Revisiting the synthesis of *trans*-[Pt(dmso)$_2$ClMe] and *cis*-[Pt(dmso)$_2$Me$_2$]: experimental and DFT studies

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Keywords

Platinum. Alkyl complexes. Synthesis. DFT calculations.

Dedication

Dedicated to the memory of Professor Pascual Royo and his outstanding contribution to organometallic chemistry.

Highlights

• The methylation of [Pt(dmso)$_2$Cl$_2$] (**1**) with SnMe$_4$ has been reexamined.

• Improved synthesis of *trans*-[Pt(dmso)$_2$ClMe] (**2**) and *cis*-[Pt(dmso)$_2$Me$_2$] (**3**).

• Reaction kinetics favors the formation of dimethyl complex **3**.

• Subsequent comproportionation of **1** and **3** yields to the formation of monomethyl **2**.

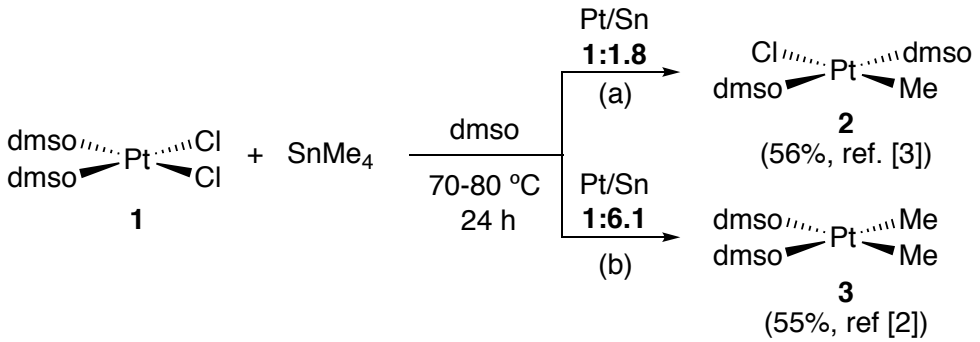
Abstract

The preparation of *trans*-[Pt(dmso)$_2$ClMe] (**2**) and *cis*-[Pt(dmso)$_2$Me$_2$] (**3**) from *cis*-[Pt(dmso)$_2$Cl$_2$] (**1**) and SnMe$_4$ has been reexamined (dmso = dimethyl sulfoxide). The information obtained from experimental and DFT studies has permitted the improvement of previously reported methods for the synthesis of both complexes in terms of reaction times, reaction yields, and atom economy. These studies show that complex **1** reacts with a first equiv of SnMe$_4$ to form *trans*-[Pt(dmso)$_2$ClMe] (**2**) as an intermediate that quickly reacts with a second equiv of SnMe$_4$ to yield *cis*-[Pt(dmso)$_2$Me$_2$] (**3**). When only 1 equiv of the organostannane reagent is added, the comproportionation of **3** with the excess of unreacted **1** leads the reaction back to the formation of *trans*-[Pt(dmso)$_2$ClMe] (**2**). The mechanism of this comproportionation has been studied using DFT calculations.

1. Introduction

The synthesis of the methyl platinum complexes *trans*-[Pt(dmso)$_2$ClMe] (**2**) and *cis*-[Pt(dmso)$_2$Me$_2$] (**3**) (dmso = dimethyl sulfoxide) was first reported by Eaborn and coworkers in 1979,[1, 2] and described in more detail for **2** by Romeo and Monsù Scolaro two decades later (Scheme 1).[3] These complexes are suitable precursors for the preparation of a wide range of organoplatinum compounds by substitution of the labile dmso ligand with N-heterocyclic carbenes,[4, 5] phosphanes,[6-10] thioxamides,[11, 12] CN-chelates,[13-16] CNN-[17] or CNC-pincers,[18, 19] N-,

S-, or P-chelates,[20] imines,[21] and other ligands. Other valuable [PtL_2ClMe] and [PtL_2Me_2] precursors, typically 1,5-cyclooctadiene[22-24] or dimethyl sulfide complexes,[25] are prepared by methods that are less convenient due to the use of very reactive methylating reagents (Li,[24, 25] Al,[22] or Mg [23]) or the involvement of synthetic steps that have to be carefully performed.



Scheme 1. Reported synthesis for complexes (a) **2** [1-3] and (b) **3** [1, 2] from *cis*-[$Pt(dmso)_2Cl_2$] (**1**) and $SnMe_4$.

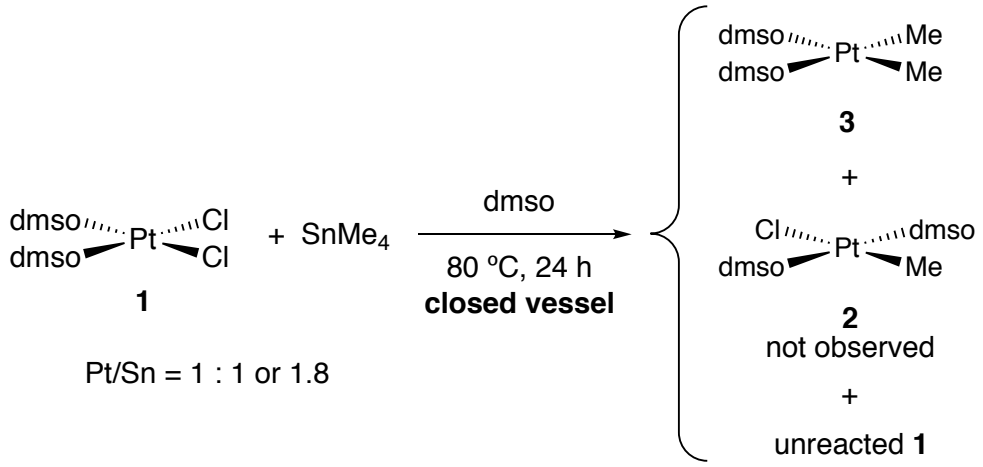
The procedure described by Eaborn for the synthesis of organoplatinum complexes is appealing due to the availability of a wide range of organotin compounds.[26] In addition, the method is simple, makes use of stable and easy to handle Pt and Sn reagents, and leads to the targeted Pt complexes in a single step in warm dmso. However, the reported yields are poor in the case of the methyl derivatives **2** and **3** (around 55%, Scheme 1).[2, 3] The method works better with more reactive $SnMe_3R$ derivatives (*e.g.*, R = aryl), which are also able to react with [$Pt(cod)Cl_2$] in chlorinated solvents.[27] Nevertheless, the organoplatinum complexes are formed faster and tend to be more stable in dimethyl sulfoxide, probably because the coordinated dmso molecules are less prone to dissociate in this solvent.[2] At this point, it is worth to mention that Vrieze and coworkers have described the preparation of [Pt(cod)ClMe] from [$Pt(cod)Cl_2$] and $SnMe_4$ (1:1), in CH_2Cl_2/MeOH (1:1) at room temperature during 24 h, with 79% yield after work up.[28]

We have studied with some detail the formation of **2** and **3** from *cis*-[$Pt(dmso)_2Cl_2$] and $SnMe_4$ in the context of our recent research interests in these complexes as starting materials.[29, 30] The results presented here have not only allowed the optimization of the procedures, but also revealed that the monomethyl complex **2** is only isolatable after the consumption of $SnMe_4$ in the conversion of half

of the starting *cis*-[Pt(dmso)$_2$Cl$_2$] into **3**, and subsequent comproportionation of the dichloro and dimethyl complexes.

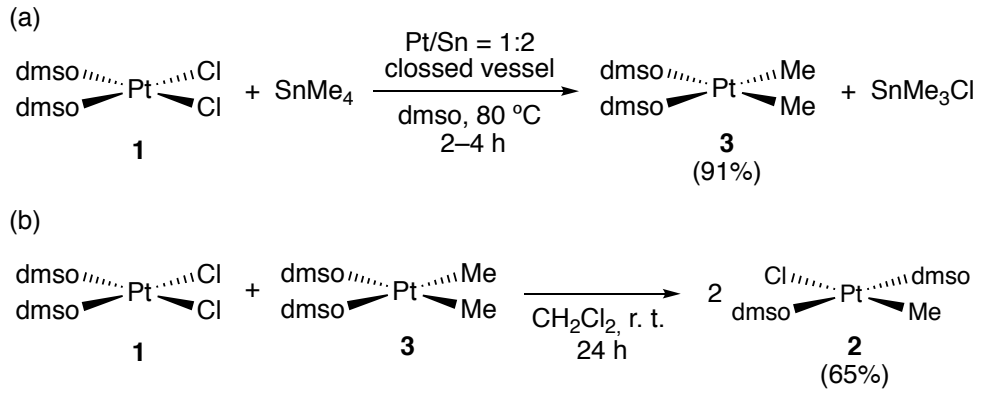
2. Results and discussion

Our initial attempts to prepare complex **2** from *cis*-[Pt(dmso)$_2$Cl$_2$] (**1**) and SnMe$_4$ following the method reported in ref [3] (Scheme 1a) afforded monomethyl complex **2** in very low yields (9% at best). The reagents were heated at 80 ºC in dimethyl sulfoxide under an inert atmosphere using, as reported, a flask equipped with a condenser. Nevertheless, the reaction outcome might be influenced by subtle experimental variables due to the low boiling point of tetramethyltin (74–75 °C). For this reason, the reaction was next performed in a closed ampoule tube under otherwise the reported conditions (*i.e.*, dmso, 80 ºC, 24 h, 1:1.8 Pt/Sn molar ratio). The outcome of the reaction was in this case a mixture of the starting dichloride **1** and the dimethyl complex **3**, instead of the expected monomethyl complex **2** (Scheme 2). When the concentration of tetramethyltin was decreased to a Pt/Sn molar ratio of 1:1, the result of the reaction barely changed except for the larger amounts of unreacted **1** observed. In consequence, an eventual formation of **3** caused by the excess of SnMe$_4$ (*i.e.*, 0.8 equiv) can be ruled out. These observations suggest that the intermediate *trans*-[Pt(dmso)$_2$ClMe] (**2**) reacts much faster with SnMe$_4$ than the starting reagent *cis*-[Pt(dmso)$_2$Cl$_2$] (**1**). This interpretation is consistent with the large *trans* effect of the methyl group opposite to the Pt–Cl bond in **2** compared to that of dmso in dichloride **1**.[31] Under this hypothesis, the formation of **2** and **3** was further examined.



Scheme 2. The reaction between **1** and $SnMe_4$ in a closed vessel.

We first monitored the formation of the dimethyl complex **3** in dmso-d_6 by ^{1}H NMR spectroscopy. The reaction mixture was heated at 80 °C in an NMR tube equipped with a J. Young valve. Surprisingly, the transformation of **1** into **3** was complete in just 3 h using only a slight excess of tetramethyltin (Pt/Sn = 1:2.5). The monomethyl complex **2** was detected as an intermediate in concentrations always below those of the dimethyl complex **3** (for instance, the ratio **2**/**3** was ≈0.2 after 1 h of reaction). Further optimization of the reaction at a 1.5-g synthetic scale showed that a stoichiometric amount of tin reagent is enough to reach almost quantitative yields (91% after isolation, Scheme 3a). Under these conditions, a colorless solution is observed at the end of the reaction without evidences of formation of Pt(0) colloids or precipitates.



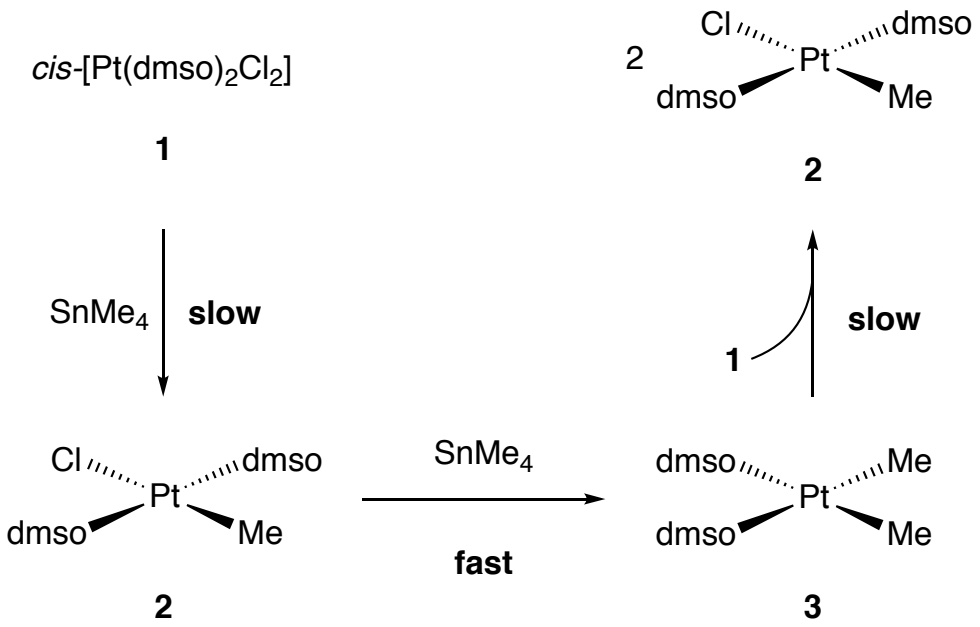
Scheme 3. Optimized conditions for the synthesis of (a) **3** and (b) **2**.

Eaborn and coworkers reported much lower yields for **3** (55% *vs.* 91%) in spite of the large excess of tetramethyltin and the longer reaction times that they employed (Scheme 1b *vs.* 3a). They suggested that the yields obtained in the synthesis of **3** and other organoplatinum derivatives were reflecting the efficiency of isolation of purified compounds rather than the efficiency of the reactions themselves.[2] Our observations show, however, that a long reaction time and a large excess of $SnMe_4$ are both counterproductive in the synthesis of **3** since both together promote the decomposition of the reaction product. Thus, a gradual darkening of the solutions due to the formation of Pt(0) colloids or precipitates was observed when the reactions were prolonged for 24 h. Darkening was also perceptible in a solution of **3** in dmso-d_6 after 10 h at 80 ºC in the presence of 3 equiv of $SnMe_4$, but the same solution was stable after 48 h at the same temperature in the absence of the organotin reagent. The isolation step poses an additional problem because complex **3** decomposes quicker in concentrated solutions. Therefore, a good control of temperature and a system assuring an efficient evacuation of dmso is important for attaining high yields. It is worth to note here that all our attempts to replace dimethyl sulfoxide with a more volatile solvent were unsuccessful.[32]

We have highlighted above that the monomethyl complex **2** was only a transient and minor intermediate in the transformation of **1** into **3** in dmso at 80 °C. Nevertheless, complex **2** was isolated by Romeo et al. in reasonable yields (56%) in the same solvent and at the same temperature (Scheme 1a).[3] As they used an open vessel and a relatively low excess of $SnMe_4$, we can consider highly probable the initial formation of a mixture of **1** and **3** under Romeo's conditions. Then, the isolation of the chloridomethyl complex **2** at the end of the reaction could be the result of a subsequent comproportionation of the dichlorido (**1**) and the dimethyl (**3**) complexes. Ligand exchanges between dimethyl and dichlorido platinum complexes have been previously applied to the preparation of other [PtL_2ClMe] complexes.[25, 27, 33, 34] Thus, we have examined the reaction between equimolar amounts of **1** and **3** in dmso-d_6 by ^{1}H NMR spectroscopy. The reaction starts only at 80 °C and the conversion into *trans*-[$Pt(dmso)_2ClMe$] (**2**) is complete after 24 h of reaction. Regrettably, yields achieved at a preparative scale under these conditions were below 30%. Once more, these low yields were associated to the formation, also noticed in the Romeo's report,[3] of platinum colloids and

precipitates during workup (*i.e.*, upon removal of the solvent under vacuum at 80 ºC). After isolation of the compound, the samples of **2** dissolved in dimethyl sulfoxide are stable at least for 48 h at 80 ºC. Therefore, decomposition of **2** seems to be favored in warm dmso under the specific conditions of the concentration step, in parallel to the behavior noted above for **3**. Due to this drawback, we tested the preparation of **2** in alternative solvents. In CH_2Cl_2, the reaction proceeded smoothly at room temperature affording complete conversions after 24 h, and complex **2** could be isolated in a 65% yield.

Scheme 4 summarizes the main points of the above discussion. The dimethyl complex **3** is the main product observed in the course of the reaction because the intermediate **2** reacts faster with $SnMe_4$ than the starting dichloride **1**. In the presence of substoichiometric amounts of alkylating agent (due to the addition of a lower stoichiometry or to the volatility of $SnMe_4$), the excess of *cis*-[$Pt(dmso)_2Cl_2$] (**1**) comproportionates with the dimethyl complex **3** in a slow reaction that selectively leads back to the monomethyl complex **2**.



Scheme 4. A general scheme of the reactions involved in the formation of *cis*-[$Pt(dmso)_2ClMe$] (**2**) from *cis*-[$Pt(dmso)_2Cl_2$] (**1**) and $SnMe_4$.

In the last part of this work, we studied the mechanism involved in the comproportionation of **1** and **3**. This reaction progresses at room temperature in CH_2Cl_2 but requires heating in dimethyl

sulfoxide. A slower reaction in the last solvent suggests that one of the steps of the reaction mechanism probably involves the dissociation of coordinated dmso. Dissociation and exchange of dmso ligands have been evidenced for [Pt(dmso)$_2$ClR] and [Pt(dmso)$_2$R$_2$] compounds (R = Me, aryl),[2] and in phosphane-dmso substitution reactions.[7] Likewise, a SMe$_2$ dissociative pathway was proposed in the synthesis of [Pt(SMe$_2$)$_2$ClMe] by a similar comproportionation approach.[21] DFT calculations were performed to confirm this hypothesis and to elucidate the full mechanism of the comproportionation reaction. The optimized structures of all complexes studied are collected in the Supplementary Information (SI). Good agreement between the computed and the X-ray structure of *cis*-[Pt(dmso)$_2$Cl$_2$] (**1**) has been observed (see Table S1 in the SI).

As it can be seen in Figure 1, the transformation studied is computed to be thermodynamically favorable and occurs with a moderate kinetic barrier in agreement with experimental observations.

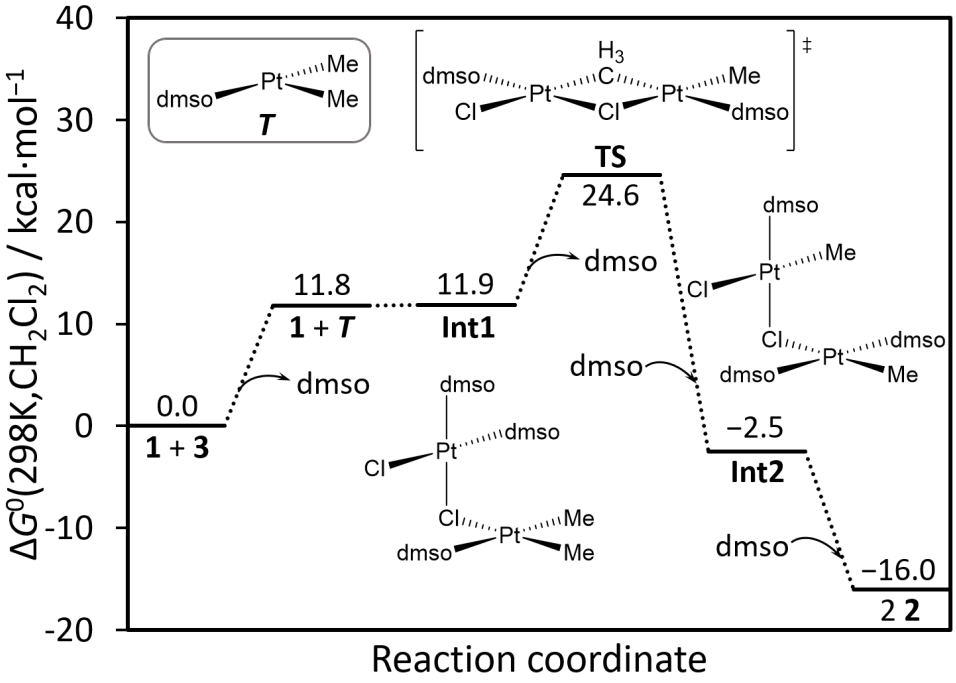


Figure 1. Gibbs Energy diagram showing the most representative minima and transition state computed at the PBE0-D3(PCM,CH_2Cl_2)/Def2TZVP level of theory for the methyl-chloro exchange process observed to occur between *cis*-[Pt(dmso)$_2$Cl$_2$] (**1**) and *cis*-[Pt(dmso)$_2$Me$_2$] (**3**). Two additional intermediates corresponding to the two minima connected through TS$_{1\text{-}2}$ are not shown in the figure for simplicity purposes (see Figures S1 and S2 for more details).

The first step is the decoordination of a dmso ligand from complex **3** to give the corresponding *cis*-[Pt(dmso)Me_2] reactive *T*-shaped intermediate, ***T*** in Figure 1. This dissociative process is thermochemically uphill (ΔH^0(298 K, CH_2Cl_2) = 25.5 kcal/mol) but entropically favored. As expected, the alternative decoordination of dmso from the starting *cis*-[Pt$(dmso)_2Cl_2$] complex is about 5 kcal/mol more disfavored (ΔH^0(298 K, CH_2Cl_2) = 30.8 kcal/mol). Once the *T*-shaped intermediate, ***T***, is formed, it would quickly react with an appropriate partner being the solvent the most reasonable one. Thus, when dmso is used as solvent, high temperatures are needed to achieve the desired conversion since the starting products are regenerated after recoordination of an additional dmso molecule. On the other hand, when the reaction is performed in dichloromethane, a molecule of solvent immediately adds to the unsaturated T-shaped intermediate *cis*-[Pt(dmso)Me_2] yielding the corresponding square planar complex [Pt(dmso)Me_2(CH_2Cl_2)]. However, the stabilization obtained with this coordination is much lower (ΔH^0(298 K,CH_2Cl_2) = −6.4 kcal/mol) than that acquired with the dmso binding (*i.e.*, −25.5 kcal/mol) and consequently, at room temperature, the dissociation of the labile CH_2Cl_2 ligand occurs easily but, similarly, is quickly replaced by a different solvent molecule located in the surroundings. Alternatively, the *T*-shaped intermediate can react bimolecularly with *cis*-[Pt$(dmso)_2Cl_2$] to form *cis*-[(Pt$(dmso)_2$Cl)(μ-Cl)(Pt(dmso)Me_2)], **Int1** in Figure 1, with a chloride ligand bridging the two Pt(II) atoms. After that, a second dmso ligand is released and then, in the crucial step, $\mathbf{TS_{1\text{-}2}}$ (see Figure 1) must be overcome to achieve the methyl-chloro exchange between the two metal centers through the inversion of the configuration of the methyl bridging ligand. The optimized structure of this transition state is shown in Figure 2 and presents an almost planar methyl ligand with a C1–H1–H2–H3 dihedral angle of C1–H1–H2–H3 = 16.4º.[35] Once this transition state has surmounted, two dmso ligands subsequently add to yield the bimolecular species **Int2** and, finally, two molecules of product **2**. Two additional intermediates, not shown in Figure 1, were located corresponding to the two minima connected through $\mathbf{TS_{1\text{-}2}}$ (see Figures S1 and S2 the SI for more details).

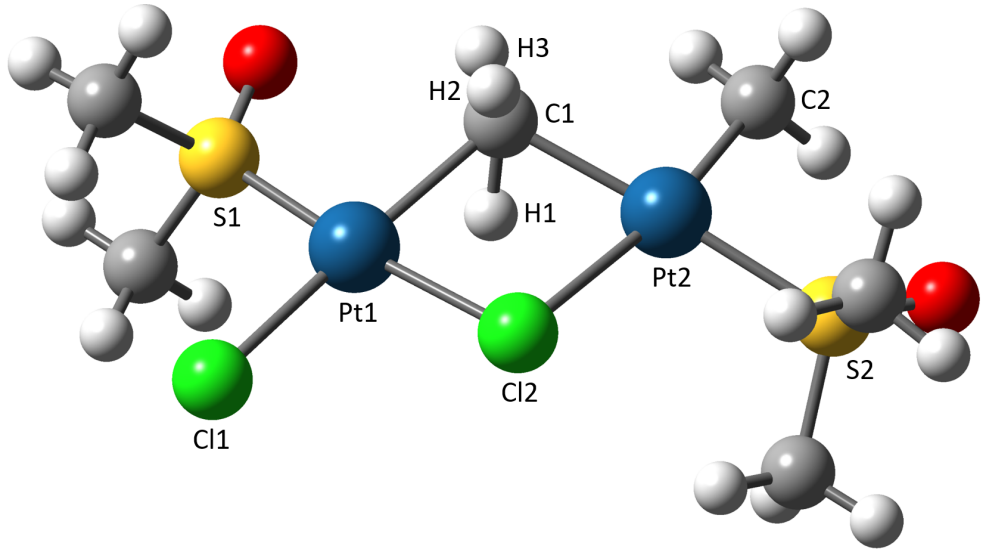


Figure 2. Optimized structure of $\mathbf{TS_{1\text{-}2}}$. Selected distances (in Å) and angles (in degrees): Pt1–Cl1 = 2.346, Pt1–S1 = 2.185, Pt1–C1 = 2.214, Pt1–Cl2 = 2.409, Pt1–Pt2 = 3.507, Pt2–Cl2 = 2.591, Pt2–C1 = 2.127, Pt2–C2 = 2.027, Pt2–S2 = 2.234, Pt1–Cl2–Pt2 = 89.0, Pt1–C1–Pt2 = 107.8, C1–Pt1–Cl2 = 79.2, C1–Pt2–Cl2 = 76.7, C1–Pt1–S1 = 95.2, S1–Pt1–Cl1 = 92.2, Cl1–Pt1–Cl2 = 93.5, Cl2–Pt2–S2 = 98.3, S2–Pt2–C2 = 91.2, C2–Pt2–C1 = 93.8, Pt1–Cl2–Pt2–C1 = 19.0, C1–H1–H2–H3 = 16.4.

3. Conclusions

In this work, we have looked for solutions to several issues associated with the methylation of $[Pt(dmso)_2Cl_2]$ (**1**) with $SnMe_4$ (low yields, low reproducibility, the need of large excesses of the organostannane, etc.). We have observed that the kinetics favors the preferential formation of *cis*-$[Pt(dmso)_2Me_2]$ (**3**), independently of the stoichiometric ratio of the reagents. Subsequent comproportionation between **1** and **3** permits the selective formation of the chloromethyl derivative *trans*-$[Pt(dmso)_2ClMe]$ (**2**). The choice of a closed vessel to avoid losses of the volatile tetramethyltin reagent, the addition of stoichiometric amounts of this reagent, the adequate selection of the solvent, and the use of reaction times as short as possible are key points to achieve high and reproducible yields. The improved procedure here reported for the synthesis of **2** and **3** affords these compounds in shorter reaction times, in higher yields, and using stoichiometric amounts of the tetramethyltin reagent. This will increase the interest of these complexes as useful starting materials for the preparation of other platinum methyl complexes.

4. Experimental section

4.1. General procedures

All reactions were performed under an argon atmosphere using standard Schlenk techniques. Unless otherwise stated, reagents and solvents were used as received from commercial sources. The complex *cis*-dichlorobis(dimethyl sulfoxide)platinum(II) was prepared as described in the literature.[3] All solvents were deoxygenated prior to use. Dimethyl sulfoxide was distilled under argon over calcium hydride and then was passed through a basic Alumina column. NMR spectra experiments were done in a Varian Mercury 300, Unity 300, or Unity 500 Plus spectrometer. Compounds **2** and **3** were characterized by comparison with their previously reported NMR data.[1-3]

*4.2. Synthesis of cis-[Pt(dmso)$_2$Me$_2$] (**3**)*

cis-[Pt(dmso)$_2$Cl$_2$] (1.604 g, 3.799 mmol), SnMe$_4$ (1.359 g, 1.05 mL, 7.599 mmol) and dmso (6 mL) were introduced into a 25 mL ampoule fitted with a PTFE valve under an argon atmosphere. The flask was completely submerged into an oil bath heated at 80 °C and the mixture was stirred until formation of a colorless solution (2–4 h). Two different methods of isolation can then be used.

Method A. The solution was carefully evaporated to dryness under vacuum at a maximum temperature of 80 °C to avoid decomposition of product. The brown solid thus obtained was washed with Et$_2$O (3 × 20 mL), dissolved in 50 mL of CH$_2$Cl$_2$ and stirred with activated charcoal (2 g) at room temperature for 30 min. After filtration, the colorless solution was dried under vacuum (30 °C, 300 mbar) to obtained complex **3** as a white solid (1.188 g, 82%).

Method B. In attempts to remove the solvent by lyophilization, we observed that complex **2** remained precipitated after unfreezing the dmso. Therefore, the solution was cooled to 40 °C, divided in four similar fractions that were transferred each one to a different 15-mL standard Eppendorf tube. The tubes were stored overnight at −20 °C and then allowed to reach room temperature. After the melting of the solvent, the white precipitate was separated by filtration. The supernatant solution can

be stored again at –20 °C overnight to recover a second crop of the product. All the portions were then combined and dissolved in dichloromethane (20 mL). The solution was evaporated to dryness under vacuum and the residue washed with diethyl ether (3 × 30 mL), filtered, and dried under vacuum for 1 h to afford **3** as a white solid (1.318 g, 91%).

*4.3. Synthesis of trans-[Pt(dmso)$_2$ClMe] (**2**).*

cis-[Pt(dmso)$_2$Cl$_2$] (0.650 g, 1.54 mmol) and *cis*-[Pt(dmso)$_2$Me$_2$] (0.588 g, 1.54 mmol) and CH_2Cl_2 (10 mL) were introduced into a 50 mL Schlenk flask under an argon atmosphere and stirred at room temperature for 24 h. Activated charcoal (1 g) was then added to the solution and the mixture was stirred at room temperature during 30 minutes. After filtration, the colorless solution was dried under vacuum (30 °C, 300 mbar), and the resulting solid was extracted with EtOH, filtered off and dried under vacuum (30 °C, 50 mbar) to give **2** as a white solid (0.804 g, 65%).

4.4. Computational details

Electronic structure calculations were performed using the PBE0 density functional[36, 37] with the D3 version of Grimme's dispersion[38] and the Def2-TZVP basis set[39] for all atoms and associated pseudopotential for Pt.[40] Geometry optimizations of all stationary points were performed without any symmetry restrictions in CH_2Cl_2 solution using the integral equation formalism of the polarizable continuum model (IEF-PCM)[41, 42] and computing analytical energy gradients. The obtained minima were characterized by performing energy second derivatives, confirming them as minima by the absence of negative eigenvalues of the Hessian matrix of the energy. Transition states were characterized by single imaginary frequency, whose normal mode corresponded to the expected motion. Computed electronic energies were corrected for zero-point energy, thermal energy and entropic effects to determine $\Delta H^0(298K,CH_2Cl_2)$ and $\Delta G^0(298K,CH_2Cl_2)$ values. All calculations were performed with the Gaussian 09 suite of programs.[43]

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Appendix A. Supplementary data

Supplementary data to this article containing figures, tables and cartesian coordinates of optimizes structures can be found online at ....

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