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2-Stannaindenes and 2-Stannaindanes

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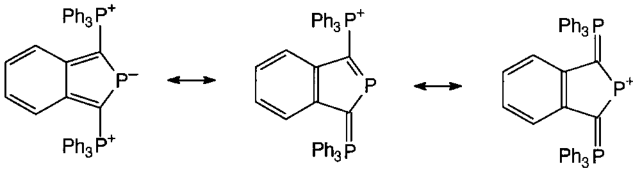
ABSTRACT

Condensation of o-xylylene bis(triphenylphosphorane) **4** *with* $[(Me_3Si)_2N]_2Sn$ *yields the 1,3-bis(triphenylphosphoranediyl)-2σ²-stannaindene* **2**, *which is orange as a solid and red in solution and which demonstrates stannylene reactivity. Alkyl bromides and iodides add to* **2** *to give the corresponding 2σ⁴-stannaindanes. In the reaction with* PCl_3, *the tin atom in* **2** *is replaced by a phosphenium ring member. A secondary product in the preparation of* **2** *is the spirocyclic 2σ⁴-stannaindane* **12**. *Its structure has been determined by X-ray analysis.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:103–108, 1998

INTRODUCTION

Heterocyclic systems analogous to thiophene but with a phosphorus or silicon atom in place of sulfur must be singly (in the case of phosphorus) or doubly (in the case of silicon) negatively charged to become isoelectronic. While examples of the first kind are well documented [1], examples of the second kind became known only recently [2,3]. In both cases, the negative charge seems at least in part to be delocalized over the ring. An electron withdrawing substituent such as a phosphonio group at a carbon ring member should further withdraw charge from the heteroatom and thus stabilize its two-coordination. This effect had been used successfully for the synthesis of a diphosphonio-isophosphindolide **1** [4–6]. We intended to use this effect now also for a doubly charged ring system and chose 1,3-bis(triphenylphosphonio)-2-stannaindenediide **2** as a target compound. Inasmuch as the two phosphonio groups compensate for the two negative charges of the ring, **2** will be a neutral compound. This zwitterionic view underlies resonance formula **2a.** Alternatively, the compound, as in **2c**, can be viewed as a stannylene with two phosphonium ylide substituents [7] and this view relates **2** to the long known diaminostannylenes [8–11].



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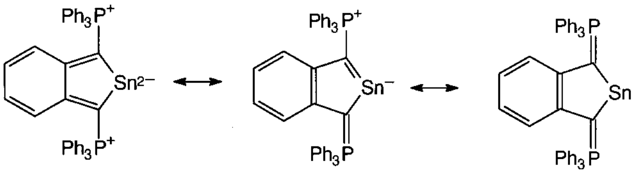

2a **2b** **2c**

RESULTS AND DISCUSSION

1,3-Bis(triphenylphosphoranediyl)-2σ²-stannaindene (**2**)

For the synthesis of **2**, several procedures were tested. In the end, the *o*-xylylene bis(triphenyl-

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Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

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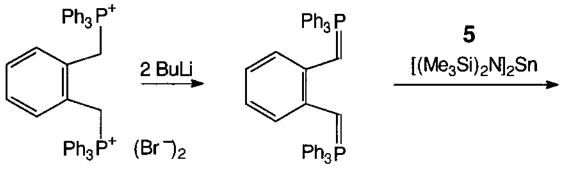
phosphorane) **4** [prepared in situ from the bis(phosphonium)bromide **3**] was condensed with a 30% excess of tetrakis(trimethylsilyl)diamino stannylene **5** [12] at 50°C for 16 hours and an isolated yield of **2** of 70% could be achieved.

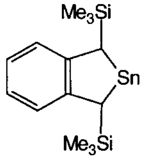


3 **4** **2**

Compound **2** crystallizes as orange-yellow rods. The substance is very sensitive to the atmosphere and immediately turns brown in contact with air. An uptake of oxygen seems to be responsible for the much-too-low carbon content found in elemental analysis. Solutions in THF or benzene display an intense red color. Solutions in acetonitrile, dichloromethane, chloroform, or carbon tetrachloride are not stable. The red color of **2** in solution parallels that of other stannylenes [12]. However, in contrast to them, the color of **2** in solution does not fade on lowering the temperature to −78°C.

The monomeric and symmetric structure of **2** in solution is confirmed by its NMR spectra (Table 1): The ^{119}Sn NMR spectrum shows a triplet at $\delta = 880.0$ with $^2J(^{119}SnP) = 126.6$ Hz. This chemical shift fits to the range known for diamino stannylenes $\delta^{119}Sn = 639–855$ [13–17]. The $^{31}P\{^1H\}$ NMR spectrum correspondingly shows a singlet at $\delta = 17.9$ with ^{117}Sn and ^{119}Sn satellites of, together, approximately 15% of the total intensity. The chemical shift $\delta^{13}C = 122.4$ of the ylidic carbon atoms in the 1,3-position of **2** is similar to $\delta^{13}C = 109.0$ [4] in **1**, its coupling to the phosphorus atoms $^{1,3}J(PC) = 41.0$ and 7.4 Hz being considerably smaller, however, than in **1**, where $^{1,3}J(PC) = 96.6$ and 14.0 Hz [4].

Two known stannylenes **6** [18] and **7** [9] offer themselves in particular for a comparison with **2**, as they possess a similar bicyclic structure.



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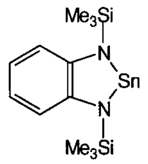

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In compound **6**, $Me_3Si–CH$ ring members take the place of $Ph_3\overset{+}{P}–\overset{-}{C}$ in the 1,3-position of **2**. They no longer offer the possibility for the tin(II) to integrate in a cyclic delocalization. Consequently, the stannylene **6** is, in fact, not known as such but forms instead a tetramer with an Sn_4 ring in the solid state as well as in solution.

In compound **7**, the $Me_3Si–CH$ entities of **6** are

TABLE 1 NMR Data of the 1,3-Bis(triphenylphosphoranediyl)-2-stannaindene and -indanes in Benzene (or^a THF); Coupling Constants J in Hz

	2-Substituents	*δ ^{119}Sn (t)*	*$^2J(^{119}SnP)$*	*$\delta^{31}P$*	*$\delta^{13}C$-1,3 (dd)*	*$^1J(PC)$*	*$^3J(PC)$*
2		880.0	126.6	18.0	122.4	41.0	7.4
8	$Cr(CO)_5$		191.6	21.5^a			
9	$Mo(CO)_5$		185.5	21.1^a			
10	S		248.7	16.1			
11	Se^b		240.0	16.6			
12		184.1	244.0	11.2			
			150.5	14.0^c			
13	Cl Ph	117.2	222.1	13.8			
14	Br Ph	150.3	219.9	13.7^a	42.9	101.4	12.3
15	Br Et^d		219.0	13.3^a			
16	Br Pr		226.9	13.3			
17	Br Bz^e	114.4^a	233.5	14.8^a	29.3^a	102.8	12.2
18	I Me		204.5	13.2			
19	I Et^f	102.5	206.0	13.1			
20	I I		236.5	17.0			

[a] in THF
[b] $\delta^{77}Se = 402.0$.
[c] Signal with half the intensity of the other.
[d] $\delta^1H = 0.80$ (t) and 0.07 (q), $^3J(HH) = 7.9$ Hz.
[e] $\delta^1H = 1.83$, $^2J(SnH) = 104.0$ Hz.
[f] $\delta^1H = 0.78$ (t) and 0.17 (q), $^3J(HH) = 8.1$ Hz.

replaced by $Me_3Si–N$ (which are isolobal to $Ph_3\overset{+}{P}–\overset{-}{C}$), and cyclic conjugation becomes possible again, but it is expected to be less effective than in **2.** The stannylene **7** has been found to form an adduct with THF from which the solvent molecule can be removed in vacuo, however.

The possibilities for reactions of **2** are hampered by its low thermal stability. Successful examples are restricted to cases where the reaction is fast and leads to a stable derivative. The stannylene complexes $2M(CO)_5$ [**8** (M = Cr) and **9** (M = Mo), see Table 1] are formed at 0°C from $(THF)M(CO)_5$ in THF solution but are not stable at room temperature. Room-temperature reactions with elemental sulfur and selenium give, among degradation products, the sulfide $(2S)_n$ = **10** and the selenide $(2Se)_n$ = **11.** The latter could be isolated but did not survive well at room temperature. According to the large coupling constant, $^2J(^{119}SnP)$ (Table 1), the tin atom in **10** and **11** is four coordinate. Consequently, **10** and **11** are not monomeric and belong to the class of σ^4-stannaindanes covered below.

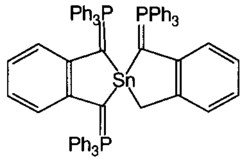
A clear-cut reaction of **2** is observed with phosphorus trichloride at −78°C wherein the tin atom in the ring is replaced by a phosphenium ring member.

$$\mathbf{2} + PCl_3 \longrightarrow \mathbf{1}\ SnCl_3$$

This result is in contrast to known reactions of other stannylenes in which PCl_3 oxidizes the tin(II) compound to the tin(IV) dichloride [19,20]. The reactions of **2** with alkyl halides and halogens are covered in the section after next.

1,3,1′-Tris(triphenylphosphoranediyl)-[2,2′]spirobi-2-stannaindane (12)

The synthesis of **2** is always accompanied by side reactions that involve the loss of triphenylphosphine from a part of **4.** As a second tin-containing product, air-sensitive red crystals of **12** were obtained from the filtrate of **2.** Compound **12** is also the major product from the thermal degradation of **2** (15 h in boiling benzene). The ^{119}Sn NMR chemical shift of **12** (δ = 184.1, Table 1) is in accord with a tetracoordinate tin atom and the double triplet signal pattern indicates a coordination with two equivalent and a third nonequivalent phosphonium ylide groups. Corresponding to this, the ^{31}P NMR spectrum shows two singlet signals of 1:2 relative intensities, both with tin satellites. No coupling between the two anisochronous phosphorus nuclei can be detected, suggesting a four-bond or longer distance between them. The observed signals are consistent with the ^{119}Sn isotopomer in an A_2BX spin system and lead to the formula shown.

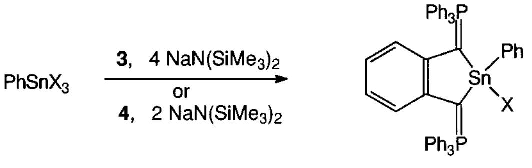


12

The structure of **12** is confirmed by a single-crystal X-ray determination that is shown in Figure 1. As a spirocyclic center, the tin atom has a strongly distorted tetrahedral coordination (Table 2) with two small endocyclic angles (84–85°) and four larger other angles (122°–124°). The bond from tin to the one tetrahedral carbon atom C1 is slightly longer (215 pm) than the bonds to the three trigonal carbon atoms C8,9,16 (210–213 pm). These carbon atoms have a planar environment with very similar angles in all three cases (C-C-Sn 109°–110°, C-C-P 124°–125°, P-C-Sn 126°–127°). Each of the two bicyclic systems joined by the central tin atom (Sn1, C1–8 and incorporating P1) and (Sn1, C9–16 and incorporating P2,3) are almost planar.

1,3-Bis(triphenylphosphoranediyl)-2σ⁴-stannaindanes (13–20)

In the presence of sodium bis(trimethylsilyl)amide, *o*-xylylene bis(phosphonium)bromide **3,** or the corresponding bisylide **4,** can be condensed with trichloro- and tribromophenylstannane to give the 2-halo-2-phenyl-σ^4-stannaindanes **13** and **14,** respectively. Along with the condensation, more or less decomposition of the ylide also takes place, as observed by the signal of PPh_3 in the ^{31}P NMR spectrum of the reaction mixture.



13, X = Cl
14, X = Br

No reaction was observed for **2** with alkyl chlorides that could have led to 2-alkyl derivatives analogous to **13.** Alkyl bromides and iodides do react, however, and yield the σ^4-stannaindanes **15–19.** As the color of the solution fades during the reaction, its progress can easily be monitored, and its rate is

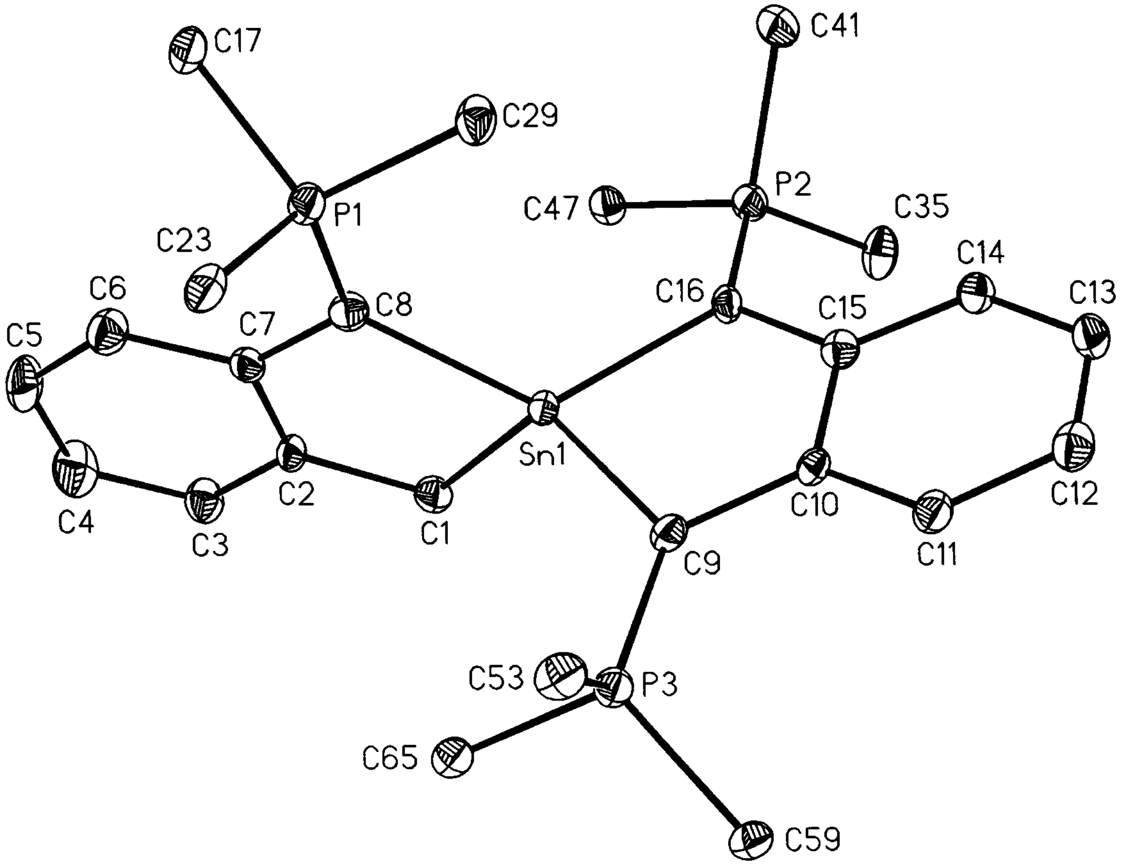
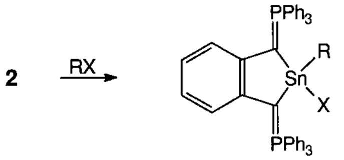


FIGURE 1 Molecular structure of **12** in the crystal of **12** · C_6H_6; thermal ellipsoids with 25% probability. Of the phenyl groups, only the ipso carbon atoms are shown. The hydrogen atoms are omitted.

TABLE 2 Relevant Bond Lengths (pm) and Bond Angles (°) of **12**

Sn1–C1	215.4(5)	C1–Sn1–C8	85.3(2)
Sn1–C8	213.4(5)	C9–Sn1–C16	84.2(2)
Sn1–C9	212.5(5)	C1–Sn1–C9	121.6(2)
Sn1–C16	210.3(4)	C1–Sn1–C16	122.6(2)
		C8–Sn1–C9	123.7(2)
C8–P1	169.0(5)	C8–Sn1–C16	124.4(2)
C9–P3	168.2(5)	Sn1–C1–C2	106.4(3)
C16–P2	168.7(5)	C1–C2–C7	120.4(4)
		C2–C7–C8	119.2(5)
C1–C2	150.7(7)	C7–C8–Sn1	108.5(3)
C2–C7	142.3(7)	C7–C8–P1	123.7(4)
C7–C8	147.8(6)	Sn1–C8–P1	127.0(3)
C9–C10	146.6(7)	Sn1–C9–P3	125.9(3)
C10–C15	144.6(7)	C10–C9–P3	125.3(4)
C15–C16	145.9(7)	Sn1–C9–C10	108.6(3)
		C9–C10–C15	118.3(4)
		C10–C15–C16	118.3(4)
		C15–C16–Sn1	109.7(3)
		C15–C16–P2	123.9(4)
		Sn1–C16–P2	126.1(3)

found to be significantly higher with alkyl iodides than with bromides.



	R	X
15	R = Et	X = Br
16	Pr	Br
17	Bz	Br
18	Me	I
19	Et	I
20	I	I

Compounds **13–19** are yellow or orange, air-sensitive solids. They are identified by their NMR spectra (Table 1). The observed chemical shift range δ^{119}Sn = 100–150 is in accord with a tetracoordinate tin atom. The ^{119}Sn NMR signal is split to a 1:2:1 triplet by a two-bond coupling to two equivalent ^{31}P nuclei $^{2}J(^{119}\mathrm{SnP})$ = 205–234 Hz, which is significantly larger than in **2.** The ^{13}C NMR signal of the 1,3-carbon ring members is found at much higher field than that of **2** (and **1**). As for **2,** the signal is split, by a one- and a three-bond ^{31}P coupling, to a double doublet. Both coupling constants are much higher than for **2** and are close to those of **1** [4] (see above).

Attempts to convert **2** into the corresponding dihalides led to complex mixtures except in the case of the addition of elemental iodine, where the diiodide **20** could be identified from the ^{31}P NMR spectrum of the reaction mixture (Table 1) and could be isolated as a dark green solid. However, it did not redissolve as such.

EXPERIMENTAL

All reactions were carried out in flame-dried glassware under argon and with use of dry solvents. NMR spectra were measured with a JEOL GSX 270 (^{31}P, ^{77}Si, ^{119}Sn) or EX 400 (^{13}C) NMR spectrometer using 85% H_3PO_4, $SeMe_2$, $SnMe_4$ (external), and $SiMe_4$ (internal) as standards.

2: To a solution of **3** (3.90 g, 4.95 mmol) in 140 mL of THF at 0°C, a 1.6 M hexane solution of butyllithium (6.2 mL, 9.95 mmol) was added dropwise within 20 minutes. The solution was stirred at room temperature for 1.5 hours and then added to a solution of **5** (3.11 g, 7.07 mmol) in 35 mL of THF at 0°C. After 16 hours of stirring at room temperature, the solvent was removed in vacuo. The residue was extracted with 70 mL of benzene. After the filtrate had been concentrated to half its volume, 120 mL of pentane were added, resulting in the formation of a yellow precipitate of **2** (2.58 g, 70%). $C_{44}H_{34}P_2Sn$ (743.4): calcd C 71.09; H 4.61, found C 69.29, H 3.78.

2 and **12:** To a solution of **3** (1.735 g, 2.20 mmol) and $SnCl_2$ (0.417 g, 2.20 mmol) in 150 mL of THF at 0°C, $NaN(SiMe_3)_2$ (1.467 g, 8.80 mmol) in 20 mL THF was added dropwise. After 25 hours of stirring at room temperature, the mixture was filtered and the filtrate was reduced to one-third of its volume. Its ^{31}P NMR spectrum showed the signals of **2** (δ = 18.0, 48% of the overall intensity), **12** (δ = 14.2 and 11.5, 37%), **4** (δ = 8.3, 2%), PPh_3 (δ = −4.7, 7%), and Ph_3PO (δ = 24.4, 3%). From this solution, **2** crystallized as orange rods that were separated after two weeks. The filtrate was further reduced in volume and gave dark red crystals of **12.**

12 from the decomposition of **2:** A solution of **2** (312 mg, 0.42 mmol) in 30 mL of benzene was heated to reflux for 8 hours and then concentrated to one-third its volume. The ^{31}P NMR spectrum showed the signals of **2** (δ = 18.2, 18% of total intensity), **12** (δ = 14.2 and 11.4, 35%), **4** (δ = 8.4, 21%), PPh_3 (δ = −4.8, 14%), and Ph_3PO (δ = 25.2, 6%).

1$SnCl_3$: On addition of PCl_3 (48 μL, 0.55 mmol) to a solution of **2** (407 mg, 0.55 mmol) in 30 mL THF, the red color faded. After having been allowed to stand for 15 hours at room temperature, the solution was concentrated to half its volume and gave the ^{31}P NMR spectrum of **1** [δ = 243.2 (t) and 17.3 (d), $^2J(PP)$ = 89.3 Hz] [4].

8 and **9:** To a THF solution of $(THF)M(CO)_5$ (M = Cr, Mo) prepared in situ at 0°C, an equimolar amount of **2** was added. After 2 hours at room temperature, the ^{31}P NMR spectrum (Table 1) was recorded.

10 and **11:** Equivalent amounts of **2** and elemental sulfur or selenium were stirred in benzene for 15 hours at room temperature. The major product was insoluble even in dichloromethane. The ^{31}P NMR spectrum of the benzene filtrate showed the signals of Ph_3PS and Ph_3PSe and those of **10** and **11** (Table 1), respectively.

13: To a solution of **3** (1.68 g, 2.13 mmol) and $PhSnCl_3$ (0.35 mL, 2.13 mmol) in 60 mL of THF at 0°C, a solution of $NaN(SiMe_3)_2$ (1.57 g, 8.53 mmol) in 10 mL of THF was added dropwise. After 3 hours of stirring at room temperature, the solvent was re-

TABLE 3 Crystal Data of **12**$\cdot C_6H_6$ and Structure Refinement

Crystal system	triclinic
Space group	P-1
a = 12.4408(1) Å	α = 75.46(1)°
b = 12.5995(1) Å	β = 86.60(1)°
c = 20.3747(2) Å	γ = 66.06(1)°
V	2822.22(3) Å^3
Z	2
d (calcd.)	1.350 Mg m^{-3}
μ	0.582 mm^{-1}
$F(000)$	1182
2θ range for data collection	2.06 to 58.80°
Index ranges	$-15 \leq h \leq 15$
	$-16 \leq k \leq 16$
	$-25 \leq l \leq 25$
Reflections collected	16,365
Independent reflections	8,872 (R_{int} = 0.0454)
Observed reflections	5,977 ($F > 4\sigma(F)$)
Weighting scheme	$w^{-1} = \sigma^2F_0^2 + (0.0000\ P)^2 + 6.9515\ P$ where $P = (F_0^2 + 2F_c^2)/3$
Data / restraints / parameters	7,280 / 18 / 694
Goodness-of-fit on F^2	1.192
Final $R1$ (4σ)	0.0494
Final $wR2$	0.0928
Largest difference peak	0.518 eÅ^{-3}
Largest difference hole	−0.550 eÅ^{-3}

moved and the residue extracted with 40 mL of benzene. By concentration of the filtrate and addition of 50 mL pentane, **13** was obtained as an orange precipitate (NMR spectra: Table 1).

14: As before, this compound was prepared from **3** (1.29 g, 1.64 mmol), $PhSnBr_3$ (0.28 mL, 1.64 mmol) and $NaN(SiMe_3)_2$ (1.20 g, 6.54 mmol). The filtrate of the reaction mixture was concentrated to 20 mL and gave, after 2 days, red crystals of **14** (NMR spectra: Table 1) $C_{50}H_{39}BrP_2Sn$ (900.4): calcd C 66.69, H 4.37; found C 64.70, H 5.20.

15–19: To a THF solution of **2** maintained at 0°C, an equimolar amount of the alkyl bromide or iodide was added. While the solution was warmed to room temperature, its red color brightened. The residue, which was left after evaporation of the solvent, was extracted with benzene. Concentration of the filtrate and addition of pentane gave a yellow to orange precipitate (NMR spectra, Table 1).

20: To a solution of **2** (310 mg, 0.42 mmol) in 25 mL of benzene, a solution of I_2 (106 mg, 0.42 mmol) in 10 mL of benzene was added, and a dark precipitate formed. The ^{31}P NMR spectrum of the filtrate showed the signals of **20** (Table 1, 61%) and of PPh_3 ($\delta = -4.8$, 31%). Addition of pentane gave more dark green precipitate.

X-ray Structure Determination of 12

For the X-ray structure analysis (at 193 K), a Siemens P4 X-ray diffractometer with SMART area detector was used employing Mo-K_α radiation and a graphite monochromator. The deep violet prism had the composition $\mathbf{12} \cdot C_6H_6$ ($C_{76}H_{61}P_3Sn$, $M = 1185.94$) and a size of $0.1 \times 0.1 \times 0.15$ mm. Crystal data and data collection parameters are given in Table 3. Structure solution program: XS (SHELXTL Vers. 5), with employment of direct methods, full-matrix least-squares on F^2, and hydrogen atoms refined as a riding model. Additional information of the crystal structure determination are deposited at the Cambridge Crystallographic Data Center (CCDC) and may be requested by quoting the name of the authors and the journal citation.

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REFERENCES

[1] F. Mathey, *Coord. Chem. Rev., 137,* 1994, 1.

[2] W. C. Joo, J.-H. Hong, S.-B. Choi, H.-E. Son, C. H. Kim, *J. Organomet. Chem., 391,* 1990, 27.

[3] W. P. Freeman, T. Don Tilley, G. P. A. Yap, A. L. Rheingold, *Angew. Chem., 108,* 1996, 960; *Angew. Chem. Int. Ed. Engl., 35,* 1996, 882, and the literature cited therein.

[4] A. Schmidpeter, M. Thiele, *Angew. Chem., 103,* 1991, 333; *Angew. Chem. Int. Ed. Engl., 30,* 1991, 308.

[5] D. Gudat, V. Bajorat, M. Nieger, *Bull. Soc. Chim. Fr., 132,* 1995, 280.

[6] Other examples of this sort are the bis(triphenylphosphonio)diphospholides and triphospholides: G. Jochem, A. Schmidpeter, H. Nöth, *Chem. Eur. J., 2,* 1996 221; H.-P. Schrödel, A. Schmidpeter, H. Nöth, M. Schmidt, *Z. Naturforsch. B, 51,* 1996 1022.

[7] The cyclic 1:1 combination of an ylide and a stannylene group proves not sufficient, however, to render a stable monomer: M. Veith, V. Huch, *J. Organomet. Chem., 308,* 1986, 263.

[8] D. H. Harris, M. F. Lappert, *J. Chem. Soc., Chem. Commun.,* 1974, 895.

[9] C. D. Schaeffer, J. J. Zuckermann, *J. Am. Chem. Soc., 96,* 1974, 7160.

[10] M. Veith, *Angew. Chem., 87,* 1975, 287; *Angew. Chem. Int. Ed. Engl., 13,* 1974, 607.

[11] D. Hänssgen, J. Kuna, B. Ross, *Chem. Ber., 109,* 1976, 1797.

[12] M. J. S. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Rivière, M. Rivière-Baudet, *J. Chem. Soc., Dalton Trans.,* 1977, 2004.

[13] B. Wrackmeyer, *J. Magn. Res., 61,* 1985, 536.

[14] K. Horchler, C. Stader, B. Wrackmeyer, *Inorg. Chim. Acta, 117,* 1986, 39.

[15] C. Stader, B. Wrackmeyer, *Z. Naturforsch. B, 42,* 1987, 1515.

[16] C. Stader, B. Wrackmeyer, *Z. Naturforsch. B, 43,* 1988, 707.

[17] B. Wrackmeyer, C. Stader, K. Horchler, *J. Magn. Res., 83,* 1989, 601.

[18] M. F. Lappert, Wing-Por-Leung, C. L. Raston, A. J. Thorne, B. W. Skelton, A. H. White, *J. Organomet. Chem., 233,* 1982, C28.

[19] M. Veith, V. Huch, *Tetrahedron Lett., 24,* 1983, 4219.

[20] M. Veith, M. Grosser, V. Huch, *Z. Anorg. Allg. Chem., 513,* 1984, 89.