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The chemistry of fumarate and maleate inhibitors with platinum hydrosilylation catalysts [1]

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Abstract

$Pt(M^{vi}M^{vi})_x$ ($M^{vi}M^{vi}$ = 1,3-divinyltetramethyl disiloxane), **1**, was reacted with dimethyl fumarate to give **2**. Compound **2** was investigated by ^1H and ^{13}C NMR spectroscopy which showed it to be a mono-nuclear platinum compound containing one dimethyl fumarate and one chelating $M^{vi}M^{vi}$ ligand. The reaction of **1** with dimethyl maleate gave **3** which was analogous in structure to the fumarate product as shown by ^1H and ^{13}C NMR spectroscopy and extended X-ray absorption fine structure spectroscopy (EXAFS). The EXAFS analysis showed the presence of Pt–C bonds and a through space close contact between Pt and the O from the carbonyl. The NMR assignments were confirmed by comparing the NMR spectra of **2** and **3** with that of $(PPh_3)Pt(M^{vi}M^{vi})$, **4**. Reaction of **2** or **3** with an excess of an Si–H-containing compound (either MD^HD^HM (MD^HD^HM = 1,3-bis(trimethylsiloxy)-1,3-dimethylsiloxane) or Et_3SiH) gave **5** in all cases. Compound **5** contains an alkyl succinate ligand. Hydrogenation of the fumarate ligand (of **2**) or of the maleate ligand (of **3**) occurs by reaction with Si–H; **5** appears to be an intermediate in the hydrogenation process. The reaction between **4**, dimethylmaleate, and MD^HD^HM also gives dimethyl succinate. Differential scanning calorimetry was used to compare the effectiveness of the inhibitors in a curable formulation composed of vinyl-stopped-polydimethyl siloxane, polydimethylsiloxanemethylhydrogen-copolymer, a platinum catalyst and either a maleate or fumarate inhibitor.

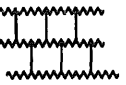
Keywords: Silicon; Platinum; Hydrosilylation; Catalysis; Inhibitors

1. Introduction

Hydrosilylation, Eq. (1), is a well known reaction for the formation of Si–C bonds [1–8]. One important application of hydrosilylation is the formation of crosslinked networks [9,10]. In the crosslinking application, Eq. (2), a polydimethylsiloxane polymer bearing at least two vinyl groups is reacted with a methylhydrogensiloxane-containing polymer in the presence of a catalyst. The letters M, D, T and Q denote $Me_3SiO–$, $–OMe_2SiO–$, $MeSi(O–)_3$ and $Si(O–)_4$ respectively [10,11]. Groups other than methyl are indicated by a superscript such as M^H and D^{vi} as for $Me_2SiHO–$ and $–OMeSi(CH=CH_2)O–$ respectively.

$$R_3SiH + H_2C{=}CHR' \xrightarrow{cat} R_3SiCH_2CH_2R' \quad (1)$$

$$M^{vi}D_xM^{vi} + MD_xD^H_yM \xrightarrow{cat} \quad (2)$$



Typical catalysts for the crosslinking reaction in Eq. (2) are low-valent platinum complexes such as **1**, commonly referred to as Karstedt's catalyst [12,13]. Complexes such as **1** are highly active; the crosslinking reaction of Eq. (2) occurs at ambient temperature in less than 1 min with as little as 10 ppm platinum.

$Pt(M^{vi}M^{vi})_x$

1

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[1] Dedicated to Professor Robert Corriu in recognition of his outstanding contributions to organosilicon chemistry.

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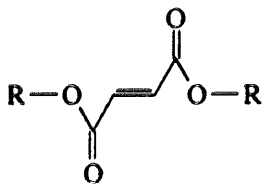
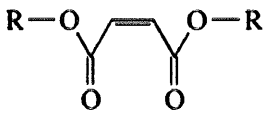
For practical purposes it is desirable to inhibit the curing reaction shown in Eq. (2) [14]. In a typical manufacturing process the vinyl-containing siloxane, Si–H-containing siloxane, filler and other additives (if any), catalyst and inhibitor are combined and the resultant mixture is expected to have some shelf stability at ambient temperature. The extent of ambient temperature shelf life depends on the industrial application, with a 24 h bath life required for paper release coatings and 6–12 month stability for conformal electronic coatings. An ideal silicone addition curable system may combine instant cure at elevated temperatures with infinite pot life at ambient temperature, sometimes designated as 'command cure' [15,16].

Inhibitors are the key to approaching ideal command cure systems. Two important inhibitor types used in commercial platinum-cured siloxanes are fumarates [17] and maleates [18].



fumarate



maleate

The mechanism of inhibition is based on the nature of the interaction of the platinum catalyst with fumarate and maleate. This report describes the chemistry that occurs between platinum complexes of type **1** with these inhibitors. Correlation between platinum–inhibitor chemistry and actual inhibitor performance in a curable polymeric system is also described.

2. Results and discussion

2.1. Reaction of Karstedt's catalyst with dimethyl fumarate or maleate

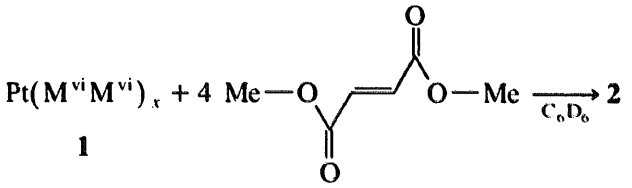
The synthesis and structure of Karstedt's catalyst has been described in detail [19,20]. Lappert and co-workers [20] have designated the product from Eq. (3) as 'Solution A'. Vacuum distillation of Solution A yields a platinum-containing oil referred to as 'Solution A Concentrate'. The ^{1}H and ^{13}C NMR spectra of Solution A Concentrate have characteristic resonances revealing both free- and platinum-bound vinyl resonances, as shown in Fig. 1. The platinum-bound vinyl resonances display additional complexity due to coupling to the 1/3 abundant spin = 1/2 ^{195}Pt nucleus. Analysis of **1** by ^{1}H and ^{13}C NMR spectroscopy and extended X-ray absorption fine structure spectroscopy (EXAFS) analysis suggested that the platinum is bound to three vinyl groups from either chelating or bridging ligands [21,22].

$$H_2PtCl_6 + M^{vi}M^{vi} \longrightarrow \underline{\text{Solution A}}$$

$$Pt(M^{vi}M^{vi})_x + M^{vi}D_xM^{vi} \qquad (3)$$

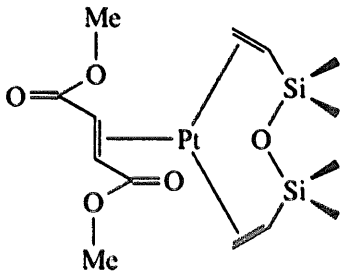
1

A C_6D_6 solution of Solution A Concentrate was reacted with four equivalents of dimethyl fumarate.



dimethyl fumarate

(4)

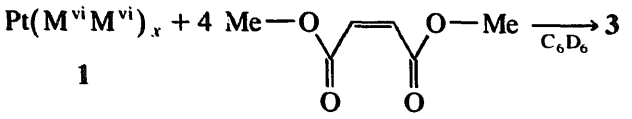


2

Both ^{1}H and ^{13}C NMR spectra showed that the resonances associated with the chelating $M^{vi}M^{vi}$ ligand of **1** were completely replaced (see Table 1 for ^{13}C data). The spectra showed the disappearance of the vinyl resonances of **1** [23] and the appearance of the resonances due to free $M^{vi}M^{vi}$. New resonances from 3 to 4.3 ppm in the ^{1}H NMR spectrum were observed and assigned to the olefinic $M^{vi}M^{vi}$ protons of the vinyl–platinum interaction in **2**. Another resonance at 4.57 ppm (J_{Pt-C} = 30 Hz) was assigned to the olefinic protons of the fumarate bound to platinum. A single new methoxy resonance was observed in both ^{1}H and ^{13}C NMR spectra (^{1}H NMR; 3.34 ppm cf. 3.26 ppm for dimethyl fumarate). Additionally, a new carbonyl resonance was observed in the ^{13}C NMR spectrum at 169.74 ppm, with a coupling constant to Pt of 21 Hz. The fumarate olefin–platinum interaction in **2** gave rise to a resonance showing ^{195}Pt satellites at 51.06 ppm, J_{Pt-C} = 89 Hz. The assignments were made using the ^{13}C NMR spin program, attached proton test. The presence of a chelating $M^{vi}M^{vi}$ ligand was further supported by the observation in both the ^{1}H and ^{13}C NMR spectra for **2** of resonances upfield of TMS associated with the silicon methyl groups. Lappert and co-workers [20,22] have shown that in a complex containing bridging and

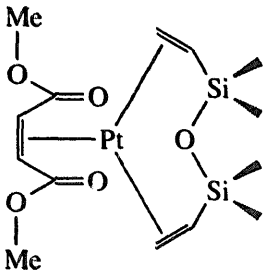
chelating $M^{vi}M^{vi}$ the bridging group is replaced upon addition of other ligands such as maleic anhydride.

In an analogous reaction, a C_6D_6 solution of Solution A Concentrate was reacted with four equivalents of dimethyl maleate (Eq. (5)). NMR analysis of the solution from Eq. (5) showed that the dimethyl maleate



dimethyl maleate

(5)



3

analog of **2** is formed, **3**. The ^1H NMR spectrum showed the presence of a new methoxy resonance at 3.43 ppm (cf. free dimethyl maleate MeO peak at 3.41 ppm). A new resonance was observed at 3.93 ppm with Pt satellites, $J_{Pt-C} = 33$ Hz, assigned to the maleate olefin–platinum bond. Additional peaks in the spectrum were present from 3.0 to 3.6 ppm and were probably due to the $M^{vi}M^{vi}$–Pt interaction. The ^{13}C NMR spectrum of **3** showed the presence of the platinum-bound maleate olefin resonance at 49.29 ppm ($J_{Pt-C} = 104$ Hz). The symmetry of the cis-bound olefin resulted in equivalent shifts for the $M^{vi}M^{vi}$ species. Note that the proposed structure has the carbonyls of the dimethyl maleate ligand pointing toward the platinum. This arrangement is supported by the new carbonyl resonance in the ^{13}C NMR spectrum at 169.27 ppm, which exhibited coupling to platinum ($J_{Pt-C} = 19$ Hz). The arrangement is further supported by the EXAFS analysis of **3** which showed the presence of both Pt–O and Pt–C bonds (($d_{Pt-C} = 2.22$ Å) and $d_{Pt-O} = 2.08$ Å, number of Pt–C bonds greater than Pt–O bonds). In the IR spectrum the carbonyl peak in **3** was unchanged from that of the free dimethyl maleate, which is consistent with a dative bond and not a covalent Pt–O bond. The above results suggest that no change in oxidation state occurs in the transformation of **1** to **3**. When the reaction solution from Eq. (5) was combined with 4 equivalents of $M^{vi}M^{vi}$ no displacement of the maleate ligand was observed.

Additional confirmation for the assignments of structures **2** and **3** came from the NMR spectroscopic analysis of $(PPh_3)Pt(M^{vi}M^{vi})$, **4** [24]. Compound **4** was

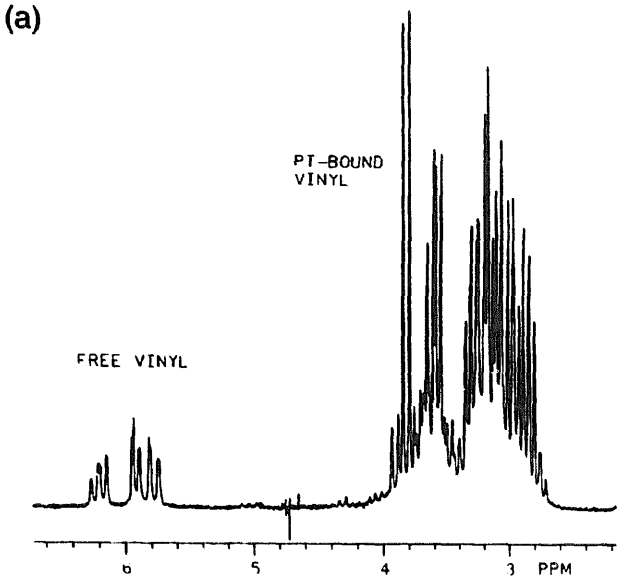
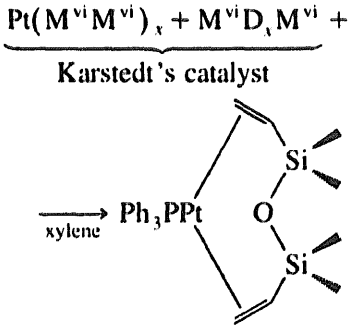


Fig. 1. (a) ^1H and (b) ^{13}C NMR spectra of Solution A Concentrate, **1**, in C_6D_6.

prepared by adding one equivalent of PPh_3 to Karstedt's catalyst solution in the presence of an excess of $M^{vi}M^{vi}$, Eq. (6).



(6)

4

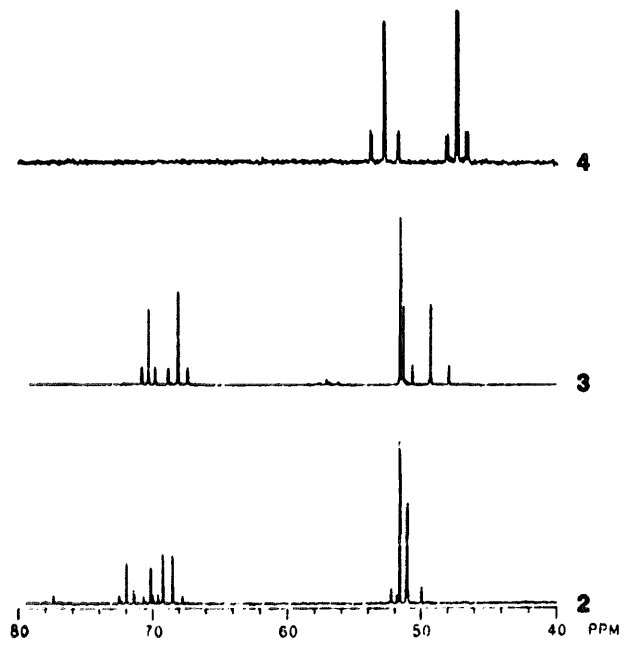


Fig. 2. ^{13}C NMR spectra from 40 to 80 ppm showing Pt-bound olefin resonances for compounds **2**, **3** and **4** in C_6D_6.

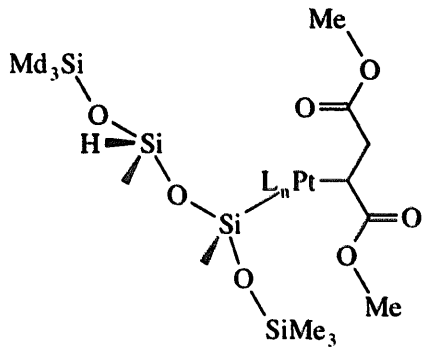
The ^{13}C NMR spectrum of **4** supports the assignments for **2** and **3**. Compounds **2**, **3** and **4** all have vinyl resonances bound to platinum, upfield of those for free vinyl. Additionally, the three compounds have similar Pt=C coupling constants (see Fig. 2 and Table 1).

2.2. Reaction of Karstedt's catalyst with fumarate or maleate and silicone hydride

Reaction of Solution A Concentrate with four equivalents of dimethyl fumarate, followed by five equivalents of MD^HD^HM, yielded a new platinum complex, **5**, Eq. (7)

MD^HD^HM

(7)



5

The ^{13}C NMR spectrum of the reaction solution from Eq. (7) showed the disappearance of the platinum-bound fumarate olefin bonds of **2**. Additionally, new carbonyl resonances were observed at 178.74 ($J_{Pt-C} = 24$ Hz) and 188.53 ($J_{Pt-C} = 20$ Hz), that is downfield from those in **2**. ^{13}C NMR spectroscopy also showed the presence of only one other resonance with Pt satellites at 41.06 ppm ($J_{Pt-C} = 15$ Hz) which may be due to the CH group in **5**. The IR spectrum of the reaction solution from Eq. (7) showed new CO stretches at 1658 and 910 cm^{-1}. GLCMS analysis indicated formation of dimethyl succinate, which was confirmed by ^1H and ^{13}C NMR spectroscopy. GLCMS analysis and NMR spectroscopy

Table 1
^{13}C NMR data for olefins and their Pt-complexes (^{13}C NMR resonances in ppm, ^{195}Pt–^{13}C coupling constant in Hz in parentheses)

Compound	Si-CH=CH_2	Si-CH=CH_2	CO_2CH_3	CO_2CH_3	C=C
Dimethyl fumarate	—	—	164.90	51.62	133.39
Dimethyl maleate	—	—	165.34	51.58	129.86
Dimethyl succinate	—	—	172.33	51.24	—
$M^{vi}M^{vi}$	132.00	139.44	—	—	—
$Pt(M^{vi}M^{vi})_x$, **1**	56.26(61)	56.46(57)	—	—	—
	56.85(58)	57.30(55)			
	57.17(59)	57.55(62)			
$Pt(M^{vi}M^{vi})$	68.47(56)	70.11(42)	169.74	51.62	51.06
(*trans*-(MeO_2C)	69.20(56)	71.94(42)	(21)		(89)
CH=CH(CO_2Me)), **2**					
$Pt(M^{vi}M^{vi})$	68.01(55)	70.23(39)	169.27	51.36	49.29
(*cis*-(MeO_2C)CH=CH(CO_2Me)), **3**			(19)		(104)
$Pt(M^{vi}M^{vi})$	47.25(57)	52.78(77)			
($P(C_6H_5)_3$), **4**					
5			178.74	53.22	
			(24)	50.03	
			188.53		
			(20)		

Solutions run in C_6D_6, referenced to the center triplet line = 128 ppm.

showed that there had been considerable hydrosilylation in the oligomers present in **1**, $M^{vi}D_xM^{vi}$.

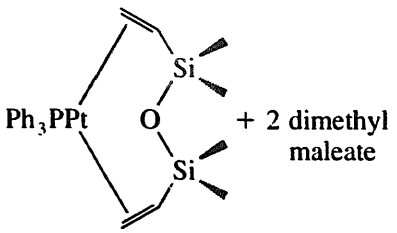
Several experiments were performed to elucidate the structure of **5**. We considered the possibility that dimethyl succinate formed a complex with platinum during the reaction in Eq. (7). However, there was no observed reaction (as determined by ^1H and ^{13}C NMR spectroscopy) between dimethyl succinate and **1**. Complex **5** was not obtained when **1** was first reacted with MD^HD^HM followed by dimethyl succinate. Thus once dimethyl succinate is formed there is no further interaction with platinum.

The proposed structure of **5** is that of the intermediate expected from the hydrogenation of fumarate olefin bound to the platinum center. Hydrogenation occurred via oxidative addition of Si–H to platinum. The identity of the ligands L (if any) in **5** are not known but clearly they are not olefinic in nature. The NMR data supported the carbon-bound succinate ligand of **5**. ^1H NMR resonances at 4.2 (d of d, $J = 16$ and 84 Hz) and 4.57 (t, $J = 30$ Hz) ppm were assigned to CH_2 and CH respectively. The diastereotopic nature of the protons on the CH_2 group in **5** gave rise to the triplet observed at 4.57 ppm.

The reaction of Eq. (7) was repeated using **3** instead of **2**. The ^1H NMR spectrum showed disappearance of the bound olefinic resonances and the appearance of peaks due to dimethyl succinate. Hydrosilylation of $M^{vi}D_xM^{vi}$ by MD^HD^HM was again observed. The NMR spectra of the platinum product from reactions of **2** or **3** in the presence of excess MD^HD^HM were identical, indicating that the same platinum product resulted from hydrogenation of maleate or fumarate by MD^HD^HM. It is noteworthy at this point that isomerization of maleate to fumarate (or fumarate to maleate) was never observed.

The reaction in Eq. (7) was repeated except that Et_3SiH (ten equivalents) was used in place of the five equivalents of MD^HD^HM. NMR spectroscopy and GLCMS analysis showed that hydrosilylation of $M^{vi}M^{vi}$ had taken place in addition to formation of dimethyl succinate. Thus, hydrogenation appears to be a general reaction regardless of the silane used.

In contrast to the chemistry with Karstedt's catalyst, **1**, there was no reaction between **4** and dimethyl maleate. It was not surprising that dimethyl maleate is unable to replace the PPh_3 ligand in **4**. When two equivalents of dimethyl maleate and two equivalents of MD^HD^HM were added to **4**, no reaction occurred in the absence of air. However, when the reaction solution was exposed to air it darkened, and clean conversion of the maleate to succinate took place, Eq. (8).



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$$+2\ MD^HD^HM \xrightarrow[C_6D_6]{\text{no air}} \text{no reaction} \qquad (8)$$

$$\xrightarrow{\text{air}} \text{dimethyl succinate 100\%}$$

Activation of phosphine-containing metal complexes by air in catalytic reactions is well known to proceed through oxidation of PPh_3 to give $O{=}PPh_3$. Formation of phosphine oxide would obviously irreversibly remove phosphine from the metal center and open a coordination site on the metal [25,26].

2.3. Use of inhibitors in a curable siloxane polymer system

The inhibitors described above provided reasonable shelf life when added to formulations. Differential scanning calorimetry (DSC) of formulations proved to be a useful method for evaluation of potential inhibitors for a command cure application. If the exotherm due to hydrosilylation (cure) occurred at too low a temperature then the formulation was likely to gel prematurely. In order to compare the inhibiting ability of maleate vs. fumarate, siloxane formulations were prepared with 35 mole equivalents of diethyl maleate and diethyl fumarate, Table 2.

Diethyl fumarate gave rise to a broader exotherm than diethyl maleate and there were two well-resolved peaks in the DSC trace. It is possible that the first peak represented hydrogenation of the fumarate olefin bond; this is supported by the measured heats of reaction.

Work is in progress to find reactivity/activity relationships between platinum inhibitors and actual perfor-

Table 2
DSC analysis of inhibited, platinum-cured siloxane

Inhibitor	Onset (°C)	Peak (°C)	Heat (J g^{-1})
Dimethyl maleate	76	94	−31.4
Diethyl maleate	77	94	−29.8
Diethyl fumarate	64	(79), 96	(−6.8) −27.2

mance in command cure formulations.

3. Experimental

3.1. General

Reactions were carried out in air or in a Vacuum Atmospheres Dry Box. ^1H and ^{13}C NMR spectra were recorded in C_6D_6, on a GE QE-300 instrument at 300.15 and 75.48 MHz respectively. IR data was collected using a Mattson Instruments Model 6020 Galaxy Series FTIR. DSC data was collected using a Perkin–Elmer 7 Series Thermal Analysis System. GLCMS data were recorded using a Jeol SX 102 high resolution, double focusing magnetic sector instrument employing a 30 m DB 5 capillary column. FDMS measurements were made using a Jeol model HX 110 instrument. Reactions between platinum solutions and inhibitors were carried out by adding the inhibitor with an Eppendorf pipettor.

3.2. EXAFS

EXAFS measurement on Pt L_{III} edge, white line corresponding to 2p $3/2 \rightarrow 5d$ transition, was performed at beamline X9B, National Synchrotron Light Source, BNL. X-ray beam energy was tuned by a Si(220) fixed-exit double crystal monochromator, and harmonics was rejected using a Ni-coated mirror. Fluorescence signals were recorded by a Canberra 13-element Ge detector. Samples of about 300 ppm Pt concentration were kept at 100 K by a close-cycle He cryostat during the measurement. The energy resolution is about 1–2 eV in this energy range. Data were corrected for detector deadtime and analyzed by EDAP (a computer program developed by J. Dong). Back scattering amplitudes and phases of Pt, Si and C used in the refinement were extracted from the corresponding model compounds.

3.3. Preparation of solution A concentrate

Solution A was prepared as described previously by reacting H_2PtCl_6 with excess $M^{vi}M^{vi}$ to give an oil composed of $M^{vi}D_xM^{vi}$, $x = 0$–9, average $x = 1$, 13 wt.% Pt [13,19]. The concentrate was prepared by taking the yellow solution A and subjecting the oil to vacuum distillation, 45–55°C, 0.01 mm Hg for 5 h. The distillation of Solution A gave 53.9 g of a more viscous and dark-brown oil, 23.9 wt.% platinum.

3.4. Solution A + dimethyl fumarate

Solution A concentrate (0.177 g, 0.217 mmol Pt) was dissolved in 0.5 ml C_6D_6 followed by addition of dimethyl fumarate (0.125 g, 0.868 mmol), **2**. ^1H NMR: −0.46 (s), −0.35 (s), 0.15 (m), 0.2, 0.3, 3.26, 3.34, 4.2 (d of d, 16 Hz, 84 Hz), 4.57 (t, 30 Hz); ^{13}C NMR: −2.89, −2.31, 0.44, 1.34, 1.40, 51.06 (t, 89 Hz), 51.62, 68.47 (t, 56 Hz), 69.20 (t, 56 Hz), 70.11 (t, 42 Hz), 71.94 (t, 42 Hz), 133.99, 164.9, 169.74 (t, 21 Hz).

After NMR analysis, MD^HD^HM (0.355 μl, 1.09 mmol) was added and the NMR recorded, **5**. ^1H NMR: 0.09, 0.12, 0.14, 0.16, 0.21, 0.36, 0.53, 2.29, 2.4, 2.7, 3.26, 3.28, 3.48, 3.78, 4.89, 5.79; ^{13}C NMR: 0.3, 0.45, 0.82, 1.0, 1.39, 5.23, 6.04, 9.95, 28.81, 32.17, 33.10, 40.68, 41.03 (t, 15 Hz), 50.02, 51.52, 53.05, 53.25, 131.75, 131.94, 133.39, 139.46, 139.61, 139.81, 165.19, 178.74 (t, 24 Hz), 187.27, 188.53 (t, 20 Hz).

3.5. Solution A + dimethyl maleate, 3

Solution A concentrate (0.178 g, 0.219 mmol Pt) was dissolved in 0.5 ml C_6D_6 and then dimethyl maleate (109 μl, 0.875 mmol) was added. ^1H NMR: −0.32, 0.82, 0.14, 0.31, 3.41, 3.43, 3.93 (t, 33 Hz), 5.88; ^{13}C NMR: −2.39, −0.39, 1.33, 49.29 (t, 104 Hz), 51.62, 68.01 (t, 55 Hz), 70.23 (39 Hz), 129.89, 165.34, 169.27 (t, 19 Hz).

After recording the NMR data, $M^{vi}M^{vi}$ (0.1 ml, 4.36 mmol) was added. There was no change in the NMR other than the addition of the $M^{vi}M^{vi}$ resonances.

Solution A concentrate (0.289 g, 0.35 mmol) was dissolved in C_6D_6 (0.5 ml) and then dimethyl maleate was added (177 μl, 1.41 mmol) followed by addition of Et_3SiH (0.559 ml, 3.5 mmol).

3.6. Synthesis of $(PPh_3)Pt(M^{vi}M^{vi})$, 4

Solution A (5 g of a 5.5% Pt solution in xylene, 2.8 mmol) was combined with $M^{vi}M^{vi}$ (5.2 g, 28 mmol) and then PPh_3 (0.75 g, 2.8 mmol). The volatile components were removed in vacuo and then the [illegible] obtained was washed with hexanes to obtain 1 g **4** (55%). ^1H NMR: 7.28 (m, 15H), 2.35 (m, 4H), 2.02 (m, 2H), 0.22 (s, 6H), −0.41 (s, 6H); ^{13}C NMR: −1.35, 1.75, 47.25 (t of d, 57 Hz, 10 Hz), 52.78 (t of d, 77 Hz, 10 Hz), 128.34, 133.68 (q, 11 Hz), 135.56 (t, 16 Hz), 136.15 (t, 16 Hz). FDMS: 643 amu, platinum isotope envelope observed.

Compound **4** (0.209 g, 0.325 mmol) was dissolved in C_6D_6 (1 ml) and then dimethyl maleate (80 μl, 0.64 mmol) was added in the glove box. ^1H and ^{13}C NMR analysis at this point showed no change. MD^HD^HM (0.21 ml, 0.64 mmol) was then added to the solution of **4** and dimethyl maleate in the glove box. NMR analysis showed that no apparent reaction occurred. After exposure to air the yellow solution turned red.

3.7. Curable silicone formulation

A vinyl-stopped polymer, $M^{vi}D_xM^{vi}$ (10 g, 200 cps) was combined with platinum in the form of Solution A

Concentrate (150 ppm Pt final concentration, 8 μmol), inhibitor and a Si–H-containing co-polymer $MD^{H}_{2}D_{x}M$ ($x = 20$, 0.5 g). The inhibitors were added at a 35 : 1 mole ratio relative to platinum: dimethyl maleate (26.5 μl), diethyl maleate 45 μl), and diethyl fumarate (45.8 μl) respectively.

References

[1] B. Marciniec, J. Gulinski, W. Urbaniak and Z.W. Kornetka, in B. Marciniec (ed.), *Comprehensive Handbook on Hydrosilylation*, Pergamon, Oxford, 1992.

[2] V.B. Pukhnarevich, E. Lukevics, L.I. Kopylova and M.G. Voronkov, *Perspectives of Hydrosilylation*, Institute of Organic Synthesis, Riga, Latvia, 1992.

[3] I. Ojima, in S. Patai and Z. Rappaport (eds.), *The Chemistry of Organic Silicon Compounds*, Vol. 2, Wiley Interscience, New York, 1989, Chapter 25, pp. 1479–1526.

[4] D.A. Armitage, in G. Wilkinson et al. (eds.), *Comprehensive Organometallic Chemistry*, Vol. 2, Pergamon, Oxford, 1982, pp. 117–120.

[5] J.L. Speier, in F.G.A. Stone and R. West (eds.), *Advances in Organometallic Chemistry*, Vol. 17, Academic Press, New York, 1979, pp. 407–447.

[6] E. Lukevics, Z.V. Belyakova, M.G. Pomeransteva and M.G. Voronkov, *J. Organomet. Chem. Libr.*, *5* (1977) 1.

[7] C. Eaborn and R.W. Bott, in A.G. MacDiarmid (ed.), *The Bond to Carbon*, Marcel Dekker, New York, 1968.

[8] J.F. Harrod and A.J. Chalk, in I. Wender and P. Pino (eds.), *Organic Synthesis via Metal Carbonyls*, Vol. 2, Wiley, New York, 1977, pp. 673–703.

[9] W. Noll, *Chemistry and Technology of Silicones*, Academic Press, New York, 1968.

[10] J. Rich, J. Cella, L. Lewis, S. Rubinsztajn, J. Stein, N. Singh and J. Wengrovius, in *Kirk–Othmer: Encyclopedia of Chemical Technology*, Wiley, New York, 4th edn., 1996, in press.

[11] J. Stein, L.N. Lewis, K.A. Smith, and K.X. Lettko, *J. Inorg. Organomet. Polym.*, *1* (1991) 325.

[12] B.D. Karstedt, US Patent 3814730, 1974; *Chem. Abstr.*, *74*, 100519.

[13] L.N. Lewis, R.E. Colborn, H. Grade, J. Garold L. Bryant, C.A. Sumpter and R.A. Scott, *Organometallics*, *14* (1995) 2202.

[14] E.W. Abel, F.G.A. Stone and G. Wilkinson, *Comprehensive Organometallic Chemistry II: A Review of the Literature 1982–1994*, Pergamon, New York, 1995.

[15] L.N. Lewis, C.A. Sumpter and J. Stein, *J. Inorg. Organomet. Polym.*, in press.

[16] L.N. Lewis, C.A. Sumpter and M. Davis, *J. Inorg. Organomet. Polym.*, *5* (1995) 377.

[17] P.Y.K. Lo, US Patent 4774111, 1988; *Chem. Abstr.*, *110*, 77596.

[18] M.E. Grenoble and R.P. Eckberg, US Patent 4448815, 1984; *Chem. Abstr.*, *101*, 39988; P.Y.K. Lo, L.E. Thayer and A.P. Wright, US Patent 4783552, 1988; Ifipat AN: 1893417.

[19] L.N. Lewis, N. Lewis, and R.J. Uriarte, in W.R. Moser and D.W. Slocum (eds.), *Homogeneous Transition Metal Catalyzed Reactions*, Adv. Chem. Ser. 230, American Chemical Society, Washington, DC, 1992, p. 541.

[20] G. Chandra, P.Y. Lo, P.B. Hitchcock and M.F. Lappert, *Organometallics*, *6* (1987) 191–192.

[21] L.N. Lewis, J. Stein, K.A. Smith, R.P. Messmer, D.G. LeGrand and R.A. Scott, in B. Marciniec and J. Chojnowski (eds.) *Progress in Organosilicon Chemistry*, Gordon & Breach, Amsterdam, 1995, p. 263.

[22] P.B. Hitchcock, M.F. Lappert and N.J.W. Warhurst, *Angew. Chem. Int. Ed. Engl.*, *30* (1991) 438.

[23] M.F. Lappert and F.P.A. Scott, *J. Organomet. Chem.*, *482* (1995) C11.

[24] G. Beuter, O. Heyke and I.-P. Lorenz, *Z. Naturforsch. Teil B:*, *46* (1991) 1694.

[25] L.N. Lewis, *J. Am. Chem. Soc.*, *108* (1986) 743.

[26] C. O'Connor and G. Wilkinson, *Tetrahedron Lett.*, (1969) 137.