Phosphane and Bis(phosphane) Ligands from Phosphinic Acids

Eric Soulier,[a] Jean-Jacques Yaouanc,[a] Pascale Laurent,[a] Hervé des Abbayes,[a] and Jean-Claude Clément*[a]

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The Boyd–Regan methodology allowed for access to various cyclic or benzylic mono- and bis(phosphinic acids) **1**–**6**. The reduction of monophosphinic acids to secondary phosphanes **7**–**9** was achieved with silanes. On the other hand, reduction of the bis(phosphinic acids) with $LiAlH_4$ led to bis(phosphanes) **12**–**13**. Various cyclic phosphanes and bis(phosphanes) were obtained by the alkylation of these secondary phosphanes (as their borane adducts). The Michael addition of the same borane adducts to vinylic phosphonates led to phosphane–phosphonates which could be hydrolysed to new hydrosoluble phosphanes.

Introduction

Phosphanes and poly(phosphanes) are among the most popular ligands. Several hundred papers have been published about them because they play a central role in coordination chemistry[1] and homogeneous catalysis.[2]

Among the numerous methods leading to such phosphanes, the reduction of phosphinic acids has been moderately exploited, perhaps because until recently a general access to phosphinic acids was not obvious. The recently described method of Regan−Boyd's group has opened the way to a large variety of such phosphinic acids from commercial hypophosphorus acid via a bis(trimethylsilyl)phosphonite intermediate.[3] This prompted us to consider their reduction as a convenient way to various secondary phosphane synthons.

Since secondary phosphanes are highly sensitive toward oxidation, the well-known air-stable phosphane−borane adducts could be valuable intermediates for an easy access, by classical methods (alkylation, Michael addition, etc.) to many tertiary mono- or bis(phosphanes) and functional phosphanes.

Results and Discussion

Phosphinic Acids

The interest in the Regan−Boyd method of synthesizing phosphinic acids lies in its versatility, which also allows Michael additions[3b] or alkylations[3c] to symmetrical or unsymmetrical phosphinic acids and, more recently to the interesting phosphorus-containing heterocycles **1** and **2** (see Table 1).

Functionalization of phenylphosphinic acid is also feasible[3d] by the same method, as depicted in Scheme 1.

We extended this straightforward and mild procedure to the preparation of other phosphinic acids. As an improvement on the Regan−Boyd method, we found it more convenient to first add an excess of ethyldiisopropylamine, since ammonium phosphinate is sparingly soluble in dichloromethane, and then wait for the dissolution of the resulting ethyldiisopropylammonium phosphinate prior to the addition of chlorotrimethylsilane. The heterocycle **3** was thus obtained from 2,2′-bis(bromomethyl)-1,1′-biphenyl (70% yield), which was previously described as a by-product in the thermal cyclization of diphosphinic acid derived from biphenyl.[4] The previously unknown (as far as we know) ferrocene-derived phosphinic acid **4** could similarly also be obtained from 1,1′-bis(chloromethyl)ferrocene. Using the same methodology, the reaction of phenylphosphinic acid with α,α′-dibromo-*m*-xylene or 2,2′-bis(bromomethyl)-1,1′-biphenyl led to the diphosphinic acids **5** or **6**, respectively.

All these acids were fully characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy (see Table 1 for selected values). As an exception, it must be noted that the ^{31}P shift of the acid **2** is found approximately 20−30 ppm upfield relative to that of the other acids. The same shielding was previously observed in a series of monocyclic phosphinic acids.[5] This is also true for the corresponding phosphanes (see below).

Reduction of Phosphinic Acids 1−6 to Secondary Phosphanes

Phosphinic acids themselves are generally more difficult to reduce than their corresponding esters or chlorides, probably because of their poor solubility in traditional solvents. Thus, a mixture $LiAlH_4/NaBH_4/CeCl_3$ reduced Ph(*o*-$MeOC_6H_4$)P(O)OEt to the corresponding phosphane−borane adduct in 91% yield, whereas the parent acid gave only a 15% yield.[6] A similar low yield was observed in the case of cyclic phosphinic acids.[7]

More interesting are the silanes, since less difference was observed between acids and their chlorides or esters. Thus,

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[a] Laboratoire de Chimie, Electrochimie Moléculaires et Chimie Analytique, CNRS UMR 6521, UFR Sciences et Techniques,
6 avenue Le Gorgeu, B. P. 809, 29285, Brest, France
Fax: (internat.) + 33-2/98016594
E-mail: jean-claude.clement@univ-brest.fr

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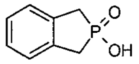
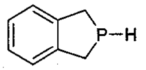
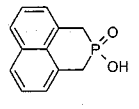
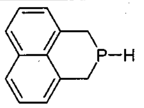
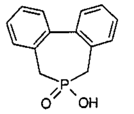
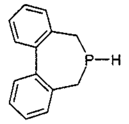
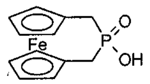
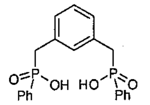
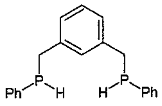
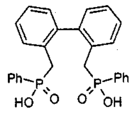
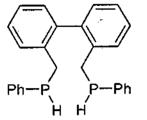
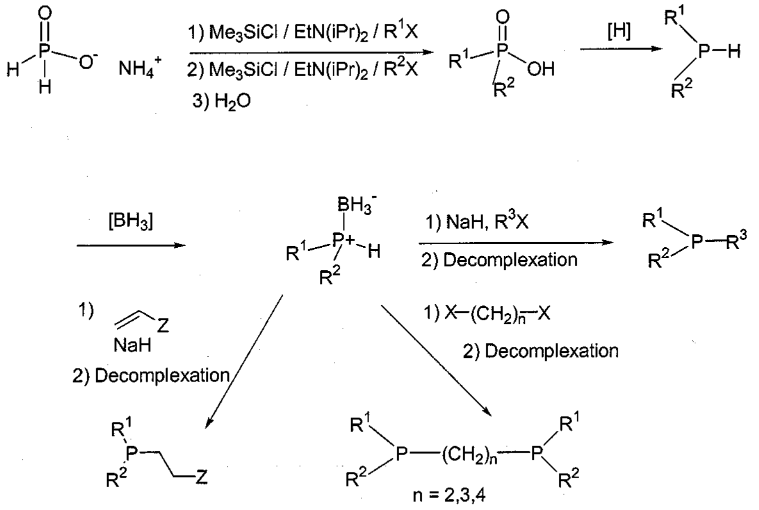
Table 1. Yields and ^{31}P NMR data for phosphinic acids and secondary phosphanes

Phosphinic acid	Yield (%)	δ (ppm) ^{31}P	Secondary phosphane	Yield (%)	δ (ppm) ^{31}P
 **1**	70	69.4	 **7**	60	–59.7
 **2**	90	39.4	 **8**	70	–82.7
 **3**	70	62.3	 **9**	70	–31.8
 **4**	43	62.5	–	–	–
 **5**	100	38.5	 **12**	46	–40.2 –40.3
 **6**	100	38.2	 **13**	54	–45.4 –45.5 –46.3 –46.3



Scheme 1

with $(C_6H_5)_2SiH_2$, Bu_2PH was obtained in 77% yield from $Bu_2P(O)OH$ compared to 95% from $Bu_2P(O)Cl$.[8] On reaction with a cyclic phosphinic acid, the same $(C_6H_5)_2SiH_2$ gave a 92% yield of secondary cyclic phosphane.[9]

In the present work, both the silanes and $LiAlH_4$ were used, depending on the starting phosphinic acid. With the monophosphinic acids **1–3**, $PhSiH_3$ was found to be convenient. After 2 h at 80–100 °C and once excess $PhSiH_3$ was removed under vacuum at room temperature, the resulting secondary phosphanes **7**, **8** and **9** were directly isolated by bulb-to-bulb distillation from the reaction mixture containing oxidized siloxanes. Since the bis(phosphinic acids) **5** and **6** were only sparingly soluble in common solvents, they were first (quantitatively) converted into their corresponding chlorides **10** and **11** with $SOCl_2$ or oxalyl chloride in dichloromethane solution. These derivatives were more soluble and were reduced with $LiAlH_4$ in THF, leading to the secondary phosphanes **12** and **13** in moderate yields.

The Borane Protection

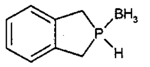
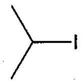
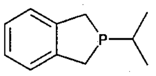
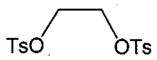
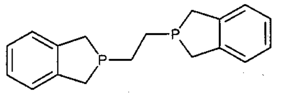
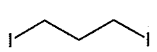
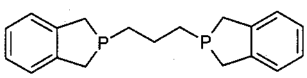
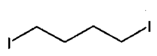
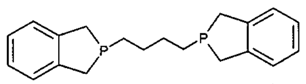
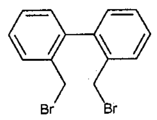
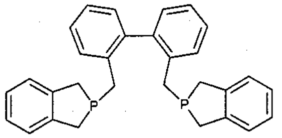
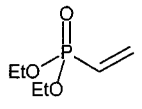
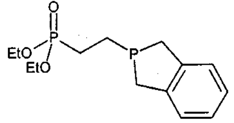
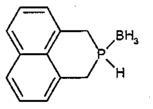
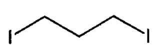
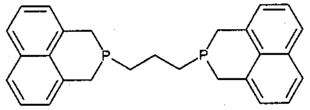
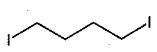
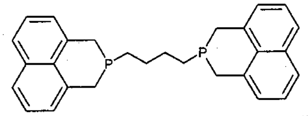
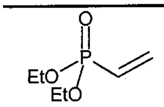
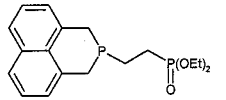
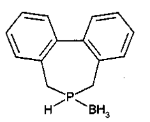
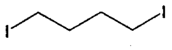
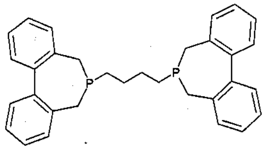
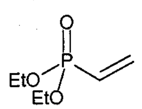
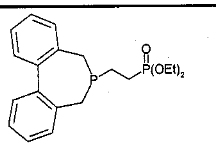
Protecting phosphanes as their borane adducts is convenient since they react readily with BH_3–THF or BH_3–SMe_2, leading to air-stable crystalline solids. They are so stable that oxidation of an adjacent functional group is feasible without oxidative cleavage of the P−B bond.[10]

In spite of this protective effect, the P−H bond remains very reactive, and phosphane−borane adducts are, for instance, good Michael donors, with[11] or without[12] base catalysis.

Deprotection is easily achieved either by heating at reflux in excess amine[11−13] or by reaction with HBF_4−OMe_2.[14]

As is the case with other alkylphosphanes, phosphanes **7−13** are very sensitive towards oxidation. Treating **7**, **8** and **9** with BH_3−THF overnight at room temperature led to the crystalline air-stable solids **14−16** (Table 2). ^{31}P NMR spectra of these adducts generally exhibit a poorly resolved multiplet in the range δ = 30−45, except for **15** (δ = −2.2). As a general rule, every derivative of the six-membered phosphinic acid **15** exhibits approximately 30 ppm shielding rel-

Table 2. Examples of tertiary phosphanes, bis(phosphanes) and phosphane−phosphonates from secondary phosphane synthons

Phosphane–borane adduct		Reactant	Phosphane		^{31}P NMR	^{13}C NMR selected C_α–P
	14			17	–1.5 (s)	31.3 (d) $^1J_{(P-C)}$ = 15.5 Hz
				18	–14.2 (s)	32.9 (d) $^1J_{(P-C)}$ = 7.4 Hz
				19	–19.2 (s)	32.9 (d) $^1J_{(P-C)}$ = 13.7 Hz
				20	–18.7 (s)	33.0 (d) $^1J_{(P-C)}$ = 13.6 Hz
				21	–8.9 (s)	32.8 (d) $^1J_{(P-C)}$ = 16.2 Hz 33.3 (d) $^1J_{(P-C)}$ = 16.1 Hz
				22	–13.3 (d) 30.8 (d) $^3J_{(P-P)}$ = 56.9 Hz	32.6 (d) $^1J_{(P-C)}$ = 14.2 Hz
	15			23	–55.9 (s)	29.4 (d) $^1J_{(P-C)}$ = 12.6 Hz
				24	–54.8 (s)	29.7 (d) $^1J_{(P-C)}$ = 11.9 Hz
				25	–51.6 (d) 31.4 (d) $^3J_{(P-P)}$ = 54.8 Hz	29.0 (d) $^1J_{(P-C)}$ = 13.6 Hz
	16			26	–28.8 (s)	28.4 (d) $^1J_{(P-C)}$ = 18.9 Hz 31.3 (d) $^1J_{(P-C)}$ = 14.6 Hz
				27	4.8 (d) 31.5 (d) $^3J_{(P-P)}$ = 56.0 Hz	30.7 (d) $^1J_{(P-C)}$ = 14.7 Hz

ative to other corresponding compounds with the same functionality (compare **2** with **1** or **3**; **24** with **20** or **26;** and **23** with **19**).

Reactivity of Phosphane−Boranes

Alkylation

From a P−H bond of a phosphane−borane complex, the generation of the P^- ion is often achieved by reaction with alkyllithium compounds.[15] In the case of compounds **14−16**, reaction with *n*BuLi led to a nonspecific deprotonation, because of the marked acidic character of the benzylic methylene groups. On the other hand, Imamoto's method (i.e. addition of one equivalent of KOH or NaH to a stoichiometric mixture of phosphane−borane and alkyl halide or tosylate) gave good to excellent results in our hands and allowed for the preparation of a variety of tertiary phosphanes and bis(phosphane−boranes) from compounds **14−16**. Unfortunately, the borane adducts of the bis(phosphanes) **12** and **13** are not reactive, and the same procedure failed, even with simpler halides such as CH_3I.

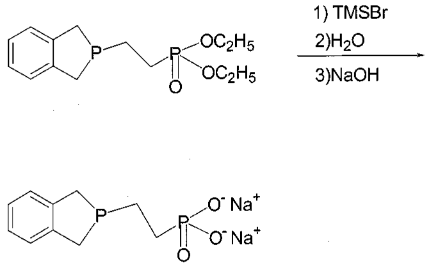
Michael Additions

Although base-catalyzed additions of primary[16] or secondary[17] phosphanes to functionally activated olefins is extensively described, we encountered some difficulties while treating phosphanes **7−9** with diethyl(vinyl)phosphonate in the presence of catalytic amounts of EtONa in ethanol, since the resulting phosphane−phosphonates were contaminated with significant quantities (up to 20%) of phosphonium−bis(phosphonates), resulting from a second addition to the vinylphosphonate, probably owing to the basic character of the phosphanes. With EtONa in THF, reaction times were exceedingly long. On the other hand, since phosphane−borane complexes add very well to activated double bonds, without[12] or with catalysts such as KOH,[7] the same protocol as for alkylations [i.e. the addition of one equivalent of NaH to a 1:1 mixture of phosphane−borane and diethyl(vinyl)phosphonate] was successfully applied to borane adducts **14−16**, thus leading to phosphonate−phosphane−borane complexes (70−93% yield).

Deprotection of Borane Complexes

Aminolysis is a common practice for the liberation of borane complexes, and exchange with diethylamine and morpholine,[7] or TMEDA and DABCO[12] is well established. However, Livinghouse et al.[14] have mentioned the failure of these procedures in the case of a very basic aliphatic bis(phosphane), and suggested the use of strong organic acids such as CF_3SO_3H or HBF_4 for that purpose. This enantioselective decomplexation was taken up by Imamoto and co-workers for chiral trialkylphosphanes.[18] In our hands, with phosphane−boranes and phosphane−phosphonate−boranes, only partial aminolysis was evident after several days (as an example, aminolysis of triphenylphosphane−borane is achieved after some hours), but with $HBF_4-O(C_2H_5)_2$, complete decomplexation was achieved overnight at room temperature. Examples of both bis(phosphanes) resulting from alkylations, and phosphane−phosphonates obtained from Michael additions are shown in Table 2.

Phosphane−phosphonates are interesting potentially hemilabile ligands. Furthermore, using the $TMSBr/H_2O/NaOH$ sequence of Roundhill et al,[19] phosphane−phosphonate **22**, for instance, was converted into its disodium phosphonic salt **28** (Scheme 2).



Scheme 2

In a CH_2Cl_2/water mixture (1:1, v/v), the salt **28** was recovered (more than 95% wt) in the water phase. Furthermore, when an aqueous solution of **28** was mixed to a CH_2Cl_2 solution of one equivalent of $Rh(cod)_2Cl_2$, the resulting Rh complex was entirely recovered in water.

Conclusion

Since many phosphinic acids are easily accessible by the Regan−Boyd method, their reduction by conventional methods leads to versatile secondary phosphanes which can be converted into a large variety of functional tertiary phosphanes and bis(phosphanes). The preparation of some related P−H functional phosphanes was recently described[20] by phosphanation (PH_3) of 2,2′-bis(halomethyl)-1,1′-biphenyls or binaphthyls. However, considering the drawbacks of using PH_3, one can think that the method described above constitutes an interesting alternative.

Experimental Section

NMR spectra were obtained with an AC 300 Bruker spectrometer, ^1H NMR at 300 MHz,^{13}C NMR at 75 MHz and ^{31}P NMR at 121 MHz, in $CDCl_3$ (unless otherwise stated). Chemical shifts (δ) are expressed in parts per million. *J* values are reported in Hz. Elemental analyses were performed by the "Service Central d'Analyse du CNRS" (Vernaison, France), or the "Service de Microanalyse de l'ICSN−CNRS" (Gif sur Yvette, France).

Phosphinic Monoacids

General Procedure: Compounds **1** and **2** were prepared as previously described.[3e]

Phosphinic Acids 3 and 4: To a solution of ammonium phosphinate (2.0 g, 24.1 mmol) in dichloromethane (160 mL) were added at 0 °C, ethyldiisopropylamine (14.7 mL, 85.8 mmol). After stirring for 20 min, trimethylsilyl chloride (10.7 mL, 85.2 mmol) was added to the mixture. The reaction mixture was stirred for 2 h at room temperature, then dihalide (1.1 equivalent) was added at 0 °C: 2,2′-bis(bromomethyl)-1,1′-biphenyl (**3**, 9.01 g, 26.5 mmol) or 1,1′-bis(chloromethyl)ferrocene (**4**, 7.50 g, 26.5 mmol). The mixture was stirred for an additional 24 h. The ethyldiisopropylammonium chloride was filtered off, and the filtrate washed twice with aqueous HCl (10%, 100 mL), then with distilled water (80 mL). After drying ($MgSO_4$), the solvent was removed under vacuum, leading to crude phosphinic acids **3** and **4** as solids which could be purified by washing with hexane.

6,7-Dihydro-6-hydroxy-5*H*-dibenzo[*c,e*]phosphepin 6-Oxide (3): ^{1}H NMR (CD_3OD): δ = 2.86 (dd, *J* = 15.2, 14.5, 2 H), 3.01 (dd, *J* = 20.6, 14.5, 2 H), 7.35−7.42 (m, 8 H). − ^{13}C NMR (CD_3OD): δ = 35.8 (d, *J* = 88.0), 128.7−141.4 (m). − $^{31}P\{^1H\}$ NMR (CD_3OD): δ = 62.3.

Ferrocenophane-Derived Phosphinic Acid 4: ^{1}H NMR ([D$_6$]DMSO): δ = 2.23 (d, *J* = 16.1, 4 H), 4.05 (s, 8 H). − ^{13}C NMR ([D$_6$]DMSO): δ = 30.7 (d, *J* = 146.1), 69.1−74.1 (m). − $^{31}P\{^1H\}$ NMR (CD_3OD): δ = 62.5.

Phosphinic Diacids

General Procedure: Ethyldiisopropylamine (5.1 mL, 29.6 mmol) and trimethylsilyl chloride (3.7 mL, 29.6 mmol) were added to a mixture of phenylphosphinic acid (2.0 g, 14.1 mmol) in dichloromethane at 0 °C. The mixture was stirred at room temperature for 2 h. α,α′-Dibromo-*m*-xylene (2.0 g, 7.7 mmol) was then added at 0 °C. The mixture was stirred at room temperature for 24 h, filtered and then washed with two portions of 10% HCl. The organic layer was dried with $MgSO_4$, and the solvent was removed under vacuum. The product was washed several times with hexane before characterization.

3-{[Hydroxy(phenyl)phosphoryl]methyl}benzyl(phenyl)phosphinic Acid (5): ^{1}H NMR (CD_3OD): δ = 3.19 (d, *J* = 17.9, 4 H), 6.86−7.02 (m, 4 H), 7.38−7.62 (m, 10 H). − ^{13}C NMR (CD_3OD): δ = 39.3 (d, *J* = 105.6), 129.1−134.0 (m). − $^{31}P\{^1H\}$ NMR (CD_3OD): δ = 38.5. − $C_{20}H_{20}O_4P_2$ (386.3): calcd. C 62.18, H 5.22; found C 61.73, H 4.91.

2,2′-Bis{[hydroxy(phenyl)phosphoryl]methyl}-1,1′-biphenyl (6): ^{1}H NMR (CD_3OD): δ = 2.80 (dd, *J* = 15.6, 15.2, 2 H), 3.01 (dd, *J* = 20.4, 15.2, 2 H), 6.42−7.75 (m, 18 H). − ^{13}C NMR (CD_3OD): δ = 35.7 (d, *J* = 95.1), 127.6−142.1 (m). − $^{31}P\{^1H\}$ NMR (CD_3OD): δ = 38.2.

Secondary Monophosphanes

General Procedure: A mixture of phosphinic acid and phenylsilane (1 equiv.) was stirred at 100 °C for 2−12 h under N_2. The phosphane was distilled under reduced pressure.

2,3-Dihydro-1*H*-isophosphindole (7): ^{1}H NMR: δ = 3.32 (dm, *J* = 189.8, 1 H), 3.06−3.18 (m, 4 H), 7.14−7.31 (m, 4 H). − ^{13}C NMR: δ = 27.6 (d, *J* = 10.0), 125.8, 143.6. − $^{31}P\{^1H\}$ NMR: δ = −59.7.

2,3-Dihydro-1*H*-benzo[*d,e*]isophospholine (8): ^{1}H NMR: δ = 3.26 (dm, *J* = 189.8, 1 H), 3.17 (d, *J* = 5.3, 4 H), 7.17−7.64 (m, 6 H). − ^{13}C NMR: δ = 23.5 (d, *J* = 10.1), 123.8−133.6 (m). − $^{31}P\{^1H\}$ NMR: δ = −82.7.

6,7-Dihydro-5*H*-dibenzo[*c,e*]phosphepin (9): ^{1}H NMR: δ = 1.74 (dm, *J* = 253.9, 1 H), 2.53−2.61 (m, 4 H), 7.26−7.33 (m, 8 H). − ^{13}C NMR: δ = 23.01 (m), 126.4−140.1 (m). − $^{31}P\{^1H\}$ NMR: δ = −31.8.

Secondary Diphosphanes

General Procedure: The bis(phosphinic acids) **5** and **6** were converted into their chlorides with excess $SOCl_2$ in CH_2Cl_2. The crude chlorides **10** and **11** were reduced to phosphanes with $LiAlH_4$ (*x* mg, 2.5 equiv.) in THF (room temperature, overnight). Hydrolysis (*x* μL H_2O, *x* μL 15% NaOH, 3 × *x* μL H_2O) then filtration and concentration gave bis(phosphanes) **12** and **13**.

3-{[Chloro(phenyl)phosphoryl]methyl}benzyl(phenyl)phosphinic Chloride (10): ^{1}H NMR: δ = 3.61 (dd, 2 H, $^2J_{P,H}$ = 5.2, $^2J_{H,H}$ = 5.2), 3.67 (dd, 2 H, $^2J_{P,H}$ = 6.8, $^2J_{H,H}$ = 5.2), 7.01−7.16 (m, 4 H), 7.43−7.72 (m, 10 H). − ^{13}C NMR: δ = 43.9 (d, 2 C, $^1J_{P,C}$ = 76.4), 128.3−132.9 (18 C). − $^{31}P\{^1H\}$ NMR: δ = 51.9, 52.0.

2,2′-Bis{[chloro(phenyl)phosphoryl]methyl}-1,1′-biphenyl (11): ^{1}H NMR: δ = 3.12−3;75 (m, 4 H), 6.37−7.58 (m, 18 H). − ^{13}C NMR: δ = 40.4 (d, $^1J_{P,C}$ = 76.8), 40.7 (d, $^1J_{P,C}$ = 76.7), 40.8 (d, $^1J_{P,C}$ = 76.8), 41.0 (d, $^1J_{P,C}$ = 76.7, 2 C, 3 diastereoisomers), 127.4−140.1 (m, 24 C). − $^{31}P\{^1H\}$ NMR: δ = 52.1, 52.5, 52.6 (2:1:1).

Phenyl{3-[(phenylphosphanyl)methyl]benzyl}phosphane (12): ^{1}H NMR: δ = 2.84−3.04 (m, 4 H), 4.02 (dm, *J* = 208.3, 1 H), 7.13−7.83 (m, 14 H). − ^{13}C NMR: δ = 31.0 (m), 126.0−140.1 (m). − $^{31}P\{^1H\}$ NMR: δ = −40.2, −40.3.

2,2′-Bis[(phenylphosphanyl)methyl]-1,1′-biphenyl (13): ^{1}H NMR: δ = 4.11 (dm, *J* = 210.6, 1 H), 2.73−3.13 (m, 4 H), 6.92−7.42 (m, 18 H). − ^{13}C NMR: δ = 29.2 (d, *J* = 17.1), 29.5 (d, *J* = 17.1), 124.8−140.7 (m). − $^{31}P\{^1H\}$ NMR: δ = −45.8, −46.7.

Secondary Phosphane−Boranes

General Procedure: To a solution of the secondary phosphanes in THF was added 1 equiv. of BH_3−THF, and the mixture was stirred overnight. The solvent was removed under vacuum and the residue washed with hexane. Phosphanes−boranes were quantitatively obtained as white powders.

1,3-Dihydro-2*H*-isophosphindolium-2-yl Trihydridoborate(1$^-$) (14): ^{1}H NMR: δ = 5.12 (q, *J* = 356.3, 1 H), −0.55 (q, *J* = 96, 3 H), 3.23 (ddd, *J* = 10.1, 7.3, 6.3, 2 H), 3.44 (ddd, *J* = 10.1, 17.3, 2.6, 2 H), 7.22−7.32 (m, 4 H). − ^{13}C NMR: δ = 28.8 (d, *J* = 39.8), 124.6, 127.5, 134.7. − $^{31}P\{^1H\}$ NMR: δ = 2.1 (q, *J* = 49).

1*H*-Benzo[*de*]isophosphinolinium-2(3*H*)-yl Trihydridoborate(1$^-$) (15): ^{1}H NMR: δ = 4.91 (q, *J* = 362.6, 1 H), 0.78 (q, *J* = 86, 3 H), 3.40 (ddd, *J* = 10.9, 16.5, 12.1, 2 H), 3.53 (dd, *J* = 7.8, 16.5, 2 H), 7.15−7.81 (m, 6 H). − ^{13}C NMR: δ = 25.0 (d, *J* = 35.0), 125.5, 127.4, 128.4, 128.7, 128.8, 134.3. − $^{31}P\{^1H\}$ NMR: δ = −24.0 (q, *J* = 54). − $C_{12}H_{14}BP$ (200): calcd. C 72.06, H 7.05; found C 70.74, H 7.66.

5,7-Dihydro-6*H*-dibenzo[*c,e*]phosphepinium-6-yl Trihydridoborate(1$^-$) (16): ^{1}H NMR: δ = 5.28 (q, *J* = 355.5, 1 H), 0.29 (q, *J* = 108, 3 H), 2.75 (m, 2 H), 3.53 (m, 2 H), 7.26−7.44 (m, 8 H). − ^{13}C NMR: δ = 23.8 (d, *J* = 34.4), 25.6 (d, *J* = 32.5), 128.0−139.9. − $^{31}P\{^1H\}$ NMR: δ = 18.2 (q, *J* = 42). − $C_{14}H_{16}BP$ (226): calcd. C 74.4, H 7.1, B 4.8, P 13.7; found C 73.0, H 7.0, B 4.6, P 13.5.

Tertiary Phosphane−Boranes and Phosphane−Borane Phosphonates

General Procedure: A suspension of NaH (1 mmol) in THF (5 mL) was added to a mixture of secondary phosphane−borane (1 mmol) and alkyl halide or diethylvinylphosphonate (1 mmol) in THF (10 mL) at 0 °C. The mixture was stirred at room temperature until the reaction was complete. THF was removed under vacuum, and dry dichloromethane was added. The mixture was treated with diluted HCl and extracted with dichloromethane. The organic layer was dried with $MgSO_4$, and the solvent removed under vacuum.

Tertiary Phosphanes and Phosphane−Phosphonates

General Procedure: To a solution of tertiary phosphane−borane or phosphane−borane−phosphonate in dichloromethane was added 5 equiv. of HBF_4−OEt_2. The mixture was stirred overnight at room temperature and a saturated aqueous sodium hydrogen carbonate solution was then added at 0 °C. The mixture was stirred for 10 min and the phosphanes or phosphane−phosphonates were then extracted with dichloromethane. The organic layer was washed with two portions of water, dried with $MgSO_4$ and the solvent was removed under vacuum.

2-Isopropyl-2,3-dihydro-1*H*-isophosphindole (17): 90% yield. − ^{1}H NMR: δ = 1.51 (sept, J = 7.0, 1 H), 3.00 (dd, J = 2.4, 17.1, 2 H) 3.24 (dd, $J_{P,H}$ = $J_{H,H}$ = 17.4, 2 H), 1.13 (dd, J = 6.9, 14.4, 6 H), 7.23−7.39 (m, 4 H). − ^{13}C NMR: δ = 23.4 (d, J = 11.5), 31.3 (d, J = 15.5), 19.2 (d, J = 17.1), 125.9, 126.6, 141.6. − ^{31}P{^{1}H} NMR: δ = −1.5.

2-[2-(1,3-Dihydro-2*H*-isophosphindol-2-yl)ethyl]-2,3-dihydro-1*H*-isophosphindole (18): 77% yield. − ^{1}H NMR: δ = 1.35−1.60 (m, 4 H), 2.81 (d, J = 17.3, 4 H), 3.24 (dd, J = 17.3, 17.3, 4 H), 7.23−8.00 (m, 8 H). − ^{13}C NMR: δ = 22.3, 32.9 (d, J = 7.4), 126.2, 127.2, 141.4. − ^{31}P{^{1}H} NMR: δ = −14.2. − $C_{18}H_{20}P_2$ (298.3): calcd. C 72.48, H 6.76; found 72.01, H 6.51.

2-[3-(1,3-Dihydro-2*H*-isophosphindol-2-yl)propyl]-2,3-dihydro-1*H*-isophosphindole (19): 81% yield. − ^{1}H NMR: δ = 1.40−1.52 (m, 4 H), 1.65 (quint, ^{3}J = 8.2, 2 H), 2.85 (d, ^{2}J = 17.2, 4 H), 3.24 (dd, $^{2}J_{P-H}$ = 17.2, 4 H), 7.23−7.40 (8 H). − ^{13}C NMR: δ = 28.0 (dd, $^{1}J_{P,C}$ = 15.1, $^{3}J_{P,C}$ = 11.2, 2 C), 32.9 (d, J = 13.7, 4 C), 22.8 (t, J = 16.1), 126.1 (2 C), 127.1 (2 C), 141.6 (2 C). − ^{31}P NMR: δ = −19.2 (s).

2-[4-(1,3-Dihydro-2*H*-isophosphindol-2-yl)butyl]-2,3-dihydro-1*H*-isophosphindole (20): 83% yield. − ^{1}H NMR: δ = 1.2−1.5 (m, 4 H), 2.85 (dd, $^{2}J_{P,H}$ = 2.0, $^{2}J_{H,H}$ = 17.6, 4 H), 3.23 (dd, $^{2}J_{P,H}$ = ^{2}J $_{H,H}$ = 17.6, 4 H), 1.3−1.75 (m, 4 H), 7.22−7.42 (m, 8 H). − ^{13}C NMR δ = 24.4 (dd, $^{2}J_{P,C}$ = $^{3}J_{P,C}$ = 13.3, 2 C), 26.2 (d, $J_{P,C}$ = 14.5, 2 C), 33.0 (d, $J_{P,C}$ = 13.6, 4 C), 126.2 (4 C), 127.2 (4 C), 141.7 (4 C). − ^{31}P NMR: δ = −18.7. − $C_{20}H_{24}P_2$ (326.3): calcd. C 73.61, H 7.41; found C 73.03, H 7.28.

2-{[2′-(1,3-Dihydro-2*H*-isophosphindol-2-ylmethyl)[1,1′-biphenyl]-2-yl]methyl}-2,3-dihydro-1*H*-isophosphindole (21): 79% yield. − ^{1}H NMR: δ = 2.36, (dd, J = 13.1, 4 H), 2.40 (dd, J = 13.1, 4 H), 2.62 (dd, $J_{H,H}$ = 16.9, $J_{P,H}$ = 53.2, 4 H), 2.94 (dd, $J_{H,H}$ = 16.9, $J_{P,H}$ = 35.7, 4 H), 7.00−7.30 (m, 16 H). − ^{13}C NMR: δ = 30.8 (d, J = 19.5), 32.8 (d, J = 16.2), 33.3 (d, J = 16.1), 125.4, 125.7, 126.0, 127.0, 127.1, 128.2, 129.6, 130.7, 136.1, 140.4, 141.4. − ^{31}P{^{1}H} NMR: δ = −8.9. − $C_{30}H_{28}P_2$ (326.3): calcd. C 79.98, H 6.26; found C 79.49, H 6.71.

2-[3-(1*H*-Benzo[*d,e*]isophospholin-2(3*H*)-yl)propyl]-2,3dihydro-1*H*-benzo[*d,e*]isophosphanylline (23): 78% yield. − ^{1}H NMR: δ = 1.00−1.12 (m, 4 H), 2.85 (dd, J = 3.5, 16.1, 4 H), 3.18 (dd, J = 5.5.16.1, 4 H), 1.30−1.50 (m, 2 H), 7.07 (d, J = 7.0, 4 H), 7.26 (dd, J = 7.0, 8.2, 4 H), 7.61 (d, J = 8.2, 4 H). − ^{13}C NMR: δ = 24.3 (dd, J = 14.9, 11.4), 29.4 (d, J = 12.6), 22.0 (t, J = 16.6), 125.3, 127.1, 128.4, 129.0, 130.6, 134.0. − ^{31}P{^{1}H} NMR: δ = −55.9.

2-[4-(1*H*-Benzo[*d,e*]isophosphanyllin-2(3*H*)-yl)butyl]-2,3-dihydro-1*H*-benzo[*d,e*]isophospholine (24): 98% yield. − ^{1}H NMR: δ = 1.05−1.15 (m, 4 H), 1.25−1.45 (m, 4 H), 2.99 (dd, $^{2}J_{P,H}$ = 2.9, $^{2}J_{H,H}$ = 15.9, 4 H), 3.30 (dd, $^{2}J_{P,H}$ = 5.6, $^{2}J_{P,H}$ = 15.9, 4 H), 7.2 (4 H), 7.35 (4 H), 7.70 (4 H). − ^{13}C NMR: δ = 22.8 (d, $J_{P,C}$ = 14.2), 27.0 (t, $^{2}J_{P,C}$ = $^{3}J_{P,C}$ = 14), 29.7 (d, $J_{P,C}$ = 11.9), 125.2, 127, 128.5, 129.8, 131.3, 133.9. − ^{31}P NMR: δ = −54.8.

6-[4-(5,7-Dihydro-6*H*-dibenzo[*c,e*]phosphepin-6-yl)butyl]-6,7-dihydro-5*H*-dibenzo[*c,e*]phosphepine (26): 87% yield. − ^{1}H NMR: δ = 1.30−1.55 (m, 4 H), 2.10−2.45 (m, 4 H), 2.40−2.80 (m, 4 H), 1.50−1.75 (m, 4 H), 6.95−7.60 (m, 16 H). − ^{13}C NMR: δ = 22.8 (d, J = 16.6), 28.4 (d, J = 18.9), 31.3 (d, J = 14.6), 27.4 (dd, J = 12.6, 12.6), 126.3−140.6 (m). − ^{31}P{^{1}H} NMR: δ = −28.8.

Diethyl 2-(1,3-Dihydro-2*H*-isophosphindol-2-yl)ethylphosphonate (22): 83% yield. − ^{1}H NMR: δ = 1.50−1.68 (m, 2 H), 1.80−1.92 (m, 2 H), 2.90 (dd, $^{2}J_{P,H}$ = 2.5, 2 H), 3.41 (t, $^{2}J_{P,H}$ = $^{2}J_{H,H}$ = 17.1, 2 H), 7.23−7.28 (m, 2 H), 7.35−7.39 (m, 2 H). − ^{13}C NMR: δ = 16.5 (dd, $^{1}J_{P,C}$ = 17.7, $^{2}J_{P,C}$ = 6.4), 22.0 (d, $^{1}J_{P,C}$ = 140.5, $^{2}J_{P,C}$ = 16.1), 32.6 (d, $J_{P,C}$ = 14.2), 126.4, 127.2, 141. − ^{31}P NMR: δ = −13.3 (d), 30.8 (d, $^{3}J_{P,P}$ = 56.9). − $C_{14}H_{22}O_3P_2$ (300.3): calcd. C 56.00, H 7.38, P 20.63; found C 55.42, H 7.10, P 21.05.

Diethyl 2-(1*H*-Benzo[*d,e*]isophosphanyllin-2(3*H*)-yl)ethylphosphonate (25): 88% yield. − ^{1}H NMR: δ = 1.35−1.45 (m, 2 H), 3.00 (dd, J = 3.6, 16.0, 2 H), 3.25 (dd, J = 5.8, 16.0, 2 H), 1.55−1.75 (m, 2 H), 7.15 (d, J = 7.0, 2 H), 7.23 (dd, J = 7.0, 8.1, 2 H), 7.61 (d, J = 8.1, 2 H). − ^{13}C NMR: δ = 15.1 (dd, J = 17.4, 6.5), 29.0 (d, J = 13.6), 21.3(dd, J = 140.3, 16.1), 125.3−134.0 (m). − ^{31}P{^{1}H} NMR: δ = −51.6 (d, J = 54.8), 31.4 (d, J = 54.8).

Diethyl 2-(5,7-Dihydro-6*H*-dibenzo[*c,e*]phosphepin-6-yl)ethylphosphonate (27): 94% yield. − ^{1}H NMR: δ = 1.51−1.70 (m, 2 H), 1.74−1.88 (m, 2 H), 2.14−2.38 (m, 2 H), 2.57−2.68 (m,2 H), 7.00−7.30 (m, 8 H). − ^{13}C NMR: δ = 17.8 (dd, ^{1}J = 19, ^{2}J = 6), 22.0 (d, ^{1}J = 140.9, ^{2}J = 16.1), 27.9 (d, J = 19.6), 30.7 (d, J = 14.7), 126.4−140.2 (12 C). − ^{31}P NMR: δ = 4.8, 31.5 (d, $^{3}J_{P,P}$ = 56).

2-(1,3-Dihydro-2*H*-isophosphindol-2-yl)ethylphosphonic Acid, Disodium Salt (28): $(CH_3)_3SiBr$ (0.4 mL; 3 mmol) was added to a solution of phosphane−phosphonate **22** (0.3 g) in CH_2Cl_2 (20 mL). After stirring for 3 h at room temperature, methanol (3 mL) was added, and the solvents were then removed under vacuum. Crude solid phosphonic acid was dissolved in water (10 mL) and neutralized with NaOH (80 mg; 2 mmol). Evaporation of water and successive washing with hexanes led to phosphonic salt **28** as a white solid (0.282 g; 98% yield). − ^{1}H NMR (D_2O): δ = 1.45−1.55 (m, 2 H), 2.97 (dd, $J_{P,H}$ = 2.8, $J_{H,H}$ = 17), 3.16 (dt, $J_{P,H}$ = $J_{H,H}$ = 17), 7.22−7.34 (m, 2 H), 7.35−7.48 (m, 2 H). − ^{13}C NMR: δ = 23.1 (dd, $^{1}J_{P,C}$ = 11.5, $^{2}J_{P,C}$ = 5.1), 28.2 (d, $^{1}J_{P,C}$ = 128.5, $^{2}J_{P,C}$ = 10.6), 34.5 (d, $J_{P,C}$ = 10.4), 129.2, 130.2, 144.5. − ^{31}P{^{1}H} NMR: δ = −15.4 (d), 22.6 (d, $^{3}J_{P,P}$ = 53.8).

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[1] For a review, see special issue on phosphorus chemistry: G. Bertrand, *Chem. Rev.* **1994**, *94*, 1161.

[2] B. Cornils, W. A. Hermann, *Applied homogeneous catalysis with organometallic compounds*, VCH, New York, **1996**.

[3] [3a] E. A. Boyd, M. Corless, K. James, A. C. Regan, *Tetrahedron Lett.* **1990**, *31*, 2933. − [3b] E. A. Boyd, A. C. Regan, K. James, *Tetrahedron Lett.* **1992**, *33*, 813. − [3c] E. A. Boyd, A. C. Regan, K. James, *Tetrahedron Lett.* **1994**, *35*, 4223. − [3d] E. A. Boyd, M. E. K. Boyd, V. M. Loh Jr, *Tetrahedron Lett.* **1996**, *37*, 1651. − [3e]E. A. Boyd, M. E. K. Boyd, F. Kerrigan, *Tetrahedron Lett.* **1996**, *37*, 5425.

[4] C. N. Robinson, W. A. Pettit, *Tetrahedron Lett.* **1972**, *49*, 4977.

[5] J-L. Montchamp, F. Tian, J. W. Frost, *J. Org. Chem.* **1995**, *60*, 6076.

[6] H. G. De Graaf, J. Dubbeldam, H. Vermeer, F. Bickelhaupt, *Tetrahedron Lett.* **1973**, *26*, 2397.

[7] T. Imamoto, T. Oshiki, T. Onozawa, T. Kusumoto, K. Sato, *J. Am. Chem. Soc.* **1990**, *112*, 5244.

[8] H. Fritzsche, U. Hasserodt, F. Korte, *Chem. Ber.* **1965**, *98*, 1681.

[9] P. De Koe, R. Van Veen, F. Bickelhaupt, *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 465.

[10] P. Pellon, *Tetrahedron Lett.* **1992**, *33*, 4451.

[11] K. Bourumeau, A-C. Gaumont, J-M. Denis, *J. Organomet. Chem.* **1997**, *529*, 205.

[12] H. Brisset, Y. Gourdel, P. Pellon, M. Le Corre, *Tetrahedron Lett.* **1993**, *34*, 4523.

[13] T. Imamoto, T. Kusumoto, N. Suzuki, K. Sato, *J. Am. Chem. Soc.* **1985**, *107*, 5301.

[14] L. Mc Kinstry, T. Livinghouse, *Tetrahedron* **1995**, *51*, 7655.

[15] See for example: [15a] M. J. Burk, J. E. Feaster, W. A. Nugent, R. L. Harlow, *J. Am. Chem. Soc.* **1993**, *115*, 10125. – [15b] H. Werner, A. Hampp, B. Windmüller, *J. Organomet. Chem.* **1992**, 169.

[16] K. Bourumeau, A-C. Gaumont, J-M. Denis, *Tetrahedron Lett.* **1997**, *38*, 1923.

[17] See for instance: [17a] R. B. King, J. C. Cloyd Jr., P. N. Kapoor, *J. Chem. Soc., Perkin Trans. 1* **1973**, 2226. – [17b] R. B. King, J. C. Cloyd Jr., *J. Am. Chem. Soc.* **1975**, *97*, 46.

[18] T. Imamoto, J. Watanabe, Y. Wada, H. Masuda, H. Yamada, H. Tsuruta, S. Matsukawa, K. Yamaguchi, *J. Am. Chem. Soc.* **1998**, *120*, 1635.

[19] S. Ganguly, J. T; Mague, D. M. Roundhill, *Inorg. Chem.* **1992**, *31*, 3500.

[20] F. Bitterer, O. Herd, M. Kühnel, O. Stelzer, N. Weferling, W. S. Sheldrick, J. Hahn, S. Nagel, N. Rösch, *Inorg. Chem.* **1998**, *37*, 6408.

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