Multinuclear NMR Study and Crystal Structure of *trans*-[PtCl$_2$(PHtBu$_2$)$_2$]

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trans-[PtCl$_2$(PHtBu$_2$)$_2$] **(1)** was thoroughly characterised by ^{1}H, ^{31}P{^{1}H} and ^{195}Pt{^{1}H} NMR spectroscopy. Two rotational conformers were found to be stable in solution at room temperature. Force field calculations confirmed that these two conformers are very similar in energy. They co-crystallise in the tetragonal space group *P*4bar as revealed by X-ray diffraction studies. The dynamics of *trans*-[PtCl$_2$(PHtBu$_2$)$_2$] is here reported together with spectroscopic evidence of a phosphido-bridged reduction product.

Introduction

As part of our continuing interest in the chemistry of low-valent transition metal complexes, we recently became interested in the coordination chemistry of metals with secondary bulky phosphanes, such as PHtBu$_2$, PHCy$_2$ and PHPh$_2$, in phosphorus-bridged binuclear systems.[1]

With the aim of investigating the behaviour of platinum(II) complexes towards alkali metal-promoted reduction we have synthesised *trans*-[PtCl$_2$(PHtBu$_2$)$_2$] **(1)** and reacted it with metallic sodium.

Results and Discussion

trans-[PtCl$_2$(PHtBu$_2$)$_2$] **(1)** was first prepared by Shaw et al. who extracted the main NMR features of the [AMX$_{18}$]$_2$ system from its ^{1}H spectrum.[2] Moreover, it was noticed that **1** exists in solution as a mixture of two conformational isomers even at room temperature[2] (Figure 1).
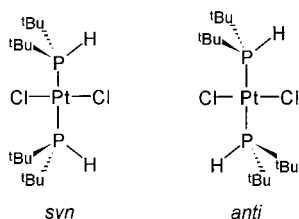

Figure 1

More recently, Goel and Ogini[3] claimed a new synthesis of **1** (as a white solid) from the reaction of K$_2$PtCl$_4$ with PtBu$_3$ in a 1:3 ratio in refluxing DMF. Contrary to Shaw's findings they observed only a broad peak (with satellites) in the ^{31}P{^{1}H} NMR spectrum at ambient temperature ($\delta = 56.8$, CH$_2$Cl$_2$) which was resolved into two peaks at 183 K.

By reaction of PtCl$_2$(PhCN)$_2$ with PHtBu$_2$ in a Pt:P ratio of 1:2 we have obtained **1** as a pale yellow solid. Its ^{1}H NMR spectrum is consistent with that reported by Shaw[2] and shows two overlapped spin systems of the [AMX$_{18}$]$_2$ type, where A is the phosphorus atom, M is the hydrogen directly bound to the phosphorus, X$_{18}$ are the *tert*-butyl hydrogens. Figure 2 shows the M part of this spectrum. The analysis of such a system, developed by Mann,[4] allowed us to obtain the spectroscopic features reported in Table 1 along with ^{1}H, ^{31}P, ^{13}C and ^{195}Pt chemical shifts.
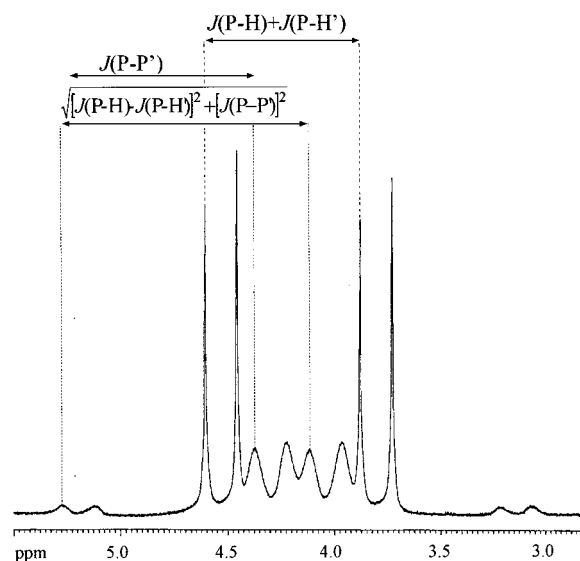

Figure 2. P-H region of the ^{1}H NMR spectrum of *syn* and *anti* conformers of complex **1** (CDCl$_3$, 295 K); see ref.[4] for the analysis of the [AMX$_{18}$]$_2$ spin system

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Table 1. NMR spectroscopic data of complex 1 (CDCl$_3$, 295 K)

	syn isomer	anti isomer
δ(tBu)	1.49	1.48
δ(**H−P**)	4.20	4.05
^1J(P−H)	362 Hz	368 Hz
^3J(P−H′)	1.5 Hz	−5 Hz
^2J(P−P′)	450 Hz	450 Hz
^3J(P−tBu)	13 Hz	11 Hz
^5J(P−tBu′)	1.6 Hz	1.7 Hz
δ(**P**−H)	49.4	56.5
^1J(P−Pt)	2429 Hz	2421 Hz
δ(**CH$_3$**)[a]	31.3	31.3
δ(**C**−P)[a]	34.9	34.9
^1J(P−C)[a]	24 Hz	24 Hz
^2J(P−C)[a]	12 Hz	12 Hz
δ(Pt)	−3738	−3767

[a] Solvent C$_6$D$_6$, 298 K.

The ^{31}P{^{1}H} NMR spectrum of **1** recorded in CDCl$_3$ at ambient temperature shows the presence of two signals with satellites at δ = 49.4 and 56.5 ascribable to the *syn* and *anti* conformers of **1**. Their *anti/syn* ratio, as assessed by the integrals in the ^{31}P NMR spectrum, was found to be equal to 1.2.

The ^{31}P{^{1}H} dynamic NMR spectrum shows the expected broadening of the signals with increasing temperature (Figure 3). A line-shape analysis[5] allowed an estimation of a lower limit of ΔG for the interconversion of the conformers equal to 18 ± 2 kcal/mol.
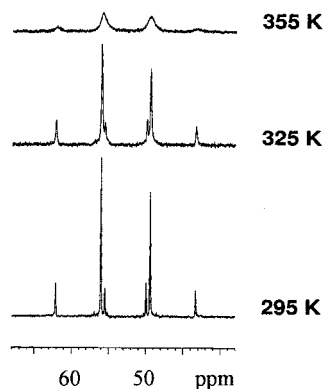

Figure 3. Variable temperature ^{31}P{^{1}H} NMR spectra of complex **1** ([D$_8$]toluene)

The ^{195}Pt{^{1}H} spectrum (Figure 4) shows the expected two triplets with Pt-P direct couplings of 2429 Hz (*syn* isomer) and 2421 Hz (*anti* isomer).

The resonance of the methyl carbons in the ^{13}C{^{1}H} NMR spectrum was found as a doublet ($^2J_{P−C}$ = 12 Hz) centred at δ = 31.3. The quaternary carbons of the coordinated phosphanes give a pseudotriplet arising from the AXX′ system (A = ^{13}C; X,X′ = ^{31}P) when $J_{XX'} \gg J_{AX}$.[6] The chemical shift is δ = 34.9, and the value of $|^1J_{P−C} + {}^3J_{P−C}|$ directly obtainable from the spectrum is 23.4 Hz.

In order to gain insight into the structure of the two (or at least of the most stable) conformers we probed the energy hypersurface with respect to the torsional position of the phosphane ligands. Molecular mechanics calculations were
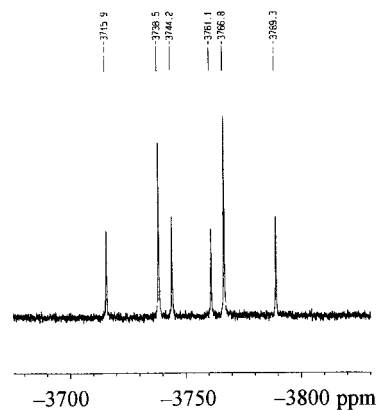

Figure 4. ^{195}Pt{^{1}H} NMR spectrum of complex **1** (CDCl$_3$, 295 K)

performed with an augmented MM2[7] force field. The torsion angles between the Cl−Pt and the P−H bonds in the PH*t*Bu$_2$ ligands were independently varied in steps of three degrees, and for each step all other intramolecular degrees of freedom were allowed to relax. The energy profile and four selected conformers are shown in Figure 5. The two geometries with both PH groups in the coordination plane of the metal centre, i.e. the *anti* (A) and the *syn* isomer (D), have almost the same energy, whereas the geometries with one (B) or two (C) P−H bonds perpendicular to the plane of coordination are energetically less favourable.

In addition to the force field calculations a crystallographic analysis was undertaken. X-ray diffraction studies were carried out on three single crystals of **1**. A ^{1}H NMR analysis of these crystals redissolved in CDCl$_3$ showed the immediate presence of both conformers.

The X-ray diffraction study revealed that **1** crystallises in the space group $P\bar{4}$ with the metal atom on the twofold axis (Wyckoff position 2*g*) and a fractional *z* coordinate of approximately 0.25. Due to this position of the most prom-
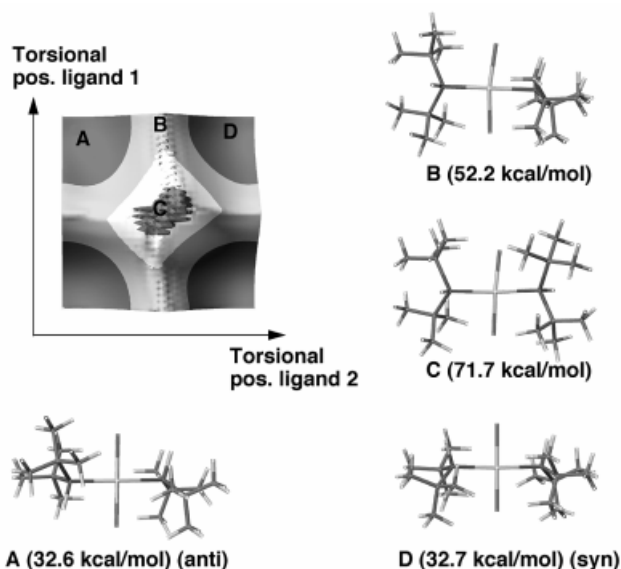

Figure 5. Profile of the energy hypersurface of **1** as a function of the torsional orientation of the phosphane ligands and the geometry of four selected conformers

inent scatterer, the intensity statistics resemble that of an *I* centred lattice: over 95% of the scattered intensity may be attributed to reflections of the type *hkl*, *h* + *k* + *l* = 2*n*.

Location of the metal, chlorine, and phosphorus atoms was straightforward. After refinement of this initial model a Fourier-difference synthesis showed electron density above and below the Pt coordination plane attributable to the carbon atoms of the phosphane ligands. Two alternative strategies were followed to deal with the electron density above and below this plane:

a) Tentative refinement as carbon positions resulted in highly anisotropic displacement parameters. Rigid bond and distance restraints had to be applied to ensure physically and chemically reasonable refinement results. In view of the site symmetry of the Pt central atom this procedure necessarily leads to an *anti* geometry although the NMR spectrum suggested the presence of both conformers in the crystal. Furthermore, the resulting angles around phosphorus were much larger than expected and in conflict with both the above mentioned force-field results and comparable structures of the PH*t*Bu$_2$ ligand[8] drawn from the CSD database.[9]

b) It was observed that the electron density closely matched the situation depicted in Figure 6 and could be explained by superposition of *anti* and *syn* (shaded) conformers, corresponding to geometries A and D, respectively, in Figure 5.
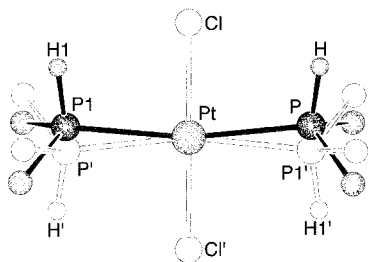

Figure 6. SCHAKAL[12] representation of the alternative orientations of **1** in the crystal; all methyl groups have been omitted, primed atoms are related to unprimed ones by the symmetry operation 1 − *x*, −*y*, *z*; a possible *syn* conformer has been emphasized by shading

The PH*t*Bu$_2$ ligand geometry was extracted from the molecular mechanics model and introduced as a rigid group in two alternative orientations. In addition to the parameters regarding Pt, Cl, and P only two overall isotropic displacement parameters for the methyl C and the phosphorus-bonded carbon atoms were refined. Despite the much smaller number of variables this second approach gave better convergence results. Figure 7 shows a PLATON view of the
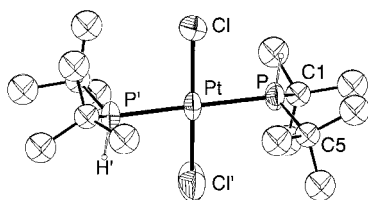

Figure 7. PLATON[13] view of the *anti* conformer of **1** with selected bond lengths [Å] and angles [deg.]: Pt−Cl 2.266(5), Pt−P 2.317(11), Pt−P−C1 112.1(7), Pt−P−C5 113.9(7), C1−P−C5 117.4

anti conformer and lists selected interatomic angles and distances.

trans-[PtCl$_2$(PH*t*Bu$_2$)$_2$] was reacted with excess sodium metal to obtain a complex mixture of compounds as revealed by ^{31}P NMR spectroscopy. Among the signals present in the ^{31}P NMR spectrum of the reaction solution a triplet centred at δ = 278.7 with satellites (J_{P-P} = 43 Hz; J_{P-Pt} = 2588 Hz) was clearly evident in the low field region (Figure 8). The values of the chemical shift and coupling constants are typical for *tert*-butyl phosphides bridging two platinum(I) atoms linked by a metal−metal bond.[7a] The presence, in the region of terminally bonded phosphanes, of a sharp triplet centred at δ = 62.0, with a coupling constant as high as 43 Hz, strongly suggests the formation of the binuclear phosphido-bridged platinum(I) complex [Pt(μ-P*t*Bu$_2$)(PH*t*Bu$_2$)]$_2$ **(2)**.
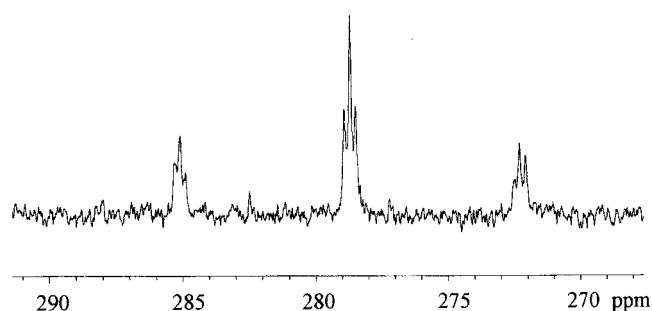

Figure 8. Phosphide resonance in the ^{31}P{^{1}H} NMR spectrum of complex **2** ([D$_8$]toluene, 295 K)

The synthesis of **2** has already been reported by Leoni, Pasquali et al. by hydride abstraction from [Pt(μ-P*t*Bu$_2$)(H)(P*t*Bu$_2$H)]$_2$ but no NMR spectroscopic data were reported, due to its low solubility.[8a] Prolonged reaction times of **1** with sodium led to decomposition into free phosphane, NaCl and platinum metal.

Experimental Section

General: All manipulations were carried out under a pure dinitrogen atmosphere, using freshly distilled and oxygen-free solvents. Di-*tert*-butylphosphane was purchased from Fluka and used as received.

Infrared spectra were recorded on a Perkin−Elmer 883 spectrometer. Elemental analyses were carried out by using a Carlo Erba model EA 1108 elemental analyser.

NMR spectra were recorded on a Bruker Avance DRX500 spectrometer; chemical shifts are referenced to Me$_4$Si (^{1}H and ^{13}C), 85% H$_3$PO$_4$ (^{31}P), and H$_2$PtCl$_6$ (^{195}Pt).

***trans*-Bis(di-*tert*-butylphosphane)dichloroplatinum(II) (1):** A suspension of [PtCl$_2$(PhCN)$_2$][10] (1.3 g, 2.8 mmol) and di-*tert*-butylphosphane (0.88 g, 6.0 mmol) in toluene (20 cm^3) was stirred at 70 °C. After a few minutes a clear yellow solution was obtained, which was cooled to room temperature and concentrated in vacuo. It was then filtered and washed three times with petroleum ether and dried in vacuo (1.3 g, 85% yield). − IR (nujol mull): $\tilde{\nu}_{max}$ = 2351m (P−H), 1365vs, 1181vs, 1023s, 901s, 813vs, 468s, 333vs (Pt−Cl) cm^{-1}. − UV/Vis (CH$_2$Cl$_2$, 1.61 × 10^{-4} mol dm^{-3}): λ$_{max}$ (ε/dm^3 mol^{-1} cm^{-1}) = 240.0 (6180), 267 (8260) and 301.0 (sh) nm.

Crystallography

Crystals of compound **1** were obtained by crystallisation from toluene. Intensity data were collected with Mo-K_α radiation (λ = 0.71073 Å, graphite monochromator) on an ENRAF-Nonius CAD4 diffractometer at 243 K on a crystal of approximate dimensions $0.13 \times 0.13 \times 0.13$ mm.

Crystal data: a = 8.906(1), c = 14.337(4) Å; V = 1137.2(4) Å^3, Z = 2, d(calcd.) = 1.63 g·cm^{-3}, μ = 6.605 mm^{-1}, F(000) = 552. 3977 Reflections were collected with the $\omega-2\theta$ scan method in the range $3.2 < \theta < 25.1$ deg. After merging symmetry equivalent data [R(int) = 0.062], 2032 independent reflections remained for structure solution by direct methods.[11] The final structure model was based on rigid-group refinement of the force field optimised PHtBu$_2$ ligand in two alternative orientations with full-matrix least-squares on F^2.[10] Convergence was reached for 2032 reflections and 50 variables at agreement factors of $wR2$ = 0.0997 (all data), $R1$ = 0.0431 [observations with $I > 2\sigma(I)$]. Max. and min. from a final Fourier map were 1.506 and -0.461 e·Å^{-3}.

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-141698. Copies of the data can be obtained free of charge on application to The Director, CCDC 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Reduction of 1 with Sodium: A suspension of *trans*-[PtCl$_2$(PHtBu$_2$)$_2$] (0.5 g, 0.9 mmol) and sodium sand (0.3 g, 13 mmol) in toluene (10 cm^3) was vigorously stirred at room temperature until a dark green suspension was obtained (about 10 h). Unreacted metallic sodium, NaCl and small amount of platinum metal were filtered off and the solution concentrated in vacuo and used for ^{31}P NMR analysis. The ^{31}P{^{1}H} NMR spectrum of the obtained orange solution showed two triplets with satellites [^{31}P{^{1}H} NMR ([D$_8$]toluene):

δ = 62.0 (t, J_{P-P} = 43 Hz, J_{P-Pt} = 4775 Hz, P$_t$), 278.7 (t, J_{P-P} = 43 Hz, J_{P-Pt} = 2588 Hz, P$_\mu$), along with less-intense signals ascribable to uncharacterised species.

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