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Reactions of a phosphavinyl Grignard reagent with main group mono-halide compounds

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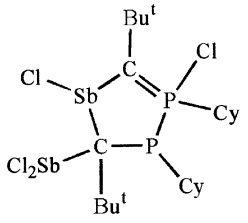
Abstract

The reactions of a phosphavinyl Grignard reagent, [CyP=C(Bu^t)MgCl(OEt$_2$)] Cy = cyclohexyl, with a variety of main group 13, 14 and 16 mono-halide compounds have been investigated. When the Grignard reagent is reacted with bromocatecholborane the terminal phosphavinyl complex, [(C$_6$H$_4$O$_2$)B{C(Bu^t)=PCy}], is formed. Related terminal phosphavinyl tin and gallium complexes, [R$_3$Sn{C(Bu^t)=PCy}], R = Me or Bu^n and [IGa{C(Bu^t)=PCy}$_2$], have been prepared by similar routes. The reaction of the Grignard reagent with PhSeCl has afforded a new λ^5,λ^5-diphosphete, [{(Bu^t)CP(Cy)(SePh)}$_2$], the mechanism of formation of which is discussed. The preparation of a phosphavinyl selenium compound, [(C$_8$H$_4$O$_2$N)P=C(Bu^t)(SePh)], is also described. All compounds have been spectroscopically characterised and several have been crystallographically authenticated.

Keywords: Phosphavinyl; Grignard; Main group; Low coordination; Phosphorus

1. Introduction

In recent years we have been systematically investigating the reactivity of phosphavinyl Grignard reagents, [RP=C(Bu^t)MgCl], R = alkyl or aryl [1], toward main group [2–4] and transition metal [5,6] halide complexes. Our original aim was to prepare terminal phosphavinyl metal complexes, which it was believed would prove useful as reagents in organophosphorus and phospha-organometallic synthesis, especially considering the wide applicability of vinyl–metal complexes in synthesis [7]. However, we have found that, although relatively stable terminal phosphavinyl complexes can be formed, e.g. [Me$_2$Sn{C(Bu^t)=PCy}$_2$] (**1**) [2] and [CyIn{C(Bu^t)=PCy}$_2$] (**2**) Cy = cyclohexyl [3], metal mediated phosphavinyl coupling reactions more commonly occur to give unusual heterocyclic or metallocage compounds, e.g. **3** [4] and **4** [3]. Although these compounds are of great interest in their own right the preparation of stable, terminal phosphavinyl-main group complexes would allow an entry into their use as reagents in synthetic techniques such as Stille type coupling reactions. It was apparent that the reaction of phosphavinyl Grignard reagents with main group monohalide compounds, R$_n$EX, R = alkyl, aryl etc., X = halide, $n = 0$–3, could afford such stable compounds, e.g. R$_n$E–C(Bu^t)=PR, which are exempt from intramolecular phosphavinyl coupling reactions. Our efforts in this area are reported herein.



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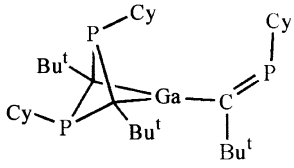

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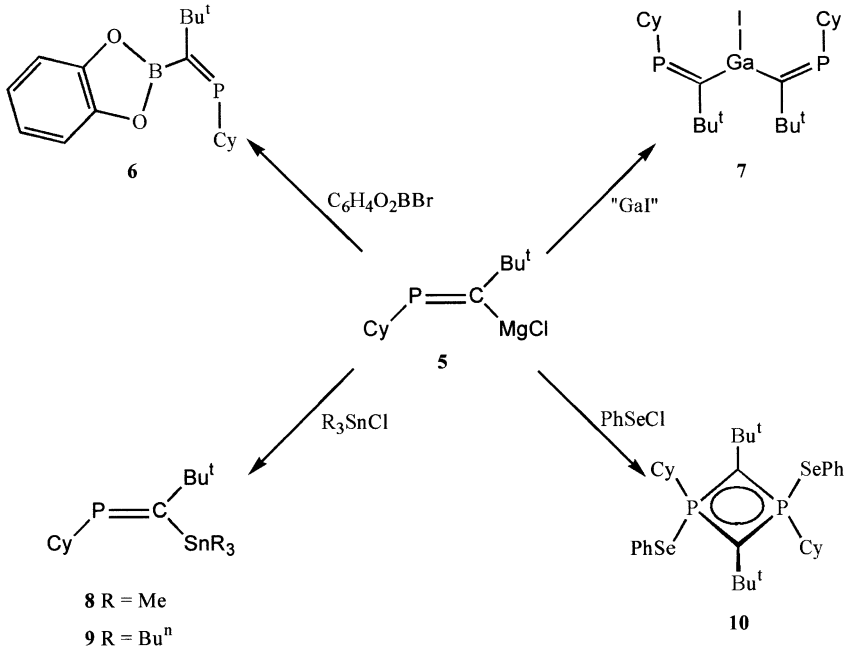
2. Results and discussion

The use of vinyl boronic acids and esters in transition metal catalysed C–C bond forming reactions, e.g. Suzuki cross couplings, is well established [8]. It seemed logical that if the phosphavinyl equivalents of these reagents could be prepared they may prove useful in organophosphorus synthesis. To this end bromocatecholborane was treated with one equivalent of [CyP=C(Bu^t)MgCl] (**5**) which led cleanly to a moderate yield (65%) of the waxy solid, **6**, after extraction of the reaction mixture with hexane (Scheme 1). Although NMR spectroscopy showed the material to be of high purity (>95%) it could be obtained analytically pure, though in lower yield (30%), by sublimation. The NMR spectroscopic data for the compound were as expected and most notably the ^{31}P-NMR spectrum exhibited a singlet at low field, 322.3 ppm, very close to that for **5** (324 ppm). An inspection of the ^{11}B-NMR spectrum of **6** revealed a singlet resonance at 31.5 ppm, which is consistent with the presence of the catecholboryl moeity.

Thallium(I) and indium(I) alkyls have found significant use as alkyl transfer reagents in organometallic synthesis [9]. Therefore, it seemed worthy to attempt the preparation of [M{C(Bu^t)=PCy}], M = Tl or In, via the reaction of **5** with MCl. In both reactions, however, metal deposition was observed and high yield formations of the known 2,4-diphosphabicyclobutane, $Cy_2P_2C_2Bu^t_2$, occurred, presumably as a result of an oxidative coupling of two phosphavinyl fragments. It is noteworthy that we have observed similar couplings in the reaction of **5** with $PbCl_2$ which also lead to deposition of the metal involved [10]. As an extension of this work the 1:1 reaction of **5** with 'GaI' was attempted. This reagent is formed via the sonication of gallium metal and half an equivalent of I_2 in toluene [11], though its actual composition is not yet known. When the reaction with **5** was carried out, gallium metal deposition was observed and the ^{31}P-NMR spectrum of the reaction mixture showed only a low field resonance at 307.2 ppm, in the normal region for phosphavinyl fragments [12]. In contrast to the corresponding Tl and In reactions, there was no formation of the coupled product, $Cy_2P_2C_2Bu^t_2$. Recrystallisation of the reaction mixture afforded a moderate yield of the Ga(III) compound, **7**, (Scheme 1). It seems that this probably forms via an intermediate, [Ga^I{C(Bu^t)=PCy}], which reacts with 'GaI' in a series of redistribution and disproportionation reactions to give **7** and two equivalents of gallium metal. The reaction occurred too rapidly for the proposed intermediate to be observed by ^{31}P-NMR spectroscopy.

Although **7** is closely related to **2**, its chloro analogue, [ClGa{C(Bu^t)=PCy}$_2$], has been proposed as a short lived intermediate in the formation of **4** from $GaCl_3$ and three equivalents of **5** [3]. In that work it was believed that [ClGa{C(Bu^t)=PCy}$_2$] underwent a rapid phosphavinyl coupling reaction and substitution of the chloride ligand with a third equivalent of **5** to give **4**. Interestingly, if **7** is treated with one equivalent of **5** no reaction occurs. It is not known why varying the nature of the halide ligands in **7** would have such a significant impact on its reactivity.

The molecular structure of **7** is depicted in Fig. 1 (Table 1). It is monomeric and as with the closely related compound, **2**, the metal centre has a trigonal-planar



Scheme 1.

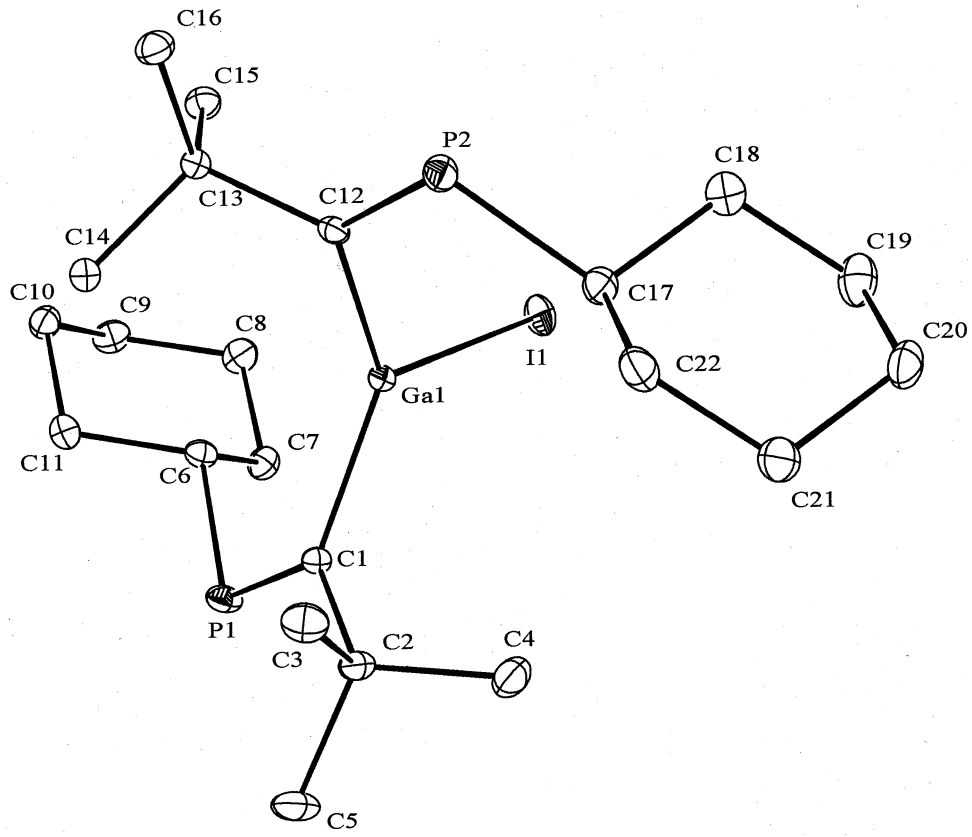


Fig. 1. Molecular structure of **7**. Selected bond lengths (Å) and angles (°): I(1)–Ga(1) 2.5364(7), Ga(1)–C(12) 1.968(2), Ga(1)–C(1) 1.973(2), P(1)–C(1) 1.674(2), P(2)–C(12) 1.671(2), C(12)–Ga(1)–C(1) 130.77(9), C(12)–Ga(1)–I(1) 114.22(6), C(1)–Ga(1)–I(1) 114.98(7), P(1)–C(1)–Ga(1) 121.17(13), P(2)–C(12)–Ga(1) 122.00(13).

coordination environment (Σ angles = 359.97°). Both the phosphavinyl fragments have retained their *Z*-stereochemistry and the two unsaturated P–C bond lengths (1.672 Å avge.) are in the normal region for localised double bonds [12]. All other bond lengths and angles within the compound are unexceptional.

The Stille cross coupling of vinyl-trialkyltin compounds with organic electrophiles in the presence of a transition metal catalyst is a powerful synthetic tool, widely utilised by organic chemists [13]. The preparation of the phosphavinyl analogues of these tin reagents could lead to their use as building blocks in the synthesis of new mono- and multi-dentate phosphorus based ligand systems using Stille methodology. The formation of these tin reagents seemed feasible given our previous preparation of the related bis-phosphavinyl tin complex, **1** [2]. This was readily achieved by reacting one equivalent of **5** with trialkyl tin chlorides to give the products, **8** and **9**, in high yields (Scheme 1). Both compounds are liquids at room temperature and can be obtained simply by filtering the reaction mixtures and removing the solvent from the filtrate in vacuo. The purity of these crude products was found by NMR spectroscopy to be greater than 98% and thus no further purification was attempted. Their ^{31}P-NMR spectra both displayed low field singlets having ^{117,119}Sn satellites with $^{2}J_{SnP}$ couplings in the expected region (**8** δ 325.2 ppm, $^{2}J_{SnP}$ 157 Hz; **9** δ 324.8 ppm, $^{2}J_{SnP}$ 144 Hz). The magnitude of these couplings were also reflected in the ^{119}Sn spectra of **8** and **9** which exhibited doublet resonances centred at −60.3 and −54.2 ppm, respectively.

Vinyl selenide compounds are useful reagents in hetero-organic synthesis [14]. Again it would be valuable to prepare the phosphavinyl analogues of these compounds and explore their utility in organic transformations. We have previously achieved this by the 1,2-additions of phenylselenyl halides to phosphaalkynes, P≡CR, R = Bu^t, adamantyl. However, although these additions were high yielding they were not stereo- or regiospecific, and thus of limited value [15]. The reaction of phenyl selenyl halides with **5** could potentially overcome this problem and lead, stereospecifically, to the *Z*-phosphavinyl complex, *Z*-[PhSe{C(Bu^t)=PCy}]. In practice, however, a very different result occurred. The 1:1 reaction of PhSeCl with **5** in diethyl ether afforded a high yield of the 1,3-λ^5,λ^5-diphosphete, **10**, after recrystallisation from hexane (Scheme 1). When this reaction was monitored by ^{31}P-NMR spectroscopy a singlet was initially observed at 320 ppm which upon warming to room temperature rapidly diminished and a new singlet appeared at 45.2 ppm which possesses ^{77}Se satellites

Table 1
Summary of crystallographic data for complexes **7**, **10** and **11**

	7	**10**	**11**
Formula	$C_{22}H_{40}GaIP_2$	$C_{34}H_{50}P_2Se_2$	$C_{19}H_{18}NO_2PSe$
M_r	563.10	678.60	402.27
a (Å)	9.5550(19)	7.803(5)	13.370(3)
b (Å)	10.915(2)	23.040(15)	8.520(2)
c (Å)	12.789(3)	18.771(13)	16.175(3)
α (°)	98.13(3)	90	90
β (°)	1105.11(3)	92.620(18)	107.64(3)
γ (°)	93.40(3)	90	90
V (Å^3)	1268.3(4)	3371(4)	1755.9(7)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$
λ (Å)	0.71073	0.71073	0.71073
T (K)	150(2)	296(2)	150(2)
Z	2	4	4
Size	0.20 × 0.20 × 0.15	0.08 × 0.05 × 0.05	0.20 × 0.20 × 0.20
Colour	Orange	Orange	Yellow
μ (mm^{-1})	2.433	2.309	2.240
F(000)	572	1408	816
Reflections collected	25 002	15 544	3948
Unique reflections	5794	4844	3561
Parameters varied	241	344	220
R $\{I > 2\sigma(I)\}$	0.0280	0.0787	0.0405
R_w {all data}	0.0648	0.2184	0.0901

with a characteristic one bond coupling ($^1J_{SeP} = 287$ Hz). We believe the mechanism of the reaction involves the initial formation of the selenophosphaalkene, CyP=C(Bu^t)(SePh), which gives rise to the singlet at 320 ppm. This rearranges, perhaps via a 1,2-selenyl shift to give a short lived λ^5-phosphaalkyne, (Cy)(PhSe)P≡CBu^t, which was not detected by NMR spectroscopy but undergoes a spontaneous [2+2] cycloaddition reaction to give **10**. This mechanism seems reasonable as there is precedent for the formation of λ^5,λ^5-diphosphetes via the cycloaddition of λ^5-phosphaalkynes [16].

The molecular structure of **10** is depicted in Fig. 2 (Table 1). The data for this crystal structure were poor due to the small size of the crystal used in the diffraction experiment and, therefore, the accuracy of the metrical parameters must be considered as low. Despite this, the structure shows the compound to contain a central planar four-membered PCPC ring in which all the P–C bond lengths are of a similar magnitude (1.736 Å avge.) and in the range expected for delocalised P–C double bonds [12]. The geometry about the ring carbon atoms is trigonal-planar and the phosphorus centres have distorted tetrahedral environments, as is the case in the few previously reported λ^5,λ^5-diphosphetes, e.g. {(PhCH$_2$)(Et$_2$N)PC(Ph)}$_2$ [17].

Although the reaction of **5** with PhSeCl did not yield a stable phosphavinyl-selenium compound, it was decided to pursue this aim by making modifications to the aforementioned non-selective 1,2-additions of phenyl selenyl halides to phosphaalkynes. To introduce more control over the isomers formed in such reactions the halide substituents in PhSeX were replaced with the bulky phthalamide group. This strategy was successful in that the reaction of *N*-phenylselenylphthalamide with P≡CBu^t in a 1:1 stoichiometry led regio- and stereospecifically to the phosphavinyl-selenium compound, **11**, in good yield (Scheme 2). The observed regiochemistry of the reaction is not surprising considering that the triple bond of the phosphaalkyne starting material is polarised, $^{\delta+}$P≡C$^{\delta-}$, whilst the stereochemistry of the addition is understandable on steric grounds.

All the spectroscopic data for **11** are consistent with its proposed formulation which was confirmed by X-ray crystallography. Its molecular structure (Fig. 3, Table 1) shows the molecule to be monomeric with the phenylselenyl group *cis*- to the phthalamide substituent. The P(1)–C(1) bond length [1.687(3) Å] is entirely consistent with a localised double bond and all other bond lengths and angles are in the expected ranges. One feature of note in the structure is the fact that the phenyl group and the 5-membered ring of the phthalamide substituent are intramolecularly 'stacked' with a centroid–centroid distance of 3.335 Å (Fig. 3b) which is consistent with previously reported π-stacking interactions [18].

3. Conclusions

In conclusion, the preparation and characterisation of a range of phosphavinyl complexes that could prove useful as reagents in organophosphorus synthesis have been investigated. This study has led to the formation of a series of terminal mono-phosphavinyl boron, tin and selenium compounds, in addition to a new 1,3-λ^5,λ^5-diphosphete. We are currently investigating the use of the prepared phosphavinyl complexes in C–C bond forming reactions (e.g. Stille and Suzuki couplings) and will report on this study in a forthcoming publication.

4. Experimental

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon or dinitrogen. Toluene, Et$_2$O, THF and hexane were distilled over potassium or NaK alloy then freeze–thaw degassed prior to use. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on either a Bruker DPX400 or JEOL Eclipse 300 spectrometer in C$_6$D$_6$ and were referenced to the residual ^{1}H or ^{13}C resonances of the solvent used (^{1}H- and ^{13}C-NMR) or to external 85%

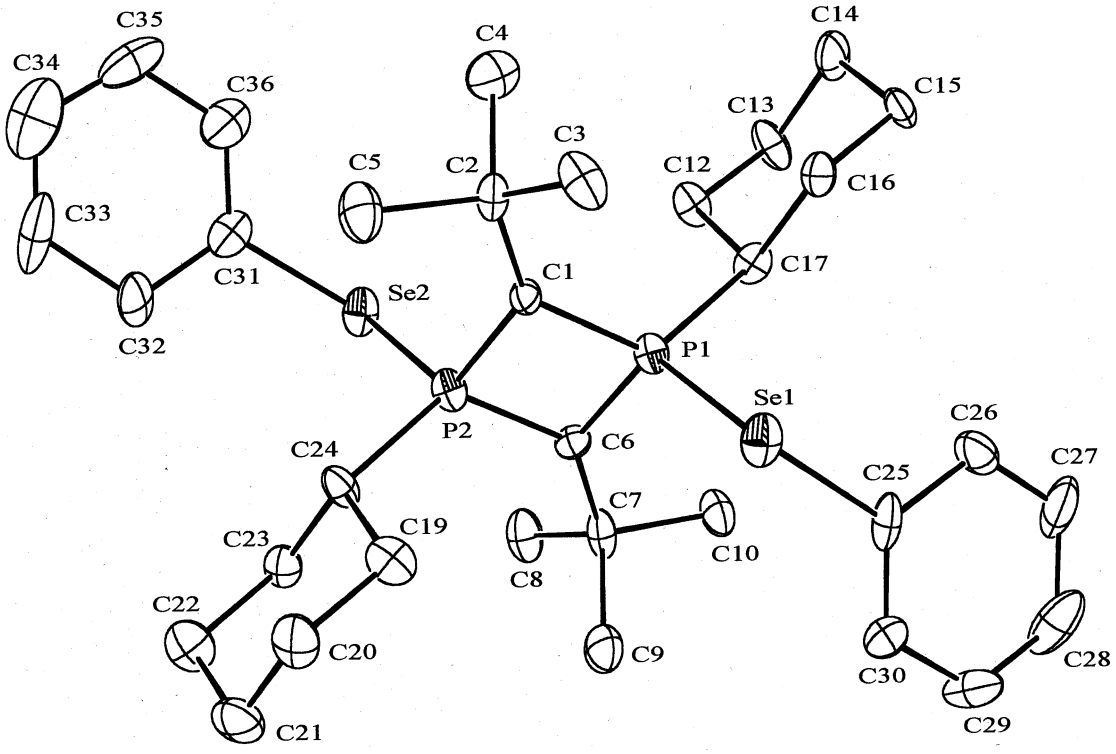
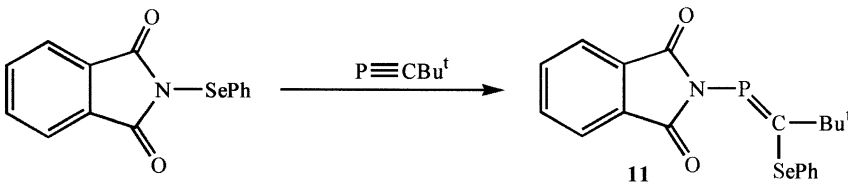


Fig. 2. Molecular structure of **10**. Selected bond lengths (Å) and angles (°): Se(1)–P(1) 2.304(4), P(1)–C(1) 1.732(13), P(1)–C(6) 1.746(13), C(1)–P(2) 1.736(13), Se(2)–P(2) 2.300(4), P(2)–C(6) 1.729(13), C(1)–P(1)–C(6) 91.7(6), C(1)–P(1)–Se(1) 106.8(5), C(6)–P(1)–Se(1) 118.1(5), P(1)–C(1)–P(2) 88.2(6), C(6)–P(2)–C(1) 92.1(6), C(6)–P(2)–Se(2) 104.8(5), C(1)–P(2)–Se(2) 117.2(5), P(2)–C(6)–P(1) 88.0(6).

H_3PO_4, 0.0 ppm (^{31}P-NMR). Mass spectra were recorded using a VG Fisons Platform II instrument under APCI conditions. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. Elemental analyses were carried out at the Warwick Analytical Service. Reproducible elemental analyses of **8**, **9** and **11** could not be obtained but the NMR spectra of the crude products showed them to have a purity of $>98\%$. Compound **5** was prepared by a literature procedure [1]. All other reagents were used as received.

4.1. $[(C_6H_4O_2)B\{C(Bu^t)=PCy\}]$ (**6**)

To a solution of bromocatecholborane (0.31 g, 1.58 mmol) in Et_2O (20 ml) at -78 °C was added **5** (0.50 g, 1.58 mmol) in Et_2O (20 ml). The resultant pale yellow solution was warmed to room temperature (r.t.) and filtered. Volatiles were removed in vacuo and the residue extracted into hexane (10 ml). The solution was then filtered and the solvent removed in vacuo to give a colourless oily solid. This was sublimed at 110 °C (0.001 mmHg) to give **6** as a colourless solid (145 mg, 30%), m.p. 57–59 °C; ^{1}H-NMR (300.5 MHz, C_6D_6, 298 K) δ 1.37 (d, 9H, $^4J_{PH}=1.7$ Hz, Bu^t), 2.24–0.97 (m, 11H, Cy), 6.79 (m, 2H, Ph), 7.08 (m, 2H, Ph); ^{31}P-NMR (121.7 MHz, C_6D_6, 298 K) δ 322.3 (s, P=C); ^{11}B-NMR (96.4 MHz, C_6D_6, 298 K) δ 31.5 (s); ^{13}C-NMR (75.6 MHz, C_6D_6, 298 K) δ 198.3 (d, $^1J_{PC}=45.0$ Hz, P=C), 148.2 (s, Ar), 122.9 (s, Ar), 112.5 (s, Ar), 41.0 (d, $^1J_{PC}=35.8$ Hz, Cy), 41.2 (d, $^2J_{PC}=16.1$ Hz, CMe_3), 31.8 (d, $^2J_{PC}=13.8$ Hz, Cy), 31.7 (d, $^3J_{PC}=15.0$ Hz, CMe_3), 26.4 (d, $^3J_{PC}=9.2$ Hz, Cy), 25.6 (s, Cy); MS APCI *m/z* 185 ($[M^+-BO_2C_6H_4]$, 20%), 115 ($[PCy^+]$, 50%), 83 ($[Cy^+]$, 95%); IR (Nujol) ν cm^{-1}: 1170 (m), 1148 (m), 1124 (s), 1094 (s), 1079 (s), 1004 (m), 956 (w), 917 (w), 881 (w), 866 (w), 848 (w); microanalysis found: C 66.88, H 8.00; Calc. for $C_{17}H_{24}BO_2P$: C 67.58, H 8.01%.



Scheme 2.

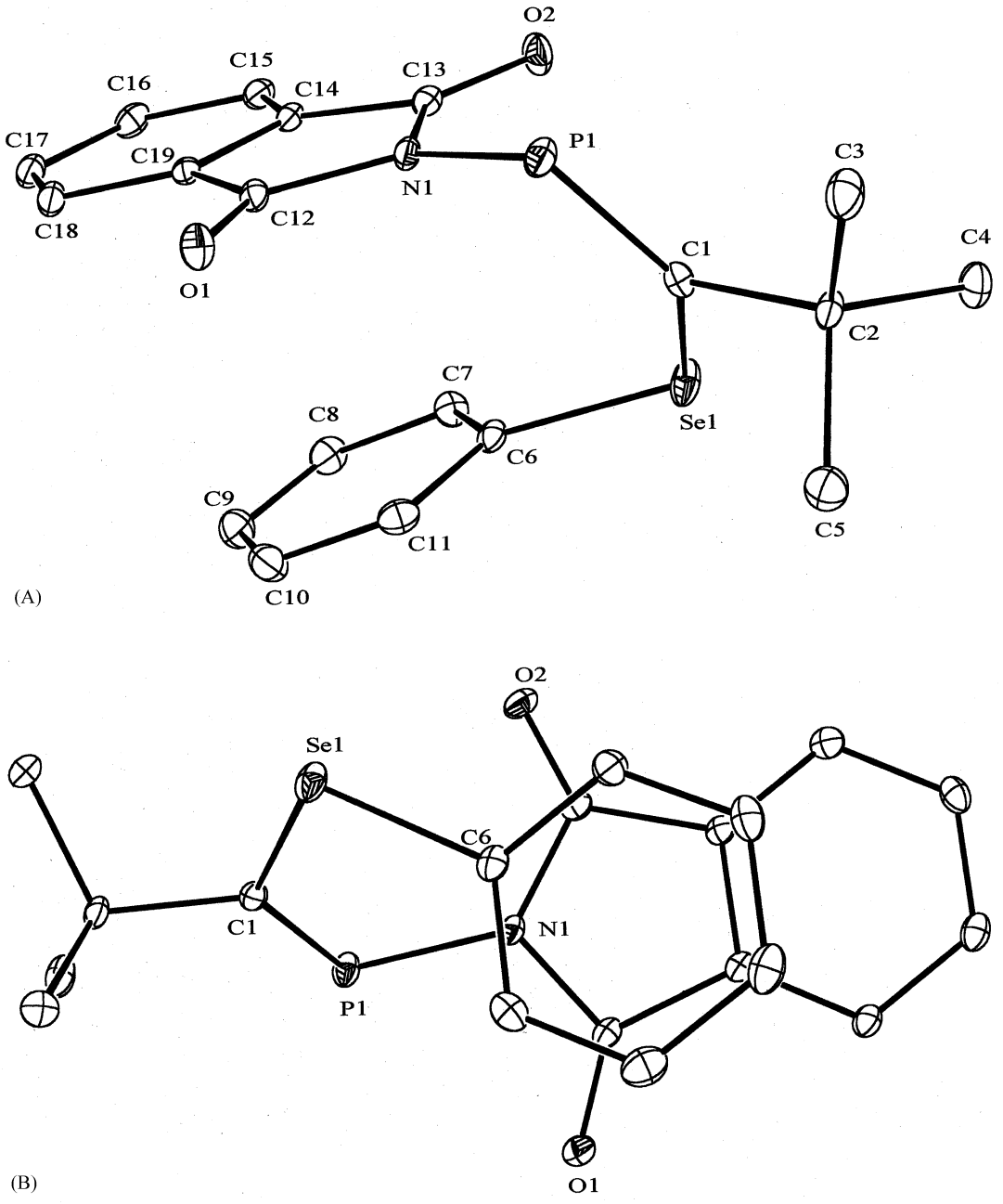


Fig. 3. Molecular structure of **11**. Selected bond lengths (Å) and angles (°): N(1)–P(1) 1.743(3), Se(1)–C(1) 1.900(3), Se(1)–C(6) 1.907(3), P(1)–C(1) 1.687(3), C(1)–Se(1)–C(6) 105.57(14), C(1)–P(1)–N(1) 105.87(15), C(2)–C(1)–P(1) 117.5(2), P(1)–C(1)–Se(1) 130.08(19).

4.2. *[IGa{C(Bu^t)=PCy}$_2$] (7)*

Gallium metal (0.13 g, 1.86 mmol) and iodine (0.24 g, 0.93 mmol) were suspended in toluene (20 ml) and placed in a ultrasonic bath for 30 min. The generated white suspension was cooled to −78 °C and **5** (0.60 g, 1.86 mmol) in toluene (20 ml) was added over 10 min. The resultant red suspension was warmed to r.t. and filtered. Volatiles were removed in vacuo and the residue extracted into hexane (10 ml). The solution was then filtered and the extract was concentrated to ca. 3 ml and placed at −30 °C to yield orange–brown crystals of **7** (0.05 g, 14%, yield based on number of mmol of I_2), m.p. 118–120 °C dec.; ^{1}H-NMR (300.5 MHz, $C_6D_5CD_3$, 298 K) δ 1.34 (d, $^4J_{PH} = 2.2$ Hz, 18H, Bu^t), 2.81–1.05 (m, 22H, Cy); ^{31}P-NMR (121.7 MHz, C_6D_6, 298 K) δ 307.2 (s, P=C); ^{13}C-NMR (75.6 MHz, C_6D_6, 298 K) 226.0 (d, $^1J_{PC} = 64.6$ Hz, P=C), 44.5 (d, $^2J_{PC} = 12.7$ Hz, *C*Me$_3$), 44.3 (d, $^1J_{PC} = 36.9$ Hz, Cy), 33.0 (d, $^3J_{PC} = 16.1$ Hz, C*Me*$_3$), 30.4 (d, $^2J_{PC} = 12.7$ Hz, Cy), 26.0 (d, $^3J_{PC} = 8.1$ Hz, Cy), 25.4 (s, Cy); MS APCI *m/z* 563 ([M$^+$], 29%), 367 ([M$^+$ −GaI], 19%); IR (Nujol) ν cm^{-1}: 1378 (s),

1358 (s), 1265 (m), 1230 (m), 1211 (w), 1190 (m), 1168 (w), 1090 (m), 1025 (m), 997 (m), 922 (s), 881 (m), 849 (s), 812 (w), 783 (w), 737 (w); microanalysis found: C 46.31, H 7.11; Calc. for $C_{22}H_{40}GaIP_2$: C 46.93, H 7.16%.

4.3. [$Me_3Sn\{C(Bu^t)=PCy\}$] (**8**)

A solution of Me_3SnCl (0.32 g, 1.58 mmol) in Et_2O (20 ml) was cooled to −78 °C and **5** (0.50 g, 1.58 mmol) in Et_2O (10 ml) was added over 10 min. The resultant pale orange–yellow solution was warmed to r.t. and filtered. Volatiles were removed in vacuo and the residue extracted into hexane (10 ml). This was then filtered and the solvent removed in vacuo to give **8** as a colourless liquid (0.50 g, 91%), ^{1}H-NMR (300.5 MHz, C_6D_6, 298 K) δ 0.33 (s, 9H, $^2J_{SnH}$ = 25.9 Hz, SnMe_3), 1.29 (d, 9H, $^4J_{PH}$ = 2.2 Hz, Bu^t), 2.34–1.10 (m, 11H, Cy); ^{31}P-NMR (121.7 MHz, C_6D_6, 298 K) δ 325.2 (s, $^2J_{SnP}$ = 156.7 Hz, P=C); ^{119}Sn-NMR (112.1 MHz, C_6D_6, 298 K) δ −60.3 (d, $^2J_{SnP}$ = 156.7 Hz); ^{13}C-NMR (75.6 MHz, C_6D_6, 298 K) δ 219.5 (d, $^1J_{PC}$ = 68.1 Hz, P=C–Sn), 43.9 (d, $^2J_{PC}$ = 16.2 Hz, CMe$_3$), 43.8 (d, $^1J_{PC}$ = 36.9 Hz, Cy), 32.2 (d, $^3J_{PC}$ = 18.5 Hz, CMe_3), 31.5 (d, $^2J_{PC}$ = 13.8 Hz, Cy), 26.5 (d, $^3J_{PC}$ = 9.2 Hz, Cy), 25.7 (s, Cy), −3.2 (d, $^1J_{SnC}$ = 160.4 Hz, $^3J_{PC}$ = 6.9 Hz, SnMe_3); MS APCI m/z 263 ([M$^+$ −Cy], 100%), 231; IR (Nujol) ν cm^{-1}: 1447 (s), 1388 (w), 1358 (s), 1260 (s), 1223 (m), 1188 (m), 1168 (w), 1096 (m), 1017 (m), 997 (w), 907 (w), 848 (m), 773 (s), 711 (m).

4.4. [$Bu^n_3Sn\{C(Bu^t)=PCy\}$] (**9**)

To a solution of Bu^n_3SnCl (120 μl, 1.58 mmol) in Et_2O (20 ml) at −78 °C was added **5** (0.20 g, 1.58 mmol) in Et_2O (10 ml) over 10 min. The resultant pale orange–yellow solution was warmed to r.t. and filtered. Volatiles were removed in vacuo and the residue extracted into hexane (10 ml). This was then filtered and the solvent removed in vacuo to give **9** as a colourless liquid (0.22 g, 74%), ^{1}H-NMR (300.5 MHz, C_6D_6, 298 K) δ 0.96 (m, 9H, Bu^n), 1.14 (m, 6H, Bu^n), δ 1.34 (d, 9H, $^4J_{PH}$ = 2.8 Hz, Bu^t), 1.36 (m, 6H, Bu^n), δ 1.58 (m, 6H, Bu^n), 2.41–0.71 (m, 11H, Cy); ^{31}P-NMR (121.7 MHz, C_6D_6, 298 K) δ 324.8 (s, $^2J_{SnP}$ = 144.3 Hz, P=C); ^{119}Sn-NMR (112.1 MHz, C_6D_6, 298 K) δ −54.2 (d, $^2J_{SnP}$ = 144.3 Hz); ^{13}C-NMR (75.6 MHz, C_6D_6, 298 K) δ 218.9 (d, $^1J_{PC}$ = 69.2 Hz, P=C–Sn), 43.8 (d, $^1J_{PC}$ = 40.4 Hz, Cy), 43.5 (d, $^2J_{PC}$ = 16.1 Hz, CMe$_3$), 32.5 (d, $^3J_{PC}$ = 18.5 Hz, CMe_3), 31.6 (d, $^2J_{PC}$ = 13.8 Hz, Cy), 29.4 (s, Bu^n), 27.6 (s, Bu^n), 26.7 (d, $^3J_{PC}$ = 9.2 Hz, Cy), 25.8 (s, Cy), 14.5 (s, Bu^n), 13.6 (s, Bu^n); MS APCI m/z 473 ([M$^+$], 11%); IR (Nujol) ν cm^{-1}: 1464 (s), 1448 (s), 1417 (w), 1388 (w), 1376 (m), 1359 (m), 1262 (w), 1206 (m), 1151 (s), 1072 (s), 1016 (s), 961 (m), 876 (w), 849 (w), 813 (s).

4.5. [$\{(Bu^t)CP(Cy)(SePh)\}_2$] (**10**)

To a solution of PhSeCl (0.30 g, 1.58 mmol) in Et_2O (20 ml) at −78 °C was added **5** (0.50 g, 1.58 mmol) in Et_2O (10 ml) over 10 min. The resultant orange solution was warmed to r.t. and filtered. Volatiles were removed in vacuo and the residue extracted into hexane (10 ml). The solution was then filtered and the solvent reduced to 5 ml and placed overnight at −30 °C to give **10** as orange–red crystals (0.43 g, 78%), m.p. 78–80 °C (dec.); ^{1}H-NMR (300.5 MHz, C_6D_6, 298 K) δ 1.40 (s, 18H, Bu^t), 2.36–1.03 (m, 22H, Cy), 6.99 (m, 2H, Ph), 7.84 (m, 4H, Ph), 8.07 (m, 4H, Ph); ^{31}P-NMR (121.7 MHz, C_6D_6, 298 K) δ 45.2 (s, $^1J_{PSe}$ = 287 Hz, CPC); ^{13}C-NMR (75.6 MHz, C_6D_6, 298 K) δ 139.4 (s, Ph), 137.7 (s, Ph), 128.7 (s, Ph), 128.4 (s, Ph), 47.3 (d, $^1J_{PC}$ = 20.8 Hz, Cy), 42.0 (t, $^2J_{PC}$ = 17.3 Hz, CMe$_3$), 34.8 (t, $^3J_{PC}$ = 8.1 Hz, CMe_3), 28.1 (s, Cy), 27.2 (t, $^3J_{PC}$ = 8.1 Hz, Cy), 26.3 (s, Cy) (P–C–P resonance not observed); MS APCI m/z 679 ([M$^+$], 100%); IR (Nujol) ν cm^{-1}: 1574 (m), 1263 (s), 1207 (w), 1167 (m), 1097 (w), 1035 (m), 1021 (m), 997 (w), 906 (m), 871 (m), 811 (w); Accurate mass MS (EI) calc. mass for $C_{34}H_{50}P_2Se_2$: 680.1718, measured mass: 680.1722.

4.6. [$(C_8H_4O_2N)P=C(Bu^t)(SePh)$] (**11**)

To a THF solution (10 ml) of *N*-phenylselenylphthalamide (0.50 g, 1.67 mmol) at −78 °C was added P≡CBu^t (0.27 ml, 1.67 mmol) over 5 min. The reaction mixture was warmed slowly to r.t. and stirred for 48 h. Removal of volatiles in vacuo and extraction into hexane (5 ml) afforded **11** as pale yellow crystals after placement at −30 °C overnight. (0.42 g, 62%), m.p. 129–132 °C; ^{1}H-NMR (300.5 MHz, $C_6D_5CD_3$, 298 K) δ 1.05 (s, 9H, Bu^t), 6.32–6.61 (m, 5H, Ph), 7.22–7.83 (m, 4H, ArH); ^{31}P-NMR (121.7 MHz, C_6D_6, 298 K) δ 237.7 (s, P=C); ^{13}C-NMR (75.6 MHz, C_6D_6, 298 K) 180.1 (s, C=O), 166.0 (d, $^1J_{PC}$ = 64.2 Hz, P=C), 137.4 (s, Ph), 136.9 (s, CCO), 135.2 (s, Ph), 130.2 (s, ArH), 126.7 (s, Ph), 128.1 (s, Ph), 120.8 (ArH), 43.1 (d, $^2J_{PC}$ = 11.7 Hz, CMe$_3$), 32.0 (d, $^3J_{PC}$ = 15.2 Hz, CMe_3), MS APCI m/z 245 ([M$^+$ −PhSe], 10%), 156 ([PhSe$^+$], 100%); IR (Nujol) ν cm^{-1}: 1576 (m), 1276 (m), 1021 (m), 734 (m).

4.7. Crystallographic studies

Crystallographic measurements were made using either an Nonius Kappa CCD (**7**), Siemens SMART CCD (**10**) or an Enraf-Nonius CAD4 diffractometer (**11**). All structures were solved using direct methods and refined on F^2 by full-matrix least-squares (SHELX-97) [19] using all unique data. All non-hydrogen atoms are anisotropic with H-atoms included in calculated positions (riding model). The data for the structure of compound **10** were weak and poor due to the small

size of the crystal and repeated attempts to grow larger crystals met with failure. However, the fact that all the spectroscopic data for this compound are consistent with its formulation leaves no doubt about the gross molecular framework of the compound.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures of **7**, **10** and **11** have been deposited with the Cambridge Crystallographic Data Centre (**7**: CCDC no. 193028; **10**: CCDC no. 193029, **11**: CCDC no. 193030). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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