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Carbodiphosphorane Isomers Based on a 1,3-Diphosphaindane Skeleton, and Their Precursors

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In a search for ring-strained carbodiphosphoranes $R_2\overline{P=C=P}R_2$, the diastereomeric bis-phosphanes **1a**(*RR, SS, RS*) and the symmetrical analogue **1c** have been converted into the corresponding cyclic methylene-bridged bis-phosphonium bromides **2a, c** and hexafluorophosphates **2b**. **2a**(*RR;SS*) and **2a**(*RS*) were separated by fractional crystallization. Treatment of **2a – c** with base (NH_3 or *n*-BuLi) yields, in a first step, the semi-ylide salts **3a – c** which, unexpectedly, undergo hydrolytic or ammonolytic cleavage at the ylidic P⩩CH⩩P bridge resulting in formation of the phosphane oxide or phosphane imine salts **5a, c** and **6a**, respectively. The second deprotonation step, using $(C_2H_5)_3P=CHCH_3$ as a transylidating agent, affords the conjugated bis-ylide **7a** in the case of **2a, 3a**(*RS*), but gives the carbodiphosphorane **4c** in the case of the methyl-free **2c, 3c**. With *n*-BuLi, **2a**(*RS*) also yields the analogous species **4a**(*RS*), probably as an $Li^{\oplus}$ adduct, as proven by its conversion into the symmetrical methylated product **8a**(*RS*). – **1c** is methylated with CH_3I at one P centre only. The resulting phosphonium salt **10** gives the mono-ylide **11** on treatment with $NaNH_2$.

Carbodiphosphoran-Isomere mit 1,3-Diphosphaindan-Gerüst und ihre Vorstufen

Bei der Suche nach ringgespannten Carbodiphosphoranen $R_2\overline{P=C=P}R_2$ wurden die diastereomeren Methyl/phenyl-bis-phosphane **1a**(*RR, SS, RS*) und ihr symmetrisches Tetraphenylanaloges **1c** zunächst in die zugehörigen methylenüberbrückten Bis-phosphonium-bromide **2a, c** und -hexafluorophosphate **2b** umgewandelt. **2a**(*RR;SS*) und **2a**(*RS*) wurden durch fraktionierende Kristallisation getrennt. Die Behandlung von **2a – c** mit den Basen NH_3 oder *n*-BuLi ergibt in erster Stufe die Semi-ylid-Salze **3a – c**, die hydrolytisch oder ammonolytisch überraschend an der P⩩CH⩩P-Brücke gespalten werden, wobei die Phosphanoxid- bzw. Phosphanimin-Salze **5a, c**, **6a** entstehen. Die zweite Stufe der Deprotonierung, ausgeführt mit dem Umylidierungs-Agens $(C_2H_5)_3P=CHCH_3$, liefert im Fall von **2a, 3a**(*RS*) das konjugierte Doppelylid **7a**, im Fall der methylfreien Salze **2c, 3c** aber das Carbodiphosphoran **4c**. Mit *n*-BuLi ergibt **2a**(*RS*) ebenfalls das analoge **4a**(*RS*), vermutlich als $Li^{\oplus}$-Addukt, wie über die Methylierung zum symmetrischen Produkt **8a**(*RS*) bewiesen werden konnte. – **1c** wird von CH_3I nur an einem Phosphorzentrum methyliert. Das entstehende Phosphoniumsalz **10** ist mit $NaNH_2$ in das Ylid **11** überführbar.

Various examples of the class of cumulated double-ylides, known as "carbodiphosphoranes" $R_3P=C=PR_3$, have been reported since the discovery of the hexaphenylated compound in 1961 [1]. The structure and stability of the systems **A** are not only markedly influenced by the

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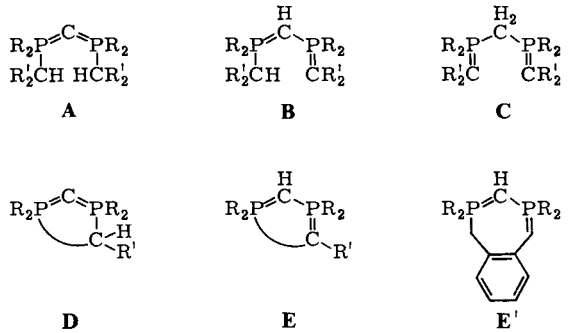
nature of the substituents R and CHR'_2 attached to the phosphorus atoms[2,3], but also in particular by ring strain in cyclic species[4-6]. Carbanion-stabilizing substituents may even cause prototropic rearrangements to afford conjugated isomeric double-ylides[7-10] (**B**). Form **B** is favoured, e.g. by benzyl, mesityl, fluorenyl, cyclopentadienyl or silylmethyl groups[7-9]. The existence of a second isomeric form **C** has not yet been conclusively confirmed[10].



A **B** **C**

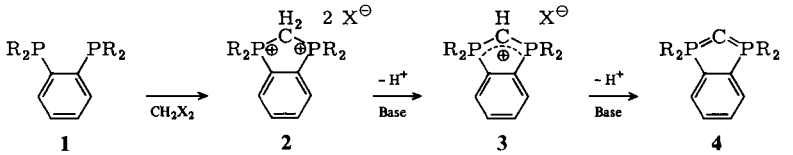
D **E** **E'**

Similar isomerism is valid for cyclic compounds **D** and **E**, as illustrated by examples like **E'**[11].

The P=C=P angles determined to date in open-chain carbodiphosphoranes[6] range from 122 to 148°. Thus these compounds show structural flexibility similar to that observed for the isoelectronic bis(triarylphosphoranylidene)ammonium cations[12], $R_3P=N=PR_3^{\oplus}$.

In the cyclic system **D** the P=C=P angle is as low as 117°, compared with 122° for the open-chain conterpart $MePh_2P=C=PPh_2Me$. In these two cases the incorporation of the P=C=P unit into the ring does not impose a strong compression of the P=C=P angle, and the two systems are of comparable stability[6].

However, five-membered ring species appear to be much less favoured than the six-membered rings, and the only example described in the literature is not very well characterized due to its limited range of stability and low solubility: $Ph_2\overline{P=C=PPh_2[CH_2]_2}$[5,13]. In order to investigate further the dependence on ring strain of carbodiphosphorane stability and isomerism, the deprotonation of cyclic bis-phosphonium cations of the type **2** was studied which might lead to compounds **3** and **4** (or possible isomers), which incorporate an *ortho*-phenylene moiety in the five-membered carbodiphosphorane ring.

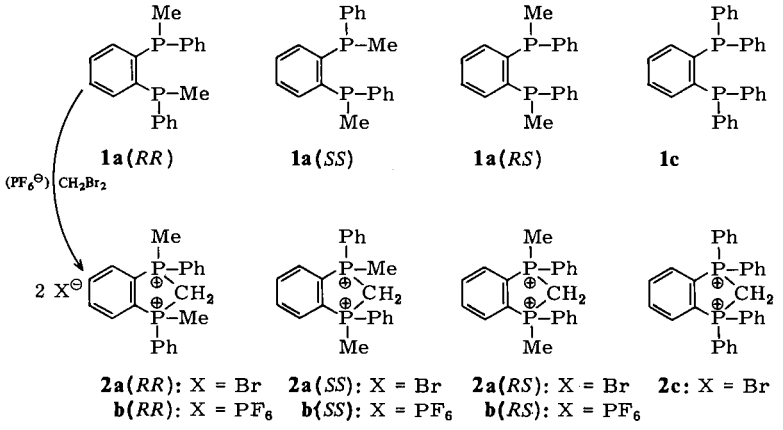


1 **2** **3** **4** (1)

In a concurrent investigation[14] the ylide formation in related 2-phosphoniaindane systems was also studied.

I. Preparation and Properties of the Phosphonium Salt Precursors

The required cyclic phosphonium salts (**2**) were prepared from the corresponding 1,2-bis(diorganophosphino)benzenes **1** and dihalomethanes as described previously for the case of **2a**(*RR, SS, RS*) where the phosphane starting compound exists as a racemic(*RR;SS*) and *meso*(*RS*) isomer mixture (**1**)[15].



(2)

2a(*RR*): X = Br **2a**(*SS*): X = Br **2a**(*RS*): X = Br **2c**: X = Br
b(*RR*): X = PF_6 **b**(*SS*): X = PF_6 **b**(*RS*): X = PF_6

The three isomers **2a** have been obtained in the earlier studies from the separated individual diphosphanes of **1a** and identified via their ^1H NMR patterns: The geminal protons of the CH_2 bridge are equivalent for the *RR, SS* isomers, but inequivalent for the *RS* isomer[15].

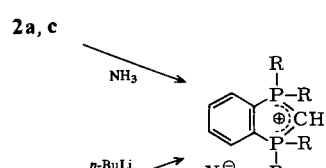
In the present study the mixture of diphosphanes **1a** (*RR, SS, RS*) was quaternized directly with CH_2Br_2, and the isomers **2a** separated by fractional crystallization. The CH_2 protons of these salts do not appear in the ^1H NMR spectra of solutions in D_2O, as they undergo rapid deuterium exchange in this solvent. In CF_3CO_2H however, the geminal inequivalence in **2a** (*RS*) is clearly evident: An ABX_2 spectrum results, which reduces to an AB spectrum under ^{31}P decoupling. The hexafluorophosphate **2b** (*RS*) shows a simple triplet in CD_3CN, apparently because of accidentally equivalent CH_2 protons under these conditions. The isomer separation described in the Experimental Section presents a significant advantage over the much more difficult procedure necessary at the stage of the phosphanes.

1c reacts with CH_2Br_2 in toluene only very slowly, and yields are still below 70% after one week at reflux temperature. The product is easily characterized by its NMR spectra (Table 1). The triplet signal of the CH_2 bridge protons disappears rapidly on addition of D_2O even in the acidic CF_3CO_2H solution, indicating again a fast deuteration of the CH_2 group. The ^{31}P signal is unaffected by this H/D exchange.

II. Single Deprotonation Reactions: Semi-ylide Phosphonium Salts

In a series of experiments with various base reagents the use of anhydrous *liquid* ammonia proved to be the method of choice, but *n*-butyllithium in an ethereal solvent is also an acceptable alternative. The dibromides **2a** react rapidly with liquid ammonia (or anhydrous ammonia solutions) with elimination of NH_4Br to produce the monobromides **3a** [See eq. (3)].

The dibromides **2a** do not react rapidly with one equivalent of *n*-BuLi in pentane; after several hours most of the starting material remains unreacted. In contrast to this, the hexafluorophosphates **2b** react immediately with *n*-BuLi even at −78 °C to give compounds **3b** in good yields.



3a (*RR*): X = Br
3a (*SS*) : X = Br
3a (*RS*) : X = Br

R = Me/Ph (3)

3b (*RR*): X = PF_6
3b (*SS*) : X = PF_6
3b (*RS*) : X = PF_6

3c: X = Br
R = Ph

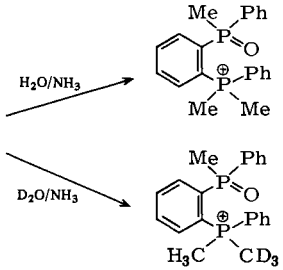
The ^1H NMR spectra show the expected changes resulting from the single deprotonation at the CH_2 bridge. The remaining proton gives a triplet signal with ca. $^2J(PH)$ = 10 Hz, a slight reduction from the 13 Hz observed for **2**. These values compare with 6 and 16 Hz for $Ph_3PCHPPh_3^{\oplus}$ and $Ph_3PCH_2PPh_3^{2\oplus}$, respectively[16,17]. The bridge proton undergoes a substantial upfield shift of 2.5 ppm, but much less than with the above open-chain analogues (4.75 ppm)[18]. Due to an increase in $^2J(PP)$, the methyl resonances change from doublets to filled-in doublets ($A_3XX'A_3'$), again accompanied by an upfield shift (0.6 ppm for *RS* and 0.3 ppm for *RR;SS*).

The bridge proton of the semi-ylide phosphonium salts **3** can still undergo proton exchange as shown by the ^1H NMR spectra of **3b** (*RS*) in CD_3CN containing excess ammonia as a base, where no PC*H*P signal can be observed.

The changes in the ^{31}P and ^{13}C NMR spectra are qualitatively similar (Tables 1, 2), though some of the trends are not in the same direction as for the open-chain analogues. The increase in $^2J(PP)$ causes the appearance of an AXX' quintet for the CH_3 signals, and $^1J(PC)$ for the P*C*P bridge is more than doubled in the conversion of **2** into **3**.

All of the semi-ylide phosphonium salts **3** readily undergo reprotonation with anhydrous HCl or CF_3CO_2H to give the starting bisphosphonium salts **2**, as identified by their NMR spectra.

The compounds **3** are unstable in aqueous solution and react with water to give the phosphane oxides **5**, which can be readily characterized by their NMR spectra (Table 1). – The geminal methyl groups at the phosphonium centre of **5a** are inequivalent due to the chiral phosphane oxide centre.



5a: X = Br
5a': X = Br (4)

In this reaction the bridge carbon becomes one of these two inequivalent PMe_2Ph methyl carbon atoms. This can be demonstrated by generating **5a** directly from **2a** (*RS*)

Table 1. ^{1}H and ^{31}P NMR Spectra[a] (δ in ppm, rel. TMS and H_3PO_4, resp.; J in Hz)

Compound	Solvent	δCH_3	$^{2}J(PH)$	$\delta CH_2/CH$	$^{2}J(PH)$	$\delta C_6H_{5/4}$	δP	$^{2}J(PP)$
2a(*RS*)	D_2O	3.08, d	14.6	[b]	–	7.6, 8.5	41.0, s	–
2a(*RR;SS*)	D_2O	2.93, d	14.6	[b]	–	7.8, 8.4	39.5, s	–
2a(*RS*)	CF_3CO_2H	2.83, d	14.4	4.18, 4.66[c]	11.0, 14.4	7.3, 8.1	–	–
2a(*RR;SS*)	CF_3CO_2H	2.70, d	14.4	4.77, t	12.6	7.5, 8.1	–	–
2b(*RS*)	CD_3CN	2.70, d	14.5	3.92, t	13.0	7.5, 8.2	–	–
2b(*RR;SS*)	CD_3CN	2.52, d	14.4	3.91, t	13.0	7.6, 8.1	–	–
2c	CF_3CO_2H	–	–	4.80, t	11.0	7.2, 8.0	30.7, s	–
3a(*RS*)	$CDCl_3$	2.63, vd	13.8	1.89, t	9.6	7.6, 8.2	29.9, s	–
3a(*RR;SS*)	$CDCl_3$	2.73, vd	13.6	1.85, br	–	7.7, 8.3	30.7, s	–
3b(*RS*)	CD_3CN	2.08, vd	14.0	1.46, t	10.0	7.5	30.9, s	–
3b(*RR;SS*)	CD_3CN	2.17, vd	14.0	1.44, t	10.0	7.5	31.5, s	–
3c	$CDCl_3$	–	–	2.26, t	9.0	8.0	31.3, s	–
5a	D_2O	1.84, d 2.41, d 2.60, d	13.5 13.0 14.0	–	–	7.3, 7.9	24.8, d 39.9, d	9
6a	$CDCl_3$	2.03, d 3.00, d 3.09, d	13.2 13.4 13.6	–	–	7.6, 8.3	25.2, d 34.6, d	6
5c	$CDCl_3$	3.45, d	14.0	–	–	7.4, 8.2	27.8, d 32.1, d	<3
7a(*RS*)	C_6D_6	0.83, br	–	–	–	6.6, m	3.9, 26.7	57
	THF	–	–	–	–	–	5.4, 27.1	58
7a(*RR;SS*)	C_6D_6	1.0, br	–	–	–	6.7, m	5.6, 27.0	57
4a(*RS*)	C_6D_6	1.66, d	12.3	–	–	6.6	28.6, s	–
	THF	–	–	–	–	–	30.8, s	–
4a(*RR;SS*)	C_6D_6	–	–	–	–	6.6	28.4, s	–
	THF	–	–	–	–	–	29.1, s	–
4b(*RR;SS*)	THF	–	–	–	–	–	30.8, s	–
4c	THF	–	–	–	–	6.8, 7.9	29.5, s	–
8a(*RS*)	$CDCl_3$	2.59, vt 1.82, t	13.6 15.0	–	–	7.7, 8.1	27.0, s	–
9a(*RS*)	CF_3CO_2H	2.81, d 1.02, dt	13.0 18.1; 7.0	4.50, dq	14.6	7.4, 8.1	46.2, s	–

[a] s = singlet, d = doublet, t = triplet, q = quartet, v = virtual, br = broad (due to exchange broadening). – [b] H/D exchange. – [c] ABX_2, $J(HH)$ = 17.3 Hz, from $\{^{31}P\}$. – [d] $N = {}^{1}J(PC) + {}^{3}J(PC)$.

Table 2. ^{13}C NMR Spectra[a] (see Table 1)

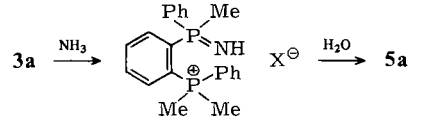
Compound	Solvent	δCH_3	$J(PC)$	δPCP	$J(PC)$	$\delta C_6H_{5/4}$
2a(*RR;SS*)	D_2O	13.81, d	53.7	–	–	109–142
2b(*RS*)	CD_3CN	8.51, dd	52.7, 1.9	17.54, t	47.4	113–137
2b(*RR;SS*)	CD_3CN	8.35, d	51.8	17.48, t	46.4	113–137
3a(*RS*)	$CDCl_3$	15.46, vt	N = 61.5[d]	–4.42, t	114.3	122–136
3a(*RR;SS*)	$CDCl_3$	15.66, vt	N = 61.5[d]	–4.74, t	114.8	122–136

in D_2O in the presence of a small amount of weak base (pyridine, e.g.). In the D_2O solution the CH_2 bridge becomes fully deuterated and upon P–C–P cleavage gives rise to an almost fully deuterated methyl group (**5a'**), showing its (weak) resonance at 2.41 ppm. The analogous experiment with **2a** (*RR;SS*) affords the weak resonance of the CD_3 group at 2.60 ppm. These results allow an unambiguous assignment of all methyl proton signals of **5a**.

Pyridine itself is not a strong enough base to induce quantitative conversion **2** → **3**. Addition of excess pyridine to solutions of **2b** (*RR;SS*) in CD_3CN only causes a downfield shift and a collapse of the multiplet structure of the CH_2 resonance, indicating rapid proton exchange and an equilibrium amount of **3b** (*RR;SS*). Pyridine thus acts only as a catalyst in the above hydrolysis.

The instability of **3** in water contrasts with the behaviour of $Ph_3PCHPPh_3^{\oplus}$, which is stable in aqueous solution. This is an indication that the compression of the PCP angle has a significant effect on the chemical properties. The mode of ring opening (at the PCP bridge instead of at a P–phenyl linkage) is also surprising. It is generally found in the base cleavage of phosphonium salts[19] that aromatic groups are displaced more readily than aliphatic groups. Clearly under ring strain the $P-\underline{C}H_2^{\ominus}$ function becomes the preferred leaving group (as compared with $C_6H_5^{\ominus}$).

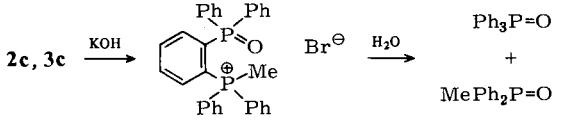
The semi-ylide phosphonium salts **3a** are also unstable in liquid ammonia, or in anhydrous ammonia solution. A new compound **6a** is produced, which contains three inequivalent methyl groups attached to phosphorus atoms. The P atoms are inequivalent and weakly coupled. **3a**(*RR;SS*) and **3a**(*RS*) yield the same product, which reacts with H_2O to produce **5a**.



6a (5)

There is, of course, a D and L form of **5a** and **6a**, but these cannot be distinguished by NMR spectroscopy.

For **2c** the liquid ammonia dehydrohalogenation is also applicable. **3c** is formed in high yield and easily characterized. Its hydrolysis and the base cleavage of **2c** (by aqueous KOH) are also initiated at the PCP bridge to give the phosphane oxide phosphonium salt first (**5c**), which finally yields triphenyl- and methyldiphenylphosphane oxide.



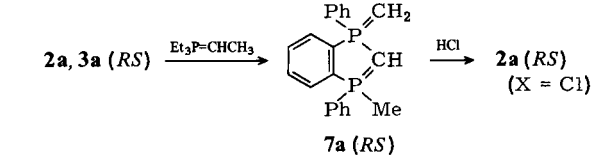
5c (6)

III. Double Deprotonation Reactions: Carbodiphosphorane Isomerism

The instability of salts **2** and **3** towards ammonia and amide cleavage (above) precludes the use of these bases for the second deprotonation step. Experiments with both

reagents produced a complex mixture of products, none of which gave **2** on reprotonation.

A reversible double deprotonation of **2a** was possible, however, by transylidation using triethylphosphonium ethylide, $Et_3P=CHCH_3$. The ^{31}P NMR spectrum of the product has an AX type pattern for two inequivalent phosphorus atoms, which shows that the conjugated double-ylide of structure **7a** has formed. Reprotonation of **7a** with nonaqueous HCl results in complete reversion to **2a** (X = Cl), in which the phosphorus atoms are again equivalent.



7a (*RS*) (7)

There is no direct evidence for the co-existence of the carbodiphosphorane isomer in this system (Formula **4**), but broad ^1H NMR signals for all non-aromatic hydrogen atoms suggest a rapid proton exchange process that may also involve a species **4**.

Such a process is quite common for mono- and polyfunctional ylides[20,21], and it has been established that this follows predominantly an intermolecular pathway with traces of acid impurity as a catalyst. Therefore it can often be retarded by addition of a strong base such as $LiAlH_4$[14].

Addition of $LiAlH_4$ to solutions of **7a** however results in gas evolution and decomposition of the compound.

Addition of small amounts of methanol as a proton source to further accelerate the proton exchange was also ineffective and caused decomposition.

The ^{31}P chemical shifts of **7a** are similar to those of other conjugated double-ylides, but $^2J(PP)$ is significantly greater than those of previously studied noncyclic compounds (Table 1)[7,8,11,22].

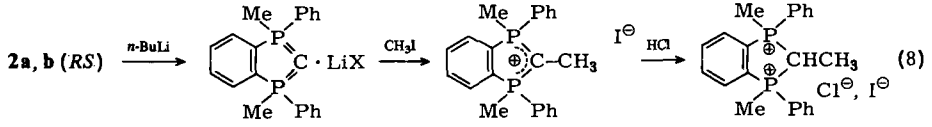
7a(*RS*), an orange microcrystalline air-sensitive solid, is too sparingly soluble in inert solvents to allow the registration of a satisfactory ^{13}C NMR spectrum. The product of the reprotonation reaction (to cation of **2a**(*RS*)) and the ^{31}P data leave no doubt, however, concerning its structure.

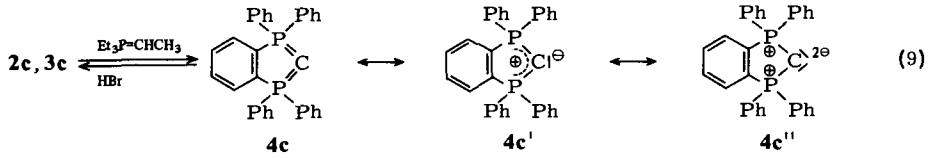
The reaction of **2a**(*RS*) with *n*-butyllithium leads to lithium-containing adducts, which are difficult to characterize. Methylation of the products in the reaction mixture affords as the main component a symmetrical species **8a**(*RS*), which may be derived from the lithium complex of a carbodiphosphorane, but a small amount of **3a**(*RS*) is also present. Treatment of this mixture with HCl in diethyl ether accordingly gives a salt precipitate consisting of mainly **9a** (*RS*) and some **2a** (*RS*).

The observations can be accounted for by the formulae in eq. (7), (8) indicating that lithium coordination shifts the prototropy equilibrium **7a** ⇌ **4a** towards the carbodiphosphorane isomer **4a**, whereas in the absence of metal salts the conjugated isomer **7a** is favoured.

2c, on treatment with $Et_3P=CHMe$ in THF at −78 °C, is converted into the cyclic carbodiphosphorane **4c**, which remains as a yellow microcrystalline solid after

evaporation of the solvent at low temperature. The compound is unstable above −30 °C and was identified through its mass spectrum (m/e = 458), its low temperature ^{1}H and ^{31}P NMR spectra and through derivatization. Ethereal HBr regenerated the starting material **2c**.





In the series **2c** – **3c** – **4c** the shift differences in the ^{31}P NMR spectra are surprisingly small: 30.7, 31.3, and 29.5 ppm, respectively. This result is in contrast to findings for related open-chain or unstrained cyclic systems, where big up-field shifts are common at least for the step semi-ylide salt/carbodiphosphorane. It therefore appears, that in the highly strained compound **4c** formulae of the type **4c'** or **4c''** should be valid, which allow for a higher positive charge at the phosphorus atoms in the ylidic species. The low thermal stability of **4c** may be one consequence of the reduced multiple bond character indicated by formulae **4c'**, **4c''**. The graphical representation in Figure 1 illustrates the marked differences in the plot of chemical shifts for three typical examples.

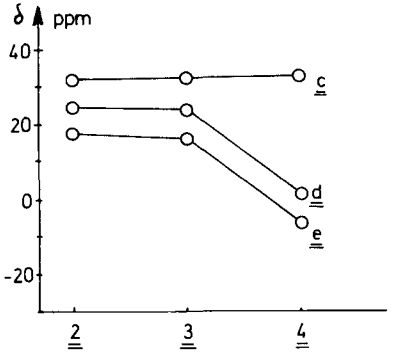
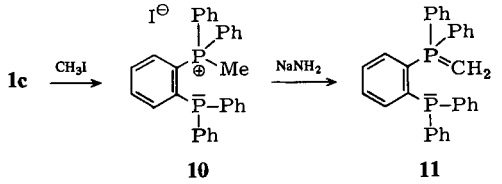


Figure 1. Plot of ^{31}P NMR chemical shifts δ[ppm] versus deprotonation state corresponding to formulae **2**, **3** and **4**. Trace **c**: **2c**, **3c**, **4c**. Trace **d**: $[Ph_2\overline{PCH_2PPh_2[CH_2]_3}]^{2\oplus}$, $[Ph_2\overline{PCHPPh_2[CH_2]_3}]^{\oplus}$, $Ph_2\overline{PCPPh_2[CH_2]_3}$. Trace **e**: $[Ph_2\overline{PCH_2PPh_2[CH_2]_4}]^{2\oplus}$, $[Ph_2\overline{PCHPPh_2[CH_2]_4}]^{\oplus}$, $Ph_2\overline{PCPPh_2[CH_2]_4}$

IV. A Mono-ylide Derived From 1c

At certain stages of the above studies reference data of related monofunctional compounds were important. For this purpose **1c** was also converted into the monophosphonium salt **10** with methyl iodide, and finally into the ylide **11**, as described in the Experimental Section. Synthetic procedures and spectral identification are straightforward.



10 **11** (10)

11 is a useful bidentate ligand. The ylide function is similar to that in $Ph_3P=CH_2$, but the complementary phosphane function further enhances the donor capacity.

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Experimental Part

General: All reactions were carried out in an atmosphere of dry, purified nitrogen, using solvents that had been dried and distilled under nitrogen. Triethylphosphane[23] and triethylphosphonium ethylide[24] were prepared by literature methods. The mixture of isomers **1a**(*RR, SS, RS*) was also obtained via the known synthetic pathway[15], but distillation of the product and separation of the isomers was not attempted, since the subsequently prepared bis-phosphonium salts **2** could readily be purified and separated by crystallization.

Apparatus: IR: Perkin Elmer 577. – NMR: Jeol C 60, Jeol FX 60, Bruker XL 90, and Bruker CXP 200.

1,2-Bis(diphenylphosphino)benzene (**1c**): 5.0 g (217 mmol) of sodium metal were added in small portions to a solution of 16.2 g (87 mmol) of diphenylphosphane in 50 ml of tetrahydrofuran. The mixture was refluxed for 2 h and filtered from unreacted metal. The clear orange-coloured filtrate was cooled to −78 °C and treated with a solution of 6.0 g (41 mmol) of 1,2-dichlorobenzene in 25 ml THF. After 2 h stirring while the mixture is warming to room temperature and two additional hours under reflux the solvent was removed and the residue crystallized from benzene/pentane. Yield 1.8 g (10%), m.p. 166 °C (lit.[25] 166.5 °C). – ^{31}P NMR (C_6D_6): δ = −14.32, s.

(RR;SS)- and (RS)-2,3-Dihydro-1,3-dimethyl-1,3-diphenyl-1,3-diphosphoniaindene dibromides (**2a**) *and bis(hexafluorophosphates)* (**2b**): Dibromomethane (22 ml, excess) was added to a crude mixture of the isomers (*RR*)-, (*SS*)- and (*RS*)-1,2-bis(methylphenylphosphino)benzene (**1a**), as obtained via a literature procedure[15] (22 g, 68 mmol). Precipitation of product began as the mixture was heated to 50 °C. At 70 °C the reaction is strongly exothermic. After 30 min at 90 °C 2-propanol (40 ml) was added to the cooled reaction mixture. On heating to 70 °C the solid became uniformly dispersed. The suspension was cooled in ice, filtered and the solid washed three times with ice-cold 2-propanol and dried in vacuo. The product (25.7 g, 76%) was dissolved in methanol (200 ml) under reflux and the solution was left to crystallize at 4 °C. Crystals of **2a** (*RS*)

were collected (8.6 g) and the filtrate was concentrated and cooled to yield a further crop (1.1 g). Total yield of **2a** (*RS*) 9.7 g (29%). – The filtrate was evaporated to dryness under vacuum to yield mainly the isomer **2a** (*RR;SS*), yield 10.8 g (32%). For the preparation of **3a** (see below) the compounds were heated in vacuo to 170°C (*RR;SS*) or 220°C (*RS*) to remove any residual methanol. The products were identified by their NMR spectra (Tables 1, 2, see also ref.[15]). The hexafluorophosphates were prepared by metathesis with $NH_4^{\oplus}$ $PF_6^{\ominus}$ in water as described previously[15]. The resulting precipitates were dried in vacuo over P_4O_{10} to yield a finely divided powder. After heating to 160°C in vacuo the samples could be used for the conversion into **3b**. The NMR spectra of the cations in **2a** and **2b** were virtually identical (Table 1).

2,3-Dihydro-1,1,3,3-tetraphenyl-1,3-diphosphoniaindene dibromide (**2c**): 4.95 g (28 mmol) of dibromomethane were added to a solution of 8.00 g (18 mmol) of **1c** in 150 ml of toluene and the reaction mixture was heated to 100°C for 10 d. Filtration and recrystallization from chloroform/methanol yielded 7.2 g (65%) of the product, m.p. 255°C (dec.).

$C_{31}H_{26}Br_2P_2$ (620.3) Calc. C 60.02 H 4.22 Found C 60.42 H 4.28

(RR;SS)- and (RS)-1,3-Dimethyl-1,3-diphenyl-3λ⁵-phospha-1-phosphoniaindene bromides (**3a**) *and hexafluorophosphates* (**3b**): 1.2 g (2.4 mmol) of **2a** (*RS*) were suspended in dichloromethane (5 ml) and the suspension was stirred at 0°C under an atmosphere of dry ammonia gas for 2 min. NH_3 and CH_2Cl_2 were then immediately removed under vacuum, and the solid residue treated with CH_2Cl_2 and filtered to remove NH_4Br. The filtrate was evaporated to dryness to give a colourless powder, yield 1.0 g (100%).

3a (*RS*): $C_{21}H_{21}BrP_2$ (415.3) Calc. C 60.74 H 5.10 Found C 58.61 H 5.37

3a(*RR, SS*) was prepared similarly from **2a**(*RR, SS*) in 92% yield, and identified via its NMR spectra.

1.6 g (2.6 mmol) of **2b** were suspended in 10 ml of tetrahydrofuran and the suspension was stirred at −78°C. To this was added dropwise 1.7 ml of a 1.60 M *n*-butyllithium (in pentane) dissolved in 10 ml of THF over a period of 15 min. The resulting suspension was warmed to room temperature, filtered, and the white solid washed with THF and vacuum dried, yield 1.0 g (80%). **3b**(*RR;SS*) crystallizes from acetonitrile/diethyl ether.

3b (*RR;SS*): $C_{21}H_{21}F_6P_3$ (480.3) Calc. C 52.51 H 4.41 Found C 52.48 H 4.46

1,1,3,3-Tetraphenyl-3λ⁵-phospha-1-phosphoniaindene bromide (**3c**): 1.83 g (2.95 mmol) of **2c** were suspended in 20 ml of dry liquid ammonia. After 1 h the ammonia was evaporated and the residue extracted with chloroform to leave behind NH_4Br. Addition of diethyl ether to the filtrate precipitated the product, yield 1.32 g (83%), m.p. 143°C (dec.).

$C_{31}H_{25}BrP_2$ (539.4) Calc. C 69.03 H 4.67 Found C 68.24 H 4.62

1,2-Didehydro-1,1,3,3-tetraphenyl-1λ⁵,3λ⁵-diphosphaindene (**4c**): A solution of 0.66 g (4.51 mmol) of triethylphosphonium ethylide in 10 ml of THF is cooled to −78°C and added to a suspension of 1.35 g (2.17 mmol) of **2c** in 10 ml THF, which is also kept at −78°C. After 1 h at −78°C the resulting yellowish-brown solution is filtered and the solvent evaporated at a temperature below −40°C. A yellow solid remains, which decomposes above −30°C.

$C_{31}H_{24}P_2$ (458.5) Molecular mass: 458, M^+ (FD-MS)

The compound is also identified by treatment with ethereal HBr, which converts it into the starting phosphonium salt **2c** as confirmed by ^1H and ^{31}P NMR spectra. For spectral data of **4c** see Table 1.

Hydrolysis of **3a**, **3b**, *and* **3c** (to give **5a**, **5b**, and **5c**): The semi-ylide salts **3a**–**c** are very unstable in aqueous solution and react immediately with water, as followed by the NMR spectra. The solu-

tions show a new AX ^{31}P NMR pattern with small ^{31}P-^{31}P coupling. After 15 min at 25°C the signals of the salts **3a** or **3b** have completely disappeared. The geminal methyl groups on the phosphonium centre of the product **5a,b** are inequivalent due to the chiral phosphane oxide centre (Table 1). – The hydrolysis of **3c** (or **2c**) requires more forcing conditions. Aqueous KOH at 80°C is also first cleaving the PCHP bridge, however, and leads eventually to the two phosphane oxides $MePh_2P=O$ and $Ph_3P=O$, as shown by NMR spectra (Table 1).

Ammonolysis of **3a** (to give **6a**): After more than a few minutes in contact with ammonia in THF, the solutions of salt **3a** show new resonances in the ^{31}P NMR spectrum. An AX pattern appears, which is very similar to that of the hydrolysis product **5a** (Table 1). It is assigned to imino analogue **6a**. This interpretation is confirmed by the hydrolysis of **6a**, which yields the oxide **5a** and ammonia. **6a** was not isolated.

cis- and trans-3-Methyl-1-methylene-1,3-diphenyl-1λ⁵,3λ⁵-diphosphaindene [**7a**(*RS*) and **7a**(*RR;SS*)]: Previously dried and powdered **2a**(*RS*) (2.1 g, 4.2 mmol) was suspended in 10 ml of THF and the suspension cooled to –78°C with stirring. 1.2 g (8.2 mmol) of $Et_3P=CHCH_3$ in 10 ml of THF were then added over a period of 5 min. A deep yellow colour developed. After 4 h stirring at –78°C and 30 min at room temperature and 20 min at 40°C the mixture was cooled and filtered. The colourless precipitate is identified as $Et_4P^{\oplus}\ Br^{\ominus}$ by its NMR spectra. It contains some unreacted **2a**(*RS*). The filtrate when concentrated in vacuo became viscous. 3 ml of benzene was added. On cooling the product **7a**(*RS*) separated as an orange micro-crystalline solid, yield 0.2 g (14%), soluble in THF, but sparingly soluble in benzene, extremely sensitive to air and moisture. $C_{21}H_{20}P_2$ (334.3) Calc. C 75.44 H 6.03 Found C 75.08 H 6.02

Treatment of THF solutions of **7a**(*RS*) with ethereal HCl gives a colourless precipitate of the phosphonium salt **2a**(*RS*), $Cl^{\ominus}$ for $Br^{\ominus}$, as the sole product, as shown by the NMR spectra. The solution is completely decolourized. *Hydrolysis* of **7a** yields the oxo-phosphonium salt **5a** (^{31}P NMR spectrum).

An analogous procedure as described for **2a**(*RS*) → **7a**(*RS*), using **2a**(*RR;SS*) gives only a yellow oil of **7a**(*RR;SS*), which could not be purified. Its treatment with ethereal HCl yields the corresponding phosphonium salt **2a**(*RR;SS*), $Cl^{\ominus}$ for $Br^{\ominus}$, however, which is an important criterion as to the identity of the material (^{31}P NMR and ^1H NMR spectra, Table 1).

Lithium bromide adducts of (R,S)- and (RR;SS)-1,2-Didehydro-1,3-dimethyl-1,3-diphenyl-1λ⁵,3λ⁵-diphosphaindene (**4a**): 2.1 g (4.2 mmol) of previously dried and powdered **2a**(*RS*) or **2a**(*RR;SS*) were suspended in 10 ml of THF and cooled to –78°C with stirring, before 5.3 ml of a 1.605 M solution of *n*-butyllithium in pentane mixed with 10 ml of THF was added dropwise (8.5 mmol) over a period of 20 min. A yellow colour developed immediately. After 27 h stirring at –78°C the reaction mixture was filtered. The solid residue consists mainly of unreacted **2a** (ca. 15%), as shown by NMR spectra. The filtrate is a thermally unstable solution of **4a**, whose ^{31}P NMR spectra were run after concentrating the solution in vacuo at 0°C. Benzene solutions were obtained after evaporating the THF solutions to dryness. An insoluble residue remains after treatment with benzene. The bright yellow filtrate is thermally more stable than the THF solution. **4a** does not crystallize.

Solutions of **4a** can be reprotonated with anhydrous HCl to produce the starting materials. NMR spectra are summarized in Tables 1, 2.

cis-1,2,3-Trimethyl-1,3-diphenyl-3λ⁵-phospha-1-phosphoniaindene iodide [**8a**(*RS*)]: To a freshly prepared THF solution of **4a**(*RS*) was added with stirring at –78°C a solution of methyl iodide in THF (excess). A precipitate formed immediately with substantial discharge of the colour of the solution. Decantation of the supernatant liquid and washing of the solid with THF yielded a product, whose NMR spectra showed that the main component was the salt **8a**(*RS*). Recrystal-

lization from CH_2Cl_2/Et_2O did not allow complete separation from unsubstituted **3a**(*RS*). – Protonation of this mixture of **8a**(*RS*) and **3a**(*RS*) with HCl in diethyl ether gave accordingly a mixture of **2a**(*RS*) and **9a**(*RS*)*), as again identified by ^1H and ^{31}P NMR spectra (Table 1).

Treatment of 1.9 g (3.1 mmol) of **2b** (*RR;SS*) in 10 ml of THF with 6.3 mmol of *n*-butyllithium in pentane/THF at –78 °C gave only the semi-ylide salt **3b**(*RR;SS*) in 30% yield (0.43 g). The properties were identical with those found previously for samples obtained from a different route (above).

[2-(Diphenylphosphino)phenyl]methyldiphenylphosphonium iodide (**10**): A solution of 11.24 g (25.2 mmol) of **1c** and 4.56 g (32.1 mmol) of methyl iodide in 150 ml of THF was stirred for 2 d at room temperature. A colourless precipitate formed which was filtered off and recrystallized from chloroform/diethyl ether, yield 14.2 g (96%), m.p. 265 °C. – ^1H NMR ($CDCl_3$): δ = 3.5, dd, $^2J(PH)$ = 14.0, $^5J(PH)$ = 2.0 Hz, CH_3; 6.76–8.00, m, $C_6H_{5/4}$. – ^{13}C NMR ($CDCl_3$): δ = 13.54, dd, $^1J(PC)$ = 63.9, $^4J(PC)$ = 19.5 Hz, CH_3; 116.9, m, $C_6H_{5/4}$. – ^{31}P NMR ($CDCl_3$): δ = 21.15 and –15.95, d each, $^3J(PP)$ = 27.5 Hz, P^V and P^{III}, resp.

$C_{31}H_{27}IP_2$ (588.4) Calc. C 63.28 H 4.62 Found C 61.54 H 4.53

[2-(Diphenylphosphino)phenyl]methylenediphenylphosphorane (**11**): A mixture of 4.3 g (7.3 mmol) of **10** and 1.3 g (33.3 mmol, excess) of sodium amide in 50 ml of anhydrous liquid ammonia was stirred for 1 h at –70 °C. The solvent was evaporated and the residue extracted with 25 ml of toluene. Evaporation of the toluene left the product in 83% yield (2.79 g), yellow-orange solid, m.p. 86–88 °C. Analytical identification was via the diphosphonium salt from re-protonation with HCl. (The NMR spectra of the products were identical with those of **10**.) – ^1H NMR ([D_8]toluene): δ = 0.38, dd, $^2J(PH)$ = 9.0, $^5J(PH)$ = 4.0 Hz, CH_2; 6.2–7.5, m, $C_6H_{5/4}$. – ^{31}P NMR ([D_8]toluene): δ = 21.7 and –15.1, d each, $^3J(PP)$ = 30.5 Hz, P^V and P^{III}, resp. – IR (Nujol): 950 cm^{-1}, ν(P=C).

*) Only one of the two possible isomers was formed (NMR).

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