Metal-Ion Induced Isomerization

First Observation of Alkali Metal Ion Induced *Trans–Cis* Isomerization of Palladium(II) Phosphane Complexes Containing Crown Ether Moieties**

Vivian Wing-Wah Yam, Xiao-Xia Lu, and Chi-Chiu Ko*

There has been growing interest in the design of allosteric host molecules that can efficiently transmit the information associated with the binding of an ion or molecule to another

---

[*] Prof. Dr. V. W.-W. Yam, Dr. X.-X. Lu, C.-C. Ko
Department of Chemistry, and
Open Laboratory of Chemical Biology of the Institute of Molecular Technology for Drug Discovery and Synthesis
The University of Hong Kong
Pokfulam Road, Hong Kong (P. R. China)
Fax: (+852) 2857-1586
E-mail: wwyam@hku.hk

[**] V.W.-W.Y. acknowledges support from The University of Hong Kong and the University Grants Committee Area of Excellence Scheme and the receipt of a Croucher Senior Research Fellowship (2000–2001) from the Croucher Foundation. C.-C.K. acknowledges the receipt of a Croucher Scholarship from the Croucher Foundation and a Li Po Chun Postgraduate Scholarship from the Li Po Chun Charitable Fund. The work has been supported by a grant from the Research Grants Council of the Hong Kong SAR, China (Project No. HKU 7120/02P). Dr. K. Lau and Dr. K. K. Cheung are gratefully acknowledged for developing the computer program for iterative fits and for solving the X-ray crystal structures, respectively.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200351178

binding site through structural changes induced on binding.[1,2] Such allosteric binding behavior not only serves as a means to control the binding or release of ions or molecules, but also provides a new strategy for the design and construction of molecular-switching devices. Although *trans–cis* thermal and photoisomerization reactions are well-known[3,4] and numerous works on photoinduced ion binding have appeared in the literature,[3] there have been no reports of metal-ion-induced or -assisted isomerization reactions brought about by allosteric interactions. In this regard, we were interested in investigating the possibility of using metal-ion complexation and allosteric interactions to induce isomerization processes. Herein, we report the unprecedented *trans–cis* isomerization of dichloropalladium(II) phosphanylcrown complexes that is induced by the binding of alkali-metal ions, as evidenced by UV/Vis, ^{1}H NMR, and ^{31}P NMR spectroscopy as well as ESI-MS, and represents a novel type of allosteric host that is the first of its kind.

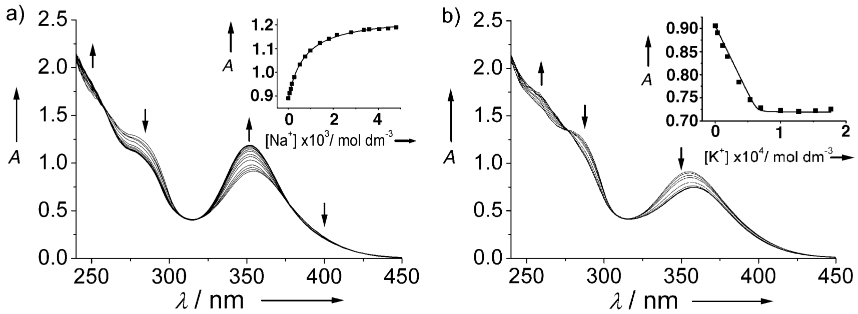


Figure 1. UV/Vis spectral changes of **1** upon addition of various concentrations of: a) $NaClO_4$ and b) KPF_6 in CH_3CN/CH_2Cl_2 (9:1 v/v, 0.1 mol dm^{-3} nBu$_4$NPF$_6$). Insert: absorbance at 355 nm (■) as a function of the concentration of Na^+ or K^+ ions with theoretical fits.

The reaction of $[PdX_2(PhCN)_2]$ with two equivalents of PPh$_2$-benzo[15]-crown-5 (PPh$_2$(B15C5)) or PPh$_2$-benzo[18]crown-6 (PPh$_2$(B18C6)) in benzene, by using a modification of literature procedures,[5] produced [PdX$_2${PPh$_2$(B15C5)}$_2$] (X = Cl, **1**;[6] Br, **2**; I, **3**) and [PdCl$_2${PPh$_2$(B18C6)}$_2$] (**4**).[5] The identities of **1**–**4** have been confirmed by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopic analysis, positive-ion FAB mass spectrometry, and satisfactory elemental analyses. The crystal structures of **1** and **2** have also been established as having a *trans* configuration by X-ray crystallographic analysis.[7]

Although the complexes exist as *trans* isomers in CD_2Cl_2, dissolution of these complexes in mixed solution of CD_3CN and CD_2Cl_2 (9:1 v/v) results in an equilibrium between the *cis* and *trans* isomers, with the *trans* form being the majority species. For example, a solution of **1** in CD_3CN/CD_2Cl_2 (9:1 v/v) shows two singlets in the ^{31}P NMR spectra (one at $\delta = 24.02$ ppm and one at $\delta = 33.26$ ppm) with an integral ratio of 3.57:1 which are ascribed to the *trans* and *cis* isomers of **1**, respectively. This assignment is consistent with the similar chemical shifts commonly observed in other related $[PdX_2L_2]$ systems (L = monodentate phosphane ligand).[8] The assignment is further supported by an increase in the intensity of the signal corresponding to the *cis* isomer at $\delta = 33.26$ upon irradiation at $\lambda = 256$ nm of a solution of **1** at −10 °C. This increase is commonly observed in the photoisomerization of *trans*-$[PdX_2L_2]$ systems.[9]

The electronic absorption spectra of solutions of **1**–**4** in CH_3CN showed high-energy bands at about 270–300 nm which are assigned as intraligand (IL) and metal-perturbed IL transitions of the phosphane ligand. The low-energy absorption bands at about 350–430 nm (with extinction coefficients of the order of 10^4 dm^3 mol^{-1} cm^{-1}), which are strongly dependent on the nature of the halides (λ_{abs}: **1**(354 nm) < **2**(374 nm) < **3**(426 nm)), were tentatively assigned as ligand-to-metal charge-transfer ($p_\pi(X) \rightarrow 4d(Pd)$; X = Cl, Br, I) transitions.

The addition of alkali-metal ions to a solution of **1** in CH_3CN/CH_2Cl_2 (9:1 v/v, 0.1 mol dm^{-3} nBu$_4$NPF$_6$) resulted in changes in the UV/Vis spectrum with well-defined isosbestic points (Figure 1). Similar spectral changes were not observed in a control experiment using a crown-free analogue [PdCl$_2${PPh$_2${3,4-(OMe)$_2$C$_6$H$_3$}}$_2$] (**5**), which indicates that these changes can be ascribed to the binding of the cations to the polyether cavity. It is interesting to note that addition of $NaClO_4$ to a solution of **1** (6.4×10^{-5} mol dm^{-3}) in CH_3CN/CH_2Cl_2 (9:1 v/v, 0.1 mol dm^{-3} nBu$_4$NPF$_6$) resulted in an increase in the absorbance and a small blue shift in the absorption energy of the low-energy band, which reached saturation at about 2.2×10^{-3} mol dm^{-3} (Figure 1 a). However, a decrease in the absorbance and a small red shift of the band were observed upon addition of KPF_6, which reached saturation at about 6.6×10^{-5} mol dm^{-3} (Figure 1 b). The UV/Vis spectral changes upon addition of other alkali-metal salts such as $LiClO_4$ to a solution of **1** are similar to that of $NaClO_4$, whereas $RbClO_4$ and $CsClO_4$ showed similar changes as KPF_6. The inserts in Figure 1 show the titration curves of **1** with $NaClO_4$ and KPF_6 together with their theoretical fits to the equation for the formation of a 1:1 adduct.[10] Stoichiometry studies indicate that **1** forms 1:1 complexes with both Na^+ and K^+ ions under the conditions studied. Addition of K^+ ions (up to a concentration of 3×10^{-4} mol dm^{-3}) to **4** gave a similar UV/Vis spectral change as that for **1** upon the addition of Li^+ and Na^+ ions, whereas addition of Cs^+ ions to **4** gave a similar spectral change as that observed for **1** upon addition of K^+ ions, that is, a decrease in the absorbance and a small red shift in the low-energy absorption band, which reached saturation at about 7.9×10^{-5} mol dm^{-3}.

Both ^{1}H and ^{31}P NMR studies were undertaken to rationalize these findings. Coordination of alkali-metal ions to both **1** and **4** was signified by downfield shifts of the crown ether protons. Interestingly, signals corresponding to the protons of *cis*-**1** initially shifted downfield upon titration with $NaClO_4$ at low concentrations, which gradually disappeared altogether upon addition of a large excess of $NaClO_4$ (ca. 500-fold), while addition of even a small amount of KPF_6 (< 1-fold) resulted in the growth of proton signals corresponding to the *cis* isomer. A more noticeable change could be observed in the ^{31}P NMR titration experiments of **1** with $NaClO_4$ and KPF_6. Figure 2 shows the changes in the ^{31}P NMR spectra of a solution of **1** in CD_3CN/CD_2Cl_2 (9:1 v/v) upon complexation of Na^+ (Figure 2a) and K^+ ions (Figure 2b). Addition of Na^+ ions initially gave rise to a slight downfield shift of the ^{31}P NMR signal, which is typical for the binding of a metal ion to the crown cavity. However, the addition of an excess of Na^+ ions (ca. 500-fold) resulted in the ^{31}P signal corresponding to the *cis* isomer at $\delta = 33.26$ disappearing, and leaving behind only the signal corresponding to the *trans* isomer. The addition of K^+ ions to **1**, in contrast, immediately gave rise to an increase in the population of the *cis* isomer, with the *cis* form becoming the predominant species as the K^+ concentration increased until saturation was reached at a $[K^+]$:[**1**] ratio of approximately unity. Similar findings were not observed in the control experiment with the crown-free analogue **5** under the same conditions, which supports the importance of the crown moieties in the specific association of the metal ions. We believe that the addition of K^+ ions, which are too large to fit into the cavity size of the benzo[15]crown-5 moiety in **1** resulted in the *trans* to *cis* isomerization of the palladium(II) complex, while addition of Na^+ ions in large excess would favor the formation of the *trans* isomer (Scheme 1). In general, benzo[15]crown-5 derivatives tend to form 2:1 (crown ether ring/metal ions) sandwich-type complexes with metal ions that are slightly greater in size than the crown ether cavity, that is, K^+, Rb^+, and Cs^+, with K^+ ions giving the best fit. Such intramolecular sandwich or tweezer binding modes in **1** would favor the conversion into the *cis* configuration, in which the two crown ether rings within the same molecule of **1** would bind to one metal ion. On the other hand, the binding of Li^+ and Na^+ ions into the cavity of benzo[15]crown-5 from solutions at high ion concentrations would favor the formation of the *trans* isomer as a consequence of electrostatic interactions arising from the binding of two metal ions to a molecule of **1**. Similarly, addition of K^+ ions, which could fit into the cavity of benzo[18]crown-6, to a solution of **4** would give rise to the formation of the *trans* isomer at high concentrations of K^+ ions, while Cs^+ ions should favor the formation of the *cis* form for a sandwich-type of binding, even at low concentrations.

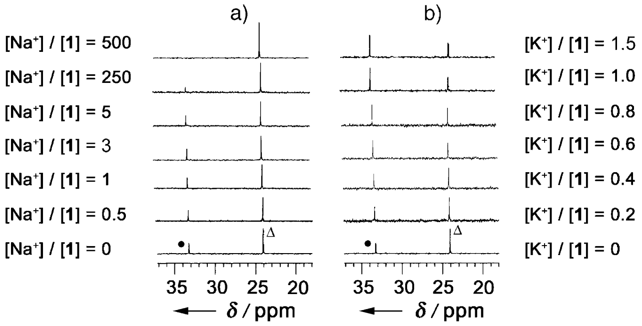


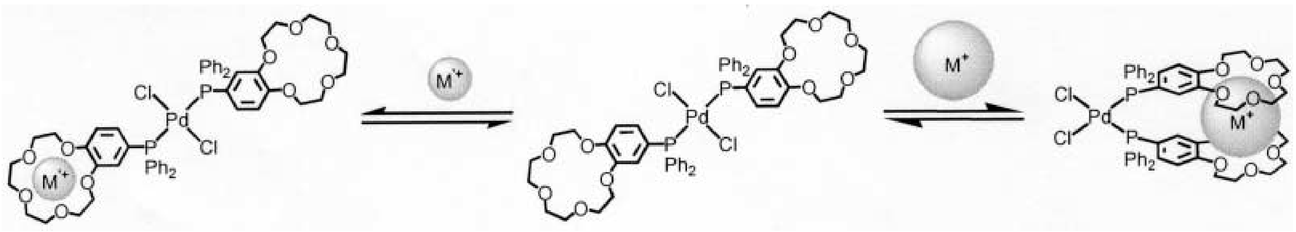
Figure 2. ^{31}P NMR (162 MHz) spectral changes of **1** (1.0×10^{-3} mol dm^{-3}) upon addition of a) $NaClO_4$ and b) KPF_6 in CD_3CN/CD_2Cl_2 (9:1 v/v) at 298 K, with signals corresponding to the *cis* (●) and *trans* (△) isomers indicated.

The log *K* values obtained from the UV/Vis spectrophotometric methods at low to moderate concentrations of Na^+ and K^+ ions, that is, under the conditions for formation of a 1:1 adduct, are 3.88 ± 0.02 for **1** with Na^+ and 4.36 ± 0.03 for **4** with K^+ ions. The close agreement of the experimental data with the theoretical fits confirms the formation of a 1:1 adduct. However, a conversion of the *trans*-**1** isomer into the *cis*-**1** form occurred in the case of the binding of K^+ ions to **1**, as indicated by ^{31}P NMR spectroscopic studies (Figure 2b). The presence of both the *trans*-**1** and *cis*-**1** isomers would require a description involving at least four species in equilibrium[11] (Scheme 2), assuming that only 1:1 **1**·M adducts are formed under the conditions studied.[12] Detailed treatment of the ^{31}P NMR data according to Scheme 2 gave K_1, K_2, and K_3 values of 0.38 ± 0.01, $1.01\times10^6\pm25000$ and $2.55\times10^5\pm6300\,\text{M}^{-1}$, respectively. The close resemblance of the experimental data to the theoretical fits confirmed the complexation stoichiometry of the K^+ ions to **1** to be 1:1 and, thus, confirmed the validity of Scheme 2. An overall equilibrium constant log *K* of 5.59 ± 0.02 was obtained for the process $M + trans\text{-}\mathbf{1} \rightleftarrows cis\text{-}\mathbf{1}\cdot M$, where $K = K_1K_2$. This result is in close agreement with a log *K* value of 5.26 ± 0.1 determined by UV/Vis spectrophotometry.

$$\begin{tikzcd}
M + trans\text{-}\mathbf{1} \arrow[r, shift left, "K_3"] \arrow[d, shift left, "K_1"] & trans\text{-}\mathbf{1}\bullet M \arrow[l, shift left] \arrow[d, shift left, "K_1'"] \\
M + cis\text{-}\mathbf{1} \arrow[r, shift left, "K_2"] \arrow[u, shift left] & cis\text{-}\mathbf{1}\bullet M \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd}$$

Scheme 2. Proposed binding equilibria between **1** and K^+ ions.

Results from the ESI mass spectrometric measurements provided direct evidence for supporting this hypothesis. In the case of **1**, only the $\{\mathbf{1}\cdot K\}^+$ adduct was observed, irrespective of the concentration of K^+ ions used, while for **4**, only $\{\mathbf{4}\cdot K\}^+$ was



Scheme 1. Schematic representation of the *trans–cis* isomerization in the presence of different metal ions.

observed at low to moderate concentrations of K^+ ions, but both the $\{\mathbf{4}\cdot K\}^+$ and $\{\mathbf{4}\cdot K_2PF_6\}^+$ ions were observed in the positive ESI-mass spectra at high concentrations of K^+ ions. Other alkali-metal ions were also examined: Only $\{\mathbf{1}\cdot M\}^+$ and $\{\mathbf{4}\cdot M\}^+$ adducts were observed at low to moderate concentrations of Li^+ and Na^+ ions, however, at high metal-ion concentrations, a small amount of the 1:2 bound adducts $\{\mathbf{1}\cdot M_2ClO_4\}^+$ and $\{\mathbf{4}\cdot M_2ClO_4\}^+$ adducts were also observed. In the case of Cs^+, however, only $\{\mathbf{1}\cdot Cs\}^+$ and $\{\mathbf{4}\cdot Cs\}^+$ appeared irrespective of the concentration of Cs^+ ions used. Similarly, for Rb^+ ions, only the $\{\mathbf{1}\cdot Rb\}^+$ adduct was observed with **1** while both $\{\mathbf{4}\cdot Rb\}^+$ and $\{\mathbf{4}\cdot Rb_2ClO_4\}^+$ ions were found with **4** at high concentrations of Rb^+ ions. In addition, **1** was found to be the most selective towards the binding of K^+ ions, while a selective preference for the binding of Cs^+ ions was observed for **4**. A likely explanation for this unprecedented ion-induced or -assisted isomerization reaction is that metal ions which are too large to fit into the size of the crown ether cavity tend to form intramolecular sandwich/tweezer complexes with the bis(crown) unit and this provides the driving force for the isomerization of the *trans* to the *cis* isomer.

In summary, the present bis(crown)-containing $[PdX_2L_2]$ system represents the first demonstration of a metal-ion-induced switching of the *trans–cis* isomerization, which may find interesting applications in the design of ion-controlled switching devices.

Received: February 13, 2003
Revised: May 26, 2003 [Z51178]

Keywords: alkali metals · crown compounds · host–guest systems · isomerization · palladium

---

[1] a) M. Takeuchi, M. Ikeda, A. Sugasaki, S. Shinkai, *Acc. Chem. Res.* **2001**, *34*, 865; b) R. Heck, F. Dumarcay, A. Marsura, *Chem. Eur. J.* **2002**, *8*, 2438; c) T. Nabeshima, Y. Yoshihira, T. Saiki, S. Akine, E. Horn, *J. Am. Chem. Soc.* **2003**, *125*, 28.

[2] a) J. Rebek, Jr., *Acc. Chem. Res.* **1984**, *17*, 258; b) T. G. Traylor, M. J. Mitchell, J. P. Ciconene, S. Nelson, *J. Am. Chem. Soc.* **1982**, *104*, 4986; c) I. Tabushi, T. Sasaki, *J. Am. Chem. Soc.* **1983**, *105*, 2901.

[3] a) H. L. Ammon, S. K. Bhattacharjee, S. Shinkai, Y. Honda, *J. Am. Chem. Soc.* **1984**, *106*, 262; b) S. Shinkai, T. Nakaji, T. Ogawa, K. Shigematsu, O. Manabe, *J. Am. Chem. Soc.* **1981**, *103*, 111; c) K. Kimura, R. Mizutani, M. Yokoyama, R. Arakawa, G. Matsubayashi, M. Okamoto, H. Doe, *J. Am. Chem. Soc.* **1997**, *119*, 2062.

[4] a) V. W. W. Yam, V. C. Y. Lau, K. K. Cheung, *J. Chem. Soc. Chem. Commun.* **1995**, 259; b) V. W. W. Yam, V. C. Y. Lau, L. X. Wu, *J. Chem. Soc. Dalton Trans.* **1998**, 1461; c) V. W. W. Yam, Y. Yang, J. X. Zhang, B. W. K. Chu, N. Y. Zhu, *Organometallics* **2001**, *20*, 4911.

[5] J. Tsuji, K. Ohno, *J. Am. Chem. Soc.* **1968**, *90*, 94.

[6] T. Okano, M. Iwahara, H. Konishi, J. Kiji, *J. Organomet. Chem.* **1988**, *346*, 267.

[7] See Supporting Information for perspective drawings and crystal structure data of **1** and **2**.

[8] J. A. Rahn, M. S. Holt, J. H. Nelson, *Polyhedron* **1989**, *8*, 897.

[9] N. W. Alcock, T. J. Kemp, F. L. Wimmer, *J. Chem. Soc. Dalton Trans.* **1981**, 635.

[10] J. Bourson, J. Pouget, B. Valeur, *J. Phys. Chem.* **1993**, *97*, 4552.

[11] See supporting information for detailed derivation and fitting procedure.

[12] Although ESI-MS could not differentiate between the formation of a 1:1 complex from a 2:2 complex, we believe that under the experimental conditions employed, in which the concentration of **1** is about 6×10^{-5} mol dm^{-3}, the formation of a 2:2 complex is unlikely. In addition, the formation of a 2:2 complex might also be entropically disadvantageous.