

Reaction of Organoboron Compounds with Platinum(II) Disolvento Complexes

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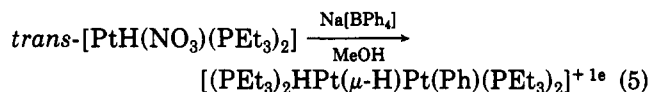
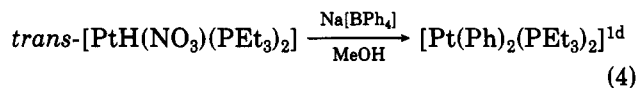
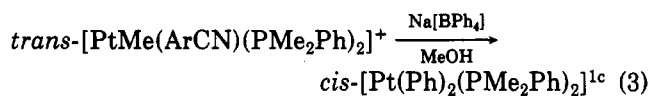
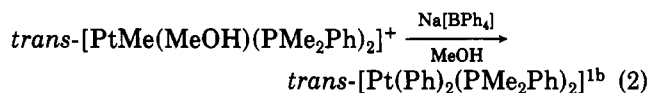
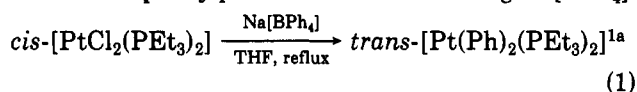
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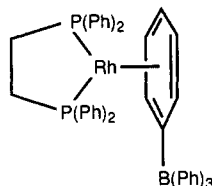
Cationic complexes $cis\text{-}[\text{Pt}(\text{S})_2\text{L}_2]^{2+}$ ($\text{L} = \text{PMe}_3, \text{PEt}_3, \text{or PPh}_3$; $\text{S} = \text{H}_2\text{O}$ or MeOH) react with arylboron derivatives ($[\text{BPh}_4]^-$, $[\text{B}(p\text{-Tol})_4]^-$, $[\text{B}(m\text{-Tol})_4]^-$, BPh_3 , $\text{B}(\text{OMe})\text{Ph}_2$, $\text{B}(\text{OMe})_2\text{Ph}$, and $\text{B}(\text{OH})_2\text{Ph}$) to give $trans\text{-}[\text{Pt}(\text{Ar})(\text{S})\text{L}_2]^+$ which are isolated and characterized as their halo derivatives $trans\text{-}[\text{PtX}(\text{Ar})\text{L}_2]$. When $\text{L} = \text{PMe}_3$, the transient formation of $cis\text{-}[\text{Pt}(\text{Ar})(\text{S})\text{L}_2]^+$ is also observed. The cation $cis\text{-}[\text{Pt}(\text{CH}_3\text{CN})_2(\text{PEt}_3)_2]^{2+}$, however, reacts with $[\text{BPh}_4]^-$ only when at least some of the solvent is hydroxylic. However the phenylation and $cis\text{-}trans$ isomerization reactions are slowed down so that the intermediate formation of $cis\text{-}[\text{Pt}(\text{Ph})(\text{CH}_3\text{CN})(\text{PEt}_3)_2]^+$ cation can be observed. It is shown that $[\text{BPh}_4]^-$ is not the phenylating agent as it decomposes to BPh_3 and C_6H_6 prior to the phenylation reaction. Other phenylboron derivatives such as BPh_3 , $\text{B}(\text{OMe})\text{Ph}_2$, $\text{B}(\text{OMe})_2\text{Ph}$, and $\text{B}(\text{OH})_2\text{Ph}$ can transfer all of their phenyl groups to platinum. It is found that the phenyl transfer is strictly regioselective; i.e., only the C atom bonded to boron is found coordinated to platinum. When $[\text{B}(\text{Me})(\text{Ph})_3]$ is used, either a methyl or a phenyl group can be transferred to platinum.

Introduction

There have been several reports in the literature¹ of the formation of phenylplatinum derivatives using $\text{Na}[\text{BPh}_4]$:



Furthermore, there are several reports of $[\text{BPh}_4]^-$ acting as a phenylating agent on complexes of rhodium,² mercury,³ ruthenium,⁴ and nickel.⁵ The rhodium complexes are particularly interesting in this context for two reasons: (1) they give well-characterized η^6 -complexes,^{2b} by reacting the disolvento complex $[\text{Rh}(\text{S})_2(\text{diphos})]^+$ (diphos = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) with $[\text{BPh}_4]^-$, the former cation being "isoelectronic" with $cis\text{-}[\text{Pt}(\text{S})_2(\text{PR}_3)_2]^{2+}$ and



(2) on heating to ca. 70 °C $[\text{Rh}(\eta^6\text{-C}_6\text{H}_5\text{-BPh}_3)(\text{diphos})]$ decomposes to $[\text{Rh}(\text{Ph})(\text{diphos})]^{2b}$

Clark and Manzer^{1c} have proposed that in the case of the phenylation of the platinum(II) complexes "the reaction probably proceeds by way of nucleophilic attack by a phenyl ring to give an intermediate π -bonded complex...."

While in the case of reaction 1 one can presume the intermediate formation of the disolvento complex $cis\text{-}[\text{Pt}(\text{THF})_2(\text{PEt}_3)_2]^{2+}$ prior to phenylation, in the cases of the other reactions only a monosolvento complex is present (reaction 2) or can be formed (reactions 3–5). In these cases an η^6 -interaction of one of the phenyl groups of $[\text{BPh}_4]^-$ would give a 20-electron intermediate or transition state. It is, however, possible that one of the other ligands (a phosphine or the "anion", i.e., H or Me) is lost prior to the η^6 -interaction. In this context it is noteworthy that in reactions 2–4 the "anionic" ligand is no longer present in the product.

In order to clarify the mechanistic pathway leading to phenylation in platinum(II) complexes, a study of the reactions of tetraarylbates with complexes $cis\text{-}[\text{Pt}(\text{S})_2(\text{PR}_3)_2]^{2+}$ was undertaken as (a) π -arene complexes could be the intermediates in reaction 1 and (b) one might be able to observe the π -interaction found in the rhodium(I) complexes.

Results

Solvento Complexes. The complexes $cis\text{-}[\text{PtCl}_2\text{L}_2]$ (1) (a, $\text{L} = \text{PMe}_3$, b, $\text{L} = \text{PEt}_3$) reacted with 2 equiv of AgCF_3SO_3 in methanol giving the corresponding solvento cations of the type $cis\text{-}[\text{Pt}(\text{S})_2\text{L}_2]^{2+}$ ($\text{S} = \text{Solvent}$) (2) (see Table I). Despite the 1:2 stoichiometry, chloride precipitation was incomplete, small amounts of Ag ions remaining in solution as evidenced by the precipitation of sparingly soluble $\text{Ag}[\text{BPh}_4]$ on addition of $\text{Na}[\text{BPh}_4]$ to these solutions. The "unreacted" chloride was present as the cation $cis\text{-}[\text{PtCl}(\text{S})\text{L}_2]^+$ (3) which also precipitated on addition of $[\text{BPh}_4]^-$. The presence of 3b ($\text{L} = \text{PEt}_3$) was confirmed by reacting 1b with 1 equiv of AgCF_3SO_3 . The ³¹P NMR spectrum of this solution showed the presence of two inequivalent P atoms, with values of ¹J(Pt,P) and ²J(P,P) that are characteristic for compounds of type 3 (see Table I).

Evaporation of a solution containing 2b ($\text{L} = \text{PEt}_3$; S as above), prepared as described above, led to the isolation of a solid that could be characterized as $cis\text{-}[\text{Pt}(\text{H}_2\text{O})_2(\text{PEt}_3)_2][\text{CF}_3\text{SO}_3]_2$ (4b) (see Experimental Section).

- (1) (a) Clark, H. C.; Dixon, K. R. *J. Am. Chem. Soc.* 1969, 91, 596. (b) Clark, H. C.; Ruddick, J. D. *Inorg. Chem.* 1970, 9, 1226. (c) Clark, H. C.; Manzer, L. E. *Inorg. Chem.* 1971, 10, 2699. (d) Deeming, A. J.; Johnson, B. F. G.; Lewis, J. J. *Chem. Soc., Dalton Trans.* 1973, 1848. (e) Bracher, G.; Grove, D. M.; Venanzi, L. M.; Bachechi, F.; Mura, P.; Zambonelli, L. *Angew. Chem., Int. Ed. Engl.* 1978, 17, 778; *Angew. Chem.* 1978, 90, 826.
 (2) (a) Schrock, R. R.; Osborn, J. A. *Inorg. Chem.* 1970, 9, 2339. (b) Albano, P.; Aresta, M.; Manassero, M. *J. Inorg. Chem.* 1980, 19, 1069.
 (3) Coates, G. E. *Organometallic Compounds*, 2nd ed.; Wiley: New York, 1960.
 (4) Haines, R. J.; Du Preez, A. L. *J. Am. Chem. Soc.* 1971, 93, 2820.
 (5) Sacconi, L.; Dapporto, P.; Stoppioni, P. *Inorg. Chem.* 1976, 15, 325.

Table I. ³¹P NMR Data for Mono- and Disolvento Complexes of Platinum(II) (S = CH₃OH or H₂O)

		δ(P ₁), ppm	¹ J(Pt,P ₁), Hz	δ(P ₂), ppm	¹ J(Pt,P ₂), Hz	² J(P ₁ ,P ₂), Hz
2a	<i>cis</i> -[Pt(S) ₂ (PMe ₃) ₂] ²⁺	-21.8 ^a	3775			
2b	<i>cis</i> -[Pt(S) ₂ (PEt ₃) ₂] ²⁺	10.1 ^a	3720			
2c	<i>cis</i> -[Pt(S) ₂ (PPh ₃) ₂] ²⁺	6.2 ^b	4068			
3b	<i>cis</i> -[Pt(Cl)(S)(PEt ₃) ₂] ⁺	7.0 ^{c,d}	3774	13.8	3553	20
6b	<i>cis</i> -[Pt(CH ₃ CN) ₂ (PEt ₃) ₂] ²⁺	7.9 ^e	3434			
7a	<i>trans</i> -[Pt(Ph)(S)(PMe ₃) ₂] ⁺	-6.3 ^a	2788			
7b	<i>trans</i> -[Pt(Ph)(S)(PEt ₃) ₂] ⁺	21.4 ^a	2805			
7c	<i>trans</i> -[Pt(Ph)(S)(PPh ₃) ₂] ⁺	27.1 ^c	3172			
11a	<i>cis</i> -[Pt(Ph)(S)(PMe ₃) ₂] ⁺	-32.6 ^{b,d}	4355	-11.6	1729	13
13b	<i>trans</i> -[Pt(<i>m</i> -Tol)(S)(PEt ₃) ₂] ⁺	20.9 ^a	2826			
14b	<i>trans</i> -[Pt(<i>p</i> -Tol)(S)(PEt ₃) ₂] ⁺	21.0 ^a	2809			
20b	<i>trans</i> -[Pt(Me)(S)(PEt ₃) ₂] ⁺	24.2 ^c	2830			

^aIn CD₃OD. ^bIn CD₂Cl₂. ^cIn CH₃OH/CD₂Cl₂. ^dThis resonance is assigned to P in the trans position to S. ^eIn CD₃CN.

However, when this solid was dissolved in methanol, it gave a solution whose NMR spectral characteristics corresponded to those of **2b** prepared in situ as described above. Silver ion free solutions of the solvento complex **2b** could be obtained by dissolving *cis*-[Pt(H₂O)₂(PEt₃)₂][CF₃SO₃]₂ (**4b**) in methanol.

The reaction of *cis*-[PtCl₂(PPh₃)₂] (**1c**) with 2 equiv of AgCF₃SO₃ in CH₂Cl₂/MeOH (1:1) gave the complex *cis*-[Pt(H₂O)₂(PPh₃)₂][CF₃SO₃]₂ (**4c**) (see Experimental Section).

When a methanolic solution of [Pt(S)₂(PMe₃)₂]²⁺ (**2a**) was treated with 2 equiv of Na[BPh₄], a white precipitate (**5a**) was formed. While this solid was relatively stable when in contact with its mother liquor, it decomposed rapidly (within minutes) upon drying. While its isolation had to be carried out at -70 °C, it did not prove possible to completely dry the solid. When **5a** was dissolved in CD₂Cl₂ at -70 °C, one could obtain satisfactory ¹H, ¹³C, and ³¹P NMR spectra for this substance. The ³¹P NMR resonances were consistent with the presence of the cationic species [Pt(S)₂(PMe₃)₂]²⁺, and integration of the appropriate resonances in the ¹H NMR spectrum showed that PMe₃ and [BPh₄]⁻ were present in the ratio 1:1. The ¹³C NMR spectrum showed only four different carbon atoms of [BPh₄]⁻; i.e., no interaction of a phenyl group of [BPh₄]⁻ with the platinum atom could be detected. Thus **5a** can be formulated as [Pt(S)₂(PMe₃)₂][BPh₄]₂. Addition of solid LiCl to a CD₂Cl₂ solution of **5a** at -70 °C resulted in the formation of *cis*-[PtCl₂(PMe₃)₂] (**1a**).

No compound of type **5** was precipitated when Na[BPh₄] was added to a methanol solution of [Pt(S)₂L₂]²⁺ (L = PEt₃) (**2b**). This solution reacted within minutes at room temperature, giving the phenylation product described in the next section.

Methanol solutions of *cis*-[Pt(S)₂(PEt₃)₂]²⁺ (**2b**) reacted with acetonitrile giving *cis*-[Pt(CH₃CN)₂(PEt₃)₂]²⁺ which could be isolated as its [BPh₄]⁻ salt *cis*-[Pt(CH₃CN)₂(PEt₃)₂][BPh₄]₂ (**6b**). This salt is thermally more stable than the corresponding species where methanol (or water) is present as the coordinated solvent.

The Phenylation Reaction. Mechanistic studies of reaction 5, to be described later, required the use of the solvent mixture CH₂Cl₂/MeOH (1:1) for solubility reasons. Thus, in order to correlate the results of those experiments with the present results, the above solvent mixture was used in the phenylation studies starting from compounds of type **2**. ³¹P NMR studies of solutions of the solvent cations **2a** and **2b** in this solvent mixture showed that the Pt complexes formed were the same as those found in pure methanol. When a solution of **2a**, dissolved in CH₂Cl₂/MeOH (1:1), was treated with Na[BPh₄], no formation of solid **5a** was observed.

Methanol or CH₂Cl₂/MeOH solutions of the solvento complexes *cis*-[Pt(S)₂L₂]²⁺ (**2a** and **2b**) reacted with

Table II. ³¹P and ¹⁹⁵Pt NMR Data for Some Arylated Compounds of the Type *trans*-[PtX(Ar)L₂]

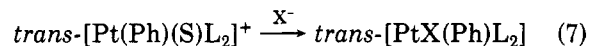
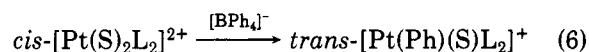
		³¹ P NMR δ (ppm)	¹ J(¹⁹⁵ Pt, ³¹ P), Hz	¹⁹⁵ Pt NMR δ (ppm)
8a	<i>trans</i> -[PtCl(Ph)(PMe ₃) ₂]	-14.5 ^a	2763	-4269
17a	<i>trans</i> -[PtCl(C ₆ D ₅)(PMe ₃) ₂]	-14.5 ^a	2763	
8b	<i>trans</i> -[PtCl(Ph)(PEt ₃) ₂]	13.6 ^a	2800	-4267
9c	<i>trans</i> -[PtBr(Ph)(PPh ₃) ₂]	23.6 ^b	3120	
10b	<i>trans</i> -[PtI(Ph)(PEt ₃) ₂]	9.0 ^c	2740	
15b	<i>trans</i> -[PtCl(<i>m</i> -Tol)(PEt ₃) ₂]	13.5 ^a	2814	-4272
16b	<i>trans</i> -[PtCl(<i>p</i> -Tol)(PEt ₃) ₂]	13.6 ^a	2807	-4277

^aIn CD₂Cl₂. ^bIn CDCl₃. ^cIn CD₃COCD₃.

[BPh₄]⁻ to give compounds that were assigned the structures *trans*-[Pt(Ph)(S)L₂]⁺ (**7a** and **7b**).

In the case of the PPh₃ analogue, for solubility reasons, the compound *cis*-[Pt(H₂O)₂(PPh₃)₂][CF₃SO₃]₂ (**4c**) was dissolved in CH₂Cl₂ and Na[BPh₄] in methanol was then added.

Compounds **7** were characterized in solution by ³¹P NMR spectroscopy (see Table I) (reaction 6). These were reacted with either LiCl, LiBr, or NaI and the products of the type *trans*-[PtCl(Ph)L₂] (**8**), *trans*-[PtBr(Ph)L₂] (**9**), or *trans*-[PtI(Ph)L₂] (**10**), respectively (reaction 7), were isolated in high yields (ca. 85%) and fully characterized (see Table II).



The phenylation reaction of compounds of type **2** was completed within 10 min at room temperature. At 0 °C completion of the reaction required ca. 30 min. while at -70 °C no phenylation occurred after several hours.

As mentioned earlier, the reaction of **2a** with Na[BPh₄] in MeOH gave a precipitate of **5a**. When this suspension was heated to reflux for ca. 5 min, complete formation of **7a** was observed. Furthermore, when solid *cis*-[Pt(S)₂(PMe₃)₂][BPh₄]₂ (**5a**) was dissolved in precooled CH₂Cl₂ and the solution was allowed to warm to 0 °C, rapid formation of *cis*-[Pt(Ph)(S)(PMe₃)₂]⁺ (**11a**) was observed. This was characterized through its NMR spectrum and transformed by addition of LiCl into the corresponding complex *cis*-[PtCl(Ph)(PMe₃)₂] (**12a**) which was also characterized by NMR spectroscopy. Complex **12a** completely isomerized to *trans*-[PtCl(Ph)(PMe₃)₂] (**8a**) within 1 h at room temperature. It follows that if in the case of **5b** the primary product has *cis* configuration, i.e., **11b**, its rate of isomerization to *trans*-[Pt(Ph)(S)(PEt₃)₂]⁺ (**7b**) must be faster than the rate of the phenylation reaction under our experimental conditions. Thus it can be con-

cluded that phenylation of compounds $cis\text{-}[\text{Pt}(\text{S})_2\text{L}_2]^{2+}$ proceeds, in all cases, by way of the intermediates $cis\text{-}[\text{Pt}(\text{Ph})(\text{S})\text{L}_2]^+$ (11) which then isomerize to the corresponding *trans* products. However, as ^{31}P NMR monitoring of the phenylation reaction did not show the presence of intermediates of type 11, it can also be deduced that isomerization occurred at a faster rate than phenylation under these conditions.

As expected, the meta- and para-substituted tetra-arylborates reacted with compound **2b** giving the corresponding aryl solvento species analogous to **7b**, which were characterized only in solution and isolated as the corresponding chloro complexes $trans\text{-}[\text{PtCl}(m\text{-Tol})(\text{PEt}_3)_2]$ (**15b**) and $trans\text{-}[\text{PtCl}(p\text{-Tol})(\text{PEt}_3)_2]$ (**16b**), respectively. These will be discussed in the next section. On the other hand, sodium tetrakis(*m*-fluorophenyl)borate, $\text{Na}[\text{B}(m\text{-FC}_6\text{H}_4)_4]$, reacted only slowly with the solvento complex **2b**. According to ^{31}P NMR spectroscopy after 20 h at room temperature about half the amount of the solvento complex **2b** was still present in solution.

Finally, BPh_3 , $\text{B}(\text{OMe})\text{Ph}_2$, $\text{B}(\text{OMe})_2\text{Ph}$, and $\text{B}(\text{OH})_2\text{Ph}$ were also capable of phenylating platinum complexes, i.e. giving **7b**, when starting from **2b**.

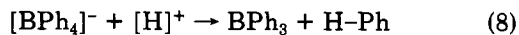
Regioselectivity of the Phenylation Reaction. During reaction 6 there is cleavage of a B-C bond and concurrent formation of a Pt-C bond, and thus one must establish whether the carbon atom bonded to platinum is the same one that was attached to boron.

As mentioned in the previous section, $\text{Na}[\text{B}(m\text{-Tol})_4]$ and $\text{Na}[\text{B}(p\text{-Tol})_4]$ reacted with the solvento complex **2b** to give the corresponding arylplatinum solvento derivatives which were transformed into **15b** and **16b**. ^1H , ^{31}P , and ^{195}Pt NMR spectroscopic studies of the reaction solutions containing either of these compounds showed that only one product was present.

The distinction between **15b** and **16b** was best done by using ^{195}Pt NMR as (1) the ^{31}P chemical shifts and $^1J(\text{Pt},\text{P})$ coupling constants of independently synthesized **15b** and **16b** proved to be identical and (2) it was difficult to detect small amounts of **15b** in **16b** or vice versa by ^1H NMR. The $\delta(\text{Pt})$ values of these two complexes differ by 5 ppm (see Table II), and thus **15b** and **16b** are clearly distinguishable. The ^{195}Pt NMR spectra of the reaction mixtures showed that, within the accuracy of the method (>98%), **15b** did not contain **16b** or vice versa.

Finally, when $cis\text{-}[\text{Pt}(\text{S})_2(\text{PMe}_3)_2]^{2+}$ (**2a**) was reacted with $\text{Na}[\text{B}(\text{C}_6\text{D}_5)_4]$, using the $\text{CH}_2\text{Cl}_2/\text{MeOH}$ solvent mixture, after the addition of LiCl only $trans\text{-}[\text{PtCl}(\text{C}_6\text{D}_5)(\text{PMe}_3)_2]$ (**17a**) was detected within the limits of sensitivity of the NMR measurements.

The Phenyating Species. In order to propose a mechanism for the phenylation reaction 6, it is important to know whether $[\text{BPh}_4]^-$ is the actual phenylating species of the solvent complexes of type **2**. This is a particularly crucial point as methanol solutions of the solvento complex **2b** are acidic (see eq 9 later) and $[\text{BPh}_4]^-$ could react according to eq 8. Indeed, the following results prove that this protonolysis takes place.



(1) BPh_3 transfers all three phenyl groups to $cis\text{-}[\text{Pt}(\text{H}_2\text{O})_2(\text{PEt}_3)_2][\text{CF}_3\text{SO}_3]_2$ (**4b**) in methanol, giving the phenylated complex **7b**, whereas $[\text{BPh}_4]^-$, $[\text{B}(m\text{-Tol})_4]^-$, or $[\text{B}(p\text{-Tol})_4]^-$ only transfer three of their four aryl groups under the same conditions. This was confirmed by reacting solutions obtained as described above: (a) with one-third equiv of BPh_3 and (b) with one-fourth equiv of $[\text{BPh}_4]^-$. In the former case only $trans\text{-}[\text{Pt}(\text{Ph})(\text{S})(\text{PEt}_3)_2]^+$ (**7b**) was observed while in the latter both the starting

Table III. Product Distribution in the Arylation Reaction Using Mixed Arylborates

		Pt complexes	composition
$\text{Na}[\text{B}(\text{C}_6\text{D}_5)_4] +$	8a	$trans\text{-}[\text{PtCl}(\text{Ph})(\text{PMe}_3)_2]$	57%
	BPh_3^a	$trans\text{-}[\text{PtCl}(\text{C}_6\text{D}_5)(\text{PMe}_3)_2]$	43%
$\text{Na}[\text{B}(\text{C}_6\text{D}_5)_4] +$	8a	$trans\text{-}[\text{PtCl}(\text{Ph})(\text{PEt}_3)_2]$	55%
	BPh_3^a	$trans\text{-}[\text{PtCl}(\text{C}_6\text{D}_5)(\text{PEt}_3)_2]$	45%
$\text{Na}[\text{B}(\text{Ph})_3(p\text{-Tol})]$	8b	$trans\text{-}[\text{PtCl}(\text{Ph})(\text{PEt}_3)_2]$	77%
	16b	$trans\text{-}[\text{PtCl}(p\text{-Tol})(\text{PEt}_3)_2]$	23%
$\text{Na}[\text{B}(\text{Ph})_3(p\text{-Tol})_3]$	8b	$trans\text{-}[\text{PtCl}(\text{Ph})(\text{PEt}_3)_2]$	24%
	16b	$trans\text{-}[\text{PtCl}(p\text{-Tol})(\text{PEt}_3)_2]$	76%
$\text{Na}[\text{B}(\text{Ph})(m\text{-FC}_6\text{H}_4)_3]$	8b	$trans\text{-}[\text{PtCl}(\text{Ph})(\text{PEt}_3)_2]$	7%
	18b	$trans\text{-}[\text{PtCl}(m\text{-FC}_6\text{H}_4)(\text{PEt}_3)_2]$	93%
$\text{K}[\text{B}(\text{Me})(\text{Ph})_3]$	7b	$trans\text{-}[\text{Pt}(\text{Ph})(\text{S})(\text{PEt}_3)_2]^+$	~50%
	20b	$trans\text{-}[\text{Pt}(\text{Me})(\text{S})(\text{PEt}_3)_2]^+$	~50%

^a A 1:1 reagent ratio was used.

material $cis\text{-}[\text{Pt}(\text{S})_2(\text{PEt}_3)_2]^{2+}$ (**2b**) and $trans\text{-}[\text{Pt}(\text{Ph})(\text{S})(\text{PEt}_3)_2]^+$ (**7b**) were present in a 1:3 ratio.

It should be noted here that although the transfer of the first phenyl group to platinum using BPh_3 on **2b** was rapid, complete transfer of all three phenyl groups required about 1 day. As the first phenylation step using $[\text{BPh}_4]^-$ occurs at a comparable rate as with BPh_3 , it follows that the cleavage of a phenyl group by a proton must be faster than the first phenylation step.

(2) When the solvento complex **2b** was reacted with one-fourth equiv of $[\text{B}(m\text{-Tol})_4]^-$ or $[\text{B}(p\text{-Tol})_4]^-$, the CH_3 resonances of toluene and compounds **13b** or **14b**, respectively, were observed in the ^1H NMR spectra of the reaction solutions.

(3) Reaction of **2b** with $[\text{B}(m\text{-FC}_6\text{H}_4)_4]^-$ (a reagent known to be insensitive to $[\text{H}]^+$, at least in H_2O at pH 2 and 50 °C according to Meisters et al.^{6b}) proceeds slowly with only ca. 50% arylation after 20 h at room temperature.

(4) $[\text{B}(\text{Ph})(m\text{-FC}_6\text{H}_4)_3]^-$ reacted completely within 3 h with the solvento complex **2b** in methanol solution forming two arylated solvento complexes that were transformed into their chloro complexes by addition of LiCl . The ^{195}Pt NMR spectrum of the product mixture showed the presence of 93% $trans\text{-}[\text{PtCl}(m\text{-FC}_6\text{H}_4)(\text{PEt}_3)_2]$ (**18b**) and 7% $trans\text{-}[\text{PtCl}(\text{Ph})(\text{PEt}_3)_2]$ (**8b**). Furthermore, **2b** with $[\text{B}(\text{Ph})(m\text{-FC}_6\text{H}_4)_3]^-$ in CD_3OD gave $\text{C}_6\text{H}_5\text{D}$ slowly over a period of 3 h as observed by ^1H NMR.

Points 3 and 4 are consistent with a slower protonolysis of the B-C bond in the $[\text{B}(m\text{-FC}_6\text{H}_4)_4]^-$ anion relative to its B-(C_6H_5) counterpart in $[\text{B}(\text{C}_6\text{H}_5)_4]^-$; i.e., $[\text{B}(\text{Ph})(m\text{-FC}_6\text{H}_4)_3]^-$ decomposes mainly to $\text{B}(m\text{-FC}_6\text{H}_4)_3$ before the arylation reaction occurs.

Taken together these results confirm that the first step in the phenylation reaction of solvento complexes of type **2** with tetraarylborates is cleavage of one aryl group by protons, as shown in reaction 8. The resulting triarylboron compound then reacts with the above solvento complex forming the arylated solvento species of type **7**.

When 1:1 mixtures of $[\text{B}(\text{C}_6\text{D}_5)_4]^-$ and $\text{B}(\text{C}_6\text{H}_5)_3$ were reacted with either $cis\text{-}[\text{Pt}(\text{S})_2(\text{PMe}_3)_2]^{2+}$ (**2a**) or $cis\text{-}[\text{Pt}(\text{S})_2(\text{PEt}_3)_2]^{2+}$ (**2b**) in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ at 0 °C, approximately equal amounts of the respective protio- and deuterio products were formed. These were transformed into and isolated as their respective chloro complexes (see Table III).

The addition of water to a mixture of the solvento complex **2b** and 2 equiv of $\text{Na}[\text{B}(m\text{-FC}_6\text{H}_4)_4]^-$ resulted in the precipitation of the hydroxy-bridged complex $[(\text{PEt}_3)_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{PEt}_3)_2][\text{B}(m\text{-FC}_6\text{H}_4)_4]_2$ (**19b**) in ca. 50% yield.

When borates with different substituents at the boron atom as $[\text{B}(\text{Me})(\text{Ph})_3]^-$, $[\text{B}(\text{Ph})_3(p\text{-Tol})]^-$, and $[\text{B}(\text{Ph})(p\text{-$

[Tol]_3^- were reacted with the solvento complex **2b**, mixtures of platinum products were observed.

The mixed *p*-tolyl-phenyl borates $[\text{B}(\text{Ph})_3(\text{p-Tol})]^-$ and $[\text{B}(\text{Ph})(\text{p-Tol})_3]^-$, respectively, reacted with the solvento complex **2b** in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ giving arylated solvento species that were isolated as the appropriate chlorides in the usual way. ^{196}Pt NMR studies showed a ratio of phenyl to tolyl as shown in Table III. It should be noted that the ratio of phenyl to tolyl in the isolated platinum complexes was about the same as it was in the used mixed borate.

The mixed alkyl-aryl boron compound $[\text{B}(\text{Me})(\text{Ph})_3]^-$ reacted with the solvento complex **2b** in methanol forming the phenylated complex **7b** and the methylated complex *trans*- $[\text{Pt}(\text{Me})(\text{S})(\text{PEt}_3)_2]^+$ (**20b**) in a ca. 1:1 ratio according to the NMR spectra.

It was also found (1) that $\text{B}(\text{OCH}_3)_2\text{Ph}$ could transfer both phenyl groups to the solvento complex **2b** giving the phenylated species **7b** and (2) that $\text{B}(\text{OCH}_3)_2\text{Ph}$ and $\text{B}(\text{OH})_2\text{Ph}$ completely transferred their phenyl groups to platinum.

However, both SiPh_4 and SnPh_4 did not react with the solvento complex **2b** under these conditions. A combination of steric factors and reduced Lewis acidity relative to BPh_3 may be responsible for this lack of reactivity.

The Phenylation Reaction Using the CH_3CN Solvento Complexes. As mentioned previously, the stable salt *cis*- $[\text{Pt}(\text{CH}_3\text{CN})_2(\text{PEt}_3)_2][\text{BPh}_4]_2$ (**6b**) could be obtained. This when dissolved in good quality but not anhydrous acetonitrile gave the corresponding phenylated product only to the extent of ca. 5% after ca. 10 h. Even after ca. 27 h ca. 95% starting material **6b** and ca. 5% of phenylated product *trans*- $[\text{Pt}(\text{Ph})(\text{CH}_3\text{CN})(\text{PEt}_3)_2]^+$ were observed. The occurrence of this reaction is likely to be due to the presence of water, the slow rate being caused by its very low concentration. This was confirmed by dissolving **6b** in $\text{CD}_3\text{CN}/\text{CH}_3\text{OH}$ (1:1). After ca. 10 h one obtained a mixture containing 34% unreacted **6b**, 44% *cis*- $[\text{Pt}(\text{Ph})(\text{S})(\text{PEt}_3)_2]^+$ (**11b**), and 22% *trans*- $[\text{Pt}(\text{Ph})(\text{S})(\text{PEt}_3)_2]^+$ (**7b**) (S in the latter two compounds could be either MeOH or CD_3CN). After ca. 27 h only the phenylated species **11b** and **7b** were present in a 44:56 ratio and after ca. 100 h only **7b** was present.

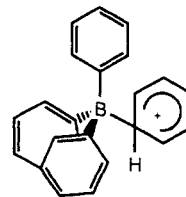
Discussion

The Solvento Complexes. Before the phenylation reaction is discussed, a comment on the nature of the solvento complexes is needed. Commercially available solvents that contain water were employed, and the latter could compete with MeOH as a ligand in the solvento complexes. It has not proved possible to establish the nature of the coordinated solvent, but, given their fast exchange, it can be assumed that both aquo and methanol complexes are present in solution. Thus, in the formulation *cis*- $[\text{Pt}(\text{S})_2(\text{PR}_3)_2]^{2+}$, S indicates either H_2O or MeOH in rapid exchange with the bulk solvent.

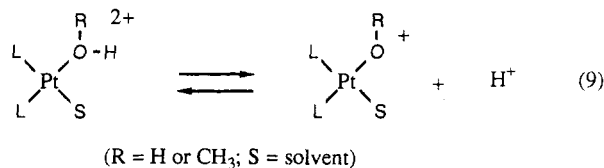
As mentioned in the Results, solid *cis*- $[\text{Pt}(\text{H}_2\text{O})_2(\text{PEt}_3)_2][\text{CF}_3\text{SO}_3]_2$ (**4b**) and *cis*- $[\text{Pt}(\text{H}_2\text{O})_2(\text{PPh}_3)_2][\text{CF}_3\text{SO}_3]_2$ (**4c**) have been obtained. This formulation is based (a) on the ^1H NMR spectrum of **4b** in CD_2Cl_2 which shows the presence of two water molecules per platinum atom and (b) the IR spectra of complexes **4b** and **4c** in CD_2Cl_2 and CDCl_3 , respectively, which clearly show bands attributable to coordinated water.

The Phenylation Reaction. The most significant feature of the reaction of $[\text{BAr}_4]^-$ with cations *cis*- $[\text{Pt}(\text{S})_2(\text{PR}_3)_2]^{2+}$ is the rapid loss of an aryl group from the boron atom. The proton-induced cleavage of an aryl group from tetraarylborates is well-documented,^{6b} with the rel-

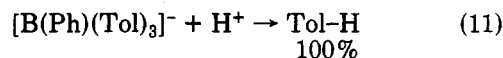
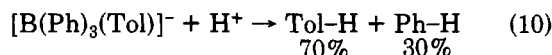
ative rates of cleavage of the different aryl substituents following: $[\text{B}(\text{p-Tol})_4]^- > [\text{BPh}_4]^- \approx [\text{B}(\text{p-ClC}_6\text{H}_4)_4]^- > [\text{B}(\text{m-FC}_6\text{H}_4)_4]^-$. Mechanistically, this reaction is described as an electrophilic attack of the proton at the carbon atom bound to boron as shown in the structure below.



It could be easily envisaged that the coordinated solvent in the cations *cis*- $[\text{Pt}(\text{S})_2(\text{PEt}_3)_2]^{2+}$ could be quite acidic because of the doubly positive charge (see eq 9) and that the protons thus released could induce the B-C cleavage.



Experiments with tetraarylborates in MeOH containing two types of aryl groups confirm the reported relative rates of B-C cleavage. Thus the following stoichiometric reactions were observed (eq 10 and 11). Thus, in the former

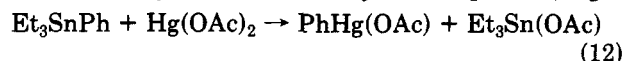


case, when 1 equiv of acid is used, a mixture of BPh_3 (70%) and BPh_2Tol (30%) is produced while in the latter case only BPhTol_2 is present. The latter compound can be isolated from the solution as its NH_3 adduct in 90% yield.

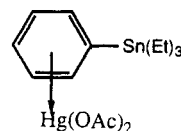
In this context the product distribution and relative rates of arylation using $[\text{B}(\text{m-FC}_6\text{H}_4)_4]^-$ and $[\text{B}(\text{Ph})(\text{m-FC}_6\text{H}_4)_3]^-$ mentioned in the earlier section are particularly relevant. Thus the extremely slow arylation reaction with the former reagent is clearly due to the slow protonolysis of $[\text{B}(\text{m-FC}_6\text{H}_4)_4]^-$ while in the latter case a phenyl group can be easily split off.

The fast B-C cleavage by protons may account for the failure to observe the formation of a π -complex between platinum and $[\text{BAr}_4]^-$. The reaction of $[\text{BPh}_4]^-$ with a platinum(II) solvento complex can be compared with the phenylation reaction of HgX_2 compounds with the same anion.¹¹ No detailed mechanistic studies of this reaction appear to have been carried out as, in most publications, the analytical aspect of this chemistry was of interest.

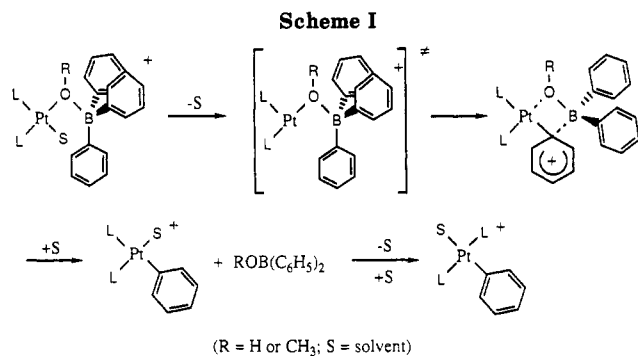
More information is available on the phenylation reaction of mercury(II) salts with aryltin compounds, e.g.¹²



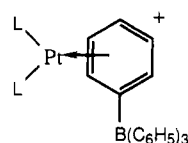
There a π -bonded intermediate of the type shown below was postulated:



(6) (a) Vandeberg, J. T.; Moore, C. E.; Cassaretto, F. P.; Posvic, H. *Anal. Chim. Acta* 1969, 44, 175. (b) Meisters, M.; Vandeberg, J. T.; Cassaretto, F. P.; Posvic, H.; Moore, C. E. *Anal. Chim. Acta* 1970, 49, 481.



In the case of our platinum dications, given the results described above, one can postulate a mechanistic pathway of the type shown in Scheme I. The formation of a π -aromatic intermediate similar to that found for rhodium could not be detected in this work. As mentioned earlier, the loss of a phenyl group from $[\text{BPh}_4]^-$ is faster than the phenylation reaction. However, our evidence does not exclude the possibility that a complex such as



could be formed, if an anhydrous aprotic solvent, S' , were used as the intermediate $\text{cis}[\text{Pt}(\text{S}')_2(\text{PR}_3)_2]^{2+}$.

The pathway outlined in Scheme I is also consistent with the regioselectivity of the reaction that shows the exclusive formation of the compound in which the carbon atom bonded to platinum is the same as that which was bonded to boron. Competitive experiments using equal amounts of BPh_3 and BTol_3 show that, as in the case for the protonation reaction, the tolyl compound reacts faster and a Pt-Tol bond is formed preferentially to the Pt-Ph bond by a factor of 3:1. The phenylating action of the other boron reagents, i.e., $\text{B}(\text{OMe})\text{Ph}_2$, $\text{B}(\text{OMe})_2\text{Ph}$, and $\text{B}(\text{OH})_2\text{Ph}$, can be described analogously to that with BPh_3 .¹³

Finally, the transfer of a methyl group from $[\text{B}(\text{Me})(\text{Ph})_3]^-$ can be interpreted in the same way, i.e., first by the loss of a phenyl group followed by alkyl or aryl transfer. In this context it should be noted that, even if one assumes that only a phenyl group is cleaved, i.e. that only BMePh_2 is formed, there is a preferential transfer of a methyl group as the two products **7b** and **20b** are formed in the approximate ratio of 1:1 (see Table III).

The discovery that the phenylation of platinum complexes $\text{cis}[\text{Pt}(\text{S}')_2(\text{PR}_3)_2]^{2+}$ by $[\text{BPh}_4]^-$ occurs via BPh_3 and not directly from the borate anion opens the question as to whether many of the phenylation reactions using $[\text{BPh}_4]^-$ previously reported really involve, as a first step, the direct transfer of a phenyl group to platinum by $[\text{BPh}_4]^-$ or whether the initial phenylating reagent is BPh_3 . This point, at least as far as reaction 5 is concerned, is under investigation and will be reported at a later date.

Experimental Section

The preparation of the platinum solvento complexes and the arylation were carried out under air. Preparation of the tetraarylborates was carried out under a nitrogen atmosphere. Elemental analyses were performed by the Microanalytical Laboratory of the Swiss Federal Institute of Technology (ETH). The solvents ("puriss" quality) were used as purchased from FLUKA AG. The ^1H and ^{31}P NMR spectra were recorded at room temperature on either a Bruker WH 90, WM 250, or AC 200 spectrometer and are referenced to internal Me_4Si and external 85% H_3PO_4 , respectively. The ^{195}Pt spectra were recorded on a Bruker

WM 250 spectrometer and are referenced to external $\text{K}_2[\text{PtCl}_6]$. For all nuclei a positive sign indicates a chemical shift downfield of the reference.

(a) Organoboron Compounds. The boron compounds $\text{Na}[\text{BPh}_4]$, $\text{B}(\text{OH})_2\text{Ph}$, and $\text{B}(\text{OMe})_3$ were purchased from FLUKA AG. $\text{Na}[\text{B}(m\text{-FC}_6\text{H}_4)_4]$,^{6a} $\text{B}(p\text{-Tol})_3$,⁷ $\text{B}(\text{OMe})\text{Ph}_2$,⁸ and $\text{B}(\text{OMe})_2\text{Ph}$ ⁹ were prepared as described in the appropriate references. Triphenylboron was precipitated from the NaOH adduct by adding dilute HCl and isolated by filtration. The tetraarylborates $\text{Na}[\text{B}(\text{C}_6\text{D}_5)_4]$, $\text{Na}[\text{B}(m\text{-Tol})_4]$, and $\text{Na}[\text{B}(p\text{-Tol})_4]$ were prepared by the method of Holzappel and Richter¹⁰ using $\text{B}(\text{OCH}_3)_3$ as starting boron compound.

Synthesis of $\text{Na}[\text{B}(\text{Ph})(m\text{-FC}_6\text{H}_4)_3]$. To a Grignard solution, prepared from 1-bromo-3-fluorobenzene (39.4 g, 0.225 mol) and magnesium turnings (5.8 g, 0.239 mol) in 200 mL of ether, was added $\text{B}(\text{OMe})_2\text{Ph}$ (11.35 g, 0.076 mol) in 50 mL of dry ether during 1 h. After additional stirring for 1 h the reaction solution was poured onto a solution of 60 g of Na_2CO_3 in 400 mL of water. The ether layer was separated and the water phase extracted twice with 300 mL of ethyl acetate. Evaporation of the combined organic layers gave a yellow oil. This was dissolved in 300 mL of ethyl acetate, dried with Na_2SO_4 , and filtered and the solvent removed. The residue was dissolved in 200 mL of ether with a small amount of acetone (ca. 10 mL), 200 mL of toluene was added, and the solution was reduced in vacuo to ca. 100 mL. The white powder was filtered off, washed with toluene and pentane, and dried. Yield: 17.3 g (0.044 mol), 58%. Anal. Calcd for $\text{C}_{24}\text{H}_{17}\text{BF}_3\text{Na}$: C, 72.76; H, 4.32. Found: C, 72.70; H, 4.65.

Synthesis of $\text{Na}[\text{B}(\text{Ph})_3(p\text{-Tol})]$. To a slurry of BPh_3 (12.9 g, 53.3 mmol) in 50 mL of dry THF was added a Grignard solution prepared from 4-bromotoluene (10 g, 58.5 mmol) and magnesium turnings (1.42 g, 58.5 mmol) in 40 mL of THF. After being stirred for 2 h at room temperature, the solution was poured on to a solution of 30 g of Na_2CO_3 in 200 mL of water. The THF phase was separated and the water phase extracted twice with 100 mL of ethyl acetate. The organic phases were combined and the solvent removed in vacuo. The residue was dissolved in 250 mL of ethyl acetate, dried with Na_2SO_4 , and filtered, the solvent removed and dried. Yield: 18.6 g (52.2 mmol), 98%. An analytically pure sample was obtained by adding toluene (6 parts) to a 5% solution of the tetraarylborate in acetone and the volume reduced in vacuo until a white precipitate was formed. The solid was filtered off, washed with ether, and dried. Anal. Calcd for $\text{C}_{25}\text{H}_{22}\text{BNa}$: C, 84.29; H, 6.22. Found: C, 84.03; H, 6.35.

Synthesis of $\text{Na}[\text{B}(\text{Ph})(p\text{-Tol})_3]$. To a slurry of $\text{B}(p\text{-Tol})_3$ (8.35 g, 29.4 mmol) in 80 mL of dry ether was added 20 mL of phenyllithium solution (2 M solution in benzene/ether (70/30), 40 mmol). After 2 h of stirring at room temperature 1 mL of water was added to destroy the excess phenyllithium. The solvent was removed and the residue dissolved in 100 mL water saturated with Na_2CO_3 . The water phase was extracted three times with 100 mL of ethyl acetate, and the combined organic phases were dried with Na_2SO_4 . The organic phase was filtered and the solvent removed. The solid was stirred for 30 min with 100 mL of ether, then filtered off, and dried. Yield: 9.22 g (24 mmol), 82%. Anal. Calcd for $\text{C}_{27}\text{H}_{20}\text{BNa}$: C, 84.39; H, 6.82. Found: C, 84.08; H, 6.49.

Synthesis of $\text{K}[\text{B}(\text{Me})(\text{Ph})_3]$. To a slurry of BPh_3 (3.5 g, 14.5 mmol) in 50 mL of dry ether was added 10 mL of methyllithium solution (1.6 M in ether, 16 mmol) and the mixture stirred for 1 h at room temperature. The excess methyllithium was then destroyed by the addition of 1 mL water and the solvent removed in vacuo. The residue was dissolved in 50 mL of water and filtered over Celite. To the clear solution was added 50 mL of water saturated with KCl to precipitate $\text{K}[\text{B}(\text{Me})(\text{Ph})_3]$, which was filtered off, washed with water, and dried. Yield: 2.6 g (8.78

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(13) A reviewer suggests that one should have considered "... the a priori possibility of an SET alternative". On the basis of our product regioselectivity, particularly that starting from *m*-tolylboron derivatives, we feel this suggestion to be unlikely.

mmol), 61%. It was recrystallized as follows: A 5% solution of the compound in acetone was mixed with a 6-fold volume of toluene and the solvent reduced under vacuum until a white precipitate formed. The precipitate was filtered off, washed with ether, and dried. Anal. Calcd for $C_{19}H_{13}BK$: C, 84.39; H, 6.82. Found: C, 84.08; H, 6.49.

(b) Platinum Complexes. The platinum complexes *cis*-[PtCl₂(PMe₃)₂] (**1a**), *cis*-[PtCl₂(PEt₃)₂] (**1b**), and *cis*-[PtCl₂(PPh₃)₂] (**1c**) were prepared by standard procedures.¹⁴ AgCF₃SO₃ (FLUKA, purum), methanol (FLUKA, puriss), acetonitrile (FLUKA, puriss), and methylene chloride (FLUKA, puriss) were used without further purification. In all cases the AgCl precipitate was filtered off over Celite.

A solution of the monocation *cis*-[PtCl(S)(PEt₃)₂][CF₃SO₃] (**3b**) was obtained by reacting 100 mg (0.2 mmol) of *cis*-[PtCl₂(PEt₃)₂] (**1b**) with 51.2 mg (0.2 mmol) of AgCF₃SO₃ in 3 mL of methanol, the mixture was stirred for 30 min and the AgCl filtered off.

Synthesis of *cis*-[Pt(H₂O)₂(PEt₃)₂][CF₃SO₃] (4b**).** A methanol (30 mL) solution of *cis*-[PtCl₂(PEt₃)₂] (**1b**) (1 g, 2 mmol) and AgCF₃SO₃ (1.03 g, 4 mmol) was stirred at room temperature for 30 min. The precipitated AgCl was filtered off and washed with methanol. From the combined methanol phases the solvent was removed by heating under vacuum to not more than 50 °C. The resulting black slurry was dissolved in 50 mL of CH₂Cl₂ and the solution filtered through Celite. Dry ether (50 mL) was added to the CH₂Cl₂ solution and the mixture cooled to 4 °C. After some colorless crystals had formed, more ether (total 200 mL) was added and crystallization completed at 4 °C. Yield: 1.38 g (1.9 mmol), 91%. Anal. Calcd for $C_{14}H_{34}F_6O_8P_2PtS_2$: C, 21.96; H, 4.48. Found: C, 22.19; H, 4.38.

Synthesis of *cis*-[Pt(H₂O)₂(PPh₃)₂][CF₃SO₃] (4c**).** To a slurry of *cis*-[PtCl₂(PPh₃)₂] (**1c**) (1 g, 1.26 mmol) in CH₂Cl₂ (20 mL) was added a methanol solution (20 mL) of AgCF₃SO₃ (650 mg, 2.53 mmol) at 0 °C. The mixture was stirred at 0 °C for 10

min. The precipitated AgCl was filtered off, and the filtrate was evaporated to dryness at 0 °C under vacuum. The colorless solid was recrystallized from CH₂Cl₂/Et₂O as above. Yield: 591 mg (0.561 mmol), 44%. Anal. Calcd for $C_{38}H_{34}O_8F_6P_2Pt$: C, 43.31; H, 3.25. Found: C, 43.60; H, 3.41.

Synthesis of *cis*-[Pt(CH₃CN)₂(PEt₃)₂][BPh₄]₂ (6b**).** To a methanol (10 mL) solution of *cis*-[Pt(H₂O)₂(PEt₃)₂][CF₃SO₃] (**4b**) (500 mg, 0.653 mmol) was added acetonitrile (1 mL), and the mixture was stirred for 5 min. A solution of Na[BPh₄] (516 mg, 1.51 mmol) in methanol (3 mL) was added. The white precipitate formed was filtered off, washed with methanol, and dried. Yield: 725 mg (0.629 mmol), 96%. Anal. Calcd for $C_{64}H_{76}N_2B_2P_2Pt_2$: C, 66.73; H, 6.65; N, 2.43. Found: C, 66.63; H, 6.85; N, 2.47.

Preparation of Solutions of the Solvento Complexes 2a and 2b. One equivalent of *cis*-[PtCl₂L₂] (L = PMe₃, **1a**; L = PEt₃, **1b**) and 2 equiv of AgCF₃SO₃ were dissolved in methanol (20 mL of solvent/mmol of *cis*-[PtCl₂L₂]), and the mixture was stirred for 30 min. The precipitated AgCl was filtered off, and an equal volume of CH₂Cl₂ was added.

The Phenylation Reaction. To the above solutions was added tetraarylborate (1 equiv), and the white suspension was stirred for 30 min at room temperature. In the case of *cis*-[Pt(S)₂(PPh₃)₂]²⁺ (**2c**), the complex *cis*-[Pt(H₂O)₂(PPh₃)₂][CF₃SO₃] (**4c**) was dissolved in CH₂Cl₂ (20 mL of solvent/mmol of **4c**), a solution of tetraarylborate (1 equiv) in methanol (20 mL/mmol) added, and the solution stirred for 30 min at room temperature. Then either LiCl, LiBr, or NaI (2 equiv) was added and the mixture stirred for another 5 min. The solution was filtered through Celite and the solvent removed. The residue was suspended in water (50 mL/mmol) and extracted twice with CH₂Cl₂ (2 × 50 mL/mmol of complex). The combined organic phases were evaporated, and the solid was recrystallized from methanol/water or acetone/water. Yields ranged from 80 to 86%.

Acknowledgment. Financial support for this work by the Swiss National Science Foundation is gratefully acknowledged.

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Synthesis, Geometrical Isomerism, and Crystal Structure of a Highly Hindered Disilene

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A disilene very resistant to air oxidation, 1,2-di(1-adamantyl)dimesityldisilene, was synthesized by solution photolysis of 2-(1-adamantyl)-2-mesitylhexamethyltrisilane. The X-ray crystal structure of the *E* isomer was determined; it crystallized in the triclinic space group *P*1, *Z* = 1, with cell dimensions *a* = 8.292 (2) Å, *b* = 10.069 (2) Å, *c* = 10.772 (2) Å, α = 105.67 (2)°, β = 93.02 (2)°, and γ = 105.68 (2)°. Irradiation of the *E* isomer in solution gave a mixture enriched in the *Z* isomer that thermally reverted to the *E* form. The activation energy of the thermal *Z*-to-*E* isomerization was 28.8 kcal mol⁻¹.

The key to synthesis of stable disilenes¹ has been protection of the Si-Si double bond by sterically hindering substituents. In general, reactivity of disilenes decreases as the size of substituents increases; for example 1,2-di-*tert*-butyldimesityldisilene (**2**) undergoes addition reactions more slowly than tetramesityldisilene (**1**).² Since the 1-adamantyl group is more sterically demanding than

tert-butyl,³ 1,2-di(1-adamantyl)dimesityldisilene (**4**) should be especially unreactive. In this paper we report the synthesis of **4**, obtained from photolysis of the trisilane Mes(Ad)Si(SiMe₃)₂ (**6**, Ad = 1-adamantyl).

Synthesis

An exchange reaction between 1-iodoadamantane and *tert*-butyllithium in pentane/ether at -70 °C was used to

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