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Organoplatinum Building Blocks for One-Dimensional Hydrogen-Bonded Polymeric Structures

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The exploitation of the hydrogen bond in the assembly of molecules in the solid state is a topic of current interest.^[1] Crystal packing of molecules can take place in a very precise manner, since the hydrogen bonds introduce a high degree of directionality and confer unique properties on the resulting molecular material.

We set out to synthesize organoplatinum complexes possessing hydrogen-bond donor (D) and hydrogen-bond acceptor (A) groups at either end of the molecule, separated by a rigid aryl spacer (**1**, Fig. 1). These features could then promote self-orga-

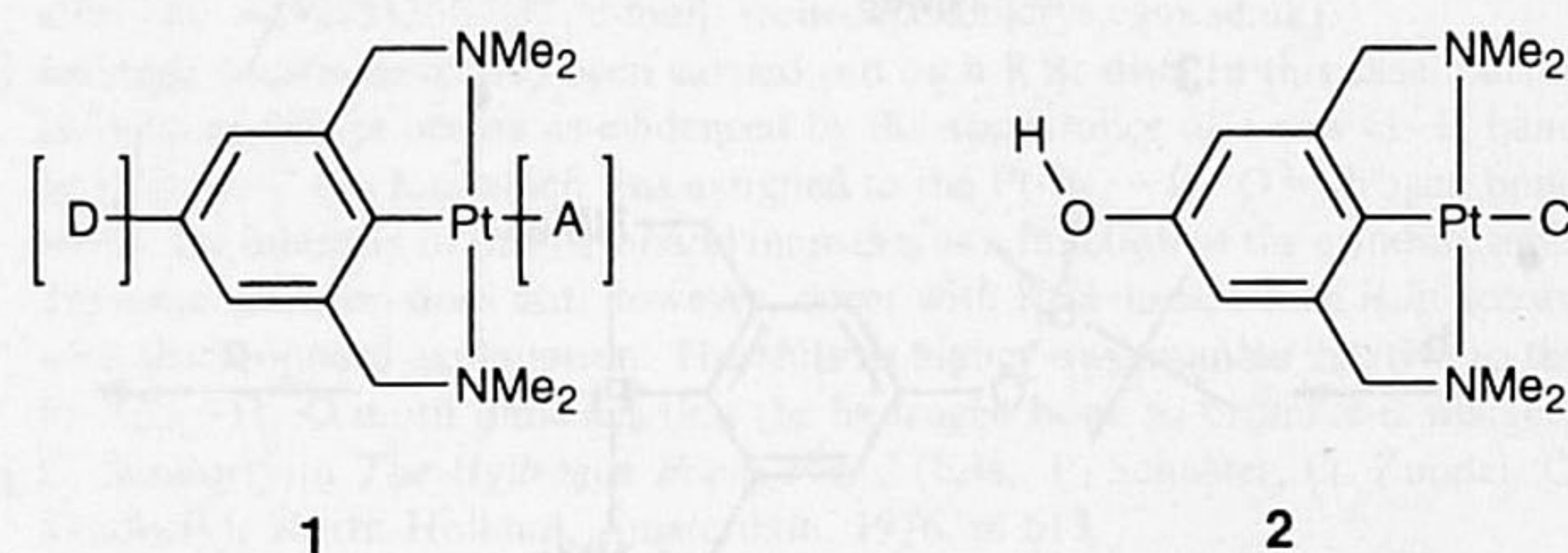


Fig. 1. Complex **2** possesses both hydrogen-bond donor [D] and hydrogen-bond acceptor [A] groups.

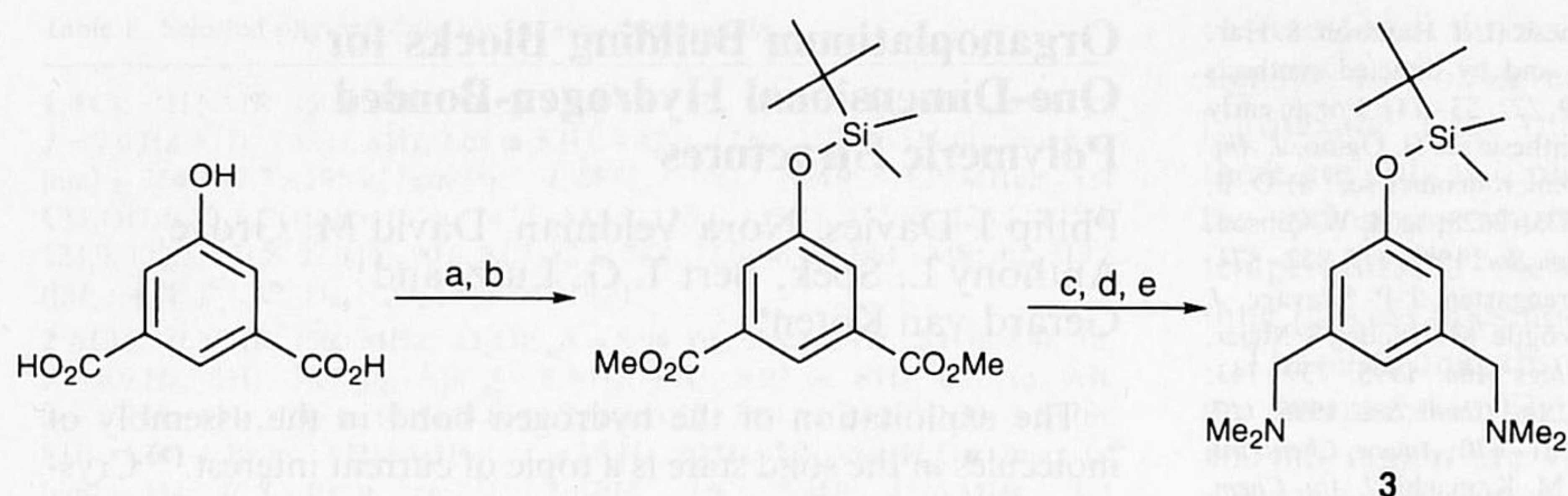
nization in the solid state through intermolecular hydrogen bonding to form a self-assembled organometallic polymeric structure containing directed, noncovalent bonds. Here we present primarily the synthesis and solid-state structure of the *para*-hydroxyaryldiamineplatinum complex **2**. This complex has all the properties required for the formation of intermolecular hydrogen bonds, namely a *para*-hydroxyl group and a potential hydrogen bond acceptor in the chloride ligand.

The synthetic strategy relies on initial synthesis of the required organic ligand (**3**) (Scheme 1) in which the hydroxyl group is protected as its *tert*-butyldimethylsilyl (TBDMS) ether.^[2] The ligand **3** was isolated in 45% yield based on the starting compound, 5-hydroxyisophthalic acid.

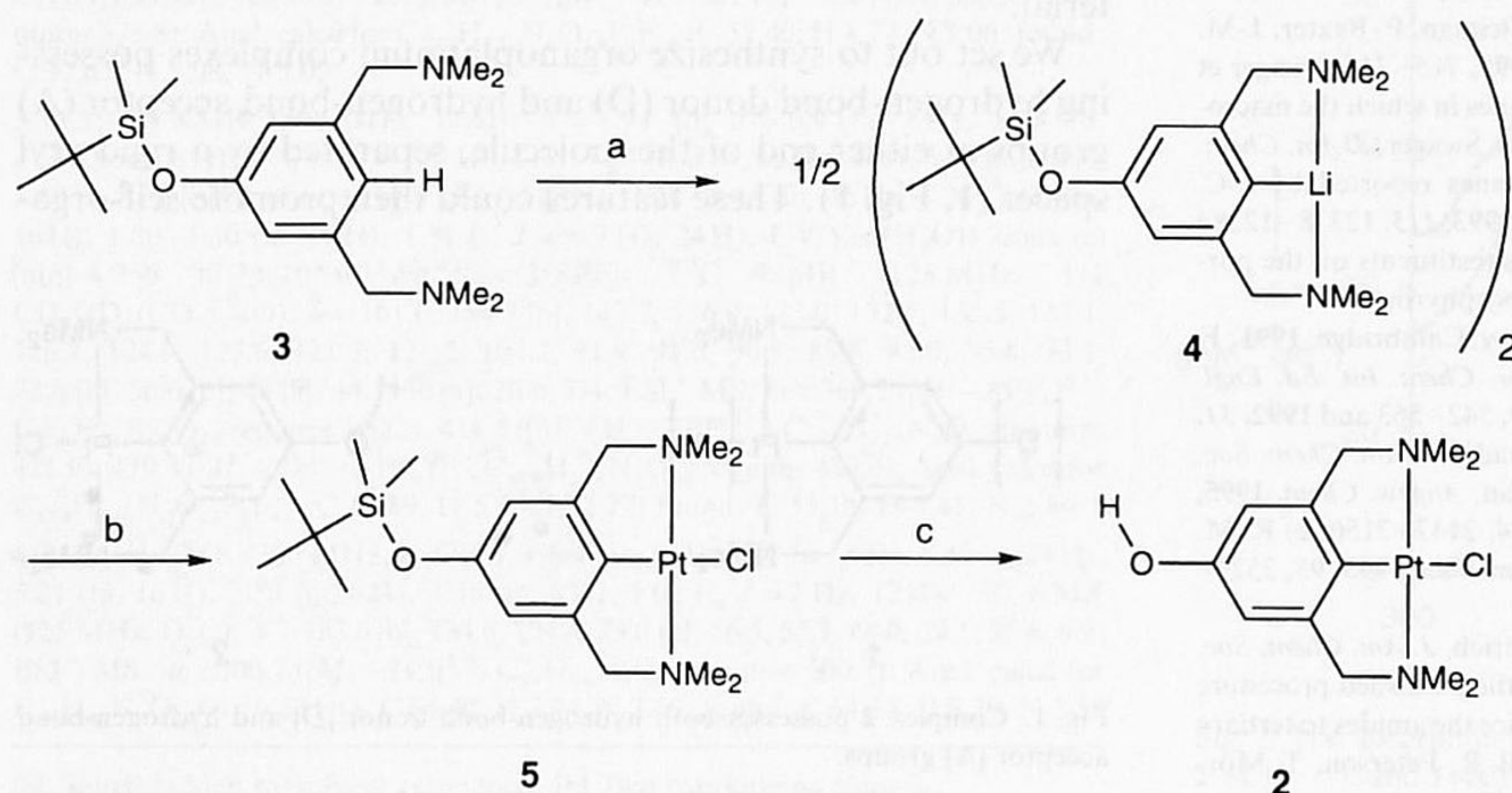
Reaction of **3** with *n*-butyllithium in hexane afforded **4** (Scheme 2) in which exclusively the position *ortho* to both CH₂NMe₂ arms was lithiated. This was established by quenching a sample of the lithiated compound with D₂O and deducing the position of deuterium incorporation by ^1H NMR spectroscopy. We propose a dimeric structure for **3** in both the solid state and in solution, based on studies of similar species.^[3]

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Scheme 1. Synthesis of the TBDMS-protected aryldiamine ligand **3**[2b]. a) MeOH, H₂SO₄, Δ; b) *t*BuMe₂SiCl, NEt₃, THF, Δ; c) LiAlH₄, Et₂O; d) MeSO₂Cl, NEt₃, CH₂Cl₂, Δ; e) NHMe₂·HCl, NEt₃, DMF.



Scheme 2. Lithiation, transmetalation, and deprotection of the aryldiamine ligand **3**. a) *n*BuLi, C₆H₁₄, -78 °C; b) [PtCl₂(SEt₂)₂], Et₂O; c) NBu₄F, THF, H₂O.

Transmetalation of **4** with [PtCl₂(SEt₂)₂] afforded the protected aryldiamineplatinum complex **5**. Reaction of **5** with tetrabutylammonium fluoride trihydrate in THF/water then afforded the *para*-hydroxyaryldiamineplatinum complex **2**.

Complex **2** self-assembles to form, in the solid state, neutral, linear, regularly repeating, one dimensional arrays through the formation of intermolecular hydrogen bonds from the phenolic hydrogen atom to the chloride ligand of an adjacent molecule of **2** (Fig. 2).^[4] A cooperative hydrogen bonding motif in which oxygen acts as both hydrogen bond donor and acceptor is not observed. All aryldiamineplatinum molecules align in the same direction in each polymer chain as a consequence of the hydrogen bonding. An equal number of individual polymer chains are, however, oriented in opposite directions, and macroscopic directionality throughout the whole crystal is therefore cancelled out. The hydroxyl hydrogen atom was located in the difference Fourier map and included in the refinement. The environment around the oxygen atom has been examined for close C–H···O contacts, and none shorter than 2.600(14) Å (O1···H9b) were found, that is, only one type of hydrogen bond motif is present. Variable-temperature infrared spectroscopic studies of **2** have been carried out to obtain further insight into the nature of the intermolecular hydrogen bonding. In the solid state at ambient temperature (296 K, Poflu mull) an O–H stretching band at 3284 cm⁻¹ shows a red-shift upon cooling (3277 cm⁻¹ at 180 K and 3270 cm⁻¹ at 87 K), a phenomenon characteristic of hydrogen bonding (Fig. 3).^[5] This temperature effect is due to a strengthening of the intermolecular hydrogen bond on cooling with concomitant weakening of the O–H bond. Shoulders on each side of the OH band originate from coupling interactions with lattice vibrations, which

occur at low wavenumber (<150 cm⁻¹).^[6] Upon cooling, the intensities of the shoulders decrease and that of the O–H mode increases significantly; this behavior is characteristic of hydrogen bonding. An IR spectrum of **2** in chloroform solution at 296 K shows a non-hydrogen-bonded O–H mode at 3598 cm⁻¹, which can be assigned to an unassociated phenolic hydroxyl group.^[7] In this spectrum there is also a residual hydrogen-bonded O–H mode at 3284 cm⁻¹. This indicates that, even in solution, there is a degree of hydrogen bonding present that can lead to the formation of dimers or higher oligomers. It is possible to calculate an approximate hydrogen-bond enthalpy (Δ*H*^o) from the difference in stretching frequency between the O–H bond observed in the solution spectrum and that in the solid-state spectrum;^[8] the value of -22.7 kJ mol⁻¹ obtained is indicative of a moderately strong hydrogen bond.

Here we have demonstrated the usefulness of the intermolecular hydrogen bond in the self-assembly of an organometallic compound in the solid state to form one-dimensional polymeric structures. Research is currently in progress to introduce chiral, identi-

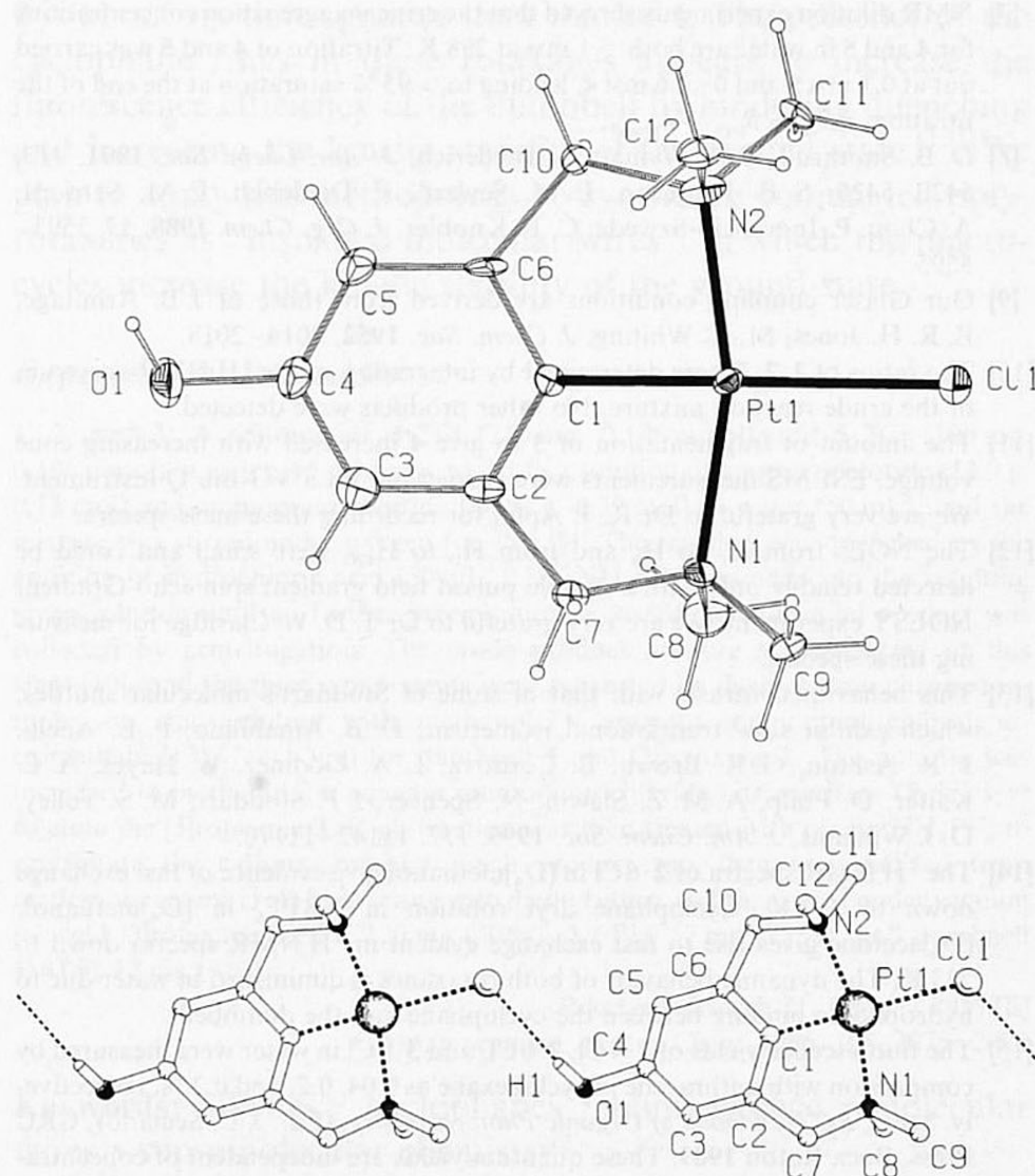


Fig. 2. Top: ORTEP plot of the structure of **2** in the solid state. Bottom: PLUTON plot showing two molecules of **2** linked by an intermolecular hydrogen bond where the hydrogen bond donor is O and the hydrogen bond acceptor is Cl. Selected bond lengths [Å] and angles [°]: Pt1–Cl1 2.434(2), Pt1–C1 1.915(9), O1–H1 0.84(13), Cl1···H1 2.32(13); Cl1···H1–O1 161(15), Pt1–Cl1···H1 115(3).

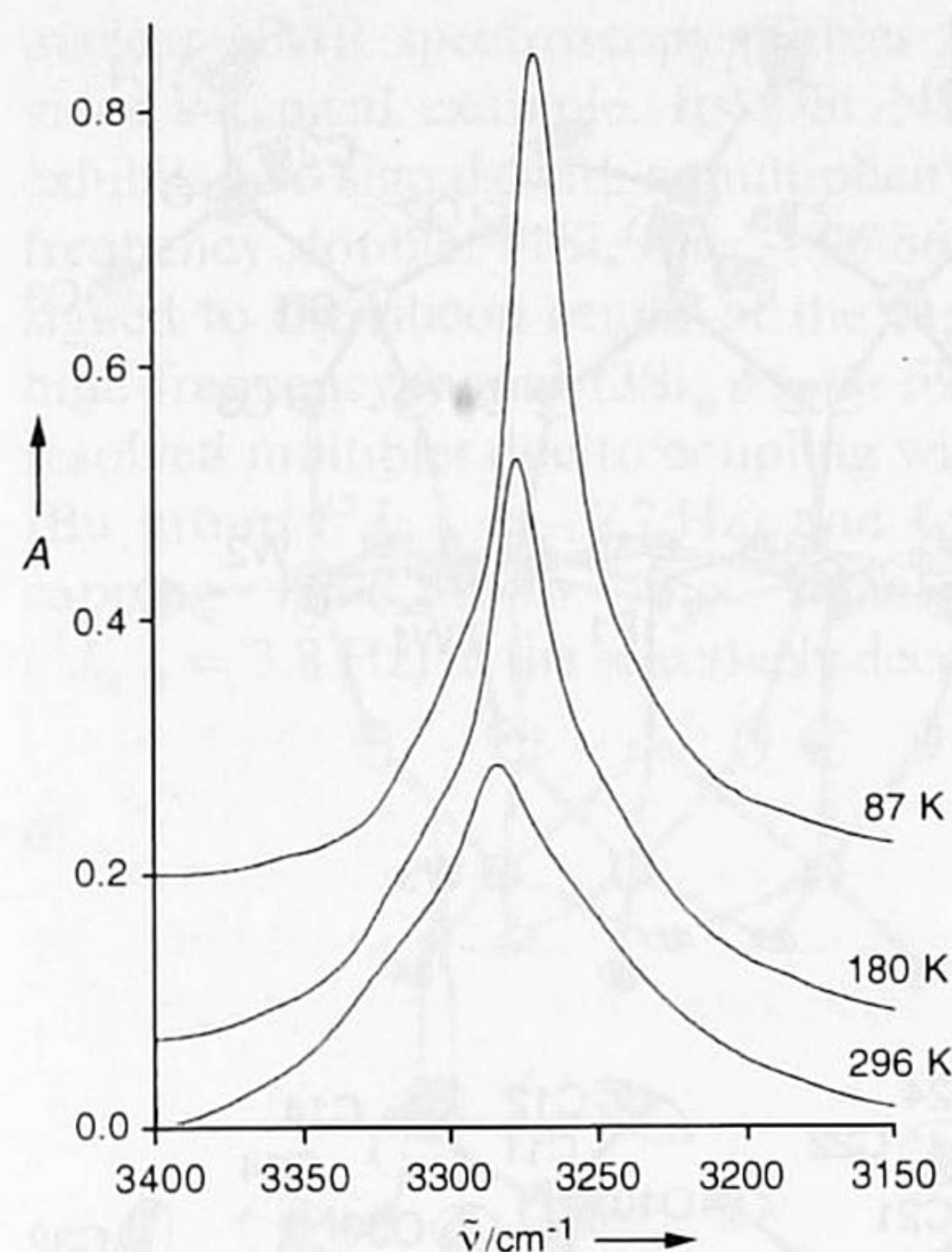


Fig. 3. The variable-temperature, solid-state infrared spectrum of **2** showing the O–H stretching region. The spectra are offset along the y axis for clarity; hence the units for the absorbance (*A*) are arbitrary.

cally configured substituents into the aryldiamine skeleton to give a noncentrosymmetric space group on crystallization, as this could give rise to desirable macroscopic properties such as optical nonlinearity.

Experimental Procedure

2: Tetrabutylammonium fluoride trihydrate (0.076 g, 0.24 mmol) was dissolved in THF (20 mL). The chloroplatinum compound **5** (0.131 g, 0.24 mmol) was added as a solid, and the mixture was stirred for 2 h at room temperature. Water (0.2 mL) was then added, and the reaction mixture stirred at room temperature for another 12 h. The precipitate that formed was collected by filtration, washed with hexane, and dried in vacuo to yield a colorless solid (0.060 g, 58%). A water-free sample for elemental analysis was obtained by drying the sample in vacuo over calcium oxide. Single crystals suitable for X-ray crystallography were grown by slow evaporation of a solution of **2** in dichloromethane/dimethylsulfoxide. Elemental analysis: calcd for $C_{12}H_{19}ClN_2OPt$: C 32.92, H 4.37, N 6.40%; found: C 33.06, H 4.42, N 6.36%; 1H NMR (200 MHz, $[D_1]chloroform/[D_6]DMSO$, 25 °C, TMS): δ = 2.55 (s, $^3J(Pt, H) = 37.4$ Hz, 12H, NMe_2), 3.49 (s, $^3J(Pt, H) = 45.8$ Hz, 4H, CH_2), 5.88 (s, 2H, aromatic), 8.00 (s, 1H, OH); ^{13}C NMR (50 MHz, $[D_1]chloroform/[D_6]DMSO$, 25 °C, TMS): δ = 154.3 (C_{para}), 143.4 ($^2J(Pt, C) = 81.0$ Hz, C_{ortho}), 133.1 ($^1J(Pt, C)$ not observed, C_{ipso}), 106.7 ($^3J(Pt, C) = 38.3$ Hz, C_{meta}), 77.3 ($^2J(Pt, C) = 62.0$ Hz, CH_2), 54.0 ($^2J(Pt, C) = 15.0$ Hz, NMe_2).

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106.1 cm $^{-1}$, 6631 reflections measured, 2936 independent ($1.7^\circ < \theta < 27.5^\circ$, ω scan, $\Delta\omega = 0.87 + 0.35 \tan \theta$, $T = 150$ K, MoK α radiation, graphite monochromator, $\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4-T diffractometer on a rotating anode. Data were corrected for Lorentzian polarization and for a linear decay of 8% of the reference reflections (212, 220, 220) during 13 h of X-ray exposure time; empirical absorption correction (DIFABS) applied as implemented in PLATON (transmission range 0.579–1.000). The structure was solved by Patterson methods and subsequent difference Fourier techniques (DIRDIF-92). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93); no observance criterion was applied during refinement. Final $R1$ value 0.0376, for 2340 reflections with $F_0 > 4.0\sigma(F_0)$, $wR2 = 0.0793$ for 2934 data, $w = 1/[\sigma^2(F_0^2) + (0.0311P)^2]$, where $P = (\text{Max}(F_0^2, 0) + 2 \times F_c^2)/3$, $S = 1.024$, for 161 parameters. Maximum and minimum residual density: 0.84, -1.08 e Å $^{-3}$. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter related to the value of the equivalent isotropic thermal parameter of their carrier atoms, by a factor of 1.5 for the methyl groups, and 1.2 for the other hydrogen atoms. The hydroxyl hydrogen was found in the difference Fourier map and allowed to refine freely. Weights were refined in the final refinement cycles. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-70. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code Int. + (1223) 336-033; e-mail: teched@chemcryst.cam.ac.uk).

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Coordination Chemistry of Polyoxometalates: Rational Synthesis of the Mixed Organosilyl Derivatives of Trivacant Polyoxotungstates α -A-[PW $_9$ O $_{34}$ (*t*BuSiO) $_3$ (RSi)] $^{3-}$ and α -B-[AsW $_9$ O $_{33}$ (*t*BuSiO) $_3$ (HSi)] $^{3-}$ *

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Derivatized polyoxometalates are expected to play an increasingly greater role in catalysis, chemotherapy, and molecular science.^[1] In particular, heteropolyoxometalates with an organic, organometalloid, or organometallic group anchored to the oxometalate backbone are attractive precursors for the synthesis of organic–inorganic hybrid materials. They were among the very first organometallic derivatives of polyoxometalates to be reported.^[2, 3a, 3b, 4a] A number of organotin derivatives of the Lindqvist,^[5] Keggin,^[3, 4] and Dawson-type^[4] structures have now been characterized. In contrast, organosilicon derivatives have received comparatively less attention. However, “Keggin-type” derivatives of general formula $[SiW_{11}O_{40}(RSi)_2]^{4-}$

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