (R′ = NO_2) are only slightly soluble. Decomposition of the bis(iminophosphoranyl)methanes takes place upon prolonged standing in water, chloroform and alcohols (complete decomposition after circa 3 days). The P-phenyl substituted compounds appear to be insensitive towards moist air: after 2 years they could be recovered unaltered. The P-methyl substituted compounds decompose slowly in air (complete decomposition after circa 2 weeks), but are thermally stable at room temperature for at least one year when stored under nitrogen.

Molecular Structure of bis(iminophosphoranyl)methanes

NMR spectroscopy. Selected ^{1}H, ^{13}C and ^{31}P NMR spectral data of the bis(iminophosphoranyl)methanes **1a–f** measured at room temperature are listed in Table I. Full data are given in the Experimental section.

In the ^{1}H NMR spectra only one signal is found for both R′ groups in **1a–1d** indicating that these groups are isochronous. The signal for the methylene protons is split into a triplet due to coupling with the two equivalent phosphorus atoms. The ^2J(P,H) of approximately 13 Hz is in the range normally found for four coordinate P^V compounds.[11] The chemical shift values of the methylene protons show a high frequency shift in going from R = Me to R = Ph. The chemical shift values for these protons in the P-phenyl substituted bis(iminophosphoranyl)methanes are hardly influenced by variation of R′ (compounds **1a**, **1c** and **1e**), indicating that the electronic properties of R′ are transmitted to the methylene group only by a σ-inductive effect and not by mesomeric effects. Thus electron delocalisation takes place in each separate iminophosphoranyl entity but is not extended to the entire molecule. These findings are in accordance with the results from X-ray studies (vide infra). In compounds **1b**, **1d** and **1f** a high frequency shift is observed in going from R′ = Me to R′ = NO$_2$,[13] i.e. with increasing −I effect of these substituents. The

TABLE I

Selected ^{1}H, ^{13}C, ^{31}P NMR[a] and IR[b] data of bis(iminophosphoranyl)methanes, $(p\text{-R}'\text{—C}_6\text{H}_4\text{—N}\text{=}\text{PR}_2)_2\text{CH}_2$

Compound			^{1}H[c]			^{13}C{^{1}H}[c,e]		^{31}P{^{1}H}	IR
	R	R′	δ(CH$_2$)	^2J(P,H)	δ(R′)	δ(CH$_2$)	^1J(P,C)	δ	$\tilde{\nu}$(P=N)
1a	Ph	Me	3.70(t)	13.6	2.17	30.5(t)	63.5	0.1	1323
1b	Me	Me	2.63(t)[g]	12.9	2.23	31.5(t)	57.4	5.6	1334
1c	Ph	OMe	3.67(t)	13.6	3.70	—	—	−2.5	1342
1d	Me	OMe	2.54(t)[g]	12.7	3.69	31.2(t)	57.4	5.4	1344
1e	Ph	NO$_2$	3.66(t)	13.6	—	[d]	[d]	1.8	1282
1f[f]	Me	NO$_2$	2.97(t)	12.7	—	[d]	[d]	14.1	1285

[a] Chemical shift values in ppm relative to Me$_4$Si for ^{1}H and ^{13}C spectra and to 85% H$_3$PO$_4$ for ^{31}p spectra. Coupling constants in Hz. Solvent CDCl$_3$. Complete spectral data: see Experimental section.

[b] KBr pellets; values in cm^{-1}.

[c] t = triplet;

[d] Not determined due to low solubility.

[e] Solvent CD$_2$Cl$_2$.

[f] Solvent CD$_3$NO$_2$.

[g] ^{1}H NMR (CD$_3$NO$_2$): **1b** δ(CH$_2$) 2.38 ppm, ^2J(P,H) = 12.9 Hz; **1d** δ(CH$_2$) 2.32 ppm, ^2J(P,H) = 12.8 Hz.

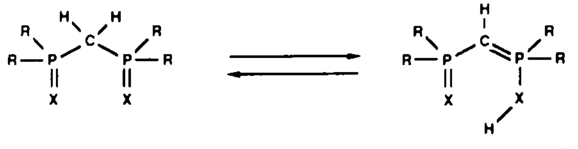
inductive effect of R′ in the P-methyl substituted compounds is more pronounced compared to the P-phenyl substituted compounds since in the latter the electronic effects are diminished by electron delocalisation into the phenyl rings.

In compounds **1b**, **1d** and **1f** the P–CH_3 protons show the X part of a $AA'X_6X'_6$ coupling pattern.[13] The intensities of the signals and the chemical shift values for compounds **1a–1f** are in agreement with predominant (>99%) presence of tautomer **1**.

The ^{13}C chemical shift assignments were made by comparison with the appropriate mono-iminophosphoranes.[14] $AA'X_2X'_2$ and $AA'X_4X'_4$ coupling patterns were found for C_{ortho} of the N-aryl groups and for C_{ortho} and C_{meta} for the P–Ph substituent respectively (**1a**). The chemical shifts and coupling constants within the aryl rings correspond to those found for mono-iminophosphoranes,[15] indicating a similar charge distribution within the phenyl and aryl substituents. Computer simulation of the $AA'X_2X'_2$ ^{13}C NMR coupling patterns for the P–CH_3 groups gives $^1J(P,C) = 77.9$ Hz, $^3J(P', C) = -8.4$ Hz and $^2J(P,P') = 27.6$ Hz for **1b** and $^1J(P,C) = 77.4$ Hz, $^3J(P',C) = -8.2$ Hz and $^2J(P,P') = 27.7$ Hz for **1d**. The signal for the methylene carbon is split into a pure triplet with $^1J(P,C) = 63.5$, 57.4 and 57.4 Hz for **1a**, **1b** and **1d** respectively, which are normal values for this type of four coordinate P^V compounds.[6]

In the ^{31}P NMR spectra only one signal is observed for the two phosphorus atoms. The chemical shift values are influenced in a similar way by variation of R′ as has been found for monomeric iminophosphoranes,[14] i.e. high frequency shifts for stronger electron withdrawing R′ groups. All NMR data clearly demonstrate that the bis(iminophosphoranyl)methanes have at least C_S symmetry in solution on the NMR timescale at room temperature.

Variable temperature NMR experiments were performed in order to establish whether a tautomeric rearrangement to **1′** occurs at low temperature, as has been found for the isoelectronic bis(methylenephosphoranyl)methane **2**.[6] No change was observed in both ^1H and ^{31}P NMR down to 193 K in CD_2Cl_2, indicating that tautomerization to **1′** does not occur and that bipm exists in the groundstate as tautomer **1** even at low temperature in solution. This difference in tautomeric behaviour with respect to the bis(methylenephosphoranyl)methane **2** can be explained by invoking the higher basicity of the phosphinylid group in **1′** compared to the phosphinimide groups in **1**.[1b,15] Hence, the tautomeric equilibrium (Equation 4) lies completely on the left hand side for bis(iminophosphoranyl)methanes (**1**). In bis(methylenephosphoranyl)methanes (**2**) the difference in basicity between the central and terminal phophinylid groups is less pronounced. Thus for compound **2** the equilibrium (Equation 4) is strongly influenced by variation of temperature and/or substituents on P and C.[6,7]



(4)

In accordance with the observations made by Aguiar *et al.* (4) the methylene protons of **1** are kinetically labile, as demonstrated by the disappearance of the triplet in the ^1H NMR spectrum in D_2O or CD_3OD solutions, due to H/D

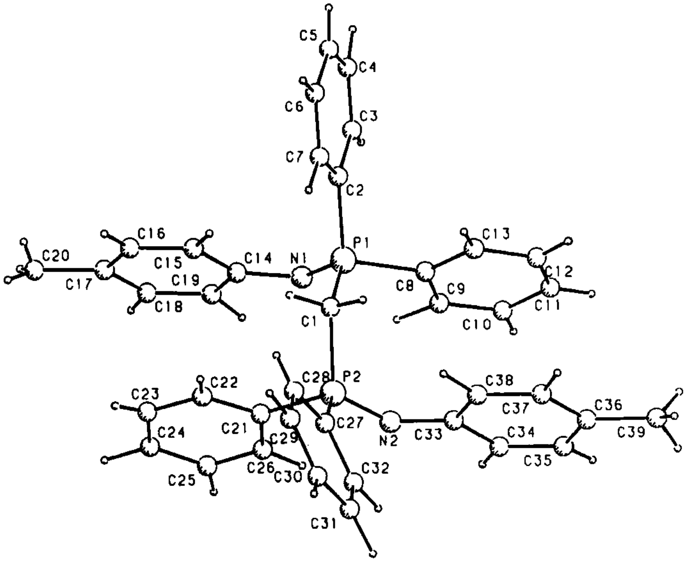


FIGURE 1 The molecular structure of $CH_2(PPh_2{=}N{-}C_6H_4{-}CH_3\text{-}4)_2$; (**1a**).

exchange reactions. In non purified commercial $CDCl_3$ enough D^+ is present to give exchange with the methylene protons.

IR spectroscopy. IR spectra (KBr) of the compounds **1a–f** show one intense absorption in the $\bar{\nu}(P{=}N)$ region (Table I). The absence of absorptions in the $\bar{\nu}(N{-}H)$, $\bar{\nu}(P{=}C)$ or $\bar{\nu}(P{-}N)$ regions indicate that bis(iminophosphoranyl)methanes have structure **1** in the solid state as well. Variation of the para substituent R′ influences $\bar{\nu}(P{=}N)$ in a similar way as has been found for mono iminophosphoranes,[1] namely a hypsochromic shift with increasing electron donating capacity of R′. Substitution of R = Ph by Me has little influence on $\bar{\nu}(P{=}N)$.

Crystal structures of $(4\text{-}CH_3{-}C_6H_4\text{-}N{=}PPh_2)_2CH_2$ (**1a**) *and* $(4\text{-}NO_2{-}C_6H_4{-}N{=}PMe_2)_2CH_2$ (**1f**): The molecular structures and the adopted numbering scheme are shown in Figures 1 and 2 for compounds **1a** and **1f** respectively. Intramolecular bond distances and bond angles are given in Table II for **1a** and in Table III for **1f**.

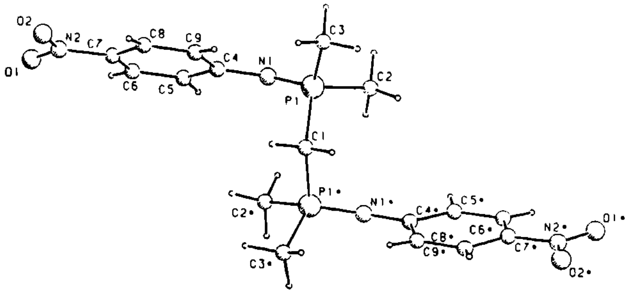


FIGURE 2. The molecular structure of $CH_2(PMe_2{=}N{-}C_6H_4{-}NO_2\text{-}4)_2$; (**1f**).

TABLE II

Bond lengths (Å) and angles (°) of the non-H atoms of **1a** (e.s.d.'s in parentheses)*

P_1-C_1	1.828(2)	$C_{16}-C_{17}$	1.372(4)
P_1-C_2	1.818(2)	$C_{17}-C_{18}$	1.377(4)
P_1-C_8	1.802(2)	$C_{17}-C_{20}$	1.519(4)
P_1-N_1	1.568(2)	$C_{18}-C_{19}$	1.385(4)
P_2-C_1	1.830(2)	$C_{21}-C_{22}$	1.377(3)
P_2-C_{21}	1.797(2)	$C_{21}-C_{26}$	1.383(3)
P_2-C_{27}	1.816(2)	$C_{22}-C_{23}$	1.375(3)
P_2-N_2	1.566(2)	$C_{23}-C_{24}$	1.372(4)
C_2-C_3	1.397(3)	$C_{24}-C_{25}$	1.351(4)
C_2-C_7	1.391(3)	$C_{25}-C_{26}$	1.379(4)
C_3-C_4	1.378(3)	$C_{27}-C_{28}$	1.395(3)
C_4-C_5	1.370(4)	$C_{27}-C_{32}$	1.391(3)
C_5-C_6	1.380(4)	$C_{28}-C_{29}$	1.384(3)
C_6-C_7	1.396(3)	$C_{29}-C_{30}$	1.365(4)
C_8-C_9	1.386(3)	$C_{30}-C_{31}$	1.388(3)
C_8-C_{13}	1.378(3)	$C_{31}-C_{32}$	1.381(3)
C_9-C_{10}	1.391(3)	$C_{33}-C_{34}$	1.401(3)
$C_{10}-C_{11}$	1.369(4)	$C_{33}-C_{38}$	1.404(3)
$C_{11}-C_{12}$	1.373(4)	$C_{33}-N_2$	1.390(2)
$C_{12}-C_{13}$	1.382(3)	$C_{34}-C_{35}$	1.390(3)
$C_{14}-C_{15}$	1.392(3)	$C_{35}-C_{36}$	1.388(3)
$C_{14}-C_{19}$	1.388(3)	$C_{36}-C_{37}$	1.390(3)
$C_{14}-N_1$	1.386(2)	$C_{36}-C_{39}$	1.512(4)
$C_{15}-C_{16}$	1.378(3)	$C_{37}-C_{38}$	1.383(3)
		C_1-H_{101}	0.95(2)
		C_1-H_{102}	0.92(2)
$C_1-P_1-C_2$	103.6(1)		
$C_1-P_1-C_8$	107.4(1)	$C_{17}-C_{18}-C_{19}$	122.3(3)
$C_1-P_1-N_1$	117.4(1)	$C_{14}-C_{19}-C_{18}$	121.2(3)
$C_2-P_1-C_8$	105.4(1)	$P_2-C_{21}-C_{22}$	121.9(2)
$C_2-P_1-N_1$	115.2(1)	$P_2-C_{21}-C_{26}$	120.1(2)
$C_8-P_1-N_1$	106.9(1)	$C_{22}-C_{21}-C_{26}$	118.0(3)
$C_1-P_2-C_{21}$	106.1(1)	$C_{21}-C_{22}-C_{23}$	122.0(3)
$C_1-P_2-N_{27}$	103.4(1)	$C_{22}-C_{23}-C_{24}$	119.1(3)
$C_1-P_2-N_2$	117.2(1)	$C_{23}-C_{24}-C_{25}$	119.5(3)
$C_{21}-P_2-C_{27}$	106.3(1)	$C_{24}-C_{25}-C_{26}$	122.0(3)
$C_{21}-P_2-N_2$	108.7(1)	$C_{21}-C_{26}-C_{25}$	119.4(3)
$C_{27}-P_2-N_2$	114.3(1)	$P_2-C_{27}-C_{28}$	124.4(2)
$P_1-C_1-P_2$	115.2(1)	$P_2-C_{27}-C_{32}$	117.2(2)
$P_1-C_2-C_3$	116.0(2)	$C_{28}-C_{27}-C_{32}$	118.4(2)
$P_1-C_2-C_7$	125.6(2)	$C_{27}-C_{28}-C_{29}$	120.3(2)
$C_3-C_2-C_7$	118.4(2)	$C_{28}-C_{29}-C_{31}$	120.8(2)
$C_2-C_3-C_4$	121.0(2)	$C_{29}-C_{30}-C_{31}$	119.8(3)
$C_3-C_4-C_5$	120.0(3)	$C_{30}-C_{31}-C_{32}$	120.0(3)
$C_4-C_5-C_6$	120.5(3)	$C_{27}-C_{32}-C_{38}$	120.8(2)
$C_5-C_6-C_7$	119.6(3)	$C_{34}-C_{33}-N_2$	116.2(2)
$C_2-C_7-C_6$	120.4(2)	$C_{34}-C_{33}-N_2$	118.6(2)
$P_1-C_8-C_9$	119.8(2)	$C_{38}-C_{33}-N_2$	125.2(2)
$P_1-C_8-C_{13}$	120.8(2)	$C_{33}-C_{34}-C_{35}$	121.2(2)
$C_9-C_8-C_{13}$	119.3(2)	$C_{34}-C_{35}-C_{36}$	122.1(2)
$C_8-C_9-C_{10}$	120.0(2)	$C_{35}-C_{36}-C_{37}$	117.0(3)
$C_9-C_{10}-C_{11}$	119.8(3)	$C_{35}-C_{36}-C_{39}$	122.3(3)
$C_{10}-C_{11}-C_{12}$	120.5(3)	$C_{37}-C_{36}-C_{39}$	120.7(3)
$C_{11}-C_{12}-C_{13}$	119.9(3)	$C_{36}-C_{37}-C_{38}$	121.4(2)
$C_8-C_{13}-C_{12}$	120.4(3)	$C_{33}-C_{38}-C_{37}$	122.0(2)
$C_{15}-C_{14}-C_{19}$	116.3(3)	$P_1-N_1-C_{14}$	128.7(1)
$C_{15}-C_{14}-N_1$	127.0(2)	$P_2-N_2-C_{33}$	126.7(1)
$C_{19}-C_{14}-N_1$	116.7(2)	$P_1-C_1-H_{101}$	107(1)
$C_{14}-C_{15}-C_{16}$	121.5(2)	$P_1-C_1-H_{102}$	108(2)
$C_{15}-C_{16}-C_{17}$	122.3(3)	$P_2-C_1-H_{101}$	109(1)
$C_{16}-C_{17}-C_{18}$	116.4(3)	$P_2-C_1-H_{102}$	104(2)
$C_{16}-C_{17}-C_{20}$	122.4(3)	$H_{101}-C_1-H_{102}$	114(2)
$C_{18}-C_{17}-C_{20}$	121.1(3)		

* C_1-H_{101} and C_1-H_{102} included.

TABLE III

Bond lengths (Å) and angles (°) of the non-H atoms of **1f** (e.s.d.'s in parentheses)*.

P_1-C_1	1.819(4)	C_5-C_6	1.377(6)
P_1-C_2	1.790(5)	C_6-C_7	1.384(7)
P_1-C_3	1.809(6)	C_7-C_8	1.355(7)
P_1-N_1	1.580(4)	C_7-N_2	1.446(5)
C_4-C_5	1.400(7)	C_8-C_9	1.371(7)
C_4-C_9	1.384(7)	N_2-O_1	1.212(6)
C_4-N_1	1.372(5)	N_2-O_2	1.209(7)
		C_1-H_1	0.93(4)
C_1-P_1-C_2	109.0(2)	C_6-C_7-C_8	119.9(4)
C_1-P_1-C_3	103.0(3)	C_6-C_7-N_2	118.8(4)
C_1-P_1-N_1	112.5(2)	C_8-C_7-N_2	121.3(4)
C_2-P_1-C_3	105.8(2)	C_7-C_8-C_9	120.5(5)
C_2-P_1-N_1	106.4(2)	C_4-N_9-C_8	122.2(5)
C_3-P_1-N_1	119.7(2)	P_1-N_1-C_4	128.9(3)
C_5-C_4-C_9	116.0(4)	C_7-N_2-O_1	120.5(4)
C_5-C_4-N_1	117.7(4)	C_7-N_2-O_2	117.7(4)
C_9-C_4-N_1	126.2(4)	O_1-N_2-O_2	121.8(4)
C_4-C_5-N_6	122.1(5)	P_1-C_1-H_1	101(3)
C_5-C_6-C_7	119.2(5)		

* C_1-H_1 included.

Both molecules consist of 2 equivalent iminophosphoranyl units bridged by a methylene group, as depicted in structure **1**. Bipm **1f** possesses molecular symmetry C_2 in the solid state. The P═N bond lengths (1.568(2) and 1.566(2) Å for **1a** and 1.580(4) Å for **1f**) are within the range normally found for iminophosphoranyl compounds containing a P═N—Ar unit.[16] They may conveniently be compared, for instance, with the bond distances of 1.567(6) Å in $Ph_3P{=}N{-}C_6H_4{-}Br$-2,[17] 1.566(7) Å in $Ph_3P{=}N{-}S{-}C_6H_3(NO_2)_2$-2,4,[18] 1.557(9) Å in $N_3P_3(NPPh_3)(NC_2H_4)_5$[19] or 1.535(9), 1.553(9) and 1.585(9) Å for $C_6(NO_2)_3(N{=}PPh_3)_3$.[20] The mean P–C_{ar} bond distances of 1.816(2) and 1.814(2) Å in **1a** lie within the range of values found for compounds with the general formula $Ph_3P{=}X$.[16] The P–C_{alk} bonds in **1f** of 1.790(5), 1.809(6) and 1.819(4) and in **1a** of 1.828(2) and 1.830(2) are a little shorter than the single bond values for P–C of 1.87 Å[21] or 1.85 Å in PMe_3,[22] but are comparable with the formal single P–C bonds in $(Me_3Si)_2C{=}PPh_2{-}CH{=}PPh_2{-}CH(SiMe_3)_2$ (1.762(4) and 1.821(4) Å), the tautomer **2'** with R = Ph and R' = R'' = $SiMe_3$.[6] The coordination geometry of the phosphorus atoms is approximately tetrahedral with bond angles at phosphorus between 103.4(1) and 117.4(1)° for **1a** and between 103.0(3) and 119.7(2)° for **1f**.

The N—C bonds (1.386(2) and 1.390(2) Å in **1a** and 1.372(5) Å in **1f**) are significantly shorter than the usually observed 1.45 Å for C(sp^2)-N(sp^2) single bonds[23] and the 1.417(11) Å for $Ph_3P{=}N{-}C_6H_4$-2-Br,[17] but longer than those found for $C_6(NO_2)_3(N{=}PPh_3)_3$ (average value 1.339(13) Å)[20] or compounds with a N–C bond order of 1.5 (1.34 Å).[23] The N–C bond distance is of the same order of magnitude as in diazaphenanthrene,[24] indicating that some electron delocalisation over the N-aryl moiety takes place. In phosphazene systems electron delocalisation results from the interaction of the $2p_\pi$ orbitals of the sp^2 hybridised nitrogen with the $3d_\pi$ orbitals of phosphorus.[25] When this delocalisation is extended to the π-system of the aryl group on nitrogen a widening of the P–N–C angle from 120° and planarity of the P-N-aryl moiety is expected. In fact this is observed for compound **1a**, where the P–N–C angles are enlarged (128.7(1) and 126.7(1)°) and the P and N atoms are only little offset from the tolyl planes: The distances of P_1 and N_1 towards the plane defined by C_{14}–C_{20} are 0.143(9) and 0.048(9) Å and of P_2 and N_2 towards the plane defined by C_{33}–C_{39} are 0.091(8) and 0.030(8) Å respectively. These geometrical features clearly demonstrate that electron delocalisation takes place separately in each iminophosphoranyl entity, and that there is no delocalisation over the entire molecule. The small angles between the phenyl planes C_8–C_{13} and C_{21}–C_{26} with the tolyl groups C_{14}–C_{20} and C_{33}–C_{39} (8.8 and 6.1° resp.) are most likely caused by sterical repulsion within the molecule. The other phenyl groups are probably forced into a position in which small angles are made with the P_1–C_1–P_2 plane (8 and 28°). In compound **1f** the electron delocalisation is restricted to the N_1-aryl-NO_2 moiety, since the atoms C_4–C_9 and N_1, N_2, O_1 and O_2 all lie within an approximate plane (maximum deviation from the plane is 0.09 Å). The electron delocalisation is not extended to the P=N entity, which is clearly demonstrated by the angle of 24° between the plane defined by C_4, N_1 and P_1 and the plane defined by C_4–C_9, N_2, O_1 and O_2, and by the distance of P_1 to this plane (0.44(2) Å).

The C_1–H bond distances are 0.95(2) and 0.92(2) Å for **1a** and 0.98(4) Å for **1f**. The coordination geometry around the methylene carbon atoms is approximately tetrahedral with bond angles at C_1 between 104 and 115.2° for **1a** and between 103 and 118.0° for **1f**.

All crystallographic data clearly demonstrate that the structural differences **1a** and **1f** are only small and can mainly be attributed to differences in electronic features of R and R′ and the consequent differences in electron delocalisation within two separate iminophosphoranyl entities.

Reactivity of **1a**

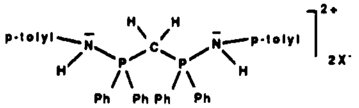
As bipm is comparable with compounds such as acetylacetone or methylenebis(phosphinoxides),[26] it is expected that it can easily be deprotonated by bases. As an example the deprotonation of **1a** was studied. If the lithium- or sodium-bis(iminophosphoranyl)methanides **3a** and **3b** could be synthesized, these would probably be suitable starting compounds for the synthesis of transition metal-bis(iminophosphoranyl)methanide complexes containing a M–C bond via transmetallation reactions.

We found that the protons of the methylene group are abstracted by the bases lithium-diisopropyl-amide (= LDA) and NaH giving **3a** and **3b** respectively. The easily achieved deprotonation with LDA or NaH is in agreement with comparable results obtained for the isostructural compounds, such as methylenebis(phosphinoxides)[26] or phosphonoacetates.[27] It has recently been shown that the lithium compound **3a** is indeed an excellent starting compound in transmetallation reactions with $[ML_2Cl]_2$ (M = Rh, Ir; L = CO, L_2 = COD)[5]. In the reaction of **1a** with BuLi decomposition into unidentifiable products took place, most likely as a result of a nucleophilic attack of BuLi on a phosphorus atom. The analogous Tl compound, which would have been a very useful reagent for transmetallation reactions with metal chlorides, could not be synthesized from **1a** and (η-C_5H_5)Tl in benzene or THF. This failure is probably due to the insolubility of (η-C_5H_5)Tl.

Reaction of **3a** or **3b** with H_2O gives **1a** in quantitative yield. Reaction of **1a** with CO_2 gave methylenebis(phosphinoxide) as well as *p*-tolyl-isocyanate and N,N'-di-*p*-tolyl-carbodiimide in an aza-Wittig reaction. Thus **1a** reacts firstly with CO_2 to form an isocyanate. The latter can react with **1a** or the oxidized product $CH_2(PPh_2{=}N\text{-}p\text{-tolyl})(PPh_2{=}O)$ to give the carbodiimide (Equation 5). This type of reaction is typical for iminophosphoranes[1a,c] and has a direct analogy to the Wittig reaction of compounds containing a C=O function with phosphinylids.

$$\begin{gathered} CH_2(PPh_2{=}N\text{-p-tolyl})_2 + CO_2 \longrightarrow \\ CH_2(PPh_2{=}O)_2 + \text{p-tolyl-N=C=O} + \text{p-tolyl-N=C=N-p-tolyl} \end{gathered} \tag{5}$$

On prolonged standing in H_2O, CH_3OH or $CHCl_3$ solutions (circa 3 days) **1a** decomposes into *p*-tolyl-amino-diphenylphosphinoxide and methyldiphenylphosphinoxide via hydrolytic cleavage of the P–C bond. Aguiar *et al.*[4] observed similar decomposition of bis(phenyl-diphenylphosphoranyl)methane (**1**, R = R' = Ph) in aqueous hydrochloric acid (Equation 2). In the reaction of **1a** with HX (X = Cl, Br) the amino(aminophosphoniummethyl)phosphonium dihalides **4a** and **b**, arising from double protonation of **1a**, were isolated. In contrast to the results of Appel *et al.*[3] and Aguiar *et al.*[4] we found that these compounds are stable in solution and in the solid state at room temperature and that hydrolysis took place only after prolonged standing in the presence of water. Under the reaction conditions employed (short reaction time in benzene or a water/benzene mixture), compounds **4a** and **4b** could be isolated in good yield. Attempts to synthesize the mono protonated amino(iminophosphoranylmethyl)phosphonium chloride **5a** from **1a** with 1 equivalent HCl failed due to proton exchange reactions between **1a**, **5a** and **4a** (Equation 6). In the ^{31}P-NMR spectrum of the reaction mixture (C_6H_6/C_6D_6) three broad signals are found at approximately 0 (**1a**), 26 (**5a**) and 29 ppm (**4a**). Work up of this mixture gave according to the IR spectrum (KBr pellet), a mixture of **1a** and **4a**. Upon dissolution of the reaction products in $CDCl_3$ an equilibrium mixture was reestablished, as indicated by the ^{1}H and ^{31}P NMR spectra, in which broad signals were found that could be assigned to **1a**, **4a** and **5a** (^{31}P: 0, 24 and 28 ppm resp.; ^{1}H NMR 3.7; 6.5 and 5.2 ppm for the methylene protons and 11.0 and 9.4 ppm for the N–H protons of **4a** and **5a** resp.)



4 a: X=Cl
b: X=Br

$$\begin{aligned} \underset{\mathbf{1a}}{CH_2(PPh_2{=}N\text{-p-tolyl})_2} &\xrightleftharpoons{HCl} \underset{\mathbf{5a}}{[CH_2(PPh_2{=}N\text{-p-tolyl})(PPh_2\text{-NH-p-tolyl})]^{+}Cl^{-}} \\ &\rightleftharpoons \underset{\mathbf{4a}}{[CH_2(PPh_2\text{-NH-p-tolyl})_2]^{2+}\cdot 2Cl^{-}} \end{aligned} \tag{6}$$

In the ^{31}P NMR spectrum of **4a** and **4b** one signal is found at approximately 29 ppm, representing a normal high frequency shift of ca 29 ppm upon protonation of the imino nitrogen.[3,28] In the ^{1}H NMR spectrum one signal has been found for the N–H protons at 10.87 and 11.30 ppm for **4a** and **4b** respectively. This signal is split into a doublet due to coupling over two bonds with one phosphorus atom. The methylene signals are found at 6.49 and 7.72 ppm for **4a** and **4b** respectively. These values are within the range normally observed for hydrogen atoms bonded to a carbon atom which is attached to two formally positively charged atoms, i.e. in $[CH_2(PPh_2—CH_2Ph)_2{\cdot}2Br^-]$[7] or $[CHMe(CPh{=}O)(CPh—OH)Br]$[29]. In their IR spectra (KBr pellets) signals are found at 2740 and 980 cm^{-1} that can be attributed to $\bar{\nu}$(N–H) and $\bar{\nu}$(P–N) of a R_3P-NHR′ group respectively.[30] In view of these data the structure of **4** may be characterized as depicted, i.e. with two discrete aminophosphonium entities.[30]

The decomposition reaction with water (vide supra) is due to nucleophilic attack of H_2O on the positively charged P atom and yields the same type of products as found by Aguiar *et al.* (Equation 2).[4] The reactivity of compound **1a** towards HCl is different with respect to $CH_2(PPh_2{=}NH)_2$ (the latter is the proposed intermediate in the reaction of $CH_2(PPh_2{=}N—SiMe_3)_2$ with HCl). Whereas **1a** reacts with HCl to give the doubly protonated compound **4a**, $CH_2(PPh_2—NH)_2$ reacts with HCl to give an amino-[phosphoranylidenamino]-phosphonium chloride (Equation 1), probably via an intermediate amino(iminophosphoranylmethyl)phosphonium chloride. The difference in reactivity of **1a** and $CH_2(PPh_2{=}NH)_2$ towards HCl may be attributed to the reduced nucleophilicity of the P=N-*p*-tolyl group in the intermediate amino(iminophosphoranylmethyl)phosphonium chloride (**5a**) due to electron delocalisation within the aryl ring.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC100 and WM250 spectrometers. ^{31}P NMR spectra were obtained on Bruker WP80 and AC100 spectrometers. Chemical shift values are in ppm relative to Me_4Si for ^{1}H and ^{13}C spectra and to 85% H_3PO_4 for ^{31}P spectra with high frequency shifts positive. Coupling constants are in Hz. IR spectra were recorded with a Perkin Elmer 283 spectrophotometer. Field Desorption (FD) mass spectra were obtained on a Varian MAT711 double focussing mass spectrometer, fitted with a 10 µm tungsten wire FD-emitter containing microneedles with an average length of 30 µm, and were performed by the Institute for Mass Spectroscopy of the University of Amsterdam. Elemental analyses were carried out by the section Elemental Analysis of the Institute for Applied Chemistry, ITC/TNO, Zeist, The Netherlands.

All the reactions and manipulations were carried out in an atmosphere of purified nitrogen, using standard Schlenk techniques. Solvents were carefully dried and distilled prior to use, unless stated otherwise.

Bis(diphenylphosphino)methane (dppm) bis(dimethylphosphino)methane (dmpm), $(iPr)_2NH$, NaH, *n*-BuLi in hexane and CF_3COOH were obtained commercially and used without purification. *p*-R-phenylazide (R = NO_2, Me, OMe)[31] and TlCp[32] were synthesized by literature procedures.

Synthesis of Bis(p-tolyl-imino-diphenylphosphoranyl)methane (**1a**). In a typical experiment 5.64 g (=83 mmol) *p*-tolylazide in 20 ml benzene was slowly added to a stirred solution of 8.0 g dppm (=42 mmol) in 50 ml benzene at 60°C. After stirring the reaction mixture for 4 hr at 60°C the solvent was removed in vacuo. The residue was washed with petroleum ether (bp. 60–80°C) and pentane and dried in vacuo giving beige **1a** in 98% yield. ^{1}H NMR ($CDCl_3$): 2.17 (6H); 3.70 (2H, t, ^2J(P,H) = 13.6 Hz); 6.42 (4H, d, ^3J(H,H) = 8.3 Hz); 6.77 (4H, d, ^3J(H,H) = 8.3 Hz); 7.23–7.46 (12H, m); 7.60–7.81 (8H, m). ^{31}P(^{1}H) NMR ($CDCl_3$): 0.1 ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): 30.5 (CH_2, t, ^1J(P,C) = 63.5 Hz); *p*-tolyl: 20.6 (CH_3); 123.3 (C_{ortho}, vt, 9.9 Hz[33]); 126.6 (C_{para}); 129.7 (C_{meta}); 148.6 (C_{ipso}); phenyl: 128.8 (C_{meta}, vd, 6.2 Hz[33]); 131.9 (C_{para}); 132.5 (C_{ortho}, vd, 4.7 Hz[33]); C_{ipso}: not observed. FD mass found: $m/z = 594$ (M^+; calcd. for $C_{39}H_{36}N_2P_2$: M = 594.68). Anal.calcd. for $C_{39}H_{36}N_2P_2$: C, 78.77; H, 6.10; N, 4.71. Found: C, 78.42; H, 6.26; N, 4.79.

Crystals suitable for crystal structure determination were obtained by diffusion of pentane into a CH_2Cl_2 solution of bis(*p*-tolyl-imino-diphenylphosphoranyl)methane at 20°C and 1 atm. All the other bis(iminophosphoranyl)methanes were synthesized according to the same procedure, unless stated otherwise.

Synthesis of Bis(p-tolyl-imino-dimethylphosphoranyl)methane (**1b**). From 2.38 g dmpm (= 17 mmol) in 10 ml benzene and 4.73 g *p*-tolylazide (= 34 mmol) in 20 ml benzene white **1b** was obtained in 80% yield after work up with Et_2O and drying in vacuo. ^1H NMR ($CDCl_3$): 1.76 (12H, vd, *J*(P,H) = 11.9 Hz[33]); 2.23 (6H); 2.63 (2H, t, ^2J(P,H) = 12.9 Hz); 6.62 (4H, d, ^3J(H,H) = 8.2 Hz); 6.94 (4H, d, ^3J(H,H) = 8.2 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 5.6 ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 17.5 (P—CH_3, vd, 69.9 Hz[33]); 31.5 (CH_2, t, ^1J(P,C) = 57.4 Hz); *p*-tolyl: 20.7 (CH_3); 122.6 (C_{ortho}, vd, 10.2 Hz[33]); 127.1 (C_{para}); 130.0 (C_{meta}); 148.4 (C_{ipso}, vd, 2.1 Hz[33]). FD mass found $m/z = 346$ (M^+; calcd. for $C_{19}H_{28}N_2P_2$: M = 346.40). Anal.calcd for $C_{19}H_{28}N_2P_2$: C, 65.88; H, 8.15; N, 8.09. Found: C, 65.49; H, 8.19; N, 8.07.

Synthesis of Bis(p-methoxy-phenyl-imino-diphenylphosphoranyl)methane (**1c**). From 1.92 g dppm (= 5 mmol) in 10 ml benzene and 1.49 g *p*-methoxy-phenylazide (= 10 mmol) in 10 ml benzene a light brown powder **1c** was obtained in 90% yield after work up with Et_2O and drying in vacuo. ^1H NMR ($CDCl_3$): 3.67 (2H, t, ^2J(P,H) = 13.6 Hz); 3.70(6H); 6.53 (8H); 7.20–7.41 (12H, m); 7.58–7.80 (8H, m). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −2.5 ppm. FD mass found: $m/z = 626$ (M^+; calcd for $C_{39}H_{36}N_2O_2P_2$: *M* = 626.68).

Synthesis of Bis(p-methoxy-phenyl-imino-dimethylphosphoranyl)methane (**1d**). 1.49 g Dmpm (= 10.9 mmol) in 10 ml benzene and 3.26 g *p*-methoxy-phenylazide (= 21.9 mmol) in 30 ml benzene gave, after work up with Et_2O, brown **1d** in circa 80% yield. ^1H NMR ($CDCl_3$): 1.71 (12H, vd, *J*(P,H) = 11.7 Hz[33]); 2.54 (2H, t, ^2J(P,H) = 12.7 Hz); 3.69 (6H); 6.57 (4H, d, ^3J(H,H) = 9.3 Hz); 6.69 (4H, d, ^3J(H,H) = 9.3 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 5.4 ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 18.1 (P—CH_3, vd, 69.3 Hz[33]); 31.2 (CH_2, t, ^1J(P,C) = 57.4 Hz); *p*-anisyl: 56.0 (OCH_3); 115.0 (C_{meta}); 123.3 (C_{ortho}, vt, 8.8 Hz[33]); 145.3 (C_{ipso}); 152.4 (C_{para}). FD mass found $m/z = 377$ ($(M-H)^+$; $C_{19}H_{28}N_2O_2P_2$ requires M = 378.39).

Synthesis of Bis(p-nitro-phenyl-imino-diphenylphosphoranyl)methane (**1e**). During the addition of 16.4 g *p*-nitro-phenylazide (= 10 mmol) in 40 ml benzene to a solution of 1.92 g dppm (= 5 mmol) in 25 ml benzene at 65°C a yellow powder precipitated. After stirring the reaction mixture for one hour at 60°C, evaporation of the solvent and washing with benzene and Et_2O a yellow solid was obtained in 90% yield. ^1H NMR ($CDCl_3$): 3.66 (2H, t, ^2J(P,H) = 13.6 Hz); 7.15–7.71 (28H, m). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 1.8 ppm. FD mass found: $m/z = 656$ (M^+; calcd for $C_{37}H_{30}N_4O_4P_2$: M = 656.62).

Synthesis of Bis(p-nitro-phenyl-imino-dimethylphosphoranyl)methane (**1f**). In the reaction of 0.634 g dmpm (= 4.7 mmol) in 10 ml benzene with 1.53 g *p*-nitro-phenylazide (= 9.3 mmol) in 50 ml benzene at 70° a yellow solid is formed. After stirring for 2 hours at 70°C the precipitate is filtered off, washed with Et_2O and dried in vacuo, giving a yellow powder in 80% yield. Crystallization from acetonitrile gave orange crystals, which were suitable for crystal structure determination. ^1H NMR (CD_3NO_2): 1.95 (12H, vd, *J*(P,H) = 12.1 Hz[33]); 2.97 (2H, t, ^2J(P,H) = 12.7 Hz); 6.70 (4H, d, ^3J(H,H) = 8.7 Hz); 7.93 (4H, d, ^3J(H, H) = 8.7 Hz). $^{31}P\{^1H\}$ NMR (CD_3NO_2): 14.1 ppm. FD mass found: $m/z = 408$ (M^+; calcd for $C_{17}H_{22}N_4O_4P_2$: M = 408.34). Anal.calcd. for $C_{17}H_{22}N_4O_4P_2$: C, 50.00; H, 5.43; N, 13.72. Found: C, 49.54; H, 5.48; N, 13.60.

Synthesis of Lithium-bis(p-tolyl-imino-diphenylphosphoranyl)methanide (**3a**). 0.84 ml of a 0.57 M LDA (= lithiumdiisopropylamide) solution in Et_2O, which was prepared from diisopropylamine and butyllithium, was added slowly to a suspension of 284.8 mg of **1a** (= 0.48 mmol) in 20 ml Et_2O. After stirring for two hours at room temperature a white solid had precipitated. After concentration to about half the volume and addition of 20 ml pentane the precipitate was filtered off under N_2 and washed with pentane yielding a white powder in quantitative yield. ^1H NMR (C_6D_6): 2.16 (6H); 3.7 (1H, br); 6.91 (20H); 7.62–7.82 (8H, m). $^{31}P\{^1H\}$ NMR (C_6D_6): 2.0 ppm.

Synthesis of Sodium-bis(p-tolyl-imino-diphenylphosphoranyl)methanide (**3b**). A suspension of 166.3 mg NaH (= 6.93 mmol) in 20 ml THF was added to a solution of 1060 mg **1a** (= 1.78 mmol) in

15 ml THF. After stirring for 1.5 hr at room temperature the yellow solution was filtered and evaporated to dryness in vacuo. After washing with pentane a light yellow powder was obtained in quantitative yield. ^{1}H NMR (C_6D_6): 2.20 (6H); 3.6 (1H, br); 6.80–6.98 (20H, m); 7.65–7.86 (8H, m). ^{31}P{^{1}H} NMR (C_6D_6): −2.3 ppm. IR ν(P═N) = 1328, 1303. Anal.calcd. for $C_{39}H_{35}N_2NaP_2$: C, 75.96; H, 5.72; N, 4.54; P, 10.05. Found: C, 75.95; H, 6.07; N, 4.27; P, 10.29.

Hydrolysis of **3a** *and* **3b**. To a solution of 0.05 mmol **3a** or **3b** in 4.5 ml C_6D_6 60 µl H_2O was added. **1a** was obtained in quantitative yield according to ^{1}H and ^{31}P NMR.

Reaction of **1a** *with* (η-C_5H_5)*Tl*. To a suspension of 108 mg (η-C_5H_5)Tl (=0.40 mmol) in 10 ml benzene, 243 mg **1a** (=0.41 mmol) was added slowly. After stirring 1 hr at room temperature no reaction was observed. Even after refluxing a mixture of (η-C_5H_5)Tl and **1a** in equimolar quantities in THF for 4 hrs no reaction had occurred.

Reaction of **1a** *with* CO_2. CO_2 gas, which was obtained by slow evaporation of solid CO_2 at room temperature, was bubbled through a solution of 171 mg **1a** (= 0.29 mmol) in 30 ml benzene at room temperature for 3/4 hour and at 60°C for another 3/4 hour. Then the solvent was removed in vacuo. The residue was washed with pentane and dried in vacuo giving a white powder, which was analysed as $CH_2(PPh_2{=}O)_2$ by IR, ^{1}H and ^{31}P NMR spectroscopy.[34] The products obtained by evaporation of the solvent of the combined washings could be identified as *p*-tolyl-N═P═O and *p*-tolyl-N═C═N-*p*-tolyl in a ratio of circa 2:1.[35]

Reaction of **1a** *with HCl.*

method 1: Dry HCl gas, obtained by addition of concentrated H_2SO_4 to NH_4Cl, was bubbled through a solution of 200 mg **1a** (= 0.34 mmol) in 25 ml benzene for 1 hour at room temperature. Then the solution was evaporated to dryness in vacuo. The residue was crystallized from acetone giving white crystals (**4a**) in circa 90% yield, which were quite soluble in water, dichloromethane and chloroform, but slightly soluble in acetone and benzene. ^{1}H NMR ($CDCl_3$): 2.13 (6H); 6.49 (2H, t, ^2J(P,H) = 15.6 Hz); 6.65 (4H, d, ^3J(H,H) = 8.6 Hz); 6.79 (4H, d, ^3J(H,H) = 8.6 Hz) 7.41–7.72(12H, m); 8.07–8.28 (8H, m); 10.87 (2H, d, ^2J(P,H) = 5.6 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): 28.7 ppm. IR: $\bar{\nu}$(N—H) = 2740 cm^{-1}; $\bar{\nu}$(P—N) = 980 cm^{-1}. Anal.calcd. for $C_{39}H_{38}Cl_2N_2P_2$: C, 70.17; H, 5.77; N, 4.20; Cl, 10.62. Found: C, 69.09; H, 5.99; N, 4.28; Cl, 10.53.

method 2: Addition of 6 ml of a 10% HCl solution in H_2O to a solution of 183.1 mg **1a** (=0.30 mmol) in 10 ml benzene gave instantaneously a white precipitate. After stirring for 5 minutes the benzene was evaporated in vacuo. The water layer was extracted with CH_2Cl_2 (2 × 5 ml). After drying and evaporation of CH_2Cl_2 **4a** was obtained in 84% yield.

1a *with* 1 *equivalent HCl*: To a solution of 265.8 mg **1a** (=0.447 mmol) in 9.5 ml benzene 2 ml of a 0.223N HCl solution in Et_2O was added. During stirring the reaction mixture a white powder precipitated. After stirring for 1.5 hr. the precipitate was filtered off. The residue could be identified as **4a**. The filtrate was evaporated to dryness. According to the IR spectrum (KBr pellet) the residual white powder was a mixture of **1a** and **4a**. In solution ($CDCl_3$) an equilibrium between **1a**, **5a** and **4a** was established as indicated by ^{1}H and ^{31}P NMR (**5a**, ^{1}H NMR: 2.1(s); 5.2(brt); 6.8(br); 7.3–8.1(br); 9.4 ppm(br); ^{31}P NMR: 24 ppm(br)).

Reaction of **1a** *with HBr*. To a solution of 173.9 mg **1a** (= 0.29 mmol) in 10 ml benzene 6 ml of a 16% HBr solution in water was added. During stirring for 10 minutes a white powder precipitated. After evaporation of the benzene the waterlayer was extracted with CH_2Cl_2 (2 × 5 ml). Evaporation of CH_2Cl_2 gave white **4b** in quantitative yield. ^{1}H NMR (C_6D_6): 1.82 (6H); 6.63 (4H, d, ^3J(H,H) = 8.2 Hz); 6.85–7.12(12H, m); 7.32 (4H, d, ^3J(H,H) = 8.2 Hz); 7.72 (2H, t, ^2J(P,H) = 14.9 Hz); 8.52–8.75 (8H, m); 11.20 (2H, d, ^2J(P,H) = 4.7 Hz). ^{31}P{^{1}H} NMR (C_6D_6): 29.1 ppm.

Crystal Structure Determinations of (4-Me-C_6H_4-$N{=}PPh_2)_2CH_2$ (**1a**) *and* (4-NO_2-C_6H_4-$N{=}PMe_2)_2CH_2$ (**1f**). For **1a** a crystal with approximate dimensions 0.13 × 0.38 × 0.40 mm was used for the crystal structure determination. The crystals were orthorhombic, space group Pcab. The unit cell had the dimensions $a = 26.602(2)$, $b = 20.521(1)$, $c = 11.8859(7)$ Å, $V = 6488.5(7)$ Å^3, $Z = 8$, D_x = 1.22 g.cm^{-3}. A total of 5492 unique reflections was measured within the range $0 \leq h \leq 31$, $0 \leq k \leq 24$, $0 \leq l \leq 13$ on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated CuKα radiation and θ-2θ scan. Of these, 4013 reflections were above the significance level of $2.5\sigma(I)$. The maximum value of $(\sin\theta)/\lambda$ was 0.59 Å^{-1}. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $75 < 2\theta < 80°$. Corrections for Lorentz and polarisation effects were applied.

The structure was determined by direct methods with the program SIMPEL.[36] The H-atom positions were derived from a ΔF synthesis. Block-diagonal least-squares refinement on F, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, converged to $R = 0.045$, $R_w = 0.066$, $(\Delta/\sigma)_{max} = 1.10$. A weighting scheme $w = (6.0 + F_{obs} + 0.01 \cdot F^2_{obs})^{-1}$ was used. An extinction correction was applied. No absorption correction was applied. A final difference Fourier map revealed a residual electron density between −0.2 and 0.4 e · Å^{-3}. For **1f** a crystal with approximate dimensions 0.15 × 0.25 × 0.35 mm was used. These crystals were monoclinic, space group C 2/c. The unit cell had the dimensions $a = 20.153(4)$, $b = 5.952(1)$, $c = 16.930(5)$ Å, $\beta = 106.24(3)°$, $V = 1949.6(6)$ Å^3, $Z = 4$ and $D_x = 1.39$ g.cm^{-3}. A total of 1875 unique reflections were measured using graphite monochromated MoKα ($\lambda = 0.71069$ Å) radiation ($2.2 \leq 2\theta \leq 50°$; $-23 \leq h \leq 23$, $0 \leq k \leq 7$, $0 \leq l \leq 20$). Of these, 1078 reflections were above the 2.5σ(I) level. The structure was solved by direct methods, by means of the symbolic addition program set SIMPEL.[36] The H-atoms were found in a ΔF synthesis. An empirical absorption correction (DIFABS)[37] was applied. Block diagonal least squares refinement, anisotropic for P, C, N and O atoms, isotropic for the H-atoms-converged to $R = 0.051$, $R_w = 0.079$ (weighting scheme $w = (4.3 + F_{obs} + 0.014 \cdot F^2_{obs})^{-1}$. In a final ΔF-synthesis the residual electron density was between −0.2 and +0.2 e · Å^{-3}. Scattering factors were taken from Cromer & Mann.[38] Anomalous dispersion for P was corrected for. All calculations were performed with XRAY76.[39]

REFERENCES

1. a) G. Singh and H. Zimmer, *Organomet. Chem. Rev.* **2,** 279 (1967); b) Yu. G. Golobolov, I. N. Zhmurova and L. F. Kasukhin, *Tetrahedron* **37,** 437 (1981); c) E. W. Abel and S. A. Mucklejohn, *Phosph. Sulf.* **9,** 235 (1981).
2. a) V. A. Gilyarov, V. Yu. Kovtun and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.* **5,** 1159 (1967). b) V. Yu Koytun, V. A. Gilyarov and M. I. Kabachnik, *Izv. Acad. Nauk SSSR, Ser. Khim.* **11,** 2612 (1972).
3. R. Appel and I. Ruppert, *Z. Anorg. Allg. Chem.* **406,** 131 (1974).
4. A. M. Aguiar, H. J. Aguiar and T. G. Archibald, *Tet. Lett.* 3187 (1966).
5. a) P. Imhoff and C. J. Elsevier, *J. Organomet. Chem.* **361,** C61 (1989); b) C. J. Elsevier and P. Imhoff, *Phosph. Sulf.* special issue on XI ICPC, Tallinn, to be published.
6. R. Appel, G. Haubrich and F. Knoch, *Chem. Ber.* **117,** 2063 (1984).
7. H. Schmidbaur, U. Deschler, B. Zimmer-Gasser, D. Neugebauer and U. Schubert, *Chem. Ber.* **113,** 902 (1980).
8. A. M. Aguiar and J. Beisler, *J. Org. Chem.* **29,** 1660 (1964).
9. H. Staudinger and J. Meyer, *Helv. Chim. Acta* **2,** 635 (1919).
10. A. V. Kirsanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 426 (1950).
11. J. R. van Wazer, Determination of Organic Structures by Physical Methods (Academic Press, New York, London, 1971) vol. 4, 323.
12. Measured in CD_3NO_2: ^{1}H NMR, **1b** $\delta(CH_2)$ 2.38 ppm, **1d** $\delta(CH_2)$ 2.32 ppm, **1f** $\delta(CH_2)$ 2.97 ppm.
13. An adequate description of these second order multiplets in dependence of the coupling constants are given by R. K. Harris, *Can. J. Chem.* **42,** 2275 (1964).
14. M. Pomerantz, D. S. Marynick, K. Rajeshwar, W.-N. Chou, L. Throckmorton, E. W. Tsai, P. C. Y. Chen and T. Cain, *J. Org. Chem.* **51,** 1223 (1986).
15. K. A. Ostaja Starzewski and H. tom Dieck, *Inorg. Chem.* **18,** 3307 (1979).
16. J. Kaiser, H. Hartung and R. Richter, *Z. Anorg. Allg. Chem.* **469,** 188 (1980).
17. M. J. E. Hewlins, *J. Chem. Soc.* B 942 (1971).
18. K. W. Chiu, J. Fawcett, R. D. W. Kemmitt and D. R. Russell, *J. Chem. Soc., Dalton Trans.* 457 (1986).
19. K. C. Kumara Swamy, M. Damodara Poojary, S. S. Krishnamurthy and H. Manohar, *J. Chem. Soc., Dalton Trans.* 1881 (1985).
20. T. S. Cameron and C. K. Prout, *J. Chem. Soc.* C 2281 (1969).
21. L. Pauling, The Chemical Bond (Cornell University Press, Ithaca, 1967).
22. D. E. C. Corbridge, Phosphorus (Elsevier, Amsterdam, 1985) 38.
23. M. Burke-Laing and M. Laing, *Acta Cryst.* **B32,** 3216 (1976).
24. H. van der Meer, *Acta Cryst.* **B28,** 367 (1972).
25. P. Schuster, *Monatsh. Chem.* **98,** 1310 (1967).
26. M. I. Kabachnik, *Dokl. Akad. Nauk. SSSR* **162,** 339 (1965).
27. T. Strzalko, J. Seyden-Penne, F. Froment, J. Croset and M.-P. Simonnin, *J. Chem. Soc., Perkin Trans. II* 783 (1987).

28. M. B. Hursthouse, N. P. C. Walker, C. P. Warrens and J. D. Woollins, *J. Chem. Soc., Dalton Trans.* 1043 (1985).
29. D. R. Clark, J. Emsley and F. Hibbert, *J. Chem. Soc., Chem. Comm.* 1252 (1988).
30. E. I. Matrosov, V. A. Gilyarov, V. Yu. Kovtun and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.* **6,** 1162 (1971).
31. L. Ugi, H. Perlinger and L. Behringer, *Chem. Ber.* 91, 2330 (1958).
32. H. Kurasowa, Compreh. Organomet. Chem. (Pergamon, Oxford, 1982) vol. **1,** 749.
33. Second order multiplet: vd = virtual doublet, vt = virtual triplet; virtual coupling constants in Hz.
34. a) J. J. Richard, K. E. Burke, J. W. O'Laughin and C. V. Banks, *J. Am. Chem. Soc.* **83,** 1722 (1961); b) L. Maier and L. C. D. Groenweghe, *J. Chem. Eng. Data* **7,** 307 (1962).
35. a) G. J. Caldow and H. W. Thompson; *Spectrochim. Acta,* **13,** 212 (1958); b) G. D. Meakins and R. J. Moss; *J. Chem. Soc.* 993 (1957).
36. H. Schenk and C. T. Kiers, Simpel 83, a program system for direct methods. Crystallographic Computing 3 (Clarendon Press, Oxford, 1985).
37. N. Walker and D. Stuart, *Acta Cryst.* **A39,** 158 (1983).
38. a) D. T. Cromer and J. B. Mann, *Acta Cryst.* **A24,** 321 (1968); b) International Tables for X-Ray Crystallography (Kynoch Press, Birmingham, 1974) vol. IV, 55.
39. J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck and H. Flack, The XRAY76 system. Tech. Rep. TR-446 (Computer Science Center, Univ. of Maryland, College Park, Maryland, 1976).