Synthesis and Structures of Zeise-type Complexes with Vinylsilane Ligands and Quantum Chemical Analysis of the Platinum–Vinylsilane Bonding

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Received March 4th, 2005.

Dedicated to Professor Herbert W. Roesky on the Occasion of his 70th Birthday

Abstract. Zeise-type complexes with vinylsilanes as π -ligands [K(18C6)][PtCl₃(η^2 -CH₂=CHX)] (X = SiMe₃, 4; SiPh₃, 5; Si(OMe)₃, 6; 18C6 = 18-crown-6) and [K(18C6)]₂[(PtCl₃)₂-{ η^2 , η^2 -(CH₂=CHSiMe₂)₂O}] (7) have been prepared by the reaction of [K(18C6)]₂[Pt₂Cl₆] (3) with the appropriate vinylsilanes. The identities of the complexes have been confirmed by NMR spectroscopy as well as for 4, 5 and (PPh₄)[PtCl₃{ η^2 -CH₂=CHSi(OMe)₃}] (6') also by single-crystal X-ray diffraction measurements. DFT calculations exhibited, that the coordination induced C=C bond

1 Introduction

Reactions with stoichiometric and catalytic formation or cleavage of silicium-element bonds in the coordination spheres of transition metals are of increasing interest to the preparative organosilicium chemistry [1, 2]. Platinum complexes may activate Si-C bonds where, in general, the tendency of cleavage is in the order $Si-C_{sp} > Si-C_{sp^2} > Si-C_{sp^3}$. Thus, the Si-C = bonds in alkynylsilanes are even susceptible towards hydrolysis in alkaline solutions [3] and the formation of platina- β -diketones [Pt₂{(COR)₂H}₂(μ -Cl)₂] from reactions of hexachloroplatinic acid and alkynylsilanes proceeds with the cleavage of $Si-C \equiv$ bonds [4]. Furthermore, in wet acetone a slow decomposition of K[PtCl₃(η^2 -CH₂= CHSiMe₃)] (1) yielding Zeise's salt and hexamethyldisiloxane was observed. This cleavage of the =CH-Si bond proved to be even catalytically [5]. Cleavage of Si-C bonds in vinyl- or alkynylsilanes by Zeise's salt or Zeise's dimer is reported to proceed via the formation of Me₃SiCl [3b, 6].

The single-crystal X-ray diffraction analysis of $[NBu_4][PtCl_3(\eta^2-CH_2=CHSiMe_3)]$ (1') exhibited a C=C bond length of 1.44(1) Å [7]. Based on the determination of the molecular structure of Si(CH=CH₂)Me₃ by gas-phase electron diffraction measurements (GED) (d(C=C) = 1.36(1) Å) [8], the coordination induced C=C bond lengthening was found to be 0.08 Å. This is much larger than the coordination induced bond lengthening of ethylene in

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lengthenings and the pyramidalization angles of the olefins in the vinylsilane complexes $[PtCl_3(\eta^2-CH_2=CHX)]^-$ (X = SiMe₃, **4c**; SiPh₃, **5c**; Si(OMe)₃, **6c**) are the same as in Zeise's anion $[PtCl_3(\eta^2-CH_2=CH_2)]^-$ (**8c**) while the amount of the π back-donation in the vinylsilane complexes **4c**-**6c** is higher than that in the ethylene complex **8c**.

Keywords: Vinylsilane complexes; Platinum complexes; DFT-calculations; Olefin bonding

Zeise's salt (0.04-0.06 Å) as shown by the comparison of the C=C bond lengths in K[PtCl₃(η^2 -CH₂=CH₂)]·H₂O (2) (neutron diffraction analysis; 1.375(4) Å) [9] with that in free ethylene (GED/IR: 1.336(3)-1.339(1) Å [10]; X-ray diffraction: 1.3124(3)-1.3142(3) Å [11]). Although these values must not be exaggerated due to uncertainties of the measurements, this may point to a strong activation of vinylsilanes by platinum(II). This receives further support from the structures of [PtX₂{Me₂(CH₂=CH)SiCH₂ECH₂Si- $(CH=CH_2)Me_2-\kappa^2 C, C', \kappa E$] (X = Br, E = Te; X = I, E = S) [12] having a coordinated and a non-coordinated vinylsilane group. In these complexes coordination induced C=C bond lengthenings of 0.08/0.13 Å were found. These two complexes and 1' are the only structurally characterized platinum(II) complexes with η^2 -CH₂=CHSiR₃ ligands. On the other hand, molecular structures of numerous platinum(II) complexes with $(\eta^2-CH_2=CH)$ - $Me_2SiOSiMe_2(\eta^2-CH=CH_2)$ ligands are known [13], showing a median of 1.415 Å for the C=C bond length (lower/ upper quartile: 1.400/1.430 Å; n = 39, n = number of observations) [14].

These findings give the background for our interest in the synthesis of Zeise-type complexes with vinylsilane ligands and their structural characterization. For the synthesis we used the reaction of $[K(18C6)]_2[Pt_2Cl_6]$ (3) [15] with vinylsilanes in methylene chloride. In an analogous way we succeeded to prepare not only an extended series of Zeise-type olefin complexes $[K(18C6)][PtCl_3(\eta^2-olefin)]$ [16] but also alkyne complexes of the type $[K(18C6)][PtCl_3(\eta^2-alkyne)]$ [17]. To gain insight into the nature of the bonding of the vinylsilane to the PtCl₃⁻ fragment quantum chemical calculations on the DFT level of theory were performed whereas different vinylsilanes $(Si(CH=CH_2)Me_3, Si(CH=CH_2)Ph_3, Si(CH=CH_2)(OMe)_3)$ have been considered.

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2 Results and Discussion

2.1 Syntheses

Reactions of the hexachlorodiplatinate $[K(18C6)]_2[Pt_2Cl_6]$ (3) with excess of the vinylsilanes $Si(CH=CH_2)Me_3$, Si(CH=CH₂)Ph₃, and Si(CH=CH₂)(OMe)₃ in methylene chloride at room temperature resulted with cleavage of the Pt-Cl-Pt bridges in the formation of Zeise-type olefin complexes 4-6 (Scheme 1). The analogous reaction with Me₂(CH₂=CH)Si-O-Si(CH=CH₂)Me₂ proceeded with the formation of the dinuclear platinum complex 7 where the divinyl disiloxane acts as a bridging μ -bis(η^2 -olefin) ligand (Scheme 1). All these reactions take advantage of the properties of the solvent (CH₂Cl₂) in which the crown ether adduct of the potassium hexachlorodiplatinate (3) is partly soluble. Furthermore, methylene chloride does not act as a concurrent donor for the vinylsilanes due to its low donor number (DN = 1 [18]) and may promote the cleavage of the Pt-Cl-Pt bridges due to its relatively high acceptor number (AN = 20.4 [18]). The complexes 4, 6, and 7 were formed in moderate to good yields (35-90 %). The reaction to form complex 5 (yield: 13 %) took more than two weeks and was accompanied by the formation of greater amounts of by-products. The identities of the complexes were confirmed by ¹H and ¹³C NMR spectroscopy and for 4 and 5 also by single-crystal X-ray diffraction analyses. In the case of the trimethylvinylsilane and trimethoxyvinylsilane complexes (4 and 6) the usage of $(PPh_4)_2[Pt_2Cl_6]$ (3') instead of 3 resulted in the formation of the requisite tetraphenylphosphonium complexes $(PPh_4)[PtCl_3(\eta^2-CH_2=CHSiR_3)]$ (R = Me, 4'; OMe, 6'). Complex 6' could be identified by X-ray diffraction analysis.

composition products. Analogously, a slow decomposition of K[PtCl₃(η^2 -CH₂=CHSiMe₃)] yielding Zeise's salt was observed [5]. Furthermore, cleavage of =C-Si bonds in vinylsilanes by catalytic amounts of Pt^{II} has been reported [3b, 6b].

2.2 NMR Spectroscopic Characterization

For the vinylic protons of complexes 4–7 spectra of higherorder were observed; chemical shifts and coupling constants given in Table 1 were obtained by spectrum simulation as ABC and ABX spin systems, respectively. As an example, in Figure 1 the experimental and simulated ¹H NMR spectra of 4 and 5 are shown. Whereas the 400 MHz spectrum of the trimethylvinylsilane complex 4 (Figure 1a) is clearly of higher order, the 500 MHz spectrum of the triphenylvinylsilane complex (Figure 1b) is a borderline case. In all cases the H,H-couplings between the vinyl protons are in the expected range: ${}^{3}J_{trans} > {}^{3}J_{cis} >> {}^{2}J_{gem}$.

Compared with the non-coordinated vinylsilanes the vinyl protons in the complexes 4–7 are high-field shifted. The coordination induced shifts (CIS; $\Delta \delta = \delta_{\text{coord.lig.}} - \delta_{\text{non-coord.lig.}}$) are between -0.97 and -1.44 ppm. In all four complexes the most high-field shifted proton has the lowest CIS. In the mononuclear complexes 4–6 the two olefinic carbon atoms shift upfield on coordination by about 60 ppm. This is higher than the CIS in the analogous complexes with non-functionalized olefins where the highfield shifts are between 40 and 55 ppm [16]. The coordination induced shifts in the dinuclear complex 7 (-46/-47 ppm) are in that range. Furthermore, coordination gives rise to a decrease in the ³J_{H,H} coupling constants by up to 5.3 Hz.



Scheme 1 Synthesis of Zeise-type complexes with vinylsilane ligands.

Complexes 4, 4', and 5 showed partial decomposition in solution (CDCl₃, CH₂Cl₂) that may be due to traces of water or HCl. The decomposition proceeded – at least in part – with cleavage of the =CH–Si bond and the formation of the anion of Zeise's salt, [PtCl₃(η^2 -CH₂=CH₂)]⁻ as shown by means of ¹H NMR spectroscopy and in an isolated case also by X-ray diffraction analysis of the decomposition product (PPh₄)[PtCl₃(η^2 -CH₂=CH₂)] (8). Although the quality of the data set was limited (see Experimental), the constitution of the complex could be determined unambiguously. In the case of the complex 4 Me₃Si–O–SiMe₃ and SiMe₃Cl were identified as de-

This may be due to the lengthening of the C–C double bonds upon coordination and in the case of the trans couplings also due to the decrease of the H–C–C–H dihedral angles as a consequence of the back-bending of the hydrogen atoms [19].

The molecular structure of 7 gives rise to expect three stereoisomers as shown in Figure 2. The coordination of one of the PtCl₃ moieties on the *re* side of the olefin and the other one on the *si* side results in the formation of the *meso* form. The coordination twice on the same side (either *re/re* or *si/si*) results in the formation of a pair of enantiomers (R, R and S, S, respectively) that are diastereomeric to

Table 1 ¹H NMR spectroscopic data obtained by spectrum simulation of higher-order multiplets of the vinylic protons in complexes $[K(18C6)][PtCl_3(\eta^2-CH_2=CHSiR_3)]$ (4-6) and in $[K(18C6)]_2[(PtCl_3)_2\{\eta^2,\eta^2-(CH_2=CHSiMe_2)_2O\}]$ (7) (δ in ppm, *J* in Hz).

	4 (R = Me)		5 (R = Ph)		$6 (\mathbf{R} = \mathbf{OMe})$		7	
	δ	$\Delta \delta^{(a)}$	δ	Δδ	δ	Δδ	Δ	Δδ
H ^{1 c)}	4.90	-1.24	5.52	-1.22	4.62	-1.14	4.88	-1.30
H^2	4.64	-1.27	4.92	-1.44	4.68	-1.38	4.63	-1.33
H^3	4.63	-1.02	4.88	-0.97	4.79	-1.12	4.62	-1.16
	^{n}J	ΔJ ^{b)}	^{n}J	ΔJ	^{n}J	ΔJ	^{n}J	ΔJ
$^{3}J_{\rm H}$ H trans	15.63	-4.79	15.29	-4.97	15.39	-5.28	15.56	-5.01
${}^{3}J_{\rm H\ H\ oic}$	11.27	-3.38	11.18	-3.42	11.45	-3.67	11.38	-3.49
${}^{2}J_{\rm H,H,gem}$	3.13	-0.60	2.99	-0.49	3.14	-0.65	3.18	-0.62

^{a)} $\Delta \delta = \delta$ (coordinated ligand) $- \delta$ (non-coordinated ligand) ^{b)} $\Delta J = {}^{n}J$ (coordinated ligand) $- {}^{n}J$ (non-coordinated ligand) ^{c)} Numbering scheme:



the *meso* form. Thus, as shown in the Figure 2, the siliciumbound methyl groups are no longer chemically equivalent. In accordance with this, in the ¹³C NMR spectrum four methyl carbon resonances were found. The shift difference a/b and c/d, respectively, is 1.0 ppm, whereas that between the two diastereomers (a/c and b/d, respectively) is very small (0.02 ppm). The signal intensity makes clear, that the complex formation is not diastereoselective. In the ¹H NMR spectrum three signals for the methyl groups were found: One broader signal at 0.49 ppm and two signals for the high-field shifted protons (0.32 ppm) with a shift difference of only 0.003 ppm.



Figure 2 Two diastereomeric forms of complex **7** due to *re/si* coordination (left, R, S isomer, *meso* form) and *re/re* coordination (right, R, R isomer). Symmetry related methyl groups are denoted with the same letter (a-d).

2.3 Structures

The structures of the vinylsilane complexes 4, 5, and 6' are shown in the Figures 3-5, selected structural parameters are presented in Table 2. Crystals of complex 4 consist of ion pairs ($[K(18C6)]^+/[PtCl_3(\eta^2-CH_2=CHSiMe_3)]^-$) with specific cation-anion interactions. The K⁺ ion has close contacts to the trans and to one of the cis chloro ligands of the trichloro(olefin)platinate anion (K…Cl1 3.290(2) Å, K…Cl2 3.185(2) Å). These distances are only slightly longer than those in the solid KCl (3.146 Å). There are no unusual contacts between these ion pairs. The shortest distance between non-hydrogen atoms is 3.446(7) Å (O6…C3'). Crystals of the triphenylvinylsilane complex 5 are built up analogously. The K…Cl contacts within the ion pair are 3.149(2) A (K···Cl2) and 3.320 (2) A (K···Cl1). The first one is even as long as those in the solid KCl (3.146 Å). There are no unusual contacts between these ion pairs. The shortest distance between non-hydrogen atoms is 3.28(1) Å (O6…C12'). Analogous ion pair formation via short K…Cl contacts has also been found in other olefin and alkyne complexes of the type [K(18C6)][PtCl₃(η^2 -olefin/alkyne)]. In the complex $(PPh_4)[PtCl_3\{\eta^2-CH_2=CHSi(OMe)_3\}]$ (6') no specific cation-anion interactions were found. Thus,



Figure 1 Experimental (bottom) and simulated (top) ¹H NMR spectrum of the vinyl region of a) complex 4 (R = Me; 400 MHz) and b) complex 5 (R = Ph; 500 MHz). # platinum satellites, * impurity.



Figure 3 Structure of $[K(18C6)][PtCl_3(\eta^2-CH_2=CHSiMe_3)]$ (4). Displacement ellipsoids are drawn at 30 % probability; H atoms were omitted for clarity.



Figure 4 Structure of $[K(18C6)][PtCl_3(\eta^2-CH_2=CHSiPh_3)]$ (5). Displacement ellipsoids are drawn at 30 % probability; H atoms were omitted for clarity.

the shortest contact between non-hydrogen atoms of the anion to a tetraphenylphosphonium cation is 3.385(8) Å (O1…C15'). The distance to another cation is only slightly longer (Cl3…C7' 3.428(5) Å).

The coordination geometry of the anions $[PtCl_3(\eta^2 CH_2 = CHSiR_3$]⁻ is as expected. The platinum atoms are square-planar coordinated by three chloro ligands and an olefin ligand that lies nearly perpendicular to the PtCl₃ plane (interplanar angles $79.8(4) - 85.7(3)^\circ$). The C=C bonds are slightly longer (1.398(8)-1.402(8) Å) than that in Zeise's salt (1.375(4) A [9]). To evaluate the coordination induced bond lengthening, these values have to be compared with the C=C bond lengths in non-coordinated vinylsilanes. These cover a broad range (structural unit CH₂=CHSiC₃: median: 1.313 Å; lower/upper quartile 1.277/1.329 Å; n = 26) and only few data are available for simple vinylsilanes (Si(CH=CH₂)₄: 1.316(2)-1.320(2) A, [20]; Si(CH=CH₂)Me₃: 1.36(1) Å [8]). Overall, on the basis of these data it is difficult to derive coordination induced bond lengthenings in these complexes. Furthermore, the co-



Figure 5 Structure of the anion $[PtCl_3{\eta^2-CH_2=CHSi(OMe)_3}]^$ in crystals of **6**'. Displacement ellipsoids are drawn at 30 % probability.

Table 2 Selected interatomic distances (in Å) and angles (in °) incomplexes [K(18C6)][PtCl_3(η^2 -CH_2=CHSiR_3)] (4, 5) and in(PPh_4)[PtCl_3{ η^2 -CH_2=CHSi(OMe)_3}] (6').

	4 (R = Me)	5 (R = Ph)	$6' \ (\mathbf{R} = \mathbf{OMe})$
Pt-Cl1	2.322(1)	2.331(2)	2.311(2)
Pt-Cl2	2.316(1)	2.293(2)	2.302(1)
Pt-Cl3	2.320(1)	2.300(2)	2.306(1)
Pt-C1	2.161(5)	2.154(7)	2.137(5)
Pt-C2	2.149(5)	2.134(6)	2.141(6)
C1-C2	1.398(8)	1.402(8)	1.402(8)
Si-C1	1.884(5)	1.861(6)	1.862(5)
Si-C3	1.874(5)	1.867(6)	$1.611(4)^{a}$
Si-C4	1.873(5)	1.889(7)	$1.640(5)^{b}$
Si-C5	1.876(5)	1.879(5)	$1.629(4)^{c}$
Si-C1-C2	127.0(4)	132.7(5)	130.2(4)
Cl2-Pt-Cl3	177.57(6)	178.95(6)	177.91(5)
Cl1-Pt-Cl2	89.68(5)	89.06(7)	89.75(5)
Cl1-Pt-Cl3	89.59(5)	90.89(7)	90.88(5)
K…Cl1	3.290(2)	3.320(2)	-
K…Cl2	3.185(2)	3.149(2)	-
Pt-C1-Si-C4	-155.9(3)	-164.8(3)	151.2(3) ^{d)}
Pt,Cl1,Cl2,Cl3/Pt,C1,C2e)	85.7(3)	79.8(4)	81.6(4)

 $^{a)}$ Si–O1. $^{b)}$ Si–O2. $^{c)}$ Si–O3. $^{d)}$ Pt–C1–Si–O2. $^{e)}$ Angle between least-square planes.

ordination induced back-bending of the substituents at the C=C carbon atoms in the complexes 4, 5, and 6' cannot be derived from the measurements: On the one side, the precision of the positions of the vinylic H atoms is too low. On the other side, quantum chemical calculations (see 2.4) indicate that the back-bending of the silyl substituents is also caused by steric effects; thus, it cannot be regarded to be a measure for the back-donation.

2.4 Quantum Chemical Calculations

In order to gain deeper insight into the nature of the sideon bonding of the vinylsilanes to platinum quantum chemical calculations on the DFT level of theory have been performed. To find out an appropriate hybrid functional and basis sets, various calculations of the anion of Zeise's salt, $[PtCl_3(\eta^2-C_2H_4)]^-$ (8c), and of Si(CH=CH₂)₄ have been performed. Comparison with the reported crystal structures of Zeise's salt [9] and tetravinylsilane [20] revealed, that the hybrid functional MPW1PW91 [21], a triple- ζ valence basis set for Pt with a polarization function added (TZVP) as provided by Ahlrichs and co-workers [22] and split-valence basis sets with a polarization function added for the other atoms (6-31G*) give a good fit between calculated and experimental values (see 3.4). The structures of the anions $[PtCl_3(\eta^2-CH_2=CHSiR_3)]^-$ (R = Me, 4c; Ph, 5c, OMe, 6c) along with the structure of Zeise's anion 8c for comparison are shown in the Figure 6. Selected geometric parameters are given in Table 3.

In general, the calculated and experimentally found structures are in a good agreement. The slightly shorter Pt-Cl bonds trans to the olefin ligands over those cis to the olefin ligands ($\Delta 0.003-0.014$ Å) can be rationalized in terms of the trans influence olefin > Cl⁻ [23] and antibonding Pt(d_{π})-Cl(p_{π}) interactions [24]. Whereas the ethylene ligand in **8c** was found to be perpendicular to the complex plane (exp.: 89.0°; calcd. from data given in [9]), in the vinylsilane complexes **4c**-**6c** the interplanar angles between the complex plane PtCl₃ and the PtC₂ plane are between 83.9 and 85.4° (exp.: 79.8(4)-85.7(3)°).

Table 3 Calculated structural parameters of vinylsilane platinate complexes $[PtCl_3(\eta^2-CH_2=CHSiR_3)]^-$ (4c-6c) and of Zeise's anion $[PtCl_3(\eta^2-CH_2=CH_2)]^-$ (8c) for comparison (interatomic distances in Å, angles in °). In parentheses the requisite values of the non-coordinated olefins (calculated on the same level of theory) are given.

	8c	$\frac{4c}{(R = Me)}$	$ \begin{array}{l} \mathbf{5c} \\ (\mathbf{R} = \mathbf{Ph}) \end{array} $	$\frac{6c}{(R = OMe)}$
 C1-C2	1 402	1 408	1 410	1 408
01 02	(1, 328)	(1,336)	(1,336)	(1, 337)
Si-C1	_	1.889	1.888	1.865
		(1.878)	(1.876)	(1.852)
Pt-C1	2.133	2.168	2.160	2.155
Pt-C2	2.133	2.136	2.131	2.132
Pt-Cl1	2.348	2.345	2.340	2.345
Pt-Cl2	2.355	2.359	2.349	2.355
Pt-Cl3	2.355	2.353	2.354	2.348
Cl2-Pt-Cl3a)	177.81	177.70	178.23	178.27
Pt,Cl1,Cl2,Cl3/Pt,C1,C2b)	90.00	83.93	84.54	85.44
$C1,H1,Si/C1-C2^{c}$	16.97 ^{d)}	20.12	23.65	23.09
	(0.00)	(0.00)	(0.47)	(0.22)
C2,H2,H3/C1-C2 ^{c)}	17.10	17.12	17.56	17.69
	(0.00)	(0.00)	(0.30)	(0.06)
\angle (Pt-C1-Si) - \angle (Pt-C1-H1)	0 ^{e)}	15	19	14
\angle (Pt-C2-H3) - \angle (Pt-C2-H2)	0	1	2	1

^{a)} All angles Cl_{trans} -Pt- Cl_{cis} are between 89.82 and 91.09°. ^{b)} Angles between least-square planes. ^{c)} Pyramidalization angle α : angle between the least-square plane (CH₂ and CHSi, respectively) and the C1-C2 axis. ^{d)} C1,H1,H4/C1-C2. ^{c)} \angle (Pt-C1-H4) – \angle (Pt-C1-H1).



Figure 6 Calculated equilibrium structures of $[PtCl_3(\eta^2-CH_2=CHX)]^-$: a) $X = SiMe_3$, 4c; b) $X = SiPh_3$, 5c; c) $X = Si(OMe)_3$, 6c; d) X = H, 8c.

As generally found in complexes having substituted olefin ligands [25], the Pt-C1 bonds are longer than the Pt-C2 bonds (Δ 0.023-0.032 Å). The coordination induced lengthening of the C=C bonds in the vinylsilane complexes 4c-6c and in the ethylene complex 8c are the same (0.071 - 0.074 A). Furthermore, for the back-bending of the olefin substituents, measured by the pyramidalization angle α (C2,H2,H3/C1-C2, see Table 3), were also found only minor differences $(17.1-17.7^{\circ})$. On the other hand, the pyramidalization angles C1,H1,Si/C1-C2 are slightly larger $(20.1-23.7^{\circ})$. But these angles cannot be regarded as a proper measure for the back-donation because the SiR₃ groups are more strongly back-bended than the hydrogen atoms H1 (\angle (Pt-C1-Si) – \angle (Pt-C1-H1) = 14-19°; for comparison: \angle (Pt-C2-H2) - \angle (Pt-C2-H3) = 1-2°, see Table 3). This could account for a larger back-donation from platinum to C1 (compared with C2) or to a steric hindrance between the bulky SiR₃ groups and the PtCl₃ moiety.

The bond dissociation energies D_e of the olefin ligands in the complexes 4c-6c and 8c

 $[PtCl_3(\eta^2\text{-}CH_2\text{=}CHX)]^- \rightarrow [PtCl_3]^- + CH_2\text{=}CHX$

were found to be 34.8 (8c, X = H) > 31.2 (4c, X = SiMe₃) > 30.2 (6c, X = Si(OMe)₃) > 24.2 (5c, SiPh₃) (values in kcal/mol; BSSE and ZPE corrected). The value calculated for 8c is in good agreement with other calculations [24, 26]. The partitioning of the bond dissociation energy D_e into a preparation term (ΔE_{prep}) and an instantaneous interaction term (ΔE_{int}) (see Ref. [27] for an explanation of the fundamental steps) shows, that the lowering of D_e from 8c to 5c is mainly caused by increasing preparation energies in the same sequence (Table 4). This can be rationalized in terms of the increasing bulkiness of the substituents H < SiMe₃ < Si(OMe)₃ < SiPh₃.

The mode of bonding of the vinylsilane ligands was examined by means of the charge decomposition analysis (CDA) of Frenking [28]. As it is clear for Zeise's salt, the low residual terms (Table 4) give evidence that also the analogous vinylsilane complexes 4c-6c can be discussed in terms of the Dewar-Chatt-Duncanson model [29]. The ratio d/b between the donation (d) and back-donation (b) proved to be in the vinylsilane complexes significantly smaller than in Zeise's anion (0.97-1.06 versus 1.25). The reason is clearly the higher $Pt \rightarrow vinylsilane back-donations$ in 4c-6c compared with $Pt \rightarrow ethylene$ back-donation in 8c. This is also confirmed by the electron populations of the π^* -orbitals of the olefins (P_{π^*}) obtained by NBO analysis [30], although the difference in the back-donation between the vinylsilane complexes 4c-6c on the one side and the ethylene complex 8c on the other side is smaller in this analysis. The higher degree of the π back-donation in 4c-6c is neither reflected in C=C bond lengthening (Δd : 0.071 - 0.074 Å in **4c**-6c versus 0.074 Å in **8c**) nor in the pyramidalization of the olefins (α : 17.1–17.7° in 4c–6c versus 17.0/17.1° in 8c) upon coordination. It is worth men**Table 4** Bond characteristics of vinylsilanes in Zeise-type complexes $[PtCl_3(\eta^2-CH_2=CHX)]^-$ (X = SiMe₃, 4c; SiPh₃, 5c; Si(OMe)₃, 6c) and in the parent complex 8c (X = H) for comparison (D_e = bond dissociation energy, ΔE_{int} = instantaneous interaction energy, ΔE_{prep} = preparation energy, all energies in kcal/mol; P_{π}/P_{π^*} = population of the π/π^* orbitals of the olefin ligands obtained by NBO analysis, values in electrons).

	8c (X = H)	$ \begin{array}{l} \mathbf{4c} \\ (\mathbf{X} = \operatorname{SiMe}_3) \end{array} $	$5c (X = SiPh_3)$	$ \begin{array}{l} \mathbf{6c} \\ (X = Si(OMe)_3) \end{array} $
D _e ^{a)}	37.6	33.3	25.9	32.2
$D_e^{(a) b)}$	34.8	31.2	24.2	30.2
$\Delta E_{int}^{a)}$	-48.7	-48.2	-47.7	-51.2
$\Delta E_{\rm prep}$	11.1	14.9	21.8	19.0
prop	Char	ge decomposit	tion	
donation (d)	0.369	0.347	0.356	0.373
back-donation (b)	0.295	0.350	0.368	0.352
repulsive	-0.626	-0.691	-0.717	-0.706
polarization				
residual term	-0.013	-0.018	-0.021	-0.027
d/b	1.25	0.99	0.97	1.06
]	NBO analysis		
P_{π} (NBO) ^{c)}	1.629 (2.000)	1.636 (1.972)	1.640 (1.967)	1.622 (1.967)
$P_{\pi^*}^{(\text{NBO})^{c)}}$	0.347 (0.000)	0.354 (0.013)	0.365 (0.012)	0.356 (0.010)

^{a)} BSSE corrected. ^{b)} ZPE corrected. ^{c)} Values of the noncoordinated olefins are given in parentheses.

tioning that recently *Kim* et al. [31] have shown that in metal-olefin complexes the electron population in π^* -antibonding orbitals (P_{π^*}) of olefin ligands is more correctly used to evaluate the degree of back-bonding than the coordination induced bond lengthening, because the latter one is caused by the degree of π -back-bonding *and* the degree of σ -bonding.

The NBO analyses of the noncoordinated olefins (calculated on the same level of theory) show for the vinylsilanes a reduced population of the π -orbitals (P_{π} : 1.967–1.972) and a partial population of the π^* -orbital (P_{π^*} : 0.010–0.013) (Table 4). This indicates hyperconjugative interactions between the π system and Si–C/Si–O bonds. In the complexes **4c–6c** one of the substituents on Si is nearly antiperiplanar to the Pt–C1 bonds (Pt–C1–Si–C4 –154.3/–151.8° **4c/5c**; Pt–C1–Si–O2 155.0°, **6c**; see Figure 6). These Si–C/Si–O bonds are significantly longer (0.013–0.027 Å) than the other ones, indicating hyperconjugative interactions. This may also exert influence on the Pt \rightarrow vinylsilane back-donation.

3 Experimental

3.1 General

All reactions were performed under Ar atmosphere using standard Schlenk techniques. Solvents were dried (Et₂O and thf over Nabenzophenone, CHCl₃, CDCl₃ and CH₂Cl₂ over CaH₂) and distilled prior to use. ¹H and ¹³C NMR spectra were recorded on Varian Gemini 200, VXR 400, and Unity Inova 500 NMR spectrometers. Chemical shifts are relative to CHCl₃ ($\delta = 7.24$) and CDCl₃ ($\delta = 77.0$) as internal references and Si(CH₃)₄ in CDCl₃ ($\delta = 0$) as external reference. If necessary, assignments of NMR signals were revealed by running spectra in APT mode. The NMR spectroscopic investigations of complexes 4–7 were performed in melted NMR tubes. IR spectra were recorded on a Galaxy FT-IR spectrometer Mattson 5030 using CsBr pellets. Microanalyses were performed by the University of Halle microanalysis laboratory using CHNS-932 (LECO) and Vario EL (elementar Analysensysteme) elemental analysers. The complex $[K(18C6)]_2[Pt_2Cl_6]$ (3) was synthesized according to a published method [15], $(PPh_4)_2[Pt_2Cl_6]$ (3') was prepared as reported in [32]. All other chemicals were commercially available.

3.2 Syntheses

3.2.1 Preparation of $[K(18C6)][PtCl_3(\eta^2-CH_2=CHSiMe_3)]$ (4)

To a suspension of $[K(18C6)]_2[Pt_2Cl_6]$ (3) (121 mg, 0.1 mmol) in CH₂Cl₂ (3 ml) Si(CH=CH₂)Me₃ (112 mg, 1.1 mmol) was added via a syringe and the reaction mixture was stirred overnight. The volume of the resulting yellow solution was reduced in vacuo to 1 ml, the precipitate was filtered off, and diethyl ether (5 ml) was added slowly to the clear filtrate. The crystals formed were filtered, washed with diethyl ether (2 × 1 ml), and dried briefly in vacuo.

Yield: 63 mg (45 %); m.p. 80-84 °C (dec.). Anal. Calc. for C₁₇H₃₆Cl₃KO₆PtSi (705.08): C, 28.96; H, 5.15; Cl, 15.08. Found: C, 29.29; H, 5.14; Cl, 14.55 %.

IR (CsBr): v 1472 (w), 1455 (w), 332 (w) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 0.26 (s+d, ²J_{Si,H} = 6.64 Hz, 9H, (CH₃)₃Si), 3.66 (s, 24H, 18C6), 4.5–4.8 (m+d, br, ²J_{Pt,H} = 64 Hz, 2H, CH₂=CHSi), 4.8–5.0 (m+d, br, ²J_{Pt,H} = 64 Hz, 1H, CH₂=CHSi). ¹³C NMR (100 MHz, CDCl₃, APT mode): δ = 0.7 (s, (CH₃)₃Si), 70.1 (s, 18C6), 73.5 (s, CH₂=CHSi), 81.4 (s, CH₂=CHSi).

Repetition of NMR measurements after 3 d revealed partial decomposition. Product composition (from ¹H NMR spectrum): [K(18C6)][PtCl₃(η^2 -CH₂=CHSiMe₃)] (4): [K(18C6)][PtCl₃(η^2 -CH₂=CH₂)] (8') : SiMe₃Cl (9) : (Me₃Si)₂O (10) \approx 33 % : 22 % : 27 % : 16 %.

¹H NMR (200 MHz, CDCl₃): $\delta = 0.04$ (s, 10), 0.27 (s, Si(CH₃)₃, 4), 0.41 (s, 9), 3.67 (s, 18C6), 4.46 (s+d, ²J_{Pt,H} = 64.74 Hz, CH₂=CH₂, 8'), 4.6–5.1 (m, SiCH=CH₂, 4). ¹³C NMR (125 MHz, CDCl₃): $\delta = -2.3$ (s), -1.7 (s), -0.5 (s), 0.5 (s+d, ¹J_{Si,C} = 53.2 Hz, (CH₃)₃Si, 4), 1.9 (s, 10), 3.2 (s+d, ¹J_{Si,C} = 57.6 Hz, 9), 64.1 (s), 68.1 (s+d, ²J_{Pt,C} = 191.9 Hz, CH₂=CH₂, 8'), 70.1 (s, 18C6), 73.4 (s+d, ¹J_{Pt,C} = 189.5 Hz, CH₂=CHSi, 4), 81.4 (s+d, ¹J_{Pt,C} = 185.2 Hz, CH₂=CHSi, 4), 81.2 (s, 9).

An analogous procedure, using $(PPh_4)_2[Pt_2Cl_6]$ (3') instead of 3, resulted in the formation of $(PPh_4)[PtCl_3(\eta^2-CH_2=CHSiMe_3)]$ (4').

¹H NMR (400 MHz, CDCl₃): $\delta = 0.07$ (s+d, ² $J_{Si,H} = 6.64$ Hz, 9H, SiCH₃), 4.25–4.52 (m+d, br, ² $J_{Pt,H} = 62.7$ Hz, 2H, CH₂=CHSi), 4.54–4.81 (m, 1H, CH₂=CHSi), 7.48–7.54 (m, 8H, *o*-CH), 7.66–7.71 (m, 8H, *m*-CH), 7.76–7.81 (m, 4H, *p*-CH). ¹³C NMR (100 MHz, CD₂Cl₂): $\delta = 0.7$ (s, CH₃Si), 73.2 (s, CH₂=CHSi), 80.4 (s, CH₂=CHSi), 117.9 (d, ¹ $J_{PC} = 89.8$ Hz, *i*-C), 131.0 (d, ³ $J_{PC} = 12.9$ Hz, *m*-C), 134.8 (d, ² $J_{PC} = 10.3$ Hz, *o*-C), 136.1 (d, ⁴ $J_{PC} = 3.0$ Hz, *p*-C). ²⁹Si NMR (100 MHz, CDcl₃): $\delta = -0.8$ (s).

From the mother liquor of this experiment, well-shaped crystals of $(PPh_4)[PtCl_3(\eta^2-CH_2=CH_2)]$ (8) suitable for single-crystal X-ray measurement were obtained.

3.2.2 Preparation of $[K(18C6)][PtCl_3(\eta^2-CH_2=CHSiPh_3)]$ (5)

A mixture of $[K(18C6)]_2[Pt_2Cl_6]$ (3) (365 mg, 0.30 mmol) and $Si(CH=CH_2)Ph_3$ (1.0 g, 3.5 mmol) in CH_2Cl_2 (10 ml) was stirred at room temperature for 17 days. The resulting dark red solution was concentrated in vacuo to 3 ml and diethyl ether (3 ml) was

added. The brown precipitate was filtered off and discarded. Then the filtrate was concentrated to 3 ml and treated with diethyl ether (3 ml) resulting in a brown precipitate that was filtered off and discarded again. This procedure was repeated two times until a yellow precipitate (5) could be isolated. This was washed with diethyl ether $(2 \times 2 \text{ ml})$ and dried briefly in vacuo.

Yield: 70 mg (13 %); m.p. 75 °C (dec.).

IR (CsBr): v 3067 (w), 2898 (m), 1472 (w), 1428 (m), 1351 (m), 1284 (w), 1249 (m), 1111 (s), 963 (m), 837 (w), 702 (m), 511 (m), 490 (w) cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ = 3.54 (s, 24H, 18C6), 4.86–4.94 (m, 2H, SiCH=CH₂), 5.49–5.54 (m, 1H, SiCH=CH₂), 7.27–7.82 (m, C₆H₅). ¹³C NMR (125 MHz, CDCl₃): δ = 69.8 (s, 18C6), 72.7/73.6 (s/s, SiCH=CH₂/SiCH=CH₂), 17.5/129.0/135.3/136.8 (s/s/s/s, C₆H₅). ²⁹Si NMR (100 MHz, CDCl₃): δ = -16.2 (s).

Further signals indicate the presence of non-reacted Si(CH= CH₂)Ph₃ (ca. 27 %) and an impurity of [K(18C6)][PtCl₃(η^2 -CH₂= CH₂)] (8') (ca. 3 %):

¹H NMR (500 MHz, CDCl₃): δ = 4.46 (s+d, ²J_{Pt,C} = 63.25 Hz, **8**'), 6.67 (dd, ³J_{H,H, trans} = 20.17 Hz, ³J_{H,H, cis} = 14.67 Hz, 1H, Ph₃SiCH=CH₂), 7.78 (dd, ³J_{H,H, trans} = 20.17 Hz, ²J_{H,H} = 3.67 Hz, 1H, Ph₃SiCH=CHH, *cis* to SiPh₃), 6.29 (dd, ³J_{H,H, cis} = 14.67 Hz, ²J_{H,H} = 3.67 Hz, 1H, Ph₃SiCH=CHH, *cis* to SiPh₃), 6.29 (dd, ³J_{H,H, cis} = 14.67 Hz, ²J_{H,H} = 3.67 Hz, 1H, Ph₃SiCH=CH=CHH, *trans* to SiPh₃). ¹³C NMR (125 MHz, CDCl₃): δ = 67.8 (s, **8**'), 127.9/ 129.6/136.0 (s/s/s, C₆H₅Si), ²⁹Si NMR (100 MHz, CDCl₃): δ = -17.3 (s, Ph₃SiCH=CH₂)

3.2.3 Preparation of $[K(18C6)][PtCl_3\{\eta^2-CH_2=CHSi(OMe)_3\}]$ (6)

To $[K(18C6)]_2[Pt_2Cl_6]$ (3) (220 mg, 0.18 mmol) in CH₂Cl₂ (6 ml) Si(CH=CH₂)(OMe)₃ (590 mg, 4.0 mmol) was added and stirred overnight. Then the solution was concentrated in vacuo to 3 ml. The brown precipitate was filtered off and to the yellow filtrate diethyl ether (3 ml) was added dropwise. The resulting pink precipitate was filtered off, the clear pale yellow filtrate was concentrated in vacuo to 1 ml. The product was obtained by adding diethyl ether (10 ml) to the solution. The filtered product was washed with diethyl ether (3 × 2 ml) and dried briefly in vacuo.

Yield: 95 mg (35%); m.p. 90–92 °C (dec.). Anal. Calc. for $C_{17}H_{36}Cl_3KO_9PtSi$ (753.08): C, 27.11; H, 4.82; Cl, 14.12. Found: C, 26.41; H, 4.95; Cl, 13.27%.

IR (CsBr): v 2096 (m), 1473 (w), 1351 (s), 1107 (s), 963 (s) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ = 3.63 (s, 24H, 18C6), 3.69 (s, 9H, OCH₃), 3.98–4.85 (m, 3H, CH₂=CHSi). ¹³C NMR (100 MHz, CDCl₃): δ = 51.1 (s, OCH₃), 68.1 (s, CH₂=CHSi), 70.1 (s, 18C6), 74.4 (s, CH₂=CHSi).

In a similar procedure, $(PPh_4)_2[Pt_2Cl_6]$ (3') was used instead of 3. From the mother liquor of this experiment well-shaped crystals of $(PPh_4)[PtCl_3\{\eta^2-CH_2=CHSi(OMe_3)\}]$ (6') suitable for single-crystal X-ray measurement could be obtained.

3.2.4 Preparation of $[K(18C6)]_2[(PtCl_3)_2\{\eta^2,\eta^2-(CH_2=CHSiMe_2)_2O\}]$ (7)

A mixture of $[K(18C6)]_2[Pt_2Cl_6]$ (3) (100 mg, 0.08 mmol) and $O[Si(CH=CH_2)Me_2]_2$ (380 mg, 2,0 mmol) in CH_2Cl_2 (3 ml) was stirred overnight at room temperature. Then the clear solution was concentrated in vacuo to 1 ml and the precipitate filtered off. To the clear yellow filtrate diethyl ether (10 ml) was added dropwise, the precipitate was filtered, washed with diethyl ether (2 × 2 ml) and dried briefly in vacuo.

Yield: 100 mg (90 %); m.p. 99 °C (dec.).

IR (CsBr): v 2898 (m), 2826 (w), 1626 (w), 1473 (w), 1453 (w), 1351 (m), 1250 (m), 1109 (s) 963 (m), 838 (m), 800 (m) cm⁻¹. ¹H NMR (400 MHz,

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CDCl₃): $\delta = 0.323$ (s, 3H, SiC*H*₃), 0.326 (s, 3H, SiC*H*₃), 0.49 (s, 6H, SiC*H*₃), 3.63 (s, 48H, 18C6), 4.60–4.65 (m, 4H, C*H*₂=CHSi), 4.85–4.92 (m, 2H, CH₂=C*H*Si). ¹³C NMR (100 MHz, CDCl₃, APT mode): $\delta = 2.48$ (s, SiC*H*₃), 2.50 (s, SiC*H*₃), 3.48 (s, SiC*H*₃), 3.50 (s, SiC*H*₃), 70.1 (s, 18C6), 73.1 (s, C*H*₂= CHSi), 80.1 (s, CH₂=CHSi). ²⁹Si NMR (99 MHz, CDCl₃): $\delta = 0.1$ (s).

3.3 X-ray structure determinations

Crystals suitable for X-ray diffraction analyses were grown from mother liquors at room temperature by slow addition of diethyl ether to a solution of the complexes in dichloromethane (4, 6') and by addition of pentane to a solution of 5 in acetone, respectively. Intensity data were collected on a STOE IPDS (4, 6') and a STOE STADI IV (5) diffractometer, respectively, using graphite monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å) at 220(2) K (4, 6') and 213(2) K (5), respectively. A summary of the crystallographic data, the data collection parameters and the refinement parameters is given in Table 5. Absorption correction for 5 was applied using ψ -scans ($T_{\min}/T_{\max} = 0.12/0.32$) and numerically for 4 ($T_{\min}/T_{\max} = 0.32/0.72$) and 6' ($T_{\min}/T_{\max} = 0.33/0.62$). The structures were solved by direct methods with SHELXS-97 [33] and refined using full-matrix least-squares routines against F^2 with SHELXL-97 [33]. Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms with isotropic displacement parameters. The positions of hydrogen atoms in 4 and 6' were found in the difference Fourier map except for the H atoms of the Me₃Si group and on C15 in 4 that were added to the model in calculated positions according to the riding model. In 5 all positions of H atoms were calculated (riding model) except those of the vinylic group (H1a/H1b, H2) that were found in the difference Fourier map. H1a/H1b were freely refined sharing the same distance and isotropic displacement parameters. Crystallographic data (excluding structure factors) for these structures have been deposited at the Cambridge Crystallographic Data Center (CCDC) as Supplementary Publication Nos. CCDC-281856 (4), CCDC-281857 (5), and CCDC-281858 (6'). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax. (internat.) +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk). Crystallographic data for $(PPh_4)[PtCl_3(\eta^2-CH_2=CH_2)]$ (8): Empirical formula $C_{26}H_{24}Cl_3PPt$,

 $M_r = 668.86$, monoclinic, $P2_1/a$, a = 25.448(4) Å, b = 7.1759(7) Å, c = 13.265(2) Å, $\beta = 91.29(2)^\circ$, V = 2421.7(6) Å³, Z = 4, μ (Mo K α) = 6.204 mm⁻¹, F(000) = 1296, θ range 2.19–25.00°, refln. coll. 9933, data/restraints/parameter 4027/1/280, $R_1 = 0.0543$ ($I > 2\sigma(I)$), $wR_2 = 0.1651$ (all data).

3.4 Computational details

All DFT calculations were performed by employing the Gaussian98 program package [34]. With various hybrid functionals and basis sets the structures of the anion of Zeise's salt (8c) and tetravinylsilane were optimized [35]. Comparison with the experimentally found structures K[PtCl₃(η^2 -C₂H₄)]·H₂O (neutron diffraction analysis) [9] and Si(CH=CH₂)₄ (single-crystal X-ray diffraction measurement) [20] revealed that the functional BHandHLYP as implemented in Gaussian98 proved to be the best to describe the structural parameters of tetravinylsilane, whereas the functional LSDA [36] performed well in describing the bond lengths in Zeise's anion. A functional satisfyingly describing both, the free vinylsilane ligand as well as the organometallic compound, was found to be Barone and Adamo's Becke-style one parameter functional using modified Perdew-Wang exchange and Perdew-Wang 91 correlation (MPW1PW91) [21]. A triple- ζ valence basis set was used for Pt with a polarization function added (TZVP) as provided by Ahlrichs and co-workers [22]; for its core orbitals an effective core potential with consideration of relativistic effects has been used [37]. For all atoms split-valence basis sets with a polarization function added were used (6-31G*). More extensive basis sets have been tested with little effect on the quality of the structure. Only TZVPP basis sets on all atoms gave significantly better results but with respect to the size of the molecules to be calculated this is inappropriate due to limited computer resources. All systems have been fully optimized without any symmetry restrictions. The resulting geometries were characterized as equilibrium structures by the analysis of the force constants of normal vibrations [35]. Electron populations were obtained by the natural bond orbital (NBO) analysis as implemented in Gaussian98 [38]. The charge decomposition analyses (CDA) were performed with the program CDA2.1 by Dapprich and Frenking [39].

 Table 5
 Crystallographic and data collection parameters for 4, 5, and 6'.

	4	5	6'
Empirical formula	C17H36Cl3KO6PtSi	C32H42Cl3KO6PtSi	C29H32Cl3O3PPtSi
$M_{\rm r}$	705.09	891.29	789.05
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a /Å	7.633(2)	13.538(1)	12.908(2)
b /Å	22.294(4)	15.732(1)	7.449(1)
c /Å	16.268(3)	18.280(3)	32.311(6)
β /°	100.99(2)	109.20(2)	95.54(2)
$V/Å^3$	2717.4(9)	3676.7(8)	3092.2(9)
Ζ	4	4	4
$D_{\rm calc} / {\rm g \ cm^{-1}}$	1.723	1.610	1.695
μ (Mo K α) /mm ⁻¹	5.683	4.219	4.916
F(000)	1392	1776	1552
Θ range /°	2.23-26.04	1.64-24.99	1.93-25.06
Refln. collected	21152	5776	16351
Refln. obs. $[I > 2\sigma(I)]$	4356	4318	4513
Refln. independent (R_{int})	5267 (0.0764)	4725 (0.0244)	5350 (0.0508)
Data/restraints/parameters	5267 / 0 / 366	4725 / 1 / 407	5350 / 0 / 451
Goodness-of-fit on F^2	1.049	1.018	1.079
$R_1, wR_2[I > 2\sigma(I)]$	0.0312, 0.0736	0.0283, 0.0737	0.0301, 0.0756
R_1, wR_2 (all data)	0.0413, 0.0774	0.0332, 0.0801	0.0385, 0.0804
Largest difference peak and hole /e $Å^{-3}$	1.012 and -1.407	0.541 and -1.155	0.839 and -0.923

Acknowledgements. The authors gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft and Merck KGaA (Darmstadt) for gifts of chemicals.

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