Anion-assisted *trans–cis* isomerization of palladium(II) phosphine complexes containing acetanilide functionalities through hydrogen bonding interactions†

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Received (in Cambridge, UK) 3rd December 2004, Accepted 19th January 2005
First published as an Advance Article on the web 26th January 2005
DOI: 10.1039/b418202b

The anion-assisted shift of *trans–cis* isomerization equilibrium of a palladium(II) complex containing acetanilide functionalities brought about by allosteric hydrogen bonding interactions has been established by UV/Vis, ^{1}H NMR, ^{31}P NMR and ESI-MS studies.

The phenomenon of *trans–cis* isomerization in square-planar d^8 metal complexes, such as those of palladium(II) and platinum(II), is well known and has been extensively studied.[1,2] Most of these studies were directed towards *trans–cis* isomerization reactions that were induced either thermally or by photochemical means. Corresponding studies involving ion-induced or assisted isomerization reaction brought about by allosteric interactions were not known. It was only recently that we reported the first system where the binding of alkali metal ions in a sandwich fashion between the bis(crown) unit of a crown ether-containing palladium(II) complex resulted in the *trans–cis* isomerization of the palladium complex.[3] As an extension of our work on the use of allosteric interactions to provide the driving force for *trans–cis* isomerization reactions, together with the growing importance of the role of anions in biological, chemical and environmental processes,[4] we are interested in investigating the possible extension of using anion complexation and allosteric interactions to promote the isomerization processes. Herein, we report the synthesis and anion-assisted *trans–cis* isomerization of a palladium(II) complex through the formation of hydrogen bonding interactions.

The complexes, $[PdCl_2(Ph_2PC_6H_4NRCOMe)_2]$ (R = H, **1**; Me, **2**), were prepared by the reaction of $[PdCl_2(PhCN)_2]$ with two equivalents of $Ph_2PC_6H_4NHCOMe$ and $Ph_2PC_6H_4NMeCOMe$ (see ESI† for detailed experimental procedures), respectively, in benzene, using a modified procedure.[5] Subsequent recrystallization from slow diffusion of diethyl ether vapor into chloroform solutions of complexes **1** and **2**, respectively, yielded **1** and **2** as pale yellow crystals. Both **1** and **2** were characterized by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy, positive-ion FAB mass spectrometry and gave satisfactory elemental analyses. The *trans* disposition of the two phosphines in the solid state was confirmed by X-ray crystallographic determination of **1** (see ESI† for perspective drawing and crystal structure data of **1**‡).

† Electronic supplementary information (ESI) available: experimental details of $Ph_2PC_6H_4NRCOMe$ (R = H and Me), characterization of **1** and **2**, and crystallographic data of **1**. See http://www.rsc.org/suppdata/cc/b4/b418202b/

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Upon dissolution of **1** in $CDCl_3$, an equilibrium mixture of the *cis* and *trans* isomers with the *trans* form being the major species (*trans*:*cis* ≈ 4:1) was observed, as revealed by the observation of two singlets in the ^{31}P NMR spectrum at δ 22.98 and 32.94 ppm, assigned as the *trans* and *cis* isomers, respectively. Similar chemical shifts have been observed in other related *trans*- and *cis*-dichloropalladium(II) phosphines.[6] This is in contrast to the related *trans*-$[PdCl_2(Ph_2PB15C5)_2]$[3] and complex **2**, where only the *trans* isomer was observed in $CDCl_3$. The observation of both *trans* and *cis* isomers in **1** but not in **2** may be attributed to the stabilization of the *cis* isomer of **1** by the formation of intramolecular hydrogen bonds between the –NH and the –C=O moieties on the adjacent acetanilides.

The electronic absorption spectrum of **1** in $CHCl_3$ showed an intense high-energy band at 260 nm, assigned as metal-perturbed intraligand (IL) transition of the phosphine ligand. With reference to previous spectroscopic studies on dihalopalladium(II) phosphines,[7] the moderately intense low-energy absorption band at 354 nm, with absorption coefficient of the order of 10^4 dm^3 mol^{-1} cm^{-1}, is assigned as a ligand-to-metal charge-transfer (p_π(Cl) → 4d(Pd)) transition.

Addition of tetra-*n*-butylammonium chloride (^{n}Bu$_4$NCl) to a solution of **1** in $CHCl_3$ resulted in changes in the UV/Vis absorption spectrum with well-defined isosbestic points (Fig. 1).

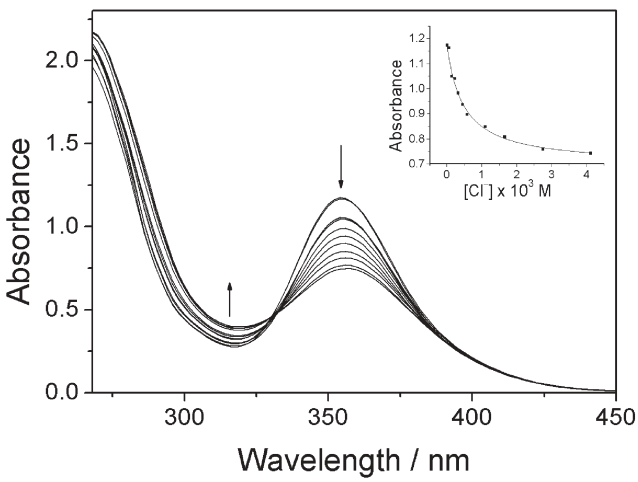
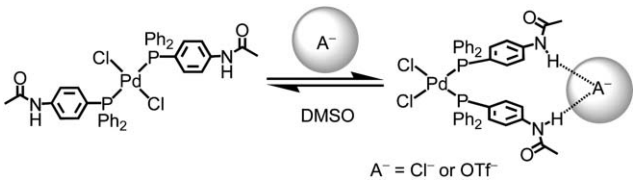


Fig. 1 UV/Vis spectral changes of **1** upon addition of ^{n}Bu$_4$NCl in $CHCl_3$. The inset shows the absorbance at 354 nm (■) as a function of the concentration of Cl^- ions with theoretical fit (—).

Similar spectral changes were not observed in a control experiment using the *N*-methylated analogue, **2**. Replacement of $^{n}Bu_4NCl$ with $^{n}Bu_4NPF_6$ did not cause any spectral changes of **1**, indicating that the changes were not attributed to ionic strength effect. It is likely that the spectral changes observed are a result of the binding of chloride ions to the amide groups present in **1** *via* the formation of hydrogen bonds. The inset in Fig. 1 shows the titration curve of **1** upon addition of $^{n}Bu_4NCl$, with its theoretical fit to the equation supporting the formation of a 1:1 adduct,[8] giving a log *K* value of 3.39.

Both ^{1}H and ^{31}P NMR studies were undertaken to rationalize these findings. The ^{1}H NMR spectrum of complex **1** in $CDCl_3$ showed two NH signals at δ 7.6 and 8.3 ppm, assigned by NOESY experiment as the *trans* and *cis* isomer, respectively. The *cis* amide proton resonance appears at a more downfield region, probably due to the presence of intramolecular hydrogen bonding between the two adjacent amide functionalities. Similar to the UV/Vis titration studies, addition of $^{n}Bu_4NCl$ to a $CDCl_3$ solution of **1** caused a change, where the amide proton resonance of both the *trans* and *cis* isomers shifted downfield initially. This is probably as a result of the formation of hydrogen bonds between the –NH amide groups and the chloride ion. Further addition of $^{n}Bu_4NCl$ resulted in the conversion of the hydrogen-bonded chloride adduct of the *trans* complex to the corresponding *cis* complex, as evidenced by the growth in the intensity of the *cis* amide proton. The greater stability of the hydrogen-bonded chloride-bound *cis* adduct would favor *cis* product formation. No further attempts were made to quantify the changes based on the integral ratios of the amide protons since they were usually very broad. Since the *cis* isomer is preferentially stabilized *via* hydrogen bond formation between the complex and the guest, addition of other guests that are capable of hydrogen bonding to the amide functionalities should lead to similar observations. Indeed, addition of $^{n}Bu_4NOTf$ increases the population of the *cis* isomer with a log *K* value of 2.61.

A more noticeable change was observed in the ^{31}P NMR titration experiments of **1** with $^{n}Bu_4NCl$ (Fig. 2). Addition of Cl^- ions led to an increase in the population of the *cis* isomer at δ 32.94 ppm and a decrease of the *trans* isomer at δ 22.98 ppm. Similar findings were not observed in a control experiment with **2** under the same conditions, thus the presence of the –NH amide groups promotes the formation of the *cis* isomer. The *trans–cis* isomerization of square-planar palladium(II) complexes is well known and the mechanism well studied.[2] In most cases, the *trans* isomer is usually the more thermodynamically favored product, however, the equilibrium of the *trans* and *cis* isomer is shifted in the case of **1** due to the preferential stabilization of the *cis* isomer by the formation of hydrogen bonds between the two –NH amide groups and the Cl^- ion (Scheme 1). Thus the formation of two intermolecular hydrogen bonds between the palladium(II) complex and the Cl^- ion results in the *cis* isomer being the more thermodynamically favored product with a *trans:cis* ratio $\approx$ 1:3. Attempts to study other anions containing hydrogen bond donors, such as $H_2PO_4^-$ in the form of its $^{n}Bu_4N^+$ salt, were unsuccessful, because they also bind to **2**, resulting in an increase of the *cis* isomer due to hydrogen bonding to the carbonyl group of the *N*-methylated amide group. It is interesting to note that the system is reversible on addition of DMSO-d_6 to a solution of **1** and $^{n}Bu_4NOTf$ in $CDCl_3$, resulting in a decrease in the *cis* isomer and an increase in the *trans* isomer. The presence of DMSO-d_6 results in the breaking of the intermolecular hydrogen bonds between the complex and guest, leading to the formation of the more thermodynamically stable *trans* isomer in the absence of the hydrogen bonded complex:guest adduct.



Scheme 1 Schematic representation of the reversible *trans–cis* isomerization of **1** in the presence of Cl^- or OTf^- ions and DMSO.

As indicated by ^{31}P NMR studies, a shift of the equilibrium from *trans* to *cis* occurred upon the addition of Cl^- ions. In fact, the presence of both the *trans*-**1** and *cis*-**1** isomers would require a description involving at least four species in equilibrium (Scheme 2), assuming that only 1:1 **1**·Cl^- adducts are formed under the conditions studied. Detailed treatment[3] of the ^{31}P NMR data according to Scheme 2 gave K_1, K_2 and K_3 values of 0.250 $\pm$ 0.004, 2410 $\pm$ 144 and 514 $\pm$ 111, respectively. The overall equilibrium constant, log *K* of 3.38, where $K = K_1K_2$, is in close agreement with the log *K* value determined by UV/Vis spectrophotometry. Negative ESI mass spectrometric measurements provided further supporting evidence for the 1:1 adduct formation. In the case of **1**, the $\{\mathbf{1}\cdot Cl\}^-$ adduct was observed, irrespective of the concentration of Cl^- ions added, while for **2**, no $\{\mathbf{2}\cdot Cl\}^-$ was observed in the negative ESI-mass spectrum.

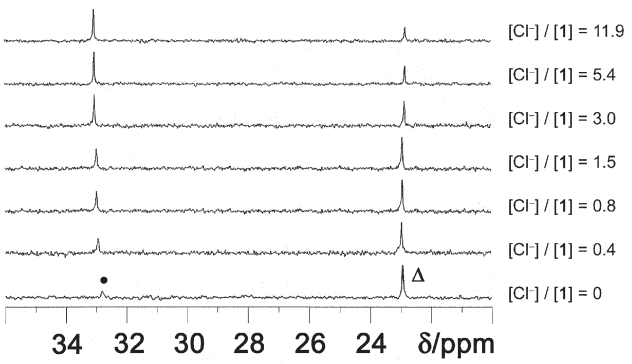
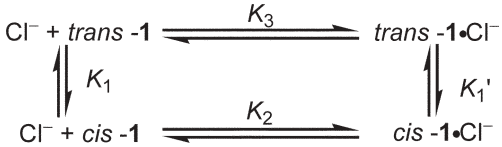


Fig. 2 ^{31}P NMR spectral changes of **1** (3.64×10^{-4} mol dm^{-3}) upon addition of $^{n}Bu_4NCl$ in $CDCl_3$ at 298 K, with the signal corresponding to the *cis* (•) and *trans* (Δ) isomers indicated.



Scheme 2 Proposed binding equilibria between **1** and Cl^- ions.

In summary, the remarkable shift of isomerization equilibrium brought about by allosteric interactions involving hydrogen bond formation has been established by UV/Vis, ^{1}H NMR, ^{31}P NMR and ESI-MS studies. The present *trans–cis* isomerization of the square-planar palladium(II) complex that is promoted *via* the binding of chloride or trifluoromethanesulfonate ions to amide functionalities through hydrogen bonding, reversible on addition of DMSO, represents another interesting demonstration of principle in manoeuvring and shifting the thermodynamic stability of the isomeric products *via* allosteric interactions.

V. W.-W. Y. acknowledges support from the University Development Fund of The University of Hong Kong, The University of Hong Kong Foundation for Educational Development and Research Limited, and the University Grants Committee of the Hong Kong Special Administrative Region, China (Project No. AoE/P-10/01). H.-S. T. acknowledges the receipt of a Postgraduate Studentship, and C.-C. K. and J. K.-Y. W. the receipt of University Postdoctoral Fellowships, both administered by The University of Hong Kong. This work has been supported by a grant from the Research Grants Council of the Hong Kong SAR, China (Project No. HKU7120/02P).

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Notes and references

‡ *Selected crystal data* for **1**, $C_{72}H_{108}Cl_4N_4O_2P_2Pd$, M_r = 1371.76, crystal size 0.40 × 0.25 × 0.20 mm, monoclinic $P2_1/n$, a = 13.641(3), b = 18.267(4), c = 15.156(3) Å, β = 92.42(3)°, V = 3773.2(14) Å^3, Z = 2, D_c = 1.207 g cm^{-3}, μ(Mo-Kα) = 0.473 mm^{-1}, F(000) = 1456, T = 301(2) K, 16043 data (5926 unique, R_{int} = 0.0472, 1.86 < θ < 25.35°), conventional R = 0.0427 [$I > 2\sigma(I)$], S = 0.922 for 394 data. Residual electron density extremes were 0.457 and −0.511 e Å^{-3}. CCDC 258649. See http://www.rsc.org/suppdata/cc/b4/b418202b/ for crystallographic data in .cif or other electronic format.

1 J. H. Nelson and D. A. Redfield, *J. Am. Chem. Soc.*, 1974, **96**, 6219; Y. J. Kim, J. I. Park, S. C. Lee, K. Osakada, M. Tanabe, J. C. Choi, T. Koizumi and T. Yamamoto, *Organometallics*, 1999, **18**, 1349; G. Alibrandi, L. M. Scolaro and R. Romeo, *Inorg. Chem.*, 1991, **30**, 4007.
2 D. Minniti, *Inorg. Chem.*, 1994, **33**, 2631; D. A. Redfield, J. H. Nelson, R. A. Henry, D. W. Moore and H. B. Jonassen, *J. Am. Chem. Soc.*, 1974, **96**, 6298; M. Cusumano, G. Guliemo, V. Ricevuto, O. Traverso and T. J. Kemp, *J. Chem. Soc., Chem. Commun.*, 1979, 775; D. G. Cooper and J. Powell, *Can. J. Chem.*, 1973, **51**, 1634.
3 V. W. W. Yam, X. X. Lu and C. C. Ko, *Angew. Chem., Int. Ed.*, 2003, **42**, 3385.
4 P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486, and references cited therein; F. P. Schmidtchen and M. Berger, *Chem. Rev.*, 1997, **97**, 1609; P. Chakrabatri, *J. Mol. Biol.*, 1993, 463.
5 J. Tsuji and K. Ohno, *J. Am. Chem. Soc.*, 1968, **90**, 94.
6 S. O. Grim and R. L. Keiter, *Inorg. Chim. Acta.*, 1970, **4**, 56.
7 C. K. Jørgensen, *Prog. Inorg. Chem.*, 1970, **12**, 101.
8 J. Bourson, J. Pouget and B. Valeur, *J. Phys. Chem.*, 1993, **97**, 4552.

