1-Triorganylstannyl-1,2,4-triphosphole: A Versatile Starting Material for Phosphorus-Rich Cage Compounds and π-Complexes

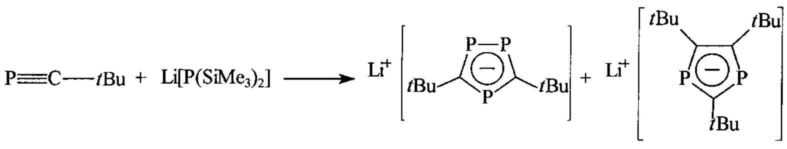
Achim Elvers,[a] Frank W. Heinemann,[a] Bernd Wrackmeyer,*[b] and Ulrich Zenneck*[a]

Dedicated to Professor Edgar Niecke on the occasion of his 60th birthday

Abstract: The reaction of Na[3,5-di-(*tert*-butyl)-1,2,4-triphospholyl] (Na-**2**) with R_3SnCl (R = Ph, Me, *n*Bu) affords the 1-triorganylstannyl-3,5-di(*tert*-butyl)-1,2,4-triphospholes **4a**–**4c** in very good yields. A rapid suprafacial [1,5]-sigmatropic shift of the $SnPh_3$ group in **4a** with $\Delta G^{\neq} = 31.5\ kJ\,mol^{-1}$ indicates a labile P–Sn bond—one of the characteristic features of **4a**–**4c**. Compound **4a** provides access to the polycyclic organophosphorus cage compound $C_4tBu_4P_5$-$SnPh_3$ (**6**) in a high-yield chemoselective and diastereospecific cycloaddition reaction; compound **4b** transfers 1,2,4-triphospholyl ligands quantitatively to Sn^{II} to form a hexaphosphastannocene derivative. Compound **4a** displaces the ethene ligands in $[CpCo(C_2H_4)_2]$ to form the stannyltriphosphole complex [Cp-(η^4-1,2,4-$C_2tBu_2P_3SnPh_3$)Co] (**10**). The absolute positive sign (reduced coupling constant ${}^1K({}^{119}Sn,{}^{31}P) < 0$) of ${}^1J({}^{119}Sn,{}^{31}P) = +1611.7$ Hz for **10** has been determined by ${}^{13}C\{{}^1H,{}^{31}P\}$ heteronuclear triple-resonance experiments. Reaction of **10** with another equivalent of $[CpCo(C_2H_4)_2]$ breaks the Sn–P bond and replaces it with a Sn–Co bond to yield the extremely slipped 34 valence electron (VE) triple-decker sandwich complex [CpCo(μ,η^5:η^2-3,5-di(*tert*-butyl)-1,2,4-triphospholyl)Co($SnPh_3$)Cp] (**11**). The central ligand exhibits unique structural features. Oxidation or thermolysis of **11** affords [Cp(1-phenyl-3,5-di(*tert*-butyl)-(η^4-1,2,4-triphosphole)Co] (**12**) by elimination of a [Cp(diphenylstannylene)Co] unit.

Keywords: cobalt · cycloadditions · cyclopentadienyl complexes · NMR · phosphorus heterocycles · tin

Introduction



1 Li-2 Li-3

Scheme 1. Preparation of triphospholyl lithium salts Li-**2** and Li-**3**.

Two principal routes to π complexes of the P-rich cyclopentadienyl ligand analogue 1,2,4-triphospholyl have been developed to date. A cyclization reaction of *tert*-butyl phosphaalkyne (**1**) in the coordination sphere of the metal atom of highly reactive complexes produces P-containing five-membered ring ligands by P atom and CR group transfer at well below room temperature.[1] Hexa- and pentaphosphaferrocene derivatives are formed besides other products from metal-vapor-based compounds such as [(η^4-1-methyl-naphthalene)(η^6-toluene)Fe] or [$(C_2H_4)_2$(η^6-toluene)Fe][2] as starting materials. This type of cyclization reaction has also been applied to other reactive iron complexes,[3] and to direct metal-vapor reactions.[4, 5] In concurrent, but independent, experiments, the reaction of the mixed alkali metal salts M[3,5-di(*tert*-butyl)-1,2,4-triphospolyl] (M-**2**) and M[2,4,5-tri(*tert*-butyl)-1,3-diphospholyl] (M-**3**) with transition metal halides was performed and yielded the same hexa- and pentaphosphaferrocene derivatives.[6] Both approaches are based on the work of Becker et al., who prepared the starting material *tert*-butyl phosphaalkyne (**1**) for the first time, as well as the mixture of the lithium salts Li[3,5-di(*tert*-butyl)-1,2,4-triphospholyl] (Li-**2**) and Li[2,4,5-tri(*tert*-butyl)-1,3-diphospholyl] (Li-**3**) (Scheme 1).[7, 8]

However, both reactions produce mixtures of substances that require separation, and the yields of the desired products are often poor, if they are formed at all. Therefore we

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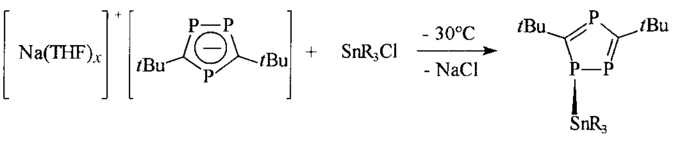
concentrated our efforts on potential specific routes for the preparation of π complexes that contain the 1,2,4-triphospholyl ligands. Our first attempt at specific ligand transfer with this particular ligand was successful with cyclopentadienyl iron cations,[9] but the observed stacking–destacking reaction sequence was limited to only a few suitable examples.[10]

Hence, the preparation of P-stannyl-substituted 1,2,4-triphosphole derivatives was tried, as these triphospholes might behave as a P-rich cyclopentadienyl analogue of stannylcyclopentadienes, which are excellent and widely applicable reagents for Cp ligand transfer reactions.[11, 12] This approach follows that of Mathey and co-workers who used stannylphosphole derivatives successfully for the preparation of π-phospholyl complexes.[13] We report the synthesis of 1-stannyltriphosphole derivatives and the structural, spectroscopic, and chemical properties of these novel compounds.[14]

Results and Discussion

Preparation of 1-stannyl-1,2,4-triphosphole derivatives (4): The reaction of a solution of Na[3,5-di(*tert*-butyl)-1,2,4-triphospholyl] (Na-**2**) with R_3SnCl (R = Ph, Me, and *n*Bu) in toluene at −30 °C afforded the 1-stannyl-3,5-di-*tert*-butyl-1,2,4-triphospholes **4a**, **4b**, and **4c** in good to almost quantitative yields (Scheme 2). To produce yields better than 80 %, the by-product Na[2,4,5-tri(*tert*-butyl)-1,3-triphospholyl] (Na-**3**) must be removed completely from the starting material by repeated recrystallization. The presence of 1,3-diphospholyl anions in such reaction mixtures reduces the yield of the desired products **4a**–**4c**, as cycloaddition reactions occur between both components.

Abstract in German: *Die Reaktion von Na[3,5-Di(tert-butyl)-1,2,4-triphospholyl] (Na-**2**) mit R_3SnCl (R = Ph, Me, nBu) liefert 1-Triorganylstannyl-3,5-di(tert-butyl)-1,2,4-triphosphol **4a**–**4c** in sehr guten Ausbeuten. Eine schnelle, sigmatrope [1,5]-Verschiebung der $SnPh_3$-Gruppe von **4a** mit ($\Delta G^{\neq}$ = 31.5 kJ mol^{-1}) gibt einen Hinweis auf eine labile P–Sn Bindung, die ein wesentliches Charakteristikum der chemischen Eigenschaften von **4a**–**4c** ist. Die Verbindung **4a** kann in hoher Ausbeute und diastereospezifisch zur Organophosphor-Käfigverbindung $C_4tBu_4P_5SnPh_3$ (**6**) umgesetzt werden und **4b** überträgt 1,2,4-Triphospholyl-Liganden quantitativ auf Sn^{II}, wobei sich ein Hexaphosphastannocen-Derivat bildet. Der Stannyltriphosphol-Komplex [Cp(η^4-1,2,4-$C_2tBu_2P_3SnPh_3$)Co](**10**) bildet sich aus **4a** und [CpCo(C_2H_4)$_2$]. Das positive Vorzeichen (reduzierte Kopplungskonstante $^1K(^{119}Sn,^{31}P) < 0$) der $^1J(^{119}Sn,^{31}P) = 1611.7$ Hz von **10** konnte über heteronucleare Tripelresonanzexperimente $^{13}C\{^1H,^{31}P\}$ bestimmt werden. Die Sn–P-Bindung von **10** kann wieder gezielt gebrochen und durch eine Sn–Co-Bindung ersetzt werden, indem man **10** mit einem zweiten Äquivalent [CpCo(C_2H_4)$_2$] umsetzt. Es wird dabei der extrem verschobene 34-Valenzelektronen (VE) Tripeldecker-Sandwichkomplex [CpCo(μ,η^5:η^2-1,2,4-$C_2tBu_2P_3$)-Co($SnPh_3$)Cp] (**11**) gebildet. Der Brückenligand weist dabei neuartige Strukturmotive auf. Unter Eliminierung einer [Cp(diphenylstannylen)Co]-Einheit bauen Luftoxidation oder Thermolyse **11** zu [Cp(1-phenyl-3,5-di(tert-butyl)-η^4-1,2,4-triphosphol)Co] (**12**) ab.*



Na – **2** R = Ph (**4a**), Me (**4b**), *n*Bu (**4c**)

Scheme 2. Preparation of compounds **4a**–**4c**.

Due to its good crystallization properties, 1-triphenylstannyl-3,5-di(*tert*-butyl)-1,2,4-triphosphole (**4a**) could be characterized completely by a single-crystal X-ray diffraction study. The novel P-stannyl triphosphole derivatives are stable up to 200 °C and soluble in common organic solvents.

Crystal structure of 4a: The structure of the tin compound **4a** was determined by X-ray diffraction in the solid state (Figure 1). The unit cell contains both enantiomers of the chiral species **4a**. The molecules of **4a** consist of a P–Sn connected $C_2tBu_2P_3$ ring and a $SnPh_3$ group. The $SnPh_3$ fragment is η-bonded by a single bond[15] to P1 as the distance Sn–P2 is too long for appreciable overlap (347.4(2) pm). The diene unit C1-P3-C2-P2 is almost planar and the last member of the ring, P1, is displaced by only 22.7(5) pm from the best plane, opposite to the position of the tin atom. Atom Sn1 on the other hand is located 182.0(8) pm away from the plane. The sum of the bond angles around P1 of 310.3° suggests a pyramidal sp^3-bonding situation with the lone pair of electrons of P1 situated out of the plane. This is in clear contrast to the more bulky P-substituted species 1-[bis(trimethylsilyl)methyl]-3,5-bis(trimethylsilyl)-1,2,4-triphosphole which is planar, and to 1-[bis(trimethylsilyl)methyl]-3,5-di(*tert*-butyl)-1,2,4-triphosphole (**5**) that has a bond angle sum of 342.3° around P1.[16, 17]

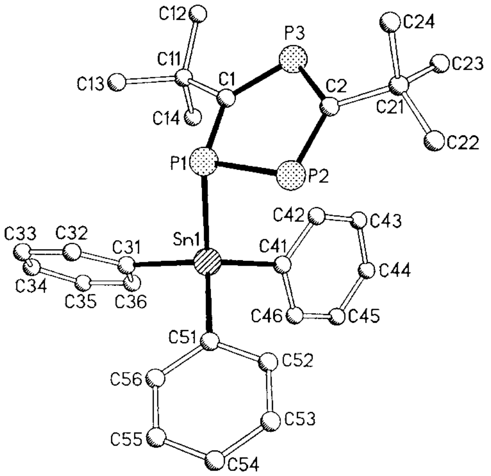


Figure 1. Molecular structure of **4a** in the solid state (one enantiomer). Selected bond angles [°]: P2-P1-Sn1 96.28(7), C1-P1-Sn1 112.7(2), C2-P2-P1 97.0(2), C1-P3-C2 102.3(2), P3-C1-P1 116.5(3),C1-P1-P2 101.3(2), P2-C2-P3 121.5(3).

The intraring bond lengths are in accord with an unambiguously diene-like character of **4a**, thus the lengths of the formal single bonds P1–C1, P3–C2, and P1–P2 are all elongated and the double bonds P2–C2 and P3–C1 are shortened with respect to the corresponding bond length of the 1,2,4-triphospholyl anion of the Li salt Li-**2** with its delocalized π bonds (Table 1). As indicated already by the less pyramidal P1 center in the 1,2,4-triphosphole derivative **5**, the diene character of the stannyltriphosphole **4a** is more pronounced, as the elongation of single bonds upon π localization is significant for **4a**, but almost absent for **5**.[16]

Table 1. Selected bond lengths [pm] of **4a**, **5**, and **2a**.

	4a	**5**[16]	**2a**[8]
P1–P2	213.1(2)	209.8(1)	211
P1–C1	178.5(5)	173.4(4)	175
P3–C1	169.8(5)	172.0(3)	175
P3–C2	177.3(5)	176.3(4)	175
P2–C2	171.2(5)	171.8(4)	175
Sn1–P1	252.1(2)		

NMR spectra and fluxional behavior of 4a: In contrast to the molecular structure of **4a** in the solid state, which would suggest an [ABC]X spin system, ($X = {}^{117/119}\mathrm{Sn}$), the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra at room temperature of **4a**–**4c** in solution show $[\mathrm{AB}_2]\mathrm{X}$ spin systems. The ^{1}H NMR spectrum of **4a** has one resonance for the two isochronic *t*Bu groups and the SnPh_3 proton resonances. Consistently, in the ^{13}C NMR spectrum only one set of resonances for the two C-*tert*-butyl units is observed and the symmetry of $^{31}\mathrm{P}-{}^{13}\mathrm{C}$ and $^{31}\mathrm{P}-{}^{1}\mathrm{H}$ coupling, as observed by ^{13}C and ^{1}H NMR, is in agreement with the observations of $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR experiments.

The ^{119}Sn NMR signal ($\delta = -104.6$) is indicative of a tetracoordinate tin atom.[18] Thus the $[\mathrm{AB}_2]\mathrm{X}$ spin system cannot be caused by a three-membered ring structure P1-Sn-P2 in solution, which would afford a coordination number of five for the tin atom.[19] Alternatively, a rapid rearrangement process was considered as the reason for the simplification of the NMR spectra. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra of **4a** were thus recorded between room temperature and −98 °C (Figure 2). On cooling, the ^{31}P(1,2) resonance with the large $^{117/119}\mathrm{Sn}-{}^{31}\mathrm{P}$ coupling (359 Hz) broadens and at −98 °C (just before the sample solidifies) two separate signals for P1 and P2 appear. Thus, the proposed ^{31}P spin subsystem [ABC] for the three P atoms exists as the slow exchange limit spectrum. Due to the broad lines, no Sn–P or P–P coupling is resolved at low temperatures. The coalescence temperature was found to be around −80 °C.

The spectroscopic findings can be interpreted by assuming a suprafacial [1,5]-sigmatropic shift of the SnPh_3 group (Scheme 3). As a consequence, the coupling constant $J({}^{31}\mathrm{P}(1,2),{}^{119}\mathrm{Sn}) = 359.0$ Hz at room temperature is the average value $\tfrac{1}{2}({}^1J + {}^2J)$Sn–P. On the basis of the estimation $|{}^1J| >> |{}^2J|$, this average value fits nicely to the data $^1J({}^{119}\mathrm{Sn},{}^{31}\mathrm{P})$ for 1-trimethylstannylphosphole derivatives (532–577 Hz).[13]

The slow exchange limit spectra are in full agreement with the molecular structure in the solid state. Since the ^{31}P NMR spectra of **4b** and **4c** at room temperature exhibit the same characteristics as those of **4a**, an analogous exchange process is also assumed in these cases. The activation energy for the stannyl exchange between P1 and P2 of **4a** was determined to be $\Delta G^{\neq} = 31.5 \pm 1\ \mathrm{kJ\,mol^{-1}}$.

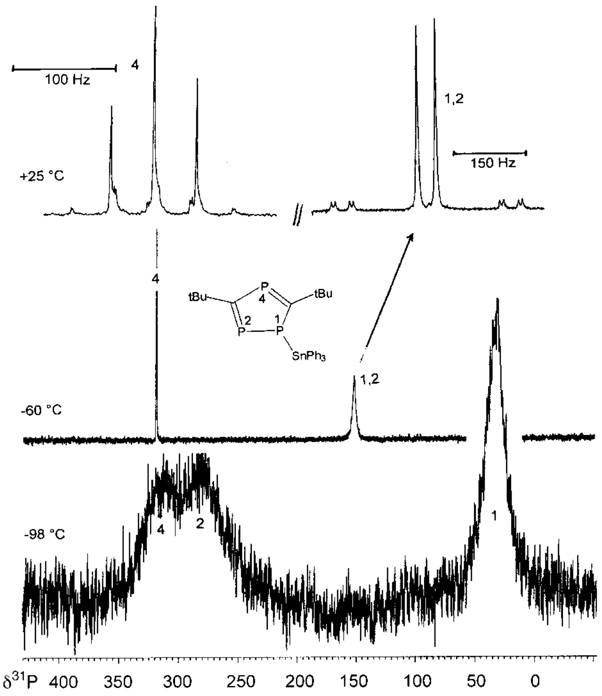


Figure 2. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra (101.3 MHz) of **4a** recorded at different temperatures. The spectrum at −98 °C was obtained just before the sample solidified.

Scheme 3. [1,5] exchange of the SnPh_3 group.

As with other stannylphosphanes,[18] a positive sign for $^1J({}^{119}\mathrm{Sn},{}^{31}\mathrm{P})$ can also be safely assumed for **4a**. This allows the sign of $^3J({}^{119}\mathrm{Sn},{}^{31}\mathrm{P})$ to be determined by a 2D $^{31}\mathrm{P}/{}^{31}\mathrm{P}$ COSY experiment by observing the tilt of the cross peaks of the tin satellites (Figure 3). A negative tilt is noted, which indicates opposite signs for $^1J({}^{119}\mathrm{Sn},{}^{31}\mathrm{P})$ and $^3J({}^{119}\mathrm{Sn},{}^{31}\mathrm{P})$ (<0!).

Cycloaddition reaction of 4a: Heterodienes with P=C double bonds are activated towards cycloaddition reactions. Sequences of inter- and intramolecular cycloaddition steps therefore play a significant part in the construction of phosphorus–carbon cage compounds.[20] To this end, compound **4a** was treated with the *tert*-butyl phosphaalkyne (**1**) in *n*-hexane at elevated temperature. After heating for 12 h at 70 °C the yellow $\mathrm{C}_4t\mathrm{Bu}_4\mathrm{P}_5\mathrm{SnPh}_3$ **6** was obtained in 80 % yield as a pure and crystalline compound (Scheme 4).

The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of **6** consists of five multiplets of equal integral values at $\delta = 330.3$, 94.9, −39.9, −88.0, and −130.0, respectively. Four inequivalent *tert*-butyl groups and one set of three phenyl groups attached to a tin atom are observed by ^{1}H and ^{13}C NMR spectroscopy. Mass spectrom-

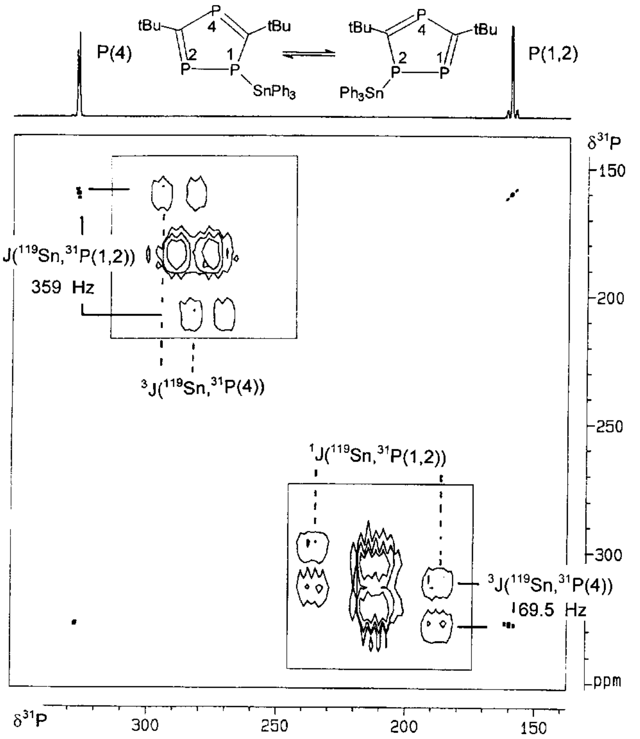


Figure 3. Contour plot of the 2D ^{1}H decoupled ^{31}P/^{31}P COSY experiment of **4a** (202.5 MHz). The regions of the cross peaks together with the tin satellites are expanded. The negative tilt[37] of the cross peaks for the tin satellites indicates that the signs of $J(^{117/119}Sn,^{31}P(1,2))$ and $J(^{117/119}Sn,^{31}P(4))$ are opposite.

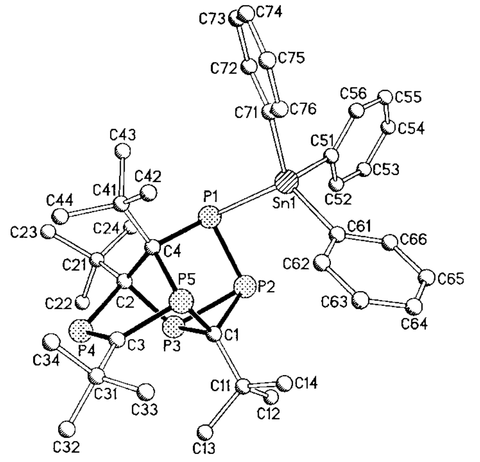
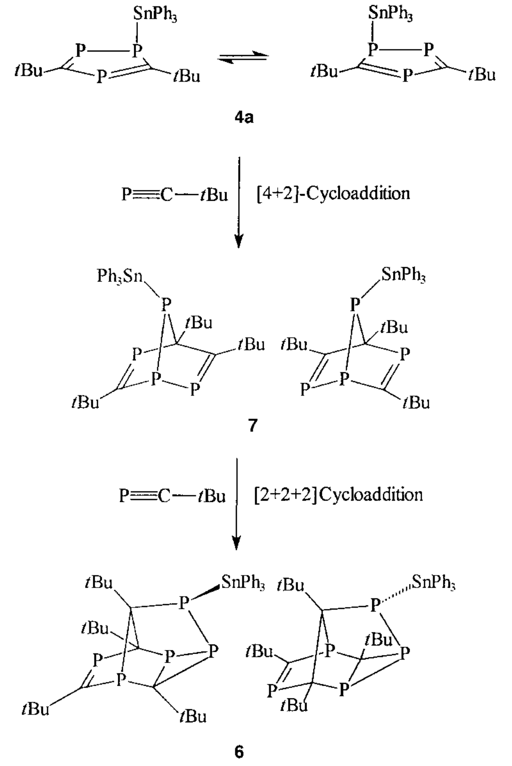


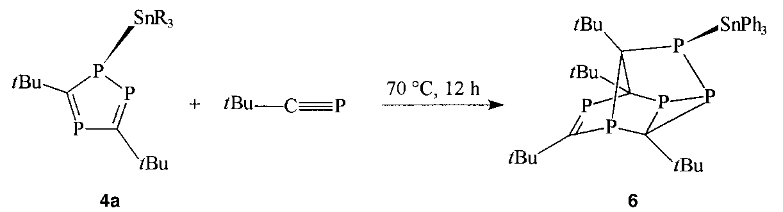
Figure 4. Molecular structure of **6** in the solid state (one enantiomer). Selected distances [pm]: Sn1–P1 252.18(9), P1–C4 188.9(3), P1–P2 215.5(1), P2–C1 186.2(3), P2–P3 220.9(1), P3–C1 183.1(3), P3–C2 191.3(3), P4–C3 167.8(3), P4–C2 188.1(3), P5–C3 183.1(3), P5–C1 185.9(3), P5–C4 188.1(3), C2–C4 159.7(4).



Scheme 5. Proposed mechanism for the formation of compound **6**.

etry and elemental analysis give further evidence of the addition of two molecules **1** to triphosphole **4a**. Besides one C=P double bond [δ^{13}C(3) = 228.7], no structural information can be deduced from the spectroscopic and analytical data due to the lack of any observable symmetry. However, the product is a single compound that is formed in high yield. X-ray crystallography solved the problem and the molecular structure of **6** in the solid state is shown in Figure 4.

As indicated by the spectra of the polycyclic cage compound, **6** is asymmetric and contains seven stereogenic centers. Surprisingly, there is only one pair of enantiomers, both of which are present in the unit cell. As the P=C double bonds are shifted by the process, every cycloaddition reaction of **4a** will block the rapid [1,5]-exchange of the SnPh$_3$ group, and the chiral, but stereochemically fluxional, molecule will be fixed as a pair of enantiomers. All consecutive reaction steps must be highly diastereoselective with *de* > 90% on the basis of the isolated yield of **6**. Therefore, a reaction mechanism can be formulated, comprising an initial Diels–Alder reaction of **4a** and **1** and a [2+2+2] cycloaddition of a second phosphaalkyne **1** to furnish the polycyclic system **6** (Scheme 5). Without this diastereoselectivity a total of 16 isomers of the same principal cage structure could have been formed. The initial [4+2] reaction step can result in two possible orientations (**A**, **B**) of the starting materials (Figure 5). Although **A** should be sterically preferred, as it avoids close contact of the *tert*-butyl groups found in case **B**, only orientation **B** is compatible with the observed end product **6**. This suggests that the reaction proceeds by orbital control



Scheme 4. Preparation of polycyclic cage compound **6**.

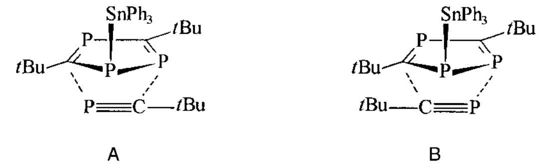


Figure 5. Possible transition states for the [4+2] cycloaddition reaction of **4a** and **1**.

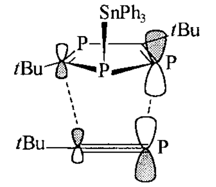


Figure 6. An orbital view of transition state **B** of Figure 5.

in both starting materials. If we take into consideration the relative expansion of the P and C p_z orbitals, the overlap between the p_z orbitals of similar nuclei is optimal (Figure 6) and leads directly to case **B** (Figure 5). That the coefficients of the HOMO and LUMO are larger at P in a phosphadiene is illustrated by the [4+2] dimerization of 2*H*-phospholes, which leads to a P–P bonded dimer.[21]

The resulting π^4-system tetraphosphanorbornadiene **7** may react again with P-alkyne **1** in a [2+2+2] step to form either a P_2C or a PC_2 three-membered ring. The P_2C ring is less strained, and alkyne **1** thus attaches to the C-bridged side of **6** (Figure 7). This step is sterically controlled, as **6** can be formed only from transition state **B** (Figure 7), where close contacts between the *tert*-butyl groups of **7** and **1** are avoided.

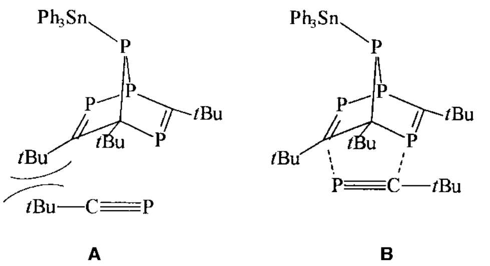
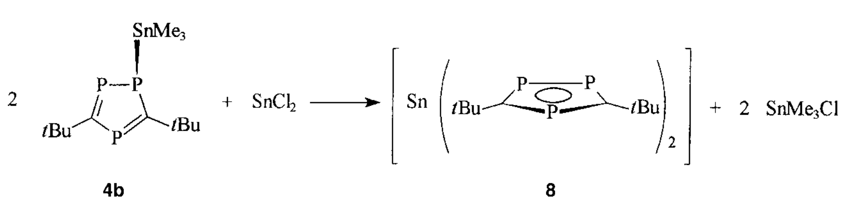


Figure 7. Possible transition states of the [2+2+2] cyclic reaction step of **7** and **1**.

Direct formation of η^5-triphospholyl complexes: Since we designed the stannyltriphospholes **4a**–**4c** for the preparation of η^5 complexes, we undertook experiments to combine π complexation of the ring with the breaking of the P–Sn σ bond. Thus, 1-trimethylstannyl-3,5-di-*tert*-butyl-1,2,4-triphosphole (**4b**) was allowed to react with $SnCl_2$ in THF, which resulted in the formation of the hexaphosphastannocene derivative $[Sn(C_2tBu_2P_3)_2]$ (**8**) in 98% yield of isolated pure material (Scheme 6). The Me_3Sn^{IV} group of starting material **4b** is eliminated together with the Cl ligand of tin(II) dichloride to form Me_3SnCl.



Scheme 6. Preparation of hexaphosphastannocene derivative **8**.

The ${}^1H$ NMR spectrum of **8** exhibits only one resonance for four equivalent *tert*-butyl groups at $\delta = 1.45$ at room temperature. The ${}^{31}P$ NMR spectrum consists of two resonances at $\delta = 266.8$ and 281.4, which are analyzed by simulation[22] as an $[AB_2]_2$ spin system. Inclusion of the ${}^{117/119}Sn$ satellites produces an $[AB_2]_2X$ spin system. The $J({}^{119}Sn,{}^{31}P)$ coupling constants are $J({}^{119}Sn,{}^{31}P(1,2)) = 91.0$ Hz and $J({}^{119}Sn,{}^{31}P(3)) = 301.0$ Hz. In contrast to those of **4a** they possess the same sign. The ${}^{119}Sn$ NMR signal of **8** at $\delta = -1718$ is very different from that of **4a**. It is close to the value observed for stannocene derivatives. We regard this finding as an indication of the dominant η^5-bonding of the triphospholyl ligands to Sn^{II}.[18, 23] However, rapid exchange processes that include smaller hapticity numbers as minor components cannot be ruled out at the moment.

Since the observation of the ${}^{13}C$ NMR signals of ring nuclei of **8** proved to be difficult, the polarization transfer technique INEPT[24] was applied to measure these signals with sufficient signal-to-noise ratio. The experiment is based on long-range coupling constants ${}^nJ({}^{13}C,{}^1H)$ with $n = 3$ (*tert*-butyl groups) in our case. The detection of the signals, including their tin satellites, is straightforward. Figure 8 shows the ${}^{13}C(3,5)$ resonances of **8**. Simulation of these spectra helped in some cases to determine the upper and lower limits of the magnitude and sign of the coupling constants $J({}^{31}P,{}^{31}P)$ of the complex spin systems.

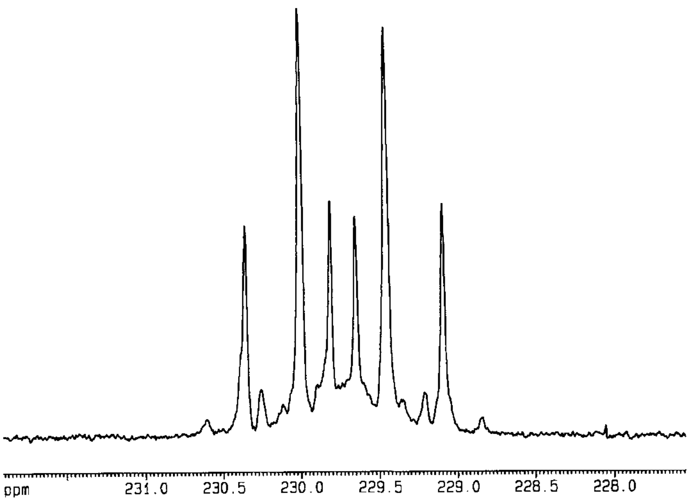
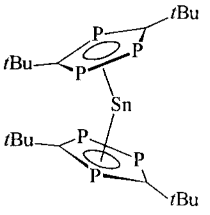
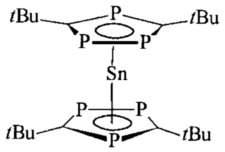


Figure 8. Part of the ${}^{13}C\{{}^1H\}$ NMR spectrum (125.8 MHz), recorded by the refocused INEPT pulse sequence, showing the ${}^{13}C(3,5)$ resonance. This spectrum can be calculated[21] as an AA'BX spin system, or together with ${}^{119}Sn$ (satellites are clearly visible) as an AA'BMX spin system.

Apart from changes in the linewidth, the NMR spectra of **8** are not temperature-dependent between room temperature and −90 °C. This points towards a fast rotation process of the cyclic ligands about the axes passing through the ring centers and the tin atom. Unfortunately, however, it does not reveal information about a bent structure of **8** or a structure with parallel ring ligands. Most known stannocene derivatives are bent (**8a**), including an example that contains one 1,2,4-triphospholyl ligand,[25] but highly substituted stannocenes with parallel rings (**8b**) have also been reported.[26, 27] As no single crystals of **8** of sufficient quality have been obtained yet, this question still remains open.

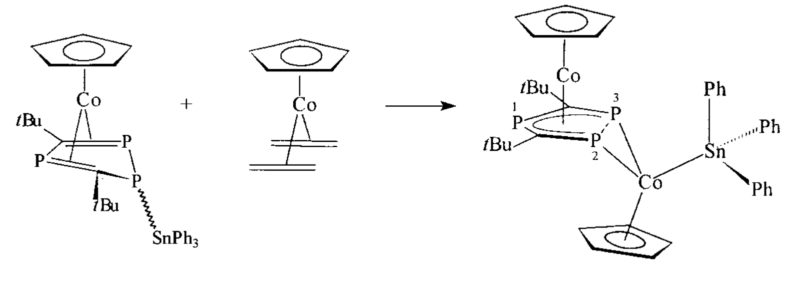


8a



8b

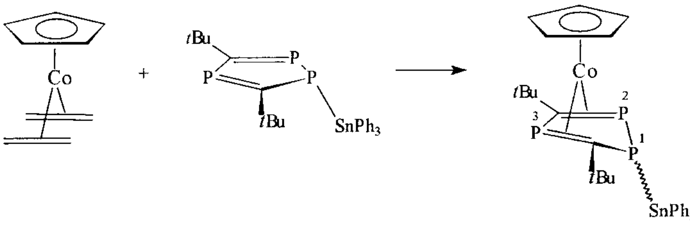
Evidently, $SnCl_2$ is a suitable reaction partner for the stannyltriphospholes **4** in order to transform them effectively into triphospholyl ligands by elimination of R_3SnCl. Metal compounds without such an anionic leaving group therefore require different reaction pathways when treated with derivatives of **4**.



10 **9** **11**

Scheme 8. Preparation of compound **11**.

Preparation of η^4-1,2,4-triphosphole complexes: To prove the above assumption, compound **4a** was allowed to react with $[CpCo(C_2H_4)_2]$ (**9**), whose pronounced reactivity is caused by the neutral and labile ethene ligands.[28] The course of this reaction is decisively dependent on the relative concentrations of the starting materials in the reaction mixture. If **9** was treated with an excess of **4a** in Et_2O/pentane (1:1) at $-40\,^{\circ}C$, $[Cp(\eta^4\text{-}C_2tBu_2P_3SnPh_3)Co]$ (**10**) was formed in 82% yield (Scheme 7).



9 **4a** **10**

Scheme 7. Synthesis of compound **10**.

The $^{31}P\{^1H\}$ NMR spectrum of **10** shows the pattern of an [ABC]X spin system with signals at $\delta = 39.0$, -9.5, and -70.4, respectively. Only one of these shows $^{117/119}Sn$ satellites for a large[18, 29] $Sn-^{31}P$ coupling ($\delta = -9.5$; $^1J(^{119}Sn,^{31}P) = +1611.7$ Hz), whereas the other $Sn-^{31}P$ coupling constants are smaller by more than one order of magnitude. This large value and the $\delta(^{13}C$ ring) data indicate localized C=P double bonds with η^4 coordination of the ring to the cobalt atom. Thus the SnR_3 unit remains within the molecule **10**, but the rapid [1,5]-shift of the free ligand no longer takes place in the complex. We have determined a positive sign of $^1J(^{119}Sn,^{31}P)$ by 1D $^{13}C\{^1H,^{31}P\}$ heteronuclear triple-resonance experiments, in which the ^{31}P transitions were irradiated selectively and the tin satellites of the $^{13}C(SnPh_3\text{-}ipso)$ signal were observed.

If **10** was treated with stoichiometric amounts of **9** at $-80\,^{\circ}C$, the dinuclear species $[Cp_2Co_2(C_2tBu_2P_3)(SnPh_3)]$ (**11**) was formed in 75% yield. Alternatively, compound **11** can be synthesized directly in 82% yield by reaction of **4a** with an excess of **9** (Scheme 8).

The spectroscopic data for **11** did not reveal unambiguous structural information (vide infra). However, it was possible to determine its structure from single crystals of **11** that were grown in pentane/THF at $-30\,^{\circ}C$ as black plates (Figure 9).

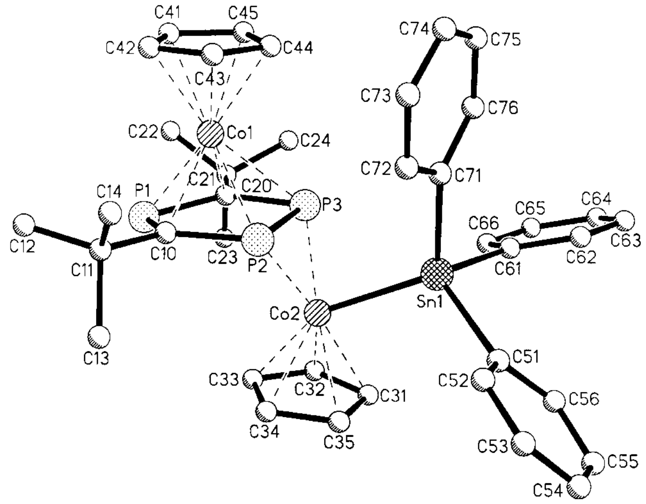


Figure 9. Molecular structure of **11**·3THF in the solid state. Selected distances [pm]: Sn1–Co2 249.97(9), Sn1–P2 336.3(2), Sn1–P3 322.6(2), Co2–P3 218.8(2), Co2–P2 219.5(2), P2–P3 233.8(2), P1–C10 176.3(6), P2–C10 178.9(5), P3–C20 179.3(6), P1–C20 177.6(6), Co1–P1 228.7(2), Co1–P2 242.1(2), Co1–P3 240.3(2), Co1–C10 208.8(5), Co1–C20 208.8(6). The THF molecules do not interact significantly with the molecules of **11** and have been omitted for clarity.

Compound **11** exhibits extraordinary structural features. It can be viewed as an extremely slipped 34 VE triple-decker sandwich complex,[30] as it contains a bridging 1,2,4-triphospholyl ring, η^5-bonded to one and η^2-bonded to the other [CpCo] unit. Because the distances Co1–P2 and Co1–P3 are longer than Co1–P1, Co1 is not situated above the center of the ring ligand, but shifted slightly away from the two bridging P atoms towards P1. If we compare this metal atom position to that of the 18 VE sandwich complex $[Cp(\eta^5\text{-}1,2,4\text{-}C_2t\text{Bu}_2P_3)Fe]$,[9] where the η^5-bonded metal atom is less perturbed, the M–P1, M–C10 and M–C20 distances are reduced for **11** and the M–P2 and M–P3 bonds are elongated.

The distance between Sn1 and both phosphorus atoms, P2 and P3, is more than 70 pm longer than the sum of the covalent radii (250 pm).[15] The triphenyltin group thus seems to be placed into an unsymmetrical μ^3-bridging position with a strong link to Co2 and weak interactions with P2 and P3. Alternatively the P–Sn bond of heterocycle **4a**, as found in the mononuclear complex **10**, may be regarded as broken in the case of the binuclear complex **11**. The incoming cobalt atom Co2 has cleaved the P–Sn bond by reaction with **10** and replaced it with the Co2–Sn bond. It thus forms a $[CpCo(SnPh_3)]$ fragment that is only η^2-coordinated to the neighboring atoms P2 and P3 opposite to the position of η^5-coordinated Co1. Because of the position of Co2, the lone pairs of electrons on P2 and P3 cannot contribute significantly to the bonding to Co2. The bridging triphospholyl ring is not fully planar. Only the fragment C20-P3-P2-C10 possesses an approximately planar conformation, but P1 is displaced by 17.6(7) pm from the best plane. The P–C bond lengths in the ring are within the range for single and double bonds. P1–C10 and P1–C20 are shorter than P2–C10 and P3–C20. The distance P2–P3 (233.8(2) pm) is slightly longer than the sum of the covalent radii (220 pm)[15] and consequently longer than the single P–P bond of free **4a**. This bond elongation indicates a reduction of the P–P bond order to a value below one, which is caused by the additional η^2 coordination of these nuclei to Co2.

To the best of our knowledge, comparable $\mu,\eta^5{:}\eta^2$-bonding modes for bridging cyclopentadienyl ligand analogues have been reported only for $[(Cp^*Fe(\mu,\eta^5{:}\eta^2\text{-}C_2t\text{Bu}_2P_3)RhCp^*(CO)]$[31] and $[(Cp^*Fe(\mu,\eta^5{:}\eta^2\text{-cyclo-}P_5)IrCp^*(CO)]$ ($Cp^* = C_5Me_5$).[32] These two examples have the same total valence electron count as **11** of 34 and exhibit a P–P bond elongation of the same magnitude for the two phosphorus atoms that bridge the two metal atoms. On the other hand, they differ strongly from **11** in the electron distribution between the two halves of the dinuclear complexes, as they have been described as the addition products of the two closely related 16 VE complex fragments Cp*RhCO or Cp*IrCO to closed shell 18 VE oligophosphaferrocene derivatives.

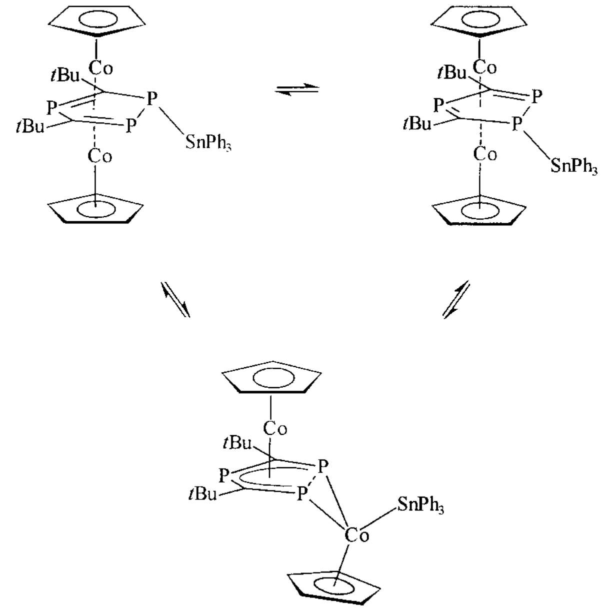
Approaching the formation of **11** in an analogous way, it may be regarded as the formal addition product of the 15 VE fragment $CpCo(SnR_3)$ to the 19 VE triphosphacobaltocene derivative $[CpCo(\eta^5\text{-}C_2t\text{Bu}_2P_3)]$. If an intramolecular charge transfer is assumed for **11** (which might be driven by the big difference in the formal electron count for the two cobalt nuclei), then a closer analogy to the compounds mentioned above may be possible. This would result in the formation of an internal salt made up of the components $[CpCo(SnR_3)]^-$ (16 VE) and $[CpCo(\eta^5\text{-}C_2t\text{Bu}_2P_3)]^+$ (18 VE). As a third qualitative alternative for the valence-electron distribution between both metal centers, the donation of the π electrons of the central ring may be regarded as having split in such a way that the electrons are transferred preferentially to the metal atom that is closer to the donating nucleus. This means that the three π electrons of C10, P1, and C20 are donated to Co1 and the two π electrons of P2 and P3 are donated mainly to Co2. This would result in the formation of two 17 VE Co centers that do interact through the p_z orbitals of P2 and P3. This strong interaction is the reason for viewing **11** as a slipped triple-decker sandwich complex and it generates the observed electronic closed-shell ground state.

The less relevant cases of unsymmetrically bridging five-membered phosphorus heterocyclic ligands have been reported for tri- and tetranuclear complexes that are composed of a 1,2-diphospha-,[33] 1,2,4-triphospha-,[34] or 1,2,3,4,5-pentaphosphaferrocene[35] partly fused with di- or trimetal carbonyl fragments. The sandwich complex units serve as four-electron donor ligands thorugh one phosphorus lone pair and the electrons of a P_2 unit of the bridging heterocycle. In two of the three cases a comparable elongation of the P–P bond is observed,[33, 35] whereas the addition of a $Ru_3(CO)_9$ unit to a 1,2,4-triphosphaferrocene derivative has no significant influence on the P–P bond length.[34]

Spectroscopic investigations: The ^{119}Sn NMR spectrum of **11** at room temperature consists of a very broad resonance at $\delta = -90$ ($h_{1/2}$ ca. 2200 Hz). This ^{119}Sn chemical shift and the fairly small coupling constants $^1J(^{119}\text{Sn},^{13}\text{C}_{\text{Ph}}) = 235.4$ Hz and $^3J(^{119}\text{Sn},^1\text{H}_{\text{Ph}}) = 34.0$ Hz are indicative of coordination number of four at the tin atom.[18] The extreme broadening of the ^{119}Sn NMR signal can be attributed to an unresolved scalar ^{119}Sn–^{59}Co coupling. The ^{59}Co NMR spectrum consists of two typically[36] extremely broad resonances at $\delta = -1845$ and -2325. The high-field signal is close to that of $[Co(Cp)_2]^+$ ($\delta(^{59}\text{Co}) = -2400$).[37] Thus, the electronic situation of the two Co atoms cannot be too different. Therefore, we prefer to view the 34 VE triple-decker sandwich complex **11** as being composed of two strongly interacting 17 VE cobalt complex fragments. An 18/16 and, even more so, a 19/15 VE combination of the cobalt atoms would result in much more pronounced splitting of the two ^{59}Co NMR signals.

The ^{31}P NMR spectrum of **11** exhibits a doublet at $\delta = 203.0$, which is accompanied by tin satellites and a triplet at $\delta = 68.4$. Compound **11** thus forms an $[AB_2]X$ spin system in solution. The high frequency shift of the ^{31}P(doublet) signal points towards a rather different bonding situation when compared with the ^{31}P data for compound **10**. Since the coupling constants $|J(\text{Sn},^{31}\text{P})|$ are of considerable magnitude, the coupling pathway through Co to a π-coordinate ^{31}P nucleus is unlikely. Thus, the NMR spectroscopic findings suggest either a highly dynamic system in which there is a P–Sn bond on average (in contrast to the molecular structure of **11** in the solid state) or a static structure with multicenter bonding between the two phosphorus atoms, cobalt, and tin (Scheme 9). The magnitude of the coupling constant $J(^{31}\text{P},^{119}\text{Sn}) = 338$ Hz is in agreement with bonding Sn–P interactions. Surprisingly, it is close to that of the fluxional starting material **4**.

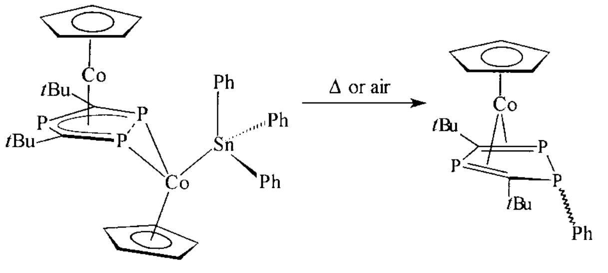
In order to obtain further evidence, temperature-dependent NMR spectra have been recorded between 20 and −100 °C. With the exception of the ^{119}Sn NMR signal, the



Scheme 9. Possible intramolecular $SnPh_3$ group exchange in **11**.

linewidths of all the other signals increase upon cooling, but no coalescence of signals or slow-exchange limit spectra have been observed. In all the spectra, the cyclopentadienyl ligands and the cobalt atoms remain nonequivalent. These observations support a static structure for **11** in solution, although a fast dynamic process cannot be ruled out. If such an exchange process of the SnR_3 group from Co2 to P1 or P2 and back again (Scheme 9) determines the behavior of **11** in solution, then the intermediate stannylated P atom must be pyramidal and the tin atom always has to move back to the same cobalt atom Co2. This question is currently being investigated through the stacking reactions of **10** with Cp-substituted $[CpCo(C_2H_4)_2]$ derivatives.

Reactivity of compound 11: Exposure of solutions of **11** to the air or prolonged heat leads to destacking and an intramolecular phenyl group transfer reaction, which yields [Cp(η^4-1-phenyl-3,5-di-*tert*-butyl-1,2,4-triphosphole)Co] (**12**) (Scheme 10). Thermal degradation of **11** produces **12** in 60 % yield, whereas oxidation gives a 43 % yield.



11 **12**

Scheme 10. Synthesis of compound **12**.

NMR spectra indicate that the product is a single compound and most probably a pair of enantiomers. As no single crystals of **12** have been obtained up to now, the position of the phenyl group is not yet clear. As noted for the η^4-1,2,4-triphosphole complex **10**, an [ABC] spin system is observed in the $^{31}P\{^1H\}$ NMR spectra, but the tin coupling is of course missing for **12**. Compounds **10** and **12** are believed to be isostructural, not only with respect to metal–ligand bonding, but also with respect to the position of the substituent at P1. Their close structural relationship is indicated by both the chemical shifts of the P nuclei and their P–P coupling constants.

Through the course of this reaction, a [Cp(diphenylstannylene)Co] unit is eliminated from **11** to allow the formation of **12**. The fate of this interesting particle is under current investigation.

Conclusion

1-Triorganylstannyl-3,5-di-*tert*-butyl-1,2,4-triphosphole derivatives **4** are readily accessible from the corresponding 1,2,4-triphospholyl sodium salts. Since the P–Sn bond is of moderate stability, compounds **4a–c** offer an interesting new route to polycyclic organophosphorus cages and to complexes with η^5-1,2,4-triphospholyl or η^4-1,2,4-triphosphole ligands. All of the reactions of **4** performed so far give good to almost quantitative yields and high chemo- and diastereoselectivity. This offers the first experimental insight into the mechanisms of some of the reactions.

Depending on the reaction partners, the stannyl group remains bonded to one of the two adjacent phosphorus atoms and is transferred quantitatively to a metal atom, or eliminated together with an anionic leaving group. A highly interesting $\mu,\eta^5{:}\eta^2$-bridging mode for the 1,2,4-triphospholyl ligand was observed in the case of the dinuclear complex **11**. If we compare the extremely slipped 34 VE triple-decker sandwich complex **11** with other triple-deckers with the same total VE count, those with carbacycles or boron heterocycles as middle decks form nonslipped, linear structures.[30] On the other hand, in the case of cyclo-P_n ($n = 5, 6$)[43] or phosphorus-rich P heterocycles as middle decks,[9, 10] 34 VE are avoided and 26 to 30 VE are found; these compounds are also nonslipped. The only exceptions to these findings are the aforementioned compounds [(Cp*Fe($\mu,\eta^5{:}\eta^2$-$C_2tBu_2P_3$)RhCp*(CO)],[31] [(Cp*Fe($\mu,\eta^5{:}\eta^2$-cyclo-P_5)IrCp*(CO)],[32] and **11**. Consequently, the reason for their pronounced slippage must be connected with the specific interaction between the phosphorus atoms of such P-rich ring ligands and transition metal atoms. In this bonding situation, the phosphorus atoms definitely do not behave as their carbon analogues.[31] As the factors that govern the limits of phosphorus-carbon analogies are not yet defined clearly, we have tried to contribute to their evaluation.

Experimental Section

All reactions were carried out in flame-dried glassware under an oxygen-free atmosphere of dry nitrogen using Schlenk techniques. Solvents were dried by standard methods and distilled under N_2. All NMR solvents were carefully dried, degassed, and stored over 4 Å molecular sieves. NMR spectra were recorded on JEOL JNM-GX 270, JEOL JNM-EX-270, JEOL

JNM-LA400, Bruker DRX500, and Bruker ARX250 instruments. ^{1}H and ^{13}C NMR chemical shifts are given relative to residual solvent peaks. ^{31}P chemical shifts are referenced to external H_3PO_4 (85 %). ^{119}Sn chemical shifts are referenced to external Me_4Sn ($\Xi(^{119}Sn = 37.290665$ MHz) and ^{59}Co chemical shifts to external $K_3[Co(CN)_6]$ (0.1 M in D_2O) ($\Xi(^{59}Co) = 23.727118$ MHz). Mass spectra were recorded on Varian MAT212 and JEOL JMS700 spectrometers. Elemental analyses were performed locally by the microanalytical laboratory of the Institut für Anorganische Chemie der Universität Erlangen–Nürnberg.

The starting materials $P(SiMe_3)_3$ and $Me_3SiP{=}C(OSiMe_3)t$Bu, used as the precursors for the preparation of the mixture of salts containing the anions **2**$^-$ M[3,5-di(*tert*-butyl)-1,2,4-triphospholyl] and **3**$^-$ M[2,4,5-tri(*tert*-butyl)-1,3-triphospholyl] were prepared by published routes.[39, 40] The sodium salt Na-**2** was prepared by modification of the route published by Nixon et al.[41] (elemental sodium was used as reducing agent) and purified by repeated recrystallization, until the by-product 1,3-diphospholyl sodium Na-**3** was removed completely. Triorganylstannyl chlorides, alkaline metals, and solvents were purchased from standard commercial sources. The stannyl components were purified by sublimation or distillation in vacuo, depending on the organyl group.

1-Triphenylstannyl-3,5-di-*tert*-butyl-1,2,4-triphosphole (4a): Triphenylstannyl chloride (0.964 g, 2.5 mmol) in toluene (20 mL) was added to a solution of 3,5-di-*tert*-butyl-1,2,4-triphospholylsodium (Na-**2**) (0.750 g, 2.3 mmol) in toluene (20 mL) at −30 °C and stirred. The reaction mixture was warmed to room temperature over 3 h and then stirred further for 1 h. Removal of the solvent under vacuum resulted in a yellow residue that was dissolved in *n*-hexane (30 mL) and filtered to yield a clear yellow solution. The solvent was removed under vacuum and the excess of triphenylstannyl chloride was sublimed (0.02 mbar, 80 °C). Yellow crystals of analytically pure **4a** (1.2 g, 87 %) were obtained after recrystallization from *n*-hexane. ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): $\delta = 1.54$ (d, $^{4}J(^{31}P,^{1}H) = 1.1$ Hz, vt, $\Sigma^{4}J(^{31}P,^{1}H) + ^{5}J(^{31}P,^{1}H) = 1.3$ Hz, 18 H; $C(CH_3)_3$), 7.54 (dd, $^{3}J(^{1}H,^{1}H) = 7.5$ Hz, $^{4}J(^{1}H,^{1}H) = 1.6$ Hz, d, $^{3}J(^{119}Sn,^{1}H) = 58$ Hz, 6 H; C_5H_6 (H_o)), 7.07–7.17 (m, 9 H; C_5H_6 ($H_m + H_p$)); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, [D$_8$]toluene, 25 °C): $\delta = 222.8$ (ddd, $^{1}J(^{31}P,^{13}C) = -65.2$ Hz, $\Sigma^{1}J(^{31}P,^{13}C) + ^{2}J(^{31}P,^{13}C) = -68.5$; C_{Ring}), 42.8 (ddd, $^{2}J(^{31}P,^{13}C) = 20.7$ Hz, $\Sigma^{2}J(^{31}P,^{13}C) + ^{3}J(^{31}P,^{13}C) = 10.3$ Hz; $C(CH_3)_3$), 36.1 (ddd, $^{3}J(^{31}P,^{13}C) = 10.3$ Hz, $\Sigma^{3}J(^{31}P,^{13}C) + ^{4}J(^{31}P,^{13}C) + 12.0$ Hz; $C(CH_3)_3$), 139.1 (d, $^{1}J(^{119}Sn,^{13}C) = 518.0$ Hz, d, $^{2}J(^{31}P,^{13}C) = 4.3$ Hz; C_5H_6 (C_i)), 137.1 (d, $^{2}J(^{119}Sn,^{13}C) = 41.4$ Hz; C_5H_6 (C_o)), 129.1 (d, $^{3}J(^{119}Sn,^{13}C) = 20.0$ Hz; C_5H_6 (C_m)), 129.8 (d, $^{4}J(^{119}Sn,^{13}C) = 13.0$ Hz; C_5H_6 (C_p)); $^{31}P\{^{1}H\}$ NMR (101.3 MHz, [D$_8$]toluene/CH_2Cl_2 1:1, 25 °C): $\delta = 327.4$ (t, $^{2}J(^{31}P,^{31}P) = 37.2$ Hz, d, $^{3}J(^{119}Sn,^{31}P) = 69.5$ Hz, 1 P; $P(3)$), 159.8 (d, $^{2}J(^{31}P,^{31}P) = 37.2$ Hz, d, $J(^{119}Sn,^{31}P) = 359.0$ Hz, 2 P; $P(1,2)$); ^{119}Sn NMR (185.6 MHz, [D$_8$]toluene, 25 °C): $\delta = -104.6$ (t, $J(^{119}Sn,^{31}P) = 359.0$ Hz, d, $^{3}J(^{119}Sn,^{31}P) = 69.5$ Hz; *Sn*Ph$_3$); MS (FD): *m*/*z* (%): 582 ([*M*]$^+$, 100); MS (EI, 70 eV): *m*/*z* (%): 582 ([*M*]$^+$, 25), 503 ([*M* − Ph]$^+$, 35), 485 ([*M* − PC*t*Bu]$^+$, 35), 426 ([*M* − 2Ph]$^+$, 20), 349 ([*M* − 3Ph]$^+$, 100), 231 ([*M* − SnPh$_3$]$^+$, 70); $C_{28}H_{33}P_3Sn$ (581.14): calcd C 57.87, H 5.72; found C 58.06, H 5.83.

1-Trimethylstannyl-3,5-di-*tert*-butyl-1,2,4-triphosphole (4b): Preparation and purification were as for compound **4a** above, but Me_3SnCl in *n*-hexane was added at 0 °C to the solution of Na-**2** in toluene. Reaction mixture: Na-**2** (0.133 g, 0.4 mmol) in toluene (20 mL) and Me_3SnCl (0.081 g, 0.4 mmol) in *n*-hexane (40 mL). Yield = 0.16 g (98 %) of **4b**; ^{1}H NMR (300.1 Hz, C_6D_6, 25 °C): $\delta = 0.31$ (9 H, $Sn(CH_3)_3$), 1.76 (d, $^{4}J(^{31}P,^{1}H) = 0.7$ Hz, 18 H; $C(CH_3)_3$); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, C_6D_6, 25 °C): $\delta = 223.4$ (ddd, $^{1}J(^{31}P,^{13}C) = 65.4$ Hz, $\Sigma^{1}J(^{31}P,^{13}C) + ^{2}J(^{31}P,^{13}C) = 71.9$; C_{Ring}), 43.0 (ddd, $^{2}J(^{31}P,^{13}C) = 21.1$ Hz, $\Sigma^{2}J(^{31}P,^{13}C) + ^{2}J(^{31}P,^{13}C) = 11.6$ Hz; $C(CH_3)_3$), 36.8 (ddd, $^{3}J(^{31}P,^{13}C) = 10.9$ Hz, $\Sigma^{3}J(^{31}P,^{13}C) + ^{4}J(^{31}P,^{13}C) = 10.9$ Hz; $C(CH_3)_3$), −1.9 (d, $^{1}J(^{119}Sn,^{13}C) = 393.1$ Hz; $Sn(CH_3)_3$); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6, 25 °C): $\delta = 319.2$ (t, $^{2}J(^{31}P,^{31}P) = 41.4$ Hz, 1 P; $P(3)$), 167.8 (d, $^{2}J(^{31}P,^{31}P) = 41.4$ Hz, d, $^{1}J(^{31}P,^{119}Sn) = 305.6$ Hz, 2 P; $P(1,2)$); MS (FD): *m*/*z* (%): 369 ([*M*]$^+$, 100); $C_{13}H_{27}P_3Sn$ (396.03): calcd C 39.53, H 6.89; found C 39.88, H 7.54.

1-Tri-*n*-butylstannyl-3,5-di-*tert*-butyl-1,2,4-triphosphole (4c): Preparation was as for compound **4a** above, but the initial temperature was 0 °C. Reaction mixture: Na-**2** (0.134 g, 0.4 mmol) in toluene (15 mL) and *n*Bu$_3$SnCl (0.134 g, 0.4 mmol) in toluene (15 mL). No crystallization of product **4c** was possible. According to the NMR spectra, the purity of the isolated material was better than 90 %. Yield = 0.18 g (90 %) of **4c**; $^{31}P\{^{1}H\}$ NMR (109.36 MHz, C_6D_6, 25 °C): $\delta = 166.03$ (d, $^{2}J(^{31}P,^{31}P) = 36$ Hz, $^{1}J(^{119}Sn,^{31}P) = 359.2$ Hz, 2 P; P(1,2)), 316.95 (t, $^{2}J(^{31}P,^{31}P) = 36$ Hz, 1 P; P(3)); $C_{22}H_{45}P_3Sn$ (522.18); MS (FD): *m*/*z*: 522 [*M*]$^+$.

Polycyclic cage compound C_4tBu$_4$P$_5$SnPh$_3$ (6): 1-Triphenyl-3,5-di-*tert*-butyl-1,2,4-triphosphole **4a** (0.559 g, 0.96 mmol) and *tert*-butyl phosphaalkyne **1** (0.192 g, 1.92 mmol) were stirred in hexane (20 mL) at room temperature. The reaction mixture was then refluxed for 12 h. After cooling, yellow crystals of **6** were formed at room temperature. Recrystallization from *n*-hexane yielded pure **6** (0.6 g, 80%). ^{1}H NMR (399.6 MHz, C_6D_6, 25 °C): $\delta = 0.89$ (s, 9 H; $C(1)(CH_3)_3$), 1.40 (s, 9 H; $C(CH_3)_3$), 1.48 (s, 9 H; $C(CH_3)_3$), 1.62 (s, 9 H; $C(CH_3)_3$), 7.12–7.24 (m, 9 H; C_6H_5 ($H_m + H_p$), 7.95 (dd, $^{3}J(^{1}H,^{1}H) = 7.9$ Hz, $^{4}J(^{1}H,^{1}H) = 1.5$ Hz, d, $^{3}J(^{1}H,^{119}Sn) = 47.9$ Hz, 6 H; C_6H_5 (H_o); $^{13}C\{^{1}H\}$ NMR (67.7 MHz, $CDCl_3$, 25 °C): $\delta = 32.6$ (m, $C(CH_3)_3$), 34.2 (m, $C(CH_3)_3$), 35.3 (m, $C(CH_3)_3$), 36.6 (m, $C(CH_3)_3$), 34.8 (m, $C(CH_3)_3$), 38.1 (m, $C(CH_3)_3$), 40.4 (m, $C(CH_3)_3$), 41.7 (m, $C(CH_3)_3$), 128.4 (s, C_6H_5 (C_p)) 129.0 (s, C_6H_5 (C_m)), 137.7 (d, $^{2}J(^{119}Sn,^{13}C) = 38.0$ Hz, C_6H_5 (C_o)), 140.5 (m, C_6H_5 (C_p)), 228.7 (m, $C(3)$); $^{31}P\{^{1}H\}$ NMR (161.7 MHz, C_6D_6, 25 °C): $\delta = 330.3$ (1 P, $P(4)$), 94.9 (1 P, $P(5)$), −39.9 (d, $^{1}J(^{31}P(1),^{31}P(2)) = 278.1$ Hz, d, $^{1}J(^{31}P,^{119}Sn) = 1074.5$ Hz, 1 P; $P(1)$), −88.0 (dd, $^{1}J(^{31}P(2),^{31}P(1)) = 278.1$ Hz, $^{1}J(^{31}P(2),^{31}P(3)) = 147.1$ Hz, 1 P; $P(2)$), −130.0 (d, $^{1}J(^{31}P(2),^{31}P(2)) = 147.1$ Hz, 1 P; $P(3)$); MS (FD): *m*/*z* (%): 782 ([*M*]$^+$, 100); $C_{38}H_{51}P_5Sn$ (782.17): calcd C 58.41, H 6.58; found C 58.35, H 6.73.

[Bis(3,5-di(*tert*-butyl)-1,2,4-triphospholyl)Sn] (Hexaphosphastannocene) (8): A solution of $SnCl_2$ (0.190 g, 1.0 mmol) in THF (10 mL) was mixed with a solution of 1-trimethylstannyl-3,5-di-*tert*-butyl-1,2,4-triphosphole (**4b**) (0.864 g, 2.1 mmol) in THF (10 mL) at 0 °C and allowed to reach room temperature over 2.5 h. Removal of the solvent under vacuum gave a brown residue that was dissolved in *n*-hexane (30 mL). Filtration gave a clear, yellow-orange solution. At −78 °C compound **8** was precipitated as small yellow needles. After recrystallization pure **8** (0.57 g) was obtained in a yield of 98 %. ^{1}H NMR (500.1 MHz, [D$_8$]toluene, 18 °C): $\delta = 1.45$ (s, 36 H; $C(CH_3)_3$); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, [D$_8$]toluene, 18 °C): $\delta = 229.7$ (ddd, $^{1}J(^{31}P(3),^{13}C) = -69.5$ Hz, $\Sigma^{1}J(^{31}P(2),^{13}C) + ^{2}J(^{31}P(1),^{13}C) = 88.0$ Hz, d, $J(^{119}Sn,^{13}C) = 66$ Hz; C_{Ring}), 42.8 (ddd, $^{2}J(^{31}P(3),^{13}C) = 20.5$ Hz, $\Sigma^{2}J(^{31}P(2),^{13}C) + ^{3}J(^{31}P(1),^{13}C) = 11.7$ Hz, d, $J(^{119}Sn,^{13}C) = 5 \pm 1$ Hz; $C(CH_3)_3$), 36.9 (ddd, $^{3}J(^{31}P(3),^{13}C) = 9$ Hz, $\Sigma^{3}J(^{31}P(2),^{13}C) + ^{4}J(^{31}P(1),^{13}C) = 4.5$ Hz; $C(CH_3)_3$); $^{31}P\{^{1}H\}$ NMR (202.5 MHz, [D$_8$]toluene, 18 °C): $\delta = 266.8$ (d, $^{2}J(^{31}P,^{31}P) = 47.0$ Hz, d, $J(^{119}Sn,^{31}P) = 91.0$ Hz, 4 P; $P(1,2)$), +281.4 (t, $^{2}J(^{31}P,^{31}P) = 47.0$ Hz, d, $J(^{119}Sn,^{31}P(3)) = 301.0$ Hz, 2 P; $P(3)$), simulated: $[A_2B]_2$ spin system: $J(A\text{-}Sn\text{-}A'') < 0.5$ Hz, $J(B\text{-}Sn\text{-}B') = \pm 8.5$ Hz, $J(B\text{-}Sn\text{-}A'') = +\ 2$ Hz. $^{1}J(A,A') > 140$ Hz; ^{119}Sn NMR (186.2 MHz, [D$_8$]toluene, 18 °C): $\delta = -1718$ (m, *Sn*); MS (FD): *m*/*z* (%): 582 ([*M*]$^+$, 10), 462 ([$(C_2t$Bu$_2$P$_3)_2$]$^+$, 60), 351 ([*M* − (C_2tBu$_2$P$_3$)]$^+$, 100); $C_{20}H_{36}P_6Sn$ (581.08) calcd C 41.34, H 6.25; found C 41.65, H 6.59.

[Cp(1-Triphenylstannyl-3,5-di-*tert*-butyl-η^4-1,2,4-triphosphole)Co] (10): [CpCo(C_2H_4)$_2$] (**9**) (0.468 g, 2.6 mmol) in Et_2O/pentane (40 mL, 1:1) was added at −40 °C to a solution of **4a** (4.591 g, 7.9 mmol) in Et_2O/pentane (40 mL, 1:1). The dark reaction mixture was allowed to reach room temperature over 2.5 h. Dark red **10** (1.50 g, 82 %) was isolated after recrystallization from *n*-hexane. ^{1}H NMR (399.7 MHz, C_6D_6, 21 °C): $\delta = 1.23$ (s, 9 H; $C(CH_3)_3$), 1.38 (s, 9 H; $C(CH_3)_3$), 4,74 (s, 5 H; C_5H_5), 7.21–7.31 (m, 9 H; C_6H_5 ($H_m + H_p$), 7.83 (d, $^{3}J(^{1}H,^{1}H) = 6.6$ Hz, d, $^{2}J(^{119}Sn,^{1}H) = 43.1$ Hz, 6 H; C_6H_5 (H_o)); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, C_6D_6, 23 °C): $\delta = 32.9$ (dd, $^{3}J(^{31}P,^{13}C) = 7.9$ Hz, $^{3}J(^{31}P,^{13}C) = 7.9$ Hz; $C(CH_3)_3$), 35.1 (dd, $J(^{31}P,^{13}C) = 8.3$, $^{3}J(^{31}P,^{13}C) = 8.3$ Hz; $C(CH_3)_3$), 38.2 (dd, $^{2}J(^{31}P,^{13}C) = 17.3$, $^{2}J(^{31}P,^{13}C) = 17.3$ Hz; $C(CH_3)_3$), 38.7 (dd, $^{2}J(^{31}P,^{13}C) = 14.8$, $^{2}J(^{31}P,^{13}C) = 13.9$ Hz; $C(CH_3)_3$), 83.5 (s, C_5H_5), 75.7 (ddd, $^{1}J(^{31}P,^{13}C) = 70.0$ Hz, $^{1}J(^{31}P,^{13}C) = 79.0$ Hz, $^{2}J(^{31}P,^{13}C) = 9.2$ Hz; $C(1)$), 145.0 (ddd, $^{1}J(^{31}P,^{13}C) = 104.8$ Hz, $^{1}J(^{31}P,^{13}C) = 77.2$ Hz, $^{2}J(^{31}P,^{13}C) = 6.4$ Hz; $C(2)$), 141.5 (d, $^{2}J(^{31}P,^{13}C) = 4.0$ Hz, d, $^{1}J(^{119}Sn,^{13}C) = 359.4$ Hz; C_5H_6 (C_i)), 138.4 (d, $^{2}J(^{119}Sn,^{13}C) = 36.0$ Hz; C_6H_5 (C_o)), 129.1 (d, $^{4}J(^{119}Sn,^{13}C) = 13.0$ Hz; C_6H_5 (C_p)), 128.9 (d, $^{3}J(^{119}Sn,^{13}C) = 45.0$ Hz; C_6H_5 (C_m)); $^{31}P\{^{1}H\}$ NMR (161.7 MHz, C_6D_6, 25 °C): $\delta = 39.02$ (dd, $^{2}J(^{31}P,^{31}P) = 38.0$ Hz, $^{2}J(^{31}P,^{31}P) = 26.3$ Hz, 1 P; $P(3)$), −9.47 (dd, $^{1}J(^{31}P,^{31}P) = 277.3$ Hz, $^{2}J(^{31}P,^{31}P) = 38.0$ Hz, d, $^{1}J(^{119}Sn,^{31}P) = 1611.7$ Hz, 1 P; $P(1)$), −70.41 (dd, $^{1}J(^{31}P,^{31}P) = 277.3$ Hz, $^{2}J(^{31}P,^{31}P) = 26.3$ Hz, d, $^{2}J(^{119}Sn,^{31}P) =$ ca. 61 Hz, 1 P; $P(2)$); ^{119}Sn NMR (186.5 MHz, CD_2Cl_2, 25 °C): $\delta = -166.5$ (ddd, $^{1}J(^{119}Sn,^{31}P) = 1613.0$ Hz, $J(^{119}Sn,^{31}P) = 28.5$ Hz, $J(^{119}Sn,^{31}P) = 60.5$ Hz; *Sn*); ^{59}Co NMR (118.6 MHz, [D$_8$]toluene, 25 °C): $\delta = -870 \pm 40$ (br, *Co*)); MS (FD): *m*/*z* (%): 706 ([*M*]$^+$, 100), 355 ([Co(C_5H_5)(C_2tBu$_2$P$_3$)]$^+$, 60); $C_{33}H_{38}CoP_3Sn$ (705.23): calcd C 56.20, H 5.43; found C 56.55, H 5.88.

[CpCo($\mu,\eta^5:\eta^2$-3,5-di-*tert*-butyl-1,2,4-triphospholyl)Co(SnPh$_3$)Cp] (11): A solution of compound **10** (0.705 g, 1 mmol) in Et$_2$O/pentane (20 mL, 1:1) was added to a solution of **9** (0.180 g, 1 mmol) in Et$_2$O/pentane (40 mL, 1:1) at -80 °C. The reaction mixture was allowed to reach room temperature over 2 h. Removal of the solvent in vacuo gave a violet residue that was redissolved in *n*-hexane (30 mL). Partial removal of the solvent resulted in the formation of a purple precipitate. Recrystallization from *n*-pentane/THF yielded **11** (0.6 g, 75 %) as almost black plates.

Treatment of compound **4a** with **9** (2.0 equiv) under analogous conditions gave product **11** in a yield of 82 %. ^{1}H NMR (500.1 MHz, C$_6$D$_6$, 25 °C): δ = 1.71 (s, 18 H; C(CH$_3$)$_3$), 4.46 (s, 5 H; C$_5$H$_5$), 4.66 (s, 5 H; C$_5$H$_5$), 7.73 (m, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7.3$ Hz, $^4J(^1\mathrm{H},^1\mathrm{H}) = 1.5$ Hz, 3 H; C$_6$H$_5$ (H$_p$)), 7.45 (br, 6 H; C$_6$H$_5$ (H$_m$)), 8.14 (dd, $^3J(^1\mathrm{H},^1\mathrm{H}) = 8.0$ Hz, $^4J(^1\mathrm{H},^1\mathrm{H}) = 1.5$ Hz, d, $^2J(^{119}\mathrm{Sn},^1\mathrm{H}) = 34$ Hz, 6 H; C$_6$H$_5$ (H$_o$)); ^{13}C{^{1}H} NMR (125.8 MHz, [D$_8$]toluene, 25 °C): δ = 164.4 (ddd, $^1J(^{31}\mathrm{P},^{13}\mathrm{C}) = 79$ Hz, $\Sigma^1J(^{31}\mathrm{P},^{13}\mathrm{C}) + {}^2J(^{31}\mathrm{P},^{13}\mathrm{C}) = 123$ Hz; C_{ring}), 42.1 (ddd, $^2J(^{31}\mathrm{P},^{13}\mathrm{C}) = 19.0$ Hz, $\Sigma^2J(^{31}\mathrm{P},^{13}\mathrm{C}) + {}^2J(^{31}\mathrm{P},^{13}\mathrm{C}) = 13$ Hz; *C*(CH$_3$)$_3$), 36.4 (ddd, $^3J(^{31}\mathrm{P},^{13}\mathrm{C}) = 10.0$ Hz, $\Sigma^3J(^{31}\mathrm{P},^{13}\mathrm{C}) + {}^4J(^{31}\mathrm{P},^{13}\mathrm{C}) = 8.0$ Hz; C(*C*H$_3$)$_3$), 86.8 (s, 5 C; *C*$_5$H$_5$), 83.3 (d, $J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 6$ Hz; *C*$_5$H$_5$), 147.1 (d, $^1J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 235.4$ Hz; C$_6$H$_5$ (C_i)), 138.3 (d, $^2J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 29.9$ Hz; C$_6$H$_5$ (C_o)), 128.8 (d, $^3J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 36$ Hz; C$_6$H$_5$ (C_m)), 128.3 (d, $^4J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 9$ Hz; C$_6$H$_5$ (C_p)); ^{31}P{^{1}H} NMR (202.5 MHz, [D$_8$]toluene, 25 °C): δ = 68.4 (t, $^2J(^{31}\mathrm{P},^{31}\mathrm{P}) = 19.5$ Hz, 1 P; *P*(3)), 203.0 (d, $^2J(^{31}\mathrm{P},^{31}\mathrm{P}) = 19.5$ Hz, d, $J(^{31}\mathrm{P},^{119}\mathrm{Sn}) = 338$ Hz, 2 P; *P*(1,2)); ^{119}Sn NMR (186.5 MHz, CD$_2$Cl$_2$, 25 °C): δ = 1.0 (br, *Sn*); ^{59}Co NMR (118.7 MHz, [D$_8$]toluene, 25 °C): δ = -1845 ± 20 (br, *Co*), -2325 ± 20 (br, *Co*); MS (FD): *m*/*z* (%): 830 ([*M*]$^+$, 100); C$_{38}$H$_{43}$Co$_2$P$_3$Sn · 3 THF (1045.50): calcd C 57.44, H 6.46; found C 55.34, H 6.14. Partial loss of THF may be the reason for the deviations between the theoretical and observed values for the analyses of **11**.

[Cp(1-phenyl-3,5-di-*tert*-butyl-η^4-1,2,4-triphosphole)Co] (12): Compound **11** (0.415 g, 0.5 mmol) was dissolved in THF/*n*-hexane (40 mL, 1:1) and refluxed for 6 h. The solution was subsequently cooled to room temperature and all the volatile components were removed under vacuum. Recrystallization from *n*-hexane yielded **12** (0.13 g, 60 %) as a dark brown powder. Due to the finely divided nature of the material, no analytically pure samples have been obtained yet. ^{1}H NMR (399.7 MHz, C$_6$D$_6$, 23 °C): δ = 1.28 (s, 9 H; C(C*H*$_3$)$_3$), 1.45 (s, 9 H; C(C*H*$_3$)$_3$), 4.86 (s, 5 H; C$_5$*H*$_5$), 7,42 (m, 2 H; C$_6$H$_5$ (H_o)), 7.15 (m, 3 H; C$_6$H$_5$ ($H_m + H_p$)); ^{13}C{^{1}H} NMR (100.4 MHz, C$_6$D$_6$, 25 °C): δ = 34.5 (dd, $^3J(^{31}\mathrm{P},^{13}\mathrm{C}) = 8.7$ Hz, $^3J(^{31}\mathrm{P},^{13}\mathrm{C}) = 8.7$ Hz; C(*C*H$_3$)$_3$), 35.4 (dd, $^3J(^{31}\mathrm{P},^{13}\mathrm{C}) = 8.4$, $^3J(^{31}\mathrm{P},^{13}\mathrm{C}) = 8.4$ Hz; C(*C*H$_3$)$_3$), 38.7 (dd, $^2J(^{31}\mathrm{P},^{13}\mathrm{C}) = 14.5$, $^2J(^{31}\mathrm{P},^{13}\mathrm{C}) = 13.1$ Hz; *C*(CH$_3$)$_3$), 39.6 (dd, $^2J(^{31}\mathrm{P},^{13}\mathrm{C}) = 17.4$, $^2J(^{31}\mathrm{P},^{13}\mathrm{C}) = 17.4$ Hz; *C*(CH$_3$)$_3$), 83.2 (s, C$_5$H$_5$)); ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$, 25 °C): δ = 34.2 (dd, $\Sigma^2J(^{31}\mathrm{P}(3),^{31}\mathrm{P}(\mathrm{A})) + {}^2J(^{31}\mathrm{P}(3),^{31}\mathrm{P}(\mathrm{B})) = 58.8$ Hz, 1 P; P(3)), 28.3 (dd, $^1J(^{31}\mathrm{P},^{31}\mathrm{P}) = 266.0$ Hz, $^2J(^{31}\mathrm{P},^{31}\mathrm{P}) = 32.9$ Hz, 1 P; P(2)), -62.7 (dd, $^1J(^{31}\mathrm{P},^{31}\mathrm{P}) = 266.0$ Hz, $^2J(^{31}\mathrm{P},^{31}\mathrm{P}) = 25.9$ Hz, 1 P; P(1)); MS (FD): *m*/*z* (%): 432 ([*M*]$^+$, 100)

X-ray structural determination of 4a, 6, and 11 · 3 THF: The data for all of the structure investigations were collected on a Siemens P4 diffractometer with Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and a graphite monochromator using ω scans. The data were corrected for Lorentz and polarization effects. An empirical absorption correction using psi scans was applied in the case of **4a** (25 reflections, $T_{\mathrm{min}} = 0.476$, $T_{\mathrm{max}} = 0.566$) and **11** · 3 THF (12 reflections, $T_{\mathrm{min}} = 0.124$, $T_{\mathrm{max}} = 0.195$), while absorption effects were neglected for **6**. The structures were solved by direct methods and refined by full-matrix least squares methods (SHELXTL 5.03).[42] Non-hydrogen atoms were refined anisotropically; the hydrogen atoms were taken from a difference Fourier calculation and were isotropically refined in the case of **4a** and **6**. For the structure of **11** · 3 THF all of the hydrogen atoms were geometrically positioned and allowed to ride on their corresponding carbon atoms. Their isotropic thermal parameters were tied to those of the adjacent carbon atoms by a factor of 1.5.

Compound **11** crystallizes with three disordered THF molecules per formula unit. No hydrogen atoms have been included in the model for the solvent molecules.

Suitable crystals for X-ray structure analyses were obtained under the following conditions. **4a**: Recrystallization from *n*-hexane at -30 °C, yellow blocks; **6**: recrystallization from *n*-hexane at room temperature, yellow blocks; **11** · 3 THF: recrystallization from *n*-pentane/THF (1:1), -30 °C, black plates. The experimental data for the X-ray diffraction studies on **4a**, **6**, and **11** are summarized in Table 2.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102683 (**4a**), CCDC-102684 (**6**), and CCDC-102685 (**11** · 3 THF). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 2. Crystal data and refinement for **4a**, **6**, and **11**.

	4a	**6**	**11**
formula	C$_{28}$H$_{33}$P$_3$Sn	C$_{38}$H$_{51}$P$_5$Sn	C$_{50}$H$_{67}$Co$_2$O$_3$P$_3$Sn
crystal size [mm]	0.50 × 0.40 × 0.40	0.50 × 0.40 × 0.30	0.80 × 0.40 × 0.30
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a [pm]	1086.9(1)	2194.9(3)	1400.2(4)
b [pm]	1122.6(1)	1012.1(2)	1832.3(3)
c [pm]	1333.0(1)	1750.6(3)	1931.1(3)
α [°]	75.79(1)	90.0	90.0
β [°]	85.88(1)	99.84(1)	99.12(2)
γ [°]	65.21(1)	90	90
V [nm^3]	1.4305(2)	3.832(1)	4.892(2)
Z	2	4	4
M_r	581.14	781.33	1045.50
ρ_{calcd} [g cm^{-1}]	1.349	1.354	1.420
F_{000}	592	1616	2160
ν(Mo$_{K\alpha}$) [mm^{-1}]	1.074	0.901	1.314
T (data coll.) [K]	293 (2)	298 (2)	190(2)
2θ range [°]	4.1 – 54.0	4.4 – 54.0	3.7 – 52.0
hkl range	−1/13, −13/13, −17/17	−28/27, −12/12, −5/22	−18/1, −23/1, −24/25
reflns measured	7125	10202	11553
reflns unique	6136	8347	9612
reflns observed[a]	4092	5222	6143
parameters	421	602	538
GooF	0.912	0.809	1.047
R (obs. refl. only)[a]	0.0509	0.0369	0.0601
*wR*2 (all refl.)	0.1552	0.0810	0.1467

[a] $F_0 \geq 4.0(F)$.

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