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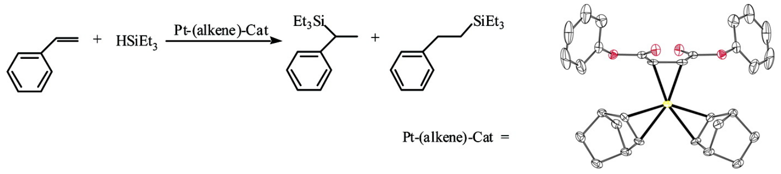

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Synthesis and Crystal Structures of Zerovalent Platinum η^2-Fumarate Bis(norbornene) Complexes and Their Application as Hydrosilylation Catalysts

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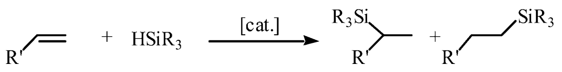
[Pt(η^2-norbornene)$_3$] reacts with a series of electron-poor alkenes, such as dimethyl maleate, maleic anhydride, several fumarates, and fumaric acid, to give platinum complexes of the type [Pt(η^2-alkene)(η^2-norbornene)$_2$]. X-ray crystal structures of [Pt(η^2-maleic anhydride)(η^2-norbornene)$_2$] and [Pt(η^2-diphenyl fumarate)(η^2-norbornene)$_2$] have been obtained. Using di-*tert*-butylfumaramide and diethyl dithiofumarate does not yield pure complexes. Addition of an excess of pyridine to [Pt(maleic anhydride)(norbornene)$_2$] yields the complex [Pt(η^2-maleic anhydride)(η^2-norbornene)(σ-*N*-pyridine)]. Whereas in the case of [Pt(η^2-norbornene)$_3$] no coordination of pyridine is observed, the complex [Pt(σ-*N*-pyridine)$_2$(η^2-tetracyanoethylene)] is readily obtained by the addition of 1 equiv of tetracyanoethylene concomitant with or immediately after the addition of pyridine. The complexes have been employed as precatalysts in the hydrosilylation of styrene by triethylsilane. The maleate and fumarate complexes are the most stable catalysts, and the various fumarate complexes do not exhibit significant differences in their catalytic behavior.

Introduction

Pure platinum(0)−alkene complexes are useful sources for ligand-free platinum and have been applied in the synthesis of many different platinum(0) complexes and have been used as catalyst precursors. The synthesis of such complexes usually starts from [Pt(cyclooctadiene)$_2$][1,2] or one of the numerous other platinum(0)−alkene complexes such as [Pt(η^2-ethene)$_3$],[2] [Pt(η^2-norbornene)$_3$],[3,4] [Pt(η^2-styrene)$_3$],[5] [Pt(dibenzylideneacetone)$_2$],[6] [Pt$_2$(η^4-divinyltetramethyldisiloxane)$_2$(μ-η^4-divinyltetramethyldisiloxane)],[7] and [Pt$_2$(η^4-hepta-1,6-diene)$_2$(μ-η^4-hepta-1,6-diene)].[8] Over the years, many other platinum(0)−alkene complexes have been reported, including a large amount of "mixed" alkene complexes, such as [Pt(η^4-cyclooctadiene)(η^2-dimethyl fumarate)],[9,10] [Pt(η^2-tetrafluoroethene)(η^2-norbornene)$_2$],[11] [Pt(η^2-2-methylnaphthoquinone)(η^2-norbornene)$_2$],[12] and [Pt$_2$(μ-η^4-*p*-benzoquinone)$_2$(η^2-norbornene)$_2$].[13]

Zerovalent platinum complexes are frequently used as catalysts for the hydrosilylation of unsaturated carbon−carbon bonds (Scheme 1).[5,12−15] However, platinum(II) catalysts can also be successfully employed in the hydrosilylation. For example, Roy and Taylor have reported some efficient platinum(II)−alkene catalysts.[16] In general, platinum(0) complexes containing weakly coordinating ligands exhibit high activities. However, the limited thermal stability of these highly active catalysts in solution is often a problem. To obtain a more stable catalyst, the use of more strongly coordinating

Scheme 1



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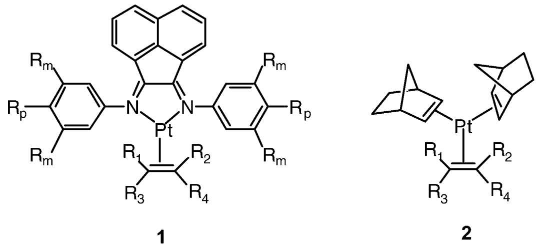
10.1021/om049913i CCC: $27.50

Chart 1



ligands is necessary. Since strongly coordinating bidentate ligands result in very low activities,[15] monodentate ligands seem to be the choice for stabilizing the platinum(0) species.

We have recently used a series of [Pt(bis(arylimino)-acenaphthene)(η^2-alkene)] ([Pt(Ar-bian)(η^2-alkene)]) complexes (**1**) (Chart 1) as catalysts in the hydrosilylation of styrene, from which it became clear that not the bidentate Ar-bian ligand but instead the monodentate alkene ligand determines the activity and stability of the catalyst.[15] A relatively stable catalyst was obtained with dimethyl fumarate as the alkene ligand, whereas maleic anhydride yielded a less stable catalyst. Since Ar-bian does not play a key role, we reasoned that replacing it by labile norbornene ligands, yielding [Pt(η^2-alkene)(η^2-norbornene)$_2$] complexes (**2**) (Chart 1), would probably generate more active catalysts. Osborn et al.[12] already observed a high activity for [Pt(η^2-2-methylnaphthoquinone)(η^2-norbornene)$_2$] in the hydrosilylation of vinylsilanes.

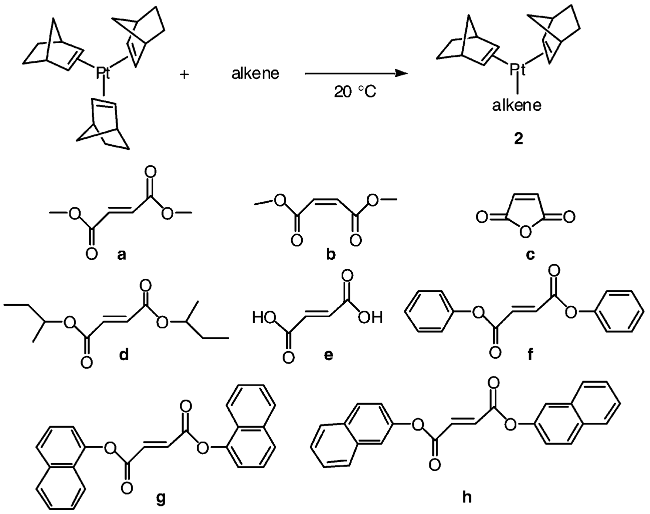
Lewis et al.[17] reported the use of some fumarates and maleates as inhibitors for hydrosilylation reactions. In this application, about 35 equiv of a fumarate or a maleate is added to a platinum catalyst and the hydrosilylation only starts above 64−77 °C. This observation indicates the relatively strong coordination of these electron-poor alkenes, which is in agreement with the Dewar, Chatt, and Duncanson model.[18,19] In zerovalent platinum complexes, the extent of π-back-donation from the metal center toward the alkene ligands is the most important contribution and the bond strength generally increases if electron-deficient alkenes are involved.

Here we report the synthesis and characterization of several new zerovalent platinum complexes of the type [Pt(η^2-alkene)(η^2-norbornene)$_2$]. Dimethyl maleate, maleic anhydride, and several fumarates were used as the electron-poor alkene ligands. The influence of the electron-withdrawing alkenes on the stability of these complexes was studied by employing them as catalysts in the hydrosilylation of styrene with triethylsilane.

Results and Discussion

Synthesis of [Pt(η^2-alkene)(η^2-norbornene)$_2$] Complexes. Green et al.[11] reported the synthesis of [Pt(η^2-tetrafluoroethene)(η^2-norbornene)$_2$] which was obtained after stirring tetrafluoroethene with [Pt(η^2-norbornene)$_3$] in light petroleum for 1 h. Osborn et al.[12] synthesized [Pt(η^2-2-methylnaphthoquinone)(η^2-norbornene)$_2$] by substitution of one norbornene ligand of [Pt(η^2-norbornene)$_3$] with 2-methylnaphthoquinone in tetrahydrofuran at room temperature. Recently, Yamamoto reported the dinuclear complex [Pt$_2$(μ-η^4-*p*-benzoquinone)$_2$(η^2-norbornene)$_2$], in which *p*-benzoquinone acts as a bridging ligand.[13] This complex was synthesized by refluxing [Pt(dba)$_2$] with 5 equiv of *p*-benzoquinone and 5 equiv of norbornene in acetone for 3 h. We used the synthetic route employed by Osborn because of its simplicity and high yield. Hence, 1 equiv of dimethyl maleate, maleic anhydride, or a fumarate was stirred with [Pt(η^2-norbornene)$_3$] at 20 °C in tetrahydrofuran or diethyl ether (Scheme 2).

Scheme 2. Synthesis of [Pt(η^2-alkene)(η^2-norbornene)$_2$] Complexes (2a−h)



The complexes **2a**−**h** were obtained as white solids or colorless crystals in 72−99% yield. All complexes are stable at 20 °C, even the complex containing fumaric acid (**2e**), which is also stable in methanol for a short period of time. The complexes containing dimethyl maleate (**2b**) and di-*sec*-butyl fumarate (**2d**) were first obtained as sticky oils, but recrystallization of these complexes from pentane at −80 °C yielded solid products. We also attempted to synthesize complexes with di-*tert*-butylfumaramide and diethyl dithiofumarate. However, for these alkenes, NMR revealed that both reactions yielded mixtures of complexes and no pure complexes could be obtained. Probably the nitrogen and the sulfur atoms in these ligands compete with the alkene ligand for coordination.

When 2 equiv of maleic anhydride or fumaric acid was used in the reaction, still only one norbornene ligand was replaced and no [Pt(η^2-alkene)$_2$(η^2-norbornene)] complexes were obtained. Conversely, Chicote et al.[10] previously reported the synthesis of platinum(0) compounds containing two or three electron-poor alkenes using [Pt(η^2-ethene)$_3$] as precursor complex. For example, [Pt(η^2-dimethyl fumarate)$_3$] was obtained by mixing 3 equiv of dimethyl fumarate with [Pt(η^2-ethene)$_3$]. In our case, when 2 equiv of styrene was added to solutions of [Pt(η^2-dimethyl fumarate)(η^2-norbornene)$_2$] and [Pt(η^2-maleic anhydride)(η^2-norbornene)$_2$] in tetrahydrofuran, no reaction was observed after stirring at 20 °C for 1 h. However, adding 2.5 equiv of pyridine to a solution of [Pt(η^2-maleic anhydride)(η^2-norbornene)$_2$] in diethyl ether yielded the novel complex [Pt(η^2-maleic anhydride)(η^2-norbornene)(σ-*N*-pyridine)]

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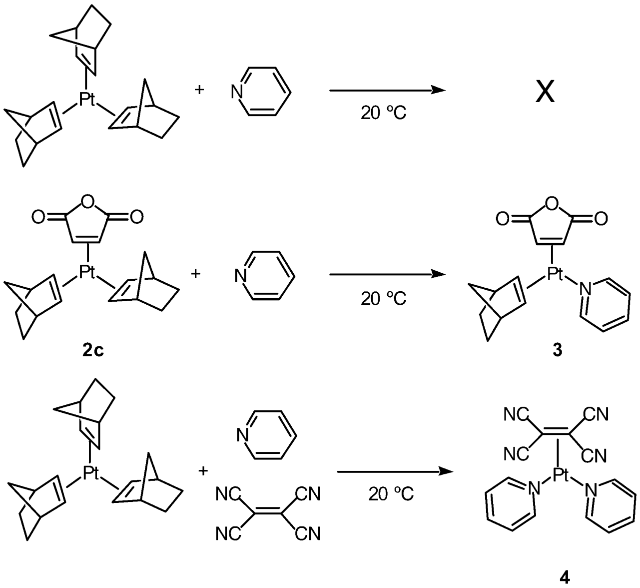
Scheme 3. Synthesis of [Pt(η^2-maleic anhydride)(η^2-norbornene)(σ-*N*-pyridine)] (3) and [Pt(σ-*N*-pyridine)$_2$(η^2-tetracyanoethylene)] (4)



(**3**) (Scheme 3). Remarkably, only one norbornene ligand was replaced, even when this complex was stirred in toluene for 16 h with 5 equiv of pyridine. This result is different from that for palladium: two pyridines readily displace norbornadiene when an excess of pyridine is added to [Pd(η^2-maleic anhydride)(η^4-norbornadiene)].[20]

Complex **3** is the first zerovalent platinum complex containing one monodentate nitrogen ligand and two alkene ligands. An NMR experiment was performed in benzene at 20 °C to study the reaction between [Pt(η^2-norbornene)$_3$] and 5 equiv of pyridine. Over 1 h, no coordination of pyridine was observed and platinum black formation was visible. Apparently, the platinum is not electrophilic enough for pyridine to coordinate. When [Pt(η^2-norbornene)$_3$] was treated with 1 equiv of tetracyanoethylene and 5 equiv of pyridine in THF, two pyridines coordinated to the platinum, yielding [Pt(σ-*N*-pyridine)$_2$(η^2-tetracyanoethylene)] (**4**) (Scheme 3). When the very electron poor tetracyanoethylene is coordinated, the platinum appears to be electrophilic enough for coordination of two pyridines. These results show the subtle balance invoked by the electron-donating and electron-withdrawing capacities of the ligands, which determine the overall stability of platinum(0) complexes.

X-ray Structure Determinations of [Pt(η^2-maleic anhydride)(η^2-norbornene)$_2$] (2c) and [Pt(η^2-diphenyl fumarate)(η^2-norbornene)$_2$] (2f). The molecular structures of [Pt(η^2-maleic anhydride)(η^2-norbornene)$_2$] (**2c**) and [Pt(η^2-diphenyl fumarate)(η^2-norbornene)$_2$] (**2f**) have been confirmed by X-ray crystallography. ORTEP plots are shown in Figure 1 (**2c**) and Figure 2 (**2f**). In both complexes the alkenes are all coordinated in one plane, similar to the situation that is found in almost all known platinum(0)−alkene complexes. In this orientation, the amount of π-back-bonding to the three alkenes is maximized.

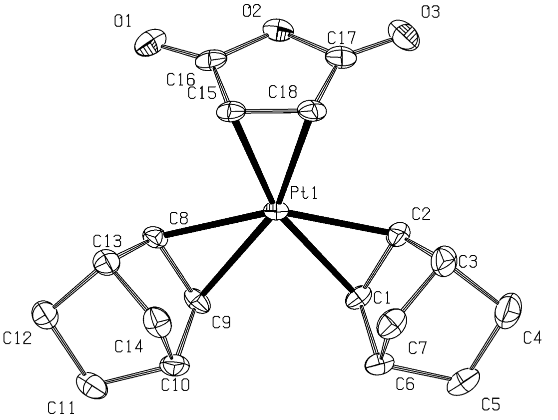


Figure 1. ORTEP plot of the molecular structure of **2c** drawn at the 50% probability level. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt1−C1, 2.246(3); Pt1−C2, 2.202(4); Pt1−C8, 2.207(4); Pt1−C9, 2.252(4); Pt1−C15, 2.104(3); Pt1−C18, 2.114(4); C1−C2, 1.388(6); C8−C9, 1.391(4); C15−C18, 1.419(6); C16−O1, 1.202(5); C17−O3, 1.193(5); C1−Pt1−C2, 36.36(15); C8−Pt1−C9, 36.33(11); C15−Pt1−C18, 39.31(16).

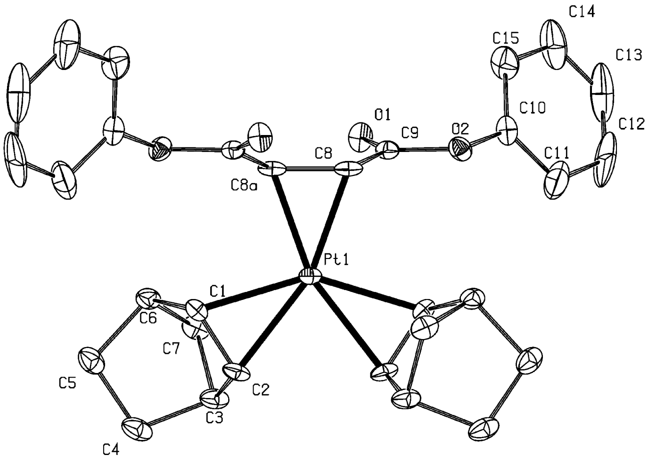


Figure 2. ORTEP plot of the molecular structure of **2f** drawn at the 30% probability level. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt1−C1, 2.206(3); Pt1−C2, 2.243(3); Pt1−C8, 2.109(2); C1−C2, 1.385(4); C8−C8a, 1.411(4); C9−O1, 1.203(3); C1−Pt1−C2, 36.25(9); C8−Pt1−C8a, 39.09(10).

Complex **2c** shows a local mirror plane that runs through atoms O2 and Pt1 and the midpoint of the bond C15═C18. The bridges of the two norbornenes are pointing in the same direction, opposite to the maleic anhydride ring. The alkene double bond length of the maleic anhydride (C15−C18) is 1.419(6) Å, which is longer than the value found in free maleic anhydride[21] (1.3322(9) Å) but fits in the range of bond lengths observed in other platinum(0) and palladium(0) complexes such as [Pt(η^4-1,5-hexadiene)(η^2-maleic anhydride)][22] (1.40(3) Å), [Pt(*N*-*tert*-butylcarbaldimino)-pyridine)(η^2-maleic anhydride)][23] (1.449(11) Å), [Pt(3,5-CF$_3$-BABAR-phos)(η^2-maleic anhydride)(η^2-norbornene)][24] (1.42(2) Å), [Pd(η^2-maleic anhydride)(σ-(N)-pyridine)$_2$][20]

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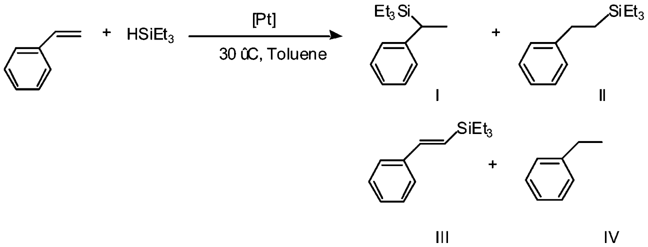
Scheme 4



(1.430 Å), and [Pt(N,N'-bis{(2,6-diisopropylphenyl)-imino}acenaphthene)(η^2-maleic anhydride)][25] (1.408(11) Å). The alkene bond lengths of the two norbornenes are 1.388(6) and 1.391(4) Å and are quite similar to the values found in [Pt(η^2-norbornene)$_3$][3,4] (1.39(3), 1.38(5), and 1,41(2) Å), [Pt$_2$(μ-η^4-p-benzoquinone)$_2$(η^2-norbornene)$_2$][13] (1.385(7) Å), and [Pt(3,5-CF$_3$-BABAR-phos)(η^2-maleic anhydride)(η^2-norbornene)][24] (1.38(2) Å). The Pt−C bond lengths of maleic anhydride (2.104(3) and 2.114(4) Å) are shorter than those of the two norbornenes (2.202(4)−2.252(4) Å). This observation, together with the longer double bond of maleic anhydride compared to norbornene, indicates a larger extent of π-back-donation from the platinum to the maleic anhydride than to the two norbornenes.

Complex **2f** is located on a crystallographic 2-fold rotation axis. The molecular structure therefore displays perfect C_2 symmetry. Different from **2c**, the bridges of the two norbornenes are in opposite direction. The alkene double bond length of the diphenyl fumarate (C8−C8a) is 1.411(4) Å, which is longer compared to the value found in free diphenyl fumarate[26] (1.307(2) Å) and is slightly smaller than the value found in [Pt(SMe)$_2$(dmphen)(diphenyl fumarate)][26] (1.444(6) Å) and [Pt(SMe)$_2$(dmphen)(diphenyl fumarate)](BF$_4$)$_2$[26] (1.446(19) Å). The alkene bond length and the Pt−C bond lengths of the norbornenes are respectively 1.385(4), 2.206(3), and 2.243(3) Å and are comparable to those of **2c**. The Pt−C bond length of diphenyl fumarate is 2.109(2) Å, which is also similar to that for **2c**. However, the elongation of the diphenyl fumarate bond (Δ = 0.104(2) Å) is larger than the value found in maleic anhydride (Δ = 0.087(4) Å), indicating that the diphenyl fumarate is more strongly coordinated.

Hydrosilylation of Styrene with Triethylsilane Catalyzed by [Pt(η^2-alkene)(η^2-norbornene)$_2$] Complexes. The hydrosilylation of styrene with triethylsilane, yielding products I and II, was monitored at 30 °C to study the stability and activity of the [Pt(η^2-alkene)(η^2-norbornene)$_2$] complexes (Scheme 4). We already employed this reaction to evaluate the catalytic performance of some platinum(0) complexes with diimine ligands[15] and with N-heterocyclic carbene ligands.[14] In the case of alkene and diimine ligands, the hydrosilylation of styrene with triethylsilane is accompanied by dehydrogenative silylation, yielding products III and IV (Scheme 1), a side reaction that has more generally been observed.[5,15] Ethylbenzene (IV), which arises by hydrogenation of styrene, is always formed in the same amount as the vinylsilane product (III). We have already reported that dehydrogenative silylation is almost completely absent when employing an in situ formed platinum 1,3-dimesityldihydroimidazol-2-ylidene catalyst.[14] So far, this is the only known platinum(0) catalyst which is capable of blocking this side reaction. The results of the catalytic hydrosilylations using the new [Pt(η^2-alkene)(η^2-norbornene)$_2$] complexes have been collected in Table 2.

Table 1. Crystallographic Data for the Crystal Structure Determinations of 2c and 2f

	2c	2f
formula	$C_{18}H_{22}O_3Pt$	$C_{30}H_{32}O_4Pt$
mol wt	481.44	651.64
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a, Å	13.050(2)	21.340(5)
b, Å	8.9621(10)	7.7477(10)
c, Å	18.093(3)	15.750(3)
β, deg	133.058(8)	102.461(18)
V, Å^3	1546.1(4)	2542.7(8)
D_{calc}, g cm^{-3}	2.0683(5)	1.7022(6)
Z	4	4
F(000)	928	1288
μ (Mo Kα), mm^{-1}	9.086	5.552
abs cor range	0.340−0.635	0.280−0.680
cryst color	colorless	colorless
cryst size, mm	0.05 × 0.10 × 0.15	0.07 × 0.18 × 0.28
θ_{min}, θ_{max}, deg	1.0, 27.5	1.0, 27.5
data set (hkl)	−16 to +16, −11 to +11, −23 to +23	−27 to +27, −10 to +9, −20 to +20
total no. of data, unique data	36 745, 3546	23 268, 2909
R_{int}	0.0595	0.0369
no. of refined params	217	171
final R1^a	0.0191 (3153 $I > 2\sigma(I)$)	0.0192 (2748 $I > 2\sigma(I)$)
final wR2^b	0.0437	0.0445
goodness of fit	1.077	1.108
$w^{-1\,c}$	$\sigma^2(F_o^2) + (0.0188P)^2 + 1.13P$	$\sigma^2(F_o^2) + (0.0153P)^2 + 3.85P$
min, max residual density, e Å^{-3}	−1.45, 0.93	−1.33, 1.14

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. ^{c} $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$.

Table 2. Hydrosilylation of Styrene with Triethylsilane^a

	catalyst	yield (%)^b	selectivity^c I:II:III (%)
1	[Pt(norbornene)$_3$]	21	2:87:11
2	[Pt(dimethyl fumarate)(nbe)$_2$] (**2a**)	50	2:84:14
3	[Pt(dimethyl maleate)(nbe)$_2$] (**2b**)	51	2:84:14
4	[Pt(maleic anhydride)(nbe)$_2$] (**2c**)	36	2:85:13
5	[Pt(di-*sec*-butyl fumarate)(nbe)$_2$] (**2d**)	52	2:84:14
6	[Pt(fumaric acid)(nbe)$_2$] (**2e**)	47	3:83:14
7	[Pt(diphenyl fumarate)(nbe)$_2$] (**2f**)	55	2:83:15
8	[Pt(di-2-naphthyl fumarate)(nbe)$_2$] (**2h**)	42	2:85:13
9	[Pt(nbe)$_3$] + 1 equiv of di-*tert*-butylfumaramide	0	
10	[Pt(nbe)$_3$] + 1 equiv of diethyl dithiofumarate	0	
11	[Pt(2-methylnaphthoquinone)(nbe)$_2$]	32	2:84:14
12	[Pt$_2$(p-benzoquinone)$_2$(nbe)$_2$]	36	2:85:13
13	[Pt(maleic anhydride)(nbe)(σ-N-pyridine)] (**3**)	0	
14	[Pt(diphenyl fumarate)(nbe)$_2$]^d (**2f**)	>99^e	2:69:29

^{a} Conditions: 0.36 mol % of catalyst, styrene to triethylsilane ratio 1.0, 30 °C, toluene. ^{b} Combined GC yield of products I−III after 6 h using n-decane as the internal standard. ^{c} Product IV was always observed in the same amount as product III and was therefore omitted. ^{d} Styrene to triethylsilane ratio 2.8. ^{e} Yield after 4 h.

From Table 2 it is obvious that, under these conditions, none of the catalysts (except **2f,** entry 14) is able

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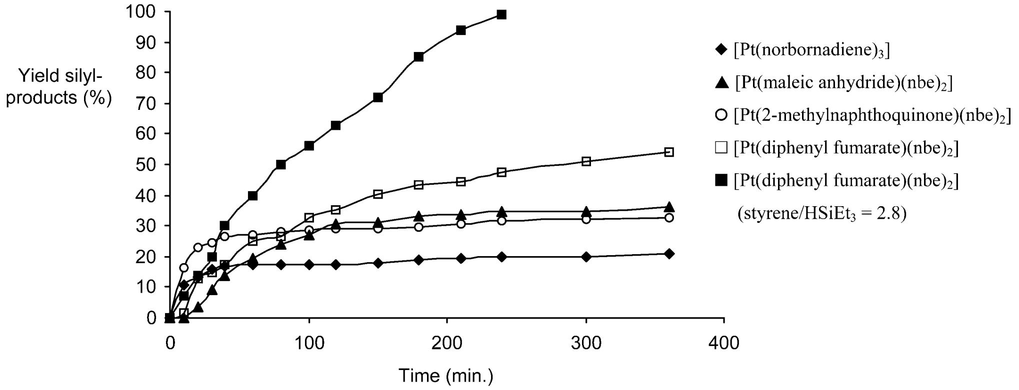

Figure 3. Hydrosilylation of styrene by triethylsilane catalyzed by [Pt(η^2-alkene)(η^2-norbornene)$_2$]. Conditions: 0.36 mol % of catalyst, styreneo triethylsilane ratio of 1 or 2.8, toluene, 30 °C. The yield is the combined GC yield of products I−III using *n*-decane as the internal standard.

to induce total conversion. We have applied a standardized styrene to hydrosilane ratio of 1 and have performed the reactions at 30 °C, which is not optimum but allows us to evaluate the differences between the platinum complexes. The reactions were performed under inert conditions, since Steffanut et al. observed a much lower rate with [Pt(η^2-2-methylnaphthoquinone)(η^2-norbornene)$_2$] when the reaction was performed in the presence of oxygen.[12] In contrast, it is already known that, for example, Karstedt's catalyst needs oxygen to become an active catalyst for some alkenes. With this catalyst, the oxygen will disrupt multinuclear platinum species that are formed when poorly stabilizing alkenes are employed.[27]

The deactivation of all catalysts due to the formation of platinum black was visible. However, the complexes containing a fumarate (**2a**,**d**−**f**,**h**, entries 2 and 5−8) or dimethyl maleate (**2b**, entry 3) deactivated much more slowly: the catalyst solutions remained clear and yellow for much longer periods than for the others. In contrast, [Pt(η^2-norbornene)$_3$] (entry 1), [Pt(η^2-2-methylnaphthoquinone)(η^2-norbornene)$_2$] (entry 11), and [Pt$_2$(μ-η^4-*p*-benzoquinone)$_2$(η^2-norbornene)$_2$] (entry 12) gave dark brown solutions immediately (due to formation of platinum particles) and consequently lower yields. Nevertheless, 2-methylnaphthoquinone and *p*-benzoquinone are still able to stabilize the platinum(0) for a short period of time and therefore give slightly higher yields than [Pt(η^2-norbornene)$_3$]. Maleic anhydride (entry 4) seems to be an intermediate ligand between quinones and fumarates or maleates. [Pt(η^2-maleic anhydride)(η^2-norbornene)(σ-*N*-pyridine)] (**3**, entry 13) did not show any activity at all. For this case, at 50 °C, no hydrosilylation was observed either. It is known that platinum complexes with bidentate ligands exhibit low activities. Probably, in this case, the maleic anhydride and pyridine remain both coordinated to the platinum during the reaction, thereby inhibiting the reaction. Also for this complex, platinum black was formed during catalysis. The reactions with the in situ formed catalysts with di-*tert*-butylfumaramide and diethyl dithiofumarate did not result in any hydrosilylation, either at 30 or at 50 °C. Probably, the nitrogen and the sulfur atoms compete with the alkene ligand for coordination, thus retarding the catalysis. Finally, [Pt(diphenyl fumarate)(norbornene)$_2$] (**2f**) was tested in the hydrosilylation with a styrene to hydrosilane ratio of 2.8 (entry 14). It is already known that platinum−alkene complexes are more stable at higher styrene concentrations,[15] and indeed a total conversion was obtained with this catalyst already after 4 h. However, this was to the detriment of the selectivity (see below).

Comparing the yields after 6 h obtained with [Pt(η^2-dimethyl fumarate)(η^2-norbornene)$_2$] (the yield is 50%) and [Pt(η^2-maleic anhydride)(η^2-norbornene)$_2$] (the yield is 36%) with those of [Pt(*p*-MeO-C$_6$H$_4$-bian)(η^2-dimethyl fumarate)][15] (yield is 41%) and [Pt(*p*-MeO-C$_6$H$_4$-bian)(η^2-maleic anhydride)][15] (yield is 31%), it becomes clear that the Ar-bian ligands decelerate the hydrosilylation to some extent. Apparently, the alkene ligand determines the catalytic behavior.

When the various catalysts were compared, no significant differences in selectivities were observed and these were similar to those of already reported catalysts, such as some [Pt(Ar-bian)(η^2-alkene)] complexes[15] and PtCl$_2$,[28] but different compared to some platinum(0)−N-heterocyclic carbene catalysts.[14] All our catalysts yielded about 2% of the branched hydrosilylated product (I), about 83−85% of the linear hydrosilylated product (II), and about 12−15% of product III due to dehydrogenative silylation. (Ethylbenzene was always formed in the same amount as III.) [Pt(η^2-norbornene)$_3$] gave a similar selectivity (entry 1). When [Pt(η^2-diphenyl fumarate)(η^2-norbornene)$_2$] was tested with a styrene to hydrosilane ratio of 2.8 (entry 14), a significantly higher yield of III was observed (29%). Other platinum−alkene and platinum−diimine catalysts[13] and also Karstedt's catalyst[29] yields similar selectivities in the hydrosilylation of styrene with triethylsilane under these conditions.

The differences in activities and stabilities between the catalysts became more clear when the reactions are followed in time. The results for [Pt(η^2-norbornene)$_3$], [Pt(η^2-maleic anhydride)(η^2-norbornene)$_2$], [Pt(η^2-2-methylnaphthoquinone)(η^2-norbornene)$_2$], and [Pt(η^2-diphenyl fumarate)(η^2-norbornene)$_2$] (with styrene to triethylsilane ratios of 1 and 2.8) are plotted in Figure 3.

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From Figure 3, it is clear that none of the catalysts suffer from an induction period; hydrosilylation starts immediately, which points to a homogeneous reaction not involving clusters or colloids. The complexes [Pt(η^2-2-methylnaphthoquinone)(η^2-norbornene)$_2$] and [Pt(η^2-norbornene)$_3$] are initially quite active catalysts, but they are not very stable, the former being somewhat more stable than the latter. [Pt(η^2-maleic anhydride)(η^2-norbornene)$_2$] is a less active catalyst but is more stable than [Pt(η^2-norbornene)$_3$]. [Pt(η^2-diphenyl fumarate)(η^2-norbornene)$_2$] is intrinsically also less active, but this complex is relatively stable. When [Pt(diphenyl fumarate)(norbornene)$_2$] was tested with a styrene to hydrosilane ratio of 2.8, the catalyst was stabilized by the high styrene concentration and total conversion was reached after 4 h.

In platinum(0) complexes, more electron-deficient alkenes are more strongly coordinated, due to the increased π-back-donation of the platinum atom to these alkenes. In the hydrosilylation, the most active catalysts contain the weakest ligands. Apparently, fumarate and maleate ligands, which yielded the most stable catalysts in our study, are more strongly coordinated to platinum(0) than maleic anhydride. This observation is in agreement with the large elongation of the diphenyl fumarate alkene bond compared to that in maleic anhydride, as is found in the crystal structures. Furthermore, maleic anhydride is a stronger alkene ligand compared to 2-methylnaphthoquinone and *p*-benzoquinone. Osborn et al.[12] used very electron poor alkenes, such as tetracyanoethylene and fumaronitrile, as ligands. These alkenes yielded very slow catalysts compared to 2-methylnaphthoquinone. It seems that in the hydrosilylation reaction, activity and stability are mutually exclusive properties of these platinum–alkene complexes: catalysts which show higher activity are less stable.

We think that the deactivation of the catalysts is caused by dissociation of all ligands, including the most tightly bound alkene, after which the platinum is not stabilized any longer. The fate of a fumarate or a maleate ligand during hydrosilylation was previously studied by Lewis et al.[17] When using an excess (35 equiv) of fumarates or maleates as inhibitors for platinum-catalyzed cross-linking reactions, they observed the formation of diethyl and dimethyl succinate, the hydrogenation products of diethyl fumarate, diethyl maleate, and dimethyl maleate. First, complexes of the type [Pt(η^2-fumarate/maleate)(η^4-divinyltetramethyldisiloxane)] were identified by NMR. During the hydrosilylation, also intermediate complexes containing alkyl succinate ligands were observed. These complexes were formed after oxidative addition of the hydrosilane, followed by insertion of the fumarate into the Pt–H bond, and can be seen as intermediates in the hydrogenation of the fumarate and maleate ligands.

Conclusions

In conclusion, several stable platinum complexes of the type [Pt(η^2-alkene)(η^2-norbornene)$_2$] were obtained. The complexes containing dimethyl maleate or a fumarate were more stable than the complex with maleic anhydride. Also, fumaric acid yielded a stable complex; in fact, all complexes are much more stable than [Pt(η^2-norbornene)$_3$]. Di-*tert*-butylfumaramide and diethyl dithiofumarate did not yield pure complexes. A second electron-poor ligand could not be added to these complexes. However, it was shown that pyridine readily replaces one norbornene in [Pt(η^2-maleic anhydride)(η^2-norbornene)$_2$], yielding the novel complex [Pt(η^2-maleic anhydride)(η^2-norbornene)(σ-*N*-pyridine)]. Remarkably, only one norbornene ligand was substituted, even with an excess of pyridine. With [Pt(η^2-norbornene)$_3$], no coordination of pyridine was observed. However, coordination of tetracyanoethylene increased the electrophilicity of the platinum to such extent that two pyridines readily coordinated, yielding [Pt(σ-*N*-pyridine)$_2$(η^2-tetracyanoethylene)]. On the basis of the results of catalytic hydrosilylation, the strength of the alkene–platinum bonds decreases in the following order: fumarate $\approx$ maleate $>$ maleic anhydride $>$ 2-methylnaphthoquinone $\approx$ *p*-benzoquinone $>$ norbornene. All catalysts deactivated during catalysis; however, it was shown that by increasing the styrene to triethylsilane ratio from 1 to 2.8, full conversion was obtained with [Pt(η^2-diphenyl fumarate)(η^2-norbornene)$_2$] as the catalyst. Due to the relatively high stability of the [Pt(η^2-fumarate)(η^2-norbornene)$_2$] complexes in the solid state, the complexes can be stored at room temperature and are consequently more easy to handle than [Pt(η^2-norbornene)$_3$]. Their higher stabilities under hydrosilylation conditions makes these complexes valuable hydrosilylation catalysts.

Experimental Section

General Considerations. All experiments were carried out by using standard Schlenk techniques under an atmosphere of 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 and ^{13}C NMR spectra were recorded at 300.1 and 75.5 MHz, respectively, on a Varian Mercury 300 and on a Varian Inova 500 spectrometer at 499.8 and 125.7 MHz, respectively. Chemical shift values are in ppm relative to external TMS with high-frequency shifts given as positive values. Abbreviations used are s = singlet, d = doublet, t = triplet, and m = multiplet; multiplicity, coupling constants (Hz), and the number of protons are given in parentheses. Fast atom bombardment (FAB) mass spectrometry measurements were carried out using a JEOL JMS SX/SX 102A four-sector mass spectrometer, coupled to a JEOL MS-MP9021D/UPD system program. The samples were loaded in a matrix solution (3-nitrobenzyl alcohol) onto a stainless steel probe and bombarded with xenon atoms with an energy of 3 keV. During the high-resolution measurements a resolving power of 10.000 (10% valley definition) was used. Triethylsilane (Acros), *n*-decane (Acros), dimethyl fumarate (Merck), dimethyl maleate (Janssen Chimica), di-*sec*-butyl fumarate (Aldrich), fumaric acid (ACL), fumaryl chloride (Acros), 1-naphthol (Aldrich), 2-naphthol (BDH), pyridine (Aldrich), and tetracyanoethylene (Fluka) were used as received. Styrene (Acros) was purified by flash chromatography on alumina immediately prior to use. Maleic anhydride (EGA) was recrystallized from dichloromethane. Diphenyl fumarate,[30] di-*tert*-butylfumaramide,[31] diethyl dithio-

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fumarate,[32] [Pt(η^2-norbornene)$_3$],[33] [Pt(η^2-2-methylnaphthoquinone)(η^2-norbornene)$_2$],[12] [Pt$_2$(μ-η^4-*p*-benzoquinone)$_2$(η^2-norbornene)$_2$],[13] [Pt(*p*-MeO-C_6H_4-bian)(η^2-dimethyl fumarate)],[15] and [Pt(*p*-MeO-C_6H_4-bian)(η^2-maleic anhydride)][15] were synthesized according to published procedures.

Synthesis of Di-1-naphthyl Fumarate (g). This compound has been reported in the literature[34] but was synthesized according to a modified procedure. A 3.45 g portion (24 mmol) of 1-naphthol was heated in 2.0 mL of toluene for 30 min at 110 °C. Then 0.92 g (6 mmol) of fumaryl chloride was added slowly. The mixture was heated at 110 °C for 2 and 1 h at 180 °C. A red solution was obtained after cooling to room temperature. The solvent was removed in vacuo and the residue washed with diethyl ether (2 × 15 mL) and methanol (3 × 10 mL) to afford **g** as a light orange powder. Yield: 0.90 g; 41%. ^{1}H NMR (499.8 MHz, CD_2Cl_2): δ 7.45 (d, $J = 7.4$ Hz, 2H, CH_{ar}), 7.56 (s, 2H, CH═CH), 7.58−7.66 (m, 6H, CH_{ar}), 7.89 (d, $J = 8.3$ Hz, 2H, CH_{ar}), 8.00 (d, $J = 9.6$ Hz, 4H, CH_{ar}). ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ 118.56 (CH), 121.51 (CH), 125.99 (CH), 127.02, 127.08 (CH), 127.30 (CH), 127.36 (CH), 128.69 (CH), 134.99 (CH═CH), 135.27, 146.83, 163.89 (C═O). MS (FAB): *m/z* 369.1122 [MH$^+$]. Anal. Calcd for $C_{24}H_{16}O_4$: C, 78.25; H, 4.38. Found: C, 78.25; H, 4.45.

Synthesis of Di-2-naphthyl Fumarate (h). A 3.46 g portion (24 mmol) of 2-naphthol was heated in 2.0 mL of toluene for 30 min at 110 °C. Then 0.92 g (6 mmol) of fumaryl chloride was added slowly. The solution was first heated for 2 h at 110 °C and then heated for 1 h at 180 °C. After the mixture was cooled to room temperature, a red solid was obtained which was washed with diethyl ether (2 × 15 mL) and methanol (3 × 10 mL), yielding product **h** as a pink powder. Yield: 0.55 g; 25%.^{1}H NMR (499.8 MHz, CD_2Cl_2): δ 7.32 (s, 2H, CH═CH), 7.33 (d, $J = 8.8$ Hz, 2H, CH_{ar}), 7.49−7.56 (m, 4H, CH_{ar}), 7.68 (s, 2H, CH_{ar}), 7.93−7.85 (m, 6H, CH_{ar}). ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ 118.96 (CH), 121.26 (CH), 126.63 (CH), 127.41 (CH), 128.24 (CH), 128.37 (CH), 130.13 (CH), 132.23, 134.27, 134.98 (CH═CH), 148.63, 163.95 (C═O). MS (FAB): *m/z* 369.1122 [MH$^+$]. Anal. Calcd for $C_{24}H_{16}O_4$: C, 78.25; H, 4.38. Found: C, 78.34; H, 4.43.

Synthesis of [Pt(η^2-dimethyl fumarate)(η^2-norbornene)$_2$] (2a). A 77.2 mg portion (162 μmol) of [Pt(nbe)$_3$] and 23.2 mg (161 μmol) of dimethyl fumarate were dissolved in 3 mL of THF. After the mixture was stirred at room temperature for 1 h, the solution was evaporated to dryness in vacuo, yielding product **2a** as a white powder. Yield: 82.0 mg; 96.0%. ^{1}H NMR (300.1 MHz, C_6D_6): δ −0.05 (d, $J = 8.9$ Hz, 2H, CH_2), 0.22 (d, $J = 8.8$ Hz, 2H, CH_2), 1.07 (d, $J = 9.1$ Hz, 4H, CH_2), 1.42 (d, $J = 9.1$ Hz, 4H, CH_2), 2.63 (s, 2H, CH), 2.95 (s, 2H, CH), 3.38 (s, 6H, CH_3), 3.44 (d, $J = 4.8$ Hz, $J_{\text{Pt−H}} = 64.0$ Hz, 2H, CH═CH nbe), 3.91 (d, $J = 4.8$ Hz, $J_{\text{Pt−H}} = 64.8$ Hz, 2H, CH═CH nbe), 4.31 (s, $J_{\text{Pt−H}} = 61.3$ Hz, 2H, CH═CH dmfu). ^{13}C NMR (75.5 MHz, C_6D_6): δ 27.28 ($J_{\text{Pt−C}} = 38.7$ Hz, CH_2), 40.18 ($J_{\text{Pt−C}} = 38.7$ Hz, CH_2), 42.19 (CH), 43.58 ($J_{\text{Pt−C}} = 104.9$ Hz, CH), 50.38 ($J_{\text{Pt−C}} = 184.1$ Hz, CH═CH), 50.74 (CH_3O), 78.53 ($J_{\text{Pt−C}} = 161.23$ Hz, CH═CH), 80.48 ($J_{\text{Pt−C}} = 162.9$ Hz, CH═CH), 171.15 ($J_{\text{Pt−C}} = 38.0$ Hz, C═O). Anal. Calcd for $C_{20}H_{28}O_4$Pt: C, 45.54; H, 5.35. Found: C, 45.64; H, 5.31.

Synthesis of [Pt(η^2-dimethyl maleate)(η^2-norbornene)$_2$] (2b). An 86.1 mg portion (180 μmol) of [Pt(nbe)$_3$] and 26.0 mg (180 μmol) of dimethyl maleate were dissolved in 2.5 mL of THF. After the mixture was stirred at room temperature for 1 h, the solution was evaporated to dryness in vacuo. The white sticky solid was recrystallized from 4.0 mL of pentane at −80 °C, yielding product **2b** as a white solid. Yield: 87.4 mg; 92.0%. ^{1}H NMR (300.1 MHz, C_6D_6): δ −0.07 (d, $J = 9.0$ Hz, 2H, CH_2), 0.15 (d, $J = 8.8$ Hz, 2H, CH_2), 1.05 (d, $J = 7.8$ Hz, 4H, CH_2), 1.41 (d, $J = 8.0$ Hz, 4H, CH_2), 2.71 (s, 4H, CH), 3.50 (s, 6H, CH_3), 3.64 (s, $J_{\text{Pt−H}} = 64.8$ Hz, 2H, CH═CH dmma), 3.83 (s, $J_{\text{Pt−H}} = 63.2$ Hz, 2H, CH═CH nbe). ^{13}C NMR (75.5 MHz, C_6D_6): δ 27.45 ($J_{\text{Pt−C}} = 40.3$ Hz, CH_2), 40.06 ($J_{\text{Pt−C}} = 41.9$ Hz, CH_2), 42.98 ($J_{\text{Pt−C}} = 104.9$ Hz, CH), 48.33 ($J_{\text{Pt−C}} = 212.9$ Hz, CH═CH), 51.10 (CH_3O), 79.50 ($J_{\text{Pt−C}} = 154.8$ Hz, CH═CH), 170.42 ($J_{\text{Pt−C}} = 37.1$ Hz, C═O). Anal. Calcd for $C_{20}H_{28}O_4$Pt: C, 45.54; H, 5.35. Found: C, 45.61; H, 5.30.

Synthesis of [Pt(η^2-maleic anhydride)(η^2-norbornene)$_2$] (2c). A 98.8 mg portion (207 μmol) of [Pt(nbe)$_3$] and 20.0 mg (204 μmol) of maleic anhydride were dissolved in 3 mL of THF. After the mixture was stirred at room temperature for 1 h, the solution was evaporated to dryness in vacuo, yielding product **2c** as a white powder. Colorless crystals of **2c** were obtained by cooling a saturated solution in ether/pentane (1:1) at −20 °C. Yield: 98.1 mg; 98%. ^{1}H NMR (300.1 MHz, C_6D_6): δ −0.27 (d, $J = 9.3$ Hz, 2H, CH_2), −0.21 (d, $J = 9.4$ Hz, 2H, CH_2), 0.86 (d, $J = 8.0$ Hz, 4H, CH_2), 1.31 (d, $J = 9.3$ Hz, 4H, CH_2), 2.65 (s, 4H, CH), 3.55 (s, $J_{\text{Pt−H}} = 64.4$ Hz, 2H, CH═CH nbe), 3.67 (s, $J_{\text{Pt−H}} = 63.3$ Hz, 2H, CH═CH ma). ^{13}C NMR (75.5 MHz, C_6D_6): δ 26.78 ($J_{\text{Pt−C}} = 42.9$ Hz, CH_2), 40.70 ($J_{\text{Pt−C}} = 37.3$ Hz, CH_2), 42.64 (CH), 46.46 ($J_{\text{Pt−C}} = 179.7$ Hz, CH═CH), 169.01 ($J_{\text{Pt−C}} = 41.4$ Hz, C═O). Anal. Calcd for $C_{18}H_{22}O_3$Pt: C, 44.91; H, 4.61. Found: C, 45.06; H, 4.68.

Synthesis of [Pt(η^2-di-*sec*-butyl fumarate)(η^2-norbornene)$_2$] (2d). A 78.9 mg portion (165 μmol) of [Pt(nbe)$_3$] and 37.7 mg (165 μmol) of di-*sec*-butyl fumarate were dissolved in 1.5 mL of THF. The solvent was evaporated after stirring at room temperature for 20 min. The white sticky solid was recrystallized from 2.0 mL of dry pentane at −80 °C, yielding product **2d** as a white solid. Yield: 100 mg; 96%. ^{1}H NMR (499.8 MHz, C_6D_6): δ −0.04 (d, $J = 8.8$ Hz, 2H, CH_2), 0.32 (d, $J = 7.7$ Hz, 2H, CH_2), 0.63 (t, $J = 7.7$ Hz, 3H, CH_3), 0.74 (t, $J = 7.7$ Hz, 3H, CH_3), 0.93 (d, $J = 6.3$ Hz, 2H, CH_2), 1.04 (d, $J = 6.4$ Hz, 2H, CH_2), 1.08 (d, $J = 9.1$ Hz, 4H, CH_2), 1.42 (d, $J = 9.0$ Hz, 4H, CH_2), 1.52−1.17 (m, 4H, CH_2), 2.67 (s, 2H, CH), 3.04 (s, 2H, CH), 3.67 (s, $J_{\text{Pt−H}} = 63.5$ Hz, 2H, CH═CH nbe), 3.83 (s, $J_{\text{Pt−H}} = 61.5$ Hz, 2H, CH═CH nbe), 4.34 (s, $J_{\text{Pt−H}} = 60.8$ Hz, 2H, CH═CH di-*sec*-butyl fumarate), 4.90 (m, 2H, CH). ^{13}C NMR (125.7 MHz, C_6D_6): δ 9.70 (CH_3), 9.91 (CH_3), 19.53 (CH_3), 19.93 (CH_3), 27.47 ($J_{\text{Pt−C}} = 43.5$ Hz, CH_2), 29.12 (CH_2), 29.29 (CH_2), 40.25 ($J_{\text{Pt−C}} = 38.7$ Hz, CH_2), 42.77 (CH), 43.65 (CH), 51.36 ($J_{\text{Pt−C}} = 174.2$ Hz, CH═CH), 51.66 ($J_{\text{Pt−C}} = 177.6$ Hz, CH═CH), 71.21 (CH), 71.40 (CH), 79.82 ($J_{\text{Pt−C}} = 170.5$ Hz, CH═CH), 170.55 ($J_{\text{Pt−C}} = 41.1$ Hz, C═O). Anal. Calcd for $C_{26}H_{40}O_4$Pt: C, 51.05; H, 6.59. Found: C, 51.18; H, 6.51.

Synthesis of [Pt(η^2-fumaric acid)(η^2-norbornene)$_2$] (2e). A 335.4 mg portion (702.3 μmol) of [Pt(nbe)$_3$] and 79.5 mg (699.6 μmol) of fumaric acid were dissolved in 7.5 mL of THF. After it was stirred at room temperature for 30 min, the mixture was evaporated. The white solid was washed with 2 × 10 mL of hexane and 5 mL of pentane and dried in vacuo, yielding the product **2e** as a white solid. Yield: 346.9 mg; 99%. ^{1}H NMR (499.8 MHz, MeOH-d_4): δ 0.20 (s, $J = 8.8$ Hz, 4H, CH_2), 1.31 (d, $J = 7.8$ Hz, 4H, CH_2), 1.73 (d, $J = 7.8$ Hz, 4H, CH_2), 2.91 (s, 2H, CH), 3.18 (s, 2H, CH), 3.66 (d, $J = 5.2$ Hz, $J_{\text{Pt−H}} = 62.8$ Hz, 2H, CH═CH nbe), 3.74 (s, $J_{\text{Pt−H}} = 61.35$ Hz, 2H, CH═CH fumaric acid), 4.27 (d, $J = 5.1$ Hz, $J_{\text{Pt−H}} = 63.9$ Hz, 2H, CH═CH nbe). ^{13}C NMR (125.7 MHz, MeOH-d_4): δ 27.97 ($J_{\text{Pt−C}} = 42.8$ Hz, CH_2), 41.10 ($J_{\text{Pt−C}} = 38.5$ Hz, CH_2), 43.06 (CH), 44.89 (CH), 51.08 ($J_{\text{Pt−C}} = 185.7$ Hz, CH═CH), 80.11 ($J_{\text{Pt−C}} = 155.86$ Hz, CH═CH), 83.05 ($J_{\text{Pt−C}} = 154.77$ Hz, CH═CH), 176.08 ($J_{\text{Pt−C}} = 38.0$ Hz, C═O). Anal. Calcd for $C_{18}H_{24}O_4$Pt: C, 43.29; H, 4.84. Found: C, 43.21; H, 4.79.

Synthesis of [Pt(η^2-diphenyl fumarate)(η^2-norbornene)$_2$] (2f). A 144.4 mg portion (300 μmol) of [Pt(nbe)$_3$] and 81.1 mg (300 μmol) of diphenyl fumarate were dissolved in 10 mL of diethyl ether. After it was stirred at room temperature for 150 min, the mixture was filtered over Celite and the Celite was flushed with 10 mL of diethyl ether. The solvent was evaporated to about 5 mL, and product **2f** was

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obtained as colorless crystals after cooling the solution to −20 °C. Yield: 140.7 mg; 72%. ^{1}H NMR (499.8 MHz, C_6D_6): δ −0.03 (d, J = 9.0 Hz, 2H, CH_2), 0.26 (d, J = 8.8 Hz, 2H, CH_2), 1.08 (d, J = 9.1 Hz, 4H, CH_2), 1.30 (d, J = 9.1 Hz, 4H, CH_2), 2.73 (s, 2H, CH), 3.02 (s, 2H, CH), 3.70 (d, J = 4.6 Hz, J_{Pt-H} = 64.2 Hz, 2H, CH=CH nbe), 3.99 (d, J = 4.8 Hz, J_{Pt-H} = 62.5 Hz, 2H, CH=CH nbe), 4.55 (s, J_{Pt-H} = 61.0 Hz, 2H, CH=CH diphenyl fumarate), 6.90 (t, J = 7.3 Hz, 2H, CH_{para}), 7.07 (t, J = 7.6 Hz, 4H, CH_{meta}), 7.15 (d, J = 8.2 Hz, 4H, CH_{ortho}). ^{13}C NMR (125.7 MHz, C_6D_6): δ 27.52 (J_{Pt-C} = 41.94 Hz, CH_2), 40.85 (J_{Pt-C} = 38.4 Hz, CH_2), 42.90 (CH), 44.17 (CH), 49.98 (J_{Pt-C} = 185.85 Hz, CH=CH), 80.96 (J_{Pt-C} = 156.50 Hz, CH=CH), 81.56 (J_{Pt-C} = 161.22 Hz, CH=CH), 122.48 (C_{ortho}), 125.80 (C_{para}), 129.80 (C_{meta}), 152.17 (C_{ipso}), 169.63 (J_{Pt-C} = 42.4 Hz, C=O). Anal. Calcd for $C_{30}H_{32}O_4Pt$: C, 55.29; H, 4.95. Found: C, 55.39; H, 4.98.

Synthesis of [Pt(η^2-di-1-naphthyl fumarate)(η^2-norbornene)$_2$] (2g). A 175.0 mg portion (370 μmol) of [Pt(nbe)$_3$] and 136.0 mg (370 μmol) of di-1-naphthyl fumarate were dissolved in 4 mL of THF, and the mixture was stirred at room temperature for 90 min. The solvent was evaporated, and the residue was washed with 10 mL of hexane and with 2 × 5 mL of pentane and dried in vacuo, yielding product **2g** as a light brown solid. Yield: 233.7 mg; 84%. ^{1}H NMR (499.8 MHz, CD_2Cl_2): δ 0.24 (d, J = 8.7 Hz, 2H, CH_2), 0.36 (d, J = 7.6 Hz, 2H, CH_2), 1.35 (d, J = 9.0 Hz, 4H, CH_2), 1.76 (d, J = 9.0 Hz, 4H, CH_2), 3.14 (s, 2H, CH), 3.30 (s, 2H, CH), 4.12 (d, J = 5.0 Hz, J_{Pt-H} = 64.5 Hz, 2H, CH=CH nbe), 4.42 (d, J = 5.0 Hz, J_{Pt-H} = 61.5 Hz, 2H, CH=CH nbe), 4.51 (s, J_{Pt-H} = 60.7 Hz, 2H, CH=CH di-1-naphthyl fumarate), 7.26 (d, J = 8.0 Hz, 2H, CH_{ar}), 7.49−7.57 (m, 6H, CH_{ar}), 7.78 (d, J = 8.0 Hz, 2H, CH_{ar}), 7.87 (d, J = 8.0 Hz, 2H, CH_{ar}), 7.92 (d, J = 8.4 Hz, 2H, CH_{ar}). ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ 27.49 (J_{Pt-C} = 42.24 Hz, CH_2), 27.56 (J_{Pt-C} = 46.88 Hz, CH_2), 40.88 (J_{Pt-C} = 36.49 Hz, CH_2), 43.49 (CH), 44.24 (CH), 48.69 (J_{Pt-C} = 187.60 Hz, CH=CH), 82.62 (J_{Pt-C} = 164.25 Hz, CH=CH), 83.59 (J_{Pt-C} = 147.00 Hz, CH=CH), 118.69 (CH), 121.92 (CH), 125.96 (CH), 126.03 (CH), 126.72 (CH), 126.96 (CH), 127.62, 128.47 (CH), 135.16, 147.48, 170.28 (C=O). Anal. Calcd for $C_{38}H_{36}O_4Pt$: C, 60.71; H, 4.83. Found: C, 60.80; H, 4.76.

Synthesis of [Pt(η^2-di-2-naphthyl fumarate)(η^2-norbornene)$_2$] (2h). A 175.0 mg portion (370 μmol) of [Pt(nbe)$_3$] and 136.0 mg (370 μmol) of di-2-naphthyl fumarate were dissolved in 4 mL of THF. After the mixture was stirred at room temperature for 90 min, the solvent was evaporated, resulting in a white solid which was washed with 10 mL of hexane and 2 × 5 mL of pentane. The desired reaction product **2h** was obtained as a white solid. Yield: 219.7 mg; 79%. ^{1}H NMR (499.8 MHz, CD_2Cl_2): δ 0.41−0.34 (m, 4H, CH_2), 1.19 (d, J = 9.0 Hz, 4H, CH_2), 1.85 (d, J = 9.0 Hz, 4H, CH_2), 3.03 (s, 2H, CH), 3.35 (s, 2H, CH), 3.71 (d, J = 4.6 Hz, J_{Pt-H} = 64.2 Hz, 2H, CH=CH nbe), 3.99 (d, J = 5.0 Hz, J_{Pt-H} = 62.1 Hz, 2H, CH=CH nbe), 4.28 (s, J_{Pt-H} = 61.6 Hz, 2H, CH=CH di-2-naphthyl fumarate), 4.55 (d, J = 5.0 Hz, J_{Pt-H} = 62.2 Hz, 2H, CH=CH nbe), 7.28 (d, J = 9.4 Hz, 2H, CH_{ar}), 7.50−7.56 (m, 4H, CH_{ar}), 7.58 (s, 2H, CH_{ar}), 7.85 (d, J = 8.0 Hz, 2H, CH_{ar}), 7.90 (d, J = 8.2 Hz, 4H, CH_{ar}). ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ 27.44 (J_{Pt-C} = 42.86 Hz, CH_2), 40.93 (J_{Pt-C} = 36.35 Hz, CH_2), 42.96 (CH), 44.30 (CH), 48.83 (J_{Pt-C} = 191.69 Hz, CH=CH), 81.66 (J_{Pt-C} = 176.22 Hz, CH=CH), 82.43 (J_{Pt-C} = 164.28 Hz, CH=CH), 119.03 (CH), 122.10 (CH), 126.15 (CH), 127.10 (CH), 128.06 (CH), 128.26 (CH), 129.68 (CH), 131.84, 134.32, 149.34, 170.63 (J_{Pt-C} = 39.44 Hz, C=O). Anal. Calcd for $C_{38}H_{36}O_4Pt$: C, 60.71; H, 4.83. Found: C, 60.84; H, 4.76.

Synthesis of [Pt(η^2-maleic anhydride)(η^2-norbornene)(σ-*N*-pyridine)] (3). A 116.8 mg portion (244 μmol) of [Pt(nbe)$_3$] and 24.0 mg (245 μmol) of maleic anhydride were dissolved in 5 mL diethyl ether, and the solution was stirred at room temperature for 30 min, yielding a white suspension. Then, 48.9 mg (618 μmol) of pyridine was added and the solution became clear. After 2 min, a white solid precipitated and the solvent was evaporated after stirring for 5 min. The solid was dried in vacuo, yielding product **3** as a white powder. Yield: 107.0 mg; 94.0%. ^{1}H NMR (499.8 MHz, CD_2Cl_2): δ 0.43 (d, J = 8.0 Hz, 2H, CH_2), 1.16 (d, J = 8.0 Hz, 4H, CH_2), 2.75 (s, 1H, CH), 2.80 (s, 1H, CH), 3.50 (d, J = 4.3 Hz, J_{Pt-H} = 53.8 Hz, 1H, CH=CH ma), 3.68 (d, J = 5.1 Hz, J_{Pt-H} = 78.1 Hz, 1H, CH=CH nbe), 3.77 (d, J = 5.1 Hz, J_{Pt-H} = 78.4 Hz, 1H, CH=CH nbe), 4.45 (d, J = 4.3 Hz, J_{Pt-H} = 78.3 Hz, 1H, CH=CH ma), 7.53 (t, J = 8.0 Hz, 2H, CH_{meta}), 7.92 (d, J = 8.0 Hz, 1H, CH_{para}), 8.66 (d, J = 8.0 Hz, J_{Pt-H} = 36.5 Hz, 2H, CH_{ortho}). ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ 27.30 (J_{Pt-C} = 55.64 Hz, CH_2), 38.01 (J_{Pt-C} = 257.14 Hz, CH=CH), 41.90 (J_{Pt-C} = 19.08 Hz, CH), 42.11 (J_{Pt-C} = 40.89 Hz, CH_2), 42.97 (J_{Pt-C} = 17.04 Hz, CH), 45.88 (J_{Pt-C} = 171.95 Hz, CH=CH), 75.05 (J_{Pt-C} = 229.29 Hz, CH=CH), 77.29 (J_{Pt-C} = 230.64 Hz, CH=CH), 126.71 (J_{Pt-C} = 36.16 Hz, C_{ortho}), 138.68 (J_{Pt-C} = 11.49 Hz, C_{para}), 153.52 (J_{Pt-C} = 12.63 Hz, C_{meta}), 171.00 (C=O), 172.28 (C=O). MS (FAB): *m*/*z* 467.0936 [MH$^+$]. Anal. Calcd for $C_{16}H_{17}NO_3Pt$: C, 41.20; H, 3.67; N, 3.00. Found: C, 41.21; H, 3.56; N, 2.96.

Synthesis of [Pt(σ-*N*-pyridine)$_2$(η^2-tetracyanoethylene)] (4). A mixture of 181.5 mg (380 μmol) of [Pt(nbe)$_3$], 48.7 mg (380 μmol) of tetracyanoethylene, and 150.3 mg (1.90 mmol) of pyridine in 5 mL of THF was stirred at room temperature for 30 min, yielding an orange solution. The solvent was evaporated and the solid was dried in vacuo, yielding product **4** as a dark orange powder. Yield: 164.6 mg; 90.0%. ^{1}H NMR (499.8 MHz, CD_2Cl_2): δ 7.53 (t, J = 7.9 Hz, 2H, CH_{meta}), 7.97 (d, J = 7.9 Hz, 1H, CH_{para}), 8.58 (d, J = 8.0 Hz, J_{Pt-H} = 33.7 Hz, 2H, CH_{ortho}). ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ 115.59 (J_{Pt-C} = 77.49 Hz, CN), 127.71 (J_{Pt-C} = 34.86 Hz, C_{ortho}), 139.87 (C_{para}), 152.31 (C_{meta}). MS (FAB): *m*/*z* 482.3835 [MH$^+$]. Anal. Calcd for $C_{16}H_{10}N_6Pt$: C, 39.92; H, 2.09; N, 17.46. Found: C, 40.02; H, 2.13; N, 17.53.

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 0.022 mmol of the appropriate platinum complex and, in the case of in situ prepared catalysts, 1 equiv of a ligand. The Schlenk tube was evacuated and filled with nitrogen three times. Then, 20 mL of toluene, 6.16 mmol of styrene, 3.08 mmol of *n*-decane, and 6.16 mmol of triethylsilane were added in this order in quick succession from syringes through the septum. The tube was immediately immersed in an oil bath, which was kept at 30 °C. Samples were taken periodically for GC analysis. Products were characterized using NMR and GC-MS. The NMR spectra of the products have already been reported in the literature.[35]

X-ray Crystal Structure Analyses. Pertinent data for the structure determinations are given in Table 1. Data were collected at 150 K on a Nonius KappaCCD diffractometer on a rotating anode (graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å). The unit-cell parameters were checked for the presence of higher lattice symmetry.[36] Intensity data were corrected for absorption using either an algorithm based on multiple measurements of symmetry-related reflections (complex **2c**) or an analytical algorithm based on crystal shape (complex **2f**). Both algorithms are incorporated in PLATON.[37] The structure of **2c** was solved with automated Patterson and subsequent difference Fourier methods using DIRDIF99.[38] The structure of **2f** was solved with direct methods using SHELSX86.[39] Both structures were refined on

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F^2 using SHELXL-97;[40] no observance criterion was applied during refinement. The hydrogen atoms directly bonded to coordinated alkene moieties were located on difference Fourier maps, and their coordinates were refined. All other hydrogen atoms were included on calculated positions riding on their carrier atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters. The isotropic displacement parameters of the hydrogen atoms were set to 1.2 times the value of the equivalent isotropic displacement parameter of their carrier atom. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 41. Validation, geometrical calculations, and illustrations were performed with PLATON.[37]

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Supporting Information Available: Further details on the crystal structures of complexes **2c** and **2f**, including atomic coordinates, displacement parameters, bond lengths and bond angles, as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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