

# (Alkyl) platinum(II) intermediates in C–H activation by platinum complexes in aqueous solution

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## Abstract

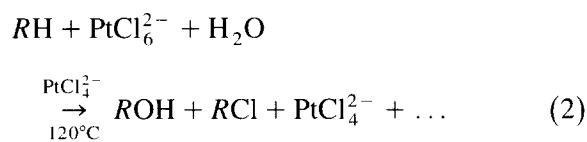
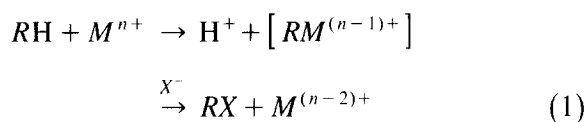
Generation of  $[\text{PtMeCl}_3]^{2-}$ , the putative first intermediate in activation of methane by  $\text{Pt}^{\text{II}}/\text{Pt}^{\text{IV}}$ , is achieved by reduction of  $\text{Na}_2[\text{PtMeCl}_5]$  in THF with cobaltocene. The monomethyl dianion is obtained, not in pure form but combined with  $[\text{PtMe}_2\text{Cl}_2]^{2-}$  and  $[\text{PtCl}_4]^{2-}$  as the mixed cobalticenium salt.  $[\text{PtMeCl}_3]^{2-}$  reacts with water to liberate  $\text{CH}_4$ ; in an acidic aqueous solution of  $[\text{PtCl}_6]^{2-}$ , it undergoes competitive protonolysis and oxidation to  $[\text{PtMeCl}_5]^{2-}$ . The relevance of this chemistry to alkane activation by platinum in aqueous solution is discussed.

*Keywords:* C–H activation; Alkane oxidation; Platinum

## 1. Introduction

The so-called electrophilic mode of alkane activation, represented schematically by Eq. (1), currently appears to be the most promising organometallic approach to practical functionalization of saturated hydrocarbons. The first well-characterized example was reported by Shilov and coworkers (Eq. (2)), and examples using other late- and post-transition metals, such as Pd and Hg, appeared subsequently. A common feature of these reactions (besides involving elements from the same region of the periodic table) is that they all operate in highly

polar media, either water or strong acid (trifluoroacetic, triflic, sulfuric) [1].

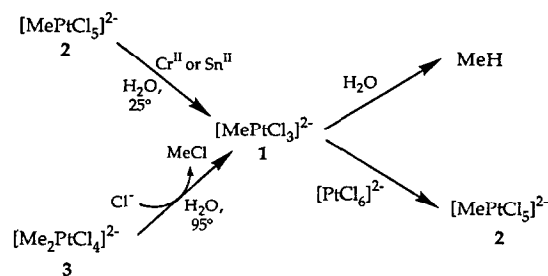
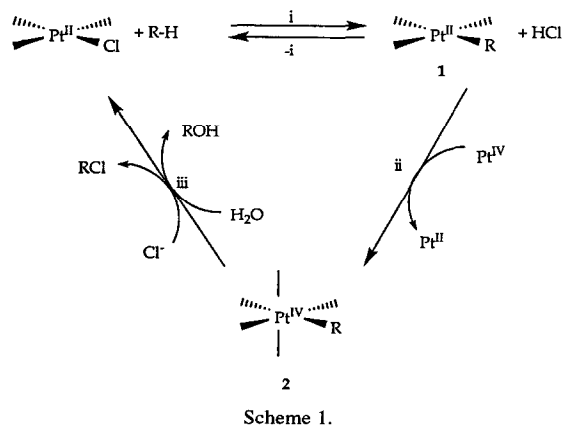


The detailed mechanism of Eq. (2) has been the subject of extensive study, both in our group and elsewhere [2]. The basic sequence of events is shown in Scheme 1, and consists of: (i) C–H activation by  $\text{Pt}^{\text{II}}$  to give an (alkyl) $\text{Pt}^{\text{II}}$  complex **1**; (ii) reaction of **1** with  $\text{PtCl}_6^{2-}$  to produce (alkyl) $\text{Pt}^{\text{IV}}$  **2**; and (iii) reaction of **2** with nucleophile ( $\text{H}_2\text{O}$  or  $\text{Cl}^-$ ) to liberate product ( $\text{ROH}$

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or RCl) and regenerate Pt<sup>II</sup>. We have established, by a combination of kinetics, isotopic labeling, and stereochemistry, that step (ii) involves electron transfer rather than alkyl transfer, and step (iii) involves nucleophilic attack by external reagent rather than intramolecular reductive elimination [2]. Less is understood about the first step, which appears to be rate-determining and hence crucial in determining activity and selectivity.

One of the difficulties in examining step (i) is the fact that the first intermediate in Scheme 1, the Pt<sup>II</sup> alkyl [RPtCl<sub>3</sub>]<sup>2-</sup> (or, perhaps, a related complex with one or more chlorides replaced by water), has to date proven elusive. There are of course many examples of Pt<sup>II</sup> alkyls with stabilizing ligands, and we have made use of them as model compounds for learning something about step (i) by investigating the microscopic reverse-protonolysis of the R–Pt<sup>II</sup> bond [3]. Since the softer ligands (amines or phosphines) needed to stabilize the complexes may significantly perturb reactivity, and since extrapolation from models is inherently ambiguous, we would much prefer to be able to work with the ligand-free version. [MePtCl<sub>3</sub>]<sup>2-</sup> (**1**) appears to have been generated as a transient species in aqueous solution by two methods: reduction of [MePtCl<sub>5</sub>]<sup>2-</sup> (**2**) by Sn<sup>II</sup> or Cr<sup>II</sup> [2], and nucleophilic displacement from [Me<sub>2</sub>PtCl<sub>4</sub>]<sup>2-</sup> (**3**) by Cl<sup>-</sup> [4]. In aqueous solution **1** is protonolyzed extremely rapidly, liberating methane, although in the



Scheme 2.

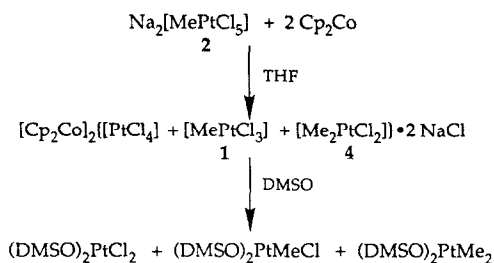
presence of [PtCl<sub>6</sub>]<sup>2-</sup> it can be competitively oxidized to **2** (Scheme 2). In this paper, we report on efforts to isolate **1**, and studies of its chemical behavior and its relevance to the functionalization of alkanes in aqueous solution.

## 2. Results and discussion

### 2.1. Preparation of methylplatinum(II) salts

As all attempts to reduce **1** in protic media led only to immediate evolution of methane [2], several approaches were examined in aprotic solvents. A methyl–platinum(II) species can be obtained by careful alkylation of [PtCl<sub>4</sub>]<sup>2-</sup> with ZnMe<sub>2</sub>, but it appears to be a dimethyl species, even when only half eq. of ZnMe<sub>2</sub> per Pt is used; nor could a monomethyl complex be generated by controlled protonolysis of the latter. (See experimental section for details.)

Reduction of **2** (as the sodium salt) proceeds readily in THF with a variety of reducing agents. Na(Hg) and Zn(Hg) both led primarily to platinum metal, while the organometallic reductants Cp<sub>2</sub>Co, Cp<sub>2</sub>\*Co, Cp<sub>2</sub>Cr and (Cp<sub>2</sub>TiCl)<sub>2</sub> all appear to reduce Pt<sup>IV</sup>, at least in part, to Pt<sup>II</sup> complexes. The best results were obtained by reduction of **2** with 2 or more eq. of cobaltocene. Slow addition of a Na<sub>2</sub>PtMeCl<sub>5</sub>/THF solution to Cp<sub>2</sub>Co (2.2–3 eq.)/THF solution results in immediate precipitation of a yellow solid. Effectively all the products precipitate out, as the supernatant exhibits no <sup>1</sup>H-NMR signals (other than the residual proton reso-



Scheme 3.

nances of THF) when THF- $d_8$  is used as solvent. The elemental analysis of the yellow solid is consistent with a nominal composition corresponding to the cobalticenium salt of **1** admixed with sodium chloride:  $(\text{Cp}_2\text{Co})_2\text{PtMeCl}_3 \cdot 2\text{NaCl}$ .

The yellow solid is insoluble in common organic solvents such as THF, methylene chloride and acetone, but is readily dissolved by DMSO- $d_6$ . The resulting homogeneous solution exhibits a number of distinct  $^1\text{H-NMR}$  signals characteristic of Pt–Me groups (readily identified by  $^{195}\text{Pt}$  satellites along with the chemical shift), as follows: (a)  $\delta$  0.88,  $^2J_{\text{PtH}} = 72$  Hz; (b)  $\delta$  0.76,  $^2J_{\text{PtH}} = 80$  Hz; (c)  $\delta$  0.60,  $^2J_{\text{PtH}} = 86$  Hz; (d)  $\delta$  0.49,  $^2J_{\text{PtH}} = 80$  Hz. A much weaker signal can also be observed at  $\delta$  1.76,  $^2J_{\text{PtH}} = 78$  Hz. These species were identified by comparison with the  $^1\text{H-NMR}$  spectra of independently prepared samples of  $(\text{DMSO})_2\text{PtMeCl}$  and  $(\text{DMSO})_2\text{PtMe}_2$  [5]. Signals (a) and (b) correspond to *cis*- and *trans*- $(\text{DMSO})_2\text{PtMeCl}$ , and (c) and (d) to the two isomers of  $(\text{DMSO})_2\text{PtMe}_2$ , respectively. The weak signal at  $\delta$  1.76 is assigned to  $\text{PtMe}_2\text{Cl}_4^{2-}$ , again by comparison to an authentic sample [4].

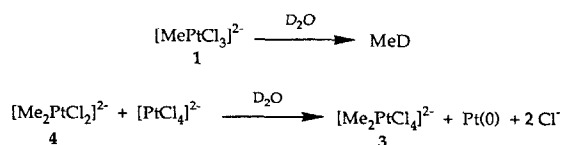
This result strongly suggests that the yellow solid is not a single species, despite the elemental analytical data. The formation of  $(\text{DMSO})_2\text{PtMeCl}$  and  $(\text{DMSO})_2\text{PtMe}_2$  upon dissolution in DMSO indicates that not only  $[\text{PtMeCl}_3]^{2-}$  but also  $[\text{PtMe}_2\text{Cl}_2]^{2-}$  is present. In fact, the monomethyl species is the minor product based on the  $^1\text{H-NMR}$  in DMSO- $d_6$ :  $(\text{DMSO})_2\text{PtMeCl}$ :  $(\text{DMSO})_2\text{PtMe}_2 \approx 3:10$ . (The ratio between *cis*- and *trans*-

$(\text{DMSO})_2\text{PtMe}_2$  varies with different experimental conditions; when  $\text{Na}_2\text{PtMeCl}_5$  is added to  $> 2.5$  eq.  $\text{Cp}_2\text{Co}$  in THF (rather than the reverse order of addition), *trans*- $(\text{DMSO})_2\text{PtMe}_2$  dominates.) Based on  $^1\text{H-NMR}$  integration (using  $\text{Cp}_2\text{Co}^+$  as internal standard), the total NMR-detectable Pt–Me species accounts for ca. 60% of the expected value. These results suggest that the yellow solid contains three complex anions: **1** and **4**, which are converted to the corresponding DMSO complexes (with some losses) on dissolution, and  $[\text{PtCl}_4]^{2-}$  to account for mass balance (Scheme 3).

## 2.2. Reaction of methylplatinum(II) salts with water

Dissolving the yellow reduction product in  $\text{D}_2\text{O}$  results in gas evolution ( $\text{CH}_3\text{D}$ ) and formation of  $[\text{PtMe}_2\text{Cl}_4]^{2-}$  (**3**), identified by  $^1\text{H-NMR}$  (see above), together with platinum metal. The yield of **3**, measured by NMR (relative to  $[\text{Cp}_2\text{Co}]^+$  as internal standard) is the same, within experimental uncertainty, as that of  $(\text{DMSO})_2\text{PtMe}_2$  when the yellow solid is dissolved in DMSO- $d_6$  (see above), suggesting that  $[\text{PtMe}_2\text{Cl}_2]^{2-}$  is quantitatively oxidized to  $[\text{PtMe}_2\text{Cl}_4]^{2-}$  while  $[\text{PtMeCl}_3]^{2-}$  undergoes protonolysis.  $\text{O}_2$  in air is not responsible for the observed oxidation: using deoxygenated  $\text{D}_2\text{O}$  to dissolve the reduction product under nitrogen leads to the same result. Formation of platinum metal implies that a  $\text{Pt}^{\text{II}}$  species, presumably  $[\text{PtCl}_4]^{2-}$ , is the oxidant ( $[\text{PtMe}_2\text{Cl}_2]^{2-}$  and  $[\text{PtCl}_4]^{2-}$  species should be present in a 1:1 ratio, as required by mass balance in the original reduction) (Scheme 4).

The differing behavior in Scheme 4, that **1** is protonolyzed whereas **4** is oxidized, could be



Scheme 4.

due to either **1** being much more water sensitive or **4** being much more susceptible to oxidation. In fact, both appear to be true, at least to some extent, although the former is probably more important here. Dissolving the yellow reduction product in slightly wet DMSO- $d_6$  resulted in gas evolution ( $\text{CH}_4$ ) and formation of  $(\text{DMSO})_2\text{PtMe}_2$  (same yield as in dry DMSO); no  $(\text{DMSO})_2\text{PtMeCl}$  was observed. This result suggests that **1** is much more water sensitive than **4**: protonolysis of  $[\text{PtMeCl}_3]^{2-}$  by water is much faster than reaction with DMSO ( $(\text{DMSO})_2\text{PtMeCl}$  itself is water stable).

Dissolving the reduction product in  $\text{D}_2\text{O}$  containing excess  $[\text{PtCl}_4]^{2-}$  still results in  $\text{CH}_3\text{D}$  evolution and no  $[\text{PtMeCl}_5]^{2-}$ . Thus oxidation of **1** by  $[\text{PtCl}_4]^{2-}$  does not compete with protonolysis, even at neutral pD and with large excess of the potential oxidant. In contrast, upon dissolving the reduction product in a  $\text{D}_2\text{O}$  solution of  $[\text{PtCl}_6]^{2-}$  (excess), an additional MePt resonance ( $\delta$  3.03,  $^2J_{\text{PtH}} = 77$  Hz) is observed along with that of **3**. This signal is identical to that of independently synthesized  $[\text{PtMeCl}_5]^{2-}$  (**2**).  $^1\text{H-NMR}$  quantitation (using sodium *p*-toluenesulfonate as internal standard) reveals that the total yield for **2** and **3** is ca. 60% based on starting **2**, and the ratio of **2**:**3**  $\approx$  3:10. Both numbers are consistent with the yield and ratio for the formation of  $(\text{DMSO})_2\text{PtMeCl}$  and  $(\text{DMSO})_2\text{PtMe}_2$  on dissolving the reduction product in DMSO, implying that at neutral pD,  $[\text{PtMeCl}_3]^{2-}$  as well as  $[\text{PtMe}_2\text{Cl}_2]^{2-}$  are completely oxidized by  $[\text{PtCl}_6]^{2-}$  to the corresponding  $\text{Pt}^{\text{IV}}$  complexes.

When the above experiment is carried out using isotopically enriched (97.3%  $^{195}\text{Pt}$ )  $[\text{PtCl}_6]^{2-}$ ,  $^1\text{H-NMR}$  spectroscopy shows that the  $^{195}\text{Pt}$  satellites of  $[\text{Pt}(\text{CH}_3)\text{Cl}_5]^{2-}$  are of normal intensity (ca. 33% of the total peak area), implying that the oxidation proceeds through electron, not alkyl transfer. This confirms the earlier finding, based on oxidation of Zeise's salt [2], that step (ii) in Scheme 1 does not involve transfer of alkyl groups between Pt centers. (As previously observed, the satellite

peaks do gradually increase if the solution is allowed to stand for 20 min or longer at room temperature. This exchange presumably results from methyl transfer between  $[\text{PtMeCl}_5]^{2-}$  and  $[\text{PtCl}_4]^{2-}$  that is generated in situ. The rate constant of this exchange has been measured [2].)

### 2.3. Competitive oxidation vs. protonolysis of $[\text{PtMeCl}_3]^{2-}$

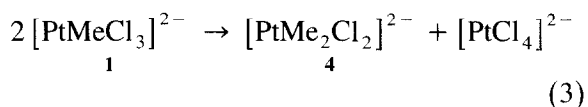
When the reduction product is dissolved in a  $\text{DCl}/\text{D}_2\text{O}$  solution of  $[\text{PtCl}_6]^{2-}$ , protonolysis of  $[\text{PtMeCl}_3]^{2-}$  competes with its oxidation by  $[\text{PtCl}_6]^{2-}$ . When the concentration of  $\text{DCl}$  is a few times higher than that of  $\text{PtCl}_6^{2-}$ ,  $\text{CH}_3\text{D}$  bubbling can be observed. By monitoring the yield of  $[\text{PtMeCl}_5]^{2-}$  while keeping  $[\text{PtCl}_6]^{2-}$  constant and varying  $[\text{DCl}]$ , the ratio of the rate constants for oxidation vs. deuterolysis,  $k_{\text{oxidation}}/k_{\text{D}^+}$ , was determined to be approximately 2.5 (see experimental section for details). The ratio  $k_{\text{oxidation}}/k_{\text{H}^+}$  was previously measured as approximately 18 at  $95^\circ\text{C}$  by Zama-shchikov and coworkers [4], using a system shown in Scheme 2 above. We have determined an isotope effect for protonolysis of **1** by carrying out the reduction of **2** by  $\text{CrCl}_2$  in a  $\text{H}_2\text{O}/\text{D}_2\text{O}$  mixture, and obtained  $k_{\text{H}}/k_{\text{D}} = 9$  at  $0^\circ\text{C}$  [6]. Applying this directly to the above result gives an apparent  $k_{\text{oxidation}}/k_{\text{H}^+} \approx 0.3$  at  $22^\circ\text{C}$ . This number should be taken as only approximate, as kinetic isotope effects measured in mixed solvents, where fractionation factors may dominate, may not translate directly to comparing results in (pure)  $\text{H}_2\text{O}$  vs.  $\text{D}_2\text{O}$  [7]. In any case, though, it is at least an order of magnitude lower than the previous ( $95^\circ\text{C}$ ) value, implying that the oxidation of **1** by  $[\text{PtCl}_6]^{2-}$  has a considerably larger activation energy than protonolysis. At the even higher temperatures (typically  $120^\circ\text{C}$ ) where alkane activation by  $\text{Pt}^{\text{II}}$  takes place, then, the oxidation of **1** to **2**, the precursor to functionalized alkane, should overwhelmingly dominate the non-productive reversion to alkane via protonolysis.

#### 2.4. Mechanism of the formation of $[\text{PtMe}_2\text{Cl}_2]^{2-}$ during reduction of **2**

There are several plausible explanations for the appearance of dimethylplatinum species in solutions made from the yellow solid obtained on reducing **2**. The close agreement of product distributions in DMSO, wet DMSO,  $\text{D}_2\text{O}$  and  $\text{D}_2\text{O}/[\text{PtCl}_6]^{2-}$  solutions rules out the possibility that methyl redistribution takes place only after the solid is redissolved, since it would be competing with various processes (DMSO substitution, protonolysis, oxidation) that presumably have quite different rates. Therefore it must take place during the reduction, prior to precipitation of the yellow cobalticinium mixed salts. The most likely mechanism for such an exchange is via a nucleophilic displacement reaction, with incipient **1** displacing  $\text{Pt}^{\text{II}}$  from unreacted **2** (Scheme 5).  $[\text{PtCl}_4]^{2-}$  is known to undergo an analogous reaction with **2** (as well as with **3** [4]), as demonstrated by  $^{195}\text{Pt}$  exchange [2], although the rate of that reaction is much slower than would be required to account for the present observation, where displacement must compete with (rather rapid) precipitation. If this explanation is correct, then, **1** must be a substantially better nucleophile than  $[\text{PtCl}_4]^{2-}$ , although the difference in solvent (THF vs.  $\text{H}_2\text{O}$ ) may also play a role.

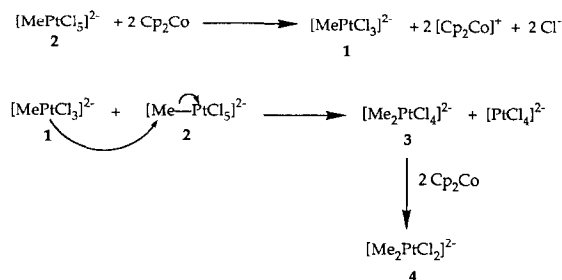
An alternate explanation would be ‘simple’ disproportionation according to Eq. (3), although it is far from clear exactly how this interchange would take place; a nucleophilic mechanism as in Scheme 5 would produce Pt

metal, which is not observed at this stage. To distinguish between these alternatives, we carried out the reduction by adding 1 eq. of  $\text{Cp}_2\text{Co}$  (THF solution) to  $\text{Na}_2\text{PtMeCl}_5$  in THF, which should keep the concentration of **2** much higher, at all stages, than the original reaction in which **2** was added to excess  $\text{Cp}_2\text{Co}$ . This results in the formation of  $[\text{PtMe}_2\text{Cl}_4]^{2-}$  as the major product,  $[\text{PtMe}_2\text{Cl}_2]^{2-}$  as the minor product, and almost no  $[\text{PtMeCl}_3]^{2-}$  (as assessed from the product distribution after dissolution in DMSO). Such a result is consistent with  $[\text{PtMe}_2\text{Cl}_2]^{2-}$  arising from nucleophilic attack of  $[\text{PtMeCl}_3]^{2-}$  on  $[\text{PtMeCl}_5]^{2-}$ ; in the alternative mechanism, the relative proportions of mono- and dimethyl products should not be much affected by inverse addition.



#### 2.5. Conclusions and implications

It seems clear that  $[\text{RPtCl}_3]^{2-}$ , the putative first intermediate in functionalization of alkanes by  $\text{Pt}^{\text{II}}/\text{Pt}^{\text{IV}}$ , is remarkably reactive, compared to its close relatives, in both thermodynamic and kinetic senses. It has not proven possible to generate the monomethyl  $\text{Pt}^{\text{II}}$  complex **1** in solution in quantities sufficient to detect. It can be trapped by rapid precipitation, but even then, only in competition with a reaction that effectively leads to disproportionation to dimethyl and methyl-free species. Similarly, **1** is much more sensitive to protonolysis than dimethyl analog **4**. (Homoleptic  $[\text{PtMe}_4]^{2-}$  is moderately stable in non-protic solution [8], unlike **1**, but is readily protonolyzed, although we do not have information on its relative susceptibility to water.) This is demonstrated not only by results above but by the fact that careful protonation of  $[\text{Bu}_4\text{N}]_2[\text{PtMe}_2\text{Cl}_2]$  with 1 eq. of HCl gives methane and unreacted **4**. The same trend may hold in ligand-stabilized analogs: the intermedi-



Scheme 5.

ate obtained by low-temperature protonation of (tmeda)PtMe<sub>2</sub> is significantly more stable to reductive elimination of methane than that from (tmeda)PtMeCl, (even though under certain conditions it is possible to prepare the latter by controlled protonolysis of the former) [6]. It should be kept in mind that protonolysis of the Pt–R bond is the microscopic reverse of the C–H bond activation reaction that initiates the entire process, so that a low activation barrier for the former implies a (relatively) low one for the latter.

Of course, a low barrier for reversible C–H activation is insufficient for productive transformations. In spite of the high sensitivity to water, **1** is a viable intermediate because it is even more rapidly oxidized to **2** by [PtCl<sub>6</sub>]<sup>2-</sup> under functionalization conditions. It appears, then, that this rather complex system succeeds in functionalizing alkanes as a consequence of a delicate balance of reactivities. [PtCl<sub>4</sub>]<sup>2-</sup> behaves as an electrophile towards alkanes, so (as a consequence of microscopic reversibility) **1** must be susceptible to electrophilic cleavage (i.e., protonolysis). However, it is competitively oxidized to **2** which is quite stable to protonolysis, instead undergoing nucleophilic cleavage [2]. Certainly the solvent, water, must play a key role in establishing this balance, along with the detailed nature of the reactive metal center.

### 3. Experimental

#### 3.1. Methylation of [PtCl<sub>4</sub>]<sup>2-</sup>

[Bu<sub>4</sub>N]<sub>2</sub>[PtCl<sub>4</sub>] was prepared by metathesis of K<sub>2</sub>[PtCl<sub>4</sub>] and [Bu<sub>4</sub>N]Cl in acetone. Under Ar, 0.35 g (0.043 mmol) of the salt was dissolved in 10 ml CH<sub>2</sub>Cl<sub>2</sub>, and 0.21 ml of 2 M ZnMe<sub>2</sub> in toluene (0.043 mmol) was added slowly. The color of the solution changed from pink-orange to dark red. After stirring for several hours, solvent was evaporated to a final volume of about 4 ml, and 20 ml pentane added; the resulting dark gray precipitate was

isolated by filtration, washed with pentane and vacuum dried. A solution in CD<sub>2</sub>Cl<sub>2</sub> exhibited a single major <sup>1</sup>H-NMR peak at δ 1.27 with satellite peaks (<sup>2</sup>J<sub>PtH</sub> = 80 Hz), but the relative intensities of that peak and [Bu<sub>4</sub>N]<sup>+</sup> signals were consistent with formulation as [Bu<sub>4</sub>N]<sub>2</sub>[PtMe<sub>2</sub>Cl<sub>2</sub>] rather than [Bu<sub>4</sub>N]<sub>2</sub>[PtMeCl<sub>3</sub>]. In agreement, addition of excess PMe<sub>3</sub> to the solution led to an NMR spectrum characteristic of a mixture of *cis*- and *trans*-PtMe<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>. When only one-half eq. of ZnMe<sub>2</sub> was used, the NMR of the resulting precipitate showed only the same signal (albeit much weaker), with no evidence of a new peak that might arise from a monomethyl complex.

Elemental analysis of the gray precipitate is inconsistent with the above formulation (Calcd. for [Bu<sub>4</sub>N]<sub>2</sub>[PtMe<sub>2</sub>Cl<sub>2</sub>]: C, 52.29; H, 10.07; N, 3.59. Found: C, 30.21; H, 5.63; N, 1.66); the low values for all three elements suggest that the precipitate contains substantial amounts of an inorganic species, possibly ZnCl<sub>2</sub>. The PMe<sub>3</sub> reaction shows fairly unequivocally, however, that some 'PtMe<sub>2</sub>' species is present.

A solution of the precipitate in CH<sub>2</sub>Cl<sub>2</sub> was treated with 1 eq. of HCl/ether at 0°C. After evaporation of solvent and redissolution in CD<sub>2</sub>Cl<sub>2</sub>, the NMR showed only the original 'PtMe<sub>2</sub>' signal (with reduced intensity relative to [Bu<sub>4</sub>N]<sup>+</sup>); again, there was no evidence at all for a new monomethyl species.

#### 3.2. Synthesis of Na<sub>2</sub>PtMeCl<sub>5</sub> · xTHF

2.0 g of K<sub>2</sub>PtMeCl<sub>5</sub> · yKCl [2] was dissolved in 10 ml water and passed through an ion-exchange resin column in the Na<sup>+</sup> form. The solution was evaporated to dryness in vacuum, and the residue dissolved in dry THF (100 ml) under N<sub>2</sub>, stirred for 15 min, and filtered. Evaporation of solvent and drying under vacuum gave 1.49 g (72%) of yellow solid, characterized as Na<sub>2</sub>PtMeCl<sub>5</sub> · xTHF, with x ≈ 2.6, by NMR. The compound in the solid state decomposes overnight at room temperature, but can be kept at –25°C without significant change for at

least months. It is stable in THF solution for several hours, but decomposes rapidly in acetone and DMSO.

### 3.3. Reduction of $\text{Na}_2\text{PtMeCl}_5$ by $\text{Cp}_2\text{Co}$

Under  $\text{N}_2$ ,  $\text{Na}_2\text{PtMeCl}_5 \cdot x\text{THF}$  (0.50 g, 0.81 mmol) was dissolved in 10 ml of THF, and the solution slowly added to 10 ml THF solution containing  $\text{Cp}_2\text{Co}$  (0.48 g, 2.5 mmol) with continuous stirring at room temperature. A yellow solid began precipitating immediately. After addition was complete, the suspension was allowed to stir for 5 min and then filtered, followed by  $5 \times 5$  ml THF wash and drying in vacuum. The yield of yellow solid was 0.635 g (97% based on the analytical formula). Anal. Calc. for  $(\text{Cp}_2\text{Co})_2\text{PtMeCl}_3 \cdot 2\text{NaCl}$ : C, 31.08; H, 2.86. Found: C, 31.21; H, 2.87. The  $^1\text{H-NMR}$  spectrum of a  $\text{DMSO-d}_6$  solution shows  $(\text{DMSO})_2\text{PtMeCl}$  and  $(\text{DMSO})_2\text{PtMe}_2$  in ca. 3:10 ratio.

### 3.4. Aqueous chemistry of $[\text{PtMeCl}_3]^{2-}$

The yellow reduction product of the preceding section (12 mg, 0.015 mmol) was dissolved in 0.6 ml  $\text{D}_2\text{O}$  containing varying amounts of  $\text{Na}_2\text{PtCl}_6$  and/or  $\text{DCl}$ , depending on the study involved. The resulting solution or suspension was agitated by a mixer for 20 min and then centrifuged. The clear supernatant was transferred to an NMR tube for analysis.

For the study of competitive oxidation/protonolysis,  $\text{DCl}$  concentrations of 0.00, 0.10, 0.13, 0.15 and 0.20 M, were used, with 0.123 M  $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ . The yield of  $[\text{PtMe}_2\text{Cl}_4]^{2-}$  (**3**) from oxidation of  $[\text{PtMe}_2\text{Cl}_2]^{2-}$  (**4**) is independent of acid concentration, so its NMR signal was used as internal  $^1\text{H-NMR}$  standard. The ratio of **2:3** is defined as  $A$ ; when  $[\text{DCl}] = 0$ ,  $[\text{PtMeCl}_3]^{2-}$  (**1**) is completely oxidized to

Table 1

Oxidation vs. protonolysis for  $[\text{PtMeCl}_3]^{2-}$  ( $[\text{PtCl}_6]^{2-} = 0.123$  M)

$[\text{DCl}]$ (M)	$A$	$k_{\text{oxidation}}/k_{\text{D}^+}$
0.00	0.280 (= $A_0$ )	–
0.10	0.214	2.64
0.13	0.198	2.56
0.15	0.182	2.26
0.20	0.174	2.67

$[\text{PtMeCl}_5]^{2-}$  (**2**) by  $[\text{PtCl}_6]^{2-}$ , so the resulting ratio ( $A_0$ ) reflects the composition of the reduction product (confirmed by the DMSO results). The ratio of rate constants is given by Eq. (4). Data are shown in Table 1.

$$\frac{k_{\text{oxidation}}}{k_{\text{D}^+}} = \frac{A}{A_0 - A} \frac{[\text{DCl}]}{[\text{PtCl}_6]^{2-}} \quad (4)$$

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