Stable Platinum(0) Catalysts for Catalytic Hydrosilylation of Styrene and Synthesis of [Pt(Ar-bian)(η^2-alkene)] Complexes

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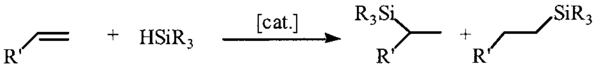
The use of alkenes and bidentate N-ligands in the platinum(0)-catalyzed hydrosilylation of styrene with triethylsilane has been evaluated. A number of bidentate N-ligands, phen, bpy, dafo, and phenyl-bian, were tested at various reaction temperatures using in situ formed catalysts with [Pt(nbe)$_3$] as a precursor. The main conclusions are: (i) ligands, such as phen, which form stable platinum(0) complexes, give lower catalytic activities compared to the ligands which form less stable complexes; (ii) a small ligand effect is observed with dafo and phenyl-bian compared to [Pt(nbe)$_3$], the precursor complex, displaying the lability of these ligands. The complex [Pt(nbe)$_3$], that only has labile alkene ligands, is an active catalyst at low temperatures. At higher temperatures, the catalyst is no longer stable and a decrease in yield is observed. Several novel complexes have been synthesized: [Pt(*m*,*m*-(CF$_3$)$_2$-C$_6$H$_3$-bian)(tcne)], [Pt(*m*,*m*-(CF$_3$)$_2$-C$_6$H$_3$-bian)(ma)], [Pt(*p*-MeO-C$_6$H$_4$-bian)(ma)], [Pt(*p*-MeO-C$_6$H$_4$-bian)(dmfu)] and [Pt(phenyl-bian)(dmfu)]. Whereas the two [Pt(Ar-bian)(ma)] complexes are intrinsically more active than the two [Pt(Ar-bian)(dmfu)] complexes, the latter are much more stable, i.e. the nature of the alkene in these complexes is an important factor in determining their catalytic behavior. Compared to [Pt(Me-nq)(nbe)$_2$], the two [Pt(Ar-bian)(dmfu)] complexes are much more stable resulting in significantly higher overall yields.

1. Introduction

The catalytic hydrosilylation of unsaturated compounds, such as alkenes, alkynes, ketones, and imines, is one of the most elegant methods for the synthesis of organosilicon compounds [Equation (1)].[1] The use of organosilicon compounds as reagents and synthons for the construction of natural products has become a powerful tool in synthesis. In addition to its use in laboratory syntheses, the hydrosilylation reaction is used in many ways in the industrial manufacture of silicon polymers, for example for the curing and modification of polyorganosiloxanes and the modification of unsaturated polymers.



(1)

Since the first report on catalyzed hydrosilylation in 1947 by Sommer et al.,[2] many efforts have been made to develop optimized catalytic systems. By now, numerous transition metal based catalysts have been reported for hydrosilylation, including metals of groups 8, 9, and 10. Platinum catalysts, especially, are very active in the hydrosilylation of unsaturated carbon−carbon bonds. The Speier catalyst,[3] H$_2$PtCl$_6$ dissolved in 2-propanol, and the Karstedt catalyst,[4] H$_2$PtCl$_6$ dissolved in tetramethyldivinyldisiloxane [(CH$_2$=CHSiMe$_2$)$_2$O], are frequently used.

However, a problem associated with these platinum catalysts is their very limited stability when exposed to hydrosilylation conditions; rapid formation of platinum colloids, that are catalytically not active, takes place. The preparative scope of Speier's catalyst is further restricted by its long and variable induction period. The nature of the catalytically active species, homogeneous vs. heterogeneous, has been questioned in the literature for a long time.[5] Recently, it has become clear that the type of platinum compound that would generate the highest activity is one in which formation of a single platinum(0) atom and concomitant loss of ligands is facile.[5] It has been observed that the Karstedt catalyst contains preponderantly [Pt$_2$(CH$_2$=CHSiMe$_2$)$_2$O]$_3$, a platinum(0) complex containing one bridging tetramethyldivinyldisiloxane ligand.[6] A widely accepted mechanism for hydrosilylation of alkenes is the Chalk−Harrod mechanism which consists of oxidative addition of a hydrosilane, insertion of an alkene into the metal−hydride bond, and reductive coupling of the alkyl and silyl fragments.[7]

Osborn et al.[8] published a series of platinum(0) complexes with the general formula [Pt(η^2-alkene)(η^4-CH$_2$=CHSiMe$_2$)$_2$O]. When naphthoquinones were used as the co-

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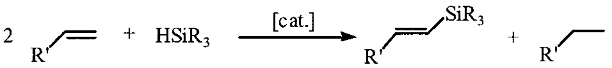
ordinating alkene, highly active catalysts were obtained. Markó et al.[9] used platinum(0) catalysts with N-heterocyclic carbenes as ligands. These catalysts were less active than the Karstedt catalyst, but side-reactions, such as isomerization and dehydrogenative silylation, were significantly suppressed. Also our group used some N-heterocyclic carbene ligands which yielded outstanding catalysts.[10]

Hydrosilylation of alkenes is often accompanied by side-reactions such as isomerization and dehydrogenative silylation. The latter can be of interest, because it produces vinylsilanes, which are very useful synthetic reagents in synthesis [Equation (2)].



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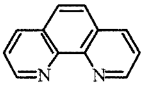
Of course, it would be desirable to have catalysts that are selective either to hydrosilylation or to dehydrogenative silylation. For instance, the catalysts $[Ru_3(CO)_{12}]$[11] and $[Fe_3(CO)_{12}]$[12] are known to be very selective towards dehydrogenative silylation of several alkenes, which is also true for rhodium(I)[13] and palladium(II) catalysts[14] when employing an excess of styrene relative to the hydrosilane or a more steric hydrosilane. Also platinum(0) catalysts can give rise to a certain extent of dehydrogenative silylation,[15,16] for which the Chalk−Harrod mechanism does not account. Therefore, other mechanisms have been proposed to explain this reaction. Characteristically, these mechanisms feature the formation of an olefin-hydride complex, arising from β-hydride elimination of a β-silylalkyl intermediate [Equation (3)]. Dissociation of the *trans*-vinylsilane yields a metal hydride complex, which is responsible for the hydrogenated product. This dissociation of the vinylsilane is favored by a high styrene concentration and by using more steric hydrosilanes.

As mentioned before, many of the known platinum(0) catalysts suffer from deactivation. For instance, Steffanut et al.[8] observed decomposition of $[Pt(\eta^2\text{-2-methylnaphthoquinone})(\eta^4\text{-}CH_2{=}CHSiMe_2)_2O]$ at temperatures higher than 20 °C. Moreover, alkene/hydrosilane ratios of two were used in their experiments, which contributes to a significantly higher catalyst stability. It would be desirable to use an alkene/hydrosilane ratio of one, but then more stable catalysts are definitely required. Thus, further manipulation of the coordination sphere of the metal center will be indispensable in order to obtain an active catalyst that is stable under the reaction conditions.

We have been interested in the use of bidentate N-ligands, especially bidentate N-ligands, for several catalytic and stoichiometric transition metal mediated carbon−element coupling reactions and for the stereoselective *cis*-hydrogenation of alkynes.[17−22] These ligands are known to stabilize platinum(0) compounds when coordinated in a bidentate manner,[23−24] yet readily give rise to free coordination sites due to their hemilability.[25−26]

An effective catalyst for hydrogenation or hydrosilylation requires a low coordination number and valence. Hence, hydrosilylation should proceed effectively for those late transition metal compounds that can readily vacate two or more coordination sites, in order to accommodate substrates, yet is able to stabilize the complex in its resting state by re-coordination of the hemilabile donor atom. In this respect, platinum based precatalysts combining a labile alkene with a hemilabile, bidentate N-ligand, specifically 1,10-phenanthroline (**1**) (phen), 2,2′-bipyridyl (**2**) (bpy), 4,5-diazafluoren-9-one (**3**) (dafo), and bis(arylimino)acenaphtene (**4**) (Ar-bian), seem to be very promising indeed for platinum(0)-catalyzed hydrosilylation.



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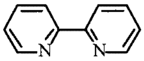

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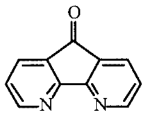

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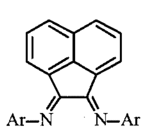

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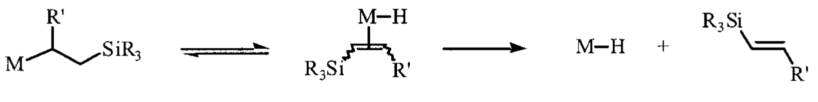
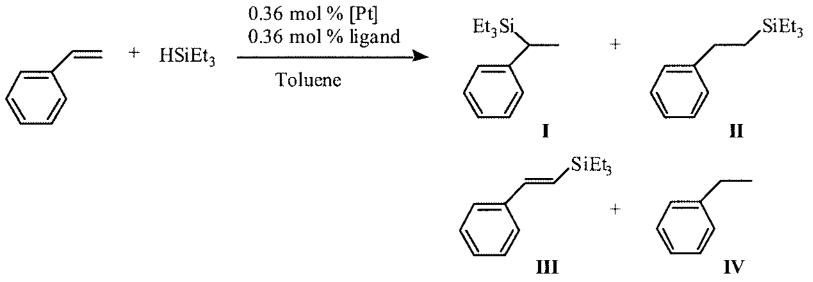
In this paper, the use of bidentate N-ligands, as ligands for Pt-catalyzed hydrosilylation of styrene with triethylsilane, is reported. The performance and stability of several in situ prepared systems, obtained from [Pt(2-norbornene)₃], [Pt(nbe)₃], with appropriate bidentate N-ligands, has been evaluated and compared with several novel $[Pt(Ar\text{-}bian)(\eta^2\text{-}alkene)]$ complexes.

2. Results and Discussion

Bidentate N-Ligands as Ligands in the Hydrosilylation of Styrene by Triethylsilane

First, the platinum(0) complex $[Pt(nbe)_3]$[27] was used as a precursor for the hydrosilylation of styrene with triethylsilane yielding products **I** and **II** (Scheme 1). The hydrosilylation of styrene is always accompanied by dehydrogenative silylation, yielding products **III** and **IV**. Throughout, ethylbenzene (**IV**) was always formed in the same amount as the unsaturated silyl product (**III**) by subsequent hydrogenation of styrene. Since the nbe ligands readily dissociate from platinum, active, coordinately unsaturated platinum(0) species are readily obtained.





Scheme 1. Hydrosilylation and dehydrogenative silylation of styrene with triethylsilane

The bidentate N-ligands are expected to coordinate to platinum immediately upon their addition, prior to the start of catalysis. Thus influencing the activity and stability of the hydrosilylation reaction. Liedtke et al.[28] also used [Pt(nbe)$_3$] as a precursor in their hydrosilylation reactions with certain phosphiranes as ligands. These experiments were performed at different temperatures and at a styrene/hydrosilane ratio of 2.8. For comparison, 2-methylnaphthoquinone (Me-nq), Osborn's ligand,[8] and bis(diphenylphosphanyl)ethane (dppe), a strongly coordinating ligand, which results in a platinum complex with low activity,[29] were also tested in this catalytic system. The results of these catalytic hydrosilylations have been collected in Table 1.

Table 1. Hydrosilylation of styrene with triethylsilane

Entry	Ligand[a]	Temp. [°C]	Yield [%][b]	Selectivity [%][c] **I/II/III**
1	–	30	91.9	2.0:67.0:31.0
		50	60.4	2.5:68.0:29.5
		100	19.7	2.7:67.6:29.7
2	Me-nq	30	92.5	2.0:66.9:31.1
		50	62.3	2.7:68.5:28.8
		100	20.7	3.0:66.0:31.0
3	phen	30	–	–
		50	–	–
		100	16.7	4.4:54.3:41.3
4	bpy	30	31.7	2.0:72.6:25.4
		50	81.7	2.6:63.9:33.5
		100	19.1	3.8:60.0:36.2
5	dafo	30	88.1	2.0:66.8:31.2
		50	69.6	2.6:65.2:32.2
		100	14.6	3.1:65.4:31.4
6	phenyl-bian	30	86.0	2.0:67.5:30.5
		50	66.0	2.6:67.8:29.6
		100	26.9	3.4:67.4:29.2
7	dppe	30	–	–
		50	–	–
		100	5.1	3.5:67.2:29.3

[a] 0.36 mol % of catalyst, styrene/triethylsilane ratio 2.8, toluene. [b] Combined GC yield, after 2 h, of products **I**, **II**, and **III** using *n*-decane as the internal standard. [c] Product **IV** was always observed in the same amount as product **III**, therefore the amount of **IV** has been omitted.

It is clear that the precursor complex [Pt(nbe)$_3$] is an active catalyst at 30 °C, but that it progressively loses its activity at higher temperatures due to deactivation of the catalyst (Entry 1). Addition of 1 equiv. of Me-nq to [Pt(nbe)$_3$] (Entry 2) gives results that are similar to those of [Pt(nbe)$_3$]: the same trend in deactivation at higher temperatures is observed and only a small increase in the yield of product **I** relative to the other products was observed. So, Me-nq is not able to act as a stabilizing ligand at higher temperatures.[8] Furthermore, the use of Me-nq does not lead to a higher yield at 30 °C compared to [Pt(nbe)$_3$] itself, which generates highly active platinum species. This observation is in agreement with the common view that single unsaturated platinum(0) atoms are highly active hydrosilylation catalysts.[5,8]

A completely different catalytic behavior is observed when 1,10-phenanthroline (phen) is used as the ligand (Entry 3). In this case, hydrosilylation only takes place at a very slow rate at 100 °C. Apparently, phen forms a very stable platinum(0) complex. This idea is supported by the fact that no significant catalyst deactivation was observed, even when running this reaction at 100 °C for 24 h, which resulted in a total yield (**I** + **II** + **III**) of 81%. The relative amount of dehydrogenative silylation has increased using phen, which can be explained by invoking the strong bidentate coordination of phen to the Pt center, favoring the dissociation of the *trans*-vinylsilane.

When bpy is used in the hydrosilylation (Entry 4), the yield obtained increases when going from 30 to 50 °C due to the increased lability of bpy with temperature. The low yield observed at 100 °C is caused by the deactivation of the catalyst at this temperature. The selectivity (**I/II/III**) obtained with this ligand changes significantly with temperature and differs from the selectivity obtained in Entries 1 and 3. Furthermore, bpy shows an increased amount of dehydrogenative silylation compared to [Pt(nbe)$_3$], but not to the same degree as phen. This can be understood from differences in the fluxional behavior of phen and bpy: by its rigidity, phen forms complexes more readily than bpy, but bpy is more flexible and can easily adapt to the η^1-coordinate structure.

The ligand dafo (Entry 5) shows a behavior completely different from phen and bpy. Only a very small decrease in yield and the same selectivity compared to [Pt(nbe)$_3$] is observed. These results indicate that dafo coordinates relatively weakly, in a bidentate fashion, to the platinum(0) atom, which is most likely due to the larger bite angle of this ligand (about 82°) compared to phen and bpy (about 77°). Indeed, Klein et al.[26] have previously observed an enhanced aptitude for dissociation of one of the donor atoms of dafo in platinum(0) and palladium(0) complexes, due to the reduced overlap between relevant metal and ligand orbitals caused by the larger bite angle. Also dimeric palladium(II) complexes have already been synthesized with dafo as a bridging ligand.[30]

Although phenyl-bian (Entry 6) possesses a bite angle similar to phen and bpy (about 77°), the catalytic results obtained with this ligand differ completely from that of phen and bpy. In fact, almost the same yield and selectivity were obtained as observed for dafo. Similarly to dafo, phenyl-bian displays a significant lability. Although platinum(0) or palladium(0) complexes in which the Ar-bian ligands act as monodentate ligands are not known, several palladium(II) complexes containing monodentate Ar-bian ligands are known.[25,31] These studies have shown that rigid bidentate N-ligands are more prone to hemilabile behavior than the more flexible ones. Assuming partial dissociation of Ar-bian in such cases may explain the observed selectivity for phenyl-bian.

Results obtained for dppe (Entry 7) again demonstrate that this bidentate phosphane ligand forms a stable chelate with platinum(0), resulting in zero activity at 30 and 50 °C and only a very low activity at 100 °C. Triphenylphosphane was also tested once in the hydrosilylation at 30 °C. After 2 h, a total yield of only 8.5% was obtained with a selectivity of 3.0:73.0:24.0 (**I/II/III**).

As mentioned before, the selectivities of platinum catalysts depend strongly on the styrene/triethylsilane ratio. For example, applying a styrene/triethylsilane ratio of 0.5 using [Pt(nbe)$_3$] as the catalyst yielded a selectivity (**I/II/III**) of 2.0:90.0:8.0. However, when a styrene/triethylsilane ratio of 6.4 was used, an enormous increase in dehydrogenative silylation was observed: 37% of product **III** was obtained. This observation supports the idea[13,14] that the dissociation of the vinylsilane is favored by a higher styrene concentration [Equation (3)]. Comparing our selectivities obtained with already reported catalysts is not straightforward since the conditions applied can have a significant influence. For example, Skoda-Földes et al.[29] obtained 12.3% of **III** with PtCl$_2$ as a catalyst and using a styrene/triethylsilane ratio of 1.0 in the hydrosilylation of styrene with triethylsilane. Employing 2.8 equiv. of styrene, we obtained 31.0% of product **III** using [Pt(nbe)$_3$] as the catalyst. However, when using a styrene/triethylsilane ratio of 1.0 with this catalyst, product **III** was observed in only 11.0%, which is almost similar to the result obtained by Skoda-Földes et al. with PtCl$_2$. Also, Dötz et al.[15] and Caseri and Pregosin[16] obtained considerable amounts of product **III** in this reaction, using [Pt(η^2-2-methylnaphthoquinone)(η^4-CH$_2$=CHSiMe$_2$)$_2$O] and *trans*-[PtCl$_2$(PhCH=CH$_2$)$_2$] as the catalyst, respectively.

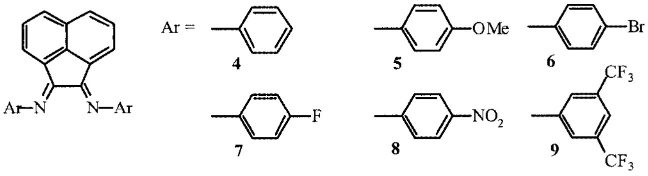
The activities of our catalysts are influenced by several reaction conditions; temperature was already discussed, but the styrene concentration also influences the reaction significantly. In general, a higher styrene concentration contributes to a higher stability of the catalyst. Consequently, when [Pt(nbe)$_3$] was used as a catalyst using a styrene/triethylsilane ratio of 1.0, a yield of only 32% was obtained after 2 h, which is rather low when compared to the 91.9% yield using a styrene/triethylsilane ratio of 2.8 (Table 1, Entry 1). However, when the reaction using a styrene/triethylsilane ratio of 1.0 was repeated, but now without 20 mL of toluene as the solvent, an increase in yield was also observed: from 32 to 88%. Caseri and Pregosin[16] reported that [Pt(styrene)$_3$] was more active than *trans*-[PtCl$_2$(PhCH=CH$_2$)$_2$] and that this complex did not show an induction period. From our results, we can say that [Pt(nbe)$_3$] also generates highly active platinum(0) species, probably similar to [Pt(styrene)$_3$][16] although we did not check if this complex is formed during catalysis.

The lability of the phenyl-bian ligand was studied in more detail by substituting the aryl groups of this ligand. Thus, ligands **4−9** were synthesized and tested in the catalytic hydrosilylation of styrene with triethylsilane at 30 °C. The results are collected in Table 2.

Table 2. Hydrosilylation of styrene with triethylsilane using Ar-bian ligands

Entry	Ligand[a]	Yield [%][b]	Selectivity [%][c] **I/II/III**
1	**4**	86.0	2.0:67.5:30.5
2	**5**	84.7	2.0:67.5:30.5
3	**6**	87.0	2.0:67.0:31.0
4	**7**	91.0	2.0:67.5:30.5
5	**8**	90.1	2.0:66.5:31.5
6	**9**	90.0	2.0:67.5:30.5

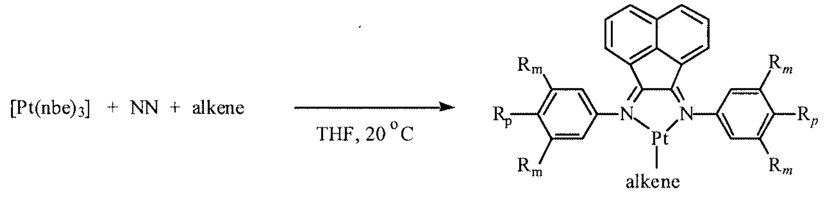
[a] 0.36 mol % of catalyst, styrene/triethylsilane ratio 2.8, toluene, 30 °C. [b] Combined GC yield, after 2 h, of products **I**, **II**, and **III** using *n*-decane as the internal standard. [c] Product **IV** was always observed in the same amount as product **III**, therefore the amount of **IV** has been omitted.



It is immediately evident from Table 2 that substitution of the Ar-bian ligands has no significant influence on the selectivity of the hydrosilylation. There seems to be a relation between the yield and the inductive effect of the *para* substituents on the aryl groups of the Ar-bian ligand, as increasing yields are observed with decreasing electron-donating ability. This can be explained by the fact that electron-donating substituents increase the basicity of the Ar-bian ligand, resulting in more stable platinum(0) complexes. As a consequence, the lowest yield is obtained for *p*-MeO-C$_6$H$_4$-bian (Entry 2), but the differences are small.

Synthesis of [Pt(Ar-bian)(η^2-alkene)] Complexes

When obtaining the catalysts in situ, there may be competition for the substrate, due to the relatively large amount (2−3 equiv.) of alkene liberated upon reaction of [Pt(nbe)$_3$] with the bidentate N-ligand (Scheme 2). On the other hand, the Ar-bian ligands are also labile. Therefore, we were inter-



10; R_m = CF_3 ; R_p = H (*m,m*-$(CF_3)_2$-C_6H_3-bian)
11; R_m = H ; R_p = OMe (*p*-MeO-C_6H_4-bian)
12; R_m = H ; R_p = H (phenyl-bian)
alkene = ma (**a**), tcne (**b**), dmfu (**c**)

Scheme 2. Synthesis of [Pt(Ar-bian)(η^2-alkene)] complexes

ested in comparing our hitherto obtained results with experiments employing predefined [Pt(Ar-bian)(η^2-alkene)] complexes as catalyst precursors in the hydrosilylation of styrene with triethylsilane. The stability of these complexes will depend on the nature of the Ar-bian ligand as well as of the alkene. Electron-donating substituents on the Ar-bian ligand, concomitant with the use of electron-poor alkenes is expected to increase the stability of complexes of this type. Van Asselt et al.[24] already synthesized several [Pt(Ar-bian)(η^2-alkene)] complexes. By employing *p*-Me-C_6H_4-bian and *o,o'*-*i*Pr_2-bian with fumaronitrile (fn), maleic anhydride (ma), and tetracyanoethylene (tcne) as coordinating alkenes, stable complexes were obtained starting from [$Pt(dba)_2$]. However, complexes with the less electron-poor dimethyl fumarate (dmfu) could not be obtained by using this method, which includes heating in THF at 45 °C for 16 h. Since our aim was the synthesis of several new complexes with alkenes like dmfu, which at the same time have Ar-bian ligands containing electron-withdrawing substituents, such as *m,m*-$(CF_3)_2$-C_6H_3-bian, we selected [$Pt(nbe)_3$] instead of [$Pt(dba)_2$] as the precursor, allowing milder reaction conditions.[23,32,33] First, the synthesis of various platinum(0) complexes of type [Pt(*m,m*-$(CF_3)_2$-C_6H_3-bian)(η^2-alkene)] was addressed by treating [$Pt(nbe)_3$] with stoichiometric amounts of the ligands. Attempts to prepare [Pt(*m,m*-$(CF_3)_2$-C_6H_3-bian)(dmfu)] were not successful. Allowing equimolar amounts of [$Pt(nbe)_3$], *m,m*-$(CF_3)_2$-C_6H_3-bian, and dmfu to react in tetrahydrofuran at room temperature led to the formation of mixtures of starting materials and reaction products. Similar results were obtained when diethyl ether instead of tetrahydrofuran was used as a solvent. In both cases, purification of the reaction product was troublesome due to its complete solubility in most common organic solvents. ^1H NMR spectroscopy of the crude reaction product suggested that ligand substitution had not been complete: large amounts of uncomplexed *m,m*-$(CF_3)_2$-C_6H_3-bian were present. Using [$Pt(cod)_2$] as starting material, [Pt{*m,m*-$(CF_3)_2$-C_6H_3-bian}(dmfu)] could not be obtained either.

Initial attempts to prepare [Pt{*m,m*-$(CF_3)_2$-C_6H_3-bian}(ma)] by adding [$Pt(nbe)_3$] to a dilute solution of equimolar amounts of *m,m*-$(CF_3)_2$-C_6H_3-bian and maleic anhydride in tetrahydrofuran were in vain. Similar to the case of [Pt{*m,m*-$(CF_3)_2$-C_6H_3-bian}(dmfu)], purification of the reaction product was tedious and ^1H NMR spectroscopy suggested incomplete ligand substitution. Better results were obtained, when *m,m*-$(CF_3)_2$-C_6H_3-bian was added to an ice cold concentrated solution of ma and [$Pt(nbe)_3$]. After washing the crude reaction product with pentane, [Pt{*m,m*-$(CF_3)_2$-C_6H_3-bian}(ma)] readily precipitated from the combined organic extract and was obtained as a pure compound.

Similarly, the synthesis of [Pt{*m,m*-$(CF_3)_2$-C_6H_3-bian}(tcne)] was straightforward and proceeded as expected. In order to probe the influence of electronic effects on the synthesis of platinum(0) complexes of type [Pt{*m,m*-$(CF_3)_2$-C_6H_3-bian}(η^2-alkene)], it was attempted to use electron-rich instead of electron-deficient alkenes. Thus, synthesis of [Pt{*m,m*-$(CF_3)_2$-C_6H_3-bian}(trimethylvinylsilane)] was attempted by stirring equimolar amounts of [$Pt(nbe)_3$], *m,m*-$(CF_3)_2$-C_6H_3-bian, and trimethylvinylsilane in tetrahydrofuran. Although nearly all of the starting materials had reacted after 4 h of stirring at room temperature, at least six different reaction products were formed as was evident from TLC and no efforts were made to further purify the crude reaction product.

Next, in order to study the influence of electronic effects on the synthesis of platinum(0) complexes of type [Pt(Ar-bian)(η^2-alkene)] and also on their catalytic hydrosilylation behavior, the synthesis of various platinum(0) complexes of type [Pt(*p*-MeO-C_6H_4-bian)(η^2-alkene)] was addressed. As opposed to the synthesis of [Pt{*m,m*-$(CF_3)_2$-C_6H_3-bian}(dmfu)], the synthesis of [Pt(*p*-MeO-C_6H_4-bian)(dmfu)] was successful and yielded the desired reaction product in excellent yield. Likewise, the synthesis of [Pt(*p*-MeO-C_6H_4-bian)(ma)] was straightforward, but the synthesis of [Pt(*p*-MeO-C_6H_4-bian)(acrylonitrile)] was more troublesome. Although TLC revealed that all of the starting materials had reacted after 2 h of stirring at room temperature, it was not possible to unambiguously characterize the residue obtained after washing the crude reaction mixture with diethyl ether/pentane. Finally, the complex [Pt(phenyl-bian)(dmfu)] was also synthesized in good yield using the same procedure.

Synthesis of [Pt(dafo)(dmfu)], [Pt(dafo)(ma)], and [Pt(dafo)(tcne)] was also addressed, but these attempts were not successful. Adding dafo to a concentrated solution of [$Pt(nbe)_3$] and 1.20 equiv. of dmfu in tetrahydrofuran did not result in the formation of [Pt(dafo)(dmfu)] after overnight stirring at reflux. None of the starting dafo had reacted, as was evident from ^{1}H NMR spectroscopy. Likewise, the synthesis of [Pt(dafo)(ma)] and [Pt(dafo)(tcne)] did not succeed. In the latter cases a slight amount of complexed dafo was observed by ^{1}H NMR spectroscopy, but the yields remained very low, in keeping with the weak ligating properties of dafo.

Hydrosilylation of Styrene by Triethylsilane Catalyzed by [Pt(Ar-bian)(η^2-alkene)] Complexes

In order to study the catalytic behavior of platinum(0) complexes of type [Pt(Ar-bian)(η^2-alkene)], [Pt{*m*,*m*-$(CF_3)_2$-C_6H_3-bian}(ma)], [Pt(*p*-MeO-C_6H_4-bian)(ma)], [Pt(*p*-MeO-C_6H_4-bian)(dmfu)], and [Pt(C_6H_5-bian)(dmfu)] were tested as catalysts in the hydrosilylation of styrene by triethylsilane, applying a styrene/triethylsilane ratio of only 1.0. The complex [Pt(Me-nq)$(nbe)_2$], an active hydrosilylation catalyst,[8] was also tested. The yields of the combined silyl products against time are shown in Figure 1.

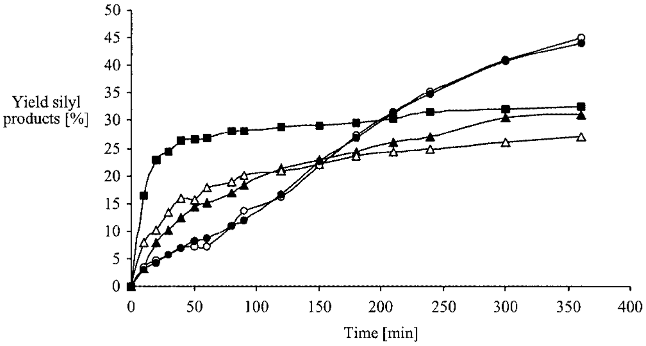


Figure 1. Hydrosilylation of styrene by triethylsilane catalyzed by [Pt(*m*,*m*-$(CF_3)_2$-C_6H_3-bian)(ma)] (open triangles), [Pt(*p*-MeO-C_6H_4-bian)(ma)] (filled triangles), [Pt(*p*-MeO-C_6H_4-bian)(dmfu)] (open circles), [Pt(C_6H_5-bian)(dmfu)] (filled circles), and [Pt(Me-nq)$(nbe)_2$] (filled squares); conditions: 0.36 mol % of catalyst, styrene/triethylsilane ratio 1.0, toluene, 30 °C; yield is the combined GC yield after 2 h of products **I**, **II**, and **III** using *n*-decane as the internal standard

From these results, it is obvious that the nature of the coordinated alkene determines the catalytic behavior of the complexes. [Pt(*p*-MeO-C_6H_4-bian)(dmfu)] and [Pt(C_6H_5-bian)(dmfu)] show an almost completely identical catalytic activity and stability. The complexes [Pt{*m*,*m*-$(CF_3)_2$-C_6H_3-bian}(ma)] and [Pt(*p*-MeO-C_6H_4-bian)(ma)] give different results compared to the two dmfu complexes: they show a higher initial activity, but decompose faster, resulting in a lower overall yield. From the synthetic experiments (see above), it is known that electron-donating substituents on the Ar-bian ligand increase the stability of the complex. However, for the two maleic anhydride complexes only a small difference in catalytic behavior is observed. In the beginning of the reaction, [Pt(*p*-MeO-C_6H_4-bian)(ma)] is slightly less active than [Pt{*m*,*m*-$(CF_3)_2$-C_6H_3-bian}(ma)], but is slightly more stable. [Pt(Me-nq)$(nbe)_2$] is a very active catalyst, but decomposition of the catalyst starts immediately after addition of triethylsilane. After 6 h, a yield of 32.5% was obtained with [Pt(Me-nq)$(nbe)_2$], which is almost similar to [Pt{*m*,*m*-$(CF_3)_2$-C_6H_3-bian}(ma)] (27.1%) and [Pt(*p*-MeO-C_6H_4-bian)(ma)] (31.1%). Although [Pt(*p*-MeO-C_6H_4-bian)(dmfu)] and [Pt(C_6H_5-bian)(dmfu)] are less active catalysts, there stability resulted in higher overall yields of 41.1% and 44.9%, respectively, after 6 h with the catalysts still being active after this time. After 24 h, a yield of 65% was obtained for [Pt(*p*-MeO-C_6H_4-bian)(dmfu)].

For all complexes, compound **II** was observed as the major product (85−87%) along with a minor amount of compound **I** (about 2%). The dehydrogenative silylation product **III** was observed in about 11−13% yield. The selectivities obtained with these catalysts were constant in time. The decreased amount of dehydrogenative silylation, compared to the reactions with in situ prepared catalysts, is caused by the lower styrene concentration compared to the other experiments, since a styrene/triethylsilane ratio of 1.0 instead of 2.8 was employed. As discussed before, the selectivities obtained are quite similar to those obtained using $PtCl_2$ as the catalyst.[29] $PtCl_2$, in fact every platinum(II) or platinum(IV) catalyst, is deemed to be reduced to a platinum(0) species. The reduction process, often of variable duration, causes the frequently observed induction periods for these catalysts.[3a] For example, using [$PtCl_2$(PhCH=CH_2)$_2$] as a catalyst, Caseri and Pregosin showed that the hydrosilylation of styrene proceeded by reduction of the Pt^{II} complex to [Pt$(styrene)_3$] with concomitant formation of 2 equiv. of R_3SiCl and 1 equiv. of ethylbenzene.[37] From Figure 1 it becomes quite obvious that our [Pt(Ar-bian)(η^2-alkene)] complexes do not suffer from an induction period; the hydrosilylation reactions start immediately after addition of the substrates. This behavior is in agreement with that observed for other platinum(0) catalysts.[8−10,16]

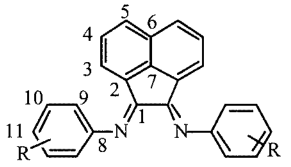
Since the palladium complexes [Pd(Ar-bian)(η^2-alkene)] are versatile catalysts for the selective hydrogenation of alkynes to (*Z*)-alkenes,[21] we also tested [Pd(*p*-MeO-C_6H_4-bian)(dmfu)] as a hydrosilylation catalyst and compared its catalytic behavior with its platinum analogue. However, it appears that this compound does not catalyze the hydrosilylation reaction at all: the complex immediately decomposed under hydrosilylation conditions in both THF and toluene at 30 °C.

Conclusion

In conclusion, several bidentate N-ligands have been evaluated in the hydrosilylation of styrene with triethylsilane at different temperatures, using in situ formed catalysts with [Pt$(nbe)_3$] as a precursor. In general, the ligands which form more stable platinum(0) complexes result in a lower catalytic activity and somewhat more dehydrogenative silylation compared to the ligands which form less stable complexes. Consequently, the precursor complex, [Pt$(nbe)_3$] itself, which has only labile alkene ligands, is an active catalyst at 30 °C and at a styrene to triethylsilane ratio of 2.8. At higher temperatures, the catalyst is no longer stable and a decrease in yield is observed when the temperature is increased. The complex [Pt(Me-nq)(nbe)$_2$], does not give significantly higher yields. Common bidentate ligands such as phen and dppe form stable complexes, resulting in no or very low hydrosilylation activity. However, for the ligands dafo and phenyl-bian, a small ligand effect is observed. Substituting the aryl groups of phenyl-bian ligand does not influence the catalysis significantly. By studying the behavior of various [Pt(Ar-bian)(alkene)] complexes, it has become clear that the nature of the alkene ligand in these complexes determines its catalytic behavior; the [Pt(Ar-bian)(ma)] complexes are intrinsically slightly more active than the two [Pt(Ar-bian)(dmfu)] complexes, however, the [Pt(Ar-bian)(dmfu)] complexes result in much more stable catalysts. The fact that the different Ar-bian ligands do not have a major influence on the catalytic behavior of the complexes demonstrates the lability of these bidentate ligands compared to several alkenes. Importantly, compared to [Pt(Me-nq)(nbe)$_2$], the two [Pt(Ar-bian)(dmfu)] complexes show an intrinsically lower activity, but are at the same time much more stable, resulting in significantly higher overall yields under similar conditions. We are at present investigating the use of alkenes as ligands in the platinum(0)-catalyzed hydrosilylation in more detail.

Experimental Section

General Remarks: All experiments were carried out by using standard Schlenk techniques under dry nitrogen. The solvents were dried according to standard procedures and distilled before use. Quantitative gas liquid chromatography (GLC) analyses were carried out with a Varian 3300 apparatus equipped with a semicapillary column (J&W, DB 5, 30 m × 1 μm) with *n*-decane as internal standard. Elemental analyses were carried out by Kolbe, Mikroanalytisches Laboratorium, Mülheim a. d. Ruhr, Germany. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at 300.1, 75.5, and 282.4 MHz, respectively, with a Varian Mercury 300 and with a Varian Inova 500 spectrometer at 499.8 and 125.7 MHz, respectively. Chemical shift values are in ppm relative to external TMS or Cl_3CF with high frequency shifts signed as positive. Abbreviations used are s = singlet, d = doublet, pst = peudotriplet, m = multiplet; multiplicity, number of protons and coupling constants (Hz) in parentheses. Triethylsilane (Acros), *n*-decane (Acros), dimethyl fumarate (Merck), tetracyanoethylene (Fluka), 1,10-phenanthroline (Aldrich), 2,2′-dipyridyl (Aldrich), triphenylphosphane (Aldrich), bis(diphenylphosphanyl)ethane (Strem), 2-methyl-2,4-naphthoquinone (Aldrich), acenaphthenequinone (Aldrich), and 4-fluoroaniline (Janssen Chimica) were used as received. Styrene (Acros) was purified by flash chromatography on alumina immediately prior to use. Maleic anhydride (EGA) was recrystallized from dichloromethane. [Pt(nbe)$_3$],[27] [Pd(*p*-MeO-C$_6$H$_4$-bian)(DMFU)],[24] phenyl-bian,[34] *p*-MeO-C$_6$H$_4$-bian,[34] *p*-Br-C$_6$H$_4$-bian,[34] *p*-NO$_2$-C$_6$H$_4$-bian,[35] and *m*,*m*-(CF$_3$)$_2$-C$_6$H$_3$-bian[35] were synthesized according to published procedures. 4.5-Diazafluoren-9-one[36] was synthesized according to the literature, but was additionally purified using column chromatography [silica, MeOH/dichloromethane (5:95)].



Bis(4-fluorophenylimino)acenaphthene (*p*-F-C$_6$H$_4$-bian, 7): The ligand was prepared analogous to the method described in the literature[36] for that of acenaphthenequinone and 4-fluoroaniline and was obtained as an orange solid. Yield: 1.81 g, 75%. ^{1}H NMR (300.1 MHz, CDCl$_3$): δ = 6.94 (d, ^3J = 7.14 Hz, 2 H, 3-H), 7.10 (m, 4 H, 9-H), 7.18 (m, 4 H, 10-H), 7.42 (pst, ^3J = 7.42 Hz, 2 H, 4-H), 7.93 (d, ^3J = 7.14 Hz, 2 H, 5-H) ppm. ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 116.52 (d, $^2J_{F,C}$ = 22.57 Hz, C-10), 119.95 (d, $^3J_{F,C}$ = 8.06 Hz, C-9), 124.10 (C-3), 127.91 (C-4), 128.48 (C-2), 129.46 (C-5), 131.47 (C-6), 142.03 (C-7), 147.71 (C-8), 160.28 (d, $^1J_{F,C}$ = 243.46 Hz, C-11), 162.00 (C-1) ppm. ^{19}F NMR (282.4 MHz, CDCl$_3$): δ = −119.31 ppm.

(σ-*N*,σ-*N*′-Bis{3,5-bis(trifluoromethyl)phenylimino}acenaphthene)-(η^{2}maleic anhydride)platinum(0) (10a): THF (2.5 mL) was added to maleic anhydride (127.0 mg, 275 μmol). The colorless solution was cooled to 0 °C, after which [Pt(nbe)$_3$] (119.5 mg, 250 μmol) was added. The solution was stirred at 0 °C for 15 min, after which *m*,*m*-(CF$_3$)$_2$-C$_6$H$_3$-bian (164.9 mg, 273 μmol) was added. Stirring was continued at 0 °C for 45 min, followed by the heating of the reaction mixture to room temperature. The orange solution was concentrated to dryness and the residue dissolved in 2 mL of dichloromethane. Pentane (20 mL) was added to the solution, after which a dark precipitate formed. The solvent was removed via a syringe and the solid was washed with pentane (4 × 20 mL) and dried in vacuo. The isolated dark purple powder was analyzed by NMR spectroscopy and appeared to be a mixture of reaction products. However, upon standing, a dark solid had precipitated from the combined organic extract. The precipitate was washed with pentane (8 × 10 mL) and dried in vacuo, after which **10a** was obtained as a dark purple powder. Yield: 96.5 mg, 43.0%. ^{1}H NMR (499.8 MHz, CD$_2$Cl$_2$): δ = 3.76 (s, $J_{Pt\text{-}H}$ = 89.84 Hz, 2 H, ma), 7.49 (d, ^3J = 7.32 Hz, 2 H, 3-H), 7.63 (pst, ^3J = 7.70 Hz, 2 H, 4-H), 8.10 (s, 2 H, 11-H), 8.21 (s, 4 H, 9-H), 8.38 (d, ^3J = 8.24 Hz, 2 H, 5-H) ppm. No ^{13}C NMR spectrum was recorded due to the low solubility and stability of the complex. ^{19}F NMR (282.4 MHz, CD$_2$Cl$_2$): δ = −63.35 ppm. $C_{32}H_{14}F_{12}N_2O_3Pt$ (897.52): calcd. C 42.82, H 1.57, N 3.12; found C 42.67, H 1.63, N 3.04.

(σ-*N*,σ-*N*′-Bis{3,5-bis(trifluoromethyl)phenylimino}acenaphthene)(η^2-tetracyanoethene)platinum(0) (10b): THF (20 mL) was added to *m*,*m*-(CF$_3$)$_2$-C$_6$H$_3$-bian (121 mg, 200 μmol), and tetracyanoethene (26.3 mg, 205 μmol). [Pt(nbe)$_3$] (92.1 mg, 193 μmol) was added to this mixture, and the solution changed color from bright orange to deep red. The mixture was stirred for 4 h at room temperature, after which the reaction was complete as was evident from TLC. The solvent was removed in vacuo and the residue washed with diethyl ether (3 × 2 mL) to afford **10b** as an orange solid. Yield: 151 mg, 81.6%. ^{1}H NMR (499.8 MHz, [D$_6$]acetone): δ = 7.80 (d, ^3J = 7.33 Hz, 2 H, 3-H), 7.85 (pst, ^3J = 7.81 Hz, 2 H, 4-H), 8.38 (s, 2 H, 11-H), 8.52 (s, 4 H, 9-H), 8.58 (d, ^3J = 8.06 Hz, 2 H, 5-H) ppm. ^{13}C NMR (125.7 MHz, [D$_6$]acetone): δ = 115.07 (CN), 123.92 (q, $^1J_{F,C}$ = 272.68 Hz, CF$_3$), 124.08 (C-9), 124.35 (C3), 125.84 (C-2), 126.78 (C-4), 130.77 (C-5), 133.18 (C-6), 134.44 (q, $^2J_{F,C}$ = 33.94 Hz, C-10), 134.45 (C-11), 149.69 (C-8), 150.07 (C-7), 176.67 (C-1) ppm. ^{19}F NMR (282.4 MHz, [D$_6$]acetone): δ = −63.57 ppm. $C_{34}H_{12}F_{12}N_6Pt$ (927.56): calcd. C 44.03, H 1.30, N 9.06; found C 44.11, H 1.36, N 9.13.

(σ-*N*,σ-*N*′-Bis{4-methoxyphenylimino}acenaphthene)(η^2-maleic anhydride)platinum(0) (11a): THF (3.5 mL) was added to *p*-MeO-C_6H_4-bian (107.3 mg, 273 µmol), and maleic anhydride (27.2 mg, 277 µmol). [Pt(nbe)$_3$] (120 mg, 251 µmol) was added to this solution after which the solution changed color from deep red to dark green. The mixture was stirred at room temperature for 60 min, and the solvent was removed in vacuo. The dark residue was washed with diethyl ether (3 × 3 mL), dried, dissolved in 5 mL of dichloromethane, and filtered through Celite Hyflo. Pentane (20 mL) was added to the filtrate followed by the formation of a dark precipitate. The solid was washed with pentane (4 × 10 mL) and dried in vacuo, after which **11a** was obtained as a brown red solid. Yield: 98.3 mg, 57.3%. ^{1}H NMR (499.8 MHz, CD_2Cl_2): δ = 3.55 (s, $J_{\text{Pt-H}}$ = 84.46 Hz, 2 H, ma), 3.93 (s, 6 H, MeO), 7.09 (d, ^3J = 9.03 Hz, 4 H, 9-H), 7.48 (pst, ^3J = 7.81 Hz, 2 H, 4-H), 7.63−7.71 (m, 6 H, 3-H and 10-H), 8.17 (d, ^3J = 8.06 Hz, 2 H, 5-H) ppm. ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ = 25.97 (ma), 55.81 (MeO), 114.45 (C-10), 123.39 (C-9), 124.97 (C-3), 127.30 (C-2), 128.94 (C-4), 130.41 (C-5), 132.19 (C-6), 141.26 (C-8), 145.50 (C-7), 160.47 (C-11), 168.64 (C-1), 174.51 (ma) ppm. $C_{30}H_{22}N_2O_5Pt$ (685.58): calcd. C 52.56, H 3.23, N 4.09; found C 52.48, H 3.20, N 3.99.

(σ-*N*,σ-*N*′-Bis{4-methoxyphenylimino}acenaphthene)(η^2-dimethyl fumarate)platinum(0) (11c): THF (20 mL) was added to *p*-MeO-C_6H_4-bian (78 mg, 199 µmol) and dimethyl fumarate (31.0 mg, 215 µmol). The solution changed color from deep red to dark green upon addition of [Pt(nbe)$_3$] (120 mg, 251 µmol). The mixture was stirred at room temperature for 90 min, after which the reaction was complete as was evident from TLC. The solvent was removed in vacuo and the dark brown residue washed with diethyl ether (2 × 3 mL) and dissolved in 5 mL of dichloromethane. The dark brown solution was filtered through Celite Hyflo and the filtrate concentrated to dryness in vacuo. The desired reaction product **11c** was obtained as a dark brown solid. Yield: 137 mg; 94.0%. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 3.40 (s, 6 H, dmfu), 3.72 (s, $J_{\text{Pt-H}}$ = 91.22 Hz, 2 H, dmfu), 3.98 (s, 6 H, MeO), 7.49 (d, ^3J = 7.42 Hz, 2 H, 3-H), 7.63 (pst, ^3J = 7.70 Hz, 2 H, 4-H), 8.10 (s, 2 H, 10-H), 8.21 (s, 4 H, 9-H), 8.14 (d, ^3J = 8.24 Hz, 2 H, 5-H) ppm. ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ = 27.29 (dmfu), 50.57 (dmfu), 56.17 (MeO), 115.07 (C-10), 123.54 (C-9), 125.72 (C-3), 129.21 (C-2), 130.11 (C-4), 130.71 (C-5), 133.43 (C-6), 134.04 (C-8), 142.62 (C-7), 160.92 (C-11), 168.93 (C-1), 176.45 (dmfu) ppm. $C_{32}H_{28}N_2O_6Pt$ (731.65): calcd. C 52.53, H 3.86, N 3.83; found C 52.34, H 3.76, N 3.95.

(σ-*N*,σ-*N*′-Bis{phenylimino}acenaphthene)(η^2-dimethyl fumarate)platinum(0) (12c): [Pt(nbe)$_3$] (0.92 g, 1.93 mmol), C_6H_5-bian (0.70 g, 2.11 mmol) and dimethyl fumarate (0.31 g, 2.15 mmol) were dissolved in THF (20 mL). The color of the solution changed to dark green immediately. The mixture was stirred at room temperature for 60 min and the solution was filtered through Celite Hyflo. The filtrate was concentrated to dryness in vacuo and was washed with a 50-mL pentane/diethyl ether (1:1) mixture and 2 × 50 mL of pentane. The desired reaction product **12c** was obtained as a dark green solid. Yield: 1.04 g; 80.0%. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 3.33 (s, 6 H, dmfu), 3.71 (s, $J_{\text{Pt-H}}$ = 93.15 Hz, 2 H, dmfu), 7.46−7.53 (m, 6 H, 3-H + 4-H + 11-H), 7.60 (m, 8 H, 9-H + 10-H), 8.21 (d, ^3J = 5.50 Hz, 1 H, 5-H), 8.23 (d, ^3J = 5.50 Hz, 1 H, 5-H) ppm. ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ = 27.93 (dmfu), 50.96 (dmfu), 122.87 (C-9), 123.76 (C-3), 128.30 (C-2), 128.62 (C-4), 129.87 (C-11), 130.16 (C-10), 130.43 (C-5), 132.7 (C-6), 145.85 (C-7), 149.19 (C-8), 169.65 (C-1), 176.47 (dmfu) ppm. $C_{30}H_{24}N_2O_4Pt$ (671.60): calcd. C 53.65, H 3.60, N 4.17; found C 53.88, H 3.74, N 4.08.

General Procedure for the Hydrosilylation of Styrene with Triethylsilane: A two-necked Schlenk tube equipped with a septum, a reflux condenser and a stirring bar was charged with the appropriate platinum complex (0.022 mmol) and, in the case of the in situ prepared catalysts, 1 equiv. of ligand. The Schlenk tube was evacuated and filled with nitrogen three times. Then toluene (20 mL), styrene (6.16 mmol or 17.24 mmol), *n*-decane (3.08 mmol), and triethylsilane (6.16 mmol) were added, in this order, in quick succession from syringes through the septum. The reactor was immediately immersed in an oil bath, which was kept at the required reaction temperature. Samples were taken periodically for GC analyses. Products were characterized using NMR spectroscopy and GC-MS.

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