Molecular Structure and Dynamics of 1,3-Distanna-2-Platina-[3]Ferrocenophanes

Max Herberhold,* Udo Steffl, Wolfgang Milius, and Bernd Wrackmeyer

Dedicated to Professor Achim Müller on the occasion of his 60th birthday

Abstract: The reaction of bis(triphenylphosphane)(ethene)platinum(0) (**1**) with organotin compounds such as hexamethyldistannane (**2**), 1,1,2,2-tetramethyl-1,2-distanna[2]ferrocenophane (**3**), bis(trimethylstannyl)ethyne (**4′**), and trimethylstannylethynyl-bis(diethylamino)borane (**4″**) affords—under liberation of ethene and cleavage of the Sn–Sn bond—the bis(triphenylphosphane)platinum(II) complexes **5a**–**8a**. Displacement of the triphenylphosphane ligands (**a**) from the 1,3-distanna-2-bis(triphenylphosphane)platina[3]-ferrocenophane (**6a**) by various chelating diphosphanes [$Ph_2P(CH_2)_nPPh_2$ with $n = 1-3$ (**b**, **c**, **d**, respectively), *cis*-$Ph_2PCH{=}CHPPh_2$ (**e**), $Fe(C_5H_4-PPh_2)_2$ (**f**), and 4,5-bis(diphenylphospinomethyl)-2,2-dimethyl-1,3-dioxalane (DIOP, **g**)] leads to the corresponding complexes **6b**–**6g** in high yield. The molecular structure of the bis(diphenylphosphanyl)methane complex, $[Pt\{(SnMe_2C_5H_4)_2Fe\}(Ph_2PCH_2PPh_2)]$ (**6b**), was determined by X-ray structural analysis. The tetrahedral distortion of the square-planar coordination sphere of the platinum atom in **6b** (10.3°) was found to be smaller than in **6a** (20.6°). All compounds were studied by multinuclear NMR spectroscopy in solution. Dynamic behavior (rotation of the PtP_2 fragment about an axis passing through the platinum atom and bisecting the $PtSn_2$ triangle) was observed by NMR spectroscopy for **5a**, **6a**, and **6g**, whereas **6b**–**6f** have more rigid structures. There is no indication of a dynamic process in the case of **7a** or **8a** in which only one Pt–Sn bond is present.

Keywords: ferrocenes · P ligands · platinum · tin · NMR spectroscopy

Introduction

It is well known that bis(phosphane)platinum(0) fragments react readily with organotin compounds to give platinum(II) complexes by oxidative addition.[1] If hexaorganodistannanes are used, two Pt–Sn bonds are formed simultaneously.[2] Thus, the reaction of $[Pt(PPh_3)_2(C_2H_4)]$ (**1**), which is a convenient source of the $[Pt(PPh_3)_2]$ fragment, with hexamethyldistannane (**2**) and 1,1,2,2-tetramethyl-1,2-distanna[2]ferrocenophane (**3**) leads to the formation of *cis*-$[Pt(SnMe_3)_2(PPh_3)_2]$ (**5a**) and *cis*-$[Pt\{(SnMe_2C_5H_4)_2Fe\}(PPh_3)_2]$ (**6a**), respectively (Scheme 1). In a similar manner **1** reacts with (1-alkynyl)-trimethylstannanes ($Me_3SnC{\equiv}CR$, **4**) to give *cis*-$[Pt(SnMe_3)(C{\equiv}CR)(PPh_3)_2]$ (R = $SnMe_3$, **7a**; $B(NEt_2)_2$, **8a**). With few exceptions,[3–5] complexes containing two Pt–Sn bonds in a Sn_2PtP_2 skeleton have not been well characterized.

In two recent communications X-ray structural analyses of the tri(*p*-tolyl)phosphane complex *cis*-$[Pt(SnMe_3)_2\{P(p\text{-tol})_3\}_2]$ (**5a′**),[4] and the 1,3-distanna-2-platina[3]ferrocenophane **6a**[5] have been reported.[19] The molecular structures of these bis(stannyl)bis(phosphane)platinum(II) complexes and their dynamic behavior are of interest, since they must be considered as the active intermediates in the Pt^0-catalyzed distannation of alkynes.[4, 5] A prominent feature of the solid-state molecular structure of both **5a′** and **6a** is the considerable tetrahedral distortion of the square-planar environment of the platinum(II) center. In solutions of **5a**, **5a′**, and **6a** a dynamic process takes place that can be best described as a rotation of the PtP_2 unit about an axis passing through the platinum atom and bisecting the Sn_2Pt triangle.[4, 5] In the present work (Scheme 1), we have studied the bis(trimethylstannyl)bis(phosphane)platinum complexes **5a** and **5b**, and we have prepared derivatives of **6a** with various chelating diphosphane ligands in order to obtain further information on the structure and the molecular dynamics of such molecules. The *cis*-(trimethylstannyl)bis(triphenylphosphane)(1-alkynyl)platinum complexes **7a** and **8a** were included in order to look for dynamic properties when only one Pt–Sn bond is present.

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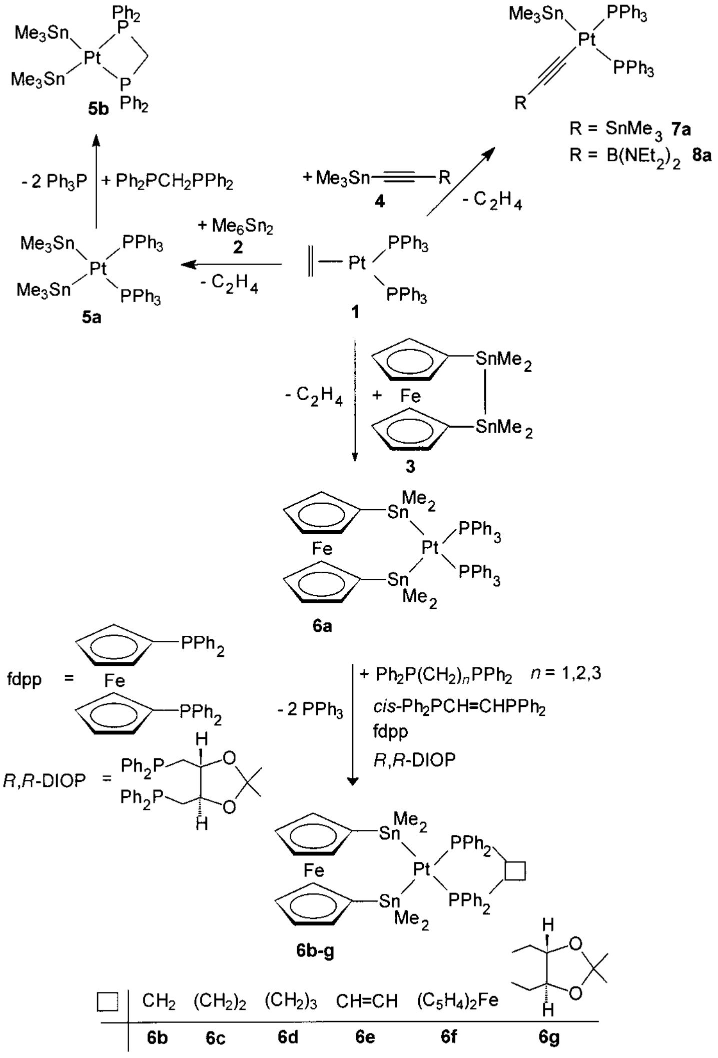
Results and Discussion

1. Synthesis of the *cis*-bis(stannyl)bis(phosphane)platinum complexes 5 and 6, and the *cis*-bis(trimethylstannyl)bis(phosphane)(1-alkynyl)platinum complexes 7a and 8a: The bis(triphenylphosphane)platinum complexes **5a**–**8a** were obtained from the reaction of bis(triphenylphosphane)(ethene)platinum (**1**) with the respective organotin compounds **2**, **3**, or **4** (Scheme 1). In the case of **8a**, the stannyl group is selectively transferred to platinum; there was no evidence for the formation of a borylplatinum derivative. It has been reported that the reaction of $[Pt(PR_3)_4]$ ($PR_3 = PPh_3$, $P(p\text{-tol})_3$, PPh_2Me) with Sn_2Me_6 affords mainly complexes with *cis* configuration analogous to **5a**.[4] However, in our hands this method proved to be unsuccessful for the synthesis of **6a**. Complexes **5b** and **6b**–**6g** were prepared by addition of the chelating diphosphane to the bis(triphenylphosphane) complexes. Two equivalents of triphenylphosphane were eliminated and separated from the less soluble platinum complexes in hexane. In the case of **5b**, the similar solubilities of **5b** and PPh_3 prevented complete separation. The complexes **5a**, **7a**, and **8a** were obtained as white powders, whereas the [3]ferrocenophanes **6a**–**g** are yellow. All complexes can be stored in an inert atmosphere for several weeks without noticeable signs of decomposition. They are moderately soluble in $CHCl_3$ or CH_2Cl_2, in which they start to decompose after a few hours, and slightly soluble in benzene or toluene; solutions with the last two solvents can be stored for a longer time. In the case of **6b**, recrystallization from CH_2Cl_2 at −15 °C gave crystalline material suitable for an X-ray structural analysis.



Scheme 1. Reaction scheme for the syntheses of compounds **5**–**8**.

Abstract in German: *Bei der Reaktion von Bis(triphenylphosphan)(ethen)platin(0) (**1**) mit Organozinn-Verbindungen wie Hexamethyldistannan (**2**), 1,1,2,2-Tetramethyl-1,2-distanna[2]ferrocenophan (**3**), Bis(trimethylstannyl)acetylen (**4′**) und Trimethylstannylethinylbis(diethylamino)boran (**4″**) entstehen - unter Freisetzung von Ethen und Spaltung der Sn-Sn-Bindung - die Bis(triphenylphosphan)platin(II)-Komplexe **5a** - **8a**. Die Verdrängung der beiden Triphenylphosphan-Liganden (**a**) aus dem 1,3-Distanna-2-bis(triphenylphosphan)platina[3]ferrocenophan (**6a**) durch verschiedene Chelat-Diphosphane ($Ph_2P(CH_2)_nPPh_2$ mit $n = 1-3$ (**b**, **c**, **d**), cis-$Ph_2PCH=CHPPh_2$ (**e**), $Fe(C_5H_4\text{-}PPh_2)_2$ (**f**), 4,5-Bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolan (DIOP, **g**)) ergibt die entsprechenden Komplexe **6b**–**6g** in hohen Ausbeuten. Die Molekülstruktur des Bis(diphenylphosphanyl)methan-Komplexes, $[Pt\{(SnMe_2C_5H_4)_2Fe\}(Ph_2PCH_2PPh_2)]$ (**6b**), wurde durch eine Röntgenstrukturanalyse bestimmt. Die tetraedrische Verzerrung der quadratisch-planaren Koordinationssphäre des Platinatoms ist in **6b** (10.3°) kleiner als in **6a** (20.6°). Alle Verbindungen wurden mit Hilfe der Mehrkern-NMR-Spektroskopie in Lösung untersucht. Ein dynamisches Verhalten (Rotation des PtP_2-Fragments um eine Achse, die durch das Platinatom verläuft und das $PtSn_2$-Dreieck halbiert) wurde NMR-spektroskopisch für **5a**, **6a** und **6g** beobachtet, während **6b**–**6f** eine starrere Struktur besitzen. Es gibt keine Hinweise auf einen dynamischen Prozeß in den Fällen **7a** oder **8a**, wo nur eine einzige Pt-Sn-Bindung vorhanden ist.*

2. X-ray structural analysis of the 1,3-distanna-2-platina[3]ferrocenophane 6b:[6] The molecular structure of **6b** is shown in Figure 1 and selected bond lengths and angles (along with those of **5a′**[4] and **6a**[5] for comparison purposes) are given in Table 1. The environments of the platinum atom in **5a′** and **6a** are rather similar as far as bond lengths and angles are concerned. However, the tetrahedral distortion in **5a′**, where the Sn-Pt-Sn and P-Pt-P planes are twisted against each other by 34.6°, is larger than in **6a** (20.6°). In **6b** the Pt–Sn bond lengths are shorter than those of **5a′** and **6a** by about 4 pm, the bond angle Sn-Pt-Sn is enlarged (89.2(1)°), whereas, as expected, the bond angle P-Pt-P is reduced (73.9(1)°), and the tetrahedral distortion is much less pronounced (10.3°). In the [3]ferrocenophanes **6a** and **6b**, the positions of the cyclopentadienyl rings deviate by 17.0° (**6a**) and 14.0° (**6b**) from an eclipsed conformation. The deviations of the Sn–C(1) bonds from the plane of the C_5H_4 rings are small, except for **6b** in which one of these bonds is shifted by 6.3° away from the Fe–Pt axis. The four-membered Pt-P-C-P ring in **6b** is not

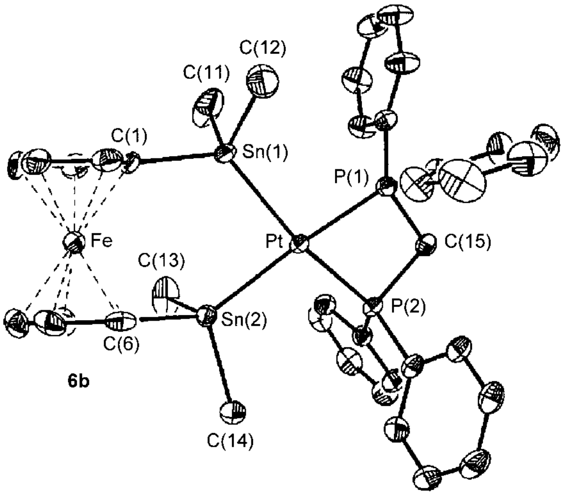


Figure 1. Molecular structure of **6b** (see Table 1 for selected bond lengths and angles).

Table 1. Selected bond lengths [pm] and angles [°] of the platinum complex **6b**, together with those of **6a**[5] and **5a′**[4] for comparison.

	6a	**6b**	**5a′**
Sn(1)–Pt	264.4(1)	260.5(1)	262.89(6)
Sn(2)–Pt	264.5(1)	259.6(1)	262.89(6)
P(1)–Pt	230.8(2)	230.6(1)	229.9(1)
P(2)–Pt	229.9(2)	229.9(2)	229.9(1)
Sn(1)–C(1)	215.7(7)	214.9(6)	–
Sn(2)–C(6)	216.0(7)	211.9(6)	–
Pt-Sn(1)-C(1)	112.7(2)	122.7(2)	–
Pt-Sn(2)-C(6)	122.7(2)	124.4(1)	–
Sn(1)-Pt-Sn(2)	82.3(1)	89.2(1)	82.91(2)
P(1)-Pt-P(2)	104.2(1)	73.9(1)	104.23(6)

exactly planar (mean deviation 9.7 pm). In contrast to the tetrahedral distortion reported here, an almost perfect square-planar geometry is typical of the majority of platinum(II) complexes; noteworthy examples are the *cis*-bis(triphenylphosphane)bis(boryl)platinum(II) complexes.[7] However, a marked tetrahedral distortion (28.5°) was also observed in the case of *cis*-$[Pt(GeMe_2Cl)_2(PEt_3)_2]$.[8] The latter result indicates that there must be influences in addition to steric repulsion that cause this particular structural feature.

3. NMR spectroscopic study of the bis(phosphane)platinum complexes 5a–8a: The ^{31}P, ^{119}Sn, and ^{195}Pt NMR data of the new complexes are listed in Table 2. Relevant ^1H and ^{13}C NMR data are given in the experimental section. The structures proposed for **5a–8a** in solution are supported by consistent NMR data sets.

The averaging of the $^2J(Sn,^{31}P)_{cis}$ and $^2J(Sn,^{31}P)_{trans}$ coupling constants is evident at room temperature for the complexes **5a** ($\Delta G^{\neq} = 39.7 \pm 1$ kJ mol^{-1}, in agreement with data reported for **5a′**[4]), **6a** (see Figure 2; $\Delta G^{\neq} = 41.8 \pm 1$ kJ mol^{-1}), and **6g** ($\Delta G^{\neq} = 49.1 \pm 2$ kJ mol^{-1}). Since the $^{195}Pt-^{31}P$ coupling is not affected, this averaging must be as a result of an intramolecular process without dissociation of Pt–P bonds.[4, 5] A transition state with a tetrahedral environment around the platinum atom has been proposed in order to explain the dynamics.[4] Alternatively, it is conceivable that the σ-electron density is delocalized in the Sn-Pt-Sn triangle, thus weakening the Pt–Sn σ bonds. This is more likely for nonchelating phosphanes or for chelating phosphanes forming a seven-membered ring system (e.g., **6g**). In the case of smaller rings the Sn-Pt-Sn bond angle is expected to widen, and Sn–Sn bonding interactions will be less favored. If only one Pt–Sn bond is present, as in the complexes **7a** and **8a**, there is no indication of such a dynamic process occurring, and such behavior is also absent in the case of *trans*-bis(trimethylstannyl)bis(phosphane)platinum complexes.[4]

In principle, the magnitude of the $^1J(^{195}Pt,^{119}Sn)$ coupling constants should reveal changes in the nature of the Pt–Sn bonds. However, these data also depend strongly on influences exerted by the particular phosphane ligand in *trans* position. The $^2J(^{119}Sn,^{117}Sn)$ geminal coupling constants across the platinum atom should reflect the bonding situation more sensitively. From the assumption that contributions of opposite signs arise from one-bond Sn–Sn and two-bond *cis*-Sn-Pt-Sn coupling pathways, the considerably smaller $^2J(^{119}Sn,^{117}Sn)$ values in the fluxional complexes **6a** (350.0 Hz) and **6g** (399.4 Hz) as compared with the more rigid complexes **6b** (542.2 Hz), **6c** (573.5 Hz), **6d** (556.6 Hz), and **6e** (542.4 Hz) can be explained. The $^1J(^{195}Pt,^{31}P)$ values for the [3]ferrocenophanes **6a–6g** range from 1774 (**6b**) to 2628 Hz (**6a**). In the case of **6b**, the smaller value is the result of significant structural changes induced by the four-membered ring.

Table 2. ^{31}P, ^{119}Sn, and ^{195}Pt NMR data[a] of the complexes **5–8**.

	5a[b]	**5b**[c]	**6a**[d]	**6b**	**6c**	**6d**	**6e**	**6f**	**6g**[e]	**7a**	**8a**[j]
$\delta^{31}P$	32.6	–31.8	31.6	–27.3	55.6	7.3	74.0	28.1	12.6	26.3[f]	23.9[k]
$^2J(^{119}Sn,^{31}P)$	652.3	–	680.0	110.8 1601.5	156.4 1591.0	195.8 1574.0	138.7 1592.5	134.6 1625.0	[e]	1606.0	1578.0
$^1J(^{195}Pt,^{31}P)$	2624.5	1750.0	2628.0	1774.0	2233.5	2332.0	2203.0	2287.5	2493.0	1855.0	1862.0
$^2J(^{31}P,^{31}P)$	[b]	–	[d]	11.4	13.2	29.1	15.4	14.6	[e]	15.7	15.3
$\delta^{119}Sn$	–16.5	–	–27.5	–25.2	–19.5	–18.4	–31.1	–24.2	–25.2	–57.5[g]	–52.9
$^2J(^{119}Sn,^{117}Sn)$	n.o.	–	350.0	542.2	573.5	556.6	542.4	n.o.	399.4	[h]	–
$^1J(^{195}Pt,^{119}Sn)$	8532.0	–	9056.0	10067.5	9330.0	9005.5	9120.0	9320.0	9529.0	8140.0[i]	8290.0
$\delta^{195}Pt$	–680.0	–	–742.3	–971.0	–858.4	–895.6	–942.8	n.m.	–795.2	–510.0	–529.0

[a] In $[D_8]$toluene or C_6D_6, at 25 °C, if not stated otherwise; coupling constants in Hz (± 1 Hz); n.o. means not observed as a result of an insufficient signal-to-noise ratio; n.m. means not measured. [b] **5a**: –70 °C; $^2J(^{119}Sn,^{31}P) = 221.2, -1569.7$ Hz; $^2J(^{31}P,^{31}P) = 16.0$ Hz. [c] Compound was not pure; the ^{31}P NMR signal and the satellites were broad, probably as the result of the presence of a small amount of Ph_3P. [d] **6a**: –40 °C; $^2J(^{119}Sn,^{31}P) = 206.0, -1574.5$ Hz, $^2J(^{31}P,^{31}P) = 16.2$ Hz. [e] At 25 °C; $^2J(^{119}Sn,^{31}P) = 202.2$, 1551.3 Hz, $^2J(^{31}P,^{31}P) = 19.4$ Hz; (coalescence at 0 °C); at +30 °C $^2J(^{119}Sn,^{31}P) = 656.4$ Hz. [f] Phosphorus located *trans* with respect to the Me_3Sn group; $\delta^{31}P(cis) = 28.1$; $^2J(^{119}Sn,^{31}P)_{cis} = 111.0$; $^1J(^{195}Pt,^{31}P)_{cis} = 2880$ Hz. [g] $\delta^{119}Sn$ (Sn–C≡) –88. 9. [h] $^4J(^{119}Sn,^{119}Sn_{C\equiv}) = 17.5$ Hz. [i] $^3J(^{195}Pt,^{119}Sn_{C\equiv}) = 278.8$ Hz. [j] In CD_2Cl_2; $\delta^{11}B = 24.3$ ($h_{1/2} = 670$ Hz). [k] Phosphorus located *trans* with respect to the Me_3Sn group; $\delta^{31}P(cis) = 27.0$; $^2J(^{119}Sn,^{31}P)_{cis} = 112.5$; $^1J(^{195}Pt,^{31}P)_{cis} = 2882. 0.$ Hz.

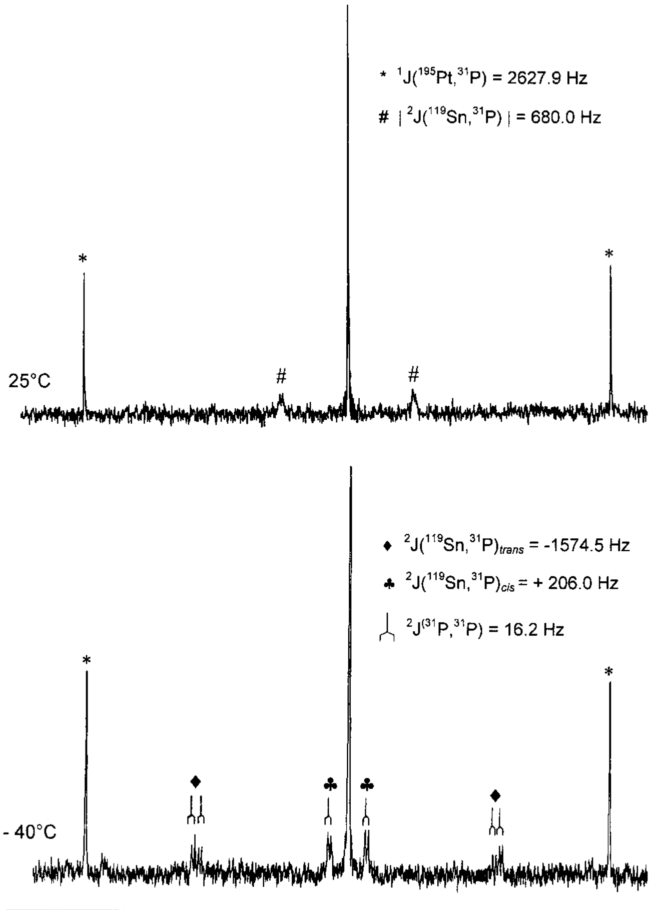


Figure 2. 101.5 MHz $^{31}P\{^1H\}$ NMR spectra of **6a**. The spectrum at 25 °C shows satellites due to averaged coupling constants $^2J(Sn,^{31}P)$, whereas the different satellites due to $^2J(Sn,^{31}P)_{cis}$ and $^2J(Sn,^{31}P)_{trans}$ are clearly resolved at −40 °C. The ^{195}Pt satellites due to $^1J(^{195}Pt,^{31}P)$ remain unaffected.

Inspection of the other data shows that $^1J(^{195}Pt,^{31}P)$ values of the more fluxional compounds **6a** and **6g** are significantly larger than for **6c**–**6f**. This trend (see also **5a**: $^1J(^{195}Pt,^{31}P) = 2624.5$ Hz) is in line with weaker Pt–Sn and stronger Pt–P bonds in the fluxional molecules. The [3]ferrocenophane structure appears to be a stabilizing factor, as becomes apparent by the smaller tetrahedral distortion in **6a** compared with **5a′**. Furthermore, conditions for fast site exchange in **6c** (101.3 MHz ^{31}P NMR; 25–100 °C) were not reached, whereas it was reported that the analogous bis(trimethylstannyl) complex shows coalescence signals already at 80 °C.[4] The $\delta^{195}Pt$ data of all complexes **5**–**8** fall into a relatively narrow range (considering the large range of $\delta^{195}Pt$ data in general[9]) between $\delta = -500$ and $\delta = -1000$. The complicated dependence of this parameter on various influences precludes a meaningful discussion.

Figure 3 shows the ^{119}Sn NMR spectrum of **7a**, which contains abundant information on ^{119}Sn chemical shifts and coupling constants. Although ^1H detected ^{119}Sn NMR spectra of the sparingly soluble complexes are attractive from the point of consumption of spectrometer time,[10] the accurate extraction of all coupling information, as in Figure 3, would have been a formidable problem. The $\delta^{31}P$ data of **5a**–**8a** are similar to those of other bis(triphenylphosphane)platinum(II) complexes. In **7a** and **8a**, the presence of the electronegative 1-alkynyl group *trans* to a Ph_3P group causes the expected increase in the magnitude of the respective coupling constants $^1J(^{195}Pt,^{31}P)$ [2880 Hz (**7a**) and 2882 Hz (**8a**)][9, 11] when compared with those of the Ph_3P ligand in a *trans* position with respect to the Me_3Sn group [$^1J(^{195}Pt,^{31}P) = 1855$ (**7a**) and 1862 (**8a**)]. The influence of the PtP_2 fragment on the ^{13}C NMR data in **6** is similar to that in other stannylplatinum complexes (see also the data for **7a** and **8a**). The ^{13}C nuclei attached to tin (C(1) and C_{Me}) become deshielded by about 4–5 ppm compared with other 1,3-distanna[3]ferrocenophanes,[12] and the magnitude of the coupling constants $^1J(^{119}Sn,^{13}C(1))$ and $^1J(^{119}Sn,^{13}C_{Me})$ is much smaller.

Conclusions and Outlook

1,2-Distanna-3-platina[3]ferrocenophanes **6b**–**6g** are now available with various chelating diphosphane ligands. These complexes should be useful for transferring the 1,1′-distannylferrocene moiety to alkynes, thus providing a route to novel 1,2-distanna[4]ferrocenophanes[13] (already shown in the case of **6a**[5]). Although metal-catalyzed distannation of alkynes will be preferable in general, it is conceivable that stoichiometric reactions of complexes of type **5** and **6** may be superior for the transformation of less reactive alkynes or other unsaturated substrates. It appears that the dynamic properties of bis(phosphane)bis(stannyl)platinum complexes described here are related to the tetrahedral distortion of the square-planar coordination sphere of the platinum atom. NMR parameters suggest that σ-electron density is delocalized in the Sn-Pt-Sn triangle, depending on the proximity of the stannyl groups. Therefore, this dynamic process is absent, if there is only one Pt–Sn bond (**7a**, **8a**) and if the stannyl groups are in mutual *trans* positions,[4] or it is less favored if the size of the chelating diphosphane enforces a larger Sn-Pt-Sn bond angle (**6b**).

Experimental Section

General: All reactions were carried out in an atmosphere of dry nitrogen, with carefully dried solvents and oven-dried glassware. Melting points: Büchi 510; EI (70 eV) mass spectra: Finnigan MAT8500; NMR spectra (^1H, ^{11}B, ^{13}C, ^{31}P, ^{119}Sn, and ^{195}Pt NMR): Bruker WP200, ARX250, and DRX500 instruments equipped with multinuclear units and variable temperature control; chemical shifts are given with respect to Me_4Si [$\delta^1H(C_6D_5H) = 7.15$, $(CHCl_3/CDCl_3) = 7.24$, $(CDHCl_2) = 5.33$, $(C_6D_5CD_2H) = 2.03$; $\delta^{13}C(C_6D_6) = 128.0$, $(CDCl_3) = 77.0$, $(CD_2Cl_2) = 53.8$, $(C_6D_5CD_3) = 20.4$], Et_2O-BF_3 [$\delta^{11}B = 0$ for $\Xi(^{11}B) = 32.083971$ MHz]; H_3PO_4, 85 % aq. [$\delta^{31}P = 0$ for $\Xi(^{31}P) = 40.480747$ MHz], Me_4Sn [$\delta^{119}Sn = 0$ for $\Xi(^{119}Sn) = 37.290665$ Mhz]; [$^{195}Pt = 0$ for $\Xi(^{195}Pt) = 21.4$ MHz].

Materials: Hexamethyldistannane **2** was used as a commercial product, and the other starting materials such as **1**,[14] **3**,[12a] and **4**[15, 16] were prepared following literature procedures. The bis(triphenylphosphane)platinum complexes **5a**[2] and **6a**[5] had been obtained before from the reaction of **1** with **2** and **3**, respectively.[5]

General method for preparing the 1,3-distanna-2-platina[3]ferrocenophanes 6b–6g: The stoichiometric amount of the chelating diphosphane (**b**)–(**g**) was added in one portion to a suspension of **6a** (0.15 g; 0.12 mmol) in toluene (10 mL), and the mixture was stirred for 12 h at room

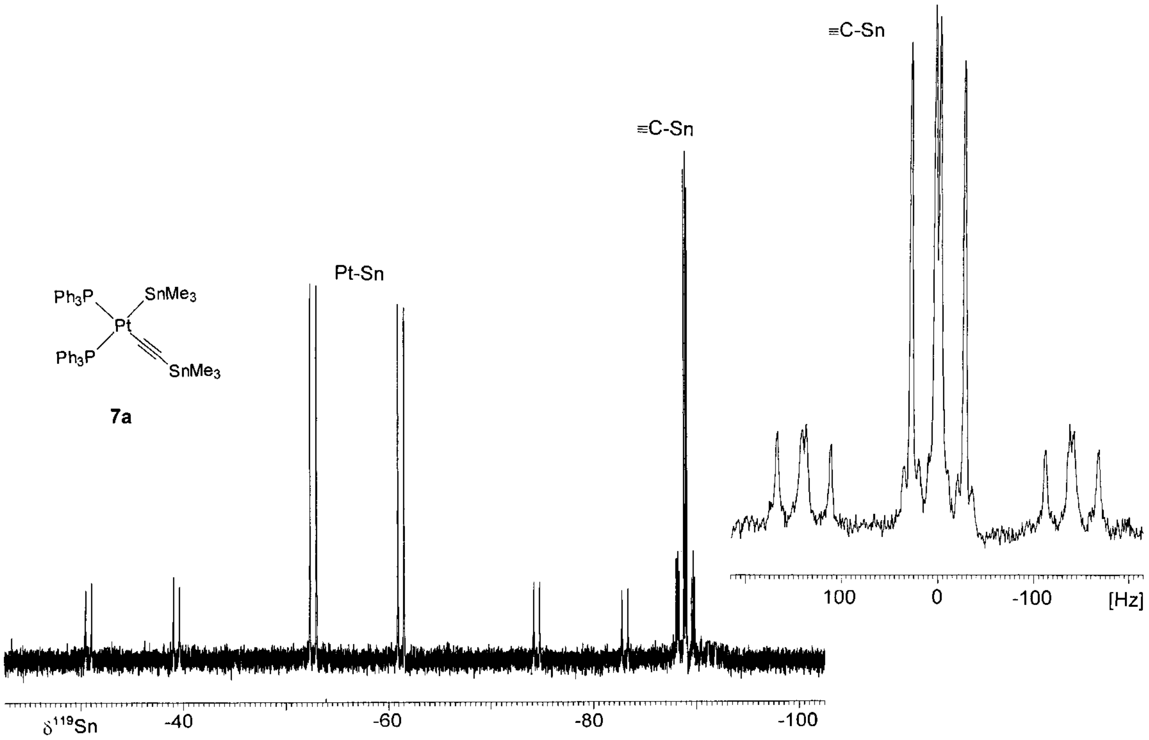


Figure 3. 186.5 MHz ^{119}Sn NMR spectrum of **7a** in C_6D_6, measured by means of the refocused INEPT pulse sequence with ^{1}H decoupling[17] (pulse repetition time 4 s, acquisition time 2 s, 6000 transients). The expected splitting of the central resonances is observed, together with ^{195}Pt satellites. In addition, the expanded region of the ^{119}Sn(C≡) resonance shows $^{117/119}$Sn satellites due to $^4J(\mathrm{Sn},\mathrm{Sn})$.

temperature. The toluene was removed in vacuo, and the residue was extracted with hexane in order to remove Ph_3P. The complexes **6b–6g** were left as yellow powders.

Compound **6b**: (92.5% yield); m.p. (decomp) 190 °C; EI MS: *m/z* (%): 1060 (20) [M^+], 1045 (100) [$M^+ - \mathrm{Me}$]; ^{1}H NMR (250 MHz, C_6D_6, 25°C): $\delta = 0.58$ (s, $^2J(^{119}\mathrm{Sn},^1\mathrm{H}) = 39.6$ Hz, $^3J(^{195}\mathrm{Pt},^1\mathrm{H}) = 10.1$ Hz, 12 H; Me_2Sn), 4.29 (m, $\Sigma^{2,4}J(^{31}\mathrm{P},^1\mathrm{H}) = 18.9$ Hz, 2 H; CH_2), 4.43 (m, 4 H; H3/4), 4.48 (m, $^3J(^{119}\mathrm{Sn},^1\mathrm{H}) = 9.4$ Hz, 4 H; H2/5), 7.0–7.6 (m, 20 H; Ph_2P); ^{13}C NMR (62.9 MHz, C_6D_6, 25 °C): $\delta = -3.2$ ($\Sigma^{3,3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 12.4$ Hz, $^1J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 196.0$ Hz, $^2J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 75.1$ Hz; Me_2Sn), 54.3 ($\Sigma^{1,3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 50.5$ Hz; CH_2), 69.6 ($^3J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 29.3$ Hz, $^4J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 8.5$ Hz; C3/4), 75.6 ($^2J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 42.3$ Hz, $^3J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 10.6$ Hz; C2/5), 78.8 ($\Sigma^{3,3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 9.5$ Hz, $^1J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 300.2$ Hz, $^2J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 104.5$ Hz; C1, FeC_5H_4), 128.7 ($\Sigma^{1,3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 46.8$ Hz; C1(Ph)), 129.0 ($\Sigma^{3,5}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 10.4$ Hz; C3/5(Ph)), 131.0 (C4(Ph)), 133.1 ($\Sigma^{2,4}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 11.6$ Hz, $^3J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 21.5$ Hz; C2/6(Ph)).

Compound **6c**: (95.7% yield); m.p. (decomp) 194 °C; EI MS: *m/z* (%): 1074 (20) [M^+], 1059 (100) [$M^+ - \mathrm{Me}$]; ^{1}H NMR (500 MHz, C_6D_6, 25°C): $\delta = 0.30$ (d, $^4J(^{31}\mathrm{P},^1\mathrm{H}) = 0.6$ Hz, $^2J(^{119}\mathrm{Sn},^1\mathrm{H}) = 39.7$ Hz, $^3J(^{195}\mathrm{Pt},^1\mathrm{H}) = 9.2$ Hz, 12 H; Me_2Sn), 1.76 (m, $\Sigma^{2,3}J(^{31}\mathrm{P},^1\mathrm{H}) = 19.8$ Hz, $^3J(^{195}\mathrm{Pt},^1\mathrm{H}) = 18.3$ Hz, 4 H; CH_2), 4.36 (m, 4 H; H3/4) and 4.37 (m, 4 H; H2/5, FeC_5H_4), 7.0–7.7 (m, 20 H; Ph_2P); ^{13}C NMR (125.8 MHz, C_6D_6, 25 °C): $\delta = -3.6$ ($\Sigma^{3,3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 16.9$ Hz, $^1J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 224.0$ Hz, $^2J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 67.4$ Hz; Me_2Sn), 33.5 ($\Sigma^{1,2}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 52.2$ Hz; CH_2), 69.8 ($^3J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 30.1$ Hz, $^4J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 3.6$ Hz; C3/4), 75.4 ($^2J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 42.1$ Hz, $^3J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 8.4$ Hz; C2/5), 78.7 ($\Sigma^{3,3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 11.5$ Hz, $^1J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 303.0$ Hz, $^2J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 90.0$ Hz; C1, FeC_5H_4), 128.8 ($\Sigma^{1,3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 48.0$ Hz; C1(Ph)), 128.9 ($\Sigma^{3,5}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 10.3$ Hz; C3/5(Ph)), 131.0 (C4(Ph)), 133.6 ($\Sigma^{2,4}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 12.6$ Hz; C2/6(Ph)).

Compound **6d**: (89.6% yield); m.p. (decomp) 187–189 °C; EI MS: *m/z* (%): 1088 (18) [M^+], 335 (100) [$\mathrm{Fe(C_5H_4)_2SnMe_2}$]$^+$; ^{1}H NMR (250 MHz, C_6D_6, 25°C): $\delta = 0.27$ (s, $^2J(^{119}\mathrm{Sn},^1\mathrm{H}) = 40.9$ Hz, $^3J(^{195}\mathrm{Pt},^1\mathrm{H}) = 6.8$ Hz, 12 H; Me_2Sn), 1.91 (m, 4 H; $P-CH_2$), 0.9 (m, 2 H; $C-CH_2$), 4.44 (m, 4 H; H3/4), 4.45 (m, 4 H; H2/5, FeC_5H_4), 7.1–7.8 (m, 20 H; Ph_2P); ^{13}C NMR (62.9 MHz, C_6D_6, 25 °C): $\delta = -2.8$ ($\Sigma^{3,3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 16.4$ Hz, $^1J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 218.3$ Hz, $^2J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 61.0$ Hz; Me_2Sn), 19.7 (-CH_2-), 27.7 ($\Sigma^{1,3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 41.1$ Hz, $^3J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 7.0$ Hz; $P-CH_2$), 69.9 ($^3J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 29.3$ Hz, $^4J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 4.2$ Hz; C3/4), 75.4 ($^2J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 39.9$ Hz, $^3J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 8.2$ Hz; C2/5), 78.8 ($\Sigma^{3,3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 9.9$ Hz, $^1J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 319.0$ Hz, $^2J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 88.9$ Hz; C1, FeC_5H_4), 128.7 ($\Sigma^{1,3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 48.2$ Hz; C1(Ph)), 128.8 ($\Sigma^{3,5}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 10.6$ Hz; C3/5(Ph)), 130.8 (C4(Ph)), 133.6 ($\Sigma^{2,4}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 12.9$ Hz, $^3J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 5.9$ Hz; C2/6(Ph)).

Compound **6e**: (67.6% yield); m.p. (decomp) 192 °C; EI MS: *m/z* (%): 1072 (15) [M^+], 1057 (100) [$M^+ - \mathrm{Me}$]; ^{1}H NMR (250 MHz, C_6D_6, 25°C): $\delta = 0.39$ (s, $^2J(^{119}\mathrm{Sn},^1\mathrm{H}) = 40.1$ Hz, $^3J(^{195}\mathrm{Pt},^1\mathrm{H}) = 6.9$ Hz, 12 H; Me_2Sn), 4.36 (m, 4 H; H3/4), 4.38 (m, 4 H; H2/5, FeC_5H_4), 6.7 (m, $\Sigma^{2,3}J(^{31}\mathrm{P},^1\mathrm{H}) = 17.3$ Hz, $\Sigma^{3,4}J(^{195}\mathrm{Pt},^1\mathrm{H}) = 16.4$ Hz, 2 H; =CH), 7.0–7.6 (m, 20 H; Ph_2P); ^{13}C NMR (62.9 MHz, C_6D_6, 25 °C): $\delta = -2.7$ ($\Sigma^{3,3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 16.5$ Hz, $^1J(^{119}\mathrm{Sn}^{13}\mathrm{C}) = 216.4$ Hz, $^2J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 62.8$; Me_2Sn), 69.9 ($^3J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 29.8$ Hz, $^4J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 4.1$ Hz; C3/4), 75.5 ($^2J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 40.0$ Hz, $^3J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 8.0$ Hz; C2/5), 78.7 ($\Sigma^{3,3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 10.6$ Hz, $^1J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 316.2$ Hz, $^2J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 90.6$ Hz; C1, FeC_5H_4), 128.8 ($\Sigma^{1,3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 45.4$ Hz; C1(Ph)), 128.6 ($\Sigma^{3,5}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 10.2$ Hz; C3/5(Ph)), 130.6 (C4(Ph)), 133.5 ($\Sigma^{2,4}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 12.4$ Hz; C2/6(Ph)), 145.9 ($\Sigma^{1,2}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 77.4$ Hz; =CH).

Compound **6f**: (44.6% yield); m.p. (decomp) 235–237 °C; EI MS: *m/z* (%): 1230 (100) [M^+]; ^{1}H NMR (250 MHz, C_6D_6, 25°C): $\delta = 0.33$ (s, $^2J(^{119}\mathrm{Sn},^1\mathrm{H}) = 40.1$ Hz, $^3J(^{195}\mathrm{Pt},^1\mathrm{H}) = 7.2$ Hz, 12 H; Me_2Sn), 4.44 (m, 4 H; H3/4), 4.46 (m, 4 H; H2/5, FeC_5H_4), 4.03–4.13 (m, 8 H; $\mathrm{Fe(C_5H_4\text{-}PPh_2)_2}$), 7.0–7.5 (m, 20 H; Ph_2P); ^{13}C NMR (62.9 MHz, C_6D_6, 25 °C): $\delta = -2.6$ ($\Sigma^{3,3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 15.2$ Hz, $^1J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 239.4$ Hz, $^2J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 54.0$ Hz; Me_2Sn), 69.7 ($^3J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 29.3$ Hz, $^4J(^{119}\mathrm{Pt},^{13}\mathrm{C}) = 6.0$ Hz; C3/4), 75.7 ($^2J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 41.2$ Hz, ($^3J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 8.2$ Hz; C2/5), 79.0 ($\Sigma^{3,3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 9.8$ Hz, $^2J(^{195}\mathrm{Pt},^{13}\mathrm{C}) = 100.2$ Hz; C1, FeC_5H_4), 72.4 ($^3J(^{31}\mathrm{P},^{13}\mathrm{C}) = 3.0$ Hz; C3/4), 74.5 ($^2J(^{31}\mathrm{P},^{13}\mathrm{C}) = 16.2$ Hz; C2/5), 76.7 (C1, ($\mathrm{Fe(C_5H_4-PPh_2)_2}$)), 128.4 ($\Sigma^{1,3}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 46.4$ Hz; C1(Ph)), 128.0 ($\Sigma^{3,5}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 10.5$ Hz; C3/5(Ph)); 131.0 (C4(Ph)), 134.3 ($\Sigma^{2,4}J(^{31}\mathrm{P},^{13}\mathrm{C}) = 12.2$ Hz; C2/6(Ph)).

Compound **6g**: (94.0% yield); m.p. (decomp) 188 °C; EI MS: *m/z* (%): 1174 (100) [M^+]; ^{1}H NMR (250 MHz, C_6D_6, 25°C): $\delta = 0.11$ (s, $^2J(^{119}Sn,^1H) = 40.2$ Hz, $^3J(^{195}Pt,^1H) = 6.3$ Hz, 6H; Me_2Sn), 0.27 (s, $^2J(^{119}Sn,^1H) = 39.6$ Hz, $^3J(^{195}Pt,^1H) = 6.9$ Hz, 6H; Me_2Sn), 1.07 (s, Me), 3.4 (m, CH_2), 4.16 (m, $\Sigma^{3,4}J(^{31}P,^1H) = 11.3$ Hz; CHO), 4.17 (m, $\Sigma^{3,4}J(^{31}P,^1H) = 11.1$ Hz; CHO), 4.38 (m, 4H; H3/4) 4.41 (m, 4H; H2/5, FeC_5H_4), 7.1–8.0 (m, 20H; Ph_2P); ^{13}C NMR (62.9 MHz, C_6D_6, 25 °C): $\delta = -1.3$ ($\Sigma^{3,3}J(^{31}P,^{13}C) = 16.4$ Hz, $^1J(^{119}Sn,^{13}C) = 219.5$ Hz, $^2J(^{195}Pt,^{13}C) = 64.6$ Hz; Me_2Sn), -2.1 ($\Sigma^{3,3}J(^{31}P,^{13}C) = 16.4$ Hz, $^1J(^{119}Sn,^{13}C) = 219.5$ Hz, $^2J(^{195}Pt,^{13}C) = 52.2$ Hz; Me_2Sn), 26.9 (Me), 37.8 ($\Sigma^{1,3}J(^{31}P,^{13}C) = 31.1$ Hz; CH_2), 78.2 ($\Sigma^{2,3}J(^{31}P,^{13}C) = 10.6$ Hz, $^4J(^{195}Pt,^{13}C) = 12.9$ Hz; CHO), 108.9 (OCO), 69.9 ($^3J(^{119}Sn,^{13}C) = 29.3$ Hz, $^4J(^{195}Pt,^{13}C) = 5.9$ Hz; C3/4), 70.0 ($^3J(^{119}Sn,^{13}C) = 29.3$ Hz, $^4J(^{195}Pt,^{13}C) = 4.7$ Hz; C3/4), 75.2 ($^2J(^{119}Sn,^{13}C) = 41.1$ Hz, $^3J(^{195}Pt,^{13}C) = 7.0$ Hz; C2/5), 75.4 ($^2J(^{119}Sn,^{13}C) = 39.9$ Hz, $^3J(^{195}Pt,^{13}C) = 5.3$ Hz; C2/5), 78.9 ($\Sigma^{3,3}J(^{31}P,^{13}C) = 9.4$ Hz, $^1J(^{119}Sn,^{13}C) = 298.1$ Hz, $^2J(^{195}Pt,^{13}C) = 93.9$ Hz; C1, FeC_5H_4), 128.8 ($\Sigma^{1,3}J(^{31}P,^{13}C) = 45.1$ Hz; C1(Ph)), 128.6 ($\Sigma^{3,5}J(^{31}P,^{13}C) = 10.1$ Hz; C3/5(Ph)), 130.3 (C4(Ph)), 135.1 ($\Sigma^{2,4}J(^{31}P,^{13}C) = 14.4$ Hz; C2/6(Ph)).

Synthesis of the alkynyl-platinum complexes 7a and 8a: A suspension of **1** (0.16 g; 0.22 mmol) in hexane (25 mL) was cooled to −78 °C and the respective alkynyltin compound **4** (0.22 mmol) was added in one portion. After warming to room temperature and stirring for 12 h, the clear solution was cooled again to −78 °C. After a further 2 h, the complexes **7a** and **8a** precipitated as white solids. They were filtered off and dried in vacuo.

Compound **7a**: (88% yield); m.p. (decomp) 110 °C; ^{1}H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 0.32$ (dd, $^4J(^{31}P,^1H) = 9.5$ Hz, 2.6 Hz, $^2J(^{119}Sn,^1H) = 44.5$ Hz, $^3J(^{195}Pt,^1H) = 9.0$ Hz, 9H; Me_3SnPt), 0.16 (s, $^2J(^{119}Sn,^1H) = 59.4$ Hz, 9H; $Me_3SnC{\equiv}$), 7.0–7.5 (m, 30H; Ph_3P); ^{13}C NMR (125.8 MHz; C_6D_6, 25 °C): $\delta = -7.3$ ($^1J(^{119}Sn,^{13}C) = 394.3$ Hz; Me_3Sn-), -3.0 (dd, $^3J(^{31}P,^{13}C) = 8.2$ Hz, 1.9 Hz, $^1J(^{119}Sn,^{13}C) = 245.0$ Hz, $^2J(^{195}Pt,^{13}C) = 63.8$ Hz; $Me_3Sn{-}Pt$), 111.9 (dd, $^2J(^{31}P,^{13}C) = 115.7$ Hz, 19.7 Hz; ${\equiv}C{-}Pt$), 122.4 (dd, $^3J(^{31}P,^{13}C) = 23.2$ Hz, 4.2 Hz, $^2J(^{195}Pt,^{13}C) = 120.0$ Hz; ${\equiv}C{-}Sn$) (measured by means of the refocused INEPT pulse sequence[17] based on $^3J(^{13}CSnC^1H) = 2.4$ Hz[18]), 134.2, 135.0, 128.1, 129.0, Ph_3P.

Compound **8a**: (92% yield); m.p. (decomp) 94 °C; ^{1}H NMR (200 MHz, CD_2Cl_2, 25 °C): $\delta = -0.26$ (dd, $^4J(^{31}P,^1H) = 9.9$ Hz, 2.8 Hz, $^2J(^{119}Sn,^1H) = 44.5$ Hz, $^3J(^{195}Pt,^1H) = 9.2$ Hz, 9H; Me_3Sn), 2.92 (q, 8H), 0.92 (t, 12H; Et_2N), 7.0–7.5 (m, 30H; Ph_3P); ^{11}B NMR (64.2 MHz; CD_2Cl_2, 25 °C): $\delta = 24.3$ ($h_{1/2} = 670$ Hz); ^{13}C NMR (50.3 MHz; CD_2Cl_2, 25 °C): $\delta = -4.2$ (dd, $^3J(^{31}P,^{13}C) = 8.9$ Hz, 2.2 Hz, $^1J(^{119}Sn,^{13}C) = 240.0$ Hz, $^2J(^{195}Pt,^{13}C) = 66.6$ Hz; Me_3Sn), 43.0, 25.0 (Et_2N), 123.5 (dd, $^2J(^{31}P,^{13}C) = 118.7$ Hz, 16.6 Hz; ${\equiv}C{-}Pt$), not observed: ${\equiv}C{-}B$, 134.0, 135.1, 128.1, 130.0, Ph_3P.

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[1] a) C. Eaborn, A. Pidcock, B. R. Steele, *J. Chem. Soc. Dalton Trans.* **1976**, 767–776; b) G. Butler, C. Eaborn, A. Pidcock, *J. Organomet. Chem.* **1978,** *144*, C23–C25; c) *ibid.* **1980,** *185*, 367–372; d) B. Cetinkaya, M. F. Lappert, J. McMeeking, D. E. Palmer, *J. Chem. Soc. Dalton Trans.* **1973**, 1202–1208; e) D. H. Harris, M. F. Lappert, J. S. Poland, W. McFarlane, *ibid.* **1975**, 311–316.

[2] M. Akhtar, H. C. Clark, *J. Organomet. Chem.* **1970,** *22*, 233–240.

[3] W. McFarlane, N. H. Rees, *J. Chem. Soc. Dalton Trans.* **1990**, 3211–3214.

[4] Y. Obora, Y. Tsuji, K. Nishiyama, M. Ebihara, T. Kawamura, *J. Am. Chem. Soc.* **1996**, *118*, 10922–10923; see also ref. [19].

[5] M. Herberhold, U. Steffl, W. Milius, B. Wrackmeyer, *Angew. Chem.* **1997**, *109,* 1545–1546; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1508–1509.

[6] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-100933. 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).

[7] a) G. Lesley, P. Nguyen, N. J. Taylor, T. B. Marder, A. J. Scott, W. Clegg, N. C. Norman, *Organometallics* **1996**, *15*, 5137–5154; b) T. Ishiyama, N. Matsuda, M. Murata, F. Ozawa, A. Suzuki, N. Miyaura, *ibid.* **1996**, *15*, 713–720.

[8] H. Yamashita, T. Kobayashi, M. Tanaka, *Organometallics* **1992**, *11*, 2330–2333.

[9] P. S. Pregosin, in *Transition Metal Nuclear Magnetic Resonance*, Elsevier, Amsterdam, **1991**, pp. 216–263.

[10] F. Kayser, M. Biesemans, M. Gielen, R. Willem, in *Advanced Applications of NMR to Organometallic Chemistry* (Eds.: M. Gielen, R. Willem, B. Wrackmeyer), Wiley, **1996**, pp. 45–86.

[11] T. G. Appleton, H. C. Clark, L. E. Manzer, *Coord. Chem. Rev.* **1973**, *10*, 335–442.

[12] a) M. Herberhold, U. Steffl, W. Milius, B. Wrackmeyer, *Angew. Chem.* **1996**, *108*, 1927–1928; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1803–1804; b) M. Herberhold, U. Steffl, W. Milius und B. Wrackmeyer, *J. Organomet. Chem.* **1997**, *533*, 109–115; c) M. Herberhold, U. Steffl, W. Milius, B. Wrackmeyer, *Z. Anorg. Allgem. Chem.* **1998**, *624*, 386–392.

[13] M. Herberhold, U. Steffl, B. Wrackmeyer, unpublished results.

[14] U. Nagel, *Chem. Ber.* **1982**, *115*, 1998–1999.

[15] B. Wrackmeyer, in *Organometallic Syntheses Vol. 4* (Eds.: R. B. King, J. J. Eisch), Elsevier, New York, **1988**, pp. 559–562.

[16] A. Sebald, B. Wrackmeyer, *J. Organomet. Chem.* **1986**, *307*, 157–165.

[17] a) G. A. Morris, R. Freeman, *J. Am. Chem. Soc.* **1979**, *101*, 760–762; b) G. A. Morris, *ibid.* **1980**, *102*, 428–429; c) D. P. Burum, R. R. Ernst, *J. Magn. Reson.* **1980**, *39*, 163–167.

[18] B. Wrackmeyer, K. Horchler, *J. Magn. Reson.* **1990**, *90*, 569–574.

[19] Note added in proof (April 1998): Twisted square-planar structures have recently also been observed for the *cis*-bis(silyl)platinum complexes *cis*-$[Pt(SiPh_2Me)_2(PMe_2Ph)_2]$ and *cis*-$[Pt(SiFMe_2)_2(PEt_3)_2]$. Both complexes show fluxional behavior on the NMR time scale: Y. Tsuji, K. Nishiyama, S. Hori, M. Ebihara, T. Kawamura, *Organometallics* **1998**, *17*, 507–512.