Efficient Homogeneous Hydrosilylation of Olefins by Use of Complexes of Pt^0 with Selected Electron-Deficient Olefins as Ligands

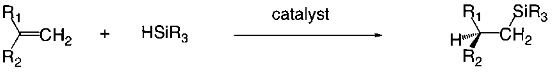
Pascal Steffanut, John A. Osborn,* Andre DeCian, and Jean Fisher*

Abstract: A family of complexes of general formula $[Pt(\eta^2\text{-}Ol_E)\{(\eta^4\text{-}CH_2{=}CHSiMe_2)_2O\}]$, where Ol_E is a di-, tri- or tetrasubstituted electron-deficient olefin such as fumaronitrile, diethylfumarate, tetracyanoethylene, ethylenetetracarboxylate, a naphthoquinone or dihydronaphthoquinone, were synthesised from the Karstedt catalyst solution containing $[Pt_2(CH_2{=}CHSiMe_2)_2O)_3]$ (**1**). The structures of these complexes were examined by ^1H, ^{13}C and ^{195}Pt NMR spectroscopy. The X-ray crystallographic structure of $[Pt(\eta^2\text{-}MeNQ)\{(\eta^4\text{-}CH_2{=}CHSiMe_2)_2O\}]$ (MeNQ = methylnaphthoquinone) was determined; the MeNQ ligand is bound to Pt by a η^2-olefin interaction. Certain of these complexes, particularly the naphthoquinone and dihydronaphthoquinone derivatives, were found to catalyse very efficiently the hydrosilylation of a variety of olefins. Tests in the presence of Hg, dibenzo[*a,e*]cyclooctatetraene or molecular oxygen indicated that the catalytic process was homogeneous in nature. The addition of excess Ol_E to the catalyst solutions greatly extended the lifetime and productivity of these catalysts, which were more efficient both in rate and overall product yield than the original Karstedt catalyst solution. Spectroscopic studies lead us to propose that the stabilising ligand Ol_E remains bound to Pt throughout the catalytic cycle; this results in increased stability and high catalytic activity.

Keywords: alkene complexes · heterogeneous catalysis · homogeneous catalysis · hydrosilylations · naphthoquinones · platinum

Introduction

Hydrosilylation of olefins is one of the most important reactions in silicon chemistry (Scheme 1).[1] Among the numerous catalysts for this reaction, the most efficient are those which involve platinum complexes, particularly the original[2] Speier catalyst, H_2PtCl_6, and the second-generation[3] Karstedt catalyst, which are presently those largely used in commercial processes. However, the detailed mechanism of the catalytic process using these Pt-based systems remains uncertain since both homogeneous and heterogeneous catalytic behaviour have been invoked. Indeed, the Pt precursors are intrinsically unstable under hydrosilylation conditions and metal-containing particles are readily formed in solution. Such observations, inter alia, have led Lewis and co-workers to suggest that colloids may be responsible for the catalytic activity.[4]



Scheme 1. The catalytic hydrosilylation of olefins.

We report here the synthesis of a family of molecular platinum(0) compounds for the hydrosilylation of olefins and studies of their catalytic activity. These catalysts are more active and more stable than the classical Karstedt catalyst systems under identical conditions and evidence is presented indicating that their catalytic action is homogeneous in nature.

Initial observations: The Karstedt catalyst solution is formed by the reaction of the diene $(CH_2{=}CHSiMe_2)_2O$ (hereafter dvtms) with H_2PtCl_6. The active catalyst precursor is probably the Pt^0 complex, $[Pt_2(CH_2{=}CHSiMe_2)_2O)_3]$ (**1**), which is preponderant in such solutions and has been characterised by an X-ray structural determination (Figure 1).[5] We note that the Karstedt catalyst solution normally used also contains an excess of dvtms.

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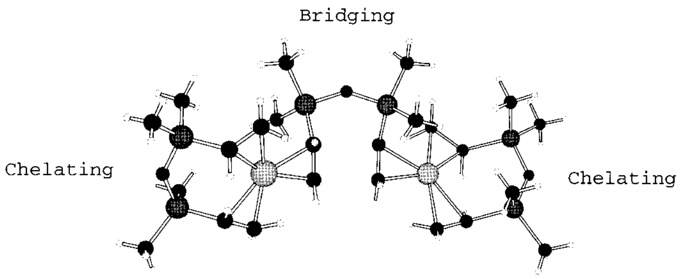

Figure 1. Chem3D representation of $[Pt_2(dvtms)_3]$.

We initially studied the Karstedt catalyst (6×10^{-6} mol) using the substrates allyl alcohol (3×10^{-3} mol) and Et_3SiH (3×10^{-3} mol) in hexane (30 mL) at 72 °C. It was observed that if the silane was added dropwise to a prepared catalyst/olefin solution, the rate of addition strongly influenced the overall yield of hydrosilylation product. Hence if the rate of dropwise addition of Et_3SiH was increased from 1.5×10^{-4} mol min^{-1} (i.e., added over 20 min) to 3×10^{-4} mol min^{-1} (added over 10 min), the final yield of product decreased from ca. 37 % to 20 %, no further reaction taking place after one hour. However if the initial olefin concentration was doubled (6×10^{-3} mol), the corresponding yields were 74 % and 62 % respectively. Similar effects were observed using styrene as substrate. Further, it was noticed that the more rapidly the silane was added, the earlier a black precipitate appeared in the solution. These observations indicated that the catalyst appeared to be less stable as the concentration of the silane increased but this effect could be compensated in part by the presence of higher concentrations of olefin substrate.

Experiments were then carried out in which the silane was added initially to the catalyst solution and the olefin added after a certain delay, *t*. Under the same standard conditions described above, a) when $t = 5$ min, the initial rate was ca. 12 equiv min^{-1} with a total yield of 48 %, b) with $t = 10$ min the rate was 5 equiv min^{-1} and the yield 40%, and c) with $t = 30$ min. the values were ca. 3.5 equiv min^{-1} and 16 %. Again we observed that the greater the value of *t*, the earlier the deposition of black material took place. If colloid particles of an optimum size were necessary for high activity,[4] then it might be anticipated that a correlation of the highest activity would occur with some optimum value of the contact time *t*, where $t > 0$. In fact we see that the initial rate of hydrosilylation always decreased with an increase in *t* and the colloids formed appeared to be much less active (if active at all) than the initial homogeneous solutions. We attempted to stabilise the colloids formed using three micelle-forming amphiphiles (sodium dodecylsulfonate (SDS), *N*-cetyl-*N,N,N*-trimethylammonium bromide and polyethyleneglycol hexadecyl ether), but the catalytic activity was either unaffected (SDS) or diminished.

We therefore redirected our attention towards the stabilisation of the molecular Pt species in solution. It is well known that phosphine complexes,[6] such as $[Pt(SiR_3)(\mu\text{-}H)(R_3P)]_2$, $[Pt(PR_3)\{(\eta^4\text{-}CH_2{=}CHSiMe_2)_2O\}]$, are less active than the Karstedt catalyst but are stable under hydrosilylation conditions at ambient temperatures. We found that when the complexes $[Pt(PR_3)\{(\eta^4\text{-}CH_2{=}CHSiMe_2)_2O\}]$ (with R = alkyl, aryl, or substituted aryl) were used as catalysts for the reaction of $HSiEt_3$ with $Et_3Si(CH{=}CH_2)$, after an induction period of ca. 1 h, the reactivity of the catalysts at 30 °C decreased in the order: R = *p*-fluorophenyl > phenyl > *m*-tolyl > cyclohexyl > *tert*-butyl. Although this trend may be a result of several factors, the catalysts with the more electron-attracting phosphines were the most efficient. We surmised that with even stronger π-acid ligands, catalysts possessing greater activity might be obtained, and therefore we synthesised Pt^0 complexes of electron-deficient olefins with this in mind.

Results and Discussion

Synthesis of $[Pt(\eta^2\text{-}Ol_E)\{(\eta^4\text{-}CH_2{=}CHSiMe_2)_2O\}]$ complexes (Ol_E = electron-deficient olefin): It had been previously reported[5] that $[Pt_2\{((CH_2{=}CH)SiMe_2)_2O\}_3]$ (**1**) reacts with maleic anhydride to form $[Pt(\eta^4\text{-dvtms})(\eta^2\text{-maleic anhydride})]$. Spectroscopic data indicated that the complex possessed a monomeric structure similar to that found for $[Pt(\eta^4\text{-1,5 hexadiene})(\eta^2\text{-maleic anhydride})]$, where an X-ray determination showed all three olefin groups coordinated to Pt in a nearly coplanar fashion.[7] The complexes $[Pt(\eta^2\text{-}C_2H_4)_2(\eta^2\text{-}C_2F_4)]$[8] and the recently described dimethylfumarate and dimethylmaleate[9] complexes have analogous structures. Interestingly, the fumarate and maleate complexes of Pt^0 were synthesised in studies with the objective of inhibiting the Pt-catalysed hydrosilylation process. We shall discuss this point later.

Using an adaptation of the reported procedure,[5] we synthesised complexes of the type $[Pt(\eta^2\text{-}Ol_E)\{(\eta^4\text{-}CH_2{=}CHSiMe_2)_2O\}]$ (Figure 2) by replacement of the bridging siloxane of $[Pt_2(CH_2{=}CHSiMe_2)_2O)_3]$ by Ol_E. The elec-

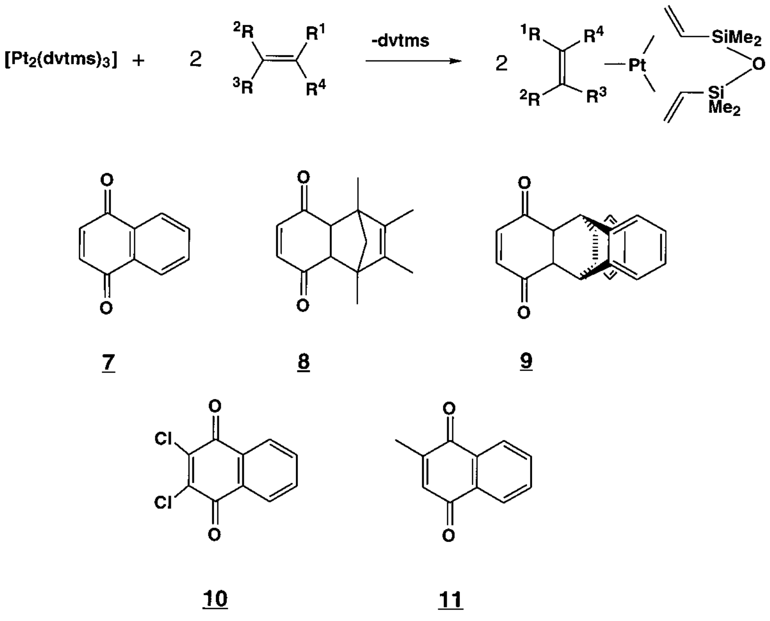

Figure 2. Substitution of $[Pt_2(dvtms)_3]$ by electrophilic olefins. The naphthoquinone ligands used and the numbers of the corresponding complexes **7**–**11** are also shown.

tron-withdrawing substituents, E, on the olefins were aryl, CN, COR or COOR. Several naphthoquinone and dihydronaphthoquinone complexes were also prepared, which we label collectively as NQ′ complexes.

In general, slightly less than one equivalent of $\mathrm{Ol_E}$ was added to a toluene or hexane solution containing **1** at 20 °C to yield the desired products as colourless (or yellow for the NQ′ complexes) microcrystalline solids. We were unable to isolate complexes of the monosubstituted olefins styrene, vinyl acetate, ethylacrylate or allyl alcohol although the styrene derivative has previously been detected in solution by ^{195}Pt NMR.[10]

The complexes $[\mathrm{Pt}(\eta^2\text{-}\mathrm{Ol_E})\{(\eta^4\text{-}\mathrm{CH_2{=}CHSiMe_2})_2\mathrm{O}\}]$ **2–11** were obtained with *trans*-disubstituted olefins such as fumaronitrile (**2**), diethylfumarate (**3**) or *trans*-(PhCO)CH=CH-(COPh) (**4**); tetrasubstituted olefins $\mathrm{(EtOOC)_2C{=}C(COOEt)_2}$ (**5**) or $\mathrm{(NC)_2C{=}C(CN)_2}$ (**6**); and the NQ′ type ligands, naphthoquinone (NQ) (**7**); 1,2,3,4-tetramethyl-4*a*,8*a*-dihydro-*endo*-1,4-methylmethanonaphthalene-5,8-dione (TND) (**8**), 9,10-dihydro-9,10-*ortho*-benzenoanthracene-1,4-dione (BAD) (**9**), dichloronaphthoquinone (DCNQ) (**10**) or methylnaphthoquinone (MeNQ) (**11**). In addition the complex $[\mathrm{Pt}(\eta^2\text{-norbornene})_2(\eta^2\text{-(MeNQ)})]$ (**12**) was prepared for comparative purposes. Details can be found in the Experimental Section.

Structures of the $[\mathrm{Pt}(\eta^2\text{-}\mathrm{Ol_E})\{(\eta^4\text{-}\mathrm{CH_2{=}CHSiMe_2})_2\mathrm{O}\}]$ complexes 2–11: Crystals of the methylnaphthoquinone complex **11** were obtained by slow evaporation of a saturated hexane solution and were analysed by X-ray diffraction methods. The structure is monoclinic with a $P2_1/n$ space group.[11] The detailed structure is shown in Figure 3 and the crystallographic data presented in Table 1.

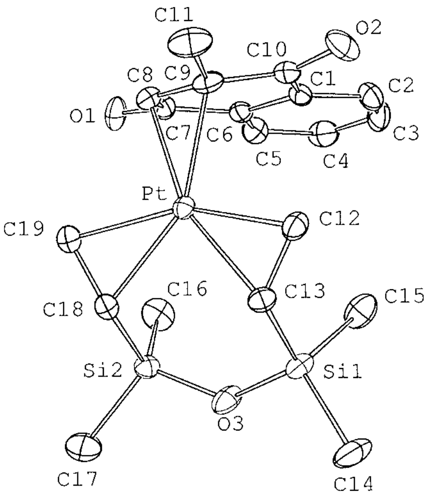

Figure 3. ORTEP plot of one molecule of **11** showing the labelling scheme used. Ellipsoids are scaled to enclose 50 % of the electronic density. Hydrogen atoms are omitted.

Table 1. X-ray crystallographic data for **11**.

formula	$\mathrm{C_{19}H_{26}O_3Si_2Pt\cdot H_2O}$
molecular weight	571.69
crystal system	monoclinic
space group	$P2_1/n$
a (Å)	9.725(3)
b (Å)	10.426(3)
c (Å)	21.348(6)
β (°)	102.76(2)
V (Å^3)	2111(2)
Z	4
colour	yellow
crystal dim (mm)	0.30 · 0.24 · 0.20
ρ_{calcd} (g cm^{-3})	1.80
$F000$	1120
μ (mm^{-1})	6.846
trans. min and max	0.6990/1.0000
T (K)	294
λ (Å)	0.71073
radiation	$\mathrm{Mo_{K\alpha}}$ graphite-monochromated
diffractometer	Enraf–Nonius CAD 4
scan mode	$\theta/2\theta$
hkl limits	0,12/ − 13,13/ − 26,27
θ limits (°)	2.5/26.98
no. of data meas.	9738
no. of data with $I > 3\sigma(I)$	3480
weighting scheme	$4F_o^2/(\sigma^2(F_o^2) + 0.0025\,F_o^4)$
no. of variables	235
R	0.033
R_w	0.042
GOF	1.053
largest peak in final difference (e Å^{-3})	1.312

The MeNQ ligand is bound solely by its olefinic double bond, leading to a closely trigonal coordination arrangement about the Pt atom as found for the other known structures of this type.[7] The electron-deficient olefin group is rotated somewhat out of the trigonal plane by an angle Θ, where Θ in this case is 17.8 ± 1.1 °. In contrast, in the benzoquinone complex [Pt(1,5-cyclooctadiene)(η^4-ditertiobutylbenzoquinone),[8] both olefinic bonds of the quinone were found to be coordinated to $\mathrm{Pt^0}$. The other notable feature of **11** is the chair conformation adopted by the $\mathrm{(CH_2{=}CHSiMe_2)_2O}$ ligand, which leads to the axial–equatorial disposition of the $\mathrm{CH_3}$ groups on the Si atoms. Similar observations have been made for the phosphine derivative, $[\mathrm{Pt}\{(\eta\text{-}\mathrm{CH_2{=}CHSiMe_2})_2\mathrm{O}\}(\mathrm{PR_3})]$.[6] The significant bond distances and angles are presented in Table 2.

Table 2. Selected bond lengths [Å]and angles [°] for **11**.

Pt–C(8)	2.162	Pt–C(12)	2.179	C(12)–C(13)	1.35
Pt–C(9)	2.174	Pt–C(13)	2.204	C(8)-Pt-C(9)	37.6
Pt–C(18)	2.231	C(8)–C(9)	1.40	C(12)-Pt-C(13)	35.9
Pt–C(19)	2.205	C(18)–C(19)	1.37	C(18)-Pt-C(19)	36.0

The ^{1}H NMR data were consistent with the stoichiometry proposed for the complexes. The $\mathrm{CH_3}$ groups on the Si atoms of the $\mathrm{(CH_2{=}CHSiMe_2)_2O}$ ligand ($\delta \approx 1$ to -2) provided further information concerning the structures in solution. If the solid-state structure found for **11** were maintained and nonfluxional in solution, four different $\mathrm{CH_3}$ resonances should be observed for all compounds if $\Theta > 0$. This was observed for complexes **2**, **4**, **5** and **6**. Since the diastereotopic $\mathrm{CH_3}$ groups on each Si atom are not equilibrated, ready dissociation of the olefin groups of the dvtms ligand by a sequential arm-off mechanism can be excluded. This is the only mechanism that

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would allow the Pt^0, which is bound to the *re* face of one diene olefinic bond and to the *si* face of the other, to gain access to the opposite faces of the diolefin. However, any rapid cyclohexane-type conformational changes of the dvtms ligand will not be observed since these would leave the CH_3 groups distinct. In the tetrasubstituted olefin complexes **5** and **6**, the presence of four CH_3 resonances indicated that the olefin must be bound rigidly at a definite angle Θ. Although a similar structure (with $\Theta > 0$) might be anticipated for **2** and **4** in solution, the ^1H NMR data cannot exclude an in-plane coordination and/or a rotational motion of the olefin since no differences in the Si–CH_3 spectrum would be observable. However in **4** the vinylic protons of the *trans*-dibenzoylethylene ligand exhibited a single resonance showing a ^2J(Pt,H) coupling of 60 Hz. Dissociation of the electron-deficient olefin cannot therefore be occurring readily, but facile rotation about the olefin axis is probably taking place.

The ^1H NMR spectrum of the NQ′ complexes **7**–**10** showed only two Si–CH_3 resonances; this can either be consistent with the solid-state structure (with $\Theta > 0$) found for **11** in which rapid olefin rotation was occurring, or a trigonal structure with $\Theta = 0$. As expected for **11**, the four Si–CH_3 resonances were distinct and coupling of ^{195}Pt with both the vinyl proton (^2J(Pt,H) = 48 Hz) and the methyl (^3J(Pt,H) = 30 Hz) on the MeNQ was observed. Again, no rapid dissociation of the MeNQ ligand can be taking place. Finally, other ^{195}Pt and ^{29}Si NMR data are given below the following section on catalysis.

Catalytic studies: The relative efficiencies of these Pt^0 complexes as hydrosilylation catalysts were compared by means of a standard reaction of $Me_3SiCH{=}CH_2$ with Et_3SiH. This reaction can also serve as a model for the cross-linking reaction used in an industrial siloxane polymer synthesis. The catalytic reactions were carried out with 30 mL of deoxygenated hexane solutions of $Me_3SiCH{=}CH_2$ (0.30 mol L^{-1}, 1000 equiv) and Et_3SiH (0.15 mol L^{-1}, 500 equiv) to which 6×10^{-6} mol of the given platinum complex was immediately added and stirred at 30 °C for 2 h. It is noteworthy that, unlike in conventional Karstedt procedures, dropwise addition of the silane was not necessary when using these catalysts. No induction period was observed and clean formation of $Me_3SiCH_2CH_2SiEt_3$ occurred with no by-products being detected by GC or NMR. The catalytic activities of the complexes **2**, **5**, **6** are compared in Figure 4 and the more active NQ′ complexes **7**, **8**, **10** and **11** in Figure 5. All reactions went to completion, the methylnaphthoquinone complex proving to be the most active.

The efficiency of these catalysts was compared with that of the Karstedt system by using equivalent Pt concentrations and measuring the time ($t_{1/2}$) needed to yield 50% of product (Table 3). It can be seen that that the NQ′ catalysts were all more active than the Karstedt catalyst solution and, moreover, no colour changes in the solution occurred during the catalytic process. The Karstedt catalyst solutions, on the other hand, quickly turned dark brown and deposited a black precipitate. We therefore carried out a comparison of the relative activities of the Karstedt catalyst and **11** over two successive runs (Figure 6).

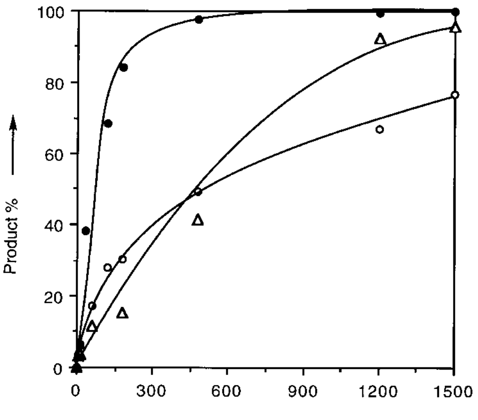

Figure 4. Activities of catalysts **2** (△), **5**(●), and **6**(○) in the hydrosilylation of triethylvinylsilane by triethylsilane at 30 °C with 6×10^{-6} mol of Pt catalyst.

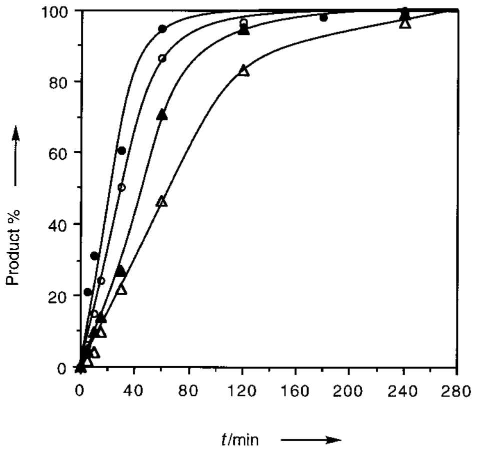

Figure 5. Activities of catalysts **7** (▲), **8** (△), **10** (○) and **11** (●) in the hydrosilylation of triethylvinylsilane by triethylsilane at 30 °C with 6×10^{-6} mol of Pt catalyst.

Table 3. Reactivities of the triolefinic complexes as catalysts in the hydrosilylation of trimethylvinylsilane by triethylsilane with 6×10^{-6} mol of platinum catalyst; $t_{1/2}$ is the time taken for 50% reaction.

Complex	Ligand	$t_{1/2}$ [min]
11	Methylnaphthoquinone (MeNQ)	22
10	Dichloronaphthoquinone (DCNQ)	30
7	Naphthoquinone (NQ)	45
8	TND	60
5	TETCE	60
6	Tetracyanoethylene (TCNE)	480
2	Fumaronitrile (FN)	585
1	Karstedt catalyst	65

After the initial typical run described above, further quantities (1000 equiv) of each of the substrates were added to the catalyst solutions. It is seen that within experimental error both catalysts were slightly less active on the second run but **11** remained approximately four times more active in terms of initial rates. This procedure was then repeated by addition of further aliquots of substrates to both catalyst systems. It was found that under these conditions the Karstedt system became inactive after approximately 2900 turnovers, whereas **11** finally produced about 4200 equivalents of

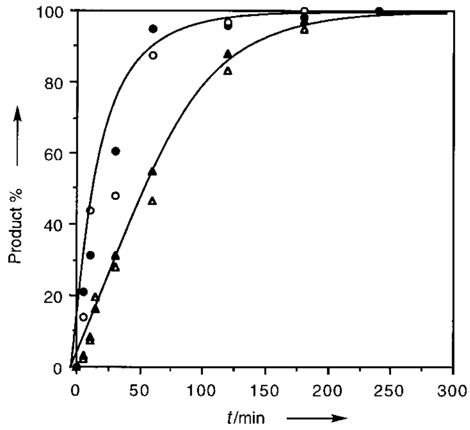

Figure 6. Activities of the first and second runs of the Karstedt catalyst (▲,△) and **11** (○,●) in the hydrosilylation of triethylvinylsilane by triethylsilane at 30 °C with 6×10^{-6} mol of Pt catalyst.

product. However over several runs the decrease in activity of **11** was gradually accompanied by a darkening of the solution with the formation of a black precipitate. We reasoned that the degradation of **11** may be occurring as a result of the loss of the stabilising MeNQ ligand and therefore studied the effect of the presence of excess MeNQ on the catalytic behaviour of **11**. Following the procedure of using successive substrate additions described above, the initial rates observed using 50-fold excess of MeNQ per Pt catalyst **11** were around 800 – 1000 turnovers h^{-1}, which were a little lower than those using **11** alone. However this activity was maintained over a much longer period, thus enabling a total turnover of ca. 26000 equiv per platinum atom. Furthermore, the colour of the catalytic solutions remained a clear yellow throughout. Increasing the additional MeNQ to 100 equiv had no further effect. The Karstedt catalyst solution contains an excess of dvtms which may reduce its efficiency somewhat but will also no doubt serve to stabilise the catalyst. Whatever the overall effect of the presence of excess dvtms on the Karstedt system may be, the productivity of **11** in the presence of excess MeNQ is more than ten times that obtained using the Karstedt catalyst under these conditions.

Tests on the catalytic reaction with mercury, dibenzo[*a*,*e*]cyclooctatetraene (DBCOT) and molecular oxygen:

a) Effect of mercury: The inhibitory effect of mercury on a catalytic reaction has been proposed as a test for the heterogeneous nature of the catalyst.[12] Mercury supposedly quenches the catalytic reactivity by forming an amalgam with the small platinum particles. Inhibition by Hg has been observed in a photoinduced hydrosilylation reaction using $CpPtMe_3$ as catalyst,[13] whereas when a surface-immobilised, monomeric, coordinatively unsaturated platinum species was involved, no inhibitory effect was seen.[14]

We found that when **11** was used as catalyst both the rate and final yield were unchanged in the presence of mercury (see Figure 7, left) which would indicate that catalysis using **11** was homogeneous throughout.

The Karstedt catalyst, under the same conditions, responded differently. In the presence of Hg, the catalyst was very active for a short period but the solutions became progressively more sombre and catalysis suddenly stopped at less than 40 % silane conversion (Figure 7, right). The Karstedt catalytic action appeared to involve two phases: an initial, active, possibly homogeneous phase that then yielded a heterogeneous system whose activity was inhibited by Hg.

b) Effect of DBCOT: It has been proposed that a phenomenological distinction between homogeneous and heterogeneous Pt catalysts can be also made by studying the effects on the catalytic process of strongly coordinating polyolefins such as DBCOT.[15] Such chelating diolefins coordinate strongly to molecular platinum(0) species, rendering them inactive in hydrosilylation or hydrogenation, whereas heterogeneous systems should be largely unaffected by their presence. Indeed using the Karstedt catalyst little lowering in rate was observed for up to 5 equiv of DBCOT, the reaction going readily to completion (Figure 8, right), indicating that the Karstedt catalyst is largely heterogeneous in action.

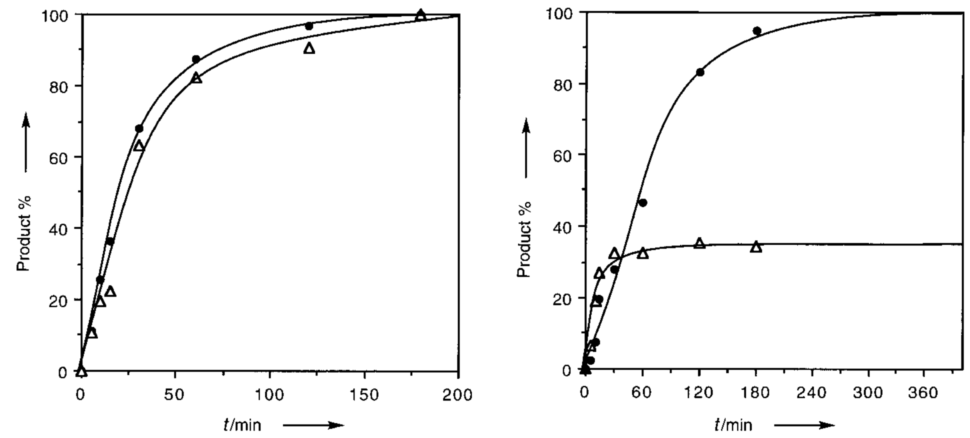

Figure 7. Effect of mercury on the Karstedt catalyst (right) and the catalyst **11** (left). Conditions: hydrosilylation of trimethylvinyl silane by triethylsilane: $T = 30\,^{\circ}C$; $[Si{-}H]_0 = 0, 5\ mol\,L^{-1}$; $[C{=}C]_0$: 0, 15 $mol\,L^{-1}$ in hexane (20 mL); 6×10^{-6} mol Pt catalyst. With 0.1 mL Hg (△), without Hg (●).

However, the addition of DBCOT (1 equiv/Pt) to catalytic solutions of **11** (Figure 8, left) caused a decrease in the initial rate by ca. 30 % (cf. Figure 7) although the reaction still went to completion. However, in the presence of 5 equiv of DBCOT per equiv Pt, a further decrease in rate was observed and the catalytic reaction stopped at 60 % conversion.

c) Effect of molecular oxygen: It has long been known that molecular oxygen can have an important effect on hydrosilylation catalysis. It was observed that small quantities of oxygen induced high activity not only for Pt but also Rh

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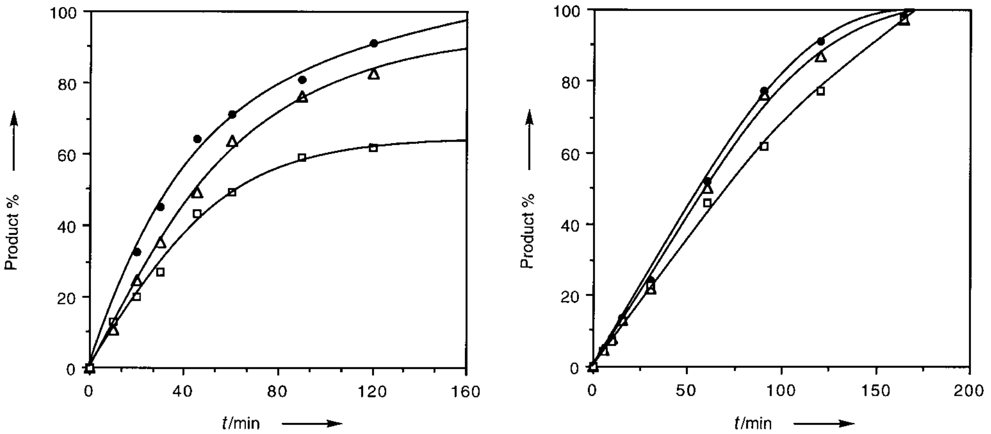


Figure 8. Effect of DBCOT on the Karstedt catalyst (right) and the catalyst **11** (left). Conditions: hydrosilylation of trimethylvinylsilane by triethylsilane: $T = 30\,^\circ C$; $[Si{-}H]_0 = 0,5\ mol\,L^{-1}$; $[C{=}C]_0$: 0,15 mol L^{-1} in hexane (20 mL); 6×10^{-6} mol Pt catalyst; (●) 1 equiv DBCOT, (△) 2 equiv DBCOT, (□) 5 equiv DBCOT.

catalysts,[16] and Lewis[4] has suggested that O_2 is required both to generate and stabilise the active platinum colloids to prevent their further agglomeration into inactive species. In contrast, oxygen was found to inhibit a molecular hydrosilylation catalyst system dramatically.[14] In Figure 9 we compare the rates of hydrosilylation with **11** and with the Karstedt catalyst under three conditions, namely under argon, argon with ca. 1% O_2, and pure O_2 (1 atm).

Using **11** the presence of even a small quantity of O_2 significantly reduced the rate and under pure O_2 the reaction stopped at 40% completion. Little change occurred in the Karstedt system on addition of 1% O_2, but a significant lowering in rate was observed using large quantities of O_2. These observations differ somewhat from those previously reported, but since the conditions used also differ direct comparisons may not be valid.

Overall the evidence indicates that catalysed hydrosilylation using the molecular Pt^0 complex **11** is homogeneous in nature. There is certainly no evidence to the contrary. However the results concerning the Karstedt catalyst are less clear-cut and, in part, contradictory; it is possible that both heterogeneous and homogeneous processes are involved, as previously suggested by Lewis.[4]

Spectroscopic studies of the catalytic reaction: Colloidal particles of platinum absorb in the visible–ultraviolet in solution; Lewis has used this property to identify their presence and their size in the reaction solutions of the Karstedt catalyst.[4] We carried out a study at 40 °C using a hexane solution of $Me_3SiCH{=}CH_2$ (0.15 mol L^{-1}) and Et_3SiH (0.07 mol L^{-1}) to which a fixed quantity of catalyst was added with [cat]/[olefin] ≈ 1/1000. The reaction followed by UV/Vis spectroscopy and glc. With **11**, the reaction was complete (by glc) after 20 min and no appreciable absorption was detected at 500–600 nm. Interestingly, however, the MeNQ ligand absorptions in **11** at 380–400 nm were modified progressively with the appearance of an isosbestic point at 350 nm, indicating the formation of a new species in solution. We confirmed previous observations that on using the Karstedt solutions there was an increase of an intense absorption in the UV/Vis which increased with time (over 20 min), and analysis of the solutions at the end of the reaction by photon correlation spectroscopy (PCS) showed the presence of particles of mean diameter of ca. 400 ± 120 nm. However, when the catalytic reaction using **11** was carried out with lower [olefin]/[SiH] ratios (1 or less), a progressive darkening of the solution occurred and PCS studies at the end of the reaction showed in this case that particles (ca. 360 ± 100 nm) had been formed. It appears that using **11** the catalyst remains stable and homogeneous as long as there is sufficient stabilising ligand present to offset the detrimental effects of large silane concentrations.

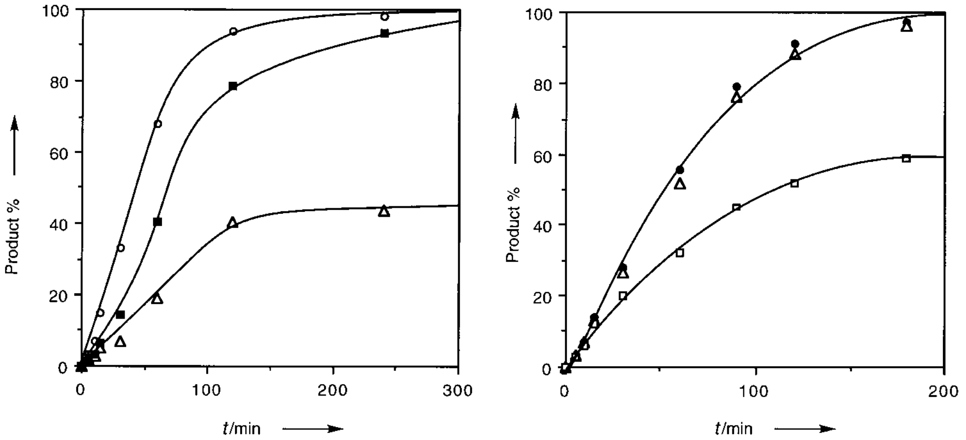
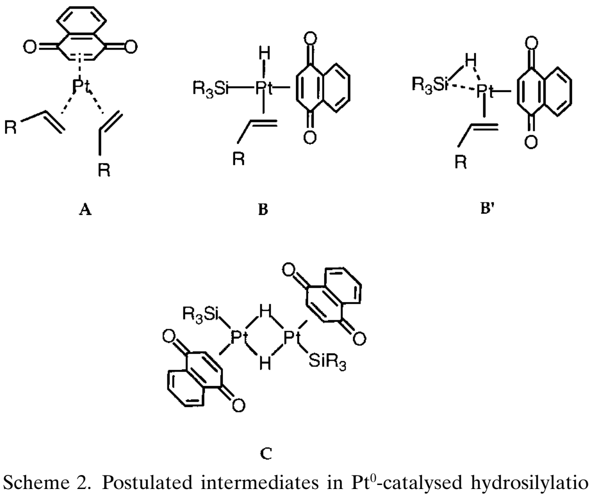


Figure 9. Oxygen effect on the Karstedt catalyst (right) and the catalyst **11** (left). Hydrosilylation of trimethylvinylsilane by triethylsilane: $T = 30\,^\circ C$; $[Si{-}H]_0 = 0,5\ mol\,L^{-1}$; $[C{=}C]_0$: 0,15 mol L^{-1} in hexane (20 mL); 6×10^{-6} mol of Pt catalyst. On right: (●) under Ar, (△) ca. 1% O_2 in Ar, (□) O_2 atm; on left: (○) under Ar, (■) ca. 1% O_2 in Ar, (△) O_2 atm.

NMR studies on the catalytic reaction: ^{195}Pt and ^{29}Si spectroscopies: Pregosin[17] studied the hydrosilylation of $[Pt(\eta^2\text{-}PhCH{=}CH_2)_3]$ by Ph_3SiH using ^{195}Pt and ^{29}Si NMR. The ^{195}Pt spectrum of $[Pt(\eta^2\text{-}PhCH{=}CH_2)_3]$ exhibited two resonances at $\delta = -5904$ and $\delta = -5886$, corresponding to two isomeric forms which, on addition of excess Ph_3SiH, gave rise to further peaks at $\delta = -5010$ and $\delta = -5017$, each of which was coupled to one ^{29}Si nucleus. It was proposed that the complexes $[Pt(\eta^2\text{-}PhCH{=}CH_2)(Ph_3Si)H]_n$ or $[Pt(\eta^2\text{-}PhCH{=}CH_2)(\eta^2\text{-}Ph_3Si\text{-}H)]_n$ ($n = 1$

or 2) were formed in these reactions. In addition the complex [Pt(η^4-1,5-cyclooctadiene)$_2$] displays a ^{195}Pt resonance at $\delta = -4636$.[18]

We found that in CD_2Cl_2/CH_2Cl_2 at 203 °K **11** showed a sharp resonance in the ^{195}Pt{^{1}H} spectrum at $\delta = -4216$ ($\Delta\nu_{1/2} = 70$ Hz) as expected for a Pt^0 complex. In the ^{29}Si NMR of **11** in CD_2Cl_2 two ^{29}Si resonances of equal intensity were observed at $\delta = 3.22$ and 3.59, both coupled to a single ^{195}Pt with ^2J(Pt,Si) = 36 Hz. These observations are consistent with the solid-state structure being preserved for **11** in solution. No noticeable change occurred in the ^{195}Pt signal on the addition of small quantities of $Me_3SiCH{=}CH_2$ (10 equiv) but when a large excess (150 equiv) was added, a signal at $\delta = -4406$ appeared. Similarly, excess $PhCH{=}CH_2$ or $CH_2{=}CH{-}CH_2OAc$ caused peaks to grow in at $\delta = -4471$ and -4523, respectively. The ^{1}H-coupled ^{195}Pt spectrum of the styrene-rich solution exhibited a complex, apparent six-line structure (relative intensities ca. 1:2:3:3:2:1) with peak separations of ca. 40 Hz which clearly resulted from coupling of ^{195}Pt to several vinyl protons, but the lack of resolution did not allow the observation of any ^3J(Pt–CH$_3$) coupling. The corresponding ^{1}H spectrum showed several methyl resonances assignable to dvtms, including signals which coincided with uncomplexed dvtms. No evidence for displacement of the methylnaphthoquinone ligand was observed. Since the ^{195}Pt chemical shift was found to vary with the nature of the olefin substrate added, a minimum of one site on Pt^0 must be occupied by this olefin. Compound **A** (Scheme 2, with NQ as ligand drawn for simplicity) would appear to be a reasonable proposition for the species formed.



Scheme 2. Postulated intermediates in Pt^0-catalysed hydrosilylation with naphthoquinones as ligands.

When Et_3SiH (5 equiv) was added to the olefin-rich solutions (150 equiv olefin) of **11**, a low-intensity peak grew in at $\delta = -4233$, which was invariant in position with the olefin used and which only disappeared when all the silane was consumed. We tentatively propose this peak results from the formation of [Pt(η^2-MeNQ)(HSiEt$_3$)]$_n$ ($n = 1$ or 2, see **C**, Scheme 2), similar to the species originally proposed by Pregosin.

Temperature stability of the Pt catalysts: Under the standard conditions at 20 °C using **11** the catalytic reactions went smoothly to completion in ca. 24 h with an initial rate, $\nu_i \approx 10.8$ mmol L^{-1}h^{-1}. At 50 °C, ν_i increased to 30.2 mmol L^{-1}h^{-1} but after 2 h the rate had greatly decreased with decomposition of the catalyst and only 68 % total conversion was finally obtained. At 73 °C, ν_i was 48 mmol L^{-1}h^{-1} but very rapid decomposition immediately took place which led to a low overall conversion (18 %). Similar observations were made for the complexes **6** and **10**.

Synthesis and catalytic activity of [Pt(η^2-norbornene)$_2$(η^2-MeNQ)] (12): It may be asked at this stage whether the dvtms in the precursor complex **11** is retained as a ligand in the active form of the catalyst or is displaced from the metal before entry into the catalytic cycle. We therefore synthesised the analogous complex [Pt(η^2-nbe)$_2$(η^2-MeNQ)] (**12**, nbe = norbornene), and tested its catalytic activity. The yellow-ochre complex was prepared by the treatment of [Pt(η^2-nbe)$_3$] with MeNQ (Figure 10) and characterised by microanalysis and NMR spectra.

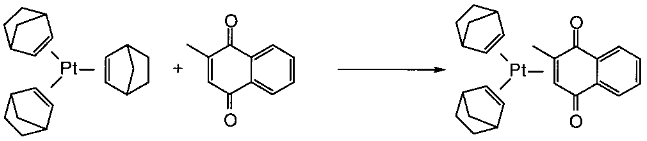


Figure 10. The synthesis of [Pt(η^2-norbornene)$_2$(η^2-(2-methylnaphthoquinone)].

The catalytic activities of **12, 11** and the Karstedt catalyst in the reaction of trimethylvinylsilane and heptamethyltrisiloxane are compared in Figure 11. At 50 % conversion the values of $t_{1/2}$ were ca. <1, 4 and 14 min, respectively, for the three catalysts; notably, the rate of reaction with **12** was considerably greater than that with **11**. The selectivity of silane addition was the same for both **12** and **11** (90 % α), slightly greater than that found for **1**.

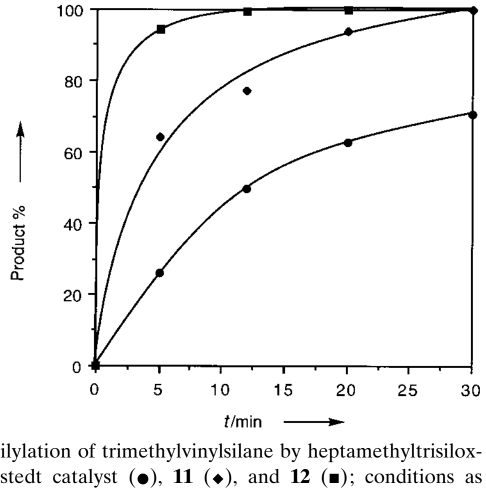


Figure 11. Hydrosilylation of trimethylvinylsilane by heptamethyltrisiloxane with the Karstedt catalyst (●), **11** (◆), and **12** (■); conditions as described in the Experimental Section.

The higher activity of **12** vis-à-vis **11** is probably a result of the greater lability of the norbornene ligand compared with dvtms which would generate the catalytically active species more readily under hydrosilylation conditions. Indeed we have found in a separate experiment that the norbornene ligands in **12** can be readily displaced by dvtms to form **11**. However, most of our studies used **11** rather than **12** because of the ease of its synthesis and high stability.

Discussion

In this paper we describe a family of Pt^0 catalysts, $[Pt(\eta^2\text{-olefin})_2(\eta^2\text{-Ol}_E)]$, where Ol_E is an electron-deficient olefin, which are efficient catalysts for the hydrosilylation of olefins. These compounds are readily synthesised and are easy-to-handle solids. Spectroscopic studies and an X-ray structural characterisation show that Ol_E is bound by a η^2-olefin interaction to Pt^0. The η^2-binding of the naphthoquinone Pt^0 complexes differs from the previously known quinone analogues where the η^4-coordination mode was observed. It was therefore expected that the analogous dihydronaphthoquinone compounds would also be stable; this was confirmed by their synthesis and use as catalysts.

The catalytic activities of this family of compounds, $[Pt(\eta^2\text{-Ol}_E)\{(\eta^4\text{-CH}_2{=}\text{CHSiMe}_2)_2O\}]$, varied greatly with the nature of Ol_E. Hence the fumaronitrile **2** and tetracyanoethylene **6** complexes were inefficient catalysts, being approximately ten times less active than the Karstedt catalyst itself under the same conditions, and thus can serve as inhibitors for the Karstedt system. However, surprisingly, all the naphthoquinone and dihydronaphthoquinone complexes, **7**–**11**, as well as the tetraester compound **5** were found to be more active than the Karstedt catalyst under the standard conditions used. The moderately π-acidic nature of the olefin function appears to induce stabilisation of the Pt species in the catalytic cycle without loss of catalytic activity. However, if this interaction becomes too strong, as in the complexes of the strongly π-acidic fumaronitrile or tetracyanoethylene ligands, the activity markedly diminishes. This is probably also the case for the dimethylfumarate and dimethylmaleate analogues which have been recently proposed as inhibitors for the Karstedt catalyst.[9] Although we find that complexes of moderately π-acidic olefins appear to provide the optimal catalyst systems there appears to be no simple quantitative correlation between the electron deficiency of the olefin and catalytic activity.

The effects of Hg, DBCOT and O_2 on the catalytic activity of **11** were consistent with homogeneous rather than heterogeneous behaviour. The corresponding tests on the Karstedt catalyst were somewhat more ambiguous, indicating the possible coexistence of both heterogeneous and homogeneous activity.

Although it is too early to propose a detailed mechanism for these catalysts, it is most reasonable to propose that the catalytic fragment $[Pt\ (\eta^2\text{-Ol}_E)]$ remains throughout the catalytic cycle. ^1H and ^{195}Pt NMR studies on model reactions of the hydrosilylation process using **11** showed that the MeNQ remained coordinated to Pt whereas dvtms was readily displaced. Similarly we have found[19] that treatment of **11** with phosphine ligands causes the displacement of the dvtms ligand, MeNQ remaining bound. The dvtms ligands in the precursor catalysts **2**–**11** therefore serve as a convenient fashion to generate $[Pt(\eta^2\text{-Ol}_E)]$ in solution. Addition of an excess of the Ol_E ligand can increases the stability and overall productivity of these catalysts with little sacrifice in rate.

The classical mechanism for hydrosilylation was proposed over thirty years ago,[20] and studies on the phosphine-modified catalysts[6] and NMR studies[18] have permitted this mechanism to be elaborated, in particular, by including dimeric intermediates. In Scheme 2 three possible intermediates of these catalysts are proposed based on our spectroscopic observations and by analogy with previous proposals. The Pt^0 complex $[(\eta^2\text{-NQ})Pt(\eta^2\text{-RCH}{=}\text{CH}_2)_2]$ (**A**) is formed by displacement of the labile dvtms ligands by the presence of excess olefin, $RCH{=}CH_2$, under catalytic conditions. The dissociation of one $RCH{=}CH_2$ ligand would give a 14 e^- Pt^0 species, which on reaction with the silane would yield either the oxidative addition product, **B**, or possibly **B′**, $[(\eta^2\text{-NQ})Pt(\eta^2\text{-RCH}{=}\text{CH}_2)(\eta^2\text{-HSiR}_3)]$, containing a σ-bonded silane ligand. Further loss of olefin from **B** (or **B′**) followed by dimerisation would lead to **C**. Preliminary kinetic data[19] indicate that both monomeric and dimeric species are probably involved in the catalytic cycle and **B** and/or **C** may then lead to products. Catalyst decomposition appears to result from the further reaction of **B** or **C** with excess silane. Since this would involve an oxidative process at Pt the greater stability of these complex catalysts (compared with the Karstedt system) may be the result of the enhanced electron-deficient character of the Pt centre resulting from the presence of the π-acidic olefin ligand.

In conclusion, although several compounds of this type were known prior to our work, their application as catalysts for hydrosilylation of olefins under mild thermal conditions had not been reported. In fact certain electron-deficient olefins had been used, paradoxically, as inhibitors for hydrosilylation catalysts. The Karstedt active species had also been generated photochemically from certain quinone complexes by photochemical labilisation of the quinone ligand. The search for appropriate ligands is an important aspect of molecular catalysis, but it is rather surprising to find an electron-deficient olefin as the ligand of choice. Given the existence of chiral naphthoquinones and the high activity of this family of molecular Pt catalysts under mild conditions, their application to enantioselective hydrosilylation can be envisaged. Further, as a source of relatively stable, unsaturated Pt^0 species these compounds may find use in synthesis and other catalytic reactions.

Experimental Section

General considerations: The preparation and handling of compounds were carried out under an argon atmosphere, using standard vacuum line and Schlenk techniques or a glovebox. All solvents were dried with the appropriate drying agents and distilled under a nitrogen atmosphere. Deuterated solvents were degassed by three freeze–pump–thaw cycles and dried over molecular sieves prior to use. NMR spectra were recorded on Bruker AM 300 (^1H, ^{31}P), and AM 400 (^{195}Pt, ^{29}Si) instruments.

Chemical shifts are reported in δ units (ppm) using the standard external references (TMS, H$_3$PO$_4$, Na$_2$PtCl$_4$). Infrared spectra were performed on a Perkin Elmer FTIR 1600 spectrometer. GC analyses of the products of the catalytic reactions were performed using a Hewlett–Packard series II 5890 gas chromatograph with a semicapillary column (HP-1, methylsilicon gum, 10 m × 0.53 mm × 2.65 mm). All GC-MS measurements were performed at the Mass Spectroscopy Service of the Chemistry Research Centre. Elemental analyses (C, H, O, Pt) were carried out at the Microanalytical Service of the Research Centre at Strasbourg or the CNRS Microanalytical Service at Vernaison (France). Photon correlation spectroscopic measurements were made with a Coulter N4 instrument. X-ray experimental data were collected on an Enraf–Nonius CAD4F diffractometer using graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 298 K.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101813. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+ 44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Synthesis of the platinum complexes: The Karstedt catalyst was obtained by stirring a solution of H$_2$PtCl$_6$ · 6H$_2$O (500 mg, 1.22×10^{-3} mol) in H$_2$O (0.2 mL) at 50 °C with tetramethyldivinylsiloxane (5 g, 0.026 mol, 6.18 mL) for 4 h. After cooling to room temperature, the solution was neutralised by 500 mg of NaHCO$_3$ and filtered, yielding the so-called solution A. The platinum concentration in this solution was measured by atomic absorption. It was supposed that the platinum in such solutions was solely in the form of Karstedt catalyst and the quantities of Karstedt catalyst used in the syntheses of the compounds described below have been calculated on this basis.

[Pt(η^2-(NC)HC=CH(CN)){(η^4-CH$_2$=CHSiMe$_2$)$_2$O}] (2): Karstedt catalyst (500 mg, 5.26×10^{-4} mol) in solution A was stirred with fumaronitrile (82 mg, 1.05×10^{-3} mol) in toluene (10 mL). The colourless solution was heated at 60 °C for 5 min, and after cooling to ambient temperature, the solvent was removed in vacuo. The resulting white powder was washed with hexamethyldisiloxane (2 × 20 mL), then tetramethyldivinylsiloxane (2 × 4 mL). After decantation and filtration, the product was dried under vacuum. Yield: 180 mg (39 %). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 3.5 - 5$ (m, 8H, CH$_2$=CH and CH=CH), −0.20, −0.26(s, 3H, SiCH$_3$), 0.42, 0.35 (s, 3H, SiCH$_3$); IR (nujol): $\tilde{\nu}$ (cm^{-1}) = 2221 (CN), 1573, 1013 (CH$_2$=CH−Si), 1254, 833, 799 (Me$_2$Si−O); m.p. 130 °C (decomp).

[Pt(η^2-(EtOOC)CH=CH(COOEt)){η^4-CH$_2$=CHSiMe$_2$)$_2$O}] (3): Diethylfumarate (158 mg, 9.20×10^{-4} mol) was added to the Karstedt catalyst (437 mg, 4.61×10^{-4} mol) in solution A. The solution was then warmed to 70 °C for 30 min. After cooling to −78 °C, colourless crystals were collected, washed twice with cold pentane (5 mL) at −78 °C and dried under vacuum. Yield: 134 mg (26 %); ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 3.5 - 4.1$ (m, 8H, CH$_2$=CH), −0.28 (s, 6H, SiCH$_3$), 0.37 (s, 6H, SiCH$_3$), 1.25 (t, 6H, CH$_3$), 4.15 (q, 4H, CH$_2$); IR (nujol): $\tilde{\nu}$ (cm^{-1}) = 1727 (C=O), 1259, 839, 794 (Me$_2$Si−O), 3040, 1000 (CH$_2$=CH−Si); m.p.: 127 °C (decomp); anal. calcd for C 34.71, H 5.46; found: C 35.20, H 5.60.

[Pt{η^2-(PhCO)CH=CH(COPh)}{η^4-(CH$_2$=CHSiMe$_2$)$_2$O}] (4): Karstedt catalyst (215 mg, 2.3×10^{-4} mol) in solution A was concentrated under vacuum over 60 min in a Schlenk tube. *trans*-Dibenzoylethylene (108 mg, 4.5×10^{-4} mol) was added to the resultant oil. The mixture was then warmed to 75 °C for 15 min and, after cooling to −78 °C, the resultant paste was washed with hexamethyldisiloxane (2 × 10 mL) and cold pentane (2 × 15 mL)(−78 °C), yielding a white powder which was then dried under vacuum. Yield: 162 mg (57 %); ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 5.74$ (s, 2H, ^2J(Pt,H): 60 Hz, CH=CH), 3.4–4.2 (m, 6H, CH$_2$=CH), 0.28 (s, 3H, SiCH$_3$), 0.23 (s, 3H, SiCH$_3$), −0.24 (s, 3H, SiCH$_3$), −0.62 (s, 3H, SiCH$_3$), 7.5 and 8.2 (m, 10H, Ar); IR (nujol) $\tilde{\nu}$ (cm^{-1}) = 1873 (CO), 1744 (CO), 1255, 836, 790 (Me$_2$Si−O), 3050, 1656, 1589, 1005 (CH$_2$=CH−Si); m.p.: 156 °C (decomp); anal. calcd for C 47.08, H 5.08; found: C 46.81, H 4.95.

[Pt{η^2-(EtOOC)$_2$C=C(COOEt)$_2$}{(η^4-CH$_2$=CHSiMe$_2$)$_2$O}] (5): The synthesis was carried out as for **4**. Yield: 102 mg (69 %); ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 3.7 - 5.2$ (m, 6H, CH$_2$=CH), −0.19 (s, 3H, SiCH$_3$), 0.05 (s, 3H, SiCH$_3$), 0.15 (s, 3H, SiCH$_3$), 0.38 (s, 3H, SiCH$_3$), 4.16 (q, 8H, CH$_2$), 1.30 (t, 12H, CH$_3$); IR (nujol): $\tilde{\nu}$ (cm^{-1}) = 1741 (CO), 1714 (CO), 1227, 837, 799 (Me$_2$Si−O), 1019 (CH$_2$=CH−Si); m.p.: 138 °C (decomp); anal. calcd for Pt 22.56; found: Pt 22.05.

[Pt{η^2-(NC)$_2$C=C(CN)$_2$}{(η^4-CH$_2$=CHSiMe$_2$)$_2$O}] (6): The synthesis was carried out as for **2**. The white solid obtained was dissolved in hexane, passed through a silica column and recovered as a white powder on removal of the hexane. Yield: 153 mg (51 %); ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = -0.36$ (s, 3H, SiCH$_3$), −0.24 (s, 3H, SiCH$_3$), 0.0 (s, 3H, SiCH$_3$), 0.09 (s, 3H, SiCH$_3$), 3.5–4.5 (m, 6H, CH$_2$=CH); IR (nujol): $\tilde{\nu}$ (cm^{-1}) = 2234 (CN), 1573, 1028 (CH$_2$=CH−Si), 1261, 839, 799 (Me$_2$Si−O); ^{195}Pt{^{1}H} NMR (85 MHz, CDCl$_3$): $\delta = -3870$; anal. calcd for C 32.12, H 3.60; found: C 32.25, H 3.57.

[Pt(η^2-napthoquinone){(η^4-CH$_2$=CHSiMe$_2$)$_2$O}] (7): Karstedt catalyst in solution A (437 mg, 4.61×10^{-4} mol) was concentrated under vacuum for 60 min in a Schlenk tube, and toluene (10 mL) was added to the resulting oil. Naphthoquinone (146 mg, 10^{-3} mol) was then added to the mixture and the green solution heated at 65 °C for 10 min. After cooling to room temperature, the mixture was stirred for 12 h. The solvent was removed under vacuum and the resultant powder was washed with tetramethyldivinylsiloxane (1 × 2 mL) and hexamethyldisiloxane (2 × 10 mL). The pale green solid was dried under vacuum. Yield: 230 mg (47 %); ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 4.95$ (s, 2H, ^2J(Pt,H): 52 Hz), 3.3–4.2 (m, 6H, CH$_2$=CH), −0.92 (s, 6H, SiCH$_3$), 0.15 (s, 6H, SiCH$_3$), 7.9 and 7.5 (m, 4H, Ar); ^{13}C NMR (200 MHz, C$_6$D$_6$): $\delta = -3.15$, 0.88 ((*C*H$_3$)$_2$Si), 60.1 (*C*H=CH−CO), 74.3 (*C*HSi), 76 (*C*H$_2$CHSi), 126, 132.9 (*C*H arom), 133.7 (C quinone), 186.53 (*C*O); IR (nujol) $\tilde{\nu}$ (cm^{-1}) = 1873 (CO) 1744 (CO), 1656, 1589 (CH$_2$=CH−Si) 1255, 836, 790 (Me$_2$Si−O); m.p.: 138 °C (decomp); anal. calcd for C 40.06, H 4.48; found: C 40.10, H 4.57.

[Pt(η^2-TND){(η^4-CH$_2$=CHSiMe$_2$)$_2$O}] (8): (TND: 1,2,3,4-tetramethyl-4*a*,8*a*-dihydro-*endo*-1,4-methylmethanonaphthalene-5,8-dione: C$_{16}$H$_{19}$O$_2$) Karstedt catalyst in solution A (420 mg, 4.5×10^{-4} mol) was concentrated under vacuum for 60 min to obtain an oil. TND (225 mg, 9.1×10^{-4} mole) was then added and the solution heated at 70 °C for 30 min. After cooling to ambient temperature the resultant solid was washed twice with hexamethyldisiloxane (2 × 5 mL) and pentane (2 × 20 mL), then dried under vacuum, yielding a white powder. Yield: 345 mg (60 %); ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 3.5 - 4.0$ (m, 6H, CH$_2$=CH), −0.35 (s, 6H, SiCH$_3$), 0.35 (s, 6H, SiCH$_3$), 4.15 (s, 2H, ^2J(Pt,H): 56 Hz, CH=CH), 2.09 (s, 2H, 2 CH), 1.54 (s, 6H, CH$_3$), 1.32 (s, 6H, CH$_3$), 0.5 (d, 2H, CH$_2$); IR (nujol) $\tilde{\nu}$ (cm^{-1}) = 1672 (CO), 1258, 839, 794 (Me$_2$Si−O), 1654, 1007 (CH$_2$=CH−Si); m.p.: 152 °C (decomp); anal. calcd for C 45.98, H 6.17; found: C 46.41, H 5.64.

[Pt(η^2-BAD){(η^4-CH$_2$=CHSiMe$_2$)$_2$O}] (9): (BAD: 9,10-dihydro-9,10-*ortho*-benzenoanthracene-1,4-dione) The synthesis was carried out as for **8** but with a longer heating period (60 min at 70 °C) to obtain a white powder. Yield: 420 mg (68 %); ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 3.2 - 4.2$ (m, 8H, CH$_2$=CH), −0.38 (s, 6H, SiCH$_3$), 0.35 (s, 6H, SiCH$_3$), 7.1 and 7.4 (m, 8H, Ar), 5 (s, 2H, ^2J(Pt,H): 56 Hz, CH=CH), 2.45 (s, 2H, 2 CH); IR (nujol): $\tilde{\nu}$ (cm^{-1}) = 1652 (CO), 1260, 835, 797 (Me$_2$Si−O); m.p.: 202 °C (decomp).

[Pt(η^2-2,3-dichloronaphthoquinone){(η^4-CH$_2$=CHSiMe$_2$)$_2$O}] (10): The synthesis was carried out as for **8** to obtain a pale yellow powder. Yield: 381 mg (70 %); ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 3.6 - 4.2$ (m, 6H, CH$_2$=CH), −0.58 (s, 6H, SiCH$_3$), 0.28 (s, 6H, SiCH$_3$), 7.52 and 8.52 (m, 4H, Ar); ^{13}C NMR (200 MHz, C$_6$D$_6$): $\delta = -2.75$ and 0.84 ((CH$_3$)$_2$Si), 85 (Cl*C*=*C*Cl), 82 (*C*H ligand), 133, 127 (*C*H arom), 206.9 (CO quinone); ^{195}Pt{^{1}H} NMR (85 MHz, CDCl$_3$): $\delta = -3100$; IR (nujol): $\tilde{\nu}$ (cm^{-1}) = 1677 (CO), 1591 (CH$_2$=CH−Si), 1259, 845, 800 (Me$_2$Si−O); m.p.: 152 °C (decomp); anal. calcd for C 35.53, H 3.64; found: C 36.18, H 3.65.

[Pt(η^2-methylnaphthoquinone){(η^4-CH$_2$=CHSiMe$_2$)$_2$O}] (11): The synthesis was carried out as for **8** but with a shorter heating period (15 min at 70 °C) to obtain a pale yellow powder. Yield: 220 mg (78 %).Crystals suitable for X-ray analysis were obtained by recrystallisation from hexane. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 5.04$ (s, 1H, ^2J(Pt,H): 48 Hz, CH=C), 2.0 (s, 3H, ^3J(Pt,H): 30 Hz, CH$_3$), 3.3–4.2 (m, 6H, CH$_2$=CH), 0.27 (s, 6H, SiCH$_3$), −0.77, −0.88 (s, 3H, SiCH$_3$), 7.9 (td, 2H, Ar), 7.5 (dd, 2H, Ar); ^{13}C NMR (200 MHz, C$_6$D$_6$): $\delta = 132.8$, 132.3, 126.2, 125.6 (*C* arom), 185.4 (*C*O), 18.2 (*C*H$_3$ quinone), 0.92–3.12 (*C*H$_3$−Si), 66 (*C*=*C*), 74, 76 (CH$_2$ siloxane), 96 (CH siloxane); ^{195}Pt{^{1}H} NMR: (85 MHz, CDCl$_3$): $\delta = -4226$; IR (nujol): $\tilde{\nu}$ (cm^{-1}): 1655 (CO), 1594 (CH$_2$=CH−Si), 836, 791

($Me_2Si{-}O$), 720 (C arom); m.p.: 144 °C (decomp); anal. calcd for C 41.95, H 4.76, Pt 33.83; found: C 41.81, H 4.77, Pt 33.70.

[Pt(η^2-norbornene)$_2$(η^2-methylnaphthoquinone)] (**12**): [Pt(norbornene)$_3$] (200 mg, 4.2×10^{-5} mol) and methylnaphthoquinone (72 mg, 4.2×10^{-5} mol) were stirred in toluene (20 mL) under an inert atmosphere and heated at 40 °C for 3 h. The solvent was then removed under vacuum and the resultant yellow-brown powder washed with pentane (2×10 mL) and dried under vacuum. Yield: 65 %; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.6$ (s, 4H, CH=CH, ^2J(Pt,H): 66 Hz), 2.9 (s, 4H, CH), 1.7 (dd, 8H, CH_2), 1.2 (dd, 4H, CH_2), 7.9 (td, 2H, CH), 7.5 (dd, 2H, CH), 4.57 (s, 1H, CH=C (naphthoquinone) ^2J(Pt,H): 50 Hz) 1.87 (s, 3H, CH_3 (naphthoquinone) ^3J(Pt,H): 34 Hz); anal. calcd for C 54.05, H 5.08; found: C 54.22, H 5.17.

Catalytic studies: Hydrosilylation reactions were carried out in Schlenk tubes equipped with septum caps under an argon atmosphere at 30 °C. In a typical experiment, the platinum catalyst (6×10^{-6} mol) was transferred to a Schlenk tube and degassed hexane (30 mL) was added under argon. The solution was stirred for 5 min and the olefin (6×10^{-3} mol) and silane (3×10^{-3} mol) were then injected in quick succession from syringes through the septum. Samples were taken by syringe periodically for GC analysis. Based on one set of measurements the data were reproducible to ca. ± 5 %.

Mercury inhibition studies: Two solutions containing 6×10^{-3} mol of trimethylvinylsilane, 6×10^{-6} mol of catalyst and 30 mL of distilled *n*-hexane were degassed and then stirred for 60 min, one solution with 1.4 g of filtered Hg and the other without Hg. Et_3SiH (3×10^{-3} mol) was then added to both solutions and the hydrosilylation process was monitored by GC analysis.

DBCOT inhibition studies: Three degassed solutions containing 6×10^{-3} mol of trimethylvinylsilane, 6×10^{-6} mol of catalyst and 30 mL of distilled *n*-hexane were prepared and 1, 2 and 5 equiv of DBCOT per platinum atom, respectively, were added to these solutions. After 60 min, Et_3SiH (3×10^{-3} mol) was added. The hydrosilylation process was then monitored by GC analysis.

Oxygen effects: Three degassed solutions containing 6×10^{-3} mol of trimethylvinylsilane, 6×10^{-6} mol of catalyst and 30 mL of distilled *n*-hexane were prepared. The catalyst (6×10^{-6} mol) was then added to the solutions under argon. The first Schlenk tube was left under argon. In the second tube, a small amount of pure oxygen (ca.2 mL) was injected. The third tube was filled entirely with oxygen. The hydrosilylation processes were then monitored by GC analysis.

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[11] Crystallographic data for **11** are given in Table 1. Diffraction data was collected at room temperature on a Nonius CAD 4-F diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation. Cell constants and orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections. Collection was achieved using $\omega/2\theta$ scans to a maximum θ value of 26 °. 9738 reflections were collected. Lorentz, polarisation and absorption corrections were applied to the data (absorption corrections from the ψ scans of 4 reflections). The structure was solved by the Patterson method. All non-hydrogen atoms were located by the heavy atom method, and were refined anisotropically. Hydrogen atoms, with the exception of the water protons, were introduced as fixed contributors with C–H = 0.95 Å, B(H) = 1.3 Beqv(C). The final cycle of full-matrix least-squares refinement was based on 4223 observed reflections ($I > 3\sigma(I)$) and converged with unweighted and weighted agreement factors of $R(F) = 0.033$ and $R(F)_w = 0.041$, respectively. All computations used OpenMolen on a DEC Alpha computer. [C. K. Fair in *MolEN, An Interactive Intelligent System for Crystal Structure Analysis*, Enraf–Nonius, Delft (the Netherlands), **1990**.] Crystal parameters, data collection details and results of the refinements are summarised in Table 2.

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