

Hydrostannylation of Phosphaalkynes[☆]

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The hydrostannylation of phosphaalkynes **8** with tin hydrides **1** depends on the stoichiometry employed: Thus, the 1,2-dihydro-1,3-diphosphetes **10** are isolated when an excess of phosphaalkyne **8** is used. On the other hand, an increase in the tin hydride concentration favors the formation of the phosphanes **11** and **12**. Synthesis of the 1,2-dihydro-1,3-diphosphetes **14** and **16** was achieved by the use of diorganotin

hydrides **13** or chloro(organo)tin hydrides **4**, respectively. An isolated and characterized by-product of the latter reaction was the phosphorus-carbon-tin cage **17**. Furthermore, the following reactions of the 1,2-dihydro-1,3-diphosphetes **10** were performed: isomerization reactions, complexation reactions with transition-metal complexes, and substitution of the hydrogen atom by iodine.

Introduction

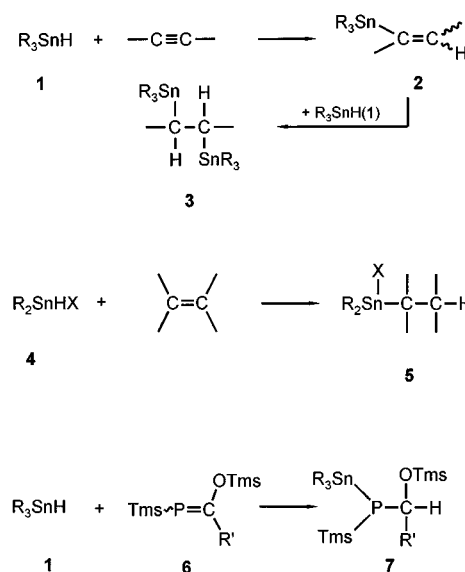
Addition reactions of organotin compounds to unsaturated systems have been known for a long time^[2]. Following the hydrostannylation of alkenes which, as a consequence of the mild reaction conditions and high selectivity, has found wide-ranging applications, the first 1,2-addition of triorganotin hydrides to acetylenes was achieved in 1959^{[3][4]}. In comparison to the hydrostannylation reactions of the corresponding olefins, the additions to C–C triple-bond systems proceed more readily. The vinyltin compounds **2** are the primary products of these reactions which then undergo, albeit somewhat delayed, addition of a second equivalent of the triorganotin hydride **1** to furnish the ditin compounds **3**. Modification of the organotin hydride by the introduction of a halogen atom to give the diorgano(halo)tin hydrides **4**^[5] provides further new possibilities for the synthesis of numerous mixed substituted organotin compounds **5**^[6].

We recently reported on hydrostannylation reactions in the chemistry of low-coordinated phosphorus, namely the selective 1,2-addition of organotin compounds to Becker-type phosphaalkenes **6** to furnish the stannylphosphanes **7**^[7].

The central theme of the present work is the reactivity of organotin hydrides and organo(halo)tin hydrides towards kinetically stabilized $\lambda^3\sigma^1$ -phosphaalkynes and the related question of whether the primary products of the 1,2-addition of tin hydrides to the P–C triple-bond system will be sufficiently stable to permit their isolation.

Reactions with Triorganotin Hydrides **1**

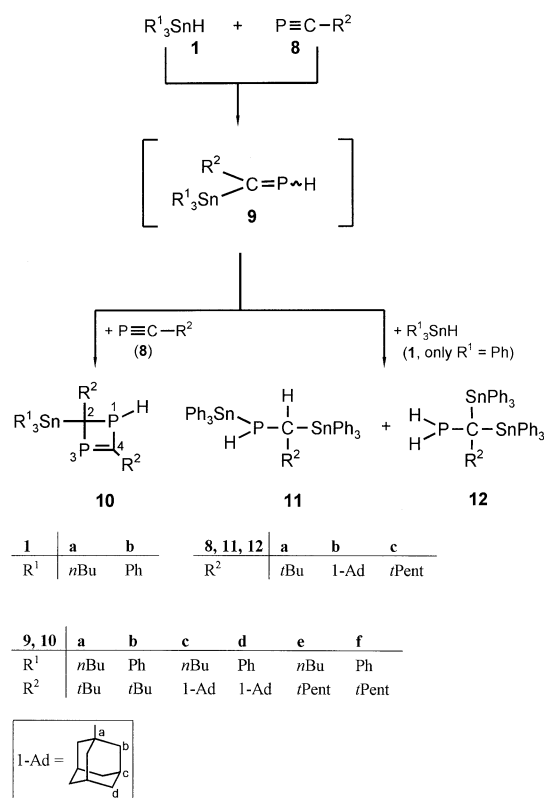
Reactions of the tin hydrides **1** with an excess of the phosphaalkynes **8a–c** in *n*-pentane at room temperature for



2 weeks gave rise to the 2-stannyl-substituted 1,2-dihydro-1,3-diphosphetes **10** in good yields. The reaction of tributyltin hydride (**1a**) with 1-adamantylphosphaalkyne (**8b**) required heating at 60°C for 4 hours for completion.

The natures of the 1,2-dihydro-1,3-diphosphetes **10a–f** were deduced from their analytical and spectroscopic data. The valency vibrations at 2160–2340 cm^{−1} in the IR spectra provided the first evidence for the presence of the PH function. A doublet of doublets at $\delta = 6.78–7.8$ with $^1J_{\text{H,P}}$ coupling constants of between 163 and 168 Hz was found in the $^1\text{H-NMR}$ spectra for these protons, which were originally bonded to the tin atoms. The splitting into a doublet of doublets and the integration values of the signals clearly demonstrate that compounds **10** are 1:2 adducts formed from one equivalent of the tin hydride **1** and two equiva-

[◇] Part 124: Ref.^[1].



lents of the phosphalkyne **8**. The proposed compositions of the products were further supported by elemental analyses or high-resolution mass spectrometry. The ^{31}P -NMR spectra each reveal the typical AX spin system for 1,2-dihydro-1,3-diphosphates^{[8][9]}. The signals for the $\lambda^3\sigma^2$ -phosphorus atoms occur in the expected low-field positions ($\delta = 369\text{--}376$) while those of the $\lambda^3\sigma^3$ -phosphorus atoms are found at $\delta = -5$ to $+3$. Both signals experience $^2J_{\text{P,P}}$ couplings of 35 to 44 Hz and appear as doublets. Thus, the existence of the structurally isomeric 1,4-dihydro-1,2-diphosphates can be excluded on the basis of the small P,P couplings^[10]. In the proton-undecoupled ^{31}P -NMR spectra the signals for the $\lambda^3\sigma^3$ -phosphorus atom are further split by $^1J_{\text{P,H}}$ couplings and those of the $\lambda^3\sigma^2$ -phosphorus atoms by $^3J_{\text{P,H}}$ couplings to give a doublet of doublets. A comparison of the measured values with those of previously known 1,2-dihydro-1,3-diphosphates^{[8][11][12]} supports the proposed constitutions. The ^{13}C -NMR spectra provide further diagnostic evidence. The doublet of doublets with large (ca. 50 Hz) and small (ca. 20 Hz) $^1J_{\text{C,P}}$ coupling constants observed at low field is characteristic for the skeletal sp^2 carbon atoms^[13]. The second skeletal carbon atoms give rise to signals in the typical sp^3 region with appreciably smaller $^1J_{\text{C,P}}$ coupling constants. The varying chemical shifts of the tin atoms in the ^{119}Sn -NMR spectra can be rationalized in terms of the differing substitution: The tin atoms of the tributyl-substituted derivatives give rise to signals in the region typical for tetraalkyl-substituted tin compounds^[14] while increasing phenyl substitution results in a stepwise shift to higher field^[15].

A more careful consideration of the structures of compounds **10** reveals the presence of two centers of chirality: In addition to the asymmetric carbon atom C2 the phosphorus atom P1 should be chiral and configurationally stable. However, only one set of signals was observed in all of the NMR spectra and therefore it must be assumed that only one diastereomer is formed in each case. An exact assignment to one of the possible isomers is not possible on the basis of the spectroscopic data.

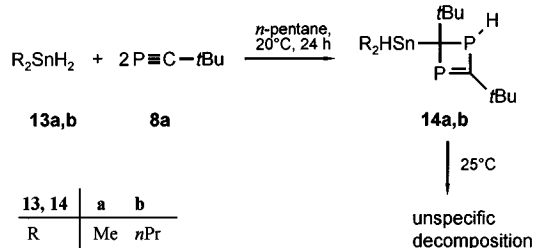
An increase in the tin hydride concentration favors the increased formation of the phosphanes **11** and **12**. When triphenyltin hydride (**1b**) was used in excess the phosphanes **11** were formed in yields exceeding 75%, while the isomeric compounds **12** were only observed as by-products (yields: $< 5\%$). In comparison to triphenyltin hydride (**1b**), the lower hydrostannylation activity of tributyltin hydride (**1a**)^[17] was not sufficient to alter the reaction course decisively in the direction of the phosphanes **11** and **12**; accordingly, the reaction mixtures contained appreciable amounts (60%) of the dihydridophosphates **10** and a separation of the individual components was not possible.

The ^{31}P -NMR and ^1H -NMR spectra are of particular diagnostic value for the structural elucidation of the distannyl-substituted phosphanes **11**. The ^{31}P -NMR spectra of **11** each contain a singlet in the region typical for stannyl-substituted phosphanes^[7] with $^1J_{\text{P},^{117,119}\text{Sn}}$ coupling constants of ca. 720 Hz. In the proton-coupled ^{31}P -NMR spectra these signals are split into doublets by $^1J_{\text{P,H}}$ couplings of ca. 200 Hz. In the ^1H -NMR spectra doublet signals at $\delta = 3.03\text{--}3.32$ with appropriate $^1J_{\text{H,P}}$ coupling constants are observed for the PH function while the protons added to carbon atoms give rise to signals at $\delta = 2.86\text{--}2.94$. The $^2J_{\text{H,P}}$ coupling constants of about 4 Hz are very small. Integration of the individual signal groups clearly shows the 1:2 ratio of phosphalkyne **8** to tin hydride **1b**. The presence of the PH function is further supported by a valency vibration at 2240 cm^{-1} in the IR spectra. The presence of two non-equivalent tin atoms is also apparent from the ^{119}Sn -NMR spectra. The triphenylstannyl groups directly bonded to phosphorus give doublet signals at $\delta = -73\text{--}75$ with $^1J_{\text{Sn,P}}$ coupling constants of ca. 730 Hz, while the signals of C-bonded tin atoms appear as singlets at $\delta = -104$. Identification of the phosphanes **12a–c**, which were not isolated, was based on direct ^{31}P -NMR-spectroscopic investigation of the reaction solutions. The chemical shifts of $\delta = -136.4$ (**12a**), -143.7 (**12b**), and -138.1 (**12c**), as well as the $^1J_{\text{P,H}}$ coupling constants [198.1 Hz (**12a**), 198.8 Hz (**12b**), 216.6 Hz (**12c**)], support the proposed structures.

The phosphalkenes **9** may be postulated as reactive intermediates in these stoichiometry-dependent reactions. These species then undergo stabilization either in a formal [2 + 2] cycloaddition to give the 1,2-dihydro-1,3-diphosphates **10** or by renewed 1,2-addition of a further equivalent of tin hydride **1** to furnish the phosphanes **11** and **12**. The preferential formation of the phosphanes **11** over **12** can be rationalized in terms of both steric and electronic factors.

Reactions with Diorganotin Dihydrides

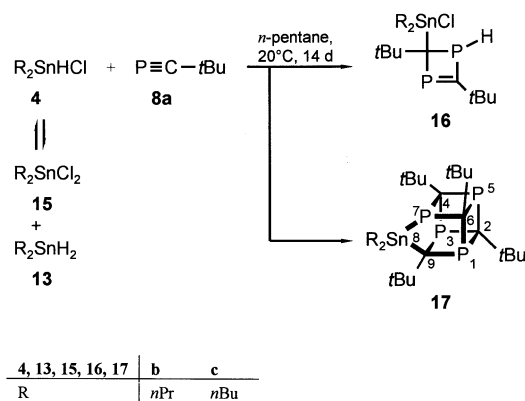
When the diorganotin dihydrides **13a, b** are allowed to react with an appreciable excess of the phosphalkyne **8a** the primary products are the 1,2-dihydro-1,3-diphosphetes **14a, b**. However, these species undergo an unspecific decomposition so that their isolation is not possible. Even so, they can be characterized by ^{31}P -NMR and IR spectroscopy through termination of the reaction after 24 hours and removal of the volatile tin hydrides **13a, b** together with the excess phosphalkyne **8a** under vacuum (oil pump).



The spectroscopic data of these compounds are in good agreement with those of the 1,2-dihydro-1,3-diphosphetes **10** discussed above. Therefore the constitutions of these hydrostannylation products may be considered as certain. One special feature resulting from the presence of the tin hydride function should be mentioned: The IR spectra contain SnH valency vibrations at $1790/1800\text{ cm}^{-1}$ in addition to the PH valency vibrations. This tin hydride function is presumably the cause of the unspecific decomposition reactions.

Reactions with Chlorodiorganotin Hydrides

Reactions of the chlorodiorganotin hydrides **4** with the phosphalkyne **8a** proceed much less selectively than those with the triorganotin hydrides **1**. In addition to the 1,2-dihydro-1,3-diphosphetes **16b, c** formed as main products, numerous by-products are observed by ^{31}P -NMR-spectroscopic monitoring of the reaction solutions. One of these by-products is the cage compound **17**. Product **17b** cannot be isolated, while **17c** has been isolated in pure form by crystallization from pentane at -20°C and completely characterized. Complete separation of the reaction mixtures into their components by either column chromatography or bulb-to-bulb distillation was not possible.



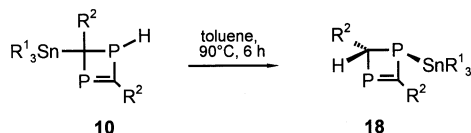
The ^1H -, ^{13}C -, ^{31}P -NMR, and IR data for the 1,2-dihydro-1,3-diphosphetes **16b, c** were taken from the crude reaction solutions and are in good agreement with those of the 1,2-dihydro-1,3-diphosphetes **10**. Thus, a detailed discussion of these data and the mechanism of the formation of the products is unnecessary in the light of the information given in the previous section.

The constitution of the cage compound **17c** was supported by mass spectrometry and elemental analysis. Linkage of the four phosphalkyne units gives rise to an A_2MX spin system in the ^{31}P -NMR spectrum. As a consequence of the C_s symmetry, the phosphorus atoms P1 and P3 are magnetically equivalent ($\delta = 221$). The signals for P5 and P7 appear at $\delta = 184$ and $\delta = -72$. The unusually low-field signals for the $\lambda^3\sigma^3$ -phosphorus atoms P1, P3, and P5 are, in fact, not surprising when one considers that the pentacyclic compound **17c** is formally derived from tetraphosphacubane, which gives a ^{31}P -NMR signal at $\delta = 257^{[18]}$. These values can be explained on the basis of the bonding model derived for tetraphosphacubane, which reveals a strong interaction between the lone electron pairs of the phosphorus atoms and the phosphorus-carbon σ bonds of the cubane skeleton. This effect is responsible for the dramatic low-field shifts of the phosphorus signals as well as the extreme high-field shifts of the signals for the skeletal carbon atoms in the ^{13}C -NMR spectrum^[19]. A further indication in favor of the proposed structure is given by the tin satellite lines in the ^{31}P -NMR spectrum: P7 exhibits a characteristic $^1J_{\text{P,Sn}}$ coupling of 744 Hz, clearly demonstrating that P7 and tin are directly adjacent^[20]. Tin satellites with $^3J_{\text{P,Sn}}$ coupling constants of 109 Hz are observed for the signal of P5. Accordingly, the ^{119}Sn -NMR signal for the tin atom ($\delta = 328$) is split into a doublet of doublets ($^1J_{\text{P,}^{119}\text{Sn}} = 784\text{ Hz}$, $^3J_{\text{P,}^{119}\text{Sn}} = 113\text{ Hz}$). As a consequence of the C_s symmetry the ^1H -NMR spectrum contains only three signals for the four *tert*-butyl groups, with an intensity ratio of 1:2:1. For the same reason the skeletal carbon atoms C4 and C6 are magnetically equivalent in the ^{13}C -NMR spectrum (pt, $\delta = 37.6$, $^1J_{\text{C,P}} = 13.5\text{ Hz}$). Carbon atom C2 gives, as required by the discussed bonding model, a signal at extremely high field ($\delta = -17.2$) (cf. skeletal carbon atom signals of tetraphosphacubane: $\delta = -29.1$)^{[18][19]}. Finally, the skeletal carbon atom C9 produces a ^{13}C -NMR signal at $\delta = 22.7$.

From a mechanistic point of view, the formation of the cage compounds **17** may be considered as a cyclooligomerization of the phosphalkyne **8a** in the coordination sphere of tin. Since the reaction of the 1,2-dihydro-1,3-diphosphete **16c** with an excess of the phosphalkyne **8a** does not lead to the formation of the homocubane **17c**, the existence of the 1,2-dihydro-1,3-diphosphete **16c** as an intermediate can be discounted. Similarly, subsequent attempts to introduce the stannyl unit into a skeletal bond of tetraphosphacubane^[18] by reaction of the latter with dibutyl(chloro)tin hydride (**4b**) were unsuccessful. Thus, a plausible mechanism involves the stepwise construction of the P/C skeleton by oligomerization of the phosphalkyne units at tin.

Thermal Isomerization of the 1,2-Dihydro-1,3-diphosphetes **10**

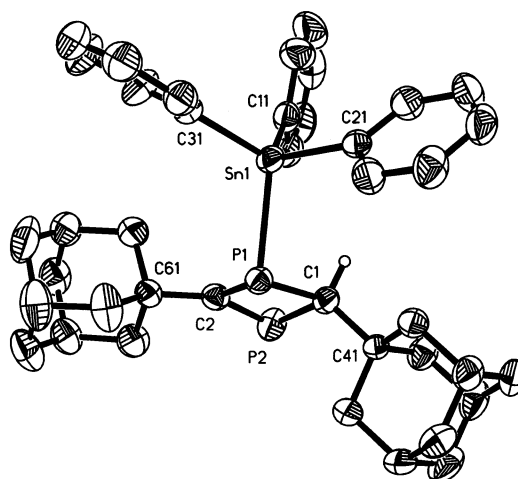
After heating of the 1,2-dihydro-1,3-diphosphetes **10a–d** in toluene at 90 °C for 6 hours, quantitative isomerization of the original 2-stannyl-substituted 1,2-dihydro-1,3-diphosphetes into the 1-stannyl-substituted derivatives **18a–d** is observed.



10, 18	a	b	c	d
R ¹	<i>n</i> Bu	Ph	<i>n</i> Bu	Ph
R ²	<i>t</i> Bu	<i>t</i> Bu	1-Ad	1-Ad

The natures of the 1,2-dihydro-1,3-diphosphetes **18** obtained were unequivocally demonstrated by mass spectrometry and elemental analysis. Evidence for the arrangement of the substituents was provided by analysis of the NMR spectra in comparison with the data for the starting compounds **10a–d**. Thus, the ³¹P-NMR signals of the λ³σ²-phosphorus atoms experienced high-field shifts of almost 20 ppm, while the signals of the λ³σ³-phosphorus atoms changed only slightly (δ = 2–3). The direct adjacency of tin to phosphorus is apparent from the tin satellites at the signal of P1 with ¹J_{P,117,119Sn} coupling constants of more than 1000 Hz and the markedly smaller ³J_{P,117,119Sn} coupling constants of 170 Hz at P3. The same couplings also appear in the ¹¹⁹Sn-NMR spectra. Because of the migration of the hydrogen atom from phosphorus to carbon the ¹H-NMR signal of this proton experiences a pronounced diamagnetic shift from δ = 7.5 to 2.6 and, instead of the original splitting into a doublet of doublets, appears merely as a doublet with a small ²J_{H,P} coupling of 1.4 Hz. The magnitude of this ²J_{H,P} coupling can be interpreted as evidence for the *trans* arrangement of **18**^[21]. In the ¹³C-NMR spectra the skeletal carbon atoms C4 give the expected doublet of doublet signals at low field (δ = 238.1–240.4; ²J_{C,P} = 53/40 Hz) while the signals of the second skeletal carbon atom appear as doublets (¹J_{C,P} = 22 to 24 Hz) at δ = 36.4–39.1 in the typical sp³ region. An X-ray crystallographic analysis of product **18d** (Figure 1) supplied final confirmation of the *trans* orientation of the adamantyl group and the triphenylstannyl group. Since only one isomer was obtained from each experiment and since the λ³σ³-phosphorus atoms should be configurationally stable^[16], the same arrangement of the substituents can also safely be assumed for the compounds **18a–c**.

The four-membered diphosphacyclobutene ring deviates slightly from planarity (sum of internal angles: 358.9°). The dihedral angle between the planes C(1)–P(1)–C(2) and C(1)–P(2)–C(2) amounts to 10.7°. The P(2)–C(2) bond length of 169.7 pm is in the typical range for P–C double bonds^[22], whereas the P(1)–C(2) single bond is somewhat shortened to 181.5 pm. The tin atom exists in a distorted tetrahedral environment.

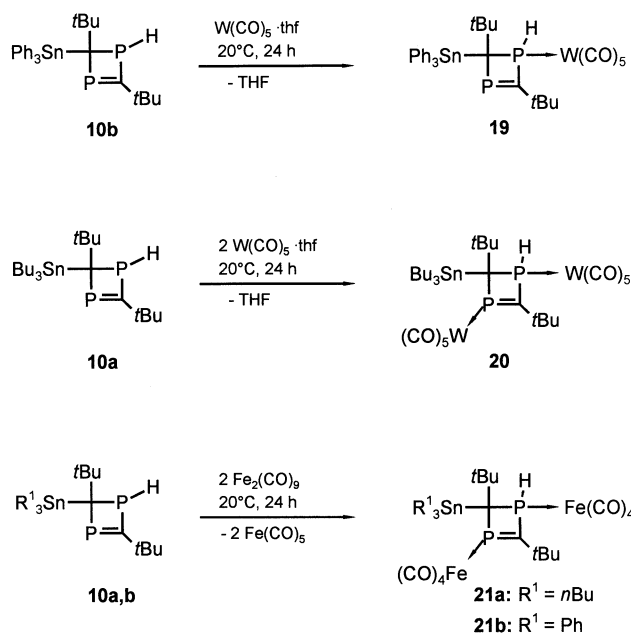
Figure 1. Molecular structure of **18d**^[a]

[a] Selected bond lengths [pm] and angles [°]: P(1)–C(2) 181.5(4), P(1)–C(1) 188.7(4), P(2)–C(2) 169.7(4), P(2)–C(1) 187.1(4), Sn(1)–C(21) 214.5(4), Sn(1)–C(31) 214.2(4), Sn(1)–C(11) 215.1(4), Sn(1)–P(1) 252.84(12); C(2)–P(1)–C(1) 82.2(2), C(2)–P(2)–C(1) 85.9(2), P(2)–C(1)–P(1) 91.2(2), P(2)–C(2)–P(1) 99.7(2), C(41)–C(1)–P(1) 118.1(3), C(41)–C(1)–P(2) 118.7(3), C(61)–C(2)–P(1) 130.0(3), C(61)–C(2)–P(2) 130.0(3), C(11)–Sn(1)–P(1) 115.27(12), C(21)–Sn(1)–P(1) 103.33(10), C(31)–Sn(1)–P(1) 113.14(10).

Complexation Behavior of **10**

Phosphane ligands have found a wide range of applications in organometallic chemistry^{[23][24]}. A common method for the preparation of phosphorus-containing transition-metal complexes comprises of a ligand-exchange reaction between phosphorus compounds and carbonyl transition-metal complexes.

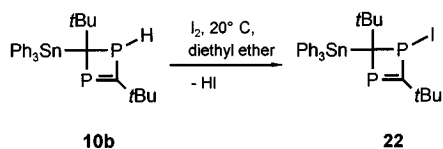
In the case of the 1,2-dihydro-1,3-diphosphetes **10**, both complexation of one phosphorus atom (→ **19**) and complete complexation of both phosphorus atoms (→ **20**) are possible using W(CO)₅·THF. Reactions of the 1,2-dihydro-1,3-diphosphetes **10a, b** with excess Fe₂(CO)₉ furnish the doubly complexed derivatives **21a, b**.



The spectroscopic characterization of the complexes **19**, **20**, and **21** is relatively simple. For the pentacarbonyltungsten complexes **19** and **20** the η^1 coordination of the metal fragment at P1 (for compound **19**) or at P1 and P3 (for compound **20**) is impressively demonstrated by the characteristic P-W couplings^[25] in the ^{31}P -NMR spectra. The complexation has only a minor influence on the ^{13}C -NMR data of the starting materials with additional characteristic signals being observed at low field for the carbonyl groups (see Experimental Section). Furthermore, CO valency vibrations appear in the IR spectra of compounds **19**, **20**, and **21**. The compositions of the products were further substantiated by mass spectrometry and elemental analysis.

Reaction of **10** with Iodine

Conversion of the PH function of the 1,2-dihydro-1,3-diphosphete **10b** into a PI function can be achieved by treatment of **10b** with a solution of iodine in diethyl ether at room temperature.



The degradation of the PH function is immediately demonstrated by the absence of the corresponding signal in the ^1H -NMR spectrum. Also, no P,H couplings can be seen in the proton-coupled ^{31}P -NMR spectrum. In comparison to that of the starting material the ^{13}C -NMR signal for C2 experiences a shift of almost 20 ppm to lower field. Finally, the increases in the $^1J_{\text{C,P}}$ coupling constants are noteworthy. The composition of the 1,2-dihydro-1,3-diphosphete **22** was substantiated by mass spectrometry and elemental analysis.

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Experimental Section

General: All experiments were carried out under argon (purity: > 99.998%) in previously evacuated and oven-dried Schlenk vessels. The solvents were anhydrous and stored under argon. – Melting points: Mettler FP 61 (heating rate: $3^\circ\text{C}/\text{min}$), uncorrected. – Elemental analyses: Perkin-Elmer EA 240. – ^1H NMR: Varian EM 360 (60 MHz), Bruker AC 200 and AMX 400; chemical shifts are relative to the solvent signals, and converted to TMS. – ^{13}C NMR: Bruker AC 200 and AMX 400; chemical shifts are relative to the solvent signals. – ^{31}P NMR: Bruker AC 200, external standard H_3PO_4 . – MS: Finnigan MAT 90 (70 eV). – IR: Perkin-Elmer 16 PC FT-IR and Perkin-Elmer 1310. – Chemicals: Triphenyltin hydride (**1b**) was prepared from triphenyltin chloride^[26], dimethyltin dihydride (**13a**)^[27], dipropyltin dihydride (**13b**)^[28], dibutyltin dihydride (**13c**)^[29], dipropyltin dichloride (**15b**)^[30], and the phosphaaacetylenes **8a**^[31], **b**^[32], **c**^[31] were prepared as described in the literature. All other starting materials were purchased from commercial suppliers.

1,2-Dihydro-1,3-diphosphetes 10. – **General Procedure:** To a solution of phosphaaalkyne **8** in pentane was added the tin hydride **1**. The mixture was stirred for two weeks at room temperature and the solvent removed under vacuum. The residue was purified by chromatography or crystallization.

2,4-Di-tert-butyl-2-tributylstannyl-1,2-dihydro-1 λ^3 ,3 λ^3 -diphosphete (10a): From **8a** (800 mg, 8 mmol) in pentane (3 ml) and **1a** (873 mg, 3 mmol); chromatography on aluminum oxide (5% H_2O) with pentane yielded **10a** (413 mg, 28%) as a yellow, non-distillable oil. – ^1H NMR (C_6D_6): δ = 0.65–1.94 (m, 45 H, Bu-H and *t*Bu-H), 6.73 (dd, $^1J_{\text{H,P}}$ = 164.7 Hz, $^3J_{\text{H,P}}$ = 21.5 Hz, 1 H, P–H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 13.5 (s, $^1J_{\text{C},^{117/119}\text{Sn}}$ = 315.7 Hz, Sn– CH_2), 13.9 (s, Sn– $[\text{CH}_2]_3$ – CH_3), 28.0 (s, SnCH_2CH_2), 29.7 [dd, $^3J_{\text{C,P}}$ = 10.1/5.8 Hz, $\text{C}(\text{CH}_3)_3$], 30.0 (s, CH_2CH_3), 30.8 [d, $^3J_{\text{C,P}}$ = 5 Hz, $\text{C}(\text{CH}_3)_3$], 36.4 (dd, $^1J_{\text{C,P}}$ = 39.2/5.5 Hz, C2), 37.1 [d, $^2J_{\text{C,P}}$ = 7.7 Hz, $\text{C}(\text{CH}_3)_3$], 39.8 [d, $^2J_{\text{C,P}}$ = 6.3 Hz, $\text{C}(\text{CH}_3)_3$], 222.56 (dd, $^1J_{\text{C,P}}$ = 52.1/23.2 Hz, C4). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = 0.7 (d, $^2J_{\text{P,P}}$ = 39.1 Hz, P–1), 375.6 (d, $^2J_{\text{P,P}}$ = 39.1 Hz, P–3). – $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C_6D_6): δ = 3.85 (s). – IR (film): $\tilde{\nu}$ = 2940, 2910, 2860, 2200 (P–H), 1455, 1355, 1210, 1110, 840 cm^{-1} . – MS; *m/z* (%): 492 (13) [M^+], 291 (39) [SnBu_3^+], 235 (76) [HSnBu_2^+], 179 (100) [H_2SnBu^+], 57 (38) [C_4H_9^+]. – $\text{C}_{22}\text{H}_{46}\text{P}_2\text{Sn}$ (491.26): calcd. C 53.8, H 9.4; found C 53.6, H 9.3.

2,4-Di-tert-butyl-2-triphenylstannyl-1,2-dihydro-1 λ^3 ,3 λ^3 -diphosphete (10b): From **8a** (4 g, 40 mmol) in pentane (5 ml) and **1b** (3.43 g, 9.8 mmol); crystallization from 3 ml of pentane at -20°C yielded **10b** (2.6 g, 48% based on **1b**) as a yellow solid with m.p. 68°C . – ^1H NMR (C_6D_6): δ = 1.16 (s, 9 H, *t*Bu-H), 1.65 (s, 9 H, *t*Bu-H), 7.42–7.48 (m, 9 H, *m*-, *p*- C_6H_5), 7.57 (dd, $^1J_{\text{H,P}}$ = 166 Hz, $^3J_{\text{H,P}}$ = 18.6 Hz, 1 H, P–H), 8.05–8.08 (m, 6 H, *o*- C_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 29.9 [d, $^3J_{\text{C,P}}$ = 3.6 Hz, $\text{C}(\text{CH}_3)_3$], 30.3 [d, $^3J_{\text{C,P}}$ = 9.0 Hz, $\text{C}(\text{CH}_3)_3$], 37.4 [d, $^2J_{\text{C,P}}$ = 7.2 Hz, $\text{C}(\text{CH}_3)_3$], 39.2 (dd, $^1J_{\text{C,P}}$ = 38.2/4 Hz, C2), 39.6 [d, $^2J_{\text{C,P}}$ = 5.4 Hz, $\text{C}(\text{CH}_3)_3$], 128.7 (s, $^2J_{\text{C},^{117/119}\text{Sn}}$ = 49.4 Hz, *o*-C), 129.2 (s, *p*-C), 138.0 (s, $^3J_{\text{C},^{117/119}\text{Sn}}$ = 35.0 Hz, *m*-C), 141.6 (s, $^1J_{\text{C},^{117/119}\text{Sn}}$ = 471.2/492.8 Hz, *ipso*-C), 224.4 (dd, $^1J_{\text{C,P}}$ = 51.6/22.9 Hz, C4). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = 2.5 (d, $^2J_{\text{P,P}}$ = 35.8 Hz, P–1), 372.1 (d, $^2J_{\text{P,P}}$ = 35.8 Hz, P–3). – $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C_6D_6): δ = –99.75 (pt, $^2J_{^{119}\text{Sn,P}}$ = 24.4 Hz). – IR (KBr): $\tilde{\nu}$ = 3040, 2920, 2180 (P–H), 1450, 1410, 1350, 1100, 840 cm^{-1} . – MS; *m/z* (%): 552 (5) [M^+], 351 (100) [SnPh_3^+], 197 (24) [SnPh^+], 57 (18) [C_4H_9^+]. – $\text{C}_{28}\text{H}_{34}\text{P}_2\text{Sn}$ (551.23): calcd. C 61.0, H 6.2; found C 61.3, H 6.2.

2,4-(Diadamant-1-yl)-2-tributylstannyl-1,2-dihydro-1 λ^3 ,3 λ^3 -diphosphete (10c): From **8b** (360 mg, 2 mmol) in pentane (2 ml) and **1a** (291 mg, 1 mmol); after stirring the reaction mixture for two weeks at room temperature the solution was heated to 60°C for 4 h; chromatography on aluminum oxide (5% H_2O) with pentane yielded **10c** (150 mg, 23%) as a yellow, non-distillable oil. – ^1H NMR (C_6D_6): δ = 1.10–2.62 (m, 57 H, Ad-H and Bu-H), 6.81 (dd, $^1J_{\text{H,P}}$ = 164 Hz, $^3J_{\text{H,P}}$ = 22 Hz, 1 H, P–H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 13.8 (s, $^1J_{\text{C},^{117/119}\text{Sn}}$ = 313.8 Hz, Sn– CH_2), 13.9 (s, Sn– $[\text{CH}_2]_3$ – CH_3), 28.1 (s, $^2J_{\text{C},^{117/119}\text{Sn}}$ = 63.0 Hz, SnCH_2CH_2), 29.2 (s, C-c), 29.5 (s, C-c), 30.2 (s, $^3J_{\text{C},^{117/119}\text{Sn}}$ = 35.3 Hz, CH_2CH_3), 37.0 (s, $2 \times \text{C-d}$), 37.4 (d, $^1J_{\text{C,P}}$ = 30.5 Hz, C-2), 38.9 (d, $^2J_{\text{C,P}}$ = 6.3 Hz, C-a), 41.2 (br. d, $^3J_{\text{C,P}}$ = 7.6 Hz, C-b), 42.1 (d, $^2J_{\text{C,P}}$ = 5.7 Hz, C-a), 43.5 (d, $^3J_{\text{C,P}}$ = 3.8 Hz, C-b), 222.6 (dd, $^1J_{\text{C,P}}$ = 51/22.4 Hz, C-4). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = –5.2 (d, $^2J_{\text{P,P}}$ = 43.6 Hz, P–1), 373.3 (d, $^2J_{\text{P,P}}$ = 43.6 Hz, P–3). – IR (film): $\tilde{\nu}$ = 2920–2800, 2160 (P–H), 1440, 1320, 1270, 1140 cm^{-1} . – MS; *m/z* (%): 649 (36) [M^+], 291 (46) [SnBu_3^+], 135 (100) [Ad^+]. – $\text{C}_{34}\text{H}_{58}\text{P}_2\text{Sn}$ (647.49): calcd. C 63.1, H 9.0; found C 63.4, H 8.9.

2,4-(Diadamant-1-yl)-2-triphenylstannyl-1,2-dihydro-1 λ^3 ,3 λ^3 -diphosphete (10d): From **8b** (300 mg, 1.7 mmol) in pentane (5 ml)

and **1b** (296 mg, 0.8 mmol); evaporation of the solvent and washing of the residue with pentane yielded **10d** (198 mg, 35%) as a yellow solid with m.p. 92°C. – ^1H NMR (C_6D_6): δ = 1.38–2.63 (m, 30 H, Ad-H), 7.20–7.41 (m, 9 H, *m*-, *p*- C_6H_5), 7.44 (dd, $^1J_{\text{H,P}}$ = 168 Hz, $^3J_{\text{H,P}}$ = 21 Hz, 1 H, P-H), 7.87–8.09 (m, 6 H, *o*- C_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 28.9 (s, C-c), 29.2 (s, C-c), 36.5 (s, C-d), 36.7 (s, C-d), 39.1 (d, $^2J_{\text{C,P}}$ = 6.5 Hz, C-a), 41.6 (br. d, $^3J_{\text{C,P}}$ = 10.0 Hz, C-b), 41.9 (d, $^2J_{\text{C,P}}$ = 5.6 Hz, C-a), 42.1 (d, $^3J_{\text{C,P}}$ = 5.6 Hz, C-b), 128.7 (s, $^2J_{\text{C,}^{117/119}\text{Sn}}$ = 49.0 Hz, *o*-C), 129.0 (s, *p*-C), 138.2 (s, $^3J_{\text{C,}^{117/119}\text{Sn}}$ = 35.3 Hz, *m*-C), 142.2 (s, $^1J_{\text{C,}^{117/119}\text{Sn}}$ = 467.4/489.1 Hz, *ipso*-C), 223.9 (dd, $^1J_{\text{C,P}}$ = 50.2/21.3 Hz, C-4), the C-2 signal could not be detected because of signal overlap. – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = –4.1 (d, $^2J_{\text{P,P}}$ = 43 Hz, P-1), 369.2 (d, $^2J_{\text{P,P}}$ = 43 Hz, P-3). – $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C_6D_6): δ = –101.43 (s). – IR (KBr): $\tilde{\nu}$ = 3030, 2940, 2865, 2818, 2180 (P-H), 1432, 1413, 1330, 1295, 1249, 715, 685 cm^{-1} . – MS; m/z (%): 708 (6) [M^+], 351 (100) [SnPh_3^+], 135 (47) [Ad^+]. – $\text{C}_{40}\text{H}_{46}\text{P}_2\text{Sn}$ (707.5): calcd. C 67.9, H 6.6; found C 67.6, H 6.5.

2,4-Di-tert-pentyl-2-tributylstannyl-1,2-dihydro-1 λ^3 ,3 λ^3 -diphosphete (10e): From **8c** (357 mg, 3.13 mmol) in pentane (5 ml) and **1a** (407 mg, 1.4 mmol); chromatography on aluminum oxide (5% H_2O) with pentane yielded **10e** (540 mg, 74%) as a yellow, non-distillable oil. – ^1H NMR (C_6D_6): δ = 0.86–1.59 (m, 45 H, *t*Pent-H and Bu-H), 6.78 (dd, $^1J_{\text{H,P}}$ = 163.04 Hz, $^3J_{\text{H,P}}$ = 20.27 Hz, 1 H, P-H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 8.0 (s, $^1J_{\text{C,}^{117/119}\text{Sn}}$ = 341.3 Hz, Sn- CH_2), 9.2 (s, CH_2CH_3), 9.6 (s, CH_2CH_3), 13.5 (s, Sn-[CH_2] $_3$ - CH_3), 24.7 [br. d, $^3J_{\text{C,P}}$ = 6.4 Hz, $\text{C}(\text{CH}_3)_2$], 25.8 [br. d, $^3J_{\text{C,P}}$ = 8.0 Hz, $\text{C}(\text{CH}_3)_2$], 27.1 (s, SnCH_2CH_2), 29.9 [s, $^3J_{\text{C,}^{117/119}\text{Sn}}$ = 21.7 Hz, $\text{Sn}(\text{CH}_2)_2\text{CH}_2\text{CH}_3$], 34.7 (dd, $^3J_{\text{C,P}}$ = 9.2/4.4 Hz, CH_2CH_3), 35.4 [d, $^2J_{\text{C,P}}$ = 7.2 Hz, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$], 36.1 (dd, $^3J_{\text{C,P}}$ = 7.2/4.0 Hz, CH_2CH_3), 38.4 (d, $^1J_{\text{C,P}}$ = 40.2 Hz, C2), 39.2 [d, $^2J_{\text{C,P}}$ = 6.4 Hz, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$], 221.0 (dd, $^1J_{\text{C,P}}$ = 52.2, 24.1 Hz, C-4). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = 1 (d, $^2J_{\text{P,P}}$ = 41 Hz, P-1), 379 (d, $^2J_{\text{P,P}}$ = 41 Hz, P-3). – IR (pentane): $\tilde{\nu}$ = 2942, 2912, 2880, 2340 (P-H), 1644, 1456 cm^{-1} . – MS; m/z (%): 520 (5) [M^+], 291 (100) [SnBu_3^+], 235 (59) [HSnBu_2^+], 177 (60) [SnBu^+], 71 (44) [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3^+$], 57 (16) [C_4H_9^+]. – HR-MS: $\text{C}_{24}\text{H}_{50}\text{P}_2\text{Sn}$: calcd. 520.2409; found 520.2385.

2,4-Di-tert-pentyl-2-triphenylstannyl-1,2-dihydro-1 λ^3 ,3 λ^3 -diphosphete (10f): From **8c** (422 mg, 3.7 mmol) in pentane (5 ml) and **1b** (123 mg, 0.35 mmol); evaporation of the solvent and washing of the residue with pentane yielded **10f** (70 mg, 34%) as a yellow solid with m.p. 86°C. – ^1H NMR (C_6D_6): δ = 0.70 (t, $^3J_{\text{H,H}}$ = 7.24 Hz, 3 H, CH_2CH_3), 0.82 (t, $^3J_{\text{H,H}}$ = 7.87 Hz, 3 H, CH_2CH_3), 0.86 [s, 3 H, $\text{C}(\text{CH}_3)_2$], 0.88 [s, 3 H, $\text{C}(\text{CH}_3)_2$], 1.27 [s, 3 H, $\text{C}(\text{CH}_3)_2$], 1.29 [s, 3 H, $\text{C}(\text{CH}_3)_2$], 7.10–7.18 (m, 9 H, *m*-, *p*- C_6H_5), 7.27 (dd, $^1J_{\text{H,P}}$ = 166.59 Hz, $^3J_{\text{H,P}}$ = 19.98 Hz, 1 H, P-H), 7.73–7.82 (m, 6 H, *o*- C_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 9.1 (s, CH_2CH_3), 9.5 (s, CH_2CH_3), 24.8 [br. s, $\text{C}(\text{CH}_3)_2$], 25.1 [br. s, $\text{C}(\text{CH}_3)_2$], 35.2 (br. s, CH_2CH_3), 35.8 (br. s, CH_2CH_3), 39.7 (d, $^1J_{\text{C,P}}$ = 6.7 Hz, C2), 41.3 [s, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$], 42.5 [s, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$], 128.4 (s, *o*-C), 128.8 (s, *p*-C), 137.8 (s, $^3J_{\text{C,}^{117/119}\text{Sn}}$ = 34.4 Hz, *m*-C), 141.6 (s, *ipso*-C), 222.7 (dd, $^1J_{\text{C,P}}$ = 52.0, 22.4 Hz, C-4). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = 3 (d, $^2J_{\text{P,P}}$ = 40 Hz, P-1), 376 (d, $^2J_{\text{P,P}}$ = 40 Hz, P-3). – IR (pentane): $\tilde{\nu}$ = 2990, 2199 (P-H), 1468, 1429, 1261, 1072, 1021, 807, 726 cm^{-1} . – MS; m/z (%): 580 (1) [M^+], 351 (100) [SnPh_3^+], 274 (20) [SnPh_2^+], 197 (62) [SnPh^+], 77 (20) [C_6H_5^+], 71 (13) [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3^+$]. – HR-MS: $\text{C}_{30}\text{H}_{38}\text{P}_2\text{Sn}$: calcd. 580.1470; found 580.1465.

1,2-Bis(triphenylstannyl)phosphanes 11a, b. – *General Procedure*: To a solution of phosphacetylene **8** in pentane was added triphenyltin hydride (**1b**). The mixture was stirred for one week at

20°C, the solvent removed under vacuum, and the residue washed several times with pentane.

[tert-Butyl(triphenylstannyl)methyl]triphenylstannylphosphane (11a): From **8a** (0.4 g, 4 mmol) in pentane (5 ml) and **1b** (6.32 g, 18 mmol) to furnish **11a** (2.6 g, 81%) as a pale yellow powder with m.p. 154°C. – ^1H NMR (C_6D_6): δ = 1.04 (s, 9 H, *t*Bu), 2.94 (d, $^2J_{\text{H,P}}$ = 4.5 Hz, 1 H, PC-H), 3.32 (d, $^1J_{\text{H,P}}$ = 196.2 Hz, 1 H, P-H), 7.05–7.13 (m, 18 H, *m*-, *p*- C_6H_5), 7.47–7.49 (m, 6 H, *o*- C_6H_5), 7.62–7.66 (m, 6 H, *o*- C_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 28.8 (d, $^1J_{\text{C,P}}$ = 36.1 Hz, PCH, ^1H coupl.: $^1J_{\text{C,H}}$ = 129.3 Hz), 32.4 [d, $^3J_{\text{C,P}}$ = 10.4 Hz, $\text{C}(\text{CH}_3)_3$], 35.4 [d, $^2J_{\text{C,P}}$ = 17.7 Hz, $\text{C}(\text{CH}_3)_3$], 129.26 (s, *o*-C), 129.30 (s, *o*-C), 129.4 (s, *p*-C), 129.6 (s, *p*-C), 137.9 (s, *m*-C), 138.1 (s, *m*-C), 139.1 (d, $^2J_{\text{C,P}}$ = 4 Hz, *ipso*-C), 140.2 (s, *ipso*-C). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = –170 (s, $^1J_{\text{P,}^{117/119}\text{Sn}}$ = 716 Hz). – $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C_6D_6): δ = –73 (d, $^1J_{^{119}\text{Sn,P}}$ = 732 Hz, P-Sn), –104 (s, PC-Sn). – IR (KBr): $\tilde{\nu}$ = 3030, 2920, 2240 (P-H), 1460, 1410, 1350, 1320, 1285, 1250, 1210, 1180, 1060, 1010, 985, 855, 750, 715, 685 cm^{-1} . – MS; m/z (%): 802 (0.2) [M^+], 451 (2) [M^+ – SnPh_3], 351 (100) [SnPh_3^+], 197 (18) [SnPh^+], 57 (9) [C_4H_9^+]. – $\text{C}_{41}\text{H}_{41}\text{PSn}_2$ (802.14): calcd. C 61.4, H 5.2; found C 61.4, H 5.2.

[Adamant-1-yl(triphenylstannyl)methyl]triphenylstannylphosphane (11b): From **8b** (0.3 g, 1.66 mmol) in pentane (5 ml) and **1b** (3.16 g, 9 mmol) to furnish **11b** (1.01 g, 75%) as a colorless powder with m.p. 185°C (dec.). – ^1H NMR (C_6D_6): δ = 1.2–1.9 (m, 15 H, Ad-H), 2.86 (d, $^2J_{\text{H,P}}$ = 3.7 Hz, 1 H, PC-H), 3.03 (d, $^1J_{\text{H,P}}$ = 198.4 Hz, 1 H, P-H), 6.9–7.25 (m, 18 H, *m*-, *p*- C_6H_5), 7.3–7.8 (m, 12 H, *o*- C_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 31.3 (s, C-c), 31.4 (d, $^1J_{\text{C,P}}$ = 39.4 Hz, PCH, ^1H coupl.: $^1J_{\text{C,H}}$ = 127.7 Hz), 38.2 (d, $^2J_{\text{C,P}}$ = 15.2 Hz, C-a), 38.6 (s, C-d), 46.7 (d, $^3J_{\text{C,P}}$ = 11.1 Hz, C-b), 130.7 (s, *o*-C), 130.9 (s, *o*-C), 131.0 (s, *p*-C), 131.2 (s, *p*-C), 139.4 (s, *m*-C), 139.7 (s, *m*-C), 140.9 (d, $^2J_{\text{C,P}}$ = 3.3 Hz, *ipso*-C), 142.8 (s, *ipso*-C). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = –175 (s, $^1J_{\text{P,}^{117/119}\text{Sn}}$ = 724 Hz). – $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C_6D_6): δ = –75 (d, $^1J_{^{119}\text{Sn,P}}$ = 731 Hz, P-Sn), –104 (s, PC-Sn). – IR (KBr): $\tilde{\nu}$ = 3030, 2910, 2840, 2240 (P-H), 1480, 1425, 1310, 1100, 1070, 1020, 1000, 890, 730, 700 cm^{-1} . – $\text{C}_{47}\text{H}_{47}\text{PSn}_2$ (880.25): calcd. C 64.1, H 5.4; found C 64.0, H 5.3.

1,2-Dihydro-1,3-diphosphetes 14a, b. – *General Procedure*: To a solution of phosphacetylene **8** in pentane was added the diorganotin dihydride **13** and the mixture stirred at room temperature for 24 h. The solvent, unreacted phosphacetylene **8**, and tin hydride **13** were removed under vacuum. Further purification by distillation, chromatography, or crystallization was not possible.

2,4-Di-tert-butyl-2-hydridodimethylstannyl-1,2-dihydro-1 λ^3 ,3 λ^3 -diphosphete (14a): From **8a** (800 mg, 8 mmol) in pentane and **13a** (452 mg, 3 mmol) to furnish **14a** (70 mg, 7%) as a yellow oil. – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = 1.9 (dd, $^1J_{\text{P,H}}$ = 161.5 Hz, $^2J_{\text{P,P}}$ = 40.9 Hz, P-1), 371.5 (dd, $^2J_{\text{P,P}}$ = 40.9 Hz, $^3J_{\text{P,H}}$ = 18.5 Hz, P-3). – IR (film): $\tilde{\nu}$ = 2930, 2910, 2170 (P-H), 1790 (Sn-H), 1450, 1350, 1250, 1240, 1050, 1010, 860, 830, 760, 620 cm^{-1} .

2,4-Di-tert-butyl-2-hydridodipropylstannyl-1,2-dihydro-1 λ^3 ,3 λ^3 -diphosphete (14b): From **8a** (800 mg, 8 mmol) in pentane and **13b** (620 mg, 3 mmol) to furnish **14b** (110 mg, 9%) as a yellow oil. – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = –0.4 (dd, $^1J_{\text{P,H}}$ = 163 Hz, $^2J_{\text{P,P}}$ = 41 Hz, P-1), 369.7 (dd, $^2J_{\text{P,P}}$ = 41 Hz, $^3J_{\text{P,H}}$ = 21 Hz, P-3). – IR (film): $\tilde{\nu}$ = 3000, 2980, 2920, 2900, 2160 (P-H), 1800 (Sn-H), 1350, 1250, 1240, 1050, 1010, 860, 830, 770, 750 cm^{-1} .

1,2-Dihydro-1,3-diphosphetes 16 and Homocubane 17. – *General Procedure*: Diorganotin dichloride **15** was dissolved in toluene (3 ml) and pentane (3 ml) and cooled to 0°C. Diorganotin dihydride

13 was added and the reaction solution was stirred for 15 min. Phosphaalkyne **8** was added. After a few hours the color of the reaction solution changed to red-brown and after 14 d the solvent was removed under vacuum. The residue was taken up in pentane (10 ml). Unreacted diorganotin dihydride **13** was crystallized at -20°C , further crystallization at -20°C yielded the homocubane **17**. Compound **17b** could not be isolated. It was not possible to purify the oils which contained the 1,2-dihydro-1,3-diphosphetes **16** as main products.

2,4-Di-tert-butyl-2-chlorodipropylstannyl-1,2-dihydro-1 λ^3 ,3 λ^3 -diphosphete (16b): From **15b** (690 mg, 2.5 mmol), **13b** (520 mg, 2.5 mmol), and **8a** (1600 mg, 16 mmol) to furnish **16b** (ca. 85%). – ^1H NMR (C_6D_6): δ = 0.85–1.9 (m, 32 H, Pr-H and *t*Bu-H), 6.82 (dd, $^1J_{\text{H,P}}$ = 166 Hz, $^3J_{\text{H,P}}$ = 20 Hz, 1 H, P–H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 18.8 (s, CH_2CH_3), 20.4 (s, SnCH_2CH_2), 23.1 (s, SnCH_2), 29.7 [dd, $^3J_{\text{C,P}}$ = 9.6/4.8 Hz, $\text{C}(\text{CH}_3)_3$], 30.6 [br. d, $^3J_{\text{C,P}}$ = 4.8 Hz, $\text{C}(\text{CH}_3)_3$], 37.1 [br. d, $^2J_{\text{C,P}}$ = 8.0 Hz, $\text{C}(\text{CH}_3)_3$], 40.2 [br. s, $\text{C}(\text{CH}_3)_3$], 43.2 (dd, $^1J_{\text{C,P}}$ = 39.0/6.0 Hz, C-2), 227.6 (dd, $^1J_{\text{C,P}}$ = 53.8/24.1 Hz, C-4). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = –5.5 (d, $^2J_{\text{P,P}}$ = 43.1 Hz, P-1), 365.7 (d, $^2J_{\text{P,P}}$ = 43.1 Hz, P-3). – IR (film): $\tilde{\nu}$ = 2930, 2842, 2200 (P–H), 1450, 1380, 1350, 1208, 1103, 1055 cm^{-1} .

2,4-Di-tert-butyl-2-dibutylchlorostannyl-1,2-dihydro-1 λ^3 ,3 λ^3 -diphosphete (16c): From **15c** (900 mg, 2.96 mmol), **14c** (696 mg, 2.96 mmol) and **8a** (2000 mg, 20 mmol) to furnish **16c** (ca. 85%). – ^1H NMR (C_6D_6): δ = 0.8–1.9 (m, 36 H, Bu-H and *t*Bu-H), 6.77 (dd, $^1J_{\text{H,P}}$ = 166.5 Hz, $^3J_{\text{H,P}}$ = 19.5 Hz, 1 H, P–H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 14.0 [s, $\text{Sn}(\text{CH}_2)_3\text{CH}_3$], 20.3 (s, SnCH_2), 27.2 (s, CH_2CH_2), 28.8 (s, CH_2CH_2), 29.7 [br. d, $^3J_{\text{C,P}}$ = 10 Hz, $\text{C}(\text{CH}_3)_3$], 30.7 [br. d, $^3J_{\text{C,P}}$ = 4.0 Hz, $\text{C}(\text{CH}_3)_3$], 37.1 [d, $^2J_{\text{C,P}}$ = 7.2 Hz, $\text{C}(\text{CH}_3)_3$], 40.2 [d, $^2J_{\text{C,P}}$ = 2.4 Hz, $\text{C}(\text{CH}_3)_3$], 43.2 (br. d, $^1J_{\text{C,P}}$ = 33.7 Hz, C-2), 227.6 (dd, $^1J_{\text{C,P}}$ = 53.0/23.3 Hz, C-4). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = –5.3 (d, $^2J_{\text{P,P}}$ = 43 Hz, P-1), 366.1 (d, $^2J_{\text{P,P}}$ = 43 Hz, P-3). – IR (film): $\tilde{\nu}$ = 2930, 2900, 2880, 2210 (P–H), 1450, 1380, 1370, 1349, 1209, 1104, 1070, 1015 cm^{-1} .

2,4,6,9-Tetra-tert-butyl-8-dibutylstanna-1,3,5,7-tetraphosphapentacyclo[4.3.0.0 2,5 .0 3,9 .0 4,7]nonane (17c): From **15c** (900 mg, 2.96 mmol), **13c** (696 mg, 2.96 mmol) and **8a** (2000 mg, 20 mmol) to furnish **17c** (210 mg, 6%) as yellow crystals with m.p. 145°C . – ^1H NMR (C_6D_6): δ = 0.87 (t, $^3J_{\text{H,H}}$ = 7.2 Hz, 6 H, $\text{CH}_2\text{--CH}_3$), 1.08 (s, 9 H, *t*Bu-H), 1.22–1.47 (m, 8 H, $\text{CH}_2\text{--CH}_2$), 1.27 (s, 18 H, *t*Bu-H), 1.5–1.61 (m, 4 H, $\text{CH}_2\text{--CH}_2$), 1.72 (s, 9 H, *t*Bu-H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = –17.2 (m, C-2), 13.6 [s, $\text{Sn}(\text{CH}_2)_3\text{CH}_3$], 18.7 (s, SnCH_2), 22.7 (m, C-9), 26.0 [m, $2 \times \text{C}(\text{CH}_3)_3$], 27.1 [m, $2 \times \text{C}(\text{CH}_3)_3$], 27.7 (s, CH_2CH_2), 30.2 (s, CH_2CH_2), 34.4 [m, $2 \times \text{C}(\text{CH}_3)_3$], 35.1 [pt, $^2J_{\text{C,P}}$ = 7.2 Hz, $2 \times \text{C}(\text{CH}_3)_3$], 37.6 (pt, $^1J_{\text{C,P}}$ = 13.5 Hz, C-4/C-6). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = –72.1 (dt, $^2J_{\text{P,P}}$ = 21.0/7.6 Hz, $^1J_{\text{P,Sn}}$ = 743.9 Hz, 1 P, P-7), 183.8 (dt, $^2J_{\text{P,P}}$ = 21.0/15.3 Hz, $^3J_{\text{P,Sn}}$ = 109 Hz, 1 P, P-5), 221.4 (dd, $^2J_{\text{P,P}}$ = 15.3/7.6 Hz, 2 P, P-1/P-3). – ^{119}Sn NMR (C_6D_6): δ = 328 (dd, $^1J_{^{119}\text{Sn,P}}$ = 784 Hz, $^3J_{^{119}\text{Sn,P}}$ = 113 Hz). – IR (KBr): $\tilde{\nu}$ = 2925, 2890, 2830, 1450, 1372, 1343, 1213, 760, 734, 696, 670 cm^{-1} . – MS; m/z (%): 634 (15) [M^+], 521 (31) [$\text{M}^+ - 2\text{Bu} + \text{H}$], 400 (14) [Cubane^+]. – $\text{C}_{28}\text{H}_{54}\text{P}_4\text{Sn}$ (633.3): calcd. C 53.1, H 8.6; found C 53.2, H 8.4.

Thermolysis of 10a–d. – **General Procedure:** The 1,2-dihydro-1,3-diphosphete **10** was dissolved in toluene (5 ml) and heated at 90°C for 6 h. Removal of the solvent yielded the 1-stannyl-substituted 1,2-dihydro-1,3-diphosphetes **18**.

trans-2,4-Di-tert-butyl-1-tributylstannyl-1,2-dihydro-1 λ^3 ,3 λ^3 -diphosphete (18a): From **10a** (413 mg, 0.84 mmol) to furnish **18a** (413 mg, 100%) as a yellow oil with b.p. $170^{\circ}\text{C}/5 \times 10^{-3}$ mbar. – ^1H NMR (C_6D_6): δ = 0.9–1.9 (m, 45 H, Bu-H and *t*Bu-H), 2.05 (s, 1 H, PC–H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 10.8 (d, $^2J_{\text{C,P}}$ =

1.2 Hz, $^1J_{\text{C},^{117/119}\text{Sn}}$ = 266.1 Hz, Sn--CH_2), 14.1 [s, $\text{Sn--}(\text{CH}_2)_3\text{--CH}_3$], 27.8 (s, SnCH_2CH_2), 28.1 [dd, $^3J_{\text{C,P}}$ = 14.0/9.4 Hz, $\text{C}(\text{CH}_3)_3$], 29.9 (s, CH_2CH_3), 31.0 [dd, $^3J_{\text{C,P}}$ = 9.3/3.9 Hz, $\text{C}(\text{CH}_3)_3$], 33.6 [d, $^2J_{\text{C,P}}$ = 6.2 Hz, $\text{C}(\text{CH}_3)_3$], 36.4 (d, $^1J_{\text{C,P}}$ = 23.1 Hz, C-2), 40.7 [pt, $^2J_{\text{C,P}}$ = 7.0 Hz, $\text{C}(\text{CH}_3)_3$], 239.8 (dd, $^1J_{\text{C,P}}$ = 51.8/39.9 Hz, C-4). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = 6.9 (d, $^2J_{\text{P,P}}$ = 39.1 Hz, $^1J_{\text{P},^{117/119}\text{Sn}}$ = 869.9 Hz, P-1), 349.4 (d, $^2J_{\text{P,P}}$ = 39.1 Hz, P-3). – ^{119}Sn NMR (C_6D_6): δ = –36 (dd, $^1J_{^{119}\text{Sn,P}}$ = 916 Hz, $^3J_{^{119}\text{Sn,P}}$ = 147 Hz). – IR (film): $\tilde{\nu}$ = 2950, 2925, 2870, 1470, 1380, 1220, 1125, 860 cm^{-1} . – MS; m/z (%): 492 (9) [M^+], 57 (77) [C_4H_9^+]. – $\text{C}_{22}\text{H}_{46}\text{P}_2\text{Sn}$ (491.26): calcd. C 53.8, H 9.4; found C 54.0, H 9.3.

trans-2,4-Di-tert-butyl-1-triphenylstannyl-1,2-dihydro-1 λ^3 ,3 λ^3 -diphosphete (18b): From **10b** (940 mg, 1.8 mmol) to furnish **18b** (940 mg, 100%) as a yellow powder with m.p. 78°C . – ^1H NMR (C_6D_6): δ = 1.17 (s, 9 H, *t*Bu-H), 1.28 (s, 9 H, *t*Bu-H), 2.83 (d, $^2J_{\text{H,P}}$ = 1.4 Hz, 1 H, PC–H), 7.21–7.31 (m, 9 H, *m*-, *p*- C_6H_5), 7.76–7.79 (dd, $^3J_{\text{H,H}}$ = 7.7 Hz, $^4J_{\text{H,H}}$ = 1 Hz, $^3J_{\text{H,Sn}}$ = 45.8 Hz, 6 H, *o*- C_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 27.8 [dd, $^3J_{\text{C,P}}$ = 7.6/4.9 Hz, $\text{C}(\text{CH}_3)_3$], 30.9 [dd, $^3J_{\text{C,P}}$ = 9.4/4.0 Hz, $\text{C}(\text{CH}_3)_3$], 33.6 [d, $^2J_{\text{C,P}}$ = 6.3 Hz, $\text{C}(\text{CH}_3)_3$], 36.7 (d, $^1J_{\text{C,P}}$ = 23.2 Hz, C-2, ^1H coupl.: $^1J_{\text{C,H}}$ = 135.7 Hz, 40.9 [dd, $^2J_{\text{C,P}}$ = 7.2/5.4 Hz, $\text{C}(\text{CH}_3)_3$], 129.1 (s, $^2J_{\text{C},^{117/119}\text{Sn}}$ = 62.8 Hz, *o*-C), 129.5 (s, $^4J_{\text{C},^{117/119}\text{Sn}}$ = 11.7 Hz, *p*-C), 138.0 (s, $^3J_{\text{C},^{117/119}\text{Sn}}$ = 35.0 Hz, *m*-C), 139.6 (d, $^2J_{\text{C,P}}$ = 2.7 Hz, *ipso*-C), 238.1 (dd, $^1J_{\text{C,P}}$ = 53.0/39.5 Hz, C-4). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = 2.8 (d, $^2J_{\text{P,P}}$ = 45.8 Hz, $^1J_{\text{P},^{119}\text{Sn}}$ = 1060.5 Hz, $^1J_{\text{P},^{117}\text{Sn}}$ = 1014.7 Hz, P-1), 353.3 (d, $^2J_{\text{P,P}}$ = 45.8 Hz, $^3J_{\text{P},^{117/119}\text{Sn}}$ = 167.9 Hz, P-3). – $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C_6D_6): δ = –157 (dd, $^1J_{^{119}\text{Sn,P}}$ = 1056 Hz, $^3J_{^{119}\text{Sn,P}}$ = 177 Hz). – IR (KBr): $\tilde{\nu}$ = 3060, 2960, 1430, 1360, 1075, 1025, 1000, 730, 700 cm^{-1} . – MS; m/z (%) = 551 (3) [M^+], 351 (81) [SnPh_3^+], 131 (100) [$\text{P}_2\text{C}_5\text{H}_9^+$], 57 (20) [C_4H_9^+]. – $\text{C}_{28}\text{H}_{34}\text{P}_2\text{Sn}$ (551.23): calcd. C 61.0, H 6.2; found C 61.3, H 6.2.

trans-2,4-(Diadamant-1-yl)-1-tributylstannyl-1,2-dihydro-1 λ^3 ,3 λ^3 -diphosphete (18c): From **10c** (200 mg, 0.31 mmol) to furnish **18c** (200 mg, 100%) as a yellow, non-distillable oil. – ^1H NMR (C_6D_6): δ = 0.9–2.3 (m, 57 H, Ad-H and Bu-H), 2.65 (s, 1 H, P–CH). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 11.0 (s, Sn--CH_2), 13.9 (s, $\text{Sn--}[\text{CH}_2)_3\text{--CH}_3$], 27.8 (s, SnCH_2CH_2), 29.1 (s, C-c), 29.2 (s, C-c), 30.0 (s, CH_2CH_3), 35.6 (d, $^2J_{\text{C,P}}$ = 5.7 Hz, C-a), 36.9 (s, Cd), 37.1 (s, C-d), 38.5 (d, $^1J_{\text{C,P}}$ = 22.9 Hz, C-2), 40.3 (dd, $^3J_{\text{C,P}}$ = 8.6/4.8 Hz, C-b), 42.9 (dd, $^2J_{\text{C,P}}$ = 6.7/3.8 Hz, C-a), 43.2 (dd, $^3J_{\text{C,P}}$ = 9.1/4.3 Hz, C-b), 240.4 (dd, $^1J_{\text{C,P}}$ = 50.6/40.1 Hz, C-4). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = 0.3 (d, $^2J_{\text{P,P}}$ = 44.0 Hz, $^1J_{\text{P},^{117/119}\text{Sn}}$ = 907.2 Hz, P-1), 340.1 (d, $^2J_{\text{P,P}}$ = 44.0 Hz, $^3J_{\text{P},^{117/119}\text{Sn}}$ = 149 Hz, P-3). – IR (film): $\tilde{\nu}$ = 2985, 2870, 2850, 1455, 1350, 1250, 1070, 875, 840 cm^{-1} . – $\text{C}_{34}\text{H}_{58}\text{P}_2\text{Sn}$ (647.49): calcd. C 63.1, H 9.0; found C 62.0, H 8.9.

trans-2,4-(Diadamant-1-yl)-1-triphenylstannyl-1,2-dihydro-1 λ^3 ,3 λ^3 -diphosphete (18d): From **10d** (198 mg, 0.28 mmol) to furnish **18d** (198 mg, 100%) as a yellow, crystalline solid with m.p. 165°C . – ^1H NMR (C_6D_6): δ = 1.2–2.15 (m, 30 H, Ad-H), 2.43 (br., 1 H, PC–H), 6.9–7.35 (m, 9 H, *m*-, *p*- C_6H_5), 7.5–7.8 (m, 6 H, *o*- C_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 28.89 (s, C-c), 28.92 (s, C-c), 35.6 (d, $^2J_{\text{C,P}}$ = 5.6 Hz, C-a), 36.5 (s, C-d), 36.9 (s, C-d), 39.1 (d, $^1J_{\text{C,P}}$ = 24.1 Hz, C-2), 40.1 (dd, $^3J_{\text{C,P}}$ = 8.0/4.1 Hz, C-b), 43.1 (dd, $^2J_{\text{C,P}}$ = 8.8/4.0 Hz, C-b), 43.4 (dd, $^2J_{\text{C,P}}$ = 6.8/3.5 Hz, C-a), 129.0 (s, *o*-C), 129.4 (s, $^4J_{\text{C},^{117/119}\text{Sn}}$ = 11.2 Hz, *p*-C), 137.7 (s, $^3J_{\text{C},^{117/119}\text{Sn}}$ = 34.5 Hz, *m*-C), 139.9 (d, $^2J_{\text{C,P}}$ = 2.4 Hz, *ipso*-C), 238.4 (dd, $^1J_{\text{C,P}}$ = 51.4/39.4 Hz, C-4). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = –5.0 (d, $^2J_{\text{P,P}}$ = 45.8 Hz, $^1J_{\text{P},^{117/119}\text{Sn}}$ = 1050.5 Hz, P-1), 349.4 (d, $^2J_{\text{P,P}}$ = 45.8 Hz, $^3J_{\text{P},^{117/119}\text{Sn}}$ = 175 Hz, P-3). – $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C_6D_6): δ = –159 (dd, $^1J_{^{119}\text{Sn,P}}$ = 1099 Hz, $^3J_{^{119}\text{Sn,P}}$ = 177 Hz). – IR (KBr): $\tilde{\nu}$ = 3030, 2870, 2820, 1460, 1430, 1410, 1330, 1300,

1250, 1090, 985, 715, 685 cm^{-1} . – MS; m/z (%): 708 (2) $[\text{M}^+]$, 700 (3) $[(\text{SnPh}_3)_2^+]$, 357 (15) $[\text{M}^+ - \text{SnPh}_3]$, 351 (100) $[\text{SnPh}_3^+]$, 135 (73) $[\text{Ad}^+]$. – $\text{C}_{40}\text{H}_{46}\text{P}_2\text{Sn}$ (707.5): calcd. C 67.9, H 6.6; found C 67.7, H 6.7.

Complexations of 10a,b with Pentacarbonyltungsten-Tetrahydrofuran. – **General Procedure:** A solution of pentacarbonyltungsten-THF was prepared by irradiation of a solution of hexacarbonyltungsten in THF (HPK, 125 W, Phillips) for 35 min. To this solution was added **10** in THF (10 ml) and the mixture was stirred at room temperature for 24 h. The solvent was then removed under vacuum and excess hexacarbonyltungsten was sublimed at 40°C under vacuum. The residue was taken up in pentane and yielded compounds **19**, **20** on crystallization at –20°C.

(2,4-Di-tert-butyl-2-triphenylstannyl-1,2-dihydro- η^1 - $1\lambda^3,3\lambda^3$ -diphosphete)pentacarbonyltungsten (**19**): From hexacarbonyltungsten (1.75 g, 5 mmol) and 1,2-dihydro-1,3-diphosphete **10b** (2.05 g, 3.72 mmol) to furnish **19** (1.46 g, 45%) as a yellow-orange, crystalline powder with m.p. 153.2°C (dec.). – ^1H NMR (C_6D_6): δ = 1.18 (s, 9 H, *t*Bu-H), 1.69 (s, 9 H, *t*Bu-H), 7.39–7.45 (m, 9 H, *m*-, *p*- C_6H_5), 7.9–8.0 (m, 6 H, *o*- C_6H_5), 9.08 (dd, $^1J_{\text{H,P}}$ = 280 Hz, $^3J_{\text{H,P}}$ = 13.8 Hz, 1 H, P-H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 29.5 [d, $^3J_{\text{C,P}}$ = 5.0 Hz, $\text{C}(\text{CH}_3)_3$], 31.3 [d, $^3J_{\text{C,P}}$ = 7.0 Hz, $\text{C}(\text{CH}_3)_3$], 37.5 [s, $\text{C}(\text{CH}_3)_3$], 39.9 [s, $\text{C}(\text{CH}_3)_3$], 45.6 (dd, $^1J_{\text{C,P}}$ = 40/13 Hz, C-2), 129.1 (s, *o*-C), 129.7 (s, *p*-C), 137.8 (s, *m*-C), 140.1 (s, *ipso*-C), 198.1 (d, $^2J_{\text{C,P}}$ = 6.4 Hz, $\text{CO}_{\text{equatorial}}$), 198.7 (d, $^2J_{\text{C,P}}$ = 18.5 Hz, CO_{axial}), 209.5 (dd, $^1J_{\text{C,P}}$ = 52/11 Hz, C-4). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = 15.3 (s, $^1J_{\text{P,W}}$ = 209 Hz, P-1), 399.2 (s, P-3). – $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C_6D_6): δ = –98.6 (m). – IR (KBr): $\tilde{\nu}$ = 3020, 2920, 2200 (P–H), 2020 (CO), 1960 (CO), 1900 (CO), 1450, 1400, 1050, 820 cm^{-1} . – MS; m/z (%) = 875 (24) $[\text{M}^+]$, 797 (100) $[\text{M}^+ - \text{Ph}]$, 553 (24) $[\text{M}^+ - \text{W}(\text{CO})_5]$, 351 (96) $[\text{SnPh}_3^+]$. – $\text{C}_{33}\text{H}_{34}\text{O}_5\text{P}_2\text{SnW}$ (875.12): calcd. C 45.3, H 3.9; found C 45.3, H 4.0.

μ -(2,4-Di-tert-butyl-2-tributylstannyl-1,2-dihydro- η^1 - $1\lambda^3,3\lambda^3$ -diphosphete)bis(pentacarbonyltungsten) (**20**): From hexacarbonyltungsten (600 mg, 1.7 mmol) and 1,2-dihydro-1,3-diphosphete **10a** (260 mg, 0.53 mmol) to furnish **20** (360 mg, 60%) as a yellow powder with m.p. 118°C (dec.). – ^1H NMR (C_6D_6): δ = 0.91–1.67 (m, 36 H, CH_2 and *t*Bu-H), 0.97 (t, $^3J_{\text{H,H}}$ = 7.24 Hz, 9 H, CH_2CH_3), 7.71 (dd, $^1J_{\text{H,P}}$ = 295.09 Hz, $^3J_{\text{H,P}}$ = 31.81 Hz, 1 H, P-H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 13.6 (s, $\text{Sn}-\text{CH}_2$), 15.1 (s, $\text{Sn}-[\text{CH}_2]_3-\text{CH}_3$), 27.7 (s, $^2J_{\text{C},^{117/119}\text{Sn}}$ = 69.1/72.3 Hz, SnCH_2CH_2), 29.8 (s, $^3J_{\text{C},^{117/119}\text{Sn}}$ = 18.5 Hz, CH_2CH_3), 31.4 [d, $^3J_{\text{C,P}}$ = 4.8 Hz, $\text{C}(\text{CH}_3)_3$], 31.5 [d, $^3J_{\text{C,P}}$ = 5.6 Hz, $\text{C}(\text{CH}_3)_3$], 36.9 [s, $\text{C}(\text{CH}_3)_3$], 39.5 [s, $\text{C}(\text{CH}_3)_3$], 51.9 (dd, $^1J_{\text{C,P}}$ = 16/8 Hz, C-2), 194.9 (dd, $^1J_{\text{C,P}}$ = 39.8/7.7 Hz, C-4), 195.8 (d, $^2J_{\text{C,P}}$ = 7.2 Hz, $\text{CO}_{\text{equatorial}}$), 196.5 (d, $^2J_{\text{C,P}}$ = 31.3 Hz, CO_{axial}), 197.9 (d, $^2J_{\text{C,P}}$ = 5.6 Hz, $\text{CO}_{\text{equatorial}}$), 198.5 (d, $^2J_{\text{C,P}}$ = 28.9 Hz, CO_{axial}). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = 6 (d, $^2J_{\text{P,P}}$ = 26 Hz, $^1J_{\text{P,W}}$ = 222 Hz, P-1), 294 (d, $^2J_{\text{P,P}}$ = 26 Hz, $^1J_{\text{P,W}}$ = 244 Hz, P-3). – IR (pentane): $\tilde{\nu}$ = 2972, 2929, 2079 (P–H), 2070 (CO), 1982 (CO), 1964 (CO), 1464, 1378, 893 cm^{-1} . – MS; m/z (%): 1138 (2) $[\text{M}^+]$, 847 (39) $[\text{M}^+ - \text{SnBu}_3]$, 813 (17) $[\text{M}^+ - \text{W}(\text{CO})_5 - \text{H}]$, 679 (53) $[\text{M}^+ - \text{SnBu}_3 - 6 \text{ CO}]$, 291 (100) $[\text{SnBu}_3^+]$, 235 (72) $[\text{HSnBu}_2^+]$, 57 (32) $[\text{C}_4\text{H}_9^+]$. – $\text{C}_{32}\text{H}_{46}\text{O}_{10}\text{P}_2\text{SnW}_2$ (1139.04): calcd. C 33.74, H 4.07; found C 32.86, H 3.90.

Complexations of 10a,b with Enneacarbonyldiiron. – **General Procedure:** To a solution of **10** in pentane (10 ml) was added enneacarbonyldiiron and the mixture stirred at room temperature for 24 h. The solution was then filtered through Celite and compounds **21** were crystallized from pentane at –78°C.

μ -(2,4-Di-tert-butyl-2-tributylstannyl-1,2-dihydro- η^1 - $1\lambda^3,3\lambda^3$ -diphosphete)bis(tetracarbonyliron) (**21a**): From enneacarbonyldiiron (1.5 g, 4 mmol) and 1,2-dihydro-1,3-diphosphete **10a** (920 mg, 1.87 mmol) to furnish **21a** (420 g, 27%) as a red-brown solid with m.p. 184°C. – ^1H NMR (CD_2Cl_2): δ = 0.95 (t, $^3J_{\text{H,H}}$ = 7.21 Hz, 9 H, CH_2CH_3), 1.21–1.66 (m, 18 H, CH_2), 1.44 (s, 9 H, *t*Bu-H), 1.45 (s, 9 H, *t*Bu-H), 7.20 (dd, $^1J_{\text{H,P}}$ = 307.25 Hz, $^3J_{\text{H,P}}$ = 30.52 Hz, 1 H, P-H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 13.7 (s, $\text{Sn}-\text{CH}_2$), 15.2 (s, $\text{Sn}-[\text{CH}_2]_3-\text{CH}_3$), 27.8 (s, $^2J_{\text{C},^{117/119}\text{Sn}}$ = 71.5 Hz, SnCH_2CH_2), 29.8 (s, $^3J_{\text{C},^{117/119}\text{Sn}}$ = 17.8 Hz, CH_2CH_3), 30.6 [dd, $^3J_{\text{C,P}}$ = 11.2/10.4 Hz, $\text{C}(\text{CH}_3)_3$], 31.1 [s, $\text{C}(\text{CH}_3)_3$], 38.2 [s, $\text{C}(\text{CH}_3)_3$], 39.8 [s, $\text{C}(\text{CH}_3)_3$], 61.9 (d, $^1J_{\text{C,P}}$ = 14.8 Hz, C-2), 195.1 (pt, $^1J_{\text{C,P}}$ = 14.4 Hz, C-4), 214.6 (d, $^2J_{\text{C,P}}$ = 11.2 Hz, CO), 217.3 (d, $^2J_{\text{C,P}}$ = 10.4 Hz, CO). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = 48 (d, $^2J_{\text{P,P}}$ = 27 Hz, P-1), 315 (d, $^2J_{\text{P,P}}$ = 26 Hz, P-3). – IR (pentane): $\tilde{\nu}$ = 2986–2843, 2068 (P–H), 2054 (CO), 1971 (CO), 1472, 1453, 1362, 1261, 1022, 907, 730 cm^{-1} . – MS; m/z (%): 828 (0.2) $[\text{M}^+]$, 660 (1) $[\text{M}^+ - \text{Fe}(\text{CO})_4]$, 492 (16) $[\text{M}^+ - 2 \text{ Fe}(\text{CO})_4]$, 291 (70) $[\text{SnBu}_3^+]$, 235 (96) $[\text{HSnBu}_2^+]$, 179 (100) $[\text{H}_2\text{SnBu}^+]$, 57 (33) $[\text{C}_4\text{H}_9^+]$. – $\text{C}_{30}\text{H}_{46}\text{Fe}_2\text{O}_8\text{P}_2\text{Sn}$ (827.02): calcd. C 43.57, H 5.61; found C 43.13, H 5.61.

μ -(2,4-Di-tert-butyl-2-triphenylstannyl-1,2-dihydro- η^1 - $1\lambda^3,3\lambda^3$ -diphosphete)bis(tetracarbonyliron) (**21b**): From enneacarbonyldiiron (400 mg, 1.1 mmol) and 1,2-dihydro-1,3-diphosphete **10b** (200 mg, 0.36 mmol) to furnish **21b** (220 mg, 69%) as a red-brown solid with m.p. 124°C. – ^1H NMR (CD_2Cl_2): δ = 1.05 (s, 9 H, *t*Bu-H), 1.60 (s, 9 H, *t*Bu-H), 7.39–7.79 (m, 15 H, C_6H_5), 7.67 (dd, $^1J_{\text{H,P}}$ = 308.18 Hz, $^3J_{\text{H,P}}$ = 28.82 Hz, 1 H, P–H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 29.7 [dd, $^3J_{\text{C,P}}$ = 11.2 Hz, $\text{C}(\text{CH}_3)_3$], 31.7 [s, $\text{C}(\text{CH}_3)_3$], 38.5 [s, $\text{C}(\text{CH}_3)_3$], 39.5 [s, $\text{C}(\text{CH}_3)_3$], 65.3 (dd, $^1J_{\text{C,P}}$ = 20.5/5.6 Hz, C-2), 129.3 (s, $^2J_{\text{C},^{117/119}\text{Sn}}$ = 53.0 Hz, *o*-C), 130.1 (s, *p*-C), 137.9 (s, $^3J_{\text{C},^{117/119}\text{Sn}}$ = 37.0 Hz, *m*-C), 139.8 (s, *ipso*-C), 196.3 (pt, $^1J_{\text{C,P}}$ = 15 Hz, C-4), 213.8 (d, $^2J_{\text{C,P}}$ = 10.4 Hz, CO), 216.6 (d, $^2J_{\text{C,P}}$ = 10.4 Hz, CO). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = 47 (d, $^2J_{\text{P,P}}$ = 34 Hz, P-1), 313 (d, $^2J_{\text{P,P}}$ = 33 Hz, P-3). – IR (KBr): $\tilde{\nu}$ = 3449, 2959, 2236 (P–H), 2072 (CO), 2057 (CO), 2007 (CO), 1981 (CO), 1945 (CO), 1450, 1428, 1360, 1211, 843 cm^{-1} . – MS; m/z (%): 887 (0.2) $[\text{M}^+ - \text{H}]$, 748 (1) $[\text{M}^+ - 5 \text{ CO}]$, 351 (100) $[\text{SnPh}_3^+]$, 169 (51) $[\text{HFe}(\text{CO})_4^+]$, 57 (55) $[\text{C}_4\text{H}_9^+]$.

2,4-Di-tert-butyl-1-iodo-2-triphenylstannyl-1,2-dihydro- $1\lambda^3,3\lambda^3$ -diphosphete (**22**): A solution of iodine (280 mg, 1.1 mmol) in diethyl ether was added dropwise to a suspension of 1,2-dihydro-1,3-diphosphete **10b** (600 mg, 1.1 mmol) in diethyl ether (5 ml). The reaction mixture was stirred 15 min at room temperature and then the solvent and all volatile compounds were removed under vacuum to furnish **22** as a yellow, non-distillable oil. Yield: about 90%. – ^1H NMR (C_6D_6): δ = 1.05 (s, 9 H, *t*Bu-H), 1.22 (s, 9 H, *t*Bu-H), 7.0–7.29 (m, 9 H, *m*-, *p*- C_6H_5), 7.87–8.12 (m, 6 H, *o*- C_6H_5). – $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ = 30.2 [d, $^3J_{\text{C,P}}$ = 4.5 Hz, $\text{C}(\text{CH}_3)_3$], 30.6 [dd, $^3J_{\text{C,P}}$ = 11.7/3.6 Hz, $\text{C}(\text{CH}_3)_3$], 38.8 [d, $^2J_{\text{C,P}}$ = 8.1 Hz, $\text{C}(\text{CH}_3)_3$], 41.5 [dd, $^2J_{\text{C,P}}$ = 7.2/2.7 Hz, $\text{C}(\text{CH}_3)_3$], 58.1 (pt, $^1J_{\text{C,P}}$ = 42.6 Hz, C-2), 130.4 (s, $^4J_{\text{C},^{117/119}\text{Sn}}$ = 13.5 Hz, *p*-C), 136.6 (s, $^2J_{\text{C},^{117/119}\text{Sn}}$ = 48.5 Hz, *o*-C), 138.8 (s, $^3J_{\text{C},^{117/119}\text{Sn}}$ = 36.8 Hz, *m*-C), 142.6 (s, *ipso*-C), 230.3 (pt, $^1J_{\text{C,P}}$ = 56.6 Hz, C-4). – $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = 5.5 (d, $^2J_{\text{P,P}}$ = 126.4 Hz, P-1), 324.9 (d, $^2J_{\text{P,P}}$ = 126.4 Hz, P-3). – IR (film): $\tilde{\nu}$ = 3035, 2930, 1460, 1420, 1355, 1065, 1015, 990, 720, 690 cm^{-1} . – MS; m/z (%): 677 (10) $[\text{M}^+]$, 351 (71) $[\text{SnPh}_3^+]$, 77 (51) $[\text{Ph}^+]$, 57 (21) $[\text{C}_4\text{H}_9^+]$.

X-ray Structural Analysis of 18d^[33]: Siemens P-4 diffractometer, graphite monochromator, Mo- K_α (λ = 0.71073 Å), structure solution by direct methods (SHELXTL-PLUS^[34]) and structure refinement by SHELXL-93^[35]. Semi-empirical absorption correction by

use of Ψ scans. Hydrogen atoms were placed in geometrically calculated positions ($d_{C-H} = 0.960$ Å). $C_{40}H_{46}P_2Sn$; $M = 707.4$ g mol $^{-1}$; monoclinic; space group $C2/c$; $a = 33.813(7)$, $b = 9.565(2)$, $c = 21.797(4)$ Å, $\beta = 101.33(3)^\circ$, $V = 6912(2)$ Å 3 ; $Z = 8$; $D_{\text{calcd.}} = 1.360$ Mg/m 3 ; $\mu = 8.59$ cm $^{-1}$; crystal size $0.30 \times 0.25 \times 0.20$ mm; ω scan: $1.23^\circ \leq \Theta \leq 26.00^\circ$. 7998 reflections collected, 6750 independent reflections ($R_{\text{int.}} = 0.0254$); max./min. transmission: 0.880/0.761; 392 parameters; $w^{-1} = [\sigma^2(F_o^2) + (0.0466P)^2 + 8.3105P]$ and $P = [(F_o^2) + 2F_c^2]/3$; $R = 0.0386$, $R_w = 0.0905$ for 6750 reflections with $I > 2\sigma(I)$ and $R = 0.0651$, $R_w = 0.1039$ for all data; residual electron density 483 enm $^{-3}$ and -433 enm $^{-3}$, GOF (on F^2) = 1.007.

☆ Dedicated to Professor Manfred Weidenbruch on the occasion of his 60th birthday.

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