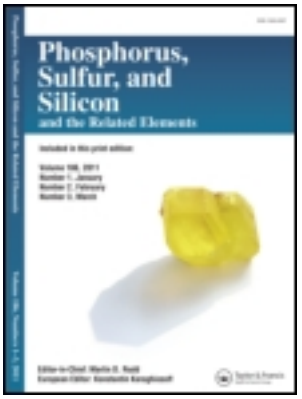

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Is the $^{1}J_{PSe}$ Coupling Constant a Reliable Probe for the Basicity of Phosphines? A ^{31}P NMR Study

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IS THE $^{1}J_{PSe}$ COUPLING CONSTANT A RELIABLE PROBE FOR THE BASICITY OF PHOSPHINES? A ^{31}P NMR STUDY

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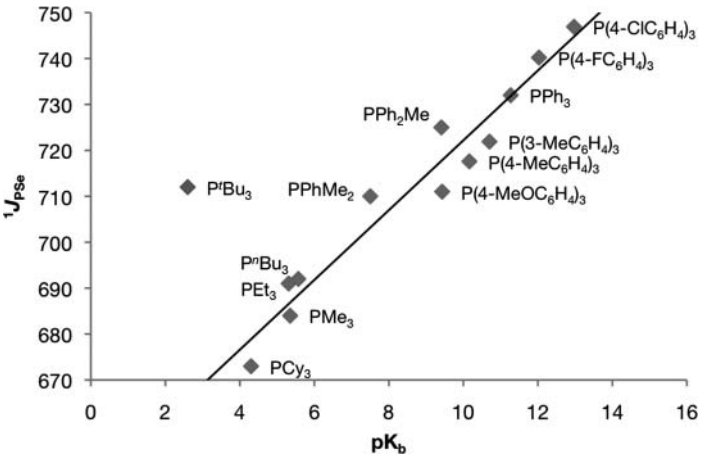
GRAPHICAL ABSTRACT



Abstract *The influence of different heteroaryl and functionalized aryl substituents on the electron-donating ability and basicity of the phosphorus atoms in heteroaryl phosphines and diphosphines has been determined by the use of the direct $^{1}J_{PSe}$ coupling constants of the corresponding selenides. The generality of the use of ^{31}P–^{77}Se spin–spin coupling constants as probe for the basicity of phosphines is discussed as well as the scope and limits of this concept.*

Keywords Phosphine selenide; heteroaryl phosphines; ^{31}P–^{77}Se spin–spin coupling constant

INTRODUCTION

Tertiary phosphines and diphosphines are widely used as ligands in transition metal complexes for catalysis and biomedical applications. The properties and reactivity of the

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D. Süslüyan thanks all the members of the institute for providing the organophosphorus compounds.
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metal can be tuned by the steric demand and the electronic effects of the phosphine ligands. Several concepts, e.g., the Tolman cone angle,[1] exist to describe the steric demand of phosphine and diphosphine ligands,[2,3] whereas electronic effects are less studied. The electron-donating ability and the electronic effect can be estimated using the ν(CO) stretching frequencies of the corresponding metal carbonyls[1] or $^1J_{PX}$ spin–spin coupling constants, X = ^{195}Pt, ^{77}Se, in the corresponding platinum complexes or selenides.[4–7] Especially for the determination of the electron-donating ability of multidentate heterophosphines, the value of $^1J_{PSe}$ is the most available of these approaches. In such multitopic ligand systems, the basicity of the phosphorus atom cannot be determined by titration as heteroatoms, e.g., nitrogen atoms, are the stronger Brønsted bases. Furthermore, it is not necessarily the phosphorus atom to act as the Lewis base and bind to, e.g., the platinum or nickel atoms, whereas the reaction with selenium gives the phosphorus selenide selectively. The value of the $^1J_{PSe}$ coupling constant for organophosphorus selenides depends on the nature of substituents at the phosphorus atom. In general, the value increases with the substituents becoming more electron-withdrawing. This value is also related to the basicity of the phosphorus atom. Again, in the case of heterophosphine compounds, the Brønsted basicity cannot be observed directly, as the heteroatoms, e.g., the N atoms of pyridinyl or imidazolyl substituents, are by far more basic; thus, titration, e.g.,would lead to the pK_{B-}value of the corresponding pyridinium phosphine or imidazolium phosphine, respectively.

RESULTS AND DISCUSSION

We are interested in the chemistry of phosphine and diphosphine compounds as ligands for water-soluble catalysts, nano-sized metal clusters, and metal-based pharmaceuticals.[8–10] We synthesized some functionalized phosphorus compounds containing functionalized phenyl groups, imidazole, and thiazole substituents as well as alkylphosphonate side chains.

In order to gain more information about the electron-donating abilities and P basicities of multifunctional phosphines and diphosphines, we have investigated the direct phosphorus-31 selenium-77 spin–spin coupling constants ($^1J_{PSe}$) of a series of multifunctional phosphorus compounds.

The selenium compounds were prepared by reaction of the corresponding phosphines with KSeCN or red selenium.[5,11] Especially, when sterically more demanding 1-methylimidazol-2-yl substituents were present in the phosphine, the reaction with KSeCN was slow and gave poor yields as compared to selenation with elemental selenium.

For the correlation of the $^1J_{PSe}$ coupling constants of the phosphine selenides and the Brønsted basicity (pK_B) of the corresponding phosphines, we used literature-known examples (Table 1). The phosphine P^{t}Bu$_3$ was not included in the correlation, as the bulky *tert*-butyl groups lead to a widening of the C-P-C angles and thus to a decrease of s-character of the lone pair. The direct spin–spin coupling constant of phosphorus to a heteronucleus is sensitive to the hybridization of the phosphorus atom: the coupling constant increases with increasing s-character. As can be seen from Figure 1, the spin–spin coupling constant $^1J_{PSe}$ of the phosphine selenides and the Brønsted basicity (pK_B) of the corresponding organophosphorus compounds correlate well, although the two compounds PPh_2Me and P(4-MeOC$_6$H$_4$)$_3$ have very similar pK_B values (9.41 and 9.43), but their selenides display a difference in $^1J_{PSe}$ of 17 Hz (with 725 and 708 Hz, respectively).

Based upon this correlation, we estimated the basicities of the phosphine and diphosphine compounds, as summarized in Tables 2 and 3. The organophosphorus compounds

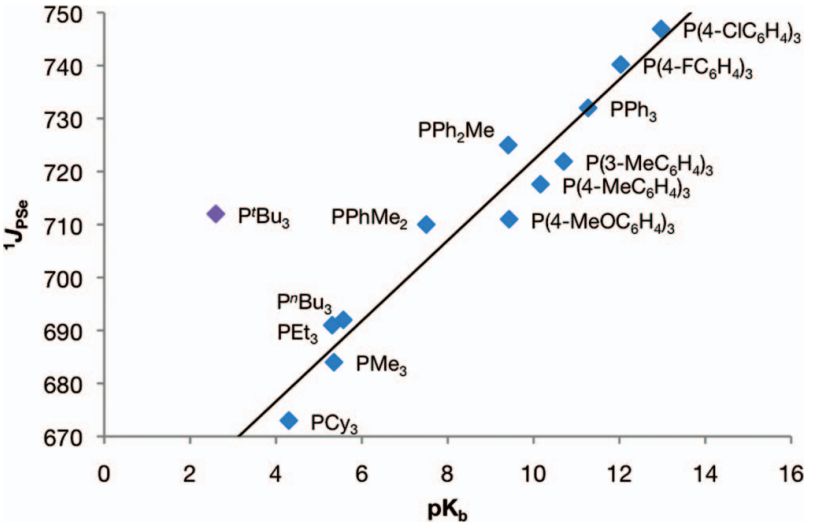


Figure 1 Correlation of $^1J_{PSe}$ and pK_B values of organophosphorus compounds. Linear regression gives $^1J_{PSe} = 7.60 \times pK_B + 646$ ($R^2 = 0.9492$); P^{t}Bu$_3$ was not included in the regression (data taken from refs. 11–17).

with heterocyclic substituents can be classified according to their substituents: compounds **2a–c** and compound **4** bearing imidazol-4(5) and imidazol-4-yl substituents, respectively, are the most basic ones ($pK_B = 9.2$–10.0), whereas the corresponding imidazol-2-yl derivatives **3a–c** and **6** and the imidazol-5-yl derivative **5** are less basic ($pK_B = 11.8$–12.9). A pronounced change in the electronic properties and in the basicity of the phosphorus atom is observed in 2-hydroxyphenyl diphenylphosphine **10** as compared to PPh_3. The basicity of phosphine **10** is more comparable to that of tris(alkyl) phosphines than to that of arylphosphines. This can be explained by the orientation of the OH group, ideally suited for the formation of a hydrogen bond toward the selenium atom and therefore favoring P^+–Se^- over P=Se.[18,19] It has to be mentioned that $^1J_{PSe}$ can differ in various solvents,

Table 1 Organophosphorus compounds used for the correlation of $^1J_{PSe}$ and pK_B (data taken from refs. 11–17)

Phosphine	$^1J_{PSe}$/Hz	$pK_{B\,(exp.)}$	$pK_{B\,(calc.)}$
PPh_3	732[a]	11.27	11.3
PPh_2Me	725[a]	9.41	10.4
$PPhMe_2$	710[a]	7.50	8.4
PMe_3	684[a]	5.35	5.0
PEt_3	691[a]	5.31	5.9
PCy_3	673[b]	4.30	3.6
P^{n}Bu$_3$	689[a]	5.57	5.7
P^{t}Bu$_3$	692[a]	2.60	6.0
P(3-MeC$_6$H$_4$)$_3$	722[b]	10.67	10.0
P(4-MeC$_6$H$_4$)$_3$	718[b]	10.16	9.5
P(4-ClC$_6$H$_4$)$_3$	747[b]	12.97	13.3
P(4-FC$_6$H$_4$)$_3$	740[b]	12.03	12.4
P(4-MeOC$_6$H$_4$)$_3$	711[b]	9.43	8.6

[a]In CH_2Cl_2. [b]In $CDCl_3$.

Table 2 ^{31}P NMR spectroscopic data and calculated P basicities for organophosphorus compounds and their selenides

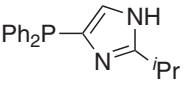
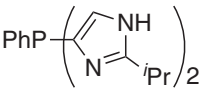
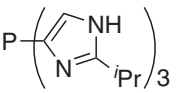
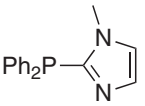
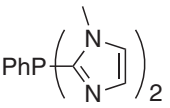
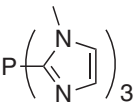
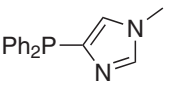
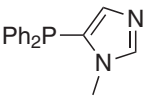
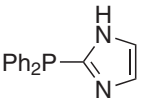
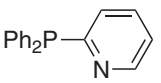
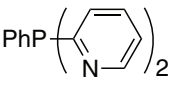
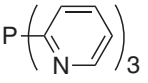
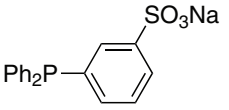
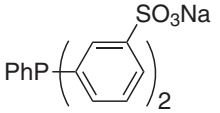
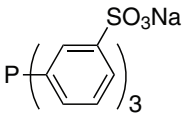
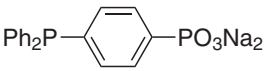
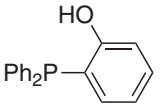
	Phosphane	δ/ppm P^{III}	δ/ppm P^{V}	$^{1}J_{PSe}$/Hz	$pK_{b(calcd.)}$
1	PPh_3	−7.12	33.71	732[d]	11.3
2a		−22.5	18.3	720[a]	9.7
2b		−55.6	0.31	716[a]	9.2
2c		−80.2	−18.5	720[a]	9.7
3a		−30.6	18.2	736[d] 741[a]	11.8 12.5
3b		−44.2	3.25	738[d] 741[a]	12.1 12.5
3c		−61.6	−12.5	741[d] 741[a]	12.5
4		−29.5	18.2	722[a]	10.0
5		−34.3	15.5	744[a]	12.9
6		−22.6	15.9	744[c]	12.9
7a		−3.9	32.5	749[a]	13.6
7b		−2.5	31.8	746[a]	13.2

Table 2 ^{31}P NMR spectroscopic data and calculated P basicities for organophosphorus compounds and their selenides *(Continued)*

	Phosphane	δ/ppm P^{III}	δ/ppm P^{V}	$^1J_{PSe}$/Hz	$pK_{b(calcd.)}$
7c		−2.6[a] −1.9[d]	30.5[a] 27.8[d]	750[a] 750[d]	13.7
8a		−3.8[a] −5.8[e]	36.5[a] 35.4[e]	738[a] 707[e]	12.1 8.0
8b		−5.0	35.1	694[e]	6.3
8c		−5.4	35.3	707[e]	8.0
9		−6.1	34.5	665[e]	2.5
10		−16.3	32.7	683[a]	4.9

[a]In methanol. [b]In ethanol. [c]In tetrahydrofuran (THF). [d]In CH_2Cl_2. [e]In H_2O.
The values of pK_B are calculated by regression data of Figure 1.

Table 3 Direct spin–spin coupling constants $^1J_{PSe}$ of homologous series of phosphines PPh_nR_{3-n} [with $^1J_{PSe}(PPh_3) = 732$ Hz[c]]

	$^1J_{PSe}$/Hz		
R	PPh_2R	$PPhR_2$	PR_3
Me	725[c]	710[c]	684[b]
Cy	725[b]	701[b]	673[b]
^{t}Bu	717[b]	708[b]	692[c]
o-Tol	732[c]	719[c]	705[b]
p-Tol	726[b]	–	715[b]
2-$MeOC_6H_4$	721[b]	718[b]	717[b]
2-furyl	754[c]	774[c]	793[c]
2-thienyl	743[c]	752[c]	757[c]
2-im^{NMe}	736[a]	738[a]	741[a]
4(5)-$im^{2\text{-}iPr}$	720[a]	716[a]	720[a]
2-py	720[b]	746[a]	750[a]

[a]In CH_3OH. [b]In $CDCl_3$. [c]In CH_2Cl_2.
Data taken from this work (see Table 2) and refs. 4, 5, 11, 14, 16, 20, and 23–26.

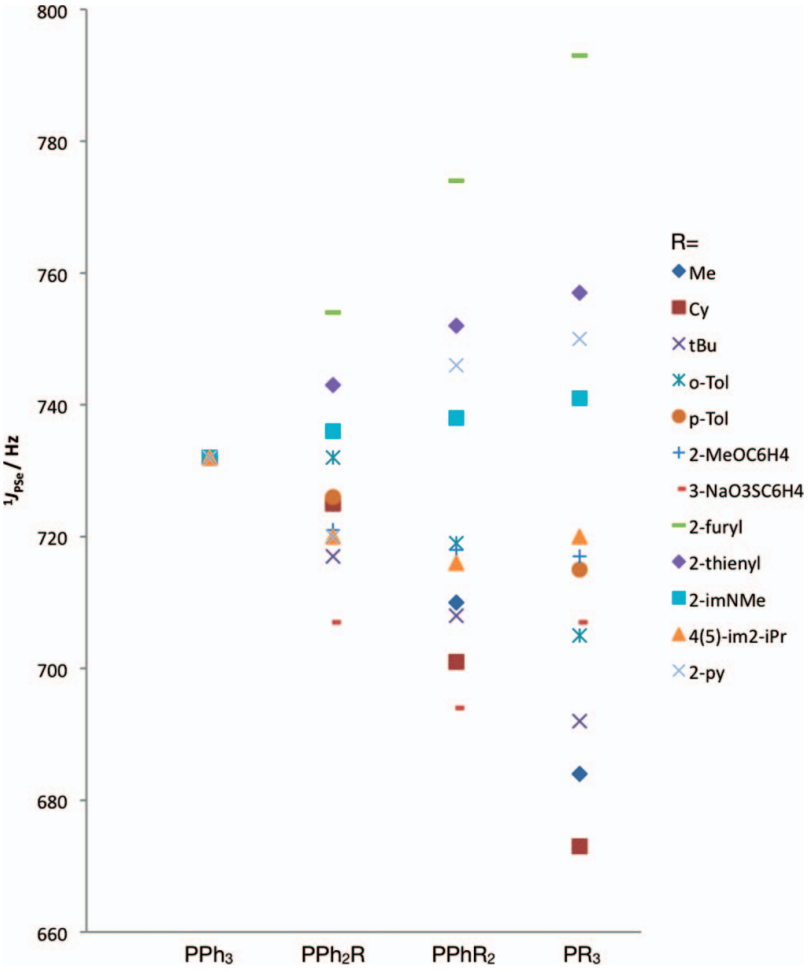
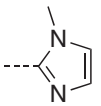
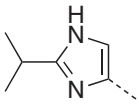
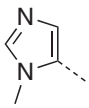
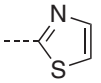
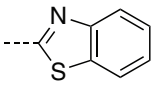
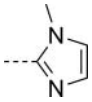
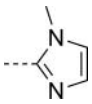


Figure 2 Direct spin–spin coupling constants $^1J_{PSe}$ of homologous series of phosphines PPh_nR_{3-n}.

especially if a direct interaction of the solvent with the selenium atom of the P=Se group occurs.[14,20–22] This has to be taken into account especially when comparing basicities of different phosphines determined in different solvents. To minimize misinterpretation of the basicities due to this effect, $^1J_{PSe}$ of homologous series of phosphines has been determined in the same solvent. The results showed that the trend of the corresponding basicities is significant.

The selenides of all compounds with three (hetero)aromatic substituents (**1**–**8**, with exception of **10**) show values for $^1J_{PSe}$ in the range of 716–750 Hz. This correlates to basicities of 9–14 in pK_B. A clear separation of electronic and steric effects can only be taken into account for a series of homologous compounds, e.g., in 4-substituted triphenylphosphine derivatives or in the series $PPh_{3-n}Me_n$ ($n = 0$–3) (Figure 1). Even in the homologous series **1**, **2a**–**c** and **1**, **3a**–**c**, no trend in $^1J_{PSe}$ can be observed. Electronic and steric effects may contribute in opposite directions. Thus, if steric parameters are altered, the $^1J_{PSe}$ spin–spin

Table 4 ^{31}P NMR spectroscopic data and calculated basicities for diphos-type compounds and their selenides

Compound $R_2P(CH_2)_2PR_2$	R	δ/ppm $P^{III,a}$	$P^{III,b}$	P^V	$^1J_{PSe}$/ Hz	pK_B (calcd.)
11a	Ph	−12.3	−12.9	37.1[b]	731[b]	11.2[b]
				36.9[c]	741[c]	12.1[c]
12		−50	−54.7	3.8[b]	740[b]	12.4
13		−63	n.o.	4.6[c]	731[c]	11.2
14		−72	−71	−4.6[b]	749[b]	13.6
15		−20	−20	17.0[b]	780[b]	17.6
16		−15	−15	21.2[b]	787[b]	18.6
$PhRP(CH_2)_2PRPh$						
17		−33	n.o.	21.0[c]	751[c]	13.8
$R_2P(CH_2)_3PR_2$						
11b	Ph	−17.2	−18.2	33.7[b]	728[b,c]	10.8
				33.4[c]		
18		−59	n.o.	3.0[c]	727[c]	10.6

[a]Diphosphane. [b]Monoselenide. [c]Diselenide. n.o.: not observed.

coupling constant is not solely sensitive to the electron-donating ability or basicity of the phosphorus atom.

Figure 2 shows the dependency of the coupling constant $^1J_{PSe}$ on the degree of substitution within a homologous series of phosphine selenides. A clear trend is observed for substituents that are not able to form hydrogen bonds or that form only weak hydrogen bonds on heteroatoms.

Hydrogen bonding in the selenide of compound **10**, observed in the solid state of the corresponding oxide,[27] is possible and may cause the trend to be far from linear. Despite those irregularities, the general trend observed here is that the introduction of electron-withdrawing substituents causes the values of $^1J_{PSe}$ to increase and that of electron-donating substituents to decrease.

The selenides of diphos-type ligands were prepared analogously to those mentioned before. An excess of selenium reagent was used to yield the diselenide compounds. However, using diphos compounds **12** and **14**–**16**, the monoselenides were obtained as the major products. The $^1J_{PSe}$ coupling constants were determined either from the mono or diselenide (Table 4).

The selenides of the imidazolyl compounds **12**–**18** show $^1J_{PSe}$ coupling constants comparable to those of the selenides of dppe (**11a**) and dppp (**11b**). However, **14** and **17** are slightly less basic as would be expected from the electron-withdrawing properties of the heteroaryl substituents. The selenides of the thiazol-2-yl and benzothiazol-2-yl derivatives **15** and **16** show remarkably high values of $^1J_{PSe}$. In the case of Se = P(2-furyl)$_3$ ($^1J_{PSe}$ = 787 Hz), an interaction between O and Se was discussed as an explanation for its unusual behavior.[4] Increasing the spacer length between the phosphorus atoms from $(CH_2)_2$ to $(CH_2)_3$ as in the selenides of dppe (**11a**) and dppp (**11b**) or in the selenides of compounds **12** and **18** leads to a decrease in $^1J_{PSe}$ of 10 ± 3 Hz. This should not be due to different electronic properties of the corresponding phosphorus atoms but to different electronic repulsion of the P═Se groups. However, the $^1J_{PSe}$ coupling constant is used as a degree for the electron-donating ability and basicity of phosphines independent of steric interference. For diphos-type compounds, this seems not to be the case, as $^1J_{PSe}$ is dependent on the degree of selenation.

CONCLUSION

We conclude that the direct spin–spin coupling constant $^1J_{PSe}$ correlates to the Brønsted basicity (pK_B) of an organophosphine only if intramolecular or intermolecular hydrogen bonding interaction is not dominant. If this is true, the direct spin–spin coupling constants $^1J_{PSe}$ of homologous series of phosphines $PR_nR'_{3-n}$ correlate in a linear manner to the degree of substitution.

EXPERIMENTAL

The phosphines were prepared according to the published procedures; the preparation of **17** and **18** proceeded analogously and will be described in detail in further publications. All experiments were carried out under an atmosphere of dry nitrogen. Solvents were purified and dried using standard techniques. ^{31}P NMR spectra were recorded on a Brucker DRX 200 and DRX 500 spectrometer. For measurement of δ_P of organophosphorus compounds and their corresponding selenides, aqueous NH_4PF_6 was used as an external standard (a sealed capillary was immersed in solution and centered). The measurement of $^1J_{PSe}$ was carried out at 20 °C (±1 °C). The accuracy of measurement of the coupling constant was ±0.5 Hz. The temperature and concentration dependence of $^1J_{PSe}$ for the selenides was not studied. The sign of the $^1J_{PSe}$ coupling constants has not been determined, but is known to be negative for phosphorus(V) selenides.[16] The EI mass spectra were recorded with a double-focussing mass spectrometer, model 311 A Varian MAT, ionization energy 70 eV. The fast atom bombardment (FAB) mass spectra were recorded with a mass spectrometer Finnigan, model MAT 8200, in a NBA matrix. Infrared spectra were recorded with a Bruker IFS 66 FT-IR spectrophotometer.

Bis(2-isopropylimidazol-4(5)-yl)phenylphosphine (2b)

To a solution of 1-diethoxymethyl-2-isopropylimidazole (10.6 g, 50.0 mmol) in 300 mL of diethyl ether, 33 mL (53 mmol) of 1.6 M *n*-butyl lithium in hexane was added at −78 °C. The solution was stirred at −78 °C for 30 min and additionally for 30 min at room temperature. After cooling to −78 °C, $PhPCl_2$ (3.39 mL, 25 mmol) in 10 mL of diethyl ether was added. The white suspension was stirred overnight at room temperature, 75 mL of conc. NH_4OH was added, and the organic layer was separated, washed with water, and dried over $MgSO_4$. After removal of the solvent, the oily residue was redissolved in 100 mL of acetone:water (10:1) and heated to reflux for 12 h. The resulting white precipitate was collected and recrystallized from methanol/acetone. Yield: 3.51 g (43%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.39$ (d, $^3J_{HH} = 7$ Hz, 12H), 3.12 (sept, $^3J_{HH} = 7$ Hz, 2H), 7.24 (m, 5H), 7.43 (d, $J_{PH} = 0.8$ Hz). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): $\delta = -63$ (s). $^{31}P\{^1H\}$ NMR (81 MHz, methanol): $\delta = -55.6$ (s). EI MS (70 eV, 240 °C): *m/z* (%) = 326 (100) $[M]^+$, 249 (18) $[M\text{-}Ph]^+$, 217 (61) $[M\text{-}im^{iPr}]^+$. $C_{18}H_{23}N_4P$ (326.38): Calcd. C, 66.2; H, 7.1; N, 17.2. Found C, 65.6; H, 7.1; N, 17.1%.

1-Methylimidazol-4-yl-diphenylphosphine (4)

A solution of 4-iodo-1-methylimidazole (1.00 g) in THF was treated with EtMgBr (0.21 g). This solution was stirred at ambient temperature for 2 h, cooled to 0 °C, and Ph_2PCl (0.96 g) was added. The suspension was stirred overnight, the solvent was removed in vacuo, and the residue was extracted with NH_3-saturated dichloromethane. The organic phase was filtered and the solvent was removed in vacuo. The residue was recrystallized from ethanol. Yield 1.01 g (78%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 4.00$ (s, 3H, NCH_3), 6.70 (s, 1H, H_{im}), 7.40–7.53 (m, 11H, Ph, H_{im}). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): $\delta = -29.5$. EI-MS (Pt, 210 °C): *m/z* = 266 $[M]^+$, 188 $[M\text{-}Ph]^+$, 183 $[M\text{-}im^{NMe}]^+$. IR (KBr): $\nu = 2963, 1581, 1478, 1433, 1261, 1095, 800\ cm^{-1}$. $C_{16}H_{15}N_2P \cdot 4/3\ H_2O$ (290.30): Calcd. C, 66.5; H, 6.7; N 9.7. Found C, 66.9; H, 6.7; N, 10.0%.

1-Methylimidazol-5-yl-diphenylphosphine (5)

A solution of 5-bromo-1-methylimidazole (1.00 g) in THF was treated with EtMgBr (0.21 g). This solution was stirred at ambient temperature for 2 h, cooled to 0 °C, and Ph_2PCl (0.96 g) was added. The suspension was stirred overnight, the solvent was removed in vacuo, and the residue was extracted with NH_3-saturated dichloromethane. The organic phase was filtered and the solvent was removed in vacuo. Yield: 0.50 g (38%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 3.61$ (s, 3H, N-C*H*$_3$), 6.75 (s, 1H, H_{im}), 7.12–7.45 (m, 10H, Ph), 7.68 (s, 1H, H_{im}). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): $\delta = -34.3$. Electrospray ionization (ESI) (CH_3OH) *m/z* (rel. Int.) = 283 (15) $[MO+H]^+$, 267 (100) $[M+H]^+$, 219 (20) $[OPPh_2OH]^+$, 183 (50) $[M\text{-}Im^{NMe}]^+$. $C_{16}H_{15}N_2P \cdot CH_2Cl_2 \cdot 2\ H_2O$ (290.30): Calcd. C, 52.7; H, 5.5; N, 7.2. Found C, 52.3; H, 5.3; N, 6.7%.

Synthesis of Selenides

The synthesis was carried out using known procedures.

- *Route A:* A solution of the phosphine (0.1 mmol) in 1 mL of the corresponding solvent (Tables 1–4) was stirred for 16 h with selenium at room temperature and the excess of selenium was removed by filtration.
- *Route B:* A solution of phosphine (0.1 mmol) in 1 mL of the corresponding solvent (Tables 1–4) was stirred for 6 h with an excess KSeCN at room temperature and the precipitate was removed by filtration. To the resulting solution, the external standard was added and the ^{31}P NMR spectrum was recorded.

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