Organometallics **1994**, *13*, 2787–2791

Reactions of Stannaphosphenes with α-Ethylene Aldehydes and Ketones

A. Kandri-Rodi, H. Ranaivonjatovo, and J. Escudié*

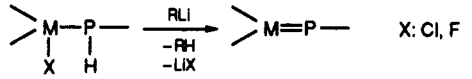
Laboratoire de Chimie des Organominéraux, URA 477 du CNRS, Université P. Sabatier, 31062 Toulouse Cedex, France

Received January 24, 1994[●]

Stannaphosphene $\mathrm{Is_2Sn{=}PAr}$ (**1**) (Is, 2,4,6-triisopropylphenyl; Ar, 2,4,6-tri-*tert*-butylphenyl) gives with various α-ethylene aldehydes and ketones exclusive [2 + 4] cycloadditions, leading to the corresponding six-membered ring stannaoxaphosphorinenes **2**–**7**. A comparison with the reactivity of germaphosphenes toward the same carbonyl compounds is described. The inversion barrier of phosphorus has been determined for cycloadducts **2** (acrolein) and **3** (methacrolein) (respectively 12.9 and 13.0 kcal/mol) by dynamic proton NMR. The very low values observed are mainly due to the large steric hindrance of groups on phosphorus. The rotational barrier of the Is group cis to the Ar group has been determined in **2** and **3**, as well as the rotational barrier of the Ar group in **2**–**4** (cycloadduct with crotonaldehyde).

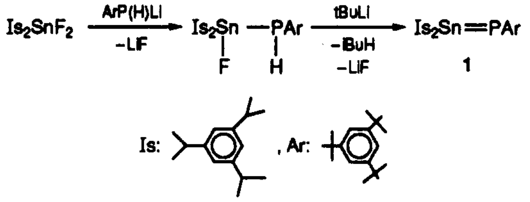
Introduction

Some stable sila-, germa-, and stannaphosphenes >M=P– (M = Si,[1] Ge[2,3] Sn[4,5]) have been synthesized some years ago, generally by dehydrohalogenation of halogenometallophosphines by lithium compounds:



Whereas the reactivity of sila- and germaphosphenes (transient[6] or stable[1–3,7]) begins to be well-known, only few reactions have been performed with stannaphosphenes,[8] and, more generally, with doubly-bonded tin compounds.[9] This is particularly due to the difficulty in the synthesis and stabilization of such derivatives.

We have recently obtained the new stannaphosphene **1**,[5] which is thermally stable and can be prepared on a large scale in excellent yield:



In this paper we describe the reactivity of **1** with α-ethylene aldehydes and ketones and compare the results obtained to those observed with other doubly-bonded main group element compounds.

Results and Discussion

Various types of reactions could occur between stannaphosphene **1** and α-ethylene aldehydes and ketones (Scheme 1):

- A [2 + 4] cycloaddition leading to a six-membered ring compound with a Sn—O bond (route a). This route seems the most likely, since it occurs with other doubly-bonded main group element compounds such as germenes,[10] stannanimines,[9e] and generally, germaphosphenes[7d] and silenes.[11] Moreover, in this last case two possible regiochemistries are observed, with oxygen bonded to silicon or to carbon.

[●] Abstract published in *Advance ACS Abstracts*, May 15, 1994.

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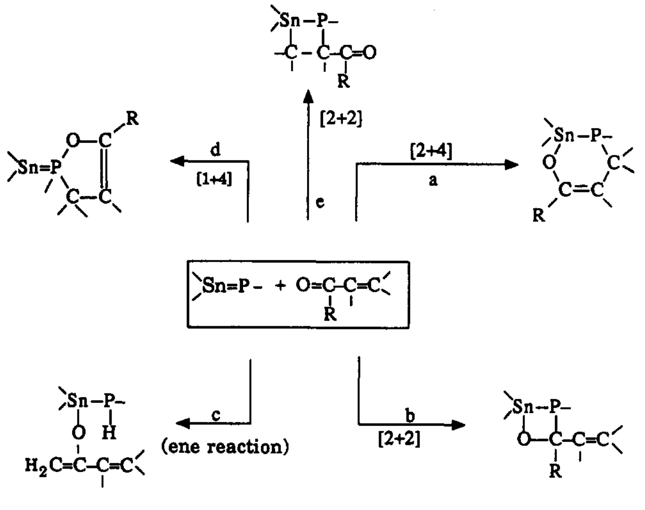
Scheme 1



(route a,b,d,e:R=H,Me
route c :R =Me)

•A [2 + 2] cycloaddition with the C=O unsaturation (route b). Such a reaction was observed with disilenes[12] and sometimes with silenes[11] and germaphosphenes.[7d]

•An ene reaction (route c) in the case of ketones, corresponding to a reaction of the enolic form, previously observed with germaphosphenes[7d] and stannanimine.[9e]

•A [1 + 4] cycloaddition involving exclusively the phosphorus atom (route d), as observed in diphosphenes.[13]

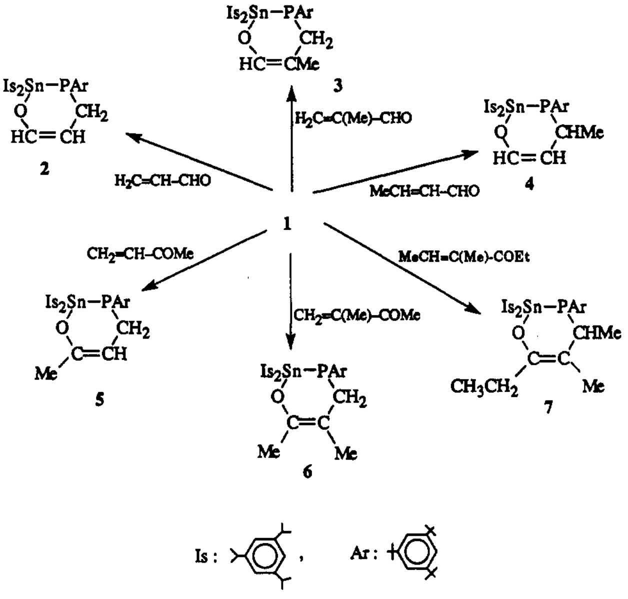
•A [2 + 2] cycloaddition involving the C=C double bond (route e). However, such a reaction has never been observed and is unlikely.

1 was allowed to react at room temperature in Et_2O with acrolein, methacrolein, crotonaldehyde (*E* isomer), methyl vinyl ketone, methyl isopropenyl ketone, and ethyl 1-methylprop-1-enyl ketone (*E* isomer) in an equivalent molar ratio. Although the charge distribution and the steric interactions are changed when the C=C double bond is differently substituted,[14] we have observed in all cases the nearly quantitative formation of six-membered ring stannaoxaphosphorinenes 2–7 resulting from a [2 + 4] cycloaddition according to route a (Scheme 2).

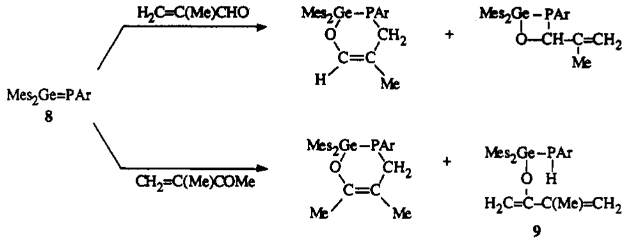
In contrast, no reaction was observed between 1 and tetramethylcyclopent-2-enone, which has a transoid unsaturated system, even after heating in a sealed tube at 80 °C during 2 h. Although the Sn–P single bond is generally reactive, a reaction of the carbonyl compound with the Sn–P bond of 2–7 does not occur, probably due to steric protection.

Only one diastereoisomer was obtained for 4 and 7. Unfortunately, we have been unable to determine the ${}^2J_{PCH}$ coupling constant (the H of the CHMe group gives a complex multiplet due to the coupling with P, CH_3, and the two ethylene hydrogens) and therefore to know the value of the dihedral angle between the direction of the lone pair and of the CH, according to a Karplus type curve.[15] However, because of the very large steric hindrance Me and Ar groups are probably in trans positions.

Scheme 2

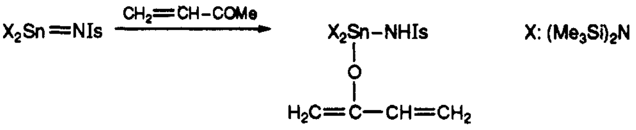


Scheme 3



As expected, only one type of regiochemistry occurs, with oxygen bonded to tin. This regiochemistry is strongly influenced by the polarities of the reactants ($Sn^{\delta+}{=}P^{\delta-}$ and $C^{\delta+}{\cdots}C{\cdots}C{-}O^{\delta-}$) and by the well-known affinity of tin for oxygen. Thus the first step of the reaction could be a nucleophilic attack of oxygen on tin, followed by a nucleophilic attack of phosphorus on the β-carbon, leading to six-membered rings.

Note that, whereas an exclusive [2 + 4] cycloaddition is observed between 1 and methyl vinyl ketone, an ene reaction occurs between a stannanimine and this same ketone:[9e]



$$X_2Sn{=}NIs \xrightarrow{CH_2{=}CH{-}COMe} X_2Sn{-}NHIs(O{-}C({=}CH_2){-}CH{=}CH_2) \qquad X: (Me_3Si)_2N$$

Large differences are also observed in the chemical behavior of germaphosphene $Mes_2Ge{=}PAr$ (8) toward α-ethylene aldehydes and ketones. Generally, six-membered ring compounds are obtained, but increasing the bulkiness of the reactants affords also four-membered ring compounds and open-chain products (Scheme 3).[7d] The sole formation of six-membered ring compounds 2–7 in the case of stannaphosphene 1 could be due to a less important steric hindrance because of longer Sn=P, Sn—C, and Sn—O bonds than Ge=P, Ge—C, and Ge—O bonds and of the reluctance of tin to form four-membered ring compounds.

Room Temperature NMR Studies

${}^{13}C$ NMR (Table 1). ${}^{13}C$ NMR spectroscopy is a good tool to prove the six-membered ring structure of the

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Table 1. ^{13}C NMR Data for **2**–**5**, Solvent $CDCl_3$ [δ (ppm), J (Hz)]

	2	3	4	5
CH_3		19.29 (d, $^3J_{CP}$: 2.8)	19.35 (d, $^2J_{CP}$: 24.7)	
C–P ($^1J_{CP}$)	26.98 (d, 30.0)	32.94 (d, 31.6)	36.55 (d, 11.8)	27.85 (d, 37.7)
C=C—O ($^2J_{CP}$)	100.02 (d, 6.5)	112.56 (d, 6.0)	113.94 (d, 7.5)	95.81 (d, 7.9)
C=*C*—O ($^3J_{CP}$)	150.76 (d, 9.4)	146.12 (d, 8.8)	151.57 (d, 7.4)	157.90 (d, 9.7)

Table 2. ^1H NMR Data for **2**–**5** at 25 °C, Solvent $CDCl_3$ [δ (ppm), J (Hz)][a]

	2	3	4	5
p-$(CH_3)_2CH$ ($^3J_{HH}$)[b,d]	1.21 (d, 6.8, 12H)	1.18 (d, 6.8, 12H)	6d are observed at 0.78, 0.94, 1.19, 1.21, 1.26, and 1.28 ($^3J_{HH}$ 6.5 Hz); ortho and para iPr could not be identified	1.17 (d, 6.9, 12H)
o-$(CH_3)_2CH$ ($^3J_{HH}$)[c,d]	1.00 (d, 6.5, 12H) 1.05 (d, 6.5, 12H)	0.93–1.07 (m, 24H)		0.96 (broad d, 6.4, 24H)
p-$(CH_3)_3C$	1.31 (s)	1.29 (s)	1.29 (s)	1.27 (s)
o-$(CH_3)_3C$	1.63 (s)	1.60 (s)	1.64 (s)	1.55 (s)
p-$CHMe_2$ ($^3J_{HH}$)[d]	2.83 (sept, 6.8, 2H)	2.81 (sept, 6.8, 2H)	2.82 (sept, 6.5, 2H)	2.80 (sept, 6.9, 2H)
o-$CHMe_2$ ($^3J_{HH}$)[d]	3.05 (sept, 6.5, 4H)	2.89–3.42 (m, 4H)	3.77 and 3.00 (broad signals)	3.06 (broad sept, 6.9, 4H)
CH_3		1.52–1.60 (m)	0.47 (dd, $^3J_{HH}$ 7.0, $^3J_{HP}$ 16.8)	
C*H*=C—O	4.60 (tdd, $^3J_{HC=CH}$ 5.7, $^3J_{H-P}$ 11.7, $^3J_{HC-CH_2}$ 6.4)		4.35 (q, $^3J_{HH}$ and $^3J_{HP}$ 5.2)	4.52 (dtq, $^3J_{HP}$ 9.6, $^3J_{HH}$ 6.8, $^4J_{HH}$ 0.8)
=C*H*—O	6.5 (tdd, $^3J_{HC=CH}$ 5.7, $^4J_{HP}$ 1.9 Hz, $^4J_{HC=CH-CH_2}$ 0.9)	6.27 (qd, broad, $^4J_{H-P}$ 3.2, $^4J_{HC=C-CH_3}$ 1.4)	6.28 (ddd, $^3J_{HC=CH}$ 5.2, $^4J_{HP}$ 3.2, $^4J_{HC=CH-CH}$ 2.2)	
H arom Is ($^4J_{SnH}$)[e]	6.97 (s, 21.6)	6.93 (s, 21.6)	6.95 (s, 21.6)	6.92 (s, 21.2)
H arom Ar ($^4J_{HP}$)	7.37 (d, 2.1)	7.31 (d, 2.0)	7.31 (d, 1.8)	7.29 (d, 2.0)

[a] Due to multiple couplings, the hydrogen(s) on the carbon bonded to phosphorus give a complex signal which has not be resolved. [b] For **2**, **3**, and **5**, only one doublet was observed: because of the distance of chiral phosphorus the two methyl signals are isochronal. [c] Two doublets should be observed for the two diastereotopic Me groups of every *o*-iPr; however they sometimes appear at 25 °C as broad signals, since at this temperature they are close to the coalescence due to the phosphorus inversion. [d] The two Is groups are equivalent at 25 °C (phosphorus inversion). [e] Satellites due to the coupling with ^{117}Sn and ^{119}Sn.

Table 3. ^{31}P and ^{119}Sn NMR Data for Compounds **2**–**7**, Solvent $CDCl_3$ [δ (ppm), J (Hz)]

	2	3	4	5	6	7
$\delta(^{31}P)$	−18.0	−16.0	2.2	−21.9	−13.4	6.7
$\delta(^{119}Sn)$	−85.6	−100.2	−84.6	−99.1	−107.2	−111.5
$^1J_{P-^{119}Sn}$	1788.6	1836.6	1960.3	1721.2	1760.6	1789.5
$^1J_{P-^{117}Sn}$	1710.1	1755.5	1874.1	1645.5	1679.3	1710.3

Table 4[a]

	rotational barrier of Ar				rotational barrier of Is		inversion barrier of P	
	o-tBu		arom H					
	T_c	ΔG^*	T_c	ΔG^*	T_c	ΔG^*	T_c	ΔG^*
2	−70	9.8	−77	9.7	−60	10.1	−4	12.9
3	−75	9.6	−82	9.4	−55	10.3	0	13.0
4[b]	+10	14.0	0	13.9				

[a] ΔG^*: ±0.2–0.3 kcal/mol. T_c: °C. [b] **4** presents very complicated spectra due to the chiral carbon bonded to phosphorus, and only the rotational barrier of the Ar group could be determined.

cycloadducts **2**–**5**. The carbon bonded to oxygen was observed at low field (~146–160 ppm with a $^3J_{CP}$ coupling constant between 7.4 and 9.7 Hz) in agreement with a sp^2 structure. In a four-membered ring stannaoxaphosphetane >Sn–(P–)–(C<)–O (if a [2 + 2] cycloaddition occurred), this carbon would appear at higher field (~80–90 ppm), as previously observed in germaoxaphosphetanes[7d] with a large $^1J_{CP}$ coupling constant. The stannaoxaphosphorinene structure was also demonstrated by the existence of a $^1J_{PC}$ coupling constant between the β-carbon and the phosphorus atom in the range 30.0–37.7 Hz, except in the special case of **4** (11.8 Hz) which has a methyl on this carbon. Broad signals are sometimes observed for o-$CHMe_2$ groups due to their slow rotation.

^1H NMR (see Table 2 and footnotes enclosed).

^{31}P NMR (Table 3). Signals for **2**–**7** are observed between +6.7 and −21.9 ppm, at a lower field than expected for a phosphorus atom bonded to a tin atom in a six-membered ring compound. This low field shift is probably due to a phosphorus atom that is less pyramidal than usual because of the very large steric hindrance. Compounds **4** and **7**, with a methyl on the carbon bonded to phosphorus and, consequently, a greater steric hindrance than **2**, **3**, **5**, and **6**, are, as expected, the most low field shifted.

The $^1J_{P-^{117/119}Sn}$ coupling constants are very large (1645–1874 and 1721–1960 Hz) compared to standard $^1J_{P-Sn}$ coupling constants (generally 800–1000 Hz).[4,5,8b,16] They are close to the values observed in tin–phosphorus double bonds (2000–2200 Hz).[4,5] Such very large constants are also probably due to the quasiplanarity of phosphorus. As expected, in each series of aldehydes and ketones, the coupling constant increases with the steric hindrance and thus with the planarity of phosphorus.

^{119}Sn NMR (Table 3). Doublets, due to the coupling with phosphorus, were observed between −85.6 and −111.5 ppm, in the normal range for a tin bonded to an oxygen in a six-membered ring derivative.

Dynamic ^1H NMR Study of 2–4

A dynamic ^1H NMR study has been performed for compounds **2**–**4** between +50 and −80 °C by following the evolution of the methyl signals of the *o*-iPr and *t*-Bu groups or of the aromatic hydrogen signals of the Ar groups. Three successive phenomena are observed in this temperature range: (a) the slow rotation of the Ar group, (b) the slow

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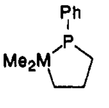
Table 5. Mass Spectroscopy (^{120}Sn) for Compounds 2–4 (EI, 70 eV) and 5 (DCI/CH$_4$)

	m/*z*	fragments	relat abundance
2	858	M$^{\bullet+}$	0.5
	816	M – iPr + 1	2
	802	Is$_2$Sn=PAr	2
	583	M – ArP + 1	2
	542	Is$_2$SnO	1
	526	Is$_2$Sn	15
	322	IsSn – 1	71
	277	ArP + 1	100
3	872	M$^{\bullet+}$	0.5
	802	Is$_2$Sn=PAr	1
	596	M – ArP	2
	552	M – ArP – iPr – 1	5
	541	Is$_2$SnO – 1	1
	526	Is$_2$Sn	14
	345	M – Is$_2$Sn – 1	1
	322	IsSn – 1	99
	277	ArP + 1	100
4	872	M$^{\bullet+}$	1
	802	Is$_2$Sn=PAr	2
	746	Is$_2$Sn=PAr – tBu + 1	1
	597	M – ArP + 1	1
	541	Is$_2$SnO – 1	5
	526	Is$_2$Sn	25
	322	IsSn – 1	100
	277	ArP + 1	44
5	872	M$^{\bullet+}$	14
	816	M – tBu + 1	11
	802	Is$_2$Sn=PAr	28
	669	M – Is	5
	596	M – ArP	6
	526	Is$_2$Sn	12
	347	M – Is$_2$Sn + 1	46
	277	ArP + 1	100

rotation of the Is group cis to the Ar group, and (c) the inversion of phosphorus (see Table 4). The rapid inversion of phosphorus at room temperature is unambiguously evidenced by the equivalence of the two triisopropylphenyl groups on tin. These groups should be inequivalent due to the presence of the chiral phosphorus atom. At low temperatures, they become inequivalent as expected.

Whereas high values are calculated for the rotational barrier of the Ar and Is groups due to the very large steric hindrance, very low values are obtained for the inversion barrier at phosphorus. In germyl- and stannylphosphines the inversion barrier generally lies in the range 19–25 kcal/mol. For example, in cyclic metallophospholanes: 21.95 kcal/mol in **12a**, 24.30 in **12b**;[19] 21.9 (**13a**), 23.1 (**13b**);[21] 19.6 (**14a**), 22.2 (**14b**).[21] In acyclic metallophosphines Me$_3$MP(Ph)iPr:[20] M = Sn, 19.3; M = Ge, 21.4. kcal/mol. Inversion barriers below 20 kcal/mol can be observed when phosphorus is substituted by two metals,[21] since it is well-known that the electronegativity of atoms bonded to phosphorus is, along with the steric effects, one of the main factors affecting the magnitude of inversion barriers. In 2 and 3, where phosphorus is bonded to only one metal atom, even lower inversion barriers than in dimetallophosphines are observed, probably mainly due to the extremely large steric hindrance caused by the bulky Ar and Is groups. Note that the value obtained for 2 (12.9 kcal/mol) is about the same as the value previously determined for 11[7d] (13.2 kcal/mol) synthesized in the reaction between acrolein and germaphosphene Mes$_2$Ge=PAr:



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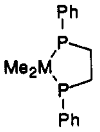

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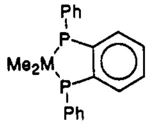
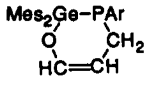
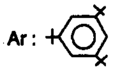


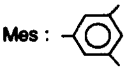
14

(a: M=Sn
b: M=Ge)

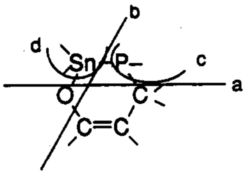


11





Mass Spectrometry. In all cases the molecular peak has been detected. Four types of fragmentation occur:



Generally, the most important (a) leads to the starting material, but formation of stannanone (b), release of phosphinidene (c), and release of stannylene (d) are also observed (Table 5).

Experimental Section

As solutions of stannaphosphene 1 are highly air- and moisture-sensitive, their syntheses and handling require high vacuum line techniques and carefully deoxygenated solvents (usually Et$_2$O, THF, pentane) which must be freshly distilled over sodium benzophenone.

^{1}H NMR spectra were recorded on Bruker AC 80, AC 200, and AC 250 instruments, respectively at 80.1, 200.1, and 250.1 MHz. ^{13}C NMR spectra were recorded on Bruker AC 200 and AC 250 instruments, respectively, at 50.3 and 62.9 MHz (referenced to TMS). ^{31}P NMR spectra were recorded on Bruker AC 80 and AC 200 instruments at 32.3 and 81.0 MHz (referenced to H$_3$PO$_4$, 85%), and ^{119}Sn NMR spectra, on a Bruker AC 200 at 74.6 MHz (referenced to Me$_4$Sn). Mass spectra were measured by EI at 70 eV on a Hewlett Packard 5989 A spectrometer, or by DCI/CH$_4$ on a NERMAG R10010 spectrometer. Melting points were determined on a Leitz microscope heating stage 250. Elemental analyses were performed by the "Service de Microanalyse de l'Ecole de Chimie de Toulouse" (Toulouse, France).

Synthesis of Stannaphosphene 1. Stannaphosphene 1 was synthesized as previously briefly described.[5] To a solution of fluorostannylphosphine Is$_2$Sn(F)P(H)Ar (1 g, 1.24 mmol) in Et$_2$O (10 mL) cooled at –78 °C was slowly added 1 equiv of *tert*-butyllithium (1.7 M in pentane). After completion of the addition, the red reaction mixture was allowed to warm to room temperature. A ^{31}P and ^{119}Sn NMR analysis showed the nearly quantitative formation of 1 ($\delta(^{31}P)$ + 170.7 ppm at 25 °C, $\delta(^{119}Sn)$ +499.5 ppm, $^{1}J_{P-^{119}Sn}$ 2208 Hz, $^{1}J_{P-^{117}Sn}$ 2110 Hz). The only byproducts, in very low percentage, can be the starting fluorostannylphosphine, the stannylphosphine Is$_2$Sn(H)P(H)Ar ($\delta(^{31}P)$ –133.3 ppm), and if the reaction is not carried out with a rigorously dried apparatus, the hydrolysis product Is$_2$Sn(OH)P(H)Ar ($\delta(^{31}P)$ –119.05 ppm). Crude solutions of 1, even without elimination of LiF, were generally used for the reactions with α-ethylene aldehydes and ketones.

General Procedure for the Reaction of α-Ethylene Aldehydes and Ketones with 1. To a red solution of 1 (prepared

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(21) (a) Couret, C.; Escudié, J.; Saint-Roch, B.; Andriamizaka, J. D.; Satgé, J. *J. Organomet. Chem.* **1982**, *224*, 247. (b) Driess, M.; Pritzkow, H.; Winkler, U. *Chem. Ber.* **1992**, *125*, 1541. (c) Hänssgen, D.; Aldoven, H.; Nieger, M. *Chem. Ber.* **1990**, *123*, 1837.

from 1 g of $Is_2Sn(F)P(H)Ar$ in Et_2O (10 mL) was slowly added, at room temperature, 1 molar equiv of α-ethylene aldehyde (acrolein, methacrolein, crotonaldehyde) or ketone (methyl vinyl ketone, isopropenyl ketone, ethyl 1-methylprop-1-enyl ketone) in the pure state or in solution in Et_2O (5 mL). The reaction mixture turned immediately from red to light yellow. After 1 h of stirring at room temperature, LiF was eliminated by filtration. ^{31}P and ^{119}Sn NMR analyses of the solution showed the formation of cycloadducts **2**–**7** in more than 80% yield. After removal of solvents in vacuo, **2**–**5** were recrystallized from pentane and obtained as pure products in the form of yellow crystals.

2: 0.48 g (45%), mp 94–95 °C. Anal. Calcd for $C_{51}H_{79}OPSn$: C, 71.29; H, 9.26. Found: C, 71.55; H, 9.60.

3: 0.54 g (50%), mp 124–125 °C.

4: 0.60 g, (55%), mp 112–113 °C. Anal. Calcd for $C_{52}H_{81}OPSn$: C, 71.63; H, 9.36. Found: C, 71.31; H, 9.33.

5: 0.38 g (35%), mp 142–143 °C. Anal. Calcd for $C_{52}H_{81}OPSn$: C, 71.63; H, 9.36. Found: C, 71.74; H, 9.68.

6 and **7** could not be completely purified but were unambiguously characterized by ^{31}P and ^{119}Sn NMR.

Acknowledgment. We thank Professors J. Satgé and C. Couret for helpful discussions.

OM940052V