A Silatrane–Platinum Complex, *trans*-[PtCl{Si(OCH$_2$CH$_2$)$_3$N}(PMe$_2$Ph)$_2$] with a Planar Nitrogen and No Si–N Bond; *X*-Ray Crystal Structure†

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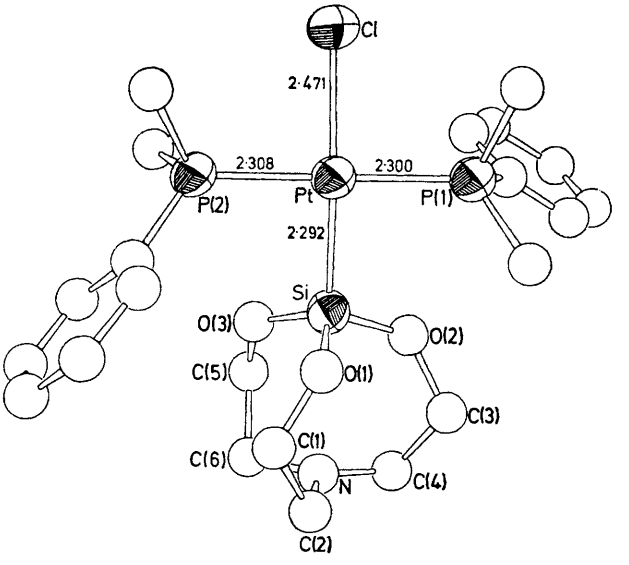
Summary An *X*-ray crystal structure analysis of *trans*-[PtCl{Si(OCH$_2$CH$_2$)$_3$N}(PMe$_2$Ph)$_2$] reveals a square-planar co-ordination geometry for platinum, a non-bonded Si–N distance of 2·89(1) Å, and trigonal-planar stereochemistry for nitrogen.

ELIMINATION of HCl from a mixture of silatrane HSi(OCH$_2$CH$_2$)$_3$N (2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]-undecane) (I) and *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] in the presence of Et$_3$N[1] gave a solution from which *trans*-[PtCl{Si(OCH$_2$-CH$_2$)$_3$N}(PMe$_2$Ph)$_2$], (II), was obtained. Recrystallisation from dichloromethane–pentane gave (II) as colourless needles, m.p. 190—191 °C, in 40% yield. The i.r. band characteristic of Si–N bonded silatranes,[2] which was at 598 cm^{-1} for (I), was not detected for (II), suggesting that the Si–N bond might not be present in the complex, and this was confirmed by an *X*-ray crystal structure analysis.

Crystal data: C$_{22}$H$_{38}$ClNO$_3$P$_2$PtSi, monoclinic, space group $P2_1/c$, a = 6·630(4), b = 17·465(6), c 22·297(6) Å, β = 97·39(2)°, Z = 4. The analysis was based on the integrated intensities of 2165 independent reflections [$I_o > 3\sigma(I_o)$] collected using Cu-K_α radiation on an automatic diffractometer, and corrected for absorption effects. Heavy atom methods were used for the solution of the phase problem with full-matrix least-squares refinement of atomic co-ordinates with anisotropic Debye–Waller factors for Pt, P, Si, and Cl atoms and isotropic thermal parameters for C, N, and O atoms. The present unweighted discrepancy



† Reprints not available.

index R_F is 0·048. A difference electron synthesis revealed no disorder of the nitrogen atom.

The molecular structure and platinum–ligand distances are shown in the Figure. Distortions from square-planar co-ordination geometry about platinum are small and the platinum–ligand distances differ only slightly from those in *trans*-[PtCl{SiMe(1-$C_{10}H_7$)Ph}(PMe_2Ph)$_2$].[3] The long Pt–Cl bond reflects the large *trans*-influence of the silicon ligand atom.[4]

TABLE. Mean bond lengths (Å) and angles (°) in silatranes $XSi(OCH_2CH_2)_3N$.

	X = Ph	X = $PtCl(PMe_2Ph)_2$
Si–N	2·132(4)	2·89(1)
Si–O	1·660(4)	1·649(9)
X–Si–O	96·3(2)	108·8(3)
O–Si–O	118·8(2)	110·1(5)
Si–O–C	123·6(4)	125·4(8)
C–C–(C, N, or O)	106·6(5)	111·7(11)
C–N–C	112·5(4)	119·7(11)

The silatrane ligand has novel structural features. The absence of a Si–N bond is evident from the long Si–N separation of 2·89(1) Å (sum of covalent radii 1·93 Å), the tetrahedral stereochemistry of silicon, and the remarkable trigonal-planar stereochemistry of nitrogen (Table). This is the first example of a silatrane which does not involve Si–N bonding, and we suggest that attachment to platinum makes the silicon sufficiently anionic for the Si–N interaction to become repulsive (sum of van der Waals radii 3·65 Å). Construction of space-filling Corey–Pauling–Koltum molecular models of the silatrane cage using tetrahedral valencies for C, N, O, and Si atoms shows that the nitrogen lone-pair must be inside the cage and very close to silicon. Molecular structures of $PhSi(OCH_2CH_2)_3N$ (Table) and related molecules[5] show that the silicon normally adopts a trigonal bipyramidal configuration, accommodating the nitrogen lone-pair by formation of a Si–N bond. The molecular models also show that structures in which the nitrogen lone-pair lies outside the cage would be severely strained; such strain is clearly evident from the C–C–C angles (117—120°) in the externally protonated 1-azabicyclo[3.3.3]undecane, $HC(CH_2CH_2CH_2)_3NH^+$.[6]

Thus, in the platinum complex, structures with the lone-pair of pyramidal nitrogen inside or outside the cage are unfavourable, whereas adoption of a trigonal-planar configuration at nitrogen permits normal angles about other atoms of the cage (Table). The model incorporating trigonal nitrogen is unstrained.

The results suggest that the nitrogen atom in the free base[5] $HC(CH_2CH_2CH_2)_3N$ is probably trigonal planar.

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