Synthesis and structural characterisation of platinum silasesquioxane complexes

Hendrikus C. L. Abbenhuis,*[a] Andrew D. Burrows,*[b] Huub Kooijman,[c] Martin Lutz,[c] Mark T. Palmer,[b] Rutger A. van Santen[a] and Anthony L. Spek[c]

[a] *Schuit Institute of Catalysis, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands. E-mail: H.C.L.Abbenhuis@tue.nl*

[b] *Dept. of Chemistry, University of Bath, Claverton Down, Bath, UK BA2 7AY. E-mail: a.d.burrows@bath.ac.uk*

[c] *Bijvoet Centre for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

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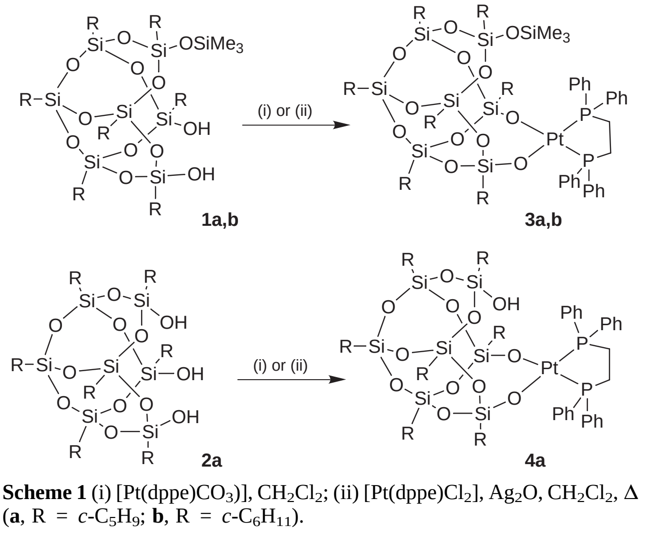
The reaction of partially condensed silasesquioxanes of the type [$R^1_7Si_7O_9(OH)_2(OR^2)$] (R^1 = *c*-C_5H_9, *c*-C_6H_{11}; R^2 = H, $SiMe_3$) with either [Pt(dppe)(CO_3)] or [Pt(dppe)Cl_2]/Ag_2O leads to the formation of [$R^1_7Si_7O_9(OR^2)O_2Pt$(dppe)], crystallographically characterised for R^1 = *c*-C_5H_9; R^2 = $SiMe_3$, providing unprecedented routes to late transition metal silasesquioxane complexes.

Currently, metallasilasesquioxanes are considered as the best soluble models for silica-supported transition metal species and an increasing number of examples of *early* transition metal compounds based on these ligands is being reported.[1] In contrast, metallasilasesquioxanes involving *late* transition metals are considerably rarer, and to date no such examples of mononuclear platinum group complexes have been characterised crystallographically. Transmetallation reactions have briefly been reported to give platinum silasesquioxane complexes,[1] though no experimental details were published and the reported transmetallations suffer from requiring the use of thallium or tetraalkylstibonium intermediates. Here we detail two simple routes to platinum silasesquioxane complexes and present the first example of an X-ray single crystal structure of a mononuclear platinum metal silasesquioxane complex.

Platinum silasesquioxane complexes can be conveniently prepared (Scheme 1) by utilising the reactivity of the acidic silasesquioxane silanol groups[2] with the carbonate functionality in [Pt(dppe)(CO_3)] [dppe = bis(diphenylphosphino)ethane].[3] In all cases the reactions are slow with full conversion only occurring after several days, but yields are good with no by-products observed.† $^{31}P\{^1H\}$ NMR spectroscopy provides a useful method for following the reactions, and resonances for the silasesquioxane derivatives **3** and **4** occur in all cases upfield and with larger ^1J(PPt) coupling constants than for [Pt(dppe)(CO_3)].‡ Both chemical shifts and ^1J(PPt) coupling constants for **3** and **4** fall within a narrow range [δ between 26 and 28, referenced to external 85% phosphoric acid, and ^1J(PPt) between 3730 and 3780 Hz]. The chemical shifts are similar to those reported previously for [Pt(dppe)($OSiMe_3)_2$] [δ 27.1, ^1J(PPt) 3595][4] and [Pt(dppe)(OMe)$_2$] [δ 28.5, ^1J(PPt) 3342][5] though the coupling constant is somewhat larger, reflecting the lower *trans* influence of the silasesquioxane. The reactivity of [Pt(dppe)(CO_3)] is in marked contrast to that of [Pt($PPh_3)_2(CO_3$)], for which no reaction with **1** was observed after several days. A similar pattern was observed in the reaction of these platinum carbonates with ethane-1,2-diol, for which the equilibrium constant was approximately 27 times greater for [Pt(dppe)(CO_3)] than for [Pt($PPh_3)_2(CO_3$)].[6]

A second useful preparative route utilises the reaction of the silasesquioxane silanol groups with the chlorides on [Pt(dppe)Cl_2] in refluxing dichloromethane in the presence of the base silver(I) oxide.[7] Again the reaction is slow, though more general than the carbonate route as it allows $PMePh_2$ analogues of **3** and **4** to be prepared.

Single crystals of complex **3a** were grown from the slow diffusion of acetonitrile into a toluene solution, and the molecular structure is shown in Fig. 1.§ The co-ordination geometry around the platinum centre is distorted square planar,



Scheme 1 (i) [Pt(dppe)CO_3)], CH_2Cl_2; (ii) [Pt(dppe)Cl_2], Ag_2O, CH_2Cl_2, Δ (**a**, R = *c*-C_5H_9; **b**, R = *c*-C_6H_{11}).

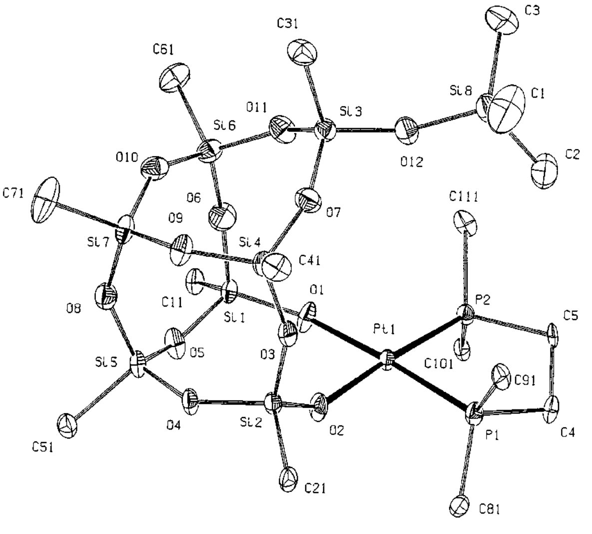


Fig. 1 Perspective ORTEP plot of **3a**. For clarity, thermal ellipsoids are shown at 50% probability; no H and only C attached to Si and P are shown. Selected interatomic distances (Å) and interbond angles (°) are: Pt–O(1) 2.031(6), Pt–O(2) 2.036(4), Pt–P(1) 2.195(2), Pt–P(2) 2.204(2), Si(1)–O(1) 1.573(6), Si(2)–O(2) 1.566(6), other Si–O 1.597(7)–1.647(7), O(1)–Pt–O(2) 90.3(2), O(2)–Pt–P(1) 90.2(2), P(1)–Pt–P(2) 86.90(8), P(2)–Pt–O(1) 92.5(2), Pt–O(1)–Si(1) 146.2(4), Pt–O(2)–Si(2) 148.3(4), Si(3)–O(12)–Si(8) 152.8(5), other Si–O–Si 140–170.

with *cis* angles ranging from 86.9 to 92.5°. The Pt–O and Pt–P distances compare well with those found in the isoelectronic compound [Pt(dppe)(OCH$_3$)$_2$] [Pt–P = 2.222(3), 2.228(3) Å, Pt–O = 2.037(7), 2.041(7) Å][5] with the slight shortening of the Pt–P bonds in complex **3a** with respect to [Pt(dppe)(OCH$_3$)$_2$] again consistent with the lower *trans* influence of the silasesquioxane. The Si–O distances in the platinum siloxy functions [Si(1)–O(1) = 1.573(6) Å; Si(2)–O(2) = 1.566(6) Å] are significantly shorter than those present in the silasesquioxane skeleton [1.597–1.647 Å; typical 1.63 Å], while in the silasesquioxane silanol **1a**, these distances are 1.619(7) and 1.616(7) Å (*vide infra*). This bond shortening may be ascribed to the absence of electron donation of the oxygen lone pairs to the electron rich platinum centre which will lead to a stronger Si–O bond by enhanced electron donation to silicon; this effect is absent or the reverse in high oxidation state early transition metal silasesquioxanes.[8]

In order to make a better evaluation of the structural features of the silasesquioxane unit present in **3a**, we determined the molecular structure of the silasesquioxane disilanol **1a** (Fig. 2); single crystals were prepared by allowing acetonitrile to diffuse slowly into a toluene solution of **1a**.§ This disilanol was found to be a monomeric compound that crystallises into two distinct isomers that differ mainly by the orientations of the, highly disordered, cyclopentyl units. Although the quality of the structure determination is poor (*R*1 = 0.1423), the conformation of the Si/O skeleton of **1a** can be discussed with regard to that present in **3a**. Such a comparison reveals that the Si/O skeletons of both compounds are remarkably similar. For instance, the intramolecular distance of the ligating oxygen atoms O(1) and O(2) in **3a** is 2.88(1) Å *versus* 2.67(1) Å in **1a**, while the intramolecular distance Si(1)–Si(3) in **3a**, which can be considered as a measure for the binding cavity, of 5.22(1) Å is virtually equal to that of 5.21(1) Å measured in **1a**. As a result, one might conclude that the silasesquioxane diol is ideally preorganised for co-ordination to a Pt(II) centre following deprotonation.

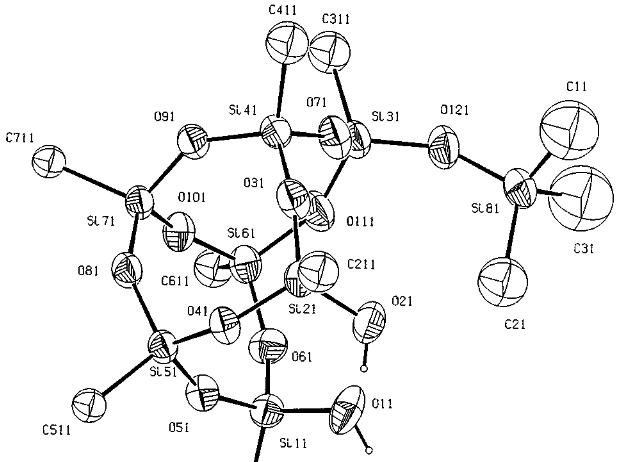


Fig. 2 Perspective ORTEP plot of one of the independent molecules of **1a**. For clarity, thermal ellipsoids are shown at 50% probability; no H and only C attached to Si are shown. Selected interatomic distances (Å) and interbond angles (°) are: Si(11)–O(11) 1.650(8), Si(21)–O(21) 1.619(8), other Si–O 1.579(10)–1.650(8), Si–O–Si 149–156.

We are currently investigating the reactivity of the hydroxyl group in **4** and those of the known silasesquioxane tetrasilanol (c-C$_7$H$_{13}$)$_6$Si$_6$O$_7$(OH)$_4$[9] with a view to preparing bimetallic metallasilasesquioxanes.

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Notes and references

† A typical preparation (**3a**): Silasesquioxane **1a** (294 mg, 0.304 mmol) was added to a solution of [Pt(dppe)(CO$_3$)] (200 mg, 0.306 mmol) in dichloromethane (20 cm^3) and the mixture stirred at room temperature (typically 7 days). The solvent was removed under reduced pressure, the crude solid washed with acetonitrile, and recrystallised from toluene–acetonitrile to give colourless crystals of **3a** (90% yield). (Anal. Found: C, 49.8; H, 6.25%; C$_{62}$H$_{96}$Si$_8$O$_{12}$P$_2$Pt requires C, 49.8; H, 6.41%). Silasesquioxane silanols **1b** and **2a** were prepared according to ref. 2 and 9, respectively. The new silasesquioxane **1a** was prepared by an identical method as reported for **1b** starting from 17.0 g of **2a**, 25 mL of Et$_3$N and 2.20 mL of Me$_3$SiCl to give 13.6 g (75%) of **1a;** ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ 4.22 (s, 2H, SiOH), 1.76–1.48 (m, 56H, C$_5$H$_9$), 1.49 (m, 7H, C$_5$H$_9$), 0.16 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C) δ 27.6–27.0 (CH$_2$), 23.7, 22.7, 22.4, 22.3, 22.1 (1 : 2 : 2 : 1 : 1 for CH), 1.7 (SiMe$_3$).

‡ *Selected spectroscopic data*: **3a**: ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ 8.06 (dq, 8H, Ph), 7.50 (t, 4H, Ph), 7.43 (m, 8H, Ph), 2.14 (m, 4H, P(CH$_2$)$_2$P), 1.72 (m, 12H, C$_5$H$_9$), 1.50 (m, 28H, C$_5$H$_9$), 1.27 (m, 4H, C$_5$H$_9$), 1.12 (m, 12H, C$_5$H$_9$), 0.92 (m, 3H, C$_5$H$_9$), 0.81 (m, 2H, C$_5$H$_9$), 0.54 (m, 2H, C$_5$H$_9$), −0.29 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C) δ 28.7 (CH$_2$P), 28.5–26.4 (other CH$_2$), 25.1, 24.2, 23.2, 23.0 (2 : 3 : 1 : 1 for CH), 1.0 (SiMe$_3$). ^{29}Si{^{1}H} NMR (79 MHz, CH$_2$Cl$_2$, 0.02 M Cr(acac)$_3$, 25 °C) δ 6.0 (SiMe$_3$), −65.1, −66.3, −66.6, −68.7 (1 : 1 : 2 : 3). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 25 °C) δ 27.1 [^1J(PPt) = 3773 Hz]. FAB-MS 1539 [M + H]$^+$. **4a**: ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ 8.0 (m, 8H, Ph), 7.5 (m, 12H, Ph), 2.2 (m, 4H, P(CH$_2$)$_2$P), 1.9–0.8 (m, 63H, C$_6$H$_9$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C) δ 29 (CH$_2$P), 28.6–26.7 (other CH$_2$), 25.10, 23.22, 23.11, 22.69, 22.60 (2 : 2 : 1 : 1 : 1 for CH). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 25 °C) δ 26.7 [^1J(PPt) = 3730 Hz].

§ *Crystal data* for **3a**: C$_{64}$H$_{96}$Si$_8$P$_2$O$_{12}$Pt·C$_2$H$_3$N, M_r = 1580.22, orthorhombic, space group *Pccn* (no. 56) with a = 47.997(4), b = 13.9845(11), c = 21.803(2) Å, V = 14634(2) Å^3, D_c = 1.434 g cm^{-3}, Z = 8, F(000) = 6544, μ(Mo-Kα) = 2.15 mm^{-1}, 13789 reflections measured, 12902 independent, (1.0° < θ < 25.00°, ω scan, T = 150 K, Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å). Hydrogen atoms were included in the refinement at calculated positions riding on their carrier atoms. Refinement of 812 parameters converged at a final $wR2$ value of 0.1439, $R1$ = 0.0525 [for 7517 reflections with $F_o > 4\sigma(F_o)$], S = 1.111. *Crystal data* for **1a**: C$_{38}$H$_{74}$Si$_8$O$_{12}$, M_r = 947.69, triclinic, space group $P\bar{1}$ (no. 2) with a = 14.5232(12), b = 15.7325(8), c = 23.4701(15) Å, α = 102.358(5), β = 97.036(6), γ = 92.941(5)°, V = 5182.2(6) Å^3, D_c = 1.215 g cm^{-3}, Z = 4, F(000) = 2040, μ(Mo-Kα) = 0.259 mm^{-1}, 17993 reflections measured, 17304 independent, (0.9° < θ < 25.34°). Data collection performed as described for compound **3a**. The reference reflections displayed a decay of 2%. Refinement of 669 parameters converged at a final $wR2$ value of 0.4489, $R1$ = 0.1423 [for 7874 reflections with $F_o > 4\sigma(F_o)$]. CCDC 182/1064. See http://www.rsc.org/suppdata/cc/1998/2627/, for crystallographic files in .cif format.

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