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ARTICLE

Pt–Me bond cleavage in the reactions of dimethylplatinum(II) complexes containing chelating phosphine ligands with organotin(IV) chlorides

Badri Z. Momeni and Sedigheh Eatezadi

Abstract: Selective Pt–Me bond activation of dimethylplatinum(II) complexes [$PtMe_2$(PP)] (PP = dppm (bis(diphenylphosphino) methane), dppe (1,2-bis(diphenylphosphino)ethane), dppp (1,3-bis(diphenylphosphino)propane)) was achieved by $SnMe_2Cl_2$ to yield the corresponding platinum(II) complexes [PtMeCl(PP)] (PP = dppm, dppe, dppp) and *cis*-[$PtCl_2$(PP)] (PP = dppm, dppp). On the other hand, the reactions of complexes [$PtMe_2$(PP)] (PP = dppm, dppe, dppp) with $SnPh_3Cl$ resulted in the selective cleavage of the Pt–Me bond to afford the methylplatinum(II) complexes [PtMeCl(PP)]. Notably, the reaction of [$PtMe_2$(dppm)] with $SnMe_2Cl_2$ and $SnPh_3Cl$ also gave the ionic A-frame complex [Pt_2Me_2(μ-Cl)(μ-dppm)$_2$]Cl. The variable-temperature ^1H and ^{31}P NMR spectroscopy shows that the cleavage of the Pt–Me bond occurs very rapidly and the short-lived platinum(IV) intermediate is difficult to detect during the reaction. An explanation is presented on the basis of the nature of the strong π-acceptance of the phosphine ligand, which resulted in the formation of a very unstable platinum(IV) intermediate.

Key words: platinum, tin, phosphine, mechanism, NMR.

Résumé : L'activation sélective de la liaison Pt–Me de complexes de diméthylplatine(II) [$PtMe_2$(PP)] (PP = dppm (bis(diphénylphosphino) méthane), dppe (1,2-bis(diphénylphosphino) éthane), dppp (1,3-bis(diphénylphosphino)propane)) par le $SnMe_2Cl_2$ conduit à la formation des complexes de platine(II) correspondants [PtMeCl(PP)] (PP = dppm, dppe, dppp) et *cis*-[$PtCl_2$(PP)] (PP = dppm, dppp). Par ailleurs, les réactions des complexes [$PtMe_2$(PP)] (PP = dppm, dppe, dppp) avec le $SnPh_3Cl$ aboutissent au clivage de la liaison Pt–Me pour donner les complexes de méthylplatine(II) [PtMeCl(PP)]. En particulier, la réaction de [$PtMe_2$(dppm)] avec le $SnMe_2Cl_2$ et le $SnPh_3Cl$ fournit aussi le complexe ionique à structure en A [Pt_2Me_2(μ-Cl)(μ-dppm)$_2$]Cl. La spectroscopie NMR du ^1H et du ^{31}P à température variable montre que le clivage de la liaison Pt–Me est très rapide et qu'il est difficile de détecter l'éphémère complexe intermédiaire de platine(IV) durant la réaction. On présente une explication fondée sur le caractère fortement π-accepteur du ligand phosphine, qui conduit à la formation d'un complexe intermédiaire de platine(IV) très instable. [Traduit par la Rédaction]

Mots-clés : platine, étain, phosphine, mécanisme, NMR.

Introduction

The mechanism of electrophilic cleavage of the metal–carbon bond plays an important role in organometallic chemistry, making it the subject of many studies over the last few decades.[1–3] For example, the Stille reaction is a palladium(0)-catalyzed coupling of organostannanes with organic electrophiles of R–X that is successfully used in organic synthesis.[4] The majority of the Pt–C bond cleavage has been focused on the reactions of alkylplatinum complexes containing phosphine ligands.[5–8] For example, the reaction of [$PtMe_2$(phosphine)$_2$] with iodine, magnesium iodide, or hydrogen chloride is a facile synthetic route to the monomethylplatinum(II) derivatives.[9] However, less is known about the mechanism of the carbon–heteroatom coupling reaction catalyzed by transition metals.[10–12] Notable catalytic C (sp^3)–O reductive coupling of the platinum(IV) center involved in the Shilov reaction affords the alcohol or alkyl chloride from the low-cost alkanes.[13]

Two mechanisms have been proposed for the cleavage of the Pt–Me bond by the electrophilic reagents. The first is the attack of an electrophile at the metal center, giving an oxidative addition/reductive elimination sequence (S_E(ox) mechanism), while the second is the direct attack at the Pt–C bond (S_E2 mechanism).[14–16] Despite the large amount of research conducted, it still remains difficult to predict the selectivity of the site of attack.[17] There are a variety of examples in literature that the Pt–Me bond cleavage occurs from the six-coordinated platinum(IV) complexes resulting from the oxidative addition reactions.[18] The most definitive evidence for an oxidative addition/reductive elimination mechanism is the detection of a platinum(IV) intermediate.[15] For example, the intermediacy of platinum(IV) hydride in the protonolysis of alkylplatinum(II) bonds is consistent with an oxidative addition/reduction elimination mechanism.[15]

There are a number of Sn(IV) halides that oxidatively add to electron-rich platinum(II) complexes containing diimine ligands.[18–21] Kuyper reported the first six-coordinated stannylplatinum(IV) complexes from the reaction of the electron-rich dimethylplatinum(II) complex [$PtMe_2$(NN)] (NN = 2,2′-bipyridine, 1,10-phenanthroline, 2,9–dimethyl-4,7-diphenyl-1,10-phenenthroline) with SnR_nCl_{4-n} ($n = 0$–3, R = Me, Ph).[22] In some cases, there is an equilibrium that is shifted towards platinum(II) complexes at room temperature.[19] Interestingly, the halide ion in halostannylplatinum(IV) complexes can act as a donor to the organotin(IV) halide because tin(IV) centers can easily adopt trigonal bipyramidal or octahedral geometries.[23] Similarly, the stannylplatinum(IV) complex containing the tridentate nitrogen ligand of [Pt($SnMe_2$Cl)Me_2{(pz)$_3$BH-*N*,*N*′,*N*″}] ((pz)$_3$BH$^-$ = tris(pyrazoyl-1-yl)borate) was prepared from the reaction of platinum(II) complex K[$PtMe_2${(pz)$_3$BH-*N*,*N*′}] with $SnMe_2Cl_2$.[24] It

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B.Z. Momeni and S. Eatezadi. Department of Chemistry, K.N. Toosi University of Technology, P.O. Box 16315-1618, Tehran 15418, Iran.
Corresponding author: Badri Z. Momeni (e-mail: momeni@kntu.ac.ir).

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has been reported that the organotin(IV) chlorides oxidatively add to platinum(0) complexes containing phosphine ligands to produce stannylplatinum(II) complexes.[25] In this context, we undertook a study of the reaction of a related series of dimethylplatinum(II) complexes containing chelating phosphine ligands with organotin(IV) chlorides of $SnMe_2Cl_2$ and $SnPh_3Cl$.

Experimental

Materials and instrumentation

All procedures were performed under an atmosphere of argon. Dichloromethane was distilled from P_2O_5 and diethyl ether was distilled from sodium/benzophenone ketyl. Acetone and the other reagents were used without further purification. NMR data were recorded using a Bruker Avance DRX 500 MHz spectrometer. ^1H and ^{31}P NMR chemical shifts are reported relative to residual solvent signal and 85% H_3PO_4, respectively. All of the chemical shifts and coupling constants are reported in ppm and Hz, respectively. The complexes $[PtMe_2(PP)]$ (PP = dppm, dppe, dppp) were prepared according to the literature.[26,27] The complexes $[PtCl_2(dppm)]$,[28] $[PtMeCl(PP)]$ (PP = dppm, dppe, dppp)[16], and $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$[26] were characterized according to the literature.

Reaction of $[PtMe_2(dppm)]$ with $SnMe_2Cl_2$

To a solution of $[PtMe_2(dppm)]$ (100 mg, 0.16 mmol) in acetone (20 mL) was added $SnMe_2Cl_2$ (72 mg, 0.33 mmol). The solution color changed to yellow and the solution was then stirred for 2 days. The solvent was removed and the resulting residue was crystallized from CH_2Cl_2 – diethyl ether to form a pale yellow solid, identified as a mixture of **2a** (major product), **4a** (minor product), and **3a** (minor product). Yield: 78%.

Reaction of $[PtMe_2(dppe)]$ with $SnMe_2Cl_2$

A mixture of $[PtMe_2(dppe)]$ (80 mg, 0.13 mmol) and $SnMe_2Cl_2$ (56 mg, 0.26 mmol) in acetone (20 mL) was stirred for 2 days. The product was filtered off and washed with diethyl ether to give a white solid, identified as **2b**. Yield: 65%.

Reaction of $[PtMe_2(dppp)]$ with $SnMe_2Cl_2$

A mixture of of $[PtMe_2(dppp)]$ (90 mg, 0.14 mmol) and $SnMe_2Cl_2$ (62 mg, 0.28 mmol) in acetone (20 mL) was stirred for 2 days. The product was filtered off and washed with diethyl ether to give a white solid, identified as **2c** (major product) and **3c** (minor product). Yield: 54%.

Reaction of $[PtMe_2(dppm)]$ with $SnPh_3Cl$

Following the same procedure as for the reaction of $[PtMe_2(dppm)]$ with $SnMe_2Cl_2$, a mixture of $[PtMe_2(dppm)]$ (100 mg, 0.16 mmol) with $SnPh_3Cl$ (126 mg, 0.33 mmol) was stirred for 3 days to give a pale yellow solid, identified as **2a** (major product) and **4a** (minor product). Yield: 68%.

Reaction of $[PtMe_2(dppe)]$ with $SnPh_3Cl$

A mixture of $[PtMe_2(dppe)]$ (80 mg, 0.13 mmol) and $SnPh_3Cl$ (99 mg, 0.26 mmol) in acetone (25 mL) was stirred for 3 days. The solvent was removed and the resulting residue was crystallized from CH_2Cl_2 – diethyl ether to form pale yellow crystals, identified as **2b**. Yield: 76%.

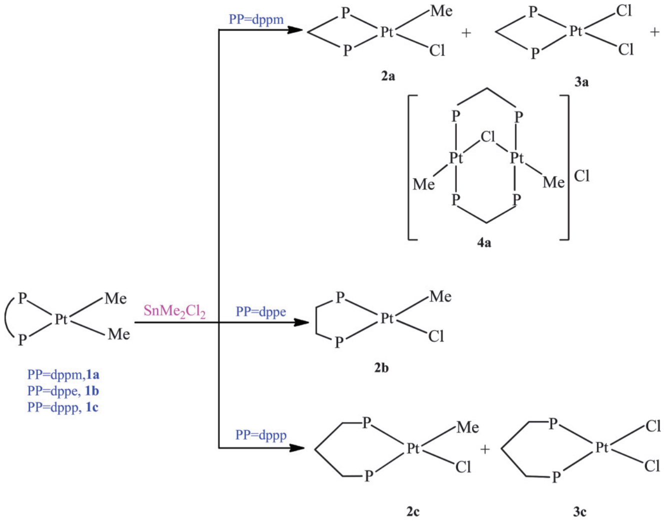
Reaction of $[PtMe_2(dppp)]$ with $SnPh_3Cl$

A mixture of $[PtMe_2(dppp)]$ (90 mg, 0.14 mmol) and $SnPh_3Cl$ (108 mg, 0.28 mmol) in acetone (20 mL) was stirred for 3 days. The resultant white solid was filtered off and washed with diethyl ether, identified as **2c**. Yield: 51%.

Variable temperature NMR studies for the reaction of $[PtMe_2(dppm)]$ with $SnMe_2Cl_2$

To a solution of solution of $[PtMe_2(dppm)]$ (15 mg, 0.025 mmol) in acetone-d_6 (0.5 mL) in an NMR tube, cooled to –84 °C, was added $SnMe_2Cl_2$ (11 mg, 0.05 mmol). The tube was then placed in the precooled probe of the NMR spectrometer at –84 °C and the ^1H and ^{31}P NMR spectra were obtained at 2–3 °C intervals from –84 to +25 °C.

Scheme 1.

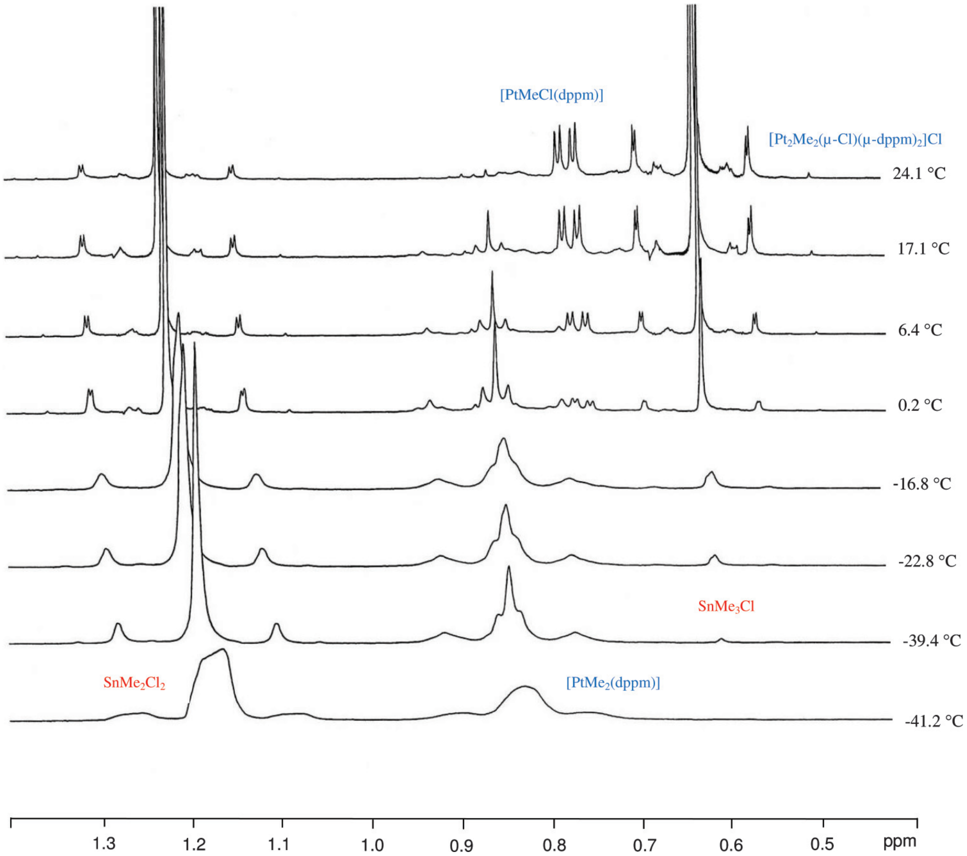


Results and discussion

The reaction of dimethylplatinum(II) complex $[PtMe_2(dppm)]$ (**1a**) with $SnMe_2Cl_2$ in a Pt:Sn 1:2 molar ratio at room temperature resulted in the formation of $[PtMeCl(dppm)]$ (**2a**), $[PtCl_2(dppm)]$ (**3a**), and $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$ (**4a**) (Scheme 1). The products were characterized based on the ^1H and ^{31}P NMR spectra.[16,26,28]

One would expect the platinum(IV) products resulting from an oxidative addition reaction of the platinum(II) complex. Initial attempts to detect the in situ platinum(IV) product resulting from an oxidative addition reaction of $[PtMe_2(dppm)]$ (**1a**) with $SnMe_2Cl_2$ at room temperature, which would give the characteristic $^2J(Pt^{IV}H)$ coupling constant, showed that no platinum(IV) product formed during the reaction. The ^1H and ^{31}P NMR spectra showed that a mixture of platinum(II) complexes **2a–4a** persist in solution that were essentially the same as the solid-state products (Scheme 1). Therefore, the variable-temperature ^1H and ^{31}P NMR spectra were obtained for the reaction of $[PtMe_2(dppm)]$ (**1a**) with $SnMe_2Cl_2$ in acetone-d_6 with an interval of 2–3 °C to detect if any platinum(IV) intermediate forms during the reaction. Due to monitoring the reaction with an interval of 2–3 °C, there were several ^1H NMR spectra. Therefore, a set of selected variable ^1H NMR spectra for the reaction of **1a** with $SnMe_2Cl_2$ in a 1:2 Pt:Sn molar ratio is shown in Fig. 1. At –82.8 °C, the ^1H NMR spectrum displayed two distinct signals at $\delta = 0.82$ and 1.11 ppm. The signal at $\delta = 0.82$ ppm appeared as a singlet with broad platinum satellites. This signal is assigned to the presence of the $[PtMe_2(dppm)]$ in solution. The signal at $\delta = 1.11$ was flanked by tin satellites with $^2J(^{119/117}SnH) = 91$ Hz due to the starting $SnMe_2Cl_2$. The magnitude of $^2J(^{119/117}SnH) = 91$ Hz is considerably larger than that reported for a solution of $SnMe_2Cl_2$ in $CDCl_3$ ($^2J(^{119}SnH) = 68.6$ Hz, $^2J(^{117}SnH) = 65.7$),[29] typical for the five-coordinated tin(IV) compounds.[19] On the other hand, the ^{31}P NMR spectrum of the solution at –73.7 °C indicated only a signal at $\delta = -41.6$ with $^1J(PtP) = 1482$ Hz due to the presence of the complex $[PtMe_2(dppm)]$ in solution. At –63.5 °C, the signal at $\delta = 0.88$ ppm displayed platinum satellites with $^2J(PtH) = 71$ Hz, typical for the starting platinum(II) complex **1a**. The chemical shift of the $SnMe_2Cl_2$ signal increased to $\delta = 1.16$ ppm with $^2J(^{119/117}SnH) = 87$ Hz at –41.2 °C; however, the Pt–Me signal appeared at $\delta = 0.82$ ppm with a decreasing in the coupling constant of $^2J(PtH) = 68$ Hz. Interestingly, there is a little increase in the chemical shift of the Sn-Me signal of $SnMe_2Cl_2$ and a decrease in the $^2J(^{119/117}SnH)$ value

Fig. 1. Selected variable ^1H NMR spectra (0.4–1.4 ppm) for the reaction of $[PtMe_2(dppm)]$ with $SnMe_2Cl_2$ in acetone-d_6.

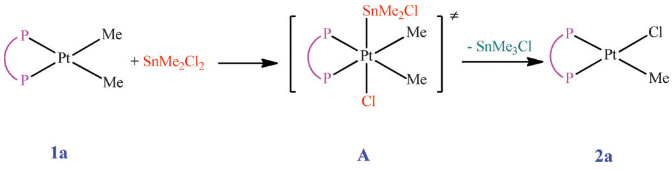


with increasing the temperature. For example, δ = 1.13 ppm with $^2J(^{119/117}SnH)$ = 91 Hz at −63.5 °C, δ = 1.15 ppm with $^2J(^{119/117}SnH)$ = 90 Hz at −50.0 °C, and δ = 1.16 ppm with $^2J(^{119/117}SnH)$ = 87 Hz at −41.2 °C. Notably, at −39.4 °C, the magnitude of $^2J(PtH)$ increased to 73 Hz as well as the magnitude of $^2J(^{119/117}SnH)$, which increased to 89 Hz. At this temperature, a small signal at δ = 0.60 ppm appeared due to the formation of $SnMe_3Cl$. At 0.2 °C, the spectrum contained two very small doublets at δ = 0.76 ppm due to the formation of [PtMeCl(dppm)] (**2a**). Note that at 6.4 °C, a very weak signal appeared at δ = 0.50 due to the formation of the A-frame dimer of $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$ (**4a**).

At none of these temperatures could any platinum(IV) intermediate be detected by ^{31}P and ^1H NMR spectroscopy. Therefore, NMR data show that the oxidative addition of $SnMe_2Cl_2$ to **1a** occurs very rapidly and the short-lived platinum(IV) intermediate is difficult to detect. The formation of the platinum(IV) intermediate would lead to a decrease in the coupling constant of $^2J(PtH)$. It can be seen that the coupling constant of $^2J(PtH)$ = 68 Hz reached a minimum at −41.2 °C. At the same time, there is an increase in the coupling constant of $^2J(SnH)$ from 87.2 to 89.4 Hz at −39.4 °C. That is suggested to be due to the oxidative addition of $SnMe_2Cl_2$ to **1a** to form a very unstable intermediate $[PtMe_2(dppm)(SnMe_2Cl)Cl]$, which could not be observed. At this temperature, the signal due to the formation of $SnMe_3Cl$ resulting from the coupling of Sn–C could be observed. It should be noted that there has been no evidence for the elimination of ethane. Therefore, the coupling of $Sn(sp^3)–C(sp^3)$ is preferred relative to $C(sp^3)–C(sp^3)$ coupling. On the basis of the NMR data, we suggest a mechanism that involves the unstable intermediate **A**, as shown in Scheme 2.

The reaction of $[PtMe_2(PP)]$ (PP = dppe, dppp) (**1b–1c**) with $SnMe_2Cl_2$ in a 1:2 Pt:Sn molar ratio proceeded similarly but in the case of **1b**, the only product was [PtMeCl(dppe)] (**2b**) (Scheme 1). Compound $SnMe_3Cl$ could also be detected in situ by ^1H NMR spectroscopy from the reactions of **1b** and **1c** with $SnMe_2Cl_2$. The complexes **1b** and **1c** were too insoluble to provide satisfactory variable-temperature NMR spectra.

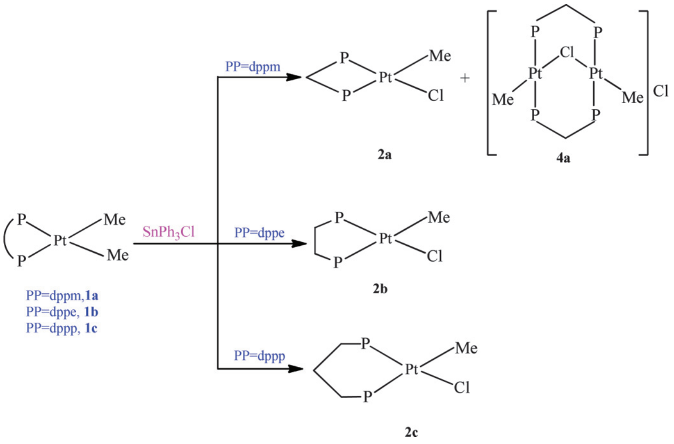
Scheme 2.



The reaction of $[PtMe_2(PP)]$ (**1a–1c**) with $SnPh_3Cl$ afforded the corresponding complexes [PtMeCl(PP)] (PP = dppm (**2a**), dppe (**2b**), or dppp (**2c**)) as well as the complex $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$ (**4a**) in the case of dppm (Scheme 3). NMR data showed that the starting complexes of **1a–1c** were in the solution to some extent after a reaction time of 2 days. However, these signals disappeared after a reaction time of 3 days. The ^1H NMR spectrum of the reaction of **1a** with $SnPh_3Cl$ displayed a signal at δ = 0.60 ppm with tin satellites, which were not well resolved. This signal is assigned to the $SnPh_3Me$ resulting from the coupling of the Sn–C bond.[30] The ^1H NMR resonance for $SnPh_3Me$ in the reactions of **1b** and **1c** with $SnPh_3Cl$ are mainly obscured by the more intense resonances of Pt–Me bonds of [PtMeCl(PP)] (**2b** and **2c**) flanked by both platinum and phosphorus satellites.

In the course of work on the effect of the molar ratios of the reactants, the reaction of $[PtMe_2(dppm)]$ with $SnMe_2Cl_2$ at a molar ratio of 1:1 was complicated, containing the presence of several unknown platinum(II) complexes in solution. In addition, the complex of $[PtCl_2(dppm)]$ was obtained from the reaction of complex **1a** with $SnMe_2Cl_2$ at a Pt:Sn 1:20 molar ratio. On the other hand, the reaction of **1a** with $SnPh_3Cl$ at a Pt:Sn 1:20 molar ratio

Scheme 3.



and a reaction time of days gave a mixture of $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$ (major product) and $[PtCl_2(dppm)]$ (minor product). Therefore, the A-frame dimer of **4a** is more stable than the monomer form of **2a** when the reaction is carried out in the presence of an excess of $SnPh_3Cl$.

Accordingly, the reaction of $[PtMe_2(dppe)]$ with $SnPh_3Cl$ resulted in the formation of complex [PtMeCl(dppe)] as the only product at a Pt:Sn 1:20 molar ratio and a reaction time of 2 days. Therefore, no $[PtMe_2(PP)]$ was observed in the case of the reaction of $[PtMe_2(PP)]$ with an excess of $SnPh_3Cl$ after 2 days.

In the oxidative addition, two bonds are formed with the metal, while its oxidation state increases by one or two units. These reactions can be reversible but the equilibrium is dependent upon the nature of electron donation abilities of ligands.[1] The ligands with strong electron donation abilities stabilize the higher oxidation states of the metals; thus, the oxidative addition is energetically favored if the L_2 is a weak π-acid ligand. We found that the reactivity of organotin(IV) chlorides towards the $[PtMe_2(PP)]$ precursors differs significantly from those of the $[PtMe_2(NN)]$ complexes. Interestingly, the Pt–Me bond cleavage occurs in the reactions of bis(phosphine)platinum(II) complexes with organotin(IV) chlorides instead of the formation of a platinum(IV) product, which is observed in the reactions of dimethylplatinum(II) complexes containing diimine ligands.[18] This is consistent with the general view that nitrogen-donor ligands are able to stabilize the platinum(IV) oxidation state better than the phosphorus-donor ligands. In light of our results, the bidentae ligand L_2 affects the energy of both the transition state and the product of the oxidative addition. On the other hand, the reductive elimination process takes place easier when the more stable product $[PtL_2MeCl]$ forms, which is observed in the case of dimethylplatinum(II) complexes containing chelating phosphine ligands. In addition, the order of the decreasing reactivity of organotin(IV) chlorides towards $[PtMe_2(PP)]$ (PP = dppm, dppe, dppp) is $SnMe_2Cl_2 > SnPh_3Cl$.

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