Pre-catalyst resting states: a kinetic, thermodynamic and quantum mechanical analyses of [$PdCl_2$(2-oxazoline)$_2$] complexes†‡§

Robert A. Gossage,*[a] Hilary A. Jenkins,[b] Nathan D. Jones,[c] Roderick C. Jones[d] and Brian F. Yates[d]

Received 4th February 2008, Accepted 28th March 2008
First published as an Advance Article on the web 7th May 2008
DOI: 10.1039/b801951g

The treatment of cold (~3 °C) methanolic solutions of Li_2PdCl_4 with two equivalents of 2-phenyl-2-oxazoline (Phox) results in the isolation of [$PdCl_2$(Phox)$_2$] (**3**). This complex undergoes remarkably slow isomerisation ($CHCl_3$-*d*) at room temperature to a corresponding thermodynamic form. In addition to a theoretical treatment (DFT), the isomerisation behaviour has been analysed both kinetically and thermodynamically. These investigations lead to the conclusion that the initially formed (*i.e.* kinetic) isomer of **3** is the *cis*-form which undergoes conversion to the corresponding thermodynamic *trans*-form *via* a dissociative (D) mechanism involving loss of a Phox ligand. The activation parameters $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are found to be +304 (±3) J K^{-1} mol^{-1} and +176 (±1) kJ mol^{-1}, respectively and indicate a high barrier to Pd–N bond cleavage under these conditions. The thermodynamic parameters show the expected endothermic nature of this process (+140 ± 17 kJ mol^{-1}) and a slight positive overall entropy ($\Delta S^{\circ} = +17 \pm 2$ J K^{-1} mol^{-1}); this latter parameter is presumably due to the formation of the lower dipole moment *trans*-product when compared to the *cis*-isomer. Calculated (DFT) values of $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ are in excellent agreement to those found experimentally. Further theoretical investigation suggests that two 14-electron three-coordinate T-shaped transition states (*i.e.*, [$PdCl_2$(Phox)]‡) are involved; the form pre-disposed to yield the thermodynamic *trans*-product following re-attachment of the released oxazoline is found to be energetically favoured. The analogous alkyloxazoline system [$PdCl_2$(Meox)$_2$] (**4**: Meox = 2-methyl-2-oxazoline) has likewise been investigated. This material gives no indication of *cis–trans* isomerisation behaviour in solution (NMR) and is shown to exist (X-ray) in the *trans*-form in the solid-state (as do previously reported crystalline samples of **3**). A DFT study of **4** reveals similar values of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ if a D type mechanism were operating to rapidly convert *cis*- to *trans*-**4**. However, a significantly higher thermodynamic stability of the *trans*-isomer relative to the *cis*-form is revealed *versus* similar calculations of the Phox derivative **3**. This suggests the possibility that (*i*) reactions of Meox with Li_2PdCl_4 may lead directly to the *trans*-form of [$PdCl_2$(Meox)$_2$] or alternatively (*ii*) that alkyloxazoline complexes such as **4** may have a different, and presumably much more rapid, mechanism for isomerisation. The results are placed into the context that isomerisation behaviour, or lack thereof, could play a key preliminary role in later substrate modification. This is due to the fact that [PdX_2(oxazoline)$_2$] compounds are well-known (pre-)catalysts for C–C bond forming chemistry.

Introduction

During the last 25 years, the use of palladium complexes in transition metal-mediated catalysis has become one of the cornerstones of synthetic chemistry.[1] Palladium-based materials are now widely used in both the regio- and enantio-selective synthesis of C–C, C–H and C–N bonds, in addition to a wide variety of other classes of bond-forming reactions.[1] Despite these advances, the nature, role and structure of the active Pd species have often remained elusive. Indeed considerable effort, both experimental and theoretical, has been applied to elucidate the nature of the reactive intermediates during substrate modification.[2] In contrast, much less attention has been paid to the "resting" state(s) of the pre-catalytic complexes that appear during, before or after catalysis has been initiated.[3]

We recently reported that a simple palladium(II) chloride complex containing a ligated monodentate oxazoline (*viz.* [$PdCl_2$(Etox-$\kappa^1N)_2$]: **1**; Etox = 2-ethyl-2-oxazoline: Fig. 1) can be used as a

[a]*The David Upton Hill Laboratories of Inorganic Chemistry, Department of Chemistry, Acadia University, Wolfville, NS, B4P 2R6, Canada. E-mail: rob.gossage@acadiau.ca; Fax: +1-902-5851114; Tel: +1-902-5851109*
[b]*Department of Chemistry, Saint Mary's University, Halifax, NS, B3H 3C3, Canada. E-mail: haj@smu.ca*
[c]*Department of Chemistry, The University of Western Ontario, 1151 Richmond Street, London, ON, N6A 5B7, Canada*
[d]*The School of Chemistry, The University of Tasmania, Private Bag 50, Hobart, Tasmania, 7001, Australia*

† Oxazoline chemistry. Part XVI. For Part XV, see ref. 7*f*.

‡ This article is dedicated to the memory of Mr. Charles R. "Chuck" Eisnor (1954–2006).

§ Electronic supplementary information (ESI) available: details of the characterization of **3** and **4**, a crystallographic information (.cif) file for complex **4** (CCDC# 657356), details and graphical representations of the kinetic plots used to characterize the isomerisation of **3** and details of all DFT calculations described herein. CCDC reference number 657356. For ESI or crystallographic data in CIF or other electronic format see DOI: 10.1039/b801951g

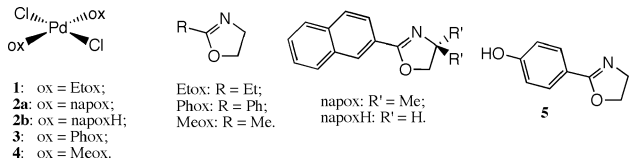


Fig. 1 Schematic representations of the compounds discussed herein.

catalyst precursor for a number of C–C bond forming reactions.[4] This material operates in open air and the addition of excess "free" oxazoline ligand is not required for good catalytic activity. In fact, this has been shown to retard the production of organic products.[4b,5] This observation suggests the presence of a key coordinatively unsaturated intermediate, either within the catalytic cycle itself and/or as an important pre-catalyst leading to the active form(s). We surmised[4b] that one such species could be the formally fourteen-electron metal complex $[PdCl_2(Etox)]^{\ddagger}$ formed *via* dissociation of one of the Etox ligands. There is currently little mechanistic or structural information on exactly how this[4] or related systems[5] operate and indeed there are few details on the properties of the pre-catalyst forms (*i.e.*, the 'resting states').[4a,5b] An important background observation to the present discussion appeared in the literature over a dozen years ago.[6] In 1994, van Koten and co-workers reported a study detailing the cyclopalladation of the naphthalene-derived oxazoline referred to hereafter as napox (*i.e.*, 4,4-dimethyl-2-{2′-naphthyl}-2-oxazoline: Fig. 1). A minor component of this work described the synthesis and isolation of the mononuclear coordination complex $[PdCl_2(napox\text{-}\kappa^1N)_2]$ (**2a**: Fig. 1), which was viewed as a possible intermediate in subsequent cyclometalation chemistry. Complex **2a** is an obvious relative of our catalyst precursor **1**. Crystalline samples of the isolated form of **2a** exist as the *trans*-isomer only (X-ray diffraction) with the coordination of napox to the Pd metal centre through the *N*-donor atom, as expected.[4,7] However, *crystalline* samples of **2a**, upon dissolution in $CDCl_3$, invariably give ^1H NMR spectra consistent with the presence of two structural forms.[6,8] This observation was attributed to the rapid formation of an equilibrium mixture of the *cis* and *trans* isomers of **2a**, although at the time detailed experiments to confirm this notion were not performed.[6] Curiously, the analogous complex devoid of methyl groups (**2b**: Fig. 1) did not give any indication (NMR) of mixed (solution *cis* ⇆ *trans*) isomer behaviour.[6]

In contrast to the nature of **2a**, our ^1H NMR examination of **1**[3,9] revealed no spectroscopic evidence for isomeric solution equilibrium (*cf.* **2b**) and a single crystal X-ray diffraction study gave, as above, only a single isomer (*i.e.*, *trans*-$[PdCl_2(Etox\text{-}\kappa^1N)_2]$).[4a] We hypothesized that perhaps the van Koten system **2a** operates differently, possibly due to the unique *electronic* nature of napox when compared with that of Etox or its 4,4-dihydro congener. This idea is based on the notion that napox is the larger of the three ligands and hence would intuitively pre-dispose a resulting $PdCl_2$ complex with a structure containing *trans*-disposed oxazolines as opposed to a more sterically encumbered *cis*-form.[10] These results are further supported by a more recent study of a simpler aryl-oxazoline complex reported by Smoliakova *et al.*, *viz.* *trans*-$[PdCl_2(Phox\text{-}\kappa^1N)_2]$ (**3**: Phox = 2-phenyl-2-oxazoline).[11] As with our Etox system (**1**) and **2b**, the authors reported only a single isomer of **3** in solution after re-crystallization and isolation; the *trans* ligand arrangement being likewise confirmed for the solid material by an X-ray diffraction study. As substituted aryl-oxazolines are readily obtained,[12] complex **3** and its analogues presented to us a useful starting point to investigate possible electronic (or other) effects on this isomerisation behaviour.[9] Thus, our initial intentions were to attempt to map out the electronic (or steric) nature of such isomer distributions. We began by re-investigating the parent material (**3**) and have found that a less stable form can be observed if accessed *via* low temperature synthesis. This material exhibits remarkably slow isomerisation behaviour (*cf.* **2a**) at room temperature (RT) but reaches an equilibrium almost completely dominated by the (solid-state) isolable *trans* isomer as reported.[11] Herein, we report a full kinetic, thermodynamic and DFT investigation of this system and include a comparative synthetic, structural and DFT study of the simplest alkyl analogue of **3**, namely $[PdCl_2(Meox\text{-}\kappa^1N)_2]$ (**4**: Meox = 2-methyl-2-oxazoline). These data support the notion that the observed isomerisation behaviour of **3** takes place *via* the dissociation of an oxazoline ligand, which is a less common route (*cf.* associative mechanism) for formally d^8 metal systems.[13] The relative energies of the isomers, as observed spectroscopically and calculated by DFT, support the observed general characteristics of the $[PdCl_2(oxazoline)_2]$ system, namely that both **3** and the alkyl-oxazoline complex **4** are thermodynamically favoured to exist in the *trans* isomeric form. The observed rate of stereomutation of *cis*- to *trans*-**3** is one of the slowest ever observed for the isomerisation of a square planar (SQP) formally Pd^{2+} halide complex. These results are further discussed in terms of the use of compounds such as **1** as catalyst precursors. In addition, the possible significance of such (low concentration) *cis* forms as important intermediates and/or resting states in subsequent substrate modification is put forward.

Experimental section

General

All reagents and solvents used in this work were of reagent grade and obtained from commercial sources; synthetic procedures were carried out using standard bench-top techniques. A stock solution (0.23 M) of Li_2PdCl_4 was obtained by dissolving an appropriate quantity of $PdCl_2$ (2.0 g: 11 mmol) in MeOH (~40 mL) in the presence of 2 equiv. (0.95 g) of LiCl. The mixture was then stirred for approximately 30 min at RT and filtered directly into a 50.00 mL volumetric flask which was subsequently filled with additional MeOH to give the required total solution volume. Complex **3** was made by an identical route to that of **4** (below) and the identity of the product confirmed by comparison to the data previously reported.[11] NMR spectra ($CDCl_3$ solution) were recorded at RT using Bruker AC-250 or Advance 300 NMR spectrometers operating at 250 MHz or 300 MHz, respectively. Chemical shift values are reported in ppm using TMS (and/or residual $CHCl_3$ solvent resonance) as internal standard. Coupling constants are reported in Hertz. Elemental analysis was performed by L.U.C.A.S., Thunder Bay, Ontario, Canada.

Synthesis of 4

A quantity of Li_2PdCl_4 (6.1 mL; 0.23 M in MeOH: 1.4 mmol) was added to further MeOH (~10 mL) and the mixture cooled to

~3 °C. Meox (0.25 g: 2.9 mmol) was then added by syringe and the dark brown mixture was then stirred for approximately 1 h. During this period, the colour of the solution changed to light yellow and an orange precipitate formed. This solid was isolated by filtration, washed with MeOH (3 × 5 mL) and thrice with Et_2O (5 mL) and then allowed to dry in air. The yield of **4** was 0.27 g (56%) in the form of an orange solid; mp: 230–232 °C (decomp.). ^{1}H NMR (250 MHz; $CDCl_3$): $\delta = 4.52$ (t, 4H, $J = 9.8$, CH_2O), 3.99 (t, 4H, $J = 9.8$, CH_2N), 2.52 (s, 6H, CH_3). Anal. calcd for $C_8H_{14}N_2O_2Cl_2Pd$: C, 27.65; H, 4.06; N, 8.06; found: C, 27.47; H, 3.73; N, 8.04%.

X-Ray crystallographic study of 4

Orange crystals of **4**, suitable for X-ray diffraction, were grown from a CH_2Cl_2 solution of **4** which had been layered with MeOH, sealed (septum) and thereafter had been left standing for several days at −22 °C. Further details of the crystallographic investigation of **4** can be found in the ESI§ including an ORTEP diagram of one of the molecules of **4**.

Crystal data. Empirical formula $C_8H_{14}C_{12}N_2O_2Pd$, M 347.51, T 223(2) K, crystal system triclinic, space group $P\bar{1}$, $a = 7.5416(8)$ Å, $\alpha = 84.997(2)°$, $b = 8.4479(9)$ Å, $\beta = 81.775(2)°$, $c = 9.6688(10)$ Å, $\gamma = 85.269(2)°$, V 605.81(11) Å^3, Z 2, final R indices [$I > 2\sigma(I)$], $R1 = 0.0278$, $wR2 = 0.0798$, R indices (all data), $R1 = 0.0306$, $wR2 = 0.0813$.

Kinetic and thermodynamic investigations of 3

The details of the kinetic and thermodynamic investigation (including concentration *versus* time plots) of complex **3** and the DFT studies of **3** and **4** and the intermediates derived thereof can be found in the ESI.§

Computational methods

Full geometry optimisations were carried out with the use of the B3LYP density functional level of theory[14–16] combined with the LANL2DZ basis set (which incorporates the Hay and Wadt[17] small-core relativistic effective core potential and double-zeta valence basis set) on Pd, and the 6-31G(d) basis set[18–20] on all other atoms. Sets of five d-functions were used in the basis sets throughout these calculations. For the optimised geometries, harmonic vibrational frequencies were calculated at the B3LYP level. All transition structures possessed one and only one imaginary frequency, and they were further characterised by following the corresponding normal mode towards each product and reactant. Single-point energies on the B3LYP/LANL2DZ:6-31G(d) optimised geometries were calculated at the B3LYP level with the LANL2 augmented:6-311+G(2d,p) basis set,[21] which incorporates the LANL2 effective core potential and augmented basis set on Pd (the large f-polarised valence basis set of Bauschlicher and coworkers[22] was used) together with the 6-311+G(2d,p) basis set[23–25] on all other atoms. Energies from these single-point calculations were combined with the zero-point vibrational energy corrections from the lower level of theory to yield $\Delta H°$ and $\Delta G°$ numbers. All calculations were carried out with the Gaussian 03 program.[26]

Results and discussion

Synthesis and characterisation of 3 and 4

We employed a modified synthesis[11] of **3** and **4** which involves protocols similar to those used previously in the production of **1** and **2a/b**.[4a,6] This involves treatment of Li_2PdCl_4 in MeOH solution with the ligand in question at a temperature below ambient. Complexes **3** and **4** are air- and moisture-stable materials in both the solid-state and in solution ($CDCl_3$, CH_2Cl_2, benzene).

The low temperature synthesis of **3** allows one to arrest the stereomutation process which is an inherent characteristic of this compound. Two distinct sets (Fig. 2 and ESI§) of signals are evident upon examination of the ^{1}H NMR spectrum ($CDCl_3$ solution) of **3** isolated in this manner. The methylene region (δ = 5.0–3.0 ppm: Fig. 2) of the ^{1}H NMR spectrum is the most provocative indicator of the presence of the two isomeric forms. The chemical shift values of the two downfield AA′BB′ (*i.e.*, pseudo-triplet pattern) signals (Fig. 2) match those reported for isolated *trans*-**3**[11] while the other set of upfield signals are previously unreported. A solution of this mixture was thereafter left at RT for approximately 24 h during which time most (>70%) of the initially more intense resonances had disappeared whilst those of known *trans*-**3** grew in intensity. No Pd "black" was observed to form under these conditions nor were any other NMR signals noted. Heating of the NMR tube in an oil bath at 60 °C for 8 h lead to virtually complete conversion (NMR) of the sample to *trans*-**3**; again there was no evidence for sample decomposition. This result confirms the observations previously reported,[11] as the minor isomer is present in less than 3% at equilibrium (RT). Presumably, the resulting solid-state crystalline phase of **3** exists, as in the case of van Koten's **2a** and our **1**, solely in the reported *trans* form.[11]

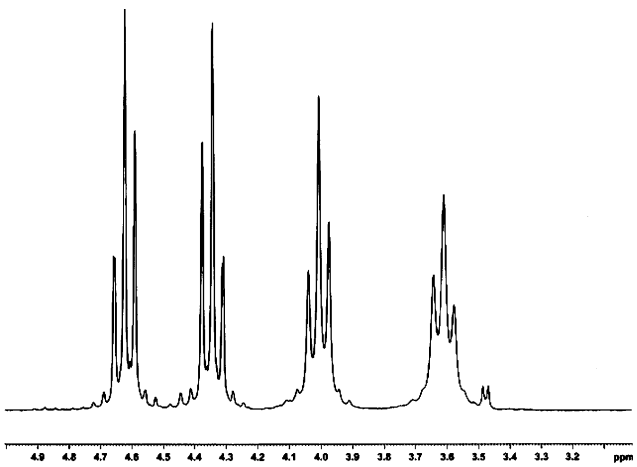


Fig. 2 A typical ^{1}H NMR spectrum in the region δ = 5.0–3.0 ppm of compound **3** at approximately a 50 : 50 *cis*/*trans* isomer ratio.

Compound **4** (Fig. 1) was isolated as described above for **3**, however no evidence (NMR) was observed for the presence of more than one isomer in solution. A determination of the solid-state structure of **4** was therefore carried out by single crystal X-ray diffraction (Table 3 and ESI§). Two different molecules of **4** are found within the unit cell; both forms have a *trans*-disposition of the two halide and two oxazoline ligands around

the metal center. The primary structural difference between the two lies in the tilting of the oxazoline ring planes relative to the Pd coordination plane, which is more pronounced in one of the forms than in the other (torsion angle for molecule 1: ∠C3–N1–Pd1–Cl1 = ~111°; molecule 2: ∠C7–N2–Pd2–Cl2 = ~97°; see ESI§). A molecular representation of one of the molecules of **4** within the unit cell can be found in Fig. 3. The bond lengths and angles of both molecules of **4** are otherwise unsurprising and are comparable with that of **1**,[4a] **2a**,[6] **3**[11] and other Pd–oxazoline complexes (*vide infra* and Table 3, below).[5b,27] Note that there is little variation within this series in terms of the Pd–Cl and Pd–N bond lengths and the angles between the atoms ligating the Pd centre (Table 3). Although the solid-state structures of free Phox, Etox or Meox are not known (these compounds all have melting points well below RT), X-ray diffraction (and DFT) data of the related compound 2-(4′-hydroxyphenyl)-2-oxazoline (**5**: Fig. 1) has been reported.[12f] Of note is the almost identical N=C (oxazoline) bond length (1.2775(14) Å) between this "free" ligand and the coordinated oxazolines found in **1**, **3** and/or **4**. This suggests little disturbance of the N–C π-system upon coordination of the Etox, Phox or Meox to Pd, as might be expected.

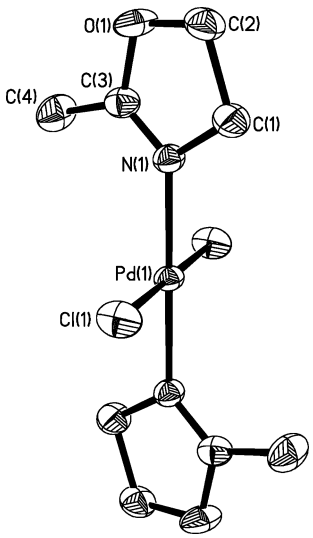


Fig. 3 A molecular representation of one of the molecules of **4** found within the unit cell.

Kinetic and thermodynamic study of 3

The initial observation of slow isomerisation of **3** (*vide supra*) recommended this as an ideal system for a kinetic study of the stereomutation process by NMR spectroscopy. The rate of disappearance of the initially major isomeric component and the complementary appearance of the known compound *trans*-**3** was found to be first-order in Pd over all concentration and temperature ranges investigated. This result effectively eliminates the possibility that the precursor to *trans*-**3** is a dimeric species or a higher order aggregate.[3a] Thus, the initial kinetic product in the synthesis of *trans*-**3** is assumed to be the cisoidal isomer (hereafter referred to as *cis*-**3**). This result lends support to van Koten's earlier hypothesis[6] that the analogous complex **2a** exists in solution as a *cis*/*trans* isomeric mixture.

The observed kinetic and thermodynamic data for the isomerisation of *cis*-**3** are given in Table 1 and Table 2. The retarding of the rate of isomerisation upon added Phox (Table 1; entry 5), in addition to the large calculated $\Delta S^{\ddagger}$ value (Table 2), strongly suggests a dissociative (D) type mechanism for this inter-conversion (Scheme 1). The first order nature of the data imply that *cis*-**3** is a mononuclear complex and thus presumably an initial (unsaturated 14-electron) intermediate **I** (*i.e.* $[PdCl_2(Phox)]^{\ddagger}$) results from the rate determining step. One assumes that **I** isomerizes rapidly to a second form **II**, which is trapped by the previously released Phox in another fast step to give the thermodynamically more stable *trans*-**3** (Scheme 1). These aspects will be further discussed in the theoretical examination below.

It has been previously established that there are three distinct mechanisms by which Pd^{2+}/Pt^{2+} systems carry out *cis–trans* isomerisation chemistry. The most common is the classical associative (A) mechanism,[10a,28–31] a somewhat more rare non-dissociative stereomutation has been established (*i.e.* an intramolecular rearrangement *via* a pseudo-tetrahedral transition state without bond rupture)[32,33] in addition to the D mechanism.[34,35] Obviously, only this latter process is characterized by a large positive $\Delta S^{\ddagger}$ value. The D process is now well-recognized, but certainly less common in SQP Pd^{2+}/Pt^{2+} ligand exchange chemistry than the A case.[10,13,28–30,36,37]

DFT characterization of *cis*/*trans*-3 and 4

The kinetic aspects of the system, as examined above, yields a high energy barrier and a dissociative process for the conversion of *cis*- to *trans*-**3** (Table 2) but we have no experimental comparison for the analogous chemistry with alkyl-oxazoline derivatives such as

Table 1 Kinetic and thermodynamic data for the *cis*-to-*trans* isomerization of **3**

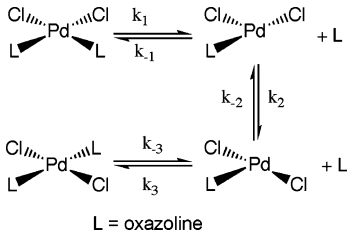
Entry	T^a/K	$10^5 k_1{}^b$/s^{-1}	$10^5 k_{-1}{}^b$/s^{-1}	K_{eq}	ΔG°/kJ mol^{-1}
1	294	0.753 (± 0.025)	0.036 (± 0.002)	21 ± 8	−7.4 ± 1.1
2	298	nm[c]		34 ± 4	−8.7 ± 0.4
3	303	7.10 (± 0.33)	0.051 (± 0.01)	140 ± 20	−12.4 ± 0.4
4	308	24.4 (± 1.9)	0.10 (± 0.03)	236 ± 22	−14.0 ± 0.3
5	308[d]	3.2		nm	
6	313	54.9 (± 2.0)		nm	

[a] Temperature ± 1 K. [b] k_1 = rate constant for the isomerization of the *cis*-to-*trans* isomer, k_{-1} = rate constant for the isomerization from the *trans*-to-*cis* isomer; k_{-1} calculated from the expression $K_{eq} = k_1/k_{-1}$; values of the equilibrium constants (K_{eq}) were determined by integration of the methylene ^{1}H NMR signals at t_{∞}. [c] nm = not measured. [d] Contains additional "free" Phox; [Phox] : [**3**]$_0$ = 1 : 3; single dataset determination.

Table 2 Calculated and observed properties of **3**

Quantity	Value[a,b]	Quantity	Value[a]
$\Delta G^{\ddagger}$	+85 ± 3 (+86.8)		
$\Delta H^{\ddagger}$	+176 ± 1 (+137.9)	ΔH°	+140 ± 17
$\Delta S^{\ddagger}$	+304 ± 3 (+171.4)	ΔS°	+17 ± 2

[a] ΔG and ΔH are reported in units of kJ mol^{-1}; ΔS values are given units of J K^{-1} mol^{-1}. [b] Calculated values (DFT) in parentheses.



Scheme 1 The proposed mechanism for the isomerisation of *cis*- to *trans*-**3**.

4. It must be assumed that this latter compound reaches isomeric equilibrium very rapidly or that the *cis* congener is not formed at all by our synthetic protocol. Any subsequent equilibrium chemistry is apparently completely (NMR) dominated by a single isomer, which is presumably the crystallographically characterised *trans*-form. The present NMR investigation likewise gives no indication of the presence or structural nature of the surmised transition states formed from **3** which we have referred to thus far simply as "**I**" and "**II**". We have therefore applied DFT[38,39] to examine the nature of these isomerisations and to confirm the thermodynamic preference, at least in the gas phase, for both **3** and **4** to exist as the crystallographically identified *trans*-isomers. We shall first discuss the isomerisation behaviour of **3**.

The DFT calculations involving complex **3** parallel the kinetic and thermodynamic observations discussed above. A representation of the lowest energy *cis*-form of **3** appears in Fig. 4 along with the complementary *trans*-form. This latter molecular geometry is very close in general molecular characteristics to the solid-state form reported previously.[11] A comparison of the important bond lengths and angles (observed and calculated) appears in Table 3. Generally, these calculated values are quite close to the observed values found in the solid-state, although the calculated gas phase values suggest slightly longer bond lengths (notably the Pd–L interactions) than those experimentally determined in the solid phase. The energy difference calculated between the *cis* and *trans* gas phase forms (ΔE = ~29 kJ mol^{-1}) implies that the *trans*-form is thermodynamically favoured,[10b,28] as observed.[11] Calculations of the 14-electron transition state complexes are also quite informative. The two calculated structural isomers of the $[PdCl_2(Phox)]^{\ddagger}$ species, which could be classified as independent T-shaped forms (**I** and **II**) are both found to be plausible structural isomers (Fig. 5). The loss of Phox from *cis*-**3** leads directly to intermediate **I** which has an approximate right angle between the two chloride ligands (calculated value of the Cl–Pd–Cl angle is 97.6°). This isomer is calculated to be approximately +3.2 kJ mol^{-1} higher in energy than isomeric form **II** (Fig. 5: calculated Cl–Pd–Cl angle of 172.4°).[40] Hence, the initial 14-electron intermediate **I** is energetically pre-disposed to rearrange to form a second structural motif (*i.e.*, **II**) that upon re-addition of released Phox would lead to *trans*-**3** (Scheme 1). We have further applied DFT methods to mimic the empirical observations above (Table 3). The calculated $\Delta G^{\ddagger}$ value (+86.8) is in excellent agreement to that found from the experimental determination. Although our calculations do admittedly underestimate the magnitude of both

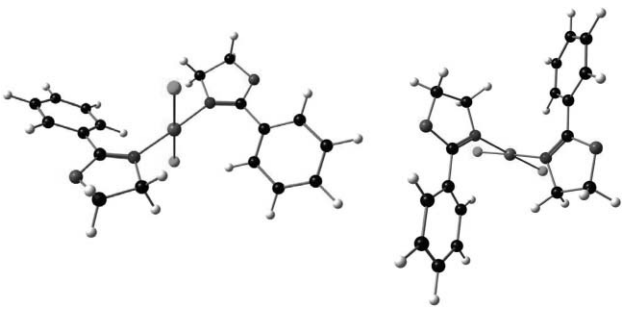


Fig. 4 Calculated (DFT) structures of *trans*- (left) and *cis*-**3** (right).

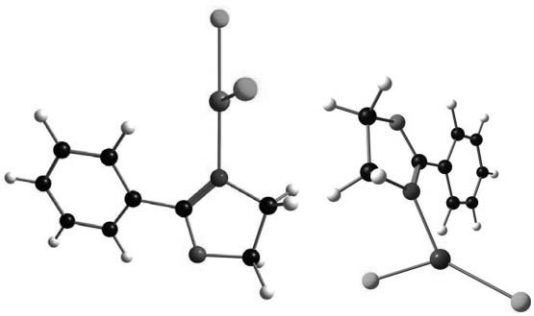


Fig. 5 Calculated (DFT) T-shaped structures of **3** following loss of a Phox ligand: initial "**I**" form (left) and form "**II**" (right).

Table 3 Calculated and observed bond lengths and angles of complexes **3** and **4**[a]

Measurement	*t*-**3**[b,c]	*t*-**3** (calc.)	*t*-**4**[b,d]	*t*-**4**[b,e]	*t*-**4** (calc)[d]	*c*-**3** (calc.)	*c*-**4** (calc.)
Pd–N	2.0074(14)	2.053	2.008(2)	2.026(2)	2.052	2.094	2.095
Pd–Cl	2.300(2)	2.3632.378	2.3011(8)	2.2876(8)	2.368	2.333	2.330
N=C	1.271(2)	1.291	1.261(4)	1.272(4)	1.286	1.290	1.287
N–Pd–N	180.0	176.5	180.00(6)	180.00(3)	180.0	93.4	93.5
Cl–Pd–Cl	180.0	180.0	180.00(4)	180.00(3)	180.0	93.2	93.3
N–Pd–Cl	89.13(5)90.87(5)	88.391.7	89.15(7)90.85(7)	89.82(7)90.18(7)	88.991.1	86.7(*c*)178.9(*t*)	86.8(*c*)179.5(*t*)

[a] Estimated standard deviations are in parentheses; bond lengths are reported in Å units; bond angles are given in degrees (°); *t* = *trans*; *c* = *cis*; calc. = calculated (gas phase) values obtained from DFT. [b] Observed (solid-state) values obtained from X-ray diffraction data. [c] Data taken from reference 11. [d] Molecule #1 in the unit cell; this work. [e] Molecule #2 in the unit cell; this work.

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, a distinctly large and positive enthalpy and entropy is theoretically determined, as observed. Possible reasons for this result are that there are solvation effects that are not accounted for in the (gas phase) calculations. Certainly our large $\Delta S^{\ddagger}$ value suggests a considerable increase in solvent randomness following ligand dissociation in addition to any possible influence of the formation of intermediate **I**.

No related isomerisation observations have been found for alkyloxazoline complex **4** although calculations of the activation energies for a possible dissocative isomerisation pathway are found to be similar to aryloxazoline complex **3**. These parameters are calculated as $\Delta G^{\ddagger} = +89.4$ kJ mol^{-1}; $\Delta H^{\ddagger} = +138.7$ kJ mol^{-1} and a $\Delta S^{\ddagger}$ value of +165.4 J K^{-1} mol^{-1}. Thus, both complexes **3** and **4** are calculated to have a fairly high barrier to isomerisation but there appears to be little difference energetically between the two species in terms of a D mechanism for interconversion. However, the ground state energy difference between *cis*-**4** and *trans*-**4** (Fig. 6) is calculated to be much larger ($\Delta E = \sim 45$ kJ mol^{-1}) than that of **3**. These data strongly suggest that the observed solution (NMR) form of **4** is most likely the structurally characterized solid-state *trans*-form.

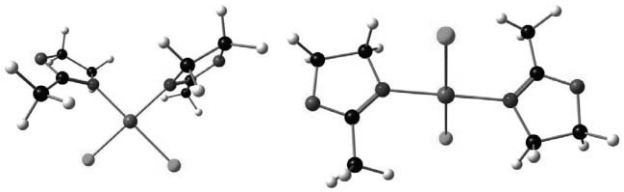


Fig. 6 Calculated (DFT) structures of *cis*- (left) and *trans*-**4** (right).

The results described above lead one to suggest two possible reasons for the different observations between **3** and **4**. Firstly, it is possible that reactions of Meox with Li_2PdCl_4 lead directly to only the *trans*-form of [$PdCl_2$(Meox)$_2$], due perhaps to a strong thermodynamic preference for this isomer. Alternatively, alkyloxazoline complexes such as **4** may have a different, and presumably much more rapid, mechanism for isomerisation and are thus kinetically biased to yield the *trans* form. The alkyloxazoline ligand Meox is certainly sterically smaller than Phox and presumably more basic.[41] The steric size of Meox could allow the Pd centre of **4** to be more accessible relative to that of **3** and thus perhaps the small alkyloxazoline ligands open up rapid associative and/or non-dissocative stereomutation pathways for isomerisation. These hypotheses suggests that there may exist a fundmental difference between aryl-, when compared to alkyl-, oxazoline PdX_2 materials.

Overall, the data generated here create a picture in which oxazoline ligand dissociation from **3** leads to a T-shaped 3-coordinate intermediate form which is energetically favoured to undergo re-arrangement to the thermodynamic *trans*-isomer upon re-attachment of the dissociated oxazoline. Our kinetic investigations of the properties of **3** have indicated a mechanistic scheme as depicted in Scheme 1. Note that in the case of $k_{-1}k_{-2} < k_2k_3$ (as suggested by the observed data and DFT) and the steady-state approximation of "free" [Phox] ≈ 0; then k_{obs} collapses to k_{ct} (*i.e.* k_1). This very situation has been previously described by Minniti.[35a] No related isomerisation observations have been found for the alkyloxazoline complex **4** although calculations of the activation energies for a potential dissocative isomerisation pathway are found to be similar to that of aryloxazoline complex **3**.

Significance and conclusions

The justification for a D mechanism for the isomerisation of **3** is supported by the observed slower kinetic profile in the presence of added Phox and the large positive value of $\Delta S^{\ddagger}$. Both the non-dissociative stereomutation and D mechanisms are usually observed in SQP systems containing ligands of high *trans*-effect (*e.g.*, silyl, alkyl, hydrido, *etc.*).[13,33–35] Thus, dissociative processes can be expected to operate under catalysis conditions due to the typical presence of intermediate complexes containing transition metal (M) bonds such as M–H, M–SiR_3 and/or M–C. In the case described here, the relatively weak *trans*-effect chloride ligand is located *trans* to the oxazoline. Dissociation of this oxazoline leads to T-shaped species such as **I** and **II**; complexes such as **3** therefore represent a rare dissociative system that does not contain ligands of high *trans*-effect.[10] This helps to explain the rather large barrier to isomerisation (in addition to the obvious requirement to cleave a Pd–N bond) and thus slow kinetic profile of the compound studied here. Many systems which utilize Pd have been suggested to include one or more key *cis–trans* isomerisation step(s) during catalysis. This is particularly noteworthy in situations leading to reductive elimination chemistry,[1,2,42] as invariably the two coupled fragments must be previously oriented in an intermediate *cis*-geometry.[43] However, situations similar to those described above are rarely considered in processes which occur before substrate activation. What is currently unknown is how the presence (or absence) of a *mixture* of catalytic precursors affects the subsequent product profiles. We have shown that in some cases mixtures of pre-catalytic *cis*/*trans* isomers can be observed but in other cases the *cis* form appears to exist, at best, at very low concentrations relative to the *trans* isomer. The relative rates at which two such isomers enter a catalytic cycle(s) however, is currently not known nor are the (ligand) steric and electronic factors that control K_{eq} between these forms. Situations such as those described above were discussed some time ago in a seminal review by Anderson and Cross,[10b] but the factors that control Pd isomeric mixtures, particularly in the solution phase, are still far from well-established.[43] As the general class of [PdX_2(oxazoline)$_n$] complexes are active mediators of C–C bond formation,[4,5] such information may be vital in improving and modifying subsequent catalysis. This investigation has further presented the concept that detailed kinetic investigations whose overall objective is to clarify aspects of catalytic cycle(s) may also have to involve study of any pre-catalyst materials. Indeed, a re-examination (DFT, K_{eq}, *etc.*) of the original van Koten napox system (**2a**/**b**) and substituted structural analogues of **3**[5a,11,12] in addition to the possible role of *cis*- and *trans*-isomers in catalysis by these materials, are currently in progress. Results of these investigations will be published in due course.

Acknowledgements

This research was supported by the generous contributions of The Killam Trusts (NDJ), The Royal Society of Chemistry (specifically in the form of a J.W.T. Jones Travelling Fellowship to RAG), the Australian Research Council, Acadia University, Saint Mary's University, The University of Western Ontario and

by The University of Tasmania. The provision of further funding, in the form of a "Discovery" Grant (RAG), from the Natural Sciences and Engineering Research Council (NSERC) of Canada is likewise acknowledged. Johnson-Matthey Inc. is thanked for a generous loan of $PdCl_2$ that was used in this work. The authors are also indebted to the assistance of Australia's Program of Advanced Computing (Australian National University, Canberra).

Notes and references

1 (*a*) J. Tsuji, *Palladium Reagents and Catalysts: New Perspectives for the 21st Century*, Wiley, Hoboken, 2nd edn, 2004; (*b*) J. J. Li and G. W. Grimble, *Palladium in Heterocyclic Chemistry*, Pergamon, Amsterdam, 2000; (*c*) R. F. Heck, *Palladium Reagents in Organic Syntheses*, Academic Press, Toronto, 1990; (*d*) A. de Meijere, *Metal-Catalyzed Cross-Coupling Reactions*, Wiley-VCH, Weinheim, 2nd edn, 2004; (*e*) A. Yamamoto, *J. Organomet. Chem.*, 2002, **653**, 5; (*f*) T. Hayashi, *J. Organomet. Chem.*, 2002, **653**, 41; (*g*) E. Negishi, *J. Organomet. Chem.*, 2002, **653**, 34; (*h*) V. Farina, V. Krishnamurthy and W. J. Scott, *Org. React. (N. Y.)*, 1997, **50**, 1; (*i*) G. Y. Li, *J. Organomet. Chem.*, 2002, **653**, 63; (*j*) A. Ricci and C. L. Sterzo, *J. Organomet. Chem.*, 2002, **653**, 177; (*k*) G. Pattenden and D. J. Sinclair, *J. Organomet, Chem.*, 2002, **653**, 261; (*l*) N. Yasuda, *J. Organomet. Chem.*, 2002, **653**, 279; (*m*) S. Kotha, K. Lahiri and D. Kashinath, *Tetrahedron*, 2002, **58**, 9633; (*n*) E. Negishi, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 233; (*o*) C. J. Elsevier, *Coord. Chem. Rev.*, 1999, **185–186**, 809; (*p*) F. Alonso, I. P. Beletskaya and M. Yus, *Tetrahedron*, 2005, **61**, 11771; (*q*) A. Suzuki, *Chem. Commun.*, 2005, 4759; (*r*) A. Suzuki, *Proc. Jpn. Acad., Ser. B*, 2004, **80**, 359; (*s*) I. P. Beletskaya and A. V. Cheprakov, *Chem. Rev.*, 2000, **100**, 3009; (*t*) J. Hassan, M. Sévignon, C. Gozzi, E. Schulz and M. Lemaire, *Chem. Rev.*, 2002, **102**, 1359; (*u*) R. Chinchilla and C. Nájera, *Chem. Rev.*, 2007, **107**, 874; (*v*) J. P. Wolfe, S. Wagaw, J.-F. Marcoux and S. L. Buchwald, *Acc. Chem. Res.*, 1998, **31**, 805; (*w*) K. Billingsley and S. L. Buchwald, *J. Am. Chem. Soc.*, 2007, **129**, 3358 and references therein; (*x*) S. Shekhar, P. Ryberg, J. F. Hartwig, J. Mathew, D. G. Blackmond, E. R. Strieter and S. L. Buchwald, *J. Am. Chem. Soc.*, 2006, **128**, 3584; (*y*) L. Penn, A. Shpruhman and D. Gelman, *J. Org. Chem.*, 2007, **72**, 3875; (*z*) S. Iyer, G. M. Kulkarni, C. Ramesh and A. K. Sattar, *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.*, 2005, **44**, 1894 and references therein; (*aa*) J. P. Knowles and A. Whiting, *Org. Biomol. Chem.*, 2007, **5**, 31 and references therein; (*bb*) C. Barnard, *Platinum Met. Rev.*, 2008, **52**, 38.

2 (*a*) For example: C. Amatore and A. Jutand, *Acc. Chem. Res.*, 2000, **33**, 314; (*b*) J. S. Mathew, M. Klussmann, H. Iwamura, F. Valera, A. Futran, E. A. C. Emanuelsson and D. G. Blackmond, *J. Org. Chem.*, 2006, **71**, 4711; (*c*) A. A. C. Braga, G. Ujaque and F. Meseras, *Organometallics*, 2006, **25**, 3647; (*d*) M. Ahlquist and P.-O. Norrby, *Organometallics*, 2007, **26**, 550; (*e*) K. C. Lam, T. B. Marder and Z. Lin, *Organometallics*, 2007, **26**, 758; (*f*) C. Amatore, B. Godin, A. Jutand and F. Lemaître, *Organometallics*, 2007, **26**, 1757; (*g*) M. Weck and C. W. Jones, *Inorg. Chem.*, 2007, **46**, 1865; (*h*) N. T. S. Phan, M. van der Sluys and C. W. Jones, *Adv. Synth. Catal.*, 2006, **348**, 609; (*i*) B. L. Oliveira and O. A. C. Antunes, *Lett. Org. Chem.*, 2007, **4**, 13; (*j*) I. J. S. Fairlamb and A. F. Lee, *Organometallics*, 2007, **26**, 4087; (*k*) L. S. Santos, G. B. Rosso, R. A. Pilli and M. N. Eberlin, *J. Org. Chem.*, 2007, **72**, 5809; (*l*) A. L. Casado, P. Espinet, A. M. Gallego and J. M. Martínez-Ilarduya, *Chem. Commun.*, 2001, 339; (*m*) K. Köhler, W. Kleist and S. S. Pröckl, *Inorg. Chem.*, 2007, **46**, 1876; (*n*) F. Ozawa, K. Kurihara, M. Fujimori, T. Hidaka, T. Toyoshima and A. Yamamoto, *Organometallics*, 1989, **8**, 180; (*o*) G. Espino, A. Kurbangalieva and J. M. Brown, *Chem. Commun.*, 2007, 1742; (*p*) R. Fazaeli, A. Ariafard, S. Jamshidi, E. S. Tabatabaie and K. A. Pishro, *J. Organomet. Chem.*, 2007, **692**, 3984.

3 (*a*) An excellent example of this phenomenon is related to the structural aspects of the resting (pre-catalytic) state of a common Pd precursor: palladium(II) acetate. This compound is rarely depicted in its correct structural form nor is this structural motif typically considered when an idealized catalytic cycle is presented. For an evaluation and discussion of the true nature of this material, see: V. I. Bakhmutov, J. F. Berry, F. A. Cotton, S. Ibragimov and C. A. Murillo, *Dalton Trans.*, 2005, 1989 and references therein; (*b*) For related studies:K. Yu, W. Sommer, J. M. Richardson, M. Weck and C. W. Jones, *Adv. Synth. Catal.*, 2005, **347**, 161; (*c*) N. D. Jones and B. R. James, *Adv. Synth. Catal.*, 2002, **344**, 1126; (*d*) I. J. S. Fairlamb, R. J. K. Taylor, J. L. Serrano and G. Sanchez, *New J. Chem.*, 2006, **30**, 1695; (*e*) K. Yu Monakhov and T. A. Stromnova, *Zh. Obshch. Khim.*, 2007, **77**, 1841 (*Russ. J. Gen. Chem.*, 2007, **77**, 1896).

4 (*a*) R. A. Gossage, H. A. Jenkins and P. N. Yadav, *Tetrahedron Lett.*, 2004, **45**, 7689; R. A. Gossage, H. A. Jenkins and P. N. Yadav, *Tetrahedron Lett.*, 2005, **46**, 5243; (*b*) C. R. Eisnor, R. A. Gossage and P. N. Yadav, *Tetrahedron*, 2006, **62**, 3395; (*c*) G. G. Cross, C. R. Eisnor, R. A. Gossage and H. A. Jenkins, *Tetrahedron Lett.*, 2006, **47**, 2245.

5 (*a*) The use of (substituted) 2-aryl-2-oxazolines in combination with palladium(II) acetate,[3a] as an *in situ* derived catalytic formulation (optimized with a 1 : 1 oxazoline : Pd ratio), has also been reported: B. Tao and D. W. Boykin, *Tetrahedron Lett.*, 2002, **43**, 4955; (*b*) For related work see: S. Lee, *J. Organomet. Chem.*, 2006, **691**, 1347; (*c*) D. W. Dodd, H. E. Toews, F. d. S. Carneiro, M.C. Jennings and N. D. Jones, *Inorg. Chim. Acta*, 2006, **359**, 2850; (*d*) S. Haneda, C. Ueba, K. Eda and M. Hayashi, *Adv. Synth. Catal.*, 2007, **349**, 833; (*e*) C. J. Dehen, K. J. Keuseman and I. P. Smoliakova, *J. Undergrad. Chem. Res.*, 2003, **3**, 91; (*f*) S. Haneda, Z. Gan, K. Eda and M. Hayashi, *Organometallics*, 2007, **26**, 6551; (*g*) A. F. Schmidt, V. V. Smirnov and A. Al-Halaiga, *Kinet. Katal.*, 2007, **48**, 412; A. F. Schmidt, V. V. Smirnov and A. Al-Halaiga, *Kinet. Katal.*, 2007, **48**, 390; (*h*) A. Svennebring, P. J. R. Sjöberg, M. Larhed and P. Nilsson, *Tetrahedron*, 2008, **64**, 1808.

6 J.-M. Valk, F. Maassarani, P. von der Sluis, A. L. Spek, J. Boersma and G. van Koten, *Organometallics*, 1994, **13**, 2320.

7 (*a*) For example: M. Gómez, G. Muller and M. Rocamora, *Coord. Chem. Rev.*, 1999, **193–195**, 769; (*b*) T. M. Barclay, I. del Río, R. A. Gossage and S. M. Jackson, *Can. J. Chem.*, 2003, **81**, 1482; (*c*) J. A. Cabeza, I. da Silva, I. del Río, R. A. Gossage, D. Miguel and M. Suárez, *Dalton Trans.*, 2006, 2450; (*d*) A. Decken, R. A. Gossage and P. N. Yadav, *Can. J. Chem.*, 2005, **83**, 1185; (*e*) D. J. Berg, C. Zhou, T. Barclay, X. Fei, S. Feng, K. A. Ogilvie, R. A. Gossage, B. Twamley and M. Wood, *Can. J. Chem.*, 2005, **83**, 449; (*f*) J. A. Cabeza, I. da Silva, I. del Río, R. A. Gossage, L. Martínez-Méndez and D. Miguel, *J. Organomet. Chem.*, 2007, **692**, 4346.

8 The reported isomer distribution ($CDCl_3$ solution) is 2 : 3; however, the structural nature (*i.e.* presumably *cis* or *trans*) of neither the dominant nor minor isomer has been unequivocally established[6].

9 R. A. Gossage, unpublished observations.

10 (*a*) R. Romeo, P. Uguagliati and U. Belluco, *J. Mol. Catal.*, 1976, **1**, 325; (*b*) G. K. Anderson and R. J. Cross, *Chem. Soc. Rev.*, 1980, 185; (*c*) J. N. Harvey, K. M. Heslop, A. G. Orpen and P. G. Pringle, *Chem. Commun.*, 2003, 278; (*d*) D. T. Richens, *Chem. Rev.*, 2005, **105**, 1961; (*e*) D. A. Redfield and J. H. Nelson, *J. Am. Chem. Soc.*, 1974, **96**, 6219; (*f*) P. J. Heard, *Chem. Soc. Rev.*, 2007, **36**, 551.

11 I. P. Smoliakova, K. J. Keuseman, D. C. Haagenson, D. M. Wellmann, P. B. Colligan, N. A. Kataeva, A. V. Churakov, L. G. Kuz'mina and V. V. Dunina, *J. Organomet. Chem.*, 2000, **603**, 86.

12 (*a*) For example: A. I. Meyers, *J. Org. Chem.*, 2005, **70**, 6137 and references therein; (*b*) K. Aoi and M. Okada, *Prog. Polym. Sci.*, 1996, **21**, 151 and references therein; (*c*) A. Decken, L. Botelho, A. L. Sadowy, P. N. Yadav and R. A. Gossage, *Acta Crystallogr., Sect. E*, 2006, **62**, o5414; (*d*) K. M. Button, R. A. Gossage and R. K. R. Phillips, *Synth. Commun.*, 2002, **32**, 363; (*e*) A. I. Meyers, *J. Heterocycl, Chem.*, 1998, **35**, 991; (*f*) V. Langer, M. Koóš, D. Gyepesová, M. Sládkovičová, J. Lustoň and J. Kronek, *Acta Crystallogr., Sect. C*, 2005, **61**, o602; (*g*) N. N. Karade, G. B. Tiwari and S. V. Gampawar, *Synlett*, 2007, 1921; (*h*) I. Mohammadpoor-Baltork, A. R. Khosropour and S. F. Hojati, *Synlett*, 2005, 2747.

13 (*a*) R. Romeo, *Comments Inorg. Chem.*, 1990, **11**, 21; (*b*) U. Frey, L. Helm, A. E. Merbach and R. Romeo, *J. Am. Chem. Soc.*, 1989, **111**, 8161.

14 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

15 P. J. Stephens, J. F. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.

16 R. H. Hertwig and W. Koch, *Chem. Phys. Lett.*, 1997, **268**, 345.

17 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.

18 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.

19 M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654.

20 P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett.*, 1972, **16**, 217.

21 K. E. Frankcombe, K. J. Cavell, B. F. Yates and R. B. Knott, *J. Phys. Chem.*, 1996, **100**, 18363.

22 S. R. Langhoff, L. G. Petterson, C. W. Bauschlicher and H. J. Partridge, *J. Chem. Phys.*, 1987, **86**, 268.
23 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.
24 A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639.
25 M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265.
26 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honsa, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, Revision B.04*, Gaussian, Inc., Pittsburgh, PA, 2003.
27 (*a*) For example: P. Braunstein, F. Naud, A. Dedieu, M.-M. Rohmer, A. DeCian and S. J. Rettig, *Organometallics*, 2001, **20**, 2966; (*b*) S. E. Denmark, R. A. Stavenger, A.-M. Faucher and J. P. Edwards, *J. Org. Chem.*, 1997, **62**, 3375; (*c*) M. Hatano, T. Asai and K. Ishihara, *Chem. Lett.*, 2006, **35**, 172; (*d*) B. S. Federov, N. I. Golovina, V. V. Arakcheeva, M. A. Fadeev, G. V. Strukov, V. V. Kedrov, G. V. Shilov and L. O. Atovmyan, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1604 (*Russ. Chem. Bull.*, 1999, **48**, 1584); (*e*) C. Thoumazet, M. Melaimi, L. Ricard and P. Le Floch, *C. R. Chim.*, 2004, **7**, 823; (*f*) M. Agostinho and P. Braunstein, *C. R. Chim.*, 2007, **10**, 666; (*g*) A. Horiuchi, E. Horn, K. Ito, T. Nakahodo, M. Watabe, T. T. Takahashi and C. A. Horiuchi, *Z. Kristallogr.-New Cryst. Struct.*, 2005, **220**, 27.
28 R. J. Cross, *Chem. Soc. Rev.*, 1985, **14**, 197.
29 (*a*) M. L. Tobe and J. Burgess, *Inorganic Reaction Mechanisms*, Longman, NY, 1999, ch. 2 and 3; (*b*) C. D. Hubbard and R. van Eldik, *J. Coord. Chem.*, 2007, **60**, 1.
30 (*a*) S. L. Queiroz and A. A. Batista, *Quim. Nova*, 1998, **21**, 193; (*b*) J. Burgess and C. D. Hubbard, *Adv. Inorg. Chem.*, 2003, **54**, 71.
31 (*a*) For example: L. Cattalini and M. Martelli, *J. Am. Chem. Soc.*, 1969, **91**, 312; (*b*) R. Roulet and C. Barbey, *Helv. Chim. Acta*, 1973, **56**, 2179; (*c*) J. J. MacDougall, F. Mathey and J. H. Nelson, *Inorg. Chem.*, 1980, **19**, 1400; (*d*) F. P. Fanizzi, F. P. Intini, L. Maresca and G. Natile, *J. Chem. Soc., Dalton Trans.*, 1990, 199; (*e*) A. W. Verstuyft and J. H. Nelson, *Inorg. Chem.*, 1975, **14**, 1501; (*f*) R. Favez and R. Roulet, *Inorg. Chem.*, 1981, **20**, 1598; (*g*) D. A. Redfield, J. H. Nelson, R. A. Henry, D. W. Moore and H. B. Jonassen, *J. Am. Chem. Soc.*, 1974, **96**, 6298; (*h*) J. H. Price, J. P. Birk and B. B. Wayland, *Inorg. Chem.*, 1978, **17**, 2245; (*i*) R. van Eldik, D. A. Palmer and H. Kelm, *Inorg. Chem.*, 1979, **18**, 572.
32 S. D. Kirik, L. A. Solovyov, A. I. Blokhin, I. S. Yakimov and M. L. Blokhina, *Acta Crystallogr., Sect. B*, 1996, **52**, 909.
33 (*a*) For example: H. Azizian, K. R. Dixon, C. Eaborn, A. Pidcock, N. M. Shuaib and J. Vinaixa, *J. Chem. Soc., Chem. Commun.*, 1982, 1020; (*b*) Y. Tsuji and Y. Obora, *J. Organomet. Chem.*, 2000, **611**, 343 and references therein.
34 (*a*) Pd^{2+} phosphine complexes: H. Kurosawa and S. Numata, *J. Organomet. Chem.*, 1979, **175**, 143; (*b*) F. Ozawa, A. Yamamoto, T. Ikariya and R. H. Grubbs, *Organometallics*, 1982, **1**, 1481.
35 (*a*) Pd^{2+} di-aryl complexes: D. Minniti, *Inorg. Chem.*, 1994, **33**, 2631; (*b*) A. L. Casado, J. A. Casares and P. Espinet, *Organometallics*, 1997, **16**, 5730; (*c*) A. L. Casado, J. A. Casares and P. Espinet, *Inorg. Chem.*, 1998, **37**, 4154; (*d*) A. C. Albéniz, A. L. Casado and P. Espinet, *Inorg. Chem.*, 1999, **38**, 2510; (*e*) G. Alibrandi, D. Minniti, L. Monsù Scolaro and R. Romeo, *Inorg. Chem.*, 1988, **27**, 318.
36 (*a*) R. Romeo, D. Minniti and M. Trozzi, *Inorg. Chem.*, 1976, **15**, 1134; (*b*) R. Favez, R. Roulet, A. A. Pinkerton and D. Schwarzenbach, *Inorg. Chem.*, 1980, **19**, 1356; (*c*) G. Alibrandi, G. Bruno, S. Lanza, D. Minniti and R. Romeo, *Inorg. Chem.*, 1987, **26**, 185; (*d*) G. Alibrandi, D. Minniti, L. Monsù Scolaro and R. Romeo, *Inorg. Chem.*, 1989, **28**, 1939; (*e*) G. Alibrandi, L. Monsù Scolaro and R. Romeo, *Inorg. Chem.*, 1991, **30**, 4007; (*f*) R. Romeo, A. Grassi and L. Monsù Scolaro, *Inorg. Chem.*, 1992, **31**, 4383; (*g*) D. Minniti, *J. Chem. Soc., Dalton Trans.*, 1993, 1343; (*h*) M. Schmülling and R. van Eldik, *Chem. Ber./Recl.*, 1997, **130**, 1791; (*i*) 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; (*j*) A. Klein, T. Schurr, A. Knödler, D. Gudat, K.-W. Klinkhammer, V. K. Jain, S. Záliš and W. Kaim, *Organometallics*, 2005, **24**, 4125; (*k*) R. Romeo, *Inorg. Chem.*, 1978, **17**, 2040; (*l*) R. Romeo, D. Minniti and M. Trozzi, *Inorg. Chim. Acta*, 1975, **14**, L15; (*m*) G. Faraone, V. Ricevuto, R. Romeo and M. Trozzi, *J. Chem. Soc. A*, 1971, 1877.
37 (*a*) For external cation assisted isomerisations, see: V. W.-W. Yam, X.-X. Lu and C.-C. Ko, *Angew. Chem., Int. Ed.*, 2003, **42**, 3385; (*b*) X.-X. Lu, H.-S. Tang, C.-C. Ko, J. K.-Y. Wong, N. Zhu and V. W.-W. Yam, *Chem. Commun.*, 2005, 1572.
38 (*a*) L. Vigo, M. Risto, E. M. Jahr, T. Bajorek, R. Oilunkaniemi, R. S. Laitinen, M. Latineen and A. Ahlgrén, *Cryst. Growth Des.*, 2006, **6**, 2376; (*b*) P. E. M. Siegbahn and R. H. Crabtree, *Mol. Phys.*, 1996, **89**, 279.
39 (*a*) W. R. Rocha and W. B. de Almeida, *J. Braz. Chem. Soc.*, 2000, **11**, 112; (*b*) W. Beck, T. M. Klapötke and W. Ponikwar, *Z. Naturforsch., B: Chem. Sci.*, 2002, **57**, 1120; (*c*) H. P. Dijkstra, M. Q. Slagt, A. McDonald, C. A. Kruithof, R. Kreiter, A. M. Mills, M. Lutz, A. L. Spek, W. Klopper, G. P. van Klink and G. van Koten, *Eur. J. Inorg. Chem.*, 2003, 830; (*d*) R. C. Jones, R. L. Madden, B. W. Skelton, V.-A. Tolhurst, A. H. White, A. M. Williams, A. J. Wilson and B. F. Yates, *Eur. J. Inorg. Chem.*, 2005, 1048; (*e*) M. Doux, N. Mézailles, L. Ricard and P. Le Floch, *Eur. J. Inorg. Chem.*, 2003, 3878; (*f*) D. Gudat, V. K. Jain, A. Klein, T. Schurr and S. Záliš, *Eur. J. Inorg. Chem.*, 2005, 4056; (*g*) H. Chermette, *Coord. Chem. Rev.*, 1998, **178–180**, 699.
40 The Y-shaped (pseudo-trigonal planar) form intermittent between **I** and **II** could not be located on the potential energies maps; this Y-form invariably collapsed into the isomer **II**.
41 (*a*) G. R. Porter, H. N. Rydon and J. A. Schofield, *Nature*, 1958, **182**, 927; (*b*) M. A. Weinberger and R. Greenhalgh, *Can. J. Chem.*, 1963, **41**, 1038; (*c*) A. Decken, C. R. Eisnor, R. A. Gossage and S. M. Jackson, *Inorg. Chim. Acta*, 2006, **359**, 1743.
42 (*a*) F. Ozawa and A. Yamamoto, *Chem. Lett.*, 1981, 289; (*b*) K. S. Yoo, C. H. Yoon and K. W. Jung, *J. Am. Chem. Soc.*, 2006, **128**, 16384; (*c*) J. A. Casares, P. Espinet, B. Fuentes and G. Salas, *J. Am. Chem. Soc.*, 2007, **129**, 3508; (*d*) L. J. Goossen, N. Rodríguez, B. Melzer, C. Linder, G. Deng and L. M. Levy, *J. Am. Chem. Soc.*, 2007, **129**, 4824; (*e*) N. Rodríguez, C. R. de Arellano, G. Asensio and M. Medio-Simón, *Chem.–Eur. J.*, 2007, **13**, 4223; (*f*) J. A. Casares, S. Coco, P. Espinet and Y.-S. Lin, *Organometallics*, 1995, **14**, 3058; (*g*) J. A. Chamizo, J. Morgado, M. Castro and S. Bernès, *Organometallics*, 2002, **21**, 5428; (*h*) N. Rodríguez, C. Ramírez de Arellano, G. Ascensio and M. Medio-Simón, *Chem.–Eur. J.*, 2007, **13**, 4223; (*i*) C. Amatore, B. Godin, A. Jutand and F. Lemaître, *Chem.–Eur. J.*, 2007, **13**, 2002; (*j*) C. Adamo, C. Amatore, I. Ciofini, A. Jutand and H. Lakmini, *J. Am. Chem. Soc.*, 2006, **128**, 6829; (*k*) S. Shashank and J. F. Hartwig, *J. Am. Chem. Soc.*, 2004, **126**, 13016; (*l*) A. M. Zawisza, S. Bouquillon and J. Muzart, *Eur. J. Org. Chem.*, 2007, 3901; (*m*) O. F. Wendt, *Curr. Org. Chem.*, 2007, **11**, 1417.
43 (*a*) For seminal discussions, see: K. Tatsumi, R. Hoffmann, A. Yamamoto and J. K. Stille, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1857; (*b*) F. Ozawa, T. Ito, Y. Nakamura and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1868; (*c*) A. Yamamoto, T. Yamamoto, S. Komiya and F. Ozawa, *Pure Appl. Chem.*, 1984, **56**, 1621; (*d*) A. Gillie and J. K. Stille, *J. Am. Chem. Soc.*, 1980, **102**, 4933; (*e*) M. Loar and J. K. Stille, *J. Am. Chem. Soc.*, 1981, **103**, 4174; (*f*) A. Moravskiy and J. K. Stille, *J. Am. Chem. Soc.*, 1981, **103**, 4182.

