trans–cis C–Pd–C rearrangement in hemicelates

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Kinetically unstable heteroleptic trans-bispalladacycles were isolated by using hemicelation. Three structures of trans isomers and five of cis isomers were characterized by X-ray diffraction analysis. The ready trans–to–cis isomerization of such hemicelates that was monitored by variable temperature NMR experiments is facilitated dynamically because the Pd(II) center can preserve its square planar coordination in a rather low lying transition state, which was localized by methods of the density functional theory. This process is not achievable in the isomerization of conventional homoleptic trans-bispalladacycles since it involves the preliminary partial chelate decoordination and an unfavorable high-lying planar trigonal coordinated – or Y-shaped-Pd(II) transition state according to DFT investigations.

Introduction

The so-called “antisymbiotic effect” proposed by Pearson is the situation where the coordination of a “soft” ligand to a “soft” metal decreases the affinity of the resulting assembly towards additional “soft” ligands. Pearson’s proposal is perhaps the very first attempt to rationalize intuitively the mutual influence of ligands within a metal’s coordination sphere and its impact on the stereochemistry of metal complexes. In the case of organometallic complexes Pearson’s proposal can also be rationalized by the mutual trans influences operating between ligands: if one considers a “soft” metal center, two metal-bound ligands of similar “softness” will prefer to be positioned cis to each other rather than trans, leaving the latter position preferably to “harder” ligands. As an empirical predictive tool, it makes the explicit drive leading to the most plausible stereochemistry(ies) of reactions placed under thermodynamic control. This issue has been addressed in the past by Vicente et al. for Pd(II) complexes of various ligands leading to the emergence of “transphobia” as another formulation of Pearson’s proposal. This peculiar stereochemical drive in Pd(II) complexes has been seldom addressed with homo- and hetero-leptic bispalladacycles, which are known to privilege mostly the cis C–Pd–C stereochemistry whereas both trans and cis stereochemistries are reportedly known for Pt homologues. It is quite interestingly, a rare case of the trans-isomer of bis-7-membered-palladacycles reported by Arlen et al. was reported to slowly convert into the cis isomer. Any may infer from Chin’s seminal report that experimental conditions (polarity, solubility of the reactants and intermediates, and temperature) are important and may influence the stereochemistry of the final d-metal complex. Indeed in the case of Pt(II) complexes the synthesis of the trans isomer, which proceeds by the formal displacements of labile L ligands and chloride by reaction of PtL2Cl2 complexes (M = Pt) with ortho-lithiated N,N-dialkylbenzamidine, is essentially observed at ambient temperature. The formation of cis isomers is related to a higher reaction temperature in Chin’s report: the synthesis of N,N-dialkylbenzamidine-based Pd(II) cis bis-chelates is more sluggish (requiring polar solvent and heating) than for the Pt analog leading to partial decomposition and formation of Pd-black alongside the compound of interest. Other reports issued by different authors on the synthesis and isolation of bispalladacycles concluded that there was exclusive formation of cis-isomers.

Apart from their possible labile character, it is worth noting that little consideration has been given to the polarity of bischelates, which might be at the root of the practical difficulty to isolate trans isomers. Similarly to the data reported for Pt analogues, isomer trans-I (Fig. 1) possesses a computed dipole moment lower than that of cis-I, which could make the former more difficult to isolate from a complex reaction mixture than the latter: μ_{comp}(trans-I) = 0.8 D and μ_{comp}(cis-I) = 6.1 D (Fig. 1a, cf. the ESI†).

Although difficult to track, the origin of the almost exclusive observation of cis isomers in bispalladacycles could result...
either from a stereospecific reaction of formation or from the isomerization of a short-lived transient trans-bispalladacycle, which has escaped in a great majority of experimentalists' trapping attempts until now.

Hemichelation\(^{14-18}\) is a mode of metal chelation with a heteroditopic ligand where a covalent coordinative bond is supplemented with a predominantly non-covalent stabilizing delocalized interaction of the metal with another metal centred moiety (Fig. 1b). For instance, a large number of 14-electron so-called T-shaped Pd and Pt complexes, long considered as elusive key intermediates in the final reductive-elimination steps of various catalyses,\(^{19}\) have been isolated under a stable cis C-Pd-C form thanks to hemichelation.\(^{14-16}\)

In this report, we show that heteroleptic trans C-Pd-C complexes can be isolated under the form of manageable Pd(II) hemichelates.\(^{14}\) Furthermore, we show that those isolable but nonetheless metastable trans isomers slowly isomerize in solution into the cis isomers with a Gibbs barrier of activation lower than that computed for the dissociative isomerization of elusive trans-1 into cis-1 with state-of-the-art static DFT-D calculations including COSMO-RS\(^{20,21}\) continuum solvation. This study shows that the accessibility to trans C-Pd-C hemichelates essentially depends on the experimental conditions, and on the solubility of the trans isomer. It counter-intuitively demonstrates also that a slightly higher degree of covalence in the Pd-Cr interaction is not a source of higher molecular cohesion and stability in such heterobimetallic complexes.

Results and discussion

The synthesis of Pd(II) hemichelates\(^{14,15}\) derived from palladacycles has been reported recently in a series of articles.\(^{16}\) Hemichelates have seldom displayed\(^ {17,18}\) propensity to disproportionation into homoletic complexes like other conventional bischelates\(^ {9,12}\) they can be considered as a new class of “electron deficient” heteroleptic bispalladacycles. Selective synthesis and isolation of trans-3 isomers (Scheme 1) was achieved by a proper choice of the reaction solvent. Reaction of the in situ formed lithium benzylc anion derived from I,\(^ {22}\) i.e. Li-1, with μ-chlorido-bridged palladacycles 2a-d (Scheme 1) at temperatures below \(-10^\circ\text{C}\) in Et\(_2\)O resulted in the precipitation of reddish solids corresponding to complexes trans-3a-d.

Isolation of pure samples was hence achieved by collection of the solid precipitate followed by careful recrystallization from chilled Et\(_2\)O solutions at \(-40^\circ\text{C}\). It must be noted that the same experiments carried out in tetrahydrofuran (THF) led to more homogeneous solutions and resulted in the exclusive formation of cis-3a-d. For the reaction of Li-1 with 2e in THF, which even required warming the reaction mixture above room temperature owing to the low solubility of the palladacycle, only cis-3e was recovered. The lack of solubility of 2e in Et\(_2\)O precluded all attempts to isolate trans-3e. trans-3a, trans-3b, trans-3c and trans-3d were isolated in 45%, 33%, 59% and 42% yields respectively. The yield was 48% for cis-3e.

Owing to the complex and reactive nature of the reaction medium, which required prolonged reaction times at various temperatures (organolithium derivatives) in situ NMR investigations were not attempted. However, all isolated complexes displayed reasonable resistance to air and moisture even though decomposition would ensue upon prolonged exposure of solutions to air. trans to cis isomerization was found to operate more rapidly with 3a and 3b than with 3c and 3d. It was found that at 298 K a benzene solution of trans-3a would convert quantitatively into cis-3a within 0.5 hours (trans/cis ratio: 22/78 after 4 h) at 273 K starting from trans-3a whereas trans-3c would require several hours to convert into the cis-isomer (trans/cis ratio: 6/94 after 19 h at 273 K).

Spectroscopic properties

Attenuated total reflectance Fourier-transform IR (ATR-FT-IR) spectroscopy carried out with solid state (amorphous powder) samples displayed the three major CO ligand stretching modes (\(\nu_{\text{aver}} \approx 1892 \text{ cm}^{-1}\)) remained similar to those of compound 1 (\(\nu_{\text{aver}} \approx 1892 \text{ cm}^{-1}\)). This result contrasts slightly with the significant frequency shifts noted for 2-methyl-
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indeny1-based Pd(n) hemichelates.\textsuperscript{14,15} \textsuperscript{13}C NMR spectra of both trans-3 in [D\textsubscript{6}]toluene (223 K) and cis-3 in [D\textsubscript{6}]benzene (298 K) displayed three distinct broad signals of the carboxyl ligands: the signals at \(\delta\) 241, 238 and 233 ppm in trans-3a-d are characteristic of the hindered Cr(CO)\textsubscript{3} tripod rotation. In the cis isomers the same signals appeared only slightly shielded at \(\delta\) 238, 236 and 232 ppm. The most significant difference between the \textsuperscript{13}C NMR spectra of trans and cis isomers was found to arise from the signal of the benzyllic carbon atom bound to the Pd centre: in trans isomers it appeared at ca. \(\delta\) 53–55 ppm, whereas in cis isomers it would show up at ca. \(\delta\) 42–44 ppm.

This significant ca. 10 ppm difference might be related to the drastic difference of the mutual trans influence operating on the benzyllic carbon ligand and the chelating ligand (N,N-dimethylbenzylamine abbr. DMBA, or arylpyridine) of the palladacycle; a drastic diminution of \(\Delta\) (Fig. 3a and d): \(\Delta\) which is consistent with the change of the distance from the Pd centre towards the Cr and the aromatic ring (not shown in Fig. 3, cf. the ESI† CCDC 1522982).

The most significant differences between trans and cis isomers are discernible from Cr–Pd and C\textsubscript{benzyl}–Pd distances (Fig. 2) that vary \((\Delta d = d\text{cis} - d\text{trans})\) in the trans \(\rightarrow\) cis transformation of 3a and 3c taken here arbitrarily as reference cases (Fig. 3a and d): \(\Delta d(\text{Cr–Pd}) = +0.17\ \text{Å} (\text{3a}), +0.20\ \text{Å} (\text{3c}), \Delta d(C\text{benzyl}–\text{Pd}) = -0.16\ \text{Å} (\text{in both 3a and 3c}).\) The Pd–N and Pd–C\textsubscript{Ar} distances are surprisingly much less impacted by the stereochemical change affecting the palladacycle and vary within the limits of the esds: \(\Delta d(\text{Pd–N}) = +0.01\ \text{Å} (\text{3a}), +0.03\ \text{Å} (\text{3c}); \Delta d(\text{Pd–C\textsubscript{Ar}}) = -0.01\ \text{Å} (\text{3a}), -0.02\ \text{Å} (\text{3c}).\) Overall, upon trans \(\rightarrow\) cis isomerization the C\textsubscript{benzyl}–Pd distance shortens, which is consistent with the change of the trans influence operated by C\textsubscript{Ar} and N atoms respectively. In all the cases the Pd coordination geometry is T-shaped\textsuperscript{23,24} and the Cr(CO)\textsubscript{3} moiety virtually “occupies” the fourth vacant coordination site expected for a square-planar Pd(n) complex. The structures depicted here are somewhat similar to those of Rh(i) hemichelates prepared from 1.\textsuperscript{18}

**In situ solution dynamic behaviour**

The trans-3a \(\rightarrow\) cis-3a and trans-3b \(\rightarrow\) cis-3b isomerizations monitored in [D\textsubscript{6}]toluene by \textsuperscript{1}H NMR spectrometry at five temperatures ranging from 275 K to 298 K at a total concentration of the analyte of ca. 3–4 \(\times\) 10\textsuperscript{-4} M were all found total and irreversible. The Eyring plots ln(k/T) = \(\beta(T^-1)\) (Fig. 4) were drawn from the values of first order reaction rates extracted from the plots of the concentration of trans-3a and trans-3b vs. time. For the trans-3a \(\rightarrow\) cis-3a system, linear fitting gave a Gibb's enthalpy of activation \(\Delta G^\ddagger\) of +21 ± 3 kcal mol\textsuperscript{-1} at 298 K \((\Delta H^\ddagger = +17.5 \pm 1.5\ \text{kcal mol}^{-1}, \Delta S^\ddagger = -11 \pm 5\ \text{cal mol}^{-1} \text{K}^{-1})\), deviations are deduced exclusively from linear regression fitting, \(R^2 = 0.97)\). A lower Gibb's enthalpy of activation of +14 kcal mol\textsuperscript{-1} at 298 K was obtained for the trans/cis-3b system \((\Delta H^\ddagger = +27 \pm 3\ \text{kcal mol}^{-1} and \Delta S^\ddagger = +44 \pm 8\ \text{cal mol}^{-1} \text{K}^{-1}, R^2 = 0.97)\). Both Eyring plots display linear behaviour that suggests that a single rate-determining step was involved.

**Theoretical investigation of the trans-3a \(\rightarrow\) cis-3a isomerization**

A DFT analysis of the reaction profile was carried out at the \(\text{B3LYP}^{25,\text{NL26/def2-QZVP/PBEh-3c13+COSMO-RS(v16)}^{20,21}\) levels to confirm the experimental values and gain deeper insight into the mechanism of the isomerization reaction. Our DFT model indeed predicts that cis-3a is more stable than trans-3a (by 4.6 kcal mol\textsuperscript{-1}; Table 1). A lower Gibbs barrier to activation \(\Delta G^\ddagger\) at 298.15 K amounts to ca. +15 kcal mol\textsuperscript{-1} (relative to trans-3a), in rather good agreement with the experimental value derived by the Eyring plot (+21 ± 3 kcal mol\textsuperscript{-1}). TS-3a results from a slight shift of the Pd centre towards the Cr and the ipso aromatic carbon and from the rotation of the palladacycle approximately around a Pd–C\textsubscript{ipso} axis. The projection of the Cr-atom along the arene–Cr axis itself is shifted off the center of the aromatic ring while palladium partly binds to the C\textsubscript{ortho} position as a consequence of the tendency of Pd(n) to preserve its square-planar coordination geometry. The Cr–Pd distance of 2.878 Å in TS-3a, which is longer than in trans-3a (2.694 Å) and cis-3a (2.832 Å), was first analysed as resulting from repulsive d–d interactions. In fact, Wiiberg bond indices \((w)\) counter-intuitively indicate that the Cr–Pd interaction is slightly more covalently binding in TS-3a \((w = 0.23)\) at the PBEh-3c level than in the cis isomer \((w = 0.19)\) but still less binding than the trans isomer \((w = 0.37)\). This effect can be explained by the trans influence exerted between Cr and C\textsubscript{Ar} (Fig. 5c). In TS-3a (cf. the

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\(\dagger\)Intrinsic reaction coordinate calculations have been performed to confirm that TS-3a effectively connects trans-3a and cis-3a on the PBEh-3c surface. We also checked that the location of this transition state is reproducible at different DFT levels. For instance, the latter has also been located on the PBE-D3/def2-SV(P) surface.

**Fig. 2** Schematic representation of the local atoms proximal to the Pd centre with the descriptors used throughout this article.
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Selected interatomic distances (Å) and angles (°) for Pd1 2.0982(19), C1

Fig. 4 Eyring plots of ln(k/T) vs. 1/T (K\(^{-1}\)) (left) for the spontaneous isomerization of (a) trans-3a into cis-3a in [D\(_8\)]-toluene and (b) trans-3b into cis-3b in [D\(_8\)]-toluene. Rate constants \(k\) were determined at various temperatures by monitoring the decay of trans isomers and their conversion into cis isomers over time. A first order kinetic law in trans-3a--b was assumed for the determination of rate constants \(k\).

ESI\(^+\), the Pd--N (2.169 Å) distance is slightly shortened as compared to reference situations computed in models trans-3a (Pd--N 2.268 Å) and cis-3a (Pd--N 2.240 Å), which suggests that no full decoordination of the N,N-dimethylamino ligand is required for the trans-3a → cis-3a isomerization to be effective.

**Table 1** Energy contributions (\(E\) in Eh, \(\Delta G\) in kcal mol\(^{-1}\))

<table>
<thead>
<tr>
<th>Species</th>
<th>(E) (B3LYP-NL/def2-QZVP)</th>
<th>(\Delta G)(^a) (COSMO-RS v16)</th>
<th>(\Delta G)(^b)</th>
<th>(\Delta G)(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-3a</td>
<td>-2416.7532</td>
<td>-15.7</td>
<td>212.4</td>
<td>-4.6</td>
</tr>
<tr>
<td>trans-3a</td>
<td>-2416.7427</td>
<td>-17.4</td>
<td>212.1</td>
<td>0.0</td>
</tr>
<tr>
<td>TS-3a</td>
<td>-2416.7184</td>
<td>-16.8</td>
<td>210.9</td>
<td>14.7</td>
</tr>
<tr>
<td>cis-I</td>
<td>-936.7736</td>
<td>-12.4</td>
<td>208.6</td>
<td>0.1</td>
</tr>
<tr>
<td>trans-I</td>
<td>-936.7754</td>
<td>-12.4</td>
<td>209.5</td>
<td>0.0</td>
</tr>
<tr>
<td>TS-I</td>
<td>-936.7813</td>
<td>-13.3</td>
<td>206.9</td>
<td>32.3</td>
</tr>
</tbody>
</table>

\(^a\) Corrections for solvation Gibbs free enthalpy computed with COSMO-RS.

\(^b\) \(\Delta G_{\text{HHHO}}\) is the sum of corrections from energy to Gibbs free enthalpy in the rigid-rotor-harmonic-oscillator approximation (RHRO) also including zero-point-vibrational energy.

\(^c\) Relative to trans-3a.

\(^d\) Relative to trans-I.
The latter shortening of the Pd–N distance is concomitant with the increase of the C\textsubscript{ortho}–Pd interaction (2.22 Å and \( w = 0.43 \) in TS-3a, 3.33 Å and \( w \approx 0 \) in cis-3a) and the decrease of the C\textsubscript{benzyl}–Pd bonding interaction (2.37 Å and \( w = 0.29 \) in TS-3a, 2.08 Å and \( w = 0.61 \) in cis-3a). The strength of the coordinative C\textsubscript{ipso}–Pd interaction (2.33 Å and \( w = 0.43 \) in TS-3a, 2.70 Å and \( w = 0.13 \) in cis-3a) also increases. Further studies of the chemical bonding within trans and cis-3a were carried out by complementary methods spanning from electron density topology analyses (QTAIM and NCI, vide infra) and by fragment-based interaction energy decomposition analyses (ETS-NOVC and EDA, vide infra).

**Electron density-based QTAIM and NCI analyses**

Complementary Quantum Theory of Atoms in Molecule (QTAIM)\(^{27}\) investigations (Fig. 6, cf. the ESI\(^\dagger\) for full details) of both trans and cis-3a revealed no bond path nor bond critical points (abbr. BCP) (3,–1) in the Cr–Pd segment. In the case of TS-3a a BCP (3,–1) was found in the Cr–Pd segment, to which was assigned a value of Cr–Pd bond ellipticity \( \varepsilon \) of 0.59 (\( V^2p = 0.0469 \)). The localization of a BCP in one Pd–Cr\textsubscript{O} bond path in both isomers is consistent with previous observations of incipient bridging CO interaction made for a number of other cis C–Pd–C hemichelates.\(^{28}\) The ellipticities \( \varepsilon \) of the main bonds around the Pd atom (Pd–C\textsubscript{Ar}, Pd–N, Pd–C\textsubscript{benzyl}) in cis-3a are close to 0 (cylindrically symmetric bonds), whereas in trans-3a Pd–C\textsubscript{benzyl} and Pd–N bonds feature some dissymmetry with \( \varepsilon \) values around 0.10.

Electron delocalization indexes \( \delta \) indicate that the electron density around the Cr(CO)\textsubscript{3} tripod is more localized within Pd–Cr and Pd–C\textsubscript{CO} diatomic segments in trans-3a (\( \delta(Cr–Pd) = 0.38 \), \( \delta(C\textsubscript{CO}–Pd) = 0.53 \) cf. the ESI\(^\dagger\) than in cis-3a (\( \delta(Cr–Pd) = 0.25 \), \( \delta(C\textsubscript{CO}–Pd) = 0.39 \) cf. the ESI\(^\dagger\)).

Interestingly, the participation of attractive interactions in the energetic differentiation between trans-3a and cis-3a (as pointed out also by EDA analyses, vide infra) can also be shown on non-covalent interaction plots (NCI plots)\(^{29}\) of the two stereoisomers (see Fig. 6). Indeed, blue regions (corresponding to such attractive interactions) are found between Pd and the Cr(CO)\textsubscript{3} fragment in the two complexes, but exhibit different distributions: in trans-3a (Fig. 6a), non-covalent interactions are essentially found between Pd and the carbonyl ligand labelled “C2”. Between Pd and “C1”, the electronic density exceeds the cutoff (0.04 a.u.), giving rise to a blue torus, normal to the Pd–C1 direction. In cis-3a (Fig. 6b), the blue domain spreads between Pd and the whole Cr(CO)\textsubscript{3} fragment (including Cr and the two carbonyl ligands labelled “C1” and “C2”). Also, red and yellow domains illustrate the existence of repulsive (steric) interactions between the Cr(CO)\textsubscript{3} fragment and the rest of the complex, in both stereoisomers. Finally, NCI plots also suggest that van der Waals interactions (green domains) are found between the DMBA ligand and the Cr(CO)\textsubscript{3} fragment, and between the DMBA and fluorenyl ligands, in both trans-3a and cis-3a.
Fragment-based analyses (ETS-NOCV and EDA)

Standard Energy Decomposition Analysis\textsuperscript{30,31} (EDA) was carried out assuming a fictitious closed-shell fragmentation corresponding to the interaction of the “prepared” palladacyclic cation with the Cr-bound fluorenyl anion, a fragmentation scheme that was used also for an Extended Transition State-Natural Orbitals for Chemical Valence (ETS-NOCV)\textsuperscript{32} analysis. The EDA indicates that the total interfragment interaction energy $\Delta E_{\text{int}}$ is by $-7$ kcal mol\textsuperscript{-1} more favorable to cis-3a (Table 2). Whereas $\Delta E_{\text{orbital}}$, $\Delta E_{\text{disp}}$, $\Delta E_{\text{Pauli}}$ are roughly similar within 1 to 3 kcal mol\textsuperscript{-1} for both complexes, the main difference arises with the value of $\Delta E_{\text{electrostatic}}$ that is by $-10$ kcal mol\textsuperscript{-1} more favourable to cis-3a. The ETS-NOCV\textsuperscript{32} analysis outlines the interactions between the Pd center and the benzylic position as well as the Cr(CO)$_3$ moiety. The electron density deformation plot displayed in Fig. 8 depicts the directionality of electron density transfer upon interaction of the two considered fragments in the subset of interacting orbitals ($\Delta \rho_{\text{int}}$) of the highest orbital interaction energy. Red lobes (mostly localized at the “fluorenyl anion”) materialize electron-density donating orbitals whereas blue ones materialize accepting orbitals (Pd–C$_{\text{benzyl}}$, Pd–Cr, Pd–C$_{\text{Ar}}$ and Pd–N segments) among which some are bonding orbitals located between the two considered fragments. Fig. 8 qualitatively suggests that the orbital interaction of the Pd centre with the Cr-bound fluorenyl anion is more delocalized in trans-3a than in cis-3a where the largest electron density buildup (blue lobes) within the Cr–Pd–C$_{\text{benzyl}}$ triangle is directed to the Pd–C$_{\text{benzyl}}$ bond. This conclusion is supported by the shortening of the C$_{\text{benzyl}}$–Pd distance (by $-0.16$ Å in the X-ray structure and by $-0.18$ Å at the PBEh-3c level) accompanying the elongation of the Cr–Pd distance (by $+0.17$ Å in the X-ray structure and by $+0.27$ Å at the PBEh-3c level), when going from trans-3a to cis-3a. Attractive interactions, at least in the first analysis, participate in the energetic differentiation between trans-3a and cis-3a. As a result, QTAIM analyses exhibit a small increase of the density at the bond critical point between Pd and C$_{\text{benzyl}}$ (by 0.04 u.a., see Table S3). Also, electron delocalisation indices $\delta$(Pd–C$_{\text{benzyl}}$) and $\delta$(Pd–C$_{\text{ipso}}$) increase (by 0.24 and 0.06, respectively) while $\delta$(Pd–Cr) decreases (by 0.17) when going from trans-3a to cis-3a.

Comparisons with homoleptic trans- and cis-bispalladacycles I

Solvent effect-corrected DFT-D computations (COSMO-RS model)\textsuperscript{33} indicate that the mechanism of the trans-I to cis-I isomerization reaction is dissociative as already suggested by Chini.\textsuperscript{11} Reaction path optimization showed that the isomeri-

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
 & trans- & cis- \\
 & 3a & 3a \\
\hline
$\Delta E$ & $-170$ & $-177$ \\
$\Delta E_{\text{int}}$ & $-124$ & $-124$ \\
$\Delta E_{\text{orbital}}$ & $-189$ & $-199$ \\
$\Delta E_{\text{electrostat}}$ & $-13$ & $-13$ \\
$\Delta E_{\text{disp}}$ & $156$ & $159$ \\
\hline
\end{tabular}
\caption{EDA analyses of trans- and cis-3a (ZORA-PBE-D3(BJ)/all electron QZ4P) according to the closed-shell fragmentation mode depicted in Fig. 7. Energies are expressed in kcal mol\textsuperscript{-1}.}
\end{table}

Fig. 7 Closed-shell fragmentation mode used in the EDA and ETS-NOCV analyses for trans-3a and cis-3a.

Fig. 8 ETS-NOCV analyses (gas-phase singlet ground state ZORA-PBE-D3(BJ)/all electron QZ4P) of the interfragment orbital interactions within trans-3a (upper) and cis-3a (lower) where the arbitrary fragments are the Cr-bound fluorenyl anion and the cationic palladacycle in their so-called “prepared” geometry (Fig. 7). The isosurfaces (0.005 e bohr\textsuperscript{-3}) depict electron deformation densities $\Delta \rho_{\text{int}}$ of the highest orbital interaction energy contribution, the red and blue colors being assigned to electron density donating and electron density receiving orbitals respectively.
zation occurs via full decoordination of one amino ligand to yield TS-I (Fig. 5d). The latter transition state is Y-shaped, i.e. of a rather unfavorable trigonal planar coordination geometry at the Pd atom (sum of the coordination angle in the trigonal geometry Σ(off) = 359.5°). In this case, according to computation, the Gibbs barrier of activation of the trans-I → cis-I isomerization lies by around 17 kcal mol⁻¹ at least above that of the trans-3a/cis-3a isomerization (Fig. 9).

This result echoes the conclusions drawn by Hoffmann et al. to rationalize the favorable energy bias for T-shaped ML₃ (where L is any ligand and M a transition metal) geometries over Y-shaped ones. In addition, it is interesting to note that still in the isomerization of trans-3a a slight contraction rather than an elongation of the Pd–N bond is necessary to operate the rotation of the palladacycle around the Cr–Pd axis and conversion to cis-3a.

Conclusion

In conclusion, this study shows that trans heteroleptic bischelates of Pd[n] can be isolated because of their lower solubility in Et₂O compared to the cis-isomers, and the crystal structures of both trans- and cis-isomers of a variety of bischelates, differing by the nature of their constitutive {C,N} chelating ligand, are reported. Variable temperature NMR experiments show that trans-3a and trans-3b are metastable and spontaneously convert into their cis-isomers, yielding new hemiche-lates containing a Pd centre of lower coordination number. This may result from the major drive operated by Pearson’s so-called “antisymbiotic effect”. The linear Eyring plots reveal that the isomerisation processes require a rather low activation barrier and that the two systems follow a first-order kinetic law (between 275 K and 298 K). DFT calculations also show that in spite of the more important contribution of covalence to the Pd···Cr(CO)₃ interaction in trans-3a, the latter is metastable and converts readily into the cis isomer in a single elementary reaction step. The present report shows that an enhanced degree of covalence between two adjacent metal centres such as in trans isomers is not a sufficient condition of persistence. Additionally, hemichelation by an arenetricarbonylchromium ligand dynamically offers in the transition state of the trans → cis isomerization process alternative coordination positions to the Pd centre, which preserves its square planar coordination and keeps the energetic barrier payload lower than in a Y-shaped system devoid of such delocalized secondary interactions, such as in TS-I. According to theory, the main consequence is that the trans–cis isomerization occurs by rotation of the palladacycle roughly around the Cr–Pd axis without partial decoordination of the {C,N} chelate.

Experimental section

General

All experiments were carried out under a dry argon atmosphere using standard Schlenk techniques or in an argon-filled glove-box when necessary. n-Butyllithium was purchased from Aldrich Chem. Co as a 1.6 M solution in hexanes, hexacarbonylchromium was purchased from ACR and fluorene (98%) was purchased from Aldrich Chem. Co. Celite 545 was purchased from VWR Prolabo. 4-(p-Butyl)-2-(p-tolyl)pyridine was prepared according to the literature procedure. The palladacycles used in this study were prepared according to literature procedures. Anhydrous tetrahydrofuran and diethyl ether were distilled from purple solutions of Na/benzophenone under argon. All other solvents were distilled over sodium or CaH₂ under argon. Deuterated solvents were dried over sodium or CaH₂ and purified by trap-to-trap techniques, degassed by freeze–pump–thaw cycles and stored under argon. ¹H and ¹³C NMR spectra were obtained on Bruker DPX 300, 400, Avance I 500 and Avance III 600 spectrometers. Chemical shifts (expressed in parts per million) were referenced against solvent peaks or external references. Full NMR spectral assignments are provided in the ESL† Infrared spectra of powdered amorphous samples were acquired with a Fourier transform-IR Bruker alpha spectrometer using an ATR solid state sample cell.

X-ray diffraction analyses

The crystals were placed in oil, and a single crystal was selected, mounted on a glass fibre and placed in a low-temperature N₂ stream. Acquisition and processing parameters are displayed in Table S1. Unless otherwise stated the structures were solved by direct methods using the program
SHELXS-97, the refinement and all further calculations were carried out using SHELXL-97. The crystal structures acquired with the Nonius Kappa CCD were solved using SIR-97 and refined with SHELXL-97. The refinement and all further calculations were carried out using SHELXL-97. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on $F^2$. A semi-empirical absorption correction was applied using SADAB in APEX2.

For cis-3a (named cis-3a-CH$_2$Cl in the .cif, CCDC 1522983), X-ray diffraction data collection was carried out on a Nonius Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N$_2$ device, using Mo-K$_\alpha$ radiation ($\lambda = 0.71073 \AA$). The crystal–detector distance was 36 mm. The cell parameters were determined (Denzo software) from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structure was solved by direct methods using the program SHELXS-2013. The refinement and all further calculations were carried out using SHELXL-2013. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on $F^2$. A semi-empirical absorption correction was applied using SADABS in APEX2, transmission factors: $T_{\text{min}}/T_{\text{max}} = 0.6562/0.87667$.

For cis-3b, X-ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N$_2$ device, using Mo-K$_\alpha$ radiation ($\lambda = 0.71073 \AA$). The crystal–detector distance was 38 mm. The cell parameters were determined (APEX2 software) from reflections taken from three sets of 12 frames, each at 10 s exposure. The structure was solved by direct methods using the program SHELXS-2013. The refinement and all further calculations were carried out using SHELXL-2013. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on $F^2$. A semi-empirical absorption correction was applied using SADABS in APEX2, transmission factors: $T_{\text{min}}/T_{\text{max}} = 0.6562/0.7456$.

For cis-3d, X-ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N$_2$ device, using Mo-K$_\alpha$ radiation ($\lambda = 0.71073 \AA$). The crystal–detector distance was 38 mm. The cell parameters were determined (APEX2 software) from reflections taken from three sets of 12 frames, each at 10 s exposure. The structure was solved by direct methods using the program SHELXS-2013. The refinement and all further calculations were carried out using SHELXL-2013. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on $F^2$. A semi-empirical absorption correction was applied using SADABS in APEX2, transmission factors: $T_{\text{min}}/T_{\text{max}} = 0.6562/0.7456$.

Synthesis of 2d

A mixture containing palladium(II) acetate (1.5 g, 6.68 mmol) and 4-(4-(tert-butyl)pyridin-2-yl)-N,N-dimethylaniline (1.7 g, 6.68 mmol) in 10 mL of dry degassed dichloromethane was stirred for 18 h at room temperature. The resulting mixture was filtered through Celite and solvents were removed from the filtrate under reduced pressure. The crude residue was dissolved in a acetone : H$_2$O (3 : 1, 20 mL) mixture and an excess of LiCl was added. After stirring at room temperature for 1 h, the resulting solution was extracted with three volumes (15 mL) of dichloromethane. The combined organic layers were dried over anhydrous MgSO$_4$ and the solvent was removed under reduced pressure. Finally recrystallisation in a dichloromethane/pentane mixture of solvents led to the expected pale yellow compound 2d (2.419 g, 3.06 mmol, 92% yield). Anal. calcd for C$_{30}$H$_{42}$Cl$_2$N$_4$Pd$_2$·1/10 CH$_2$Cl$_2$: C, 51.26; H, 5.32; N, 7.01. Found: C, 51.13; H, 5.37; N, 6.97. HRMS-ESI (m/z): [M + Na]$^+$ calcd for C$_{30}$H$_{42}$Cl$_2$N$_4$Pd$_2$, 789.0929; found, 789.0872. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 9.90 (d, $J = 6.2$ Hz, 1H, H$_4$), 7.43 (d, $J = 8.6$ Hz, 1H, H$_7$), 7.33 (d, $J = 2.1$ Hz, 1H, H$_{10}$), 6.44 (dd, $J = 8.6$, 2.5 Hz, 1H, H$_3$), 6.40 (dd, $J = 6.3$, 2.1 Hz, 1H, H$_2$), 5.66 (d, $J = 2.5$ Hz, 1H, H$_{10}$), 2.41
(s, 6H, H17, H16), 0.96 (s, 9H, H14, H15, H13). 13C NMR (101 MHz, C6D6 + Pyr-d5, 298 K) δ 166.5 (C3), 162.2 (C4), 158.2 (C11), 152.3 (C1), 150.7 (C6), 134.8 (C6), 124.4 (C2), 117.5 (C2), 116.5 (C10), 113.5 (C6), 108.5 (C6), 39.7 (C17, C16), 34.8 (C12), 30.1 (C14, C15, C13) (Fig. 10).

**Standard procedure for the synthesis of trans-3 compounds**

Tricarbonyl(η6-fluorene)chromium(0), i.e. 1, was dissolved in diethyl ether (5 mL) and treated with n-BuLi at −40 °C under argon. The resulting solution was transferred after 30 min via a cannula to another Schlenk vessel containing a diethyl ether (3 mL) solution of the corresponding μ-chloro-bridged palladacycle 2. The resulting mixture was stirred for 2 h and the temperature was slowly raised to −10 °C. During this time product trans-3 precipitated out of the solution as a reddish solid. The solvent was subsequently removed and the residue was washed with cold diethyl ether (15 mL). Filtration through Celite and recrystallization from a dichloromethane/pentane mixture of solvents afforded the product as a red solid.

**Standard procedure for the isomerization of trans-3 into cis-3 complexes**

trans-3 was dissolved under argon in dry benzene (5 mL) and stirred at 40 °C for 2 hours, which led to the quantitative formation of cis-3.

**Synthesis of complexes trans-3a and cis-3a**

Tricarbonyl(η6-fluorene)chromium(0), i.e. 1, (0.200 g, 0.66 mmol), n-BuLi (0.45 mL, 0.73 mmol), bis(μ-chlorido)(η6-N,N-dimethylaminophenylbenzenemethane-κC,N-palladium(η1) (0.186 g, 0.34 mmol): trans-3a (0.160 g, 0.30 mmol, 45% yield). Calculated for C25H23CrNO3Pd: C, 55.42; H, 3.91; N, 2.58. Found: C, 55.39; H, 4.22; N, 2.79. HRMS-ESI (m/z): [M + 1H]+ cycled for C25H23CrNO3Pd, 542.0034; found, 541.9968. trans-3a: IR (cm−1) ν(CO): 1944 (s), 1876 (s), 1839 (vs). 1H NMR (600 MHz, C6D6, 298 K) δ 7.43 (d, J = 6.8 Hz, 1H, H14), 7.43 (d, J = 6.8 Hz, 1H, H11), 1.43 (s, J = 6.4 Hz, 2H, H12a), 5.44 (s, J = 6.3 Hz, 1H, H18), 1.47 (s, J = 6.6 Hz, 2H, H18). 13C NMR (151 MHz, C6D6, 223 K) δ 241.3 (C16), 238.3 (C13), 234.1 (C14), 163.0 (C17), 147.8 (C23), 146.6 (C12), 139.0 (C19), 129.0 (C7), 128.4 (C3), 124.8 (C10), 124.2 (C20), 122.3 (C24), 121.9 (C21), 121.0 (C3), 118.0 (C4), 114.2 (C8), 102.4 (C13), 91.3 (C6), 90.7 (C12), 90.3 (C3), 89.8 (C11), 74.5 (C23), 54.2 (C1), 52.0 (C25), 51.6 (C24). cis-3a: IR (cm−1) ν(CO): 1940 (s), 1886 (s), 1843 (vs). 1H NMR (600 MHz, C6D6, 298 K) δ 8.23 (d, J = 7.4 Hz, 1H, H18), 7.17–7.67 (m, 1H, H4), 7.22 (td, J = 7.4, 1.5 Hz, 1H, H19), 7.26–7.24 (m, 1H, H5), 7.10 (td, J = 7.2 Hz, 1H, H3a), 6.97–6.90 (m, 2H, H3a, H4), 5.42 (d, J = 6.5 Hz, 1H, H5), 5.29 (d, J = 6.4 Hz, 1H, H22), 4.99 (td, J = 6.4 Hz, 1H, H10), 4.85 (s, 1H, H10), 4.23–4.14 (m, 1H, H11), 3.58 (d, J = 12.9 Hz, 1H, H23a), 2.82 (d, J = 12.9 Hz, 1H, H23b), 2.33 (s, 3H, H34), 2.17 (s, 3H, H35). 13C NMR (151 MHz, C6D6, 301 K) δ 237.3 (bs, C16), 236.2 (bs, C15), 232.7 (bs, C14), 160.9 (C7), 151.0 (C5), 147.4 (C24), 133.2 (C18), 130.0 (C9), 129.4 (C5), 125.9 (C24), 124.0 (C30), 123.5 (C21), 122.9 (C25), 122.5 (C24), 121.1 (C5), 108.8 (C6), 108.5 (C13), 94.9 (C12), 92.8 (C20), 90.2 (C11), 88.4 (C9), 73.0 (C23), 50.1 (C25), 48.8 (C24), 41.5 (C1) (Fig. 11).
**Synthesis of complexes trans-3c and cis-3c**

1. (0.200 g, 0.66 mmol), n-BuLi (0.45 mL, 0.73 mmol), bis-μ-chlorido][4-t-buty1-(4-N,N-dimethylaminophenylene)pyridine-k(C,N)]palladium(η) (0.267 g, 0.34 mmol): trans-3d (0.184 g, 0.28 mmol, 42% yield). Caled for C32H27CrNO3Pd, 632.0504; found, C32H27CrNO3Pd, 632.0503.

2. 1H NMR (600 MHz, C6D6, 293 K) δ 8.64 (d, J = 5.8 Hz, 1H, H12), 8.31 (d, J = 7.8 Hz, 1H, H11), 5.56 (d, J = 6.7 Hz, 1H, H21), 5.46 (s, 1H, H32), 0.74 (s, 9H, H30, H31, H33, H34), 4.34 (t, J = 6.6 Hz, 1H, H11′), 4.31 (s, 1H, H1′), 1.42 (td, J = 6.5 Hz, 1H, H30, H31, H33, H34).

3. **Fig. 12** Atom numbering schemes for NMR assignments in trans (left) and cis (right)-3c.

4. **Fig. 13** Atom numbering schemes for NMR assignments in trans (left) and cis (right)-3c.

5. **Synthesis of complexes trans-3d and cis-3d**

1. (0.200 g, 0.66 mmol), n-BuLi (0.45 mL, 0.73 mmol), bis-μ-chlorido][4-t-buty1-(4-N,N-dimethylaminophenylene)pyridine-k(C,N)]palladium(η) (0.267 g, 0.34 mmol): trans-3d (0.184 g, 0.28 mmol, 42% yield). Caled for C32H27CrNO3Pd, 632.0504; found, C32H27CrNO3Pd, 632.0503.

2. 1H NMR (600 MHz, C6D6, 293 K) δ 8.64 (d, J = 5.8 Hz, 1H, H12), 8.31 (d, J = 7.8 Hz, 1H, H11), 5.56 (d, J = 6.7 Hz, 1H, H21), 5.46 (s, 1H, H32), 0.74 (s, 9H, H30, H31, H33, H34), 4.34 (t, J = 6.5 Hz, 1H, H30, H31, H33, H34).
Synthesis of compound cis-3e

1 (0.200 g, 0.66 mmol), n-BuLi (0.45 mL, 0.73 mmol), THF (5 mL), bis(μ-chlorido)(8-methylquinolynyl)κC6Npalladium(II)43 (0.199 g, 0.35 mmol, 48% yield). Calcd for C26H17CrNO3Pd, 571.4541; found, 571.9518. IR (cm−1) ν(CO): 1931 (s), 1873 (s), 1849 (vs).1H NMR (600 MHz, C6D6, 298 K) δ 8.72 (dd, J = 4.9, 1.6 Hz, 1H, H23), 7.69 (d, J = 7.9 Hz, 1H, H4), 7.52 (d, J = 7.1 Hz, 1H, H1), 7.40 (d, J = 7.5 Hz, 1H, H3), 7.26–7.19 (m, 2H, H5, H23), 7.11–7.05 (m, 2H, H4, H20), 6.95 (d, J = 8.0 Hz, 1H, H10), 6.35 (dd, J = 8.2, 4.9 Hz, 1H, H3), 5.56 (d, J = 6.6 Hz, 1H, H20), 5.33 (d, J = 6.5 Hz, 1H, H12), 5.08 (t, J = 6.4 Hz, 1H, H10), 4.74 (s, H, H3), 4.30 (t, J = 6.4 Hz, 1H, H11), 4.25 (d, J = 13.9 Hz, 1H, H17a), 3.69 (d, J = 13.9 Hz, 1H, H17b).13C NMR (126 MHz, C6D6, 293 K) δ 238.1 (bs, C16), 237.9 (bs, C15), 232.9 (bs, C14), 153.4 (C26), 152.3 (C25), 151.3 (C12), 151.2 (C18), 136.9 (C23), 130.3 (C2), 129.6 (C20), 129.6 (C5), 129.5 (C22), 127.5 (C20), 123.6 (C19), 122.2 (C4), 121.8 (C18), 121.7 (C24), 121.3 (C6), 109.2 (C7), 107.9 (C13), 94.3 (C12), 92.3 (C10), 90.1 (C11), 89.4 (C9), 38.9 (C17), 34.6 (C1) (Fig. 15).

Quantum theory of atoms in molecules (QTAIM) and non-covalent interaction (NCI) plots

For QTAIM analyses,27 the wavefunctions were recalculated by performing single point calculations at the PBE057/SDD level (i.e. with the def2-TZVP68 basis set on all elements plus a small core Effective Core Potential (ECP) on Pd) on PBEh-3c geometries. Wavefunction files (“.wfx” format) were generated, including additional atomic core electron densities to represent the ECP-modeled electrons. These calculations were performed with the Gaussian09 (revision D0159) package. Then, the electron density (ρ), the Laplacian of the electron density (∇2ρ) and the bond ellipticity (ε) at bond critical points were computed, along with delocalization indexes (δ(A,B)) between selected pairs of atoms. These calculations were performed with the AIMAll package (version 16.01.09).60 Combined graphical representations of QTAIM and NCI analyses (shown in Fig. 6 and S30 in the ESI†) were performed at the PBE0/SDD level on PBEh-3c optimized structures, using the AIMstudio module of AIMAll, by mapping the magnitude of the reduced density gradient (so called |RDG|) isosurface with the function constructed as the electron density multi-
plied by the sign of the second Hessian eigenvalue (referred to as sign(λ2)) i.e. following the definition from Johnson and co-workers.§

ETS-NOCV and EDA analyses

Computations were performed with methods of the density functional theory using the SCM-ADF2014.01 package. The PBE65 functional implemented in the Amsterdam Density Functional package64 (ADF2014 version) and augmented with Grimme’s DFT-D3(BJ) implementation of dispersion with a Becke–Johnson (BJ) damping function50 was used in the optimizations of trans and cis-3a geometries. Preliminary geometry optimizations by energy gradient minimization were carried out in all cases with integration grid accuracy comprised between 4.5 and 7.5, an energy gradient convergence criterion of 10−3 au and a tight to very tight SCF convergence criterion. Counterpoise correction for the basis set superposition error (BSSE) was neglected throughout this study. Unless otherwise stated all computations were carried out using scalar relativistic corrections within the zeroth order regular approximation for relativistic effects with ad hoc all-electron (abbr. ae) single and quadruple polarization function triple and quadruple-ζ Slater type basis sets (ae-TZP and ae-QZ4P).53 Extended Transition State-Natural Orbitals for Chemical Valence (ETS-NOCV) analyses32 as well as calculations of vibrational modes were performed with optimized geometries using ADF2014 subroutines. Energy decomposition analyses30 were carried out using ADF2014 subroutines; it was noted that the quality of the basis set was not affecting (energy variation from TZP to QZ4P < 2%) the computed interfragment interaction energies. Vibrational modes were analytically computed to verify that the optimized geometries were related to energy minima: statistical thermodynamic data at T = 298.15 K and P = 1 atm. Representations of molecular structures and isosurfaces were produced with ADFview2014.

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Notes and references


§ We note that single points at the PBE-D3(BJ)/def2-TZVPP level on PBEh-3c optimized structures (see Table S3 in the ESI) show that the contribution of the damped – DJ(BJ) dispersion correction (+0.7 kcal mol−1) to the overall relative energies of cis-3a vs. trans-3a (~5.5 kcal mol−1) is very small, and slightly stabilizes trans-3a over cis-3a.