

Molecular insight into the non-innocence of a silica-support: the structure of a platinum–silsesquioxane derivative

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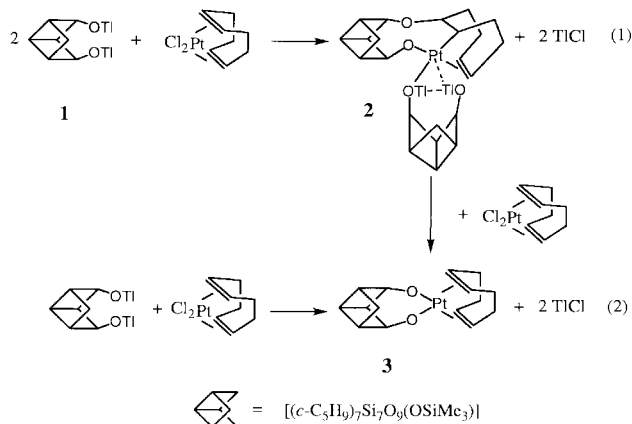
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The cyclooctadiene ligand within the square planar Pt(II) complex [PtCl₂(C₈H₁₂)] undergoes nucleophilic attack from a siloxo group of the thalated polyhedral silsesquioxane [(c-C₅H₉)₇Si₇O₉(OSiMe₃)(OTf)₂], to yield [(c-C₅H₉)₁₄Si₁₄O₁₈(OSiMe₃)₂O₄(η⁴-C₈H₁₂)PtTl₂]; given the analogy between the silsesquioxane moiety and a silica surface, the presence of an SiO–C bond between the siloxo-cage and the Pt-bound olefinic ring is significant in the context of surface non-innocence in heterogeneous catalysis.

Metalla-derivatives of partially condensed silsesquioxanes (POSS) provide an appropriate manifold for gaining molecular insight into the nature of silica-supported heterogeneous catalysts.¹ Complexes of metallic POSS with centres are known to display close structural and chemical resemblance to their heterogeneous counterparts.¹ Here, we wish to report the structure of a highly novel mixed-metal silsesquioxane complex [(c-C₅H₉)₇Si₇O₉(OSiMe₃)₂(η⁴-C₈H₁₂)PtTl₂] **2** that displays an unprecedented siloxo-metallacycle derived from the formal oxidative-addition of a Pt–OSi bond across a carbon–carbon double bond of a coordinated diolefin. Such interaction models a direct involvement of a ‘non-innocent’ silica surface into the activation of an unsaturated substrate. To date, no other molecular model for such ‘support–catalytic center’ interaction had been reported.

Upon addition of [PtCl₂(cod)] (cod = cycloocta-1,5-diene) to a benzene solution containing 2 equivalents of [(c-C₅H₉)₇Si₇O₉(OSiMe₃)(OTf)₂] **1**,² the mixed-metal compound **2** is formed in low yield (ca. 6%) (Scheme 1).[†] Compound **2** may also be isolated by fast addition of [PtCl₂(cod)] to an equimolar solution of **1**, followed by rapid work-up of the reaction mixture. Conversely, if [PtCl₂(cod)] is added slowly to an equimolar benzene solution of **1** and the mixture allowed to stand for 56 h, elimination of 2 equivalents of TfCl is observed and the metalla-silsesquioxane [(c-C₅H₉)₇Si₇O₉(OSiMe₃)₂O₂Pt(η⁴-C₈H₁₂)] **3** can be isolated in moderate yield (53%) (Scheme 1). Compound **2** has also been found to react with 1 equivalent of [PtCl₂(cod)] to give **3**.



Scheme 1

Compound **2** was initially characterised by its ¹H NMR spectrum in C₆D₆ which clearly indicates that the Pt(cod) moiety is coordinated to the silsesquioxane cage. However, a complete elucidation of the structure based on the NMR data is hindered by the overlap of cyclopentyl and cyclooctadienyl resonances. The molecular structure of compound **2** was elucidated by single-crystal X-ray diffraction analysis (Fig. 1).[‡]

Compound **2** consists of two silsesquioxane moieties bridged by a trinuclear (C₈H₁₂)PtTl₂ core. The metallic unit shows a Tl–Pt distance of 3.7382(13) Å and a Tl–Pt distance of 3.2393(15) Å. The central thallium atom [Tl(1)] forms an angle with its neighbours of 63°43'. The geometry at the platinum metal, excluding the thallium contact, is square planar with mean deviation from the plane of 0.1712 Å. The thallium atom sits above the plane, forming an angle with the perpendicular to the plane of 27°. The Pt(II) centre completes its coordination sphere with two Pt–O bonds [2.142(9) and 2.064(10) Å], one Pt–C σ bond [2.05(3) and 2.16(4) Å, in the two disordered rings present in the solid state structure] and a Pt–C=C π bond [with Pt–C distances of 2.10(2) Å]. Such coordination results form the cyclooctadiene ring having undergone nucleophilic attack from a siloxo moiety. The structural disorder results from the SiO–nucleophilic attack occurring at both possible sites of the C=C 1,2-double bond. The oxidative addition yields reaction both on Pt–C and a SiO–C bond [O–C 1.55(3) Å]. The C–C distances of 1.53(3) and 1.49(3) Å in the disordered structure show substantial lengthening with respect to the coordinated olefinic C=C bond [1.36(2) Å]. Both oxygen atoms involved in the Pt–O bonds are also involved in a Tl–O bond [2.514(11) and 2.681(11) Å]. This μ₂-siloxo-binding mode contributes one electron to the overall electron count for the platinum centre. The apparent electron deficiency at the Pt(II) centre may be taken to explain the presence of the thallium–platinum contact. Thallium(I)–platinum(II) bonds are known,³ although in scarce

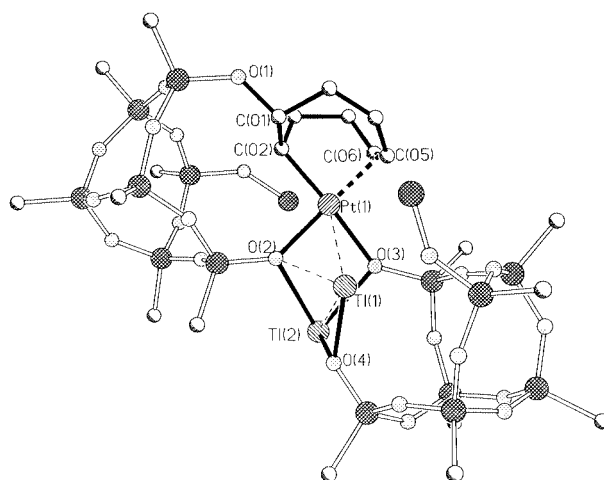


Fig. 1 Molecular structure of **2**. No H and only *ipso* carbons of cyclopentyl rings are shown for clarity. Only one of the two disordered cod rings is shown for clarity. See text for selected bond lengths and angles.

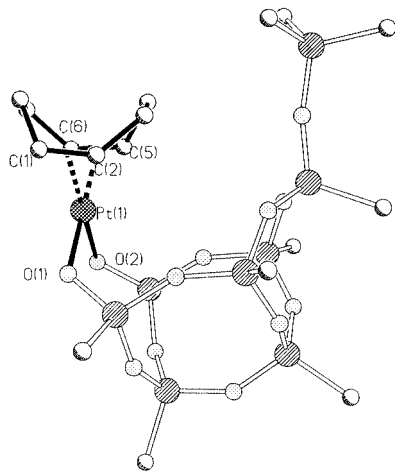


Fig. 2 Molecular structure of **3**. No H atoms and only *ipso* carbons of cyclooctenyl rings are shown for clarity. Selected interatomic distances (Å) and angles (°) (CNT is the centroid of the coordinated double bond): Pt1–O1 1.987(5), Pt1–O2 1.990(5), Pt1–C1 2.16, Pt1–C2 2.139, Pt1–C5 2.143(7), Pt1–C6 2.131(7), Pt1–CNT1 2.015, Pt1–CNT2 2.021, C1–C2 1.376(10), C5–C6 1.387(11); O2–Pt1–O1 90.4(2), O1–Pt1–CNT1 90.3(3), CNT1–Pt1–CNT2 89.4(3).

number. They vary in length between 2.860 Å^{3c} and 3.135 Å,^{3b} making the presently reported one the longest to date. The bonding geometry encountered here is reminiscent of those previously reported, with the Tl–Pt vector approaching the perpendicular of the square planar Pt(II) complex.^{3b}

The most striking feature of compound **2** is the presence of a σ bond between the siloxane frame and the metal coordinated cyclooctenyl ligand. To our knowledge, this would appear to be the first derivative that displays activation of a metal ligand by the silsesquioxane frame. The only two previously reported platinum silsesquioxanes are [(*c*-C₅H₉)₇Si₇O₉(OSiMe₃)O₂Pt(dppe)]⁴ (dppe = diphenyldiphosphinoethane) and [(*c*-C₆H₁₁)₇Si₇O₉(OSiMe₃)O₂Pt(η^4 -C₈H₁₂)].^{1b} While no experimental details are available for the latter, the former has been fully characterised, and consists of a square planar Pt(dppe) complex of the dipodal silsesquioxane cage. The chemistry at the platinum centre can be described as resulting from the exchange of two chloride ions from the appropriate Pt(II) salt with a dipodal silsesquioxane frame, with no other variation in the remaining coordination sphere of the metal centre. This reaction, which is the most used synthetic strategy for obtaining metalla silsesquioxanes,^{1c} has been applied successfully in this work and compound **3** obtained [see reaction (2) in Scheme 1].§ This has been characterised by analytical and spectroscopic techniques, and its molecular structure determined by a single crystal X-ray diffraction study (Fig. 2),‡ making it the first organometallic platinum-silsesquioxane structurally characterised.

The structure of **3** is similar to the dppe derivative described above. The Pt(cod) moiety retains most of its structural characteristics upon grafting onto the silanol. The presence of two distinct ¹H NMR resonances for the olefinic protons confirms the asymmetry in the ring-coordination arising from the presence of the POSS cage. This complex is also related to the complex [(η^4 -cod)Pt(OSiPh₃)₂],⁵ obtained from the reaction of [PtCl₂(cod)] with triphenylsilanol.

The structures of compounds **2** and **3** shed considerable light into the nature of silica-supported platinum-based catalysts. With compound (η^4 -cod)Pt(OSiPh₃)₂,⁵ they are the only reported organometallic siloxo complexes of platinum(II), and therefore constitute the only available models for silica supported organoplatinum catalysts. Such heterogeneous sys-

tems are of interest, given their use as catalysts in the heterogeneous hydrogenolysis of hydrocarbons.⁵ As with supported heterogeneous catalysts in general, the molecular structure of their active site is seldom known with precision. In such materials the activity is normally believed to reside at the metal centre, although the existence of a 'support-effect' in the solid state has been invoked.⁶ Compound **3** shows no interaction of the 'silica-like' silsesquioxane frame with the coordinated unsaturated substrate. Such structural motif models a catalyst supported on an *inactive* silica surface, and modeled in POSS chemistry. In contrast, compound **2** exemplifies the opposite situation; the coordinated unsaturated bond establishes a direct bond with the 'silica-like' part of the metalla-POSS emphasising the possible non-innocence of a silica surface.

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Notes and references

† *Synthesis of 2*: solid [PtCl₂(cod)] (20 mg, 0.054 mmol) was added to a benzene solution (5 mL) of **1** prepared *in situ* from [(*c*-C₅H₉)₇Si₇O₉(OSiMe₃)(OH)₂] (100 mg, 0.106 mmol).² The immediate precipitation of a fine white powder ensued. After 5 h of stirring, the suspension was filtered off and the colorless supernatant was dried under vacuum. The residue was extracted with benzene (3 mL) and, by slow diffusion of MeCN in the solution, pale yellow needles were obtained and studied by X-ray diffraction. δ_{H} (C₆D₆): 4.35 (br m, 2H, CH=CH), 4.15 (m, 1H, CHCH=CH), 3.15 (br, 1H, CHOSi), 2.40 (m, 2H), 2.15 (m, 2H), 1.80–1.30 [br m, *c*-CH(CH₂)₂], 0.90 [br m, 7H, *c*-CH(CH₂)₂], 0.15 [m, 9H, Si(CH₂)₃].

‡ *Crystal data*: for **2**: C₈₄H₁₅₆O₂₄PtSi₁₆Tl₂, *M* = 2603.36, triclinic, space group *P* $\bar{1}$ *a* = 14.613(2), *b* = 19.703(2), *c* = 20.723(2) Å, α = 98.04(4), β = 101.92(4), γ = 92.99(3)°, *U* = 5760.3(11) Å³, *Z* = 2, μ = 4.229 mm⁻¹, *T* = 180(2) K, 14691 independent reflections, final *R* index [*I*_o > 2 σ (*I*_o)] = 0.0803, *R*' = 0.2040, GOF = 1.045.

For **3**: C₄₆H₈₄O₁₂PtSi₈, *M* = 1248.94, triclinic, space group *P* $\bar{1}$, *a* = 11.0900(4), *b* = 11.7050(4), *c* = 23.3350(9) Å, α = 75.9010(19), β = 80.6610(19), γ = 83.003(2)°, *U* = 2888.16(18) Å³, *Z* = 2, μ = 2.649 mm⁻¹, *T* = 230(2) K, 10099 independent reflections, final *R* index [*I*_o > 2 σ (*I*_o)] = 0.0530, *R*' = 0.1228, GOF = 1.010. CCDC 182/1618. See <http://www.rsc.org/suppdata/cc/b0/b000992j/> for crystallographic files in .cif format.

§ *Synthesis of 3*: a benzene solution (5 mL) of [PtCl₂(cod)] (45 mg, 0.120 mmol) was added dropwise to a benzene solution (10 mL) of **1** prepared as above from [(*c*-C₅H₉)₇Si₇O₉(OSiMe₃)(OH)₂] (115 mg, 0.121 mmol). An immediate precipitation of a fine white powder ensued. After 48 h of stirring, the suspension was filtered off and the pale yellow supernatant was dried under vacuum. The residue was extracted with benzene (3 mL) and dried again leaving a white powder (32 mg, yield as **3**: 53%). By slow diffusion of MeCN in a benzene solution, pale yellow needles were obtained and studied by X-ray diffraction. *Elemental analysis* for C₄₆H₈₄O₁₂PtSi₈: found (calc.): C, 43.89 (44.24); H, 6.98 (6.78). δ_{H} (C₆D₆) 5.12 (m, 2H, CH_a=CH_b), 4.94 (m, 2H, CH_c=CH_d), 2.82 (br, 2H, CH₂ in cod), 2.64 (m, 2H, CH₂ in cod), 2.14 (m, 4H, CH₂ in cod), 1.76 (br, 7H, CH₂ in *c*-C₅H₉), 1.40 (br, 7H, CH₂ in *c*-C₅H₉), 0.98 (br m, 7H, CH in *c*-C₅H₉), 0.11 [m, 9H, Si(CH₃)₃].

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