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Activation of C–H bond by *cis*-[Pt(NO₃)₂(PPh₃)₂], cyclometallation of tetramethylthiourea

Serena Fantasia ^a, Mario Manassero ^{b,*}, Alessandro Pasini ^{a,*}

^a Dipartimento di Chimica Inorganica Metallorganica e Analitica, via G. Venezian 21, 20133 Milano, Italy ^b Dipartimento di Chimica Strutturale e Stereochimica Inorganica, via Venezian 21, 20133 Milano, Italy

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Abstract

Reaction of *cis*-[Pt(NO₃)₂(PPh₃)₂] with tetramethylthiourea (tmtu) affords [Pt(PPh₃)₂(tmtu^{*})]NO₃, in which tmtu^{*} is tetramethylthiourea deprotonated at one methyl group. An X-ray investigation has shown that tmtu^{*} is cyclometallated with Pt–S and Pt–CH₂ bonds. The likely role of dissociation of the labile nitrato ligands, to give cationic intermediates, is outlined. © 2003 Elsevier B.V. All rights reserved.

Keywords: Cyclometallated tetramethylthiourea; Platinum-nitrato-phosphine complex; X-ray structure

1. Introduction

Inter- and intramolecular activation of C–H bonds on platinum(II) is a topic of great interest and continuing investigations [1–4]. Here we present a case of such an activation of a methyl group of tetramethylthiourea (tmtu) on the *cis*-Pt(PPh₃)₂ species which gives rise to a Pt(II) complex with cyclometallated tmtu* [tmtu*, (CH₃)₂NC(S)N(CH₃)CH₂⁻]. Although a crystallographically characterised Pt(IV) derivative of tmtu* has been reported [5], to our knowledge this is the first example of a Pt(II) complex with cyclometallated tmtu*.

2. Experimental

2.1. General

All manipulations were carried out in the air. Solvents and reagents were used as received. NMR spectra were recorded on a Bruker Avance DRX 300 instru-

ment. δ values in ppm are relative to Me₄Si, H₃PO₄ and [PtCl₆]²⁻. *cis*-[Pt(NO₃)₂(PPh₃)₂] was prepared according to [9].

2.2. Synthesis of bis-triphenilphosphinetetramethylthioureato(C,S)platinum(II) nitrate

Equimolar amounts of tmtu (0.059 g, 0.44 mmol) and *cis*-[Pt(NO₃)₂(PPh₃)₂] were dissolved in 30 ml of CH₂Cl₂. The yellow solution was refluxed for 5 h until the colour faded. Concentration under reduced pressure gave 0.305 g (76%) of the product. Elemental analysis: found: C, 54.0; H, 4.2; N, 4.3. C₄₁H₄₁N₃O₃P₂PtS requires: C, 53.9; H, 4.5; N, 4.6.

2.3. X-ray crystallography

Crystal data: C₄₃H₄₃Cl₆N₃O₃P₂PtS, M = 1151.66, triclinic, space group P1 (no. 1), a = 9.644(1), b = 10.902(1), c = 12.077(1) Å, $\alpha = 74.99(1)$, $\beta = 85.46(1)$, $\gamma = 87.42(1)^\circ$, U = 1222.2(2) Å³, z = 1. Bruker SMART Area Detector, ω scan, T = 296 K, full-matrix least squares refinement on all reflections (9258, Friedel pairs not merged), $R_2 = 0.125$ and $R_{2w} = 0.139$ on F^2 , conventional $R_1 = 0.062$ on 7200 reflections ($I > 2\sigma(I)$). R_2 of the enantiomorph = 0.164.

^{*}Corresponding authors. Tel.: +39-02-26680676; fax: +39-02-2362748.

E-mail addresses: alessandro.pasini@unimi.it (S. Fantasia), mario.manassero@unimi.it (M. Manassero).

The atomic co-ordinates of the structure model have been deposited with the Cambridge Crystallographic Data Centre.

3. Results

3.1. General

During our work on platinum(II) complexes with sulfur donor ligands [6–9], we had the occasion of allowing tmtu to react with *cis*-[Pt(NO₃)₂(PPh₃)₂] (1) in CH₂Cl₂ or CHCl₃. Whichever the tmtu/Pt molar ratio ratio used (from 0.8 to 2.5), we obtained the same compound **2**, whose analysis was consistent with the stoichiometry Pt/(PPh₃)₂/tmtu/NO₃, with the nitrato group anionic [ν (NO₃) 1380 cm⁻¹]. These results suggested ionisation of tmtu, consequently we grew crystals suitable for X-ray diffraction studies by diffusion of disopropyl ether into a CHCl₃ solution of **2**. The crystals were of poor quality, but we attempted a diffraction study in order to elucidate the nature of the complex.

3.2. Description of the structure of 2.2CHCl₃

The structure consists of the packing of $[Pt(PPh_3)_2 (tmtu^*)]^+$ cations, NO_3^- anions and CHCl₃ molecules in the molar ratio 1:1:2.

Ρt



An ORTEP view of the cation is shown in Fig. 1. Selected interatomic distances and angles are reported in the figure caption. The metal atom is four coordinate with two cis phosphine groups, one sulfur atom and one carbon atom of cyclometallate tmtu*. The coordination geometry is square planar with a slight tetrahedral distortion, maximum displacements from the best plane being +0.106(12) and -0.103(3) Å for C(2) and S, respectively. The penta-atomic metallacycle is essentially planar, with maximum distances from the best plane of +0.051(12) and -0.068(10) Å for C(2) and N(1), respectively. The two Pt–P bond lengths are in the range found for PPh3 trans to alkyl carbon [10] and to Scoordinated thiourea [11-13]. Bond parameters involving the tmtu* ligand can be compared with those found in the octahedral Pt(IV) complex [Pt(tmtu*)₂Br₂], 3 [5]. Thepresent Pt–S bond length, 2.298(3) Å is very similar to those found in 3 $(2.313(2) \text{ Å for both tmtu}^*)$. On the contrary, the Pt-C distance found here, 2.15(1) Å, is significantly longer than those found in 3, 2.031(7) and 2.045(9) A, probably because of the stronger trans-influence of phosphorus with respect to that of bromine and/or the different oxidation state of Pt. The bites of the chelating tmtu^{*} ligands are $83.3(4)^{\circ}$ here and 83.6(2)and $86.2(2)^{\circ}$ in compound **3**.

3.3. NMR spectral characterisation

The ³¹P NMR spectrum (CDCl₃ solution) shows two doublets with J_{P-P} 22.9 Hz, centred at 17.14 ppm (J_{Pt-P}, 2022 Hz) and 22.22 ppm (J_{Pt-P} 3462 Hz). The latter doublet is assigned to P *trans* to S on the basis of literature data [11], the other is assigned to P *trans* to CH₂. Pt–P coupling constants were confirmed in the ¹⁹⁵Pt NMR spectrum (δ – 4796.8 ppm, doublet of doublet).

There are three resonances attributable to the tmtu^{*} moiety in the ¹H NMR spectrum (CDCl₃ solution): at 3.02 ppm (s, 6H); 3.08 (s, 3H) and a complex signal centred at 3,50 ppm (2H), which shows ¹⁹⁵Pt satellites (J_{Pt-H} 60.0 Hz). Upon irradiation of the ³¹P resonance at 17.1 ppm (P *trans* to CH₂), such signal becomes a doublet with a 4.98 Hz separation. A doublet, with 3.73 Hz separation, is also obtained by irradiation of the resonance of the phosphorus *trans* to S (i.e. *cis* to CH₂). Coupling of the CH₂ protons with both P atoms was confirmed by an heteronuclear multiple quantum correlation (HMQC) experiment which showed cross peaks with both P resonances. Both ³¹P and ¹H spectra are unchanged in the temperature range 250–320 K.

The ¹³C NMR spectrum is interesting since all C atoms of tmtu* display coupling with the phosphorus atoms. Chemical shifts of tmtu* are: 43.5 ppm (uncoordinated N(CH₃)₂, J_{P-C}, 1.3 Hz); 46.0 (NCH₃ adjacent to CH₂, J_{P-C}, 3.9 Hz; J_{Pt-C}, 52.0 Hz); 56.2 (CH₂, J_{P-C}, 88.9 Hz; J_{Pt-C}, 540.9 Hz); 183.0 (C=S, J_{P-C}, 18.2 Hz). Note that the CH₂ group is coupled only to one P

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atom, in contrast to the coupling with both P atoms observed for the protons of such group. Note also the small but clearly discernible ⁴J of the N(CH₃)₂ carbon atoms, which also show barely detectable Pt satellites as shoulders. No Pt–C coupling was observed for C = S, the signal is rather weak, however, and Pt satellites may be buried in the background.

3.4. Formation studies

Formation of compound 2 was followed by ³¹P NMR spectroscopy, (at 300 k). Immediately after the addition of one equivalent of tmtu to a CHCl₃ solution of the nitrato complex 1, (δ , 3.62 ppm, J_{Pt-P}, 4010 Hz [9]), a new species, 4, which shows two doublets $(J_{P-P}, 19.5)$ Hz), at 1.70 ppm (J_{Pt-P}, 3830 Hz) and 18.95 ppm, (J_{Pt-P}, 3225 Hz) starts to grow. We assign the two doublets to cis-[Pt(NO₃)(PPh₃)₂(tmtu-S)]⁺, (with S-coordinated tmtu) with the 1.70 signal due to P trans to ONO₂, on account of its chemical shift and Pt-P coupling constant similar to that of the nitrato complex [9], while the 18.95 ppm doublet is assigned to P trans to S, in accordance with literature data [11]. Coordination of tmtu is also confirmed by the shift of the resonance of the CH₃ protons, in the ¹H NMR spectrum, from 3.09 ppm (in free tmtu) to 3.17 ppm (singlet). Both spectra show also faint traces of the resonances of the product, which becomes clearly visible after 20 min. No other signal, including resonances attributable to hydrido species, was detected.

If the reaction mixture is treated with water, its layer is acidic, suggesting the formation of nitric acid whose presence in the CH_2Cl_2 phase was confirmed by mass spectrometry: injection of the CH_2Cl_2 solution into a helium gas flow quadrupole mass spectrometer [14] gave a signal at m/z 63.

4. Discussion

Activation of the C–H bond in the case here reported is favoured by the stabilisation of the final product, achieved by the formation of a five membered chelate ring, but also by the use of labile nitrato ligands which,



Scheme 1.

upon dissociation, give rise to cationic complexes, capable of C–H activation [15,16]. A likely reaction path is depicted in Scheme 1. Substitution of one nitrato group by tmtu-S gives intermediate 4, detected by NMR spectroscopy (see above). Dissociation of the second NO_3^- ligand can give rise to the (undetected) species 5 with an agostic C–H interaction. The high positive charge of 5 will favour deprotonation of an NCH₃ group to give 2 and HNO₃.

Two main mechanisms have been proposed for the activation of C–H bonds on Pt(II) [1–3,17]: oxidative addition of C–H to give a transient Pt(IV)–H species, which will eventually give the Pt(II) product by reductive elimination, and electrophilic activation of a η^2 -C–H labile intermediate which could be formed by dissociation of one nitrato group. Although our results seem in accordance with the latter mechanism, the former cannot be ruled out, since the transient Pt(IV)–H intermediate could be too short living to be detected. Clearly more detailed studies are needed to wholly understand the mechanism of this reaction, as well as its scope.

Supplementary material

All crystallographic data have been deposited with the Crystallographic Data Centre, CCDC No. 222321.

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