Transition Metal Stannyl Complexes, 12[◇]

Chelate-Assisted Oxidative Addition of Phenyl- and Alkyltin Groups to Nickel and Platinum

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Reaction of $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) with two equivalents of $Ph_2PCH_2CH_2SnPh_3$ or of $(Ph_3P)_2Pt(C_2H_4)$ with two equivalents of $Ph_2PCH_2CH_2SnR_3$ (R = Ph, Me, Bu) results in the immediate formation of the complexes $(R_3SnCH_2CH_2Ph_2P)M[PPh_2CH_2CH_2SnPh_2(M\text{–}Sn)](R)$ (M = Ni, Pt) with a *cis* arrangement of the two phosphorus atoms. The structure of $(Me_3SnCH_2CH_2Ph_2P)Pt[PPh_2CH_2CH_2SnMe_2(Pt\text{–}Sn)](Me)$ was confirmed by an X-ray structure analysis. In the presence of PPh_3, this complex shows dynamic behavior in solution due to $Ph_2PCH_2CH_2SnMe_3$/PPh_3 exchange. When the phosphanylalkylstannanes $Ph_2PCH_2CH_2SnPh_{3-x}Me_x$ (x = 1, 2) are employed in the reaction with $Ni(COD)_2$ or $(Ph_3P)_2Pt(C_2H_4)$, the Sn–Ph groups are more prone to oxidative addition than the Sn–Me groups. When $Ni(COD)_2$ is treated with one equivalent of $Ph_2PCH_2CH_2SnPh_3$ and PR'_3 (PCy_3 or PMe_2Ph) each, the complexes $(R'_3P)M(PPh_2CH_2CH_2SnPh_2)(Ph)(M\text{–}Sn)$ are formed. Heating of $(Ph_3SnCH_2CH_2Ph_2P)Ni[PPh_2CH_2CH_2SnPh_2(Ni\text{–}Sn)](Ph)$ to 70 °C induces the oxidative addition of a Sn–Ph group of the dangling ligand, and *cis*-$Ni[PPh_2CH_2CH_2SnPh_2(Ni\text{–}Sn)]_2$ is obtained. The same complex is formed upon reaction of $Ni(COD)_2$ with $Ph_2PCH_2CH_2SnPh_2H$. Reaction of $Ni(COD)_2$ with $Ph_2PCH_2CH_2SnMe_3$ results in the immediate formation of *trans*-$Ni[(PPh_2CH_2CH_2SnMe_2(Ni\text{–}Sn)]_2$.

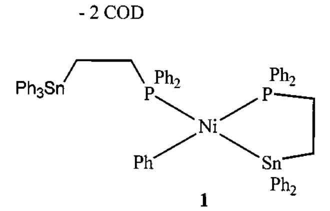
Contrary to Sn−H bonds that readily add to a variety of transition-metal complex fragments,[2] there are only few examples for the oxidative addition of non-activated Sn−C bonds. For example, $SnPh_4$ only adds to electron-rich fragments such as $(Ph_3P)_2Pt$ to give $(Ph_3P)_2Pt(SnR_3)(Ph)$.[3][4][5] Sn−Me bonds are even less reactive than Sn−Ph bonds.[6] The weaker Sn−C bonds in alkynylstannanes also add to less electron-rich metal centers.[7][8]

One of the possibilities to promote oxidative addition reactions is "chelate assistance", introduced by Stobart et al. for phosphanylalkylsilyl ligands with Si−H bonds.[9] We previously used this option to add Sn−C bonds to electron-rich Pd and Pt fragments[10] as well as to the less reactive $Fe(CO)_4$ fragment,[11] using ligands of the type $Ph_2P(CH_2)_nSnR_3$. Richmond et. al. observed reversible Sn−Ph addition in the reaction of a $SnPh_3$-substituted ethylenediamine derivative with $W(CO)_3(CH_3CN)_3$.[12] The concept was also extended to Si−Si and Si−Sn bonds.[13][14]

In the present paper, we first describe the reaction of $Ni(COD)_2$ with $Ph_2PCH_2CH_2SnR_3$. The results led us to re-examine some of our experiments with Pt compounds and to correct some of our previous results.[10]

Results and Discussion

When $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) was treated with two equivalents of $Ph_2PCH_2CH_2SnPh_3$ in THF, the color of the yellow solution changed to deep orange, and a broad signal in the ^{31}P-NMR spectrum at $\delta \approx 28$ indicated the immediate formation of phosphanenickel complexes. Additional stirring for 2.5 h resulted in the almost quantitative formation of the oxidative addition product **1** (Eq. 1) according to the ^{31}P-NMR spectrum.



(1)

1

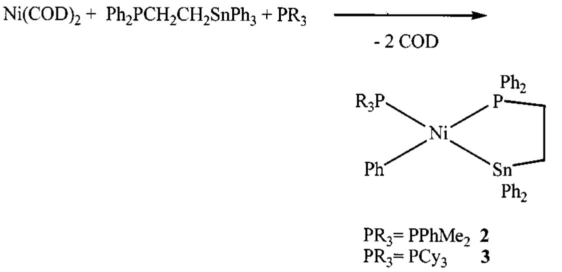
We were not able to separate traces of $Ph_2P(O)CH_2CH_2SnPh_3$ and unreacted $Ph_2PCH_2CH_2SnPh_3$. However, the structure of the complex was unequivocally confirmed by multinuclear NMR spectroscopy. The spectra are discussed in detail in the following paragraph because they are representative for most of the complexes reported in this paper.

[◇] Part 11: Ref.[1].

The $^{31}P\{^1H\}$-NMR spectrum of **1** showed the expected two doublet signals of an AB system. The resonance at $\delta = 58.3$ is attributed to the phosphorus atom in a five-membered ring because of the significant downfield shift of ca. 32 ppm relative to the resonance of the other phosphorus nucleus at $\delta = 26.1$. This downfield shift is a well-known phenomenon upon chelation,[15] and was also observed in the related Pt complexes $Pt[Ph_2PCH_2CH_2SiR_2(\mathit{Pt-Si})]_2$[9] and $(Ph_3P)Pt(Ph_2PCH_2CH_2SiR_2)(SiR_3)(\mathit{Pt-Si})$.[13] The $^2J_{PNiP}$ coupling constant of 6.1 Hz proved the *cis* disposition of the phosphorus nuclei. The $J_{117/119SnP}$ coupling constant of 219.8 Hz between the Sn and P nucleus at $\delta = 58.3$ of the chelate ring is typical for the *cis* position of both nuclei. On the other hand, the signal at $\delta = 26.1$ showed the typical *trans*-$^2J_{SnNiP}$ (^{117}Sn: 1065.9 Hz; ^{119}Sn: 1109.3 Hz) and an additional set of Sn satellites attributed to the $^3J_{117/119SnCCP}$ coupling within the dangling ligand. The NMR data confirm the *trans* position of the non-chelated ligand and the metal-bonded tin atom. The ^{119}Sn-NMR spectrum corroborates the assignment of the phosphorus resonances by showing a doublet of doublets at $\delta = 23.6$ for the tin atom bound to nickel, with *trans* $^2J_{119SnNiP}$ of 1116.9 Hz and J_{SnP} of 223 Hz. This resonance is distinctly shifted downfield by ca. 120 ppm relative to the resonance at $\delta = -97.6$ for the non-coordinated $SnPh_3$ group. This resonance appears as a doublet with the appropriate $^3J_{119SnCCP}$ of 183.8 Hz.

The ^{1}H-NMR spectrum lacked essential structural information because the methylene proton signals appear as complex multiplets superimposing each other (see Experimental Section). The only interesting feature is the resonance of the protons of the *Ni*-bonded phenyl group. Their multiplet was significantly shifted to higher field ($\delta = 6.75-7.05$), compared to the other phenyl resonances. This highfield shift seems to be a typical phenomenon for complexes of this kind because it is also reported for $(CO)_3Fe(Ph_2PCH_2CH_2SnPh_2)(Ph)(\mathit{Fe-Sn})$[11] and $(Ph_3P)Pt(Ph_2PCH_2CH_2SnPh_2)(Ph)(\mathit{Pt-Sn})$.[10] The ^{13}C-NMR spectrum confirms that there are two different phosphanylalkylstannane units in the molecule because of two separate resonances for the $SnCH_2$ and the PCH_2 group. While the resonances for the methylene carbon atoms of the dangling ligand appear as doublets due to the coupling with the phosphorus atom within the ligand, the resonances of the CH_2 groups of the chelating ligand appear as doublet of doublets because of the additional coupling with the other phosphorus nucleus. This observation seems reasonable if one takes into account that in this case the second phosphorus atom is in a kind of *transoid* position with respect to the carbon nuclei while in the first case the second phosphorus nucleus is *cisoid*. In the very complex range of the phenyl carbon signals no assignment for the *ipso*-carbon atom of the metal-bonded phenyl group was possible.

Since the second $Ph_2PCH_2CH_2SnPh_3$ in **1** just acts as a monodentate ligand, we also treated $Ni(COD)_2$ with a 1:1 mixture of $Ph_2PCH_2CH_2SnPh_3$ and $PPhMe_2$ or PCy_3 (Eq. 2). $(PhMe_2P)Ni(Ph_2PCH_2CH_2SnPh_2)(Ph)(\mathit{Ni-Sn})$ (**2**) was formed in 90% yield (^{31}P NMR) together with **1** and a small amount of $PhP(O)Me_2$ as by-products.



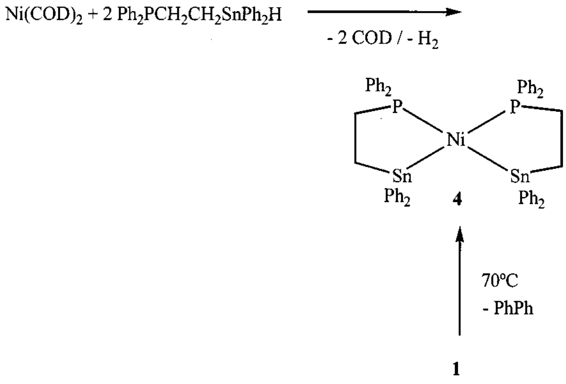
(2)

Unfortunately, **2** was even more difficult to purify than **1**. The reaction of PCy_3 resulted in almost quantitative formation of $(Cy_3P)Ni(Ph_2PCH_2CH_2SnPh_2)(Ph)(\mathit{Ni-Sn})$ (**3**) (^{31}P-NMR). It was possible to isolate the complex analytically pure as a yellow-brown powder by column chromatography. Contrary to **1**, it was even possible to assign the resonance for the *ipso*-carbon atom of the metal-bonded phenyl group. It appears at $\delta = 155.6$ (dd) with two $^2J_{PNiC}$ couplings of 59.2 and 7.9 Hz due to the *trans*- and *cis*-phosphorus nuclei. These values are in good agreement with those found for the *ipso*-carbon atom in $(Me_3P)_2Ni[CH_2C(CH_3)_2C_6H_4(\mathit{Ni-C})]$ ($\delta = 171.1$, *trans*-$^2J_{PNiC} = 79$ Hz).[16]

In the reaction with $Ph_2PCH_2CH_2SnPh_3$, nickel resembles platinum and does not parallel the reactivity pattern of palladium that formed the product of a double oxidative SnPh addition and consecutive reductive biphenyl elimination, *trans*-$Pd[Ph_2PCH_2CH_2SnPh_2(\mathit{Pd-Sn})]_2$.[10] Therefore, the possibility to induce a second SnPh oxidative addition was probed. Crude **1** was dissolved in toluene and heated to about 70°C for 9 h. Monitoring the reaction by ^{31}P-NMR spectroscopy showed a new singlet resonance at $\delta = 63.3$ with a double set of tin satellites. The coupling constants of 930.1 Hz (^{119}Sn), 891.0 Hz (^{117}Sn), and 161.1 Hz ($^{119/117}$Sn) are in the typical range for a *trans*- and a *cis*-tin nucleus relative to the phosphorus atoms, thus excluding *trans*-$Ni[Ph_2PCH_2CH_2SnPh_2(\mathit{Ni-Sn})]_2$.

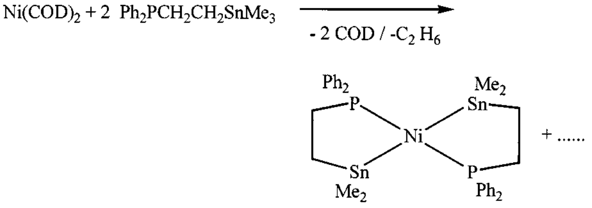
The singlet resonance in the ^{31}P-NMR spectrum is due to two equivalent phosphorus nuclei in molecules where both tin atoms are ^{118}Sn isotopes. A doublet-of-doublet resonance at $\delta = 56.8$ was observed (*trans*-$J_{119SnP} = 933.3$ and *cis*-$J_{119SnP} = 164.0$ Hz) in the ^{119}Sn-NMR spectrum. Even if one takes into account that the values given for the couplings are based on a first-order interpretation of the spectra because the resolution was too poor to observe all couplings needed for a interpretation as an ABXY spin system, the data clearly indicate the formation of the *cis* product **4** resulting from the oxidative addition of a second Sn−Ph bond (Eq. 3). Unfortunately, the course of the reaction was not completely straightforward because some decomposition occurred, and the resulting product still contained small amounts of **1** besides the impurities present in the starting complex.

We therefore prepared **4** independently from $Ni(COD)_2$ with two equivalents of $Ph_2PCH_2CH_2SnPh_2H$, utilizing the fact that Sn−H bonds are more prone to oxidative addition than Sn−C bonds. On addition of the phosphanylalkylstannane at room temperature, the color of the solution changed immediately, and gas evolution was observed after a short period. The yellow oil resulting after work-up showed the same resonances in the ^{31}P- and ^{119}Sn-NMR spectra as were observed in the thermal reaction of **1**. This proves that for SnH the second oxidative addition is facilitated, as expected (Eq. 3).



(3)

In the reaction of $Pd(PPh_3)_4$ with either $Ph_2PCH_2CH_2SnPh_3$ or $Ph_2PCH_2CH_2SnMe_3$, the *trans* complexes $Pd[PPh_2CH_2CH_2SnR($*Pd−Sn*$)]_2$ were formed.[10] Because of the somewhat surprising formation of the *cis* product **4** from **1** at elevated temperatures the question arises which isomer is obtained when $Ph_2PCH_2CH_2SnMe_3$ is treated with $Ni(COD)_2$ (Eq. 4).



(4)

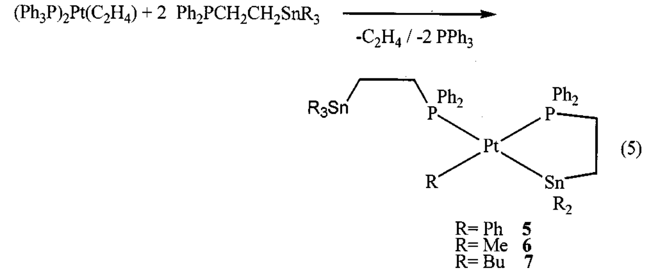
The ^{31}P-NMR spectrum of the residue obtained after removal of all volatiles showed two resonances. The one at δ = 30.6 with an Sn coupling of 149 Hz was assigned to $Ph_2P(O)CH_2CH_2SnMe_3$ as shown by the ^{31}P-NMR spectrum of a sample of $Ph_2P(O)CH_2CH_2SnMe_3$, independently prepared by oxidation of the phosphane with H_2O_2. Despite of the fact that all solvents were thoroughly dried and degassed, and air was excluded as far as possible by standard Schlenk techniques, it was impossible to suppress the formation of phosphane oxides completely. The fact that Ni^0 complexes, that are intermediates in the reactions, are very good catalysts in the phosphane oxidation by oxygen may be the reason that even very small traces of air led to significant phosphane oxidation. The singlet resonance at δ = 41.5 was assigned to *trans*-$Ni[Ph_2PCH_2CH_2SnMe_2($*Ni−Sn*$)]_2$ because of the typical *cis* coupling to $^{117/119}$Sn of 137.9 Hz and the equivalence of the two phosphorus nuclei (if both are ^{118}Sn). The *trans* conformation was confirmed by the virtual triplet observed in the ^{119}Sn spectrum at δ = 5.9 due to the inequivalence of the two phosphorus atoms in molecules with a ^{118}Sn and a ^{119}Sn nucleus. The triplet pattern is caused by the fact that $^2J_{SnNiP}$ and the "mixed" $^2J_{SnNiP}/^3J_{SnCCP}$ coupling constant have approximately the same value. Thus, in the case of $Ph_2PCH_2CH_2SnMe_3$, the outcome of the reaction of $Ni(COD)_2$ parallels that of Pd.

Comparing the higher reactivity of Sn−Ph bonds with that of Sn−Me it is somewhat surprising that elevated temperatures are needed to induce oxidative addition of a second Sn−Ph bond while the addition of a second Sn−Me bond takes place at room temperature. This may have steric reasons. Steric effects may also be responsible for the formation of different isomers in both reactions. In the reaction of the $SnPh_3$ derivative, the stereochemical outcome of the reaction is probably controlled by electronic reasons because all atoms bonded to the Ni center are equally substituted by phenyl groups. Contrary to that, steric factors may dominate in the reaction of the trimethylstannyl derivative, leading to the *trans* arrangement that minimizes the steric repulsion between the bulkier phosphane substituents.

The ligand $Ph_2PCH_2CH_2SnPh_2Me$ offers the possibility of either Sn−Ph or Sn−Me addition. Unfortunately, the reaction carried out as before was not straightforward. Nevertheless, the evolution of small amounts of gas was observed during the reaction. The ^{31}P-NMR spectrum of the residue after work-up showed two characteristic doublet resonances at δ = 57.9 and 25.3 ($^2J_{PNiP}$ = 6.1 Hz) for the main product. The reasonably close agreement of the NMR data with those of **1** (δ = 58.3, 26.1; $^2J_{PNiP}$ = 6.1 Hz) suggested that $(MePh_2SnCH_2CH_2Ph_2P)Ni[(PPh_2CH_2CH_2SnPhMe)($*Ni−Sn*$)](Ph)$ with a dangling phosphanylalkylstannane ligand is the main product. The tin satellites at the downfield signal with J_{SnP} = 213 Hz supported this interpretation. However, due to the poor resolution of the spectrum no tin satellites at the highfield signal were observed. A compound with a singlet resonance at δ = 42.5 was formed as a minor product. No tin satellites were resolved at this signal, but it can be supposed that due to the chemical shift and the gas evolution observed during reaction, *trans*-$Ni[Ph_2PCH_2CH_2SnPh_2($*Ni−Sn*$)]_2$ may be the by-product.

The somewhat different results for the oxidative addition of Sn−C bonds to Ni^0 compared to Pd^0 and the fact that we had found complexes of the type $(R_3SiSiR_2CH_2CH_2Ph_2P)Pt[PPh_2CH_2CH_2SiR_2($*Pt−Si*$)](SiR_3)$ in our previous investigations on chelate-assisted Si−Si oxidative addition to $(Ph_3P)_2Pt(C_2H_4)$, we re-checked the experiments on the Sn−C addition of phosphanylalkylstannanes to Pt^0 published by us some years ago.[10] First, we treated $(Ph_3P)_2Pt(C_2H_4)$ with two molar equivalents of $Ph_2PCH_2CH_2SnPh_3$ according to the published procedure and observed almost quantitative formation of a complex with the ^{31}P-NMR data in good agreement with those previously assigned to $(Ph_3P)Pt[Ph_2PCH_2CH_2SnPh_2($*Pt−Sn*$)](Ph)$ as product of this reaction. However, on scrutinizing the better data obtained now, we have to correct the assignment. Instead of the PPh_3 derivative, the complex

$(Ph_3SnCH_2CH_2Ph_2P)Pt[PPh_2CH_2CH_2SnPh_2($*Pt−Sn*$)](Ph)$ (**5**) was formed (Eq. 5).



(5)

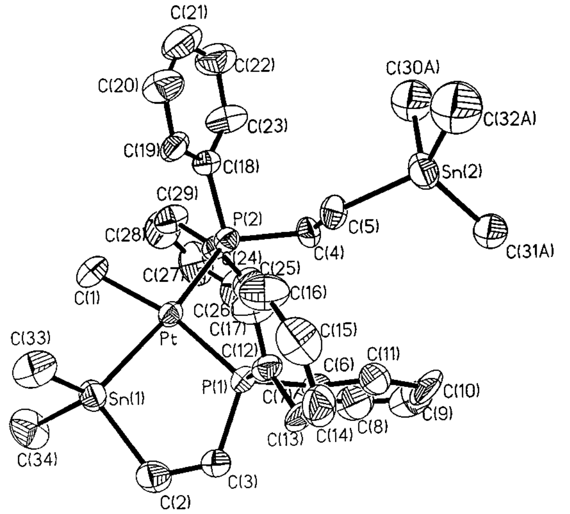
This is confirmed by the fact that a coupling to Sn (179.9 Hz) in the typical range for a $^3J_{SnCCP}$ was now observed at the resonance for the phosphorus of the non-chelated ligand. The ^{119}Sn-NMR spectrum also corroborates that there is a dangling phosphanylalkylstannane ligand because there is an additional doublet at $\delta = -97.5$ with the correct phosphorus coupling besides the doublet of doublets resonance for the chelated tin nucleus at $\delta = 97.2$. Complex **5** corresponds to the analogous Ni complex **1**. It therefore seemed reasonable to study whether a second oxidative Sn−Ph addition is also possible for Pt. However, a toluene solution of **5** heated to 70°C for 10 h and then analyzed by ^{31}P-NMR spectroscopy did not indicate any formation of the product of a second oxidative addition.

This led us to re-examine also the reaction of two equivalents $Ph_2PCH_2CH_2SnMe_3$ with $(Ph_3P)_2Pt(C_2H_4)$, for which we had previously postulated the formation of the Pt^{IV} complex $Pt[PPh_2CH_2CH_2SnMe_2($*Pt−Sn*$)]_2(Me)_2$.[10] On inspection of the better spectroscopic data obtained now we realized that the formerly observed doublet resonance in the ^{119}Sn-NMR spectrum is contradicting the proposed structure. The product was instead the Pt^{II} complex $(Me_3SnCH_2CH_2Ph_2P)Pt[PPh_2CH_2CH_2SnMe_2($*Pt−Sn*$)]$(Me) (**6**) (Eq. 5). The spectrum of the yellow oil left after removal of all volatiles from the reaction mixture mainly showed two broad resonances at $\delta \approx 55$ and 27, and a broad signal at $\delta = -3$ in the ^{31}P-NMR spectrum. The signals sharpened on lowering the temperature, and at 240 K the dynamic process was completely frozen. At this temperature, the expected spectrum for **6**, the typical AB pattern with the corresponding Sn satellites, was observed in addition to a sharp resonance for free PPh_3. The fact that the resonances of the dangling phosphorus ligand and the PPh_3 continually broaden on rising the temperature from 240 K to 360 K while the resonance of the ring-integrated phosphorus first broadens to a much smaller extend, and then re-sharpens (starting at about 310 K) indicates that the dynamic process is a $Ph_2PCH_2CH_2SnMe_3/PPh_3$ exchange at the Pt^{II} center. This suggestion is in agreement with results obtained for the complexes *cis*-$(Ph_3P)_2Pt(SiR_3)(H)$ where similar interchange processes with excess PPh_3 were observed[17]. The authors also observed the phenomenon that the resonance of the PPh_3 ligand *cis* to the silyl ligand that does not take part in the dynamic process is only slightly broadened.

To elucidate the role of the PPh_3 in the dynamic process, **6** was independently prepared from $Pt(COD)_2$. As expected, the product **6** formed in almost quantitative yield showed no dynamic features at room temperature because of the absence of PPh_3. On addition of PPh_3, a dynamic process was initiated similar to that observed for the product resulting from the reaction of $(Ph_3P)_2Pt(C_2H_4)$ at room temperature.

Colorless crystals of **6** suitable for an X-ray crystal structure analysis were obtained by diffusion of heptane into a concentrated benzene solution of the complex. The structure analysis proved the *cis* arrangement of the two phosphorus ligands with one dangling phosphanylalkylstannane (Figure 1). The Pt−C(1) distance [214 (1) pm] is in the normal range for $Pt-CH_3$ compounds (202−220 pm).[18]The Pt−Sn(1) bond length of 259.36(8) pm is significantly shorter than that in *trans*-$(Ph_3P)_2Pt(SnPh_3)(H)$ (265.4 pm).[19] This difference is reasonable if one takes into account the different influence of a hydride and a phosphane ligand. The P(1)−Pt−P(2) angle is widened [104.30(9)°] due to the steric repulsions between the bulky phenyl groups at the phosphorus atoms. This distortion from the regular square-planar arrangement is compensated by the angles C(1)−Pt−P(2), C(1)−Pt−Sn(1) and P(1)−Pt−Sn(1) being smaller than 90° [87.8(3), 85.3(3), and 82.55(7)°]. The latter is partially due to chelation. The methyl groups at the tin atom of the dangling ligand are disordered in the crystal.

Figure 1. ORTEP diagram of **6**; the hydrogen atoms are omitted for clarity[a]



[a] Selected bond lengths [pm] and angles [°]: Pt−C(1) 213.7(11), Pt−P(1) 227.4(3), Pt−P(2) 232.7(3), Pt−Sn(1) 259.36(8), Sn(1)−C(2) 213.7(11), P(1)−C(3) 184.5(10), P(2)−C(4) 187.2(9), Sn(2)−C(5) 213.1(10), Sn(1)−C(33) 213.0(11), Sn(1)−C(34) 215.0(12); C(1)−Pt−P(1) 167.4(3), C(1)−Pt−P(2) 87.8(3), P(1)−Pt−P(2) 104.30(9), C(1)−Pt−Sn(1) 85.3(3), P(1)−Pt−Sn(1) 82.55(7), P(2)−Pt−Sn(1) 173.13(7), C(33)−Sn(1)−C(34) 104.4(5), C(33)−Sn(1)−C(2) 109.2(5), C(34)−Sn(1)−C(2) 106.4(5), C(33)−Sn(1)−Pt 118.2(3), C(34)−Sn(1)−Pt 115.6(4), C(2)−Sn(1)−Pt 102.5(3), C(24)−P(2)−Pt 110.8(3), C(18)−P(2)−Pt 115.3(4), C(4)−P(2)−Pt 121.3(4), C(12)−P(1)−C(3) 103.7(5), C(6)−P(1)−C(3) 100.2(4), C(12)−P(1)−Pt 114.6(3), C(6)−P(1)−Pt 120.0(4), C(5)−C(4)−P(2) 114.8(7), C(3)−C(2)−Sn(1) 107.9(8), C(2)−C(3)−P(1) 113.2(7), C(4)−C(5)−Sn(2) 113.9(7).

Attempts to induce the oxidative addition of one of the SnMe bonds of the dangling ligand by heating a toluene solution of **6** to about 90°C for 10 h failed. The ^{31}P-NMR spectrum did not indicate any reaction.

Contrary to the results obtained for Ni^0, an increase of the steric bulk at the Sn atom by changing the methyl groups in the phosphanylethylstannane against butyl groups did not influence the general outcome of the reaction. Besides the main product $(Bu_3SnCH_2CH_2Ph_2P)Pt[PPh_2CH_2CH_2SnBu_2(\mathit{Pt-Sn})](Bu)$ (**7**) (formed in 90% yield according to the ^{31}P-NMR spectrum), a minor amount of $(Ph_3P)Pt[PPh_2CH_2CH_2SnBu_2(\mathit{Pt-Sn})](Bu)$ was observed as a by-product [^{31}P NMR(C_6D_6): $\delta = 53.9$ (d, $^2J_{PPtP} = 9.7$ Hz, $J_{117/119SnP} = 105.0$ Hz, $^1J_{PtP} = 1914.1$ Hz), 32.1 (d, $^2J_{PPtP} = 9.7$ Hz, $^2J_{119SnNiP} = 1666.3$ Hz, $^2J_{117SnPtP} = 1597.9$, $^1J_{PtP} = 2119.2$].

The use of the previously unknown derivative $Ph_2PCH_2CH_2SnMe_2Ph$, synthesized similar to its congeners by radical addition of $PhMe_2SnH$ to $CH_2{=}CHPPh_2$, led to the formation of $(PhMe_2SnCH_2CH_2Ph_2P)Pt[PPh_2CH_2CH_2SnMe_2(\mathit{Pt-Sn})](Ph)$ (**8**) and thus corroborates the fact that SnPh addition is favored over SnMe addition. The exclusive formation of the product of Sn−Ph activation was proven in the ^{1}H-NMR spectrum by a slightly broadened singlet resonance for the methyl groups at the metal-bonded Sn with a coupling to platinum of 7.3 Hz. This coupling constant was too small a value for $^2J_{PtCH}$, but in good agreement with a $^3J_{PtSnCH}$ coupling. The proton signals of the Pt−Ph moiety once again show the significant high-field shift and appear at $\delta = 6.87-6.98$. The ^{13}C-NMR spectrum in the range for the sp^2-carbon atoms and their Pt satellites is very complex. Therefore, no assignments are possible. The complexes **7** and **8** are not dynamic at room temperature in the presence of PPh_3.

Conclusions

The present and our previous results on corresponding palladium complexes,[10] allow to draw a complete picture on the reactivity pattern of $Ph_2PCH_2CH_2SnR_3$ (R = Me, Ph) with complexes of the zero-valent metals of the nickel triad. For R = phenyl, the reactivity of $Ni(COD)_2$ parallels that of $(Ph_3P)_2Pt(C_2H_4)$. Complexes of the type $(Ph_3SnCH_2CH_2Ph_2P)M[PPh_2CH_2CH_2SnPh_2(\mathit{M-Sn})](Ph)$ [M = Ni (**1**), Pt (**5**)], with a dangling $Ph_2PCH_2CH_2SnR_3$ ligand and a *cis* disposition of the two phosphorus atoms, were formed in both cases. For the nickel complex **1**, the oxidative addition of an Sn−Ph bond of the dangling $Ph_2PCH_2CH_2SnR_3$ ligand was observed at elevated temperatures during which the *cis* arrangement of the phosphorus atoms was retained. The resulting complex is *cis*-$Ni[PPh_2CH_2CH_2SnPh_2(\mathit{Ni-Sn})]_2$ (**4**). The same reaction was not observed for the corresponding Pt complex **5**. The higher reactivity of Ni for the formation of the second chelate ring by oxidative addition of an Sn−Ph bond of the dangling phosphanylalkylstannyl ligand is somewhat surprising, because the heavier metals in a group are more prone to oxidative addition reactions. The driving force for the formation of **4** from **1** therefore may be the easier reductive elimination of biphenyl from the intermediate Ni^{IV} complex.

In the corresponding reactions of the tri*methyl*stannyl derivative $Ph_2PCH_2CH_2SnMe_3$ the reactivity pattern of $Ni(COD)_2$ parallels that of $Pd(PPh_3)_4$. In both cases the bischelated complexes *trans*-$M[PPh_2CH_2CH_2SnMe_2(\mathit{M-Sn})]_2$ were formed, while the reaction with $(Ph_3P)_2Pt(C_2H_4)$ stopped at the stage of the mono-chelated complex *cis*-$(Me_3SnCH_2CH_2Ph_2P)Pt[(PPh_2CH_2CH_2SnMe_2)(\mathit{Pt-Sn})](Me)$ (**6**). The change in geometry of $Ni[PPh_2CH_2CH_2SnMe_2(\mathit{Ni-Sn})]_2$ compared to the $SnPh_2$ derivative (**4**) is probably caused by steric effects overriding the electronic preference of the *cis* isomer.

When the phosphanylalkylstannanes $Ph_2PCH_2CH_2SnPh_{3-x}Me_x$ (x = 1, 2) are employed, there is the possibility of either Sn−Ph or Sn−Me oxidative addition. For both Ni^0 and Pt^0, the Sn−Ph groups are more prone to oxidative addition than the Sn−Me groups, as was previously observed by us for Fe complexes.[11]

Complex **6**, whose structure was unambiguously confirmed by an X-ray structure analysis, showed dynamic behavior in the presence of PPh_3 that may be attributed to a $PPh_3/Ph_2PCH_2CH_2SnMe_3$ exchange process.

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Experimental Section

All operations were carried under dry and oxygen-free argon by standard Schlenk-tube techniques. All solvents were dried by standard procedures, saturated with argon and stored over molecular sieves. The THF used was freshly distilled from potassium. The phosphanylalkylstannanes were synthesized according to literature procedures[11][20] from $Ph_2P(C_2H_3)$ and $HSnR_3$. − The NMR spectra were recorded with a Bruker AC 250 spectrometer. ^{1}H- and ^{13}C-NMR data were referenced against the solvent resonances, while ^{31}P- and ^{119}Sn-NMR data were referenced against the external standards 85% H_3PO_4 and $SnMe_4$. Integrations of the ^{1}H-NMR signals are omitted if there are overlaps with residual proton resonances of the deuterated solvents (especially C_6D_6). − DSC analyses were performed with a Shimadzu Thermal Analyzer DSC 50. The expression J_{XY} is used for those cases where coupling is possible through different nuclei.

Preparation of $(Ph_3SnCH_2CH_2PPh_2)Ni(Ph)[Ph_2PCH_2CH_2SnPh_2(Ni-Sn)]$ (**1**): An amount of 922 mg (1.63 mmol) of $Ph_2PCH_2CH_2SnPh_3$ was added to a solution of 213 mg (0.77 mmol) of $Ni(COD)_2$ in 25 ml of THF. The color of the yellow solution immediately turned to deep orange. After additional 2.5 h of stirring at room temperature, the reaction mixture was yellowish brown. Then the solvent and most of the COD was removed in vacuo at 40°C, leaving a slightly oily golden brown residue that contained **1** as the main product, according to the ^{31}P-NMR spectrum. Neither recrystallisation nor column chromatography on silica with common organic solvents resulted in analytically pure samples of **1**. − ^{31}P NMR (101.25 MHz, C_6D_6): $\delta = 58.3$ (d, $^2J_{PNiP} = 6.1$ Hz, $J_{117/119SnP} = 219.8$ Hz), 26.1 (d, $^2J_{PNiP} = 6.1$ Hz, $^2J_{119SnNiP} = 1109.3$ Hz, $^2J_{117SnNiP} = 1065.9$ Hz, $^3J_{SnCCP} = 183.0$ Hz). − ^{119}Sn NMR (93.276 MHz, C_6D_6) δ 23.6 (dd, $^2J_{SnNiP} = 1116.7$ Hz, $J_{SnP} = 223$ Hz), −97.6 (d, $^3J_{SnCCP} = 183.8$ Hz). − ^{13}C NMR (62.90 MHz, C_6D_6): $\delta = 3.9$ (d, $SnCH_2$, $^2J_{PCC} = 5.1$ Hz), 6.3 (dd, $SnCH_2$, $^{2}J_{\mathrm{PCC}}$ = 31.7 Hz, J_{PC} = 13.4 Hz), 23.7 (d, PCH_2, $^{1}J_{\mathrm{PC}}$ = 11.5 Hz), 32.6 (dd, PCH_2, $^{1}J_{\mathrm{PC}}$ = 24.5 Hz, J_{PC} = 7.9 Hz), 127.8−146.5 (C_6H_5). − ^{1}H NMR (250.130 MHz, C_6D_6): δ = 1.01−1.38 (m, overlapping $SnCH_2$), 1.59−1.84 (m, PCH_2), 2.40−2.61 (m, PCH_2), 6.75−7.05 (m, NiC_6H_5), 7.00−7.62 (m, C_6H_5).

Preparation of (PhMe$_2$P)Ni(Ph)[Ph$_2$PCH$_2$CH$_2$SnPh$_2$(Ni−Sn)] (**2**): A solution of 51 mg (0.37 mmol) of $PhPMe_2$ and 207 mg (0.37 mmol) of $Ph_2PCH_2CH_2SnPh_3$ in 6 ml of THF was added to a solution of 101 mg (0.37 mmol) of $Ni(COD)_2$ in 10 ml of THF. The mixture turned orange and, during further stirring for 4 h, yellow-brown. After removal of all volatiles, a sticky yellowish brown residue was obtained. It contained 90% of **2** and some **1** and $PhP(O)Me_2$ according to the NMR spectra. − ^{31}P NMR (101.25 MHz, C_6D_6): δ = 60.0 (d, $^{2}J_{\mathrm{PNiP}}$ = 4.2 Hz, $J_{\mathrm{117/119SnP}}$ = 239.0 Hz), −6.8 (d, $^{2}J_{\mathrm{PNiP}}$ = 4.2 Hz, $^{2}J_{\mathrm{119SnNiP}}$ = 1199.5 Hz, $^{2}J_{\mathrm{117SnNiP}}$ = 1150.3 Hz). − ^{119}Sn NMR (93.276 MHz, C_6D_6): δ = 35.0 (dd, $^{2}J_{\mathrm{SnNiP}}$ = 1199.1 Hz, J_{SnP} = 239.1 Hz). − ^{13}C NMR (62.90 MHz, C_6D_6): δ = 6.2 (dd, $SnCH_2$, $^{2}J_{\mathrm{PCC}}$ = 31.1 Hz, $^{3}\mathrm{J}_{\mathrm{PNiSnC}}$ = 11.0 Hz), 12.9 (d, PCH_3, $^{1}J_{\mathrm{PC}}$ = 22.6 Hz), 32.9 (dd, PCH_2, $^{1}J_{\mathrm{PC}}$ = 33.0 Hz, $^{3}\mathrm{J}_{\mathrm{PNiPC}}$ = 9.2 Hz, 126.7−146.8 (C_6H_5). − ^{1}H NMR (250.130 MHz, C_6D_6): δ = 0.73 (d, PCH_3, $^{2}J_{\mathrm{PCH}}$ = 6.1 Hz), 1.17−1.33 (m, $SnCH_2$), 2.59−2.78 (m, PCH_2), 6.90−7.73 (m, C_6H_5).

Preparation of (Cy$_3$P)Ni(Ph)[Ph$_2$PCH$_2$CH$_2$SnPh$_2$(Ni−Sn)] (**3**): A solution of 258 mg (0.92 mmol) of PCy_3 and 518 mg (0.92 mmol) of $Ph_2PCH_2CH_2SnPh_3$ in 5 ml benzene was added to a suspension of 252 mg (0.92 mmol) of $Ni(COD)_2$ in 15 ml of heptane. A red-brown solution formed almost immediately. After additional stirring for 4 h, during which the color slightly lightened, the solution was filtered through glass wool. From the resulting deep red solution all volatiles were removed in vacuo. The remaining golden-red oil was chromatographed on silica gel with Et_2O/petroleum ether (1:50). The complex **3** was eluted as a deep yellow zone. After removal of the solvent, 620 mg (75%) of **3** was obtained as a brown-yellow powder. M.p. 69°C (dec.). − $C_{50}H_{62}P_2NiSn$ (902.3): calcd. C 66.6, H 6.93; found C 65.9, H 6.81. − ^{31}P NMR (101.250 MHz, C_6D_6): δ = 51.9 (d, $^{2}J_{\mathrm{PNiP}}$ = 8.6 Hz, J_{119SnP} = 222.2 Hz, J_{117SnP} = 206 Hz), 22.5 (d, $^{2}J_{\mathrm{PNiP}}$ = 8.6 Hz, $^{2}J_{\mathrm{119SnNiP}}$ = 1036.3 Hz, $^{2}J_{\mathrm{117SnNiP}}$ = 991.2 Hz). − ^{119}Sn NMR (93.276 Hz, C_6D_6): δ = 16.7 (dd, $^{2}J_{\mathrm{119SnNiP}}$ = 1036.3 Hz, $^{2}J_{\mathrm{119SnNiP}}$ = 218.7 Hz). − ^{13}C NMR (62.90 MHz, C_6D_6): δ = 5.2 (dd, $SnCH_2$, $^{2}J_{\mathrm{PCC}}$ = 29.6 Hz, $^{3}J_{\mathrm{PNiSnC}}$ = 12.2 Hz), 32.7 (dd, PCH_2 $^{1}J_{\mathrm{PC}}$ = 31.4 Hz, $^{2}J_{\mathrm{PNiPC}}$ = 6.9 Hz), 34.7 (d, $^{1}J_{\mathrm{PC}}$ = 11.6 Hz), 30.7 (s), 27.8 (d, J_{PC} = 9.4 Hz), 26.8 (s), signals of PCy_3, 121.1−156.2 (C_6H_5), 155.6 (dd, NiC, $^{2}J_{\mathrm{PNiC}}$ = 59.2 Hz, $^{2}J_{\mathrm{PNiC}}$ = 7.9 Hz). − ^{1}H NMR (250.130 MHz, C_6D_6): δ = 0.93−0.98 (m, $SnCH_2$, 2 H), 1.15 (s, br.) 1.51−1.80 (m) (cyclohexyl, 33 H), 2.65−2.87 (m, PCH_2, 2 H), 6.95−7.10 (m, NiC_6H_5), 7.07−7.79 (m, C_6H_5).

Thermal Reaction of **1**: An amount of 350 mg of the crude complex **1** was dissolved in 20 ml of toluene and heated in a sealed Schlenk tube for 9 h to 70°C. Then the solvent was removed in vacuo. The oily yellowish brown residue was analyzed by ^{31}P- and ^{119}Sn-NMR spectroscopy, which showed partial formation of Ni[Ph$_2$PCH$_2$CH$_2$SnPh$_2$(*Ni−Sn*)]$_2$ (**4**) and some decomposition. The reaction products could not be separated. The NMR data are given in the next paragraph.

Preparation of Ni[(Ph$_2$PCH$_2$CH$_2$SnPh$_2$(Ni−Sn)]$_2$ (**4**) *from Ph$_2$*PCH$_2$CH$_2$SnPh$_2$H: A solution of 400 mg (0.82 mmol) of $Ph_2PCH_2CH_2SnPh_2H$ in 6 ml of THF was added to a yellow solution of 108 mg (0.41 mmol) of $Ni(COD)_2$ in 10 ml of THF. The reaction mixture immediately turned red, and a gas was evolved. During additional 3 h of stirring, the color of the solution lightened to yellowish brown with further weak gas evolution. Then all volatiles were removed in vacuo leaving a yellowish brown oily residue containing **4** in about 85% yield, as confirmed by ^{31}P- and ^{119}Sn-NMR spectroscopy. Washing the residue twice with 3 ml of pentane each left a slightly oily yellowish brown powder that still contained some impurities that could not be removed. − ^{31}P NMR (101.250 MHz, C_6D_6): δ = 63.3 (s, $^{2}J_{\mathrm{119SnNiP}}$ = 930.5 Hz, $^{2}J_{\mathrm{117SnNiP}}$ = 891.1 Hz, $J_{\mathrm{117/119SnP}}$ = 161.1 Hz. − ^{119}Sn NMR (93.276 MHz, C_6D_6): δ = 56.8 (dd, $^{2}J_{\mathrm{PNiSn}}$ = 933.3 Hz, J_{SnP} = 164.0 Hz).

Reaction of Ni(COD)$_2$ with Ph$_2$PCH$_2$CH$_2$SnMe$_3$: A solution of 1.47 g (3.86 mmol) of $Ph_2PCH_2CH_2SnMe_3$ in 8 ml of THF was added to a solution of 532 mg (1.93 mmol) of $Ni(COD)_2$ in 40 ml of THF. The resulting red solution was stirred for 3 h during which a gas evolved and the color of the solution deepened. The red-brown solution was concentrated in vacuo, and the resulting yellow-brown slightly sticky residue was analyzed by ^{31}P- and ^{119}Sn-NMR spectroscopy. − ^{31}P NMR (101.250 MHz, C_6D_6): δ = 41.5 (s, J_{SnP} = 137.9 Hz). − ^{119}Sn NMR (93.276 MHz, C_6D_6): δ = 5.9 (t).

Reaction of Ni(COD)$_2$ with Ph$_2$PCH$_2$CH$_2$SnPh$_2$Me: A solution of 1.08g (2.16 mmol) of $Ph_2PCH_2CH_2SnPh_2Me$ in 5 ml of THF was added to 297 mg (1.08 mmol) $Ni(COD)_2$, dissolved in 20 ml of THF. The deep red solution was stirred for 4 h while a small amount of gas was evolved. Removal of all volatiles in vacuo left a brown oil. − ^{31}P NMR (101.250 MHz, C_6D_6): δ = 57.9 (d, $^{2}J_{\mathrm{PNiP}}$ = 6.1 Hz, $J_{\mathrm{117/119SnP}}$ = 213 Hz), 25.3 (d, $^{2}J_{\mathrm{PNiP}}$ = 6.1 Hz).

Preparation of (Ph$_3$SnCH$_2$CH$_2$Ph$_2$P)Pt[PPh$_2$CH$_2$CH$_2$SnPh$_2$-(Pt−Sn)](Ph) (**5**): A solution of 193 mg (0.35 mmol) of $Ph_2PCH_2CH_2SnPh_3$ in 3 ml of benzene was added to a solution of 117 mg (0.17 mmol) of $(Ph_3P)_2Pt(C_2H_4)$ in 12 ml of benzene. An immediate color change to bright yellow and gas evolution occurred. The solution was stirred for additional 10 h at room temperature, resulting in a pale yellow solution. A yellow oil remained after removal of all volatiles in vacuo. Complex **5** was obtained as a pale yellow powder on washing the oil three times with 5 ml of petroleum ether each at 0°C and drying in vacuo. Yield 128 mg (57%). M.p. 95°C (dec.). − $C_{64}H_{58}P_2PtSn_2$ (1321.6): calcd. C 58.2, H 4.42; found C 57.9, H 4.30. − ^{31}P NMR (101.250 MHz, C_6D_6): δ = 51.8 (d, $^{2}J_{\mathrm{PPtP}}$ = 11.0 Hz, $^{1}J_{\mathrm{PtP}}$ = 2020.2 Hz, J_{SnP} = 115.0 Hz), 24.1 (d, $^{2}J_{\mathrm{PPtP}}$ = 11.0 Hz, $^{1}J_{\mathrm{PtP}}$ = 2184.9 Hz, $^{2}J_{\mathrm{119SnPtP}}$ = 1712.6 Hz, $^{2}J_{\mathrm{117SnPtP}}$ = 1635.7 Hz, $^{3}J_{\mathrm{SnCCP}}$ = 179.4 Hz). − ^{119}Sn NMR (93.276 MHz, C_6D_6): δ = 97.2 (dd, $^{2}J_{\mathrm{119SnPtP}}$ = 1711.5 Hz, J_{119SnP} = 117.0 Hz), −97.5 (d, $^{3}J_{\mathrm{119SnCCP}}$ = 180.6 Hz). − ^{13}C NMR (62.90 MHz, C_6D_6): δ = 4.1 (d, $^{2}J_{\mathrm{PCC}}$ = 7.5 Hz, $SnCH_2$), 5.2 (dd, $^{2}J_{\mathrm{PCC}}$ = 23.6 Hz, $^{3}J_{\mathrm{PPtSnC}}$ = 12.0 Hz, $SnCH_2$), 24.4 (d, $^{1}J_{\mathrm{PC}}$ = 20.8 Hz, PCH_2) 36.6 (dd, $^{1}J_{\mathrm{PC}}$ = 37.5 Hz, J_{PC} = 8.8 Hz, PCH_2), 124.3−156.3 (C_6H_5, no assignment was possible due to different phenyl groups and Pt satellites). − ^{1}H NMR (250.130 MHz, C_6D_6): δ = 0.80−1.28 (m, overlapping, 4 H, $SnCH_2$), 2.15−2.32 (m, 2 H, PCH_2), 2.45−2.68 (m, 2 H, PCH_2), 6.78−7.73 (m, C_6H_5).

Preparation of (Me$_3$SnCH$_2$CH$_2$Ph$_2$P)Pt[PPh$_2$CH$_2$CH$_2$SnMe$_2$-(Pt−Sn)](Me) (**6**). − *Method a:* A solution of 128 mg (0.17 mmol) of $(Ph_3P)_2Pt(C_2H_4)$ in 10 ml of benzene was treated with 130 mg (0.35 mmol) of $Ph_2PCH_2CH_2SnMe_3$ in 4 ml of benzene at room temperature for 12 h. After removal of the solvent in vacuo, an orange oil remained. The product was crystallized from a concentrated benzene solution by heptane diffusion as pale yellow crystals in 55% yield (89 mg). M.p. 132°C. − $C_{34}H_{46}P_2PtSn_2$ (949.2): calcd. C 43.0, H 4.88, found C 43.4, H 4.65.

Method b: To a beige solution of 131 mg (0.32 mmol) of $Pt(COD)_2$ in 3 ml of benzene, 242 mg (0.64 mmol) of

$Ph_2PCH_2CH_2SnMe_3$ was added, resulting in a color change to yellow-brown. On stirring for 16 h, the color of the reaction mixture became lighter. All volatiles were removed in vacuo after filtration through glass wool, and the remaining slightly oily solid was washed twice at 0°C with 3 ml of pentane each. After drying, **6** was obtained as a beige powder (210 mg, 69%).

^{31}P NMR (101.250 MHz, C_6D_6): $\delta = 55.9$ (d, $^2J_{PPtP} = 7.3$ Hz, $^1J_{PtP} = 2152.2$ Hz, $J_{SnP} = 108.6$ Hz), 27.9 (d, $^2J_{PPtP} = 7.3$ Hz, $^1J_{PtP} = 2065.5$ Hz, $^2J_{119SnPtP} = 1726.2$ Hz, $^2J_{117SnPtP} = 1696.8$ Hz, $^3J_{SnCCP} = 213.6$ Hz). − ^{119}Sn NMR (93.276 MHz, C_6D_6): $\delta = 147.2$ (dd, $^2J_{119SnPtP} = 1732.1$ Hz, $J_{119SnP} = 111.9$ Hz), −29.5 (d, $^3J_{119SnCCP} = 218.7$ Hz). − ^{13}C NMR (62.90 MHz, [D$_8$]toluene): $\delta = -11.7$ (dd, *trans*-$^2J_{PPtC} = 82.9$ Hz, *cis*-$^2J_{PPtC} = 7.6$ Hz, $PtCH_3$), −9.6 (s, $SnCH_3$), −6.5 (d, $^3J_{PPtSnC} = 8.2$ Hz, $^2J_{PtSnC} = 78.5$ Hz, $SnCH_3$), 5.8 (s, br., $SnCH_2$), 6.1 (d, $J_{PC} = 13.1$ Hz, $SnCH_2$), 25.4 (d, br., $^1J_{PC} = 12.0$ Hz, PCH_2), 39.4 (dd, $^1J_{PC} = 39.2$ Hz, $J_{PC} = 8.7$ Hz, PCH_2). − ^{1}H NMR (250.130 MHz, [D$_8$]toluene): $\delta = -0.11$ (s, $^2J_{SnCH} = 51.3$ Hz, 9 H, $SnCH_3$), 0.55 (s, $^2J_{SnCH} = 41.5$ Hz, $SnCH_3$, 6H), 0.65 (d, $^3J_{PPtCH} = 6.1$ Hz, $PtCH_3$), 0.71− 0.95 (m, $SnCH_2$), 1.44−1.52 (m, $^2J_{117/119SnCH} \approx 59$ Hz, 2 H, $SnCH_2$), 2.03−2.12 (m, PCH_2), 2.48−2.61 (m, PCH_2, 2 H), 6.98−7.75 (m, C_6H_5).

Preparation of (Bu$_3$SnCH$_2$CH$_2$Ph$_2$P)Pt[PPh$_2$CH$_2$CH$_2$SnBu$_2$-(Pt−Sn)](Bu) (**7**): The reaction was carried out in benzene as described for **6**, using 160 mg (0.22 mmol) of $(Ph_3P)_2Pt(C_2H_4)$ and 227 mg (0.45 mmol) of $Ph_2PCH_2CH_2SnBu_3$. Removal of all volatiles in vacuo resulted in a yellow oil (consisting of **7** in about 90% yield according to the ^{31}P-NMR spectrum). By washing the oil twice with 8 ml of pentane each and drying in vacuo, a yellow powder was obtained that contained **7** and only traces of impurities according to the ^{31}P-NMR spectrum. − ^{31}P NMR (101.25 MHz, C_6D_6): $\delta = 53.2$ (d, $^2J_{PPtP} = 9.3$ Hz, $^1J_{PtP} = 1899.5$ Hz, $J_{117/119SnP} = 110.2$ Hz), 27.9 (d, $^2J_{PPtP} = 9.3$ Hz, $^1J_{PtP} = 2097.2$ Hz, $^2J_{119SnPtP} = 1671.2$ Hz, $^2J_{117SnPtP} = 1596.7$ Hz, $^3J_{119SnCCP} = 185.6$ Hz, $^3J_{117SnCCP} = 178.2$ Hz). − ^{119}Sn NMR (93.276 MHz, C_6D_6): $\delta = 175.8$ (dd, $^2J_{119SnPtP} = 1673.4$ Hz, $J_{119SnP} = 111.9$ Hz), −4.8 (d, $^3J_{PCC119Sn} = 185.7$ Hz). − ^{1}H NMR (250.130 MHz, C_6D_6): $\delta = 0.75-1.96$ (complex overlapping multiplets of butyl groups and $SnCH_2$), 2.20−2.51 (m, PCH_2), 2.65−2.80 (m, PCH_2) 6.99−7.90 (m, C_6H_5).

Preparation of (PhMe$_2$SnCH$_2$CH$_2$Ph$_2$P)Pt[PPh$_2$CH$_2$-CH$_2$SnMe$_2$(Pt−Sn)](Ph) (**8**): An amount of 123 mg (0.16 mmol) of $(Ph_3P)_2Pt(C_2H_4)$ and 144 mg (0.16 mmol) of $Ph_2PCH_2CH_2SnMe_2Ph$ was treated as described above. After removal of all volatiles, the yellow oil was analyzed by multinuclear NMR which indicated the almost quantitative formation of **8** according to ^{31}P NMR. − ^{31}P NMR (101.250 MHz, C_6D_6): $\delta = 52.8$ (d, $^2J_{PPtP} = 11.0$ Hz, $^1J_{PtP} = 2116.0$ Hz, $J_{117/119SnP} = 104.1$ Hz), 24.4 (d, $^2J_{PPtP} = 11.0$ Hz, $^1J_{PtP} = 2046.2$ Hz, $^2J_{119SnPtP} = 1572,3$ Hz, $^2J_{117SnPtP} = 1503.7$ Hz, $^3J_{119/117SnCCP} = 200.0$ Hz). − ^{119}Sn NMR (93.276 MHz, C_6D_6): $\delta = 161.2$ (dd $^2J_{119SnPtP} = 1572.9$ Hz, $J_{119SnP} = 104.4$ Hz) −25.5 (d, $^3J_{119SnCCP} = 208.0$ Hz). − ^{13}C NMR (62.90 MHz, C_6D_6): $\delta = -11.1$ [s, $Sn(CH_3)_2Ph$], −7.4 [d, $^3J_{PPtSnC} = 6.9$ Hz, $^2J_{PtSnC} = 74.9$ Hz, $Sn(CH_3)_2$], 3.7 (d, $^2J_{PCC} = 7.4$ Hz, $SnCH_2$), 6.6 (d, $^2J_{PCC} = 16.2$, $SnCH_2$), 25.4 (d, br., $^1J_{PC} = 18.5$ Hz, PCH_2) 37.6 (dd, $^1J_{PC} = 38.4$ Hz, $J_{PC} = 8.8$ Hz, PCH_2), 121.9−156.6 (C_6H_5, no assignment possible due to different phenyl groups and Pt satellites). − ^{1}H NMR (250.13 MHz, C_6D_6): $\delta = 0.04$ (s, $^2J_{SnCH} = 53.0$ Hz, 6 H, $SnCH_3$), 0.36 (s, br, $^3J_{PtSnCH} = 8.1$ Hz, 6 H, $SnCH_3$), 0.58−0.73 (m, $SnCH_2$), 1.05−1.19 (m, $SnCH_2$), 2.09−2.21 (m, 2 H, PCH_2), 2.53−2.67 (m, 2 H, PCH_2), 6.87−6.98 (m, 5 H, PtC_6H_5), 7.10−7.86 (m, C_6H_5).

X-ray Structure Analysis of **6**: Triclinic, space group $P1$, $a = 1241.42(1)$, $b = 1280.91(2)$, $c = 1578.98(3)$ pm, $\alpha = 66.396(1)$, $\beta = 69.796(1)$, $\gamma = 66.749(1)°$, $V = 2060.91 \cdot 10^6(3)$ pm^3, $d_{calcd.} = 1.655$ g cm^{-3} for $Z = 2$. $F(000) = 1000$, $\mu(\text{Mo-}K_\alpha) = 4.690$ mm^{-1}, $\lambda = 71.073$ pm, $T = 302$ K, crystal size = 0.5 × 0.4 × 0.25 mm. A crystal was sealed in a glass capillary and mounted on a Siemens SMART diffractometer with a CCD area detector. A hemisphere of data was collected by a combination of three sets of exposures (17343 reflections). Each set had a different ϕ angle for the crystal, and each exposure took 15 s and covered 0.3° in ω ($2.9° \leq 2\Theta \leq 60.1°$). The crystal-to-detector distance was 3.85 cm. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was applied (11897 unique reflections). The structure was solved by the Patterson method (SHELS86). Refinement was carried out with the full-matrix least-squares method based on F^2 (SHELXL93) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. Refinement converged at $R_1 = 0.0595$ [for 1847 reflections with $I > 2\sigma(I)$], $wR_2 = 0.1344$ $\{w = [\sigma^2(F_o)^2 + (0.0 \cdot x\, P)^2 + x \cdot P]^{-1}$, where $P = (F_o{}^2 + 2F_c{}^2)/3\}$; final GOF = 0.511. The final difference map showed no peak larger than +2.008 e $^{-3}$ and no hole larger than −1.243 e $^{-3}$.[21]

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[21] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge C82 1EZ, UK [fax: int. code +(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk] quoting the depository number CCDC-101015.

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