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The synthesis and complexation of a bis(phosphavinyl)tin compound

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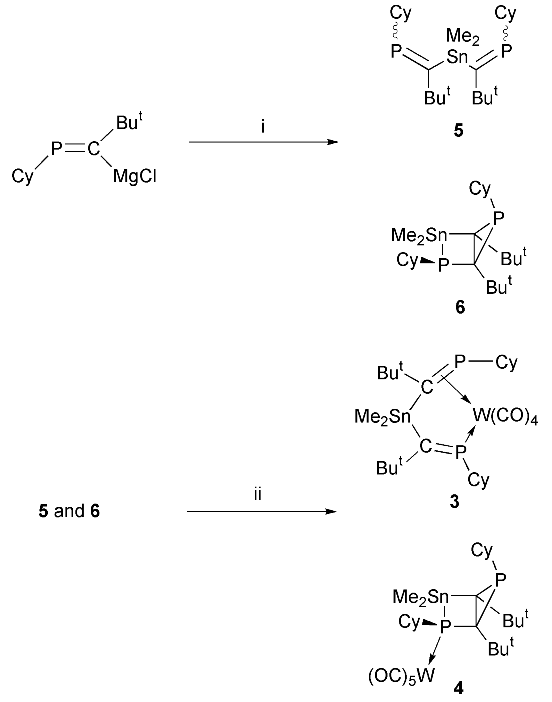
The first bis(phosphavinyl)tin and stannadiphosphabicyclo[2.1.0]pentane compounds, readily prepared from the reaction of a phosphavinyl Grignard reagent with $SnMe_2Cl_2$, have been used as ligands in the formation of two crystallographically characterised complexes.

Main group vinyl complexes have been widely utilised as reagents in both organic and organometallic synthesis.[1] It might be expected that main group phosphavinyl complexes, *i.e.* $[M\{-C(R)=P(R)\}_n]$ **1**, M = main group element, would have a similar range of uses in organophosphorus and phospha-organometallic synthesis, especially considering the close analogy between phosphorus and the valence isoelectronic CR fragment.[2] We have recently reported the regio- and stereo-selective syntheses of a range of substituted phosphavinyl Grignard reagents, *e.g.* $[Z\text{-}Mg(Cl)\{-C(Bu^t)=PCy\}]$ **2** Cy = cyclohexyl,[3] which we saw as potential transfer reagents in the synthesis of compounds of the type **1**. In particular we are interested in the preparation of phosphavinyl tin complexes given the wide applicability of vinyl tin compounds to a number of organic transformations which include the Stille reaction.[4] To date there is only one example of a related phosphaalkenyl tin complex, $[Sn(NMe_2)\{N(SiMe_3)_2\}_2\{C(SiMe_3)=P(NR_2)\}]$, NR_2 = 2,2,6,6-tetramethylpiperidino,[5] though the transient species, $[SnR_3\{-C(R)=PH\}]$, R = alkyl or aryl, have been implicated as intermediates in the formation of several phospha-organo-tin compounds.[6] Herein, we report the outcome of the reaction of **2** with $SnMe_2Cl_2$ which has afforded the first examples of both a bis(phosphavinyl)tin compound and a stannadiphosphabicyclo[2.1.0]pentane, the latter of which is formed *via* an unexpected phosphavinyl coupling reaction.

Reaction of $SnMe_2Cl_2$ with two equivalents of **2** in diethyl ether yields an oily mixture of products after stirring overnight. A ^{31}P NMR analysis of this mixture suggested that it was comprised of two major components which could not be separated using standard techniques. Consequently, the mixture was treated with an excess of $[W(CO)_5(THF)]$ in THF and the reaction products chromatographed. Two partially overlapping bands were collected from the column and recrystallised from diethyl ether to afford orange crystals of **3** and yellow crystals of **4** in low to moderate yields (Scheme 1). Both compounds are thermally robust and can be handled in air indefinitely.

The most informative spectroscopic data come from their $^{31}P\{^1H\}$ NMR spectra † which for the major product, **3**, shows a two line pattern with the low field signal (δ 253.9) occurring in the normal region for localised phosphaalkenyl fragments.[7] This signal possesses ^{183}W satellites with a coupling of 232 Hz that is indicative of a one bond P–W interaction. The high field signal (δ 77.6) is in the expected region for η^2-coordinated phosphaalkenyl moieties.[7] The minor product, **4**, also displays a two line pattern in its $^{31}P\{^1H\}$ NMR spectrum, the low field signal (δ 29.5) of which is clearly associated with the tungsten coordinated phosphorus atom as it possesses both $^{117,119}Sn$ and ^{183}W satellites.



Scheme 1 Reagents and conditions: i, 1/2 $SnMe_2Cl_2$; ii, $W(CO)_5$(THF).

From an examination of the ^{31}P NMR spectrum of the reaction mixture prior to treatment with $[W(CO)_5(THF)]$ it is clear that the two major products in the mixture are the bis(phosphavinyl)tin compound, **5** (δ 299), and the heterobicycle, **6** (δ 42, $^1J_{PSn}$ 194 Hz; δ −106). It could not be determined if **5** exists as the *Z,Z*- or *E,E*-isomer, both of which would give a singlet in their ^{31}P NMR spectra, though the *Z,Z*-form is the more likely. In addition, we have not been able to elucidate the mechanism of formation of **6** but it seems probable that this involves one of the isomeric forms of **5** which undergoes a phosphavinyl coupling reaction and subsequent rearrangement.

The molecular structures of **3** and **4** (Fig. 1 and 2) ‡ are consistent with their solution spectroscopic data and in the case of **3** a novel mixed bonding mode exists in which the bis(phosphavinyl)tin ligand is coordinated to a $W(CO)_4$ fragment in an η^1-fashion through P(1) and an η^2-fashion through the P(2)–C(14) double bond. As a result of the side-on coordination this bond is considerably lengthened [1.754(5) Å] relative to normal localised P–C double bonds, *e.g.* P(1)–C(3) [1.666(5) Å]. It is, however, evident that the bis(phosphavinyl)tin ligand in **3** exists as its *E,Z*-isomer and therefore **5** has undergone an isomerisation upon coordination to the $W(CO)_4$ fragment. This isomerisation has precedent in metallophosphaalkene chemistry[7] and is not surprising given the weakness of the π-component of the P=C bond. The X-ray crystal structure of **4** is of low accuracy but does show it to possess a strained stannadiphosphabicyclo[2.1.0]pentane core with all bond lengths normal for single bonded interactions. From the angles

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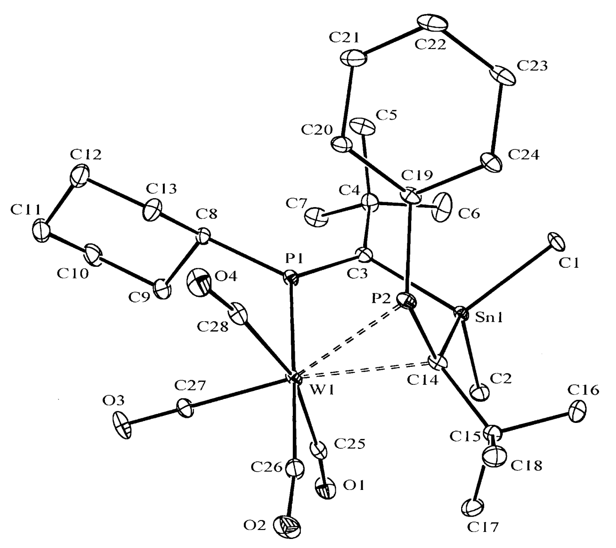

Fig. 1 Molecular structure of **3**. Selected bond lengths (Å) and angles (°): P(1)–C(3) 1.666(5), P(2)–C(14) 1.754(5), P(1)–W(1) 2.501(2), P(2)–W(1) 2.6384(17), C(14)–W(1) 2.481(6); Sn(1)–C(3)–P(1) 108.7(3), Sn(1)–C(14)–P(2) 120.0(3), C(3)–P(1)–W(1) 123.1(2), C(14)–W(1)–P(2) 39.91(12).

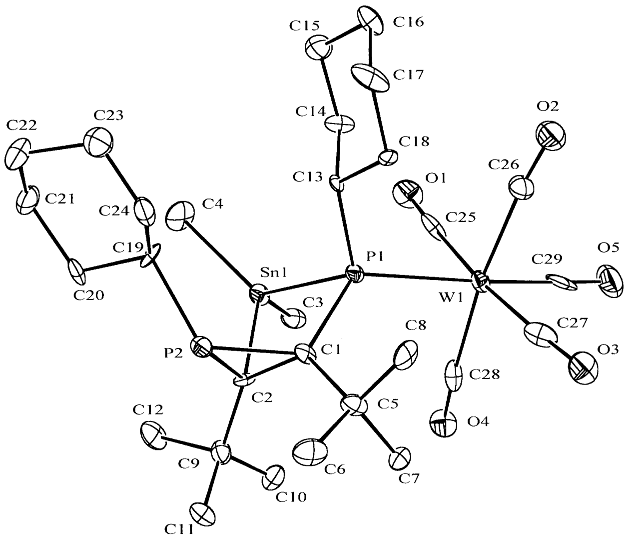

Fig. 2 Molecular structure of **4**. Selected bond lengths (Å) and angles (°): Sn(1)–P(1) 2.506(6), Sn(1)–C(2) 2.17(2), P(1)–C(1) 1.90(2), P(2)–C(1) 1.91(2), P(2)–C(2) 1.89(2); Sn(1)–P(1)–C(1) 81.4(6), P(1)–Sn(1)–C(2) 73.9(5), P(1)–C(1)–C(2) 105.5(13), Sn(1)–C(2)–C(1) 98.6(12), C(1)–P(2)–C(2) 51.2(9).

within the four membered ring it is safe to assume there is a high degree of p-character to the bonding within the ring, which would explain why no two-bond PP or SnP couplings are observed in the $^{31}P\{^{1}H\}$ NMR spectrum of **4**.

In related work we have investigated the reaction of **2** with $SnCl_2$ or $SnCl_4$ in an attempt to form homoleptic phosphavinyl tin compounds. Interestingly, however, both reactions lead to an oxidative coupling of the phosphavinyl fragment and formation of the highly strained 2,4-diphosphabicyclo[1.1.0]butane, $P_2(Cy)_2C_2(Bu^t)_2$. The results of this study, our efforts to elucidate the mechanism of formation of **6** and the use of phosphavinyl tin compounds in Stille reactions will form the basis of a forthcoming publication.

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Notes and references

† Synthesis and spectroscopic data for **3** and **4**: A solution of **2** (0.50 g, 2.05 mmol) in Et_2O (25 ml) was added to $SnMe_2Cl_2$ (0.24 g, 1.08 mmol) in Et_2O (25 ml) at −50 °C. The resulting solution was warmed slowly to room temperature, stirred overnight and volatiles removed *in vacuo* to yield a yellow oil which consisted of several inseparable phosphorus-containing products (see text). The oil was dissolved in THF (5 ml) and added to a solution of $[W(CO)_5(THF)]$ (1.9 mmol) in THF (50 ml). After 18 h volatiles were removed *in vacuo* and the residue chromatographed (Kieselgel, Et_2O–hexane 50 : 50) and partially overlapping yellow and orange fractions collected. These were concentrated *in vacuo* to yield orange crystals of **3** (yield 42% approx., mp 123–126 °C on single crystal) and yellow crystals of **4** (yield 18% approx., mp 163–168 °C dec. on single crystal). Data for **3**: $^{31}P\{^{1}H\}$ NMR (145.8 MHz, C_6D_6) δ 77.6 (s, P(2)), 253.9 (s, P(1), $^{1}J_{PW}$ 232 Hz); ^{1}H NMR (400 MHz, C_6D_6) δ 0.48 (s, 3H, SnMe), 0.69 (s, 3H, SnMe), 0.95 (s, 9H, Bu^t), 1.22 (s, 9H, Bu^t) 0.71–2.12 (m, 22H, Cy); APCI-MS: *m*/*z* 783 ($M^+ - CO$, 100%), 516 ($M^+ - W(CO)_4$, 73%); IR (Nujol, ν/cm^{-1}) 2027 m, 1951 s, 1939 s; Data for **4**: $^{31}P\{^{1}H\}$ NMR (145.8 MHz, C_6D_6) δ −108.7 (s, P(2)), 29.5 (s, P(1) $^{1}J_{SnP}$ 190, $^{1}J_{PW}$ 226 Hz); ^{1}H NMR (400 MHz, C_6D_6) δ 0.74 (s, 3H, SnMe), 0.82 (s, 3H, SnMe), 0.91 (s, 9H, Bu^t), 1.24 (s, 9H, Bu^t), 0.76–1.95 (m, 22H, Cy); APCI-MS: *m*/*z* 516 ($M^+ - W(CO)_5$, 100%), 366 ($P_2Cy_2C_2Bu^t{}_2$, 44%); IR (Nujol, ν/cm^{-1}) 2035 m, 1980 s, 1928 m; reproducible microanalyses proved difficult to obtain due to the partial co-crystallisation of **3** and **4**.

‡ Crystal data for **3**: $C_{28}H_{46}O_4P_2SnW$, $M = 811.13$ triclinic, space group $P\bar{1}$, $a = 10.759(9)$, $b = 11.445(8)$, $c = 16.379(6)$ Å, $\alpha = 103.38(5)$, $\beta = 98.22(5)$, $\gamma = 112.86(7)°$; $V = 1746(2)$ Å^3, $Z = 2$, $D_c = 1.543$ g cm^{-3}, $F(000) = 800$, $\mu(\text{Mo-K}\alpha) = 41.25$ cm^{-1}, 150(2) K, 6261 unique reflections, *R* (on *F*) 0.0342, *wR* (on F^2) 0.0919 ($I > 2\sigma I$). **4**: $C_{29}H_{46}O_5P_2SnW$, $M = 839.14$, monoclinic, space group $C2/c$, $a = 35.7212(10)$, $b = 10.3448(12)$, $c = 20.0542(15)$ Å, $\beta = 90.239(11)°$; $V = 7410.5(10)$ Å^3, $Z = 8$, $D_c = 1.504$ g cm^{-3}, $F(000) = 3312$, $\mu(\text{Mo-K}\alpha) = 38.92$ cm^{-1}, 293(2) K, 4436 unique reflections, *R* (on *F*) 0.0997, *wR* (on F^2) 0.2474 ($I > 2\sigma I$). All crystallographic measurements were made using an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods and refined on F^2 by full matrix least squares (SHELX 97)[8] using all unique data. All non-hydrogen atoms are anisotropic with H-atoms included in calculated positions (riding model). Empirical absorption corrections were carried out by the DIFABS method.[9] CCDC reference number 186/2154.

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