Mechanistic insights into the tropo-inversion of the biphenyl moiety in chiral bis-amido phosphites and in their palladium(II) complexes

Alessandro Passera,a,b,c Anna Iuliano,b,* Jesús J. Pérez-Torrentea and Vincenzo Passarellia,d,*

Chiral bis-amido phosphites L1 and L2 containing a dianimobiphenyl unit and a chiral alkoxy group derived from either (–)-menthol or 3-acetoxy deoxycholic methyl ester have been synthesised. Both L1 and L2 react with PdCl2(NCPh)2 affording di- or mononuclear derivatives of formula trans-[Pd(μ-Cl)Cl(L)]2 (1a, L = L1; 1b, L = L2) or trans-PdCl2(L)2 (2a, L = L1; 2b, L = L2) depending on the Pd:L molar ratio. The crystal structure of (M,P)-1a confirms the trans arrangement of the ligands L1 and shows an unusual puckering of the Pd2(μ-Cl)2 core (46°). Both the ligands L1 and L2 and its complexes (1, 2) are fluxional in solution as a consequence of the tropo-inversion of the dianimobiphenyl unit. For L1, L2, 1a and 2a a combined study including variable temperature 31P{1H} NMR spectroscopy and line shape analysis, Eyring plots and DFT calculations have shed light on the mechanism of the tropo-inversion.

Introduction

Metal complexes of chiral tropos, i.e. chirally flexible, ligands have proven to work as effective asymmetric catalysts in different enantioselective reactions1 and they result attractive since no resolution is required. In these complexes the conformational control of the tropo unit is obtained by the transfer of the chiral information from an enantiomer of a stereochemically stable ligand, through the coordination sphere of the metal centre,2 or by means of the chiral control exerted by an enantiopure moiety, possessing fixed stereogenic elements, covalently linked to the flexible unit.3 In both cases the conformational preference is allied to the effectiveness of the chiral stereochemically stable moiety to transfer the chiral information, but sometimes it can be triggered by the substrate of the reaction in the course of the catalytic cycle.4 In this last case the tropo-inversion phenomenon (interconversion of the two diastereomers) plays a crucial role, allowing a diastereomeric mixture to be converted in a single diastereomer of the tropos catalytic complex. Therefore, the study and the elucidation of the tropo-inversion mechanism is fundamental to the design of these ligands and their corresponding dynamic enantioselective catalysts.

So far this kind of study has been carried out on free ligands, existing as enantiomeric mixture,5 and on metal complexes of 2,2'-bis(diphenylphosphane)-1,1'-biphenyl.6 By contrast, to the best of our knowledge, the study of tropo-inversion on ligands asymmetrically activated by means of covalent bond(s) to a stereochemically stable subunit and on their metal complexes has received less attention. Indeed only a limited number of studies on the stereodynamic characteristics of phosphites and phosphine9 has been reported so far. In addition, a computational study on the stereodynamic properties of tropos quaternary ammonium salts has also been reported.9 Following our longstanding interest in the design of tropos ligands and in the use of their metal complexes as chiral catalysts, we now focused on the chiral bis-amido phosphites L1 and L2 (Scheme 1), where the chiral stereochemically stable subunit is a derivative of natural compounds, namely (–)-menthol and 3-acetoxy deoxycholic methyl ester. The presence of two P–N bonds, which increase the electronic density on the phosphorus atom, makes bis-amido phosphites more appropriate than parent phosphites to prepare palladium complexes with applications to enantioselective C–C

\[ \text{Scheme 1} \]

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Electronic Supplementary Information (ESI) available: Kinetic constants, Eyring plots, 31P{1H} NMR spectra of L2, 1b and 2b, atomic coordinates and views of the calculated structures.
The chiral bis-amido phosphites L1 and L2 and their palladium(II) complexes, by a combined approach based on NMR spectroscopy and DFT calculations, aimed at elucidating the tropo-inversion mechanism of both free and coordinated ligands.

Results and Discussion

Bis-amido phosphites. The chiral bis-amido phosphites L1 and L2 were prepared in good yields starting from N,N′-dimethyl-1,1′-diaminobiphenyl (C1), phosphorus trichloride, and a chiral enantiomerically pure alcohol, namely (−)-menthol (R1OH) and 3-acetoxy deoxycholic methyl ester (R2OH) (Scheme 2). The chiral bis-amido phosphites L1 and L2 were obtained following the two-step route 1 in Scheme 2 going through: a) the preparation of the bis-amido chlorophosphite C2, and b) the reaction of C2 with (−)-menthol (R1OH) and 3-acetoxy deoxycholic methyl ester (R2OH) (Route 2).

Ligand L1 was obtained following the two-step route 1 in Scheme 2: (a) the preparation of the bis-amido chlorophosphite C2, and (b) the reaction of C2 with (−)-menthol (R1OH). On the other hand the bulkier ligand L2 was obtained by reaction of N,N′-dimethyl-1,1′-diaminobiphenyl (C1) and the dichlorophosphite PCl2(OH2)2, resulting from the reaction of PCl3 and R2OH (Scheme 2, route 2). It is noteworthy that uncharacterized byproducts and low yields were observed when R1OH was reacted with PCl3. Also, the reaction of C2 with R1OH was extremely slow and low yields of L2 were achieved even after 72 h of reaction, probably due to the high steric demand of R1OH and its consequent low nucleophilicity.

Selected NMR data for L1 and L2 are given in Table 1. One 31P resonance was observed for both L1 and L2 indicating that at room temperature a fast exchange should exist between the two diastereomers (vide infra), one with the M configuration and the other with the P configuration of the biphenyl moiety (see ESI-Figure S1). Remarkably, both L1 and L2 contain two non-equivalent NMe groups (Table 1) as a result of the diastereotopic environment created by the chiral alkoxy substituents. Also, 3JHPO and 2JCP coupling constants were observed in the 1H and 13C signals of the NMe and the POCH groups.

Variable temperature NMR measurements for both L1 and L2 showed that the tropo-inversion at the biphenyl moiety can be slowed down enough to observe the (M)- and (P)-diastereomers. Figure 1 shows the 31P{1H} NMR spectra of L1 in the range 224–294 K (toluene-d8). Interestingly, at 224 K three resonances could be reliably identified, namely one for one diastereomer (175.7 ppm, 67%, either M or P), and two overlapped for the other [179.23 (17%); 179.21 ppm (16%), Figure 1]. Upon rising the temperature up to 234 K the signals at 179.23 and 179.21 ppm merge resulting in only one well-shaped resonance at 178.9 ppm. On these bases, these two resonances could be reasonably assigned to two exchanging conformers of one diastereomer of L1, tentatively those containing the substituents of the alkoxy moiety at axial and equatorial positions, respectively. Upon further rising the temperature the coalescence of the signals is observed between 274 and 284 K. As for L2, at 188 K two 31P resonances are observed at 165.2 (52%) and 170.1 (48%) ppm and the coalescence of the signals is achieved around 248 K (see ESI-Figure S2). Both for L1 and L2, the line shape analysis of the 31P{1H} signals provided the kinetic constants for the equilibrium (M)-L1⎯(P)-L (see ESI-Table S1) and the activation parameters were finally obtained by means of the Eyring plot (L1, ΔH‡ = +14.6±0.3; ΔS‡ = +6.5±1.1; ΔG‡298K = +12.7±0.6 kcal mol⁻¹; L2, ΔH‡ = +8.4±0.05 kcal mol⁻¹; ΔS‡ = −10.4±0.2 cal mol⁻¹ K⁻¹; ΔG‡298K = −11.3±0.1 kcal mol⁻¹; see ESI-Figure S3). The calculated small activation enthalpies and the activation entropies close to zero nicely point at a non-dissociative
mechanism, reasonably ruling out any bond breaking in the course of the tropo-inversion of both L1 and L2.

In order to clarify the mechanism of the tropo-inversion of L1, DFT calculations were undertaken. The calculated structures of (M)-L1, (P)-L1 and of the transition states for the (M)-L1⇌(P)-L1 equilibrium are shown in Figure 2. In view of the NMR data (vide supra), both conformers, namely one with equatorial and the other with axial arrangements of the substituents of the alkoxy moiety, have been considered. Not surprisingly, the structures featuring the substituents at the equatorial positions are more stable than those with the substituents at the axial positions. Interestingly, the small energy difference between the two conformers nicely fit in with the presence of one axial conformer in solution at 224 K, as suggested by the above mentioned NMR data.

Two non-equivalent transition state structures have been encountered for both the axial and the equatorial conformers. As a common characteristic, the calculated transition states feature a nearly flat biphenyl unit. Nevertheless, taking the plane containing the phosphorus and the nitrogen atoms as the reference, the structures of t-TS_I-II and t-TS_III-IV feature a trans arrangement of the oxygen atom with respect to the biphenyl moiety, while the structures of c-TS_I-II and c-TS_III-IV feature a cis arrangement. The flat biphenyl moiety reasonably results from the internal rotation around the carbon-carbon bond joining the two phenyl ring. Yet two independent molecular motions should be responsible for the above mentioned trans and cis arrangements. Taking the diastereomer II (P-eq) as an example (Figure 3), the phenyl ring of II labeled as b is trans to the oxygen whereas that labeled as a is cis. Thus, looking at the model molecule in Figure 3, t-TS is the result of turning the cis phenyl ring a clockwise around the C(sp²)-C(sp²) bond, while c-TS results from turning the trans phenyl ring b anticlockwise.

In view of the Gibbs free energy profile shown in Figure 2, despite the fact that fast equilibria between equatorial and axial conformers should occur in solution, the tropo-inversion should take place preferentially via the transition state c-TS_I-II involving the equatorial conformer.
In the case of L2 (see ESI-Figure S4), similarly to L1, two non-equivalent transition states were calculated for the tropo-inversion (M)-L2=(P)-L2 (ΔG°298 K = +1.8 kcal mol⁻¹), namely with either a cis (ΔG°298 K = +19.2 kcal mol⁻¹) or a trans (ΔG°298 K = +12.2 kcal mol⁻¹) arrangement of the oxygen atom with respect to the flat biphenyl moiety. Thus, like for L1, the tropo-inversion should take place preferentially via the transition state with a cis arrangement of the oxygen atom and the inverting biphenyl moiety.

**Synthesis of palladium(II) complexes.** L1 and L2 react with PdCl₂(NCPh₂) affording high yields of the dinuclear complexes trans-[Pd(μ-Cl)(Cl)]₂ (1a, L = L1; 1b, L = L2) or the mononuclear complexes trans-PdCl₂(L)₂ (2a, L = L1; 2b, L = L2) depending on the L:Pd molar ratio (Scheme 3). Interestingly, when the reaction of L1/L2 with PdCl₂(NCPh₂) in 1:1 molar ratio was monitored by ³¹P NMR spectroscopy, the formation of 2a/2b was observed first, followed by the quantitative formation of 1a/1b. Accordingly 1a/1b was almost quantitatively obtained when 2a/2b was reacted with PdCl₂(NCPh₂) (1:1). Further, 1a/1b readily reacts with L1/L2 (1:2) affording 2a/2b.

As a general remark, the proposed trans arrangement in 1a/1b and 2a/2b should be the consequence of the high steric demand of L1 and L2. Indeed, cis isomers of 1a and 2a were calculated to be less stable (vide infra) than the trans ones, and, as for L2, molecular models of the putative cis isomers of both 1b and 2b showed that parts of the ligands L2 would overlap.

¹H DOSY measurements were carried out at room temperature on solutions of L1, L2, and the corresponding complexes 1a/1b and 2a/2b (Table 2). In each case all the diastereomers (vide infra) exhibit identical diffusion coefficients and the differences among the calculated hydrodynamic radii nicely fit in with the proposed structure of the complexes. Indeed the hydrodynamic radii of the metal complexes 1a/1b and 2a/2b are significantly bigger than that of the corresponding uncomplexed ligands. Further the mononuclear complexes 2a and 2b exhibit smaller hydrodynamic radii than the corresponding dinuclear derivatives 1a and 1b, respectively.

**Dinuclear palladium(II) complexes.** Single crystals of (M,P)-1a were obtained by slow evaporation of a toluene solution of 1a. Figure 4 shows the ORTEP view of the dinuclear complex and

![Figure 4. ORTEP view of (M,P)-[Pd(μ-Cl)(Cl)L]. (1a) in 1a·C₂H₆ with the definition of the puckering angle (θ of the Pd₃(μ-Cl)₃ moiety. Ellipsoids are at the 50% of probability and hydrogen atoms are omitted for clarity.](image-url)

**Table 2. Selected ¹H DOSY data obtained on toluene solutions (η = 0.56 mPa s) at 298 K with an approximate concentration of 1.0·10⁻² M.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>D·10⁻⁰ (m² s⁻¹)</th>
<th>r₂⁺ (Å)</th>
</tr>
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<tbody>
<tr>
<td>L1</td>
<td>8.18</td>
<td>4.4</td>
</tr>
<tr>
<td>1a</td>
<td>5.22</td>
<td>7.5</td>
</tr>
<tr>
<td>2a</td>
<td>5.46</td>
<td>7.1</td>
</tr>
<tr>
<td>L2</td>
<td>7.24</td>
<td>5.4</td>
</tr>
<tr>
<td>1b</td>
<td>3.75</td>
<td>10.4</td>
</tr>
<tr>
<td>2b</td>
<td>4.72</td>
<td>7.7</td>
</tr>
</tbody>
</table>

* calculated from the Stokes-Einstein equation D = kₜ T/(6πη r₂⁺); ² benzene solution (η = 0.60 mPa s).

Table 3 contains selected bond lengths and angles. The palladium centres of (M,P)-1a are joined by two bridging chlorine atoms and feature a slightly distorted square planar coordination with a trans arrangement of the L1 ligands on the Pd₂(μ-Cl) core. Palladium-chlorine and palladium-phosphorus bond lengths along with the trans arrangement of the two phosphorus atoms are similar to those observed in related structures. Nevertheless the observed puckered conformation of the Pd₂(μ-Cl) core in (M,P)-1a (θ 46.7°) is unusual. A survey of the CCDC database has shown that as for now only a few examples of complexes of general formula trans-[Pd₂(μ-Cl)(P-donor)] have a puckered Pd₂(μ-Cl) core (θ 34–69°), whereas the largely most common conformation is planar or almost planar. Interestingly the complex featuring the highest puckering angle (θ 68.8°) contains a bidentate diphosphano ligand spanning the two trans positions of the bimetallic core. In addition, it should be noted that also the solid state structure of complexes of formula cis-[Pd₂(μ-Cl)(P-donor)] with bidentate phospho ligands spanning the cis positions contains a puckered core (θ 58-64°) as a consequence of the severe constraint imposed by the bidentate ligand. Pd₃-Pd distances in the range 2.91-3.34 Å have been reported for complexes [Pd₂(μ-Cl)(P-donor)₃] in association with the puckering, indicating that metal-metal interactions could eventually exist (palladium Van der Waals
radius 1.63 Å.\textsuperscript{16} When dealing with the dinuclear complex (M,P)-1a the Pd···Pd distance of 3.2526(5) Å reasonably rules out any intermetallic interaction.\textsuperscript{17}

The geometry of nitrogen atoms in (M,P)-1a are almost planar. Indeed the distance from each nitrogen atom to the least square plane containing the directly bonded atoms, namely methyl carbon, phenyl ipso carbon and phosphorus, is in the range 0.13–0.20 Å, and accordingly the sum of the bond angles slightly (< 4°) deviate from 360°. Also, both the N–C\textsuperscript{ipso} bond lengths (av. 1.44 Å) and the observed dihedral angle between the aromatic C\textsubscript{6} ring and the least square plane containing nitrogen, methyl-carbon, phenyl ipso-carbon, and phosphorus [N(1), 86.7°; N(2), 56.3°; N(3), 64.2°; N(4), 79.0°] suggest a negligible delocalization of the lone pair of the nitrogen on the aromatic ring. Further, the observed phosphorus-nitrogen bonds (av. 1.65 Å) are significantly shorter than phosphorus-nitrogen single bonds (ca. 1.77 Å), thus pointing at that the P–N bond should exhibit some degree of multiple bond.\textsuperscript{18}

The \textsuperscript{31}P(\textsuperscript{1}H) NMR spectrum of 1a in toluene-d\textsubscript{8} at 293 K (Figure 5, Table 4) shows four resonances indicating the presence of three diastereomers, namely (M,P)-1a (δ\textsubscript{p} 86.2, 88.3, ppm, total 50%), (M,M)-1a and (P,P)-1a (δ\textsubscript{p} 85.9, 20%; 88.7 ppm, 30%). Also the \textsuperscript{31}P(\textsuperscript{1}H) NMR signals are broad (Δ\textsubscript{1/2} = 10 Hz, av.) suggesting that the troppo-inversion is operative at room temperature. As a confirmation, upon rising the temperature up to 383 K the signals further broaden and their coalescence can be envisaged at about 383 K (Figure 5). More interestingly, on lowering the temperature, the line width diminishes and at 253 K the four bond phosphorus-phosphorus coupling constant of (M,P)-1a could eventually be observed (J\textsubscript{ph} = 3.0 Hz).

Similarly to 1l, each diastereomer of 1a contains two non-equivalent NMe groups per ligand, and as for the alkoxymoiety four partially overlapping non-equivalent POCH signals are observed (Table 4). Figure 6 shows selected regions of the \textsuperscript{1}H, the \textsuperscript{1}H\textsuperscript{31}P and the \textsuperscript{1}H \textsuperscript{31}P HMBC NMR spectra at 233 K with the proposed assignment. Further selected \textsuperscript{1}H and \textsuperscript{13}C NMR data are given in Table 4.

The solution behaviour of 1b is similar to that of 1a. Indeed, at 273 K the \textsuperscript{31}P(\textsuperscript{1}H) NMR spectrum of 1b contains four signals suggesting the existence of three diastereomers namely (M,M)-1b, (P,P)-1b (86.4 ppm 31%, 86.3 ppm, 37%) and (M,P)-1b (86.2, 84.9, total 32%). Also, the line width at 273 K (20 Hz, av.) and the unique broad \textsuperscript{31}P(\textsuperscript{1}H) NMR resonance at 85.0 ppm at 366 K (Δ\textsubscript{1/2} = 70 Hz) confirm that the troppo-inversions (M,M)-1b ⇌ (M,P)-1b and (M,P)-1b ⇌ (P,P)-1b are operative (see ESI-Figure S2).

In order to gain insights into the solution behaviour of 1a, the line shape analysis\textsuperscript{12} of its \textsuperscript{31}P(\textsuperscript{1}H) NMR spectra was undertaken. Two kinetic constants, namely one for the equilibrium (M,M)-1a ⇌ (M,P)-1a and another for the equilibrium (M,P)-1a ⇌ (P,P)-1a, were used in the course of the line shape analysis\textsuperscript{12} (see ESI-Table S2). As a result, the activation parameters obtained from the Eyring plots for the two processes (i): ΔH\textsubscript{a}=+10.12±0.05 kcal mol\textsuperscript{−1}; ΔS\textsubscript{a}=-19.9±0.1 cal mol\textsuperscript{−1} K\textsuperscript{−1}; ΔG\textsubscript{298 K}\textsuperscript{a}=+16.1±0.1 kcal mol\textsuperscript{−1}; ii: ΔH\textsubscript{a}=+8.23±0.04 kcal mol\textsuperscript{−1}; ΔS\textsubscript{a}=-23.9±0.1 cal mol\textsuperscript{−1} K\textsuperscript{−1}; ΔG\textsubscript{298 K}\textsuperscript{a}=+15.4±0.1 kcal mol\textsuperscript{−1}.

Table 3. Selected bond lengths [Å] and angles (°) for [PdCl\textsubscript{2}]+[C(12-25)-N(3)-P(2)-Pd(1)-1a in C\textsubscript{6}H\textsubscript{6}]

<table>
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<th>Bond/Angle</th>
<th>Length [Å]</th>
<th>Angle [°]</th>
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<tbody>
<tr>
<td>N(4)-P(2)</td>
<td>1.646(4)</td>
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<tr>
<td>Cl(2)-Pd(2)</td>
<td>2.3277(13)</td>
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<tr>
<td>Cl(2)-Pd(2)</td>
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<tr>
<td>Cl(3)-Pd(1)</td>
<td>2.2763(14)</td>
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</tr>
<tr>
<td>Cl(4)-Pd(2)</td>
<td>2.2752(14)</td>
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</tr>
<tr>
<td>N(1)-P(1)</td>
<td>1.645(4)</td>
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<td>P(2)-Pd(2)</td>
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<tr>
<td>Pd(1)-Pd(2)</td>
<td>3.2526(5)</td>
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</tr>
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</table>

Table 4. Selected \textsuperscript{1}H, \textsuperscript{13}C and \textsuperscript{31}P NMR data of 1a (toluene-d\textsubscript{8}, 233 K).

<table>
<thead>
<tr>
<th>Bond/Chemical Shift</th>
<th>δ\textsubscript{p} [ppm]</th>
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<tr>
<td>(M,M)</td>
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<tr>
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</table>
probably as a consequence of the steric congestion around the coordinated ligand is higher than that of the free ligand, inverting ligand. In addition the activation barrier of the ligand is scarcely affected by the configuration of the non-dissociative pathway for the tropo-inversion of 1a as a consequence of the puckering of Pd2(μ-Cl)2 core eventually on its fluxional behaviour in solution. The relative stability of the four isomers Va, Vb, Vla, and Vlb of formula (M,P)-[Pd(μ-Cl)Cl(L1)]2 was first addressed (Figure 7, calculated structures are shown in ESI). It should be noted that Va/Vb and Vla/Vlb are genuine pairs of isomers. Indeed, as a consequence of the puckering of Pd2(μ-Cl)2 in Va/Vb, the trans-[Pd(μ-Cl)Cl(P-donor)]2 backbone is chiral. On the other hand, the puckered structure cis-[Pd(μ-Cl)Cl(P-donor)]2 is achiral, nevertheless the presence of two different P-donor diastereomers, namely (M)-L1 and (P)-L1, makes the structures Vla and Vlb pseudoasymmetric. The trans isomers Va and Vb are significantly more stable than the cis isomers Vla and Vlb thus confirming that the trans arrangement of two L1 ligands on the Pd2(μ-Cl)2 core should be preferred over the cis one. In addition, Va is virtually superimposable to the solid state structure of (M,P)-1a and accordingly it is more stable than the trans isomer Vb. As far as the solution behaviour is concerned, Va and Vb should interconvert by means of a non-dissociative mechanism resembling the flapping of cyclobutane. Indeed the transition state TS_Va-Vb for Va=Vb features an almost planar Pd2(μ-Cl)2 core (Figure 7) and the calculated barrier (+6.9 kcal mol−1) is low enough to be easily overcome all over the range of temperature explored in the NMR measurements, thus preventing the direct observation of Va and Vb in solution. Similarly to trans-(M,P)-[PdCl(μ-Cl)(L1)]2, two pairs of isomers exist also for the diastereomers trans-(M,M)-[PdCl(μ-Cl)(L1)]2 and trans-(P,P)-PdCl(μ-Cl)(L1)]2, namely Vlla/Vlb and Vlla/Vlb, respectively (Figure 8, calculated structures are shown in ESI). Further, like for Va and Vb, the equilibria Vlla=Vlb and Vlla=Vlb feature easily affordable barriers (< +8 kcal mol−1, Figure 8) and the corresponding transition stability of the four isomers Va, Vb, Vla, and Vlb of formula (M,P)-[Pd(μ-Cl)Cl(L1)]2 was first addressed (Figure 7, calculated structures are shown in ESI). It should be noted that Va/Vb and Vla/Vlb are genuine pairs of isomers. Indeed, as a consequence of the puckering of Pd2(μ-Cl)2 in Va/Vb, the trans-[Pd(μ-Cl)Cl(P-donor)]2 backbone is chiral. On the other hand, the puckered structure cis-[Pd(μ-Cl)Cl(P-donor)]2 is achiral, nevertheless the presence of two different P-donor diastereomers, namely (M)-L1 and (P)-L1, makes the structures Vla and Vlb pseudoasymmetric. The trans isomers Va and Vb are significantly more stable than the cis isomers Vla and Vlb thus confirming that the trans arrangement of two L1 ligands on the Pd2(μ-Cl)2 core should be preferred over the cis one. In addition, Va is virtually superimposable to the solid state structure of (M,P)-1a and accordingly it is more stable than the trans isomer Vb. As far as the solution behaviour is concerned, Va and Vb should interconvert by means of a non-dissociative mechanism resembling the flapping of cyclobutane. Indeed the transition state TS_Va-Vb for Va=Vb features an almost planar Pd2(μ-Cl)2 core (Figure 7) and the calculated barrier (+6.9 kcal mol−1) is low enough to be easily overcome all over the range of temperature explored in the NMR measurements, thus preventing the direct observation of Va and Vb in solution. Similarly to trans-(M,P)-[PdCl(μ-Cl)(L1)]2, two pairs of isomers exist also for the diastereomers trans-(M,M)-[PdCl(μ-Cl)(L1)]2 and trans-(P,P)-PdCl(μ-Cl)(L1)]2, namely Vlla/Vlb and Vlla/Vlb, respectively (Figure 8, calculated structures are shown in ESI). Further, like for Va and Vb, the equilibria Vlla=Vlb and Vlla=Vlb feature easily affordable barriers (< +8 kcal mol−1, Figure 8) and the corresponding transition
states TS_VIIa-VIIb and TS_VIIia-VIIib exhibit an almost planar Pd₂(μ-Cl)₂ core (see ESI). The overall Gibbs free energy profile of the equilibria VIIa/b=Va/b=VIIia/b and the structures of the affordable transition states (t-TS_Va-VIIa and t-TS_Vb-VIIIb) for the tropo-inversion in 1a is shown in Figure 9. Notably the most stable diastereomers VIIb (M,M), Va (M,P) and VIIia (P,P) interconvert by means of a combined sequence of tropo-inversions, namely VIIia=Va and VIIib=Villa, and flapping of the Pd₂(μ-Cl)₂ core, namely VIIia=Villa, Va=Vib, and VIIib=Villa (Figure 9).

Like for free L1, taking the PN₄ plane of the inverting ligand as the reference, two non-equivalent arrangements of the oxygen atom with respect to the biphenyl unit have been encountered in the calculated transition states, namely, trans (t-TS) or cis (c-TS). Nevertheless, at variance with L1, the lowest barrier for both (M,M)= (M,P) and (M,P)= (P,P) tropo-inversions in trans-[PdCl(μ-Cl)(L1)]₂ corresponds to a trans arrangement of oxygen and biphenyl unit (t-TS_Va-VIIa and t-TS_Vb-VIIIb, Figure 9), which is in agreement with the reduced steric congestion around the Pd₂(μ-Cl)₂ moiety in comparison with that in the other transition states considered in this study (see ESI).

Mononuclear palladium(II) complexes. The solution behaviour of the mononuclear complex trans-PdCl₂(L1)₂ (2a) is similar to that described for 1a. Indeed, at 266 K the ¹¹³C{¹H} NMR spectrum of 2a contains four signals (119.1, 10% (M,M or P,P), 117.2, 51% (P,P or M,M); 116.7 and 115.9 ppm, total 39% (M,P)) suggesting the presence of the three diastereomers (M,M)-2a, (M,P)-2a and (P,P)-2a (Figure 10). Also, two non-equivalent NMe groups have been assigned to the diastereomer (M,P)-2a (δH, δC: 3.44, 42.8, 3.42, 42.3; and 3.40, 40.2, 3.34, 39.7), along with the corresponding ¹H signals for the POCH protons (δH, δC: 5.22, 79.7; 5.36, 80.0; 5.53, 78.9; 5.57, 79.2).

Figure 8. (M,M)- and (P,P)-diastereomers (Villa/Vilb, Villa/Viliib) of trans-[PdCl(μ-Cl)(L1)]₂ (1a) and the Gibbs free energy profiles for Villa=Vilb and Villa=Viliib (kcal mol⁻¹, 298 K).

Figure 9. (A) Gibbs free energy profile for the tropo-inversion in trans-[PdCl(μ-Cl)(L1)]₂ (kcal mol⁻¹, 298 K). (B) Calculated structures of the transition states t-TS_Va-VIIa and t-TS_Vb-VIIIb. (C) Overall reaction scheme of tropo-inversions and flapping of the Pd₂(μ-Cl)₂ core.
The line width observed in the $^{31}$P($^1$H) NMR spectrum at 296 K ($\Delta\nu_{1/2}$ = 8 Hz, av.) and the evolution of the signals on rising the temperature indicate that the tropo-inversion is operative in solution (Figure 10). The line shape analysis was carried out using two independent constants (see ESI-Table S3), namely one for $\Delta$($\alpha$) and the other for $\Delta$($\beta$), and the activation parameters were obtained by the Eyring plots (i: $\Delta H^\ddagger$=+14.6±0.1 kcal mol$^{-1}$; $\Delta S^\ddagger$ =–3.7±0.3 cal mol$^{-1}$ K$^{-1}$; $\Delta G^\ddagger_{298 K}$=+15.7±0.2 kcal mol$^{-1}$; ii: $\Delta H^\ddagger$=14.83±0.09 kcal mol$^{-1}$; $\Delta S^\ddagger$=–2.7±0.3 cal mol$^{-1}$ K$^{-1}$, $\Delta G^\ddagger_{298 K}$=+15.7±0.2 kcal mol$^{-1}$, see ESI-Figure S6). Similarly to 1a, the small values of activation enthalpy and the negative values of activation entropy suggest that the tropo-inversion is non-dissociative in 2a, as well. Further, like for 1a, also in 2a the inversion of one ligand is scarcely affected by the configuration of the non–inverting ligand and the activation barrier of the coordinated ligand is higher than that of the free ligand, probably for steric reasons.

DFT calculations were carried out in order to shed light on the fluxional processes of 2a in solution. Figure 11 shows the calculated structures of the diastereoisomers IXa ($M,M$), Xa-c ($M,P$) and Xla-b ($P,P$). As a common characteristic, a mutual trans arrangement of the oxygen atoms with respect to the equatorial plane is generally adopted and the absolute value of dihedral angle O–P···P–O is approx. 160° (av.). It is worth a mention that, at variance with 1a, rotamers of the ($P,M$)- and ($P,P$)-diastereomers have been considered. Indeed Xa, Xb and Xc, on one hand, and Xla and Xlb, on the other, as for the dihedral angles Pd-P-O-CH ($\alpha$) and P-O-CCH-CCH$_2$ ($\beta$) (see ESI for the structures of all the rotamers considered in this study). Similarly to 1a, the rotation around the C(sp$^2$)-C(sp$^2$) bond between the two phenyl groups should be responsible for the tropo-inversion of L1 in trans-PdCl$_2$(L1)$_2$ (2a). Indeed accessible transition states featuring almost planar biphenyl units were encountered, and taking the N-P-N plane of the inverting ligand as the reference, trans and cis arrangements of the oxygen atom and the inverting biphenyl unit were observed (see ESI). In an ideal sequential picture starting from the ($M,M$)-diastereomer IXa, the only affordable transition

**Figure 10.** Vertically stacked $^{31}$P($^1$H) NMR spectra of 2a in toluene-d$_8$ at different temperatures.

**Figure 11.** (top) Selected structures of diastereomers of 2a and relative Gibbs free energies (kcal mol$^{-1}$). For each ligand and structure, the dihedral angles Pd-P-O-C ($\alpha$) and P-O-CCH-CCH$_2$ ($\beta$) are given (deg). (bottom) Overall reaction scheme for the tropo-inversion of L1 in 2a and activation Gibbs free energies (kcal mol$^{-1}$, relative to IXa).
state for the tropo-inversion \((M,M)^{\equiv}(P,P)\) is \(t\)-TS\(_{\text{IXa-Xa}}\) (+17.1 kcal mol\(^{-1}\)) and \(Xa\) forms as a result of the inversion. Next, \(Xa\) could convert into the more stable rotamer \(Xc\) by means of the rotations around the \(P-O\) and \(O-C\) bonds (cf. \(\alpha\) and \(\beta\) in Figure 11). At variance with \((M,M)^{\equiv}(P,M)\) the tropo-inversion \((P,M)^{\equiv}(P,P)\) may take place via different pathways. Indeed the transition states \(t\)-TS\(_{\text{Xa-Xla}}\), \(t\)-TS\(_{\text{Xb-Xlb}}\), \(c\)-TS\(_{\text{Xb-Xlb}}\)

and \(c\)-TS\(_{\text{Xc-Xlb}}\) are accessible (Figure 11). Notably, similarly to \(Xa\), once \(Xa\) forms as the outcome of the inversion process \(Xa\rightarrow Xla\), \(Xa\) should convert into \(Xlc\) by means of the rotations around the \(P-O\) and the \(O-C\) bonds. Any attempt to estimate the barriers of the transformations \(Xa\rightarrow Xc\) and \(Xa\rightarrow Xlb\) was unsuccessful, nevertheless they are reasonably expected to be smaller than those of the tropo-inversion. Figure 11 shows the overall reaction scheme for the tropo-inversion in \(2a\). For the sake of comparison, additional rotamers as well as the transition states found at higher energies are shown in ESI.

The deoxycholyl derivative \(2b\) exhibit a solution behaviour similar to \(2a\) (see ESI-Figure S2). At 293 K two overlapping \(^{31}\)P resonances were observed at 113.98 (\(\Delta\nu_{1/2} = 25\) Hz, 64 %) and 114.03 ppm (\(\Delta\nu_{1/2} = 120\) Hz, 36 %), while at 203 K the \(^{31}\)P NMR spectrum shows four \(^{31}\)P signals (111.8, 5 %; 114.9, 74 %; 115.5 and 113.9, 21 %). Also at 338 K one well shaped \(^{31}\)P resonance (113.4 ppm, 6.0 Hz) was observed along with one \(1^H\) signal for POCH (\(\delta_1\), 4.84; \(\delta_2\), 80.3 ppm) and one \(1^H\) signals for the exchanging NMe groups (\(\delta_3\), 3.55; \(\delta_4\), 41.5 ppm).

Interestingly at 193 K additional minor signals can be observed in the \(^{31}\)P NMR suggesting that minor rotamers/conformers of the above mentioned diastereomers are observed as a consequence of the higher steric demand of the deoxycholyl substituents making slower the rotational/conformational equilibria (see ESI-Figure S2).

**Conclusions**

The tropo-inversion of the biphenyl moiety in \(L1\) and \(L2\), and of their palladium complexes \(\text{trans-PdCl}_2(L)_2\) (\(2a/2b\)) and \(\text{trans-Pd[µ-Cl][Cl]}(L)_1\) (\(1a/1b\)) have been investigated.

In all the cases NMR spectroscopy indicates that the tropo-inversion is operative at room temperature and all the diastereomers are present in solution. As for \(L1\), \(L2\), \(\text{trans-Pd[µ-Cl][Cl]}(L)_1\) (\(1a\)), and \(\text{trans-PdCl}_2(L)_2\) (\(2a\)), the \(^{31}\)P(\(1^H\)) NMR line shape analysis indicates that the mechanism of the tropo-inversion is non-dissociative and that higher activation barriers are observed upon coordination of \(L1\) to palladium (\(1a\) and \(2a\)). Remarkably the inversion of one ligand in both \(1a\) and \(2a\) is scarcely affected by the configuration of the non-inverting ligand. DFT calculations have pointed out that two transition states are possible. As a matter of fact, both a \(trans\) and a \(cis\) arrangement of the oxygen atom with respect to the nitrogen-phosphorus-nitrogen plane of the inverting biphenyl group can be observed. Depending on the steric congestion either the \(cis\) or the \(trans\) arrangement is the most favorable. Based on the DFT calculations, additional conformational/rotational equilibria for the diastereomers of \(1a/1b\) or \(2a/2b\) should be operative in solution.

**Experimental**

Triethylamine and pyridine were refluxed over calcium hydride and distilled. Dichloromethane, toluene and hexane were obtained oxygen- and water-free from a Solvent Purification System (Innovative Technologies). Phosphorus trichloride (Aldrich) was distilled and degassed by freeze-pump-thaw cycling. Benzene-\(d_6\) and toluene-\(d_8\) were dried over sodium and degassed by freeze-pump-thaw cycling. The other commercial reagents were used as received without further purification. \(N,N’\)-dimethyl-1,1’-biphenyl-2,2’-diamine \((C1)\) and \(\text{PdCl}_2(\text{NCPh})_2\) \((\text{C}10)\) were prepared as previously reported. NMR spectra were acquired on a Bruker AV400 spectrometer (400.13 MHz for \(1^H\)). The chemical shift values are referred to SiMe\(_4\) \((1^H\) and \(1^C\)) and \(\text{H}_3\text{PO}_4\) (\(\text{C}1^P\)) as external standards. The following abbreviations were used: singlet (s), doublet (d), triplet (t), quartet (q), nonet (n), multiplet (m), doublet-of-doublets (dd), doublet-of-doublets-of-doublets (ddd), triplet-of-doublets (td), doublet-of-triplet (dt), broad signal (bs). Due to the fluxional behaviour of \(1a/b\) and \(2a/b\), broad and partially merged \(1^H\) and \(1^C\) signals were observed at room temperature thus preventing any reliable assignment to be carried out at that temperature. On this basis, the NMR data of \(1a\) and \(2a\) are given at 266 K and 233 K, respectively, namely in the slow exchange limit, where sharp \(1^H\) and \(1^C\) signals were observed. On the other hand, as for \(1b\) and \(2b\), \(1^H\) and \(1^C\) sharp signals were observed only in the fast exchange limit, thus their NMR data are given at 366 K and 338 K, respectively. The diffusion experiments were carried out at 298 K using the stimulated echo pulse sequence \(\text{C}21\) and the data were analysed using the T1/T2 relaxation module of the suite Bruker Topspin\({\textregistered}\). Carbon, hydrogen and nitrogen analyses were performed using a Perkin-Elmer 240B microanalyzer.

**Synthesis of \(L1\) and \(L2\)**

**\(L1\)** At 273 K a solution of \(\text{PCL}_3\) (1.3 mL, 15 mmol) in toluene (15 mL) was added dropwise to a solution of \(N,N’\)-dimethyl-1,1’-diphenyl-2,2’-diamine \((C1)\) (1.0 g, 9.47 mmol) and pyridine (2.3 mL, 28 mmol) in toluene (55 mL). After 1 h stirring at room temperature, the resulting precipitate was filtered off and the volatiles were evaporated from the filtrate under reduced pressure giving 6-chloro-5,7-dimethyl-6,7-dihydro-5H-dibenzo[d,f][1,3,2]diazaphsphepine \((C2)\) (1.97 g, 276.70 g mol\(^{-1}\), 75 % yield, \(\delta_1\), 206.6, 298 K, \(\delta_2\), 276.2 as an oil which was used without further purifications. Compound \(C2\) was dissolved in toluene (20 mL) and pyridine (1.7 mL, 21 mmol) was added at room temperature. The mixture was cooled to 213 K and a solution of (-)-menthol (1.11 g, 7.10 mmol) in toluene (10 mL) was added dropwise. The resulting mixture was warmed up to room temperature and stirred for 14 h. The precipitate was filtered off and all volatiles were removed from the filtrate under vacuum, giving \(L1\) as colourless solid (2.80 g, 99 % yield). Anal. calc. for \(\text{C}_2\text{H}_3\text{N}_3\text{OP}\) (396.51 g mol\(^{-1}\)): C, 72.70; H, 8.39; N, 7.07. Found: C, 72.69; H, 8.38; N, 7.05.
**Synthesis of trans-[Pd(µ-Cl)(L)2]** (L = L1, 1a; L = L2, 1b)

A colorless solution of the ligand (0.75 mmol) in toluene (6 mL) was added to a red solution of PdCl2(NCPh)2 (0.75 mmol) in toluene (30 mL). After 1 h stirring, the solvent was removed under reduced pressure and the deep yellow-orange solid was washed with hexane (3 x 3 mL) and finally dried under vacuum.

**trans-[Pd(µ-Cl)(L)2]** (1a, 407.5 mg, 95% yield). Anal. calcld for C48H66Cl4N4O2P2P (1147.67 g mol⁻¹): C, 50.23; H, 5.80; N, 4.88. Found: C, 50.24; H, 5.78; N, 4.87. NMR data are given according to the numbering scheme used for L1 (vide supra).

**1H NMR** (298 K, toluene-d8): δ: 7.93 (d, JHH=7.6 Hz, 4H, a, a'), 7.31 (d, JHH=7.6 Hz, 4H, b, b'), 7.26 (d, JHH=7.5 Hz, 4H, c, c'), 6.58 (d, JHH=7.4 Hz, 4H, d, d), 6.34 (d, JHH=6.2 Hz, 4H, e, e'), 5.78 (d, JHH=5.4 Hz, 4H, f, f'), 4.95 (s, 8H, 9H, NEt), 2.83 (d, JHH=12.0 Hz, 4H, NEt'), 2.30 (m, 4H, 1H, 3), 2.22 (m, 1H, 23), 1.93 (m, 2H, 17, 22), 1.86-1.75 (m, 5H, 2, 4, 8/9, 15, 16), 1.72 (s, 3H, CH3CO), 1.72-1.49 (m, 6H, 1, 2/4, 6/7, 11, 14, 15), 1.46-1.07 (m, 9H, 2/4, 5, 6/7, 8/9, 11, 16, 20, 22), 1.03 (d, JHH=6.2 Hz, 3H, 21), 1.03-0.94 (m, 2H, 6, 7), 0.85 (m, 1H, 1), 0.82 (s, 3H, 18), 0.62 (s, 3H, 19). 13C{1H} NMR (298 K, C6D6): δ: 173.7 (24), 169.6 (C=O), 130.0 (d'), 130.4 (d), 128.3 (b/b'), 128.2 (b/b'), 124.7 (c/c'), 124.4 (c'/c'), 123.8 (d, JCP=0.8 Hz, a/a'), 123.5 (d, JCP=0.9 Hz, a/a'), 77.5 (d, JCP=12.2 Hz, 12), 74.0 (3), 51.0 (OCH3), 48.2 (14), 46.4 (17), 42.1 (5), 37.7 (d, JCP=34.9 Hz, NEt'), 37.6 (d, JCP=34.1 Hz, NEt), 36.3 (20), 36.1 (8/9), 35.4 (1), 33.9 (8/9), 32.7 (2/4), 31.4 (22), 31.3 (23), 28.1 (16), 27.52 (2/4), 27.45 (d, JCP=7.2 Hz, 11), 27.0 (d, JCP=3.9 Hz, 15), 26.7 (6/7), 24.3 (6/7), 23.2 (18), 21.1 (Me(CO)), 18.1 (d, JCP=6.2 Hz, 21), 12.8 (19). 31P{1H} NMR (298 K, C6D6): δ: 164.9.

**L2. Ligand L2 was synthesized according to a modification of the previously reported procedure.** Phosphorus trichloride (1.2 mL, 14 mmol) was added to a solution of 3-acyetoxy deoxycyethyl methyl ester (2.00 g, 4.46 mmol) in dichloromethane (10 mL). After 24 h stirring all volatiles were removed in vacuum and the resulting colourless solid (C3, δφ 181.6, 298 K C6D6) was dissolved in toluene (5 mL). Afterwards a solution of N,N’-dimethyl-1,1’-biphenylyl-2,2’-diamine (C1, 946 mg, 4.46 mmol) and triethyamine (1.9 mL, 14 mmol) in 25 mL of toluene was added. The resulting mixture was refluxed for 16 h and then filtered. All volatiles were removed from the filtrate in vacuum yielding a colourless solvent (2.98 g, 97 % yield). Anal. calcld for C48H66Cl4N4O2P2P (688.89 g mol⁻¹): C, 71.48; H, 8.34; N, 4.07. Found: C, 71.59; H, 8.37; N, 4.06.

1H NMR (298 K, C6D6): δ: 7.43 (dd, JHH=7.6 Hz, 4H, a, a'), 7.38 (dd, JHH=7.5 Hz, 5H, b), 7.29 (dd, JHH=7.5 Hz, 4H, c), 7.15 (dd, JHH=7.5 Hz, 6H, d), 4.82 (s, 8H, 9H, NEt), 2.83 (d, JHH=12.0 Hz, 4H, NEt'), 2.29 (m, 4H, 1H, 3), 2.17 (m, 1H, 23), 2.13 (m, 2H, 17, 22), 1.86-1.75 (m, 5H, 2, 4, 8/9, 15, 16), 1.72 (s, 3H, CH3CO), 1.72-1.49 (m, 6H, 1, 2/4, 6/7, 11, 14, 15), 1.46-1.07 (m, 9H, 2/4, 5, 6/7, 8/9, 11, 16, 20, 22), 1.03 (d, JHH=6.2 Hz, 3H, 21), 1.03-0.94 (m, 2H, 6, 7), 0.85 (m, 1H, 1), 0.82 (s, 3H, 18), 0.62 (s, 3H, 19). 13C{1H} NMR (298 K, C6D6): δ: 173.7 (24), 169.6 (C=O), 130.0 (d'), 130.4 (d), 128.3 (b/b'), 128.2 (b/b'), 124.7 (c/c'), 124.4 (c'/c'), 123.8 (d, JCP=0.8 Hz, a/a'), 123.5 (d, JCP=0.9 Hz, a/a'), 77.5 (d, JCP=12.2 Hz, 12), 74.0 (3), 51.0 (OCH3), 48.2 (14), 46.4 (17), 42.1 (5), 37.7 (d, JCP=34.9 Hz, NEt'), 37.6 (d, JCP=34.1 Hz, NEt), 36.3 (20), 36.1 (8/9), 35.4 (1), 33.9 (8/9), 32.7 (2/4), 31.4 (22), 31.3 (23), 28.1 (16), 27.52 (2/4), 27.45 (d, JCP=7.2 Hz, 11), 27.0 (d, JCP=3.9 Hz, 15), 26.7 (6/7), 24.3 (6/7), 23.2 (18), 21.1 (Me(CO)), 18.1 (d, JCP=6.2 Hz, 21), 12.8 (19). 31P{1H} NMR (298 K, C6D6): δ: 164.9. **Synthesis of trans-[Pd(µ-Cl)(L)2]** (L = L1, 1a; L = L2, 1b)
4.74 (m, 1H, 3), 3.47 (s, OCH3), 3.41 (bs, NMe, NMe’), 2.43 (m, 23), 2.34 (m, 23), 2.07-0.87 (m, 29H), 1.72 (s, CH2(C=O)), 1.26 (bs, 21), 0.82 (s, 18), 0.67 (s, 19). 13C{1H} NMR (366 K, toluene-d8): δ: 173.2 (24), 168.8 (C=O), 137.1 (e/f), 129.9 (c), 128.8 (b), 128.7 (d), 125.0 (a), 85.0 (d, 1JCP=9.0 Hz, 12), 73.5 (3), 50.3 (OCH3), 46.9 (14), 46.6 (17), 41.9 (5), 40.5 (NMe, NMe’), 36.3 (8/9/20), 35.0 (8/9/20), 34.7 (8/9/20), 32.6 (1), 31.9 (23), 30.9 (22), 27.8, 27.5, 27.4, 27.3, 26.6, 24.1, 22.3 (18), 20.5 (CH2(C=O)), 18.3 (21), 12.4 (19). 31P{1H} NMR (366 K, toluene-d8): δ: 85.0.

Synthesis of trans-PdCl2(L2) (L = L1, 2a; L = L2, 2b)

A colorless solution of the ligand (1.0 mmol) in toluene (8 mL) was added to a red solution of PdCl2(NCPh2) (0.50 mmol) in toluene (20 mL). After 15 min stirring, the solvent was removed under reduced pressure and the yellow-orange solid was washed with hexane (3 x 4 mL) and finally dried under vacuum.

Trans-PdCl2(L1)2 (2a, 470.6 mg, 97 % yield). Anal. calcld for C48H66Cl4N4O2P2Pd2·C7H8: C, 63.34; H, 7.38; N, 3.59. NMR data are given according to the numbering scheme used for the parent carbon atom.

Calculations were performed with SHELX-97 programs, included in the APEX2 package. The X–ray diffraction study was obtained by slow evaporation of a toluene solution of 1a. Intensities were collected using a Bruker SMART APEX-DUO diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) following standard procedures. Intensities were integrated and corrected for absorption effects using the SAINTE27 and SADABS28 programs, included in the APEX2 package. The structure was solved by the Patterson's method. All non-hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters (1.2uatom for the parent carbon atom). Calculations were performed with SHELX-9729 program implemented in the WinGX package.30

Conflicts of interest

There are no conflicts to declare.
Acknowledgements

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Notes and references

§ For brevity, only the configuration of the biphenyl unit in L1, L2, and in the corresponding complexes will be specified, the configuration of the alkylo substituents being invariant (see ESIFigure S1 for the assignment of the M and P descriptors).

§§ For the sake of comparison, cis-(M,P)-PdCl2(L1)2, i.e. the cis isomer of Xa, was found to be less stable (∆H = +10.9 kcal mol⁻¹), thus suggesting that, like for the dinuclear complexes [PdCl(µ-isomer of P)]2, the trans arrangement is clearly disfavoured with respect to the cis one, reasonably as a consequence of the high steric demand of L1.


12. The line shape analyses have been carried out using the program DNMR3 (D. S. Stephenson, G. Binsch J. Magn. Reson. 1978, 30, 625) included in Spinworks 3.0 by the Chemistry NMR Lab, University of Manitoba Winnipeg, Manitoba Canada.


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