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Syntheses, Dynamic Behaviour and Theoretical Studies of [(Piperidinomethyl)-silyl]methyl-Cyclopalladated Dimetallic Complexes

Victoria P. Colquhoun,[a] Daniel Schildbach,[a] Raquel Martín-Romo,[b] Carsten Strohmann,*[a] and Fernando Villafañe*[b]

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The cationic complex [Pd{$CH_2SiPh_2(CH_2NC_5H_{10})$-κ$^2C,N$}-$(NCMe)_2$]$BF_4$ ($CH_2NC_5H_{10}$ = piperidinomethyl) is obtained from the reaction of [Pd{$CH_2SiPh_2(CH_2NC_5H_{10})$-κ$^2C,N$}(μ-Cl)]$_2$ with $TlBF_4$ in the presence of NCMe. It reacts with KO_2CCH_3 leading to the dimetallic complex [Pd{CH_2SiPh_2-$(CH_2NC_5H_{10})$-κ$^2C,N$}(μ-O_2CCH_3-κO:κ′O)]$_2$, which exists only as the *transoid* isomer in solution. A dynamic process due to inversion of the acetato bridges is detected by variable-temperature ^{1}H NMR spectroscopy. The reaction of the same parent complex with Kdmpz (dmpz = dimethylpyrazolate) leads to the dinuclear complex [Pd{CH_2SiPh_2-$(CH_2NC_5H_{10})$-κ$^2C,N$}(μ-dmpz-κN:κ′N)]$_2$, which in solution exists as a mixture of *cisoid* and *transoid* isomers, but no inversion of the bridging pyrazolato groups has been observed. The reaction between equimolar amounts of these two complexes in CH_2Cl_2 affords low yields of the expected mixed acetato/pyrazolato-bridged complex [Pd$_2${CH_2SiPh_2-$(CH_2NC_5H_{10})$-κ$^2C,N$}$_2$(μ-O_2CCH_3-κO:κ′O)(μ-dmpz-κN:κ′N)]. The mixed chlorido-pyrazolato-bridged complex [Pd$_2${CH_2-$SiPh_2(CH_2NC_5H_{10})$-κ$^2C,N$}$_2$(μ-Cl)(μ-dmpz-κN:κ′N)] is obtained by mixing equimolar amounts of the parent dichlorido- and bis(dimethylpyrazolato)-bridged dinuclear complexes, and exhibits a dynamic process in solution corresponding to the inversion of the bridges. Only the *cisoid* isomers are detected for both dimetallic complexes with mixed bridging ligands. The experimental findings of the preferred *transoid* or *cisoid* structure in these dinuclear Pd complexes were supported by quantum chemical calculations.

Introduction

The chemistry of palladacycles has been one of the most active fields of research on transition-metal organometallic chemistry during the last decades.[1] There are different reasons for this development, such as the potential applications of palladacycles, which range from their use as precursors for novel organic compounds[2] to the design of new materials[3] or drugs.[4] Some chiral complexes have been used as chiral resolving agents,[5] and more recently, some palladacycles have been investigated as catalysts in C–C coupling reactions.[6] The latter aspect, which has been developed in the last few years, is undoubtedly one of the main reasons for the renewed interest in these complexes. However, it is now evident that the role of the palladacycle consists in feeding Pd^0 nanoparticles to the reaction mixture, which seem to be the real catalysts of these processes.[7]

As part of our systematic studies on metalated organosilanes, we are studying the structure and reactivity of {[(aminomethyl)silyl]methyl}metal compounds,[8] and we reported the first {[diphenyl(piperidinomethyl)silyl]methyl}-palladium(II) complexes.[9] The incorporation of a silicon atom into the palladacycle serves a double function: stabilizing the metalated carbon atom by polarisation effects, and preventing β-elimination. Moreover, the substituents at the nitrogen centre play a second, important role, as they allow the introduction of stereochemical information. This is achieved by using chiral amines in the ligand synthesis. Thereby, diastereomerically highly enriched {[(aminomethyl)silyl]methyl}lithium compounds with a stereogenic metalated carbon atom with a specific configuration can be synthesised.[8d,10]

The palladacycle complexes obtained so far with the [diphenyl(piperidinomethyl)silyl]methyl ligand were synthesised from the parent chlorido-bridged [Pd{$CH_2SiPh_2(CH_2NC_5H_{10})$-κ$^2C,N$}(μ-Cl)]$_2$ (**1**), which was obtained by the reaction of the appropriate organolithium reagent and *trans*-[$PdCl_2(SMe_2)_2$].[9b] As is common for chlorido-bridged palladacycles, the structure of this dimetallic complex is planar, and in solution a slow exchange equilibrium between the *cisoid* and the *transoid* isomer was detected on the NMR timescale. Both isomers differ in the relative orientation of the palladacycles.[9b]

Following these studies, we were interested in the synthesis of new dimetallic complexes with the [diphenyl(piperidinomethyl)silyl]methyl ligand containing other anionic

[a] IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid,
47005 Valladolid, Spain
Fax: +34-983-423-013
E-mail: fervilla@qi.uva.es
[b] Technische Universität Dortmund, Anorganische Chemie, Otto-Hahn-Straße 6, 44227 Dortmund, Germany
Fax: +49-231-755-7062
E-mail: mail@carsten-strohmann.de

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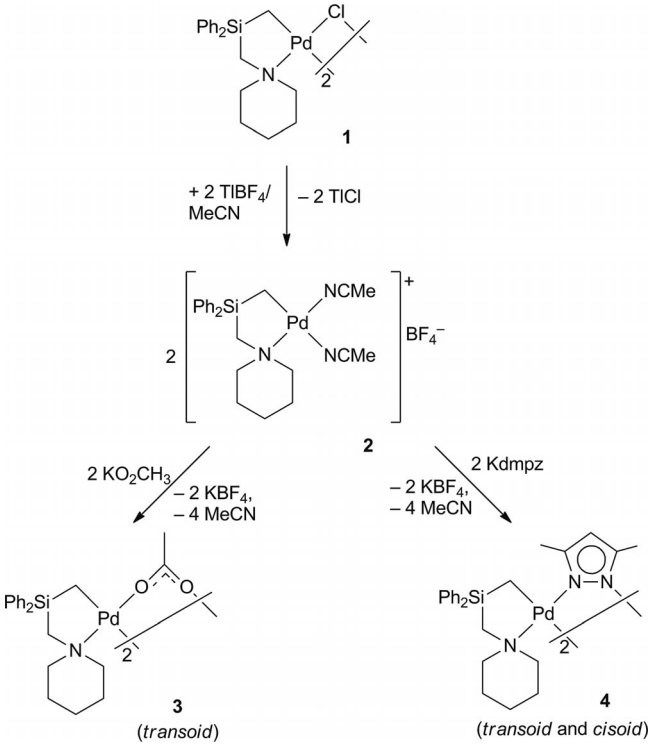
bridging ligands, such as acetato or pyrazolato groups. The geometry and electronic features of this type of dimetallic palladacycles are well known,[1] therefore we decided to complete this study by also obtaining complexes with two mixed bridging ligands. To support the experimental observations, we decided to complete this study with quantum chemical calculations. Surprisingly, theoretical studies on this type of complexes are scarce.[11]

Results and Discussion

Synthesis, Structure and Dynamic Behaviour of Dimetallic Palladium Complexes

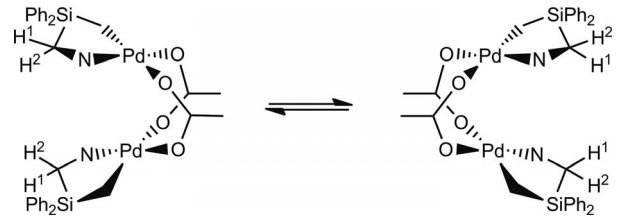
There are many examples of palladacycles with bridging acetato groups. Therefore, the synthesis of an acetato-bridged complex incorporating the [diphenyl(piperidinomethyl)silyl]methyl moiety was our first target. However, we were unable to obtain a pure acetato-bridged complex by treating **1** with different acetate salts, as the final product could not be obtained completely free of the starting material. Finally, the acetato-bridged complex **3** could be obtained in pure form by treating the cationic precursor $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})\text{-}\kappa^2C,N\}(NCMe)_2]BF_4$ (**2**), with KO_2CCH_3 (Scheme 1).



Scheme 1. Syntheses of acetato- and dmpz-bridged cyclopalladated dimetallic complexes.

The cationic complex **2** is easily obtained in thf upon treatment of complex **1** with equimolar amounts of $TlBF_4$ in the presence of acetonitrile. This reaction leads to the precipitation of TlCl, and compound **2** is obtained from the solution. Its spectroscopic data (see Experimental Section) support the proposed geometry, but no analytical data of the solid product or a ^{13}C NMR spectrum could be obtained, because of the high instability of this complex both as a solid and in solution, even at low temperatures. This instability precluded the isolation of the pure complex. However, compound **2** could be used as an in situ starting material directly obtained from the reaction mixture. Thereby, the complex is stabilized by a large amount of MeCN.

The reaction of **2** with a slight excess of KO_2CCH_3 leads to $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})\text{-}\kappa^2C,N\}(\mu\text{-}O_2CCH_3\text{-}\kappa O{:}\kappa' O)]_2$ (**3**), which is isolated as a pale yellow solid. The expected coordination of the acetato group as a bridging ligand is immediately confirmed by the IR spectrum, since the difference between both CO stretching absorptions (177 cm^{-1}) is typical for this coordination pattern.[12] Only the *transoid* isomer is detected in solution, which is revealed by the observation of only one singlet for the methyl group of the bridging acetato group in the ^1H NMR spectrum. Most of the signals in the ^1H NMR spectrum are very broad at room temperature, but are sharpened at 333 K, indicating the presence of a dynamic process in solution. The observation of only one singlet for the $SiCH_2N$ protons at this temperature indicates an averaged structure. However, these protons are diastereotopic at 253 K. At this temperature no dynamic process is observed and the signals of only one species are found, corresponding to two (indistinguishable) enantiomers (Scheme 2). This dynamic process had been previously studied in detail for other acetato-bridged complexes.[13] It is assumed to proceed by the cleavage of one of the coordinating bonds of an acetato bridge, followed by rotation of the Pd–O bond in the remaining bridge and the renewed formation of the double bridge.[13] The activation energy of this process seems to be lower for **3** than for most of the cyclopalladated complexes with bridging acetato groups reported so far, which are usually described as "rigid".[14] Usually only the *transoid* isomer is detected in solution,[13d,15] although mixtures containing mainly the *transoid* isomer with a minor amount of the *cisoid* isomer have also been reported.[13c,14b,16]



Scheme 2. Dynamic process detected in solution between the two enantiomers of **3** showing diastereotopic $SiCH_2N$ protons (piperidine groups are omitted for clarity).

In order to gain more information on the factors that determine the stereochemistry of these cyclopalladated dimetallic species, we decided to synthesise a new dimetallic complex with a different bridging ligand. Therefore, complex **2** was treated with an equimolar amount of Kdmpz, leading to $[Pd\{CH_2SiPh_2(CH_2NC_5H_{10})\text{-}\kappa^2C,N\}(\mu\text{-dmpz-}$

κ*N*:κ′*N*)]$_2$ (**4**), which was isolated as colourless crystals. The structure of this complex could be confirmed by an X-ray diffraction analysis, which is shown in Figure 1. Table 1 lists selected bond lengths and angles.

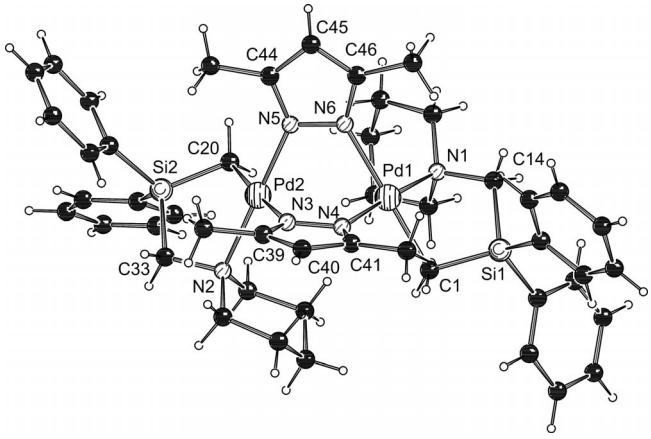


Figure 1. Molecular structure and numbering scheme of compound **4** in the crystal (SCHAKAL[18] plot, additional hexane molecule has been omitted for clarity).

Table 1. Selected bond lengths [Å] and angles [°] of compound **4**.

C1–Si1	1.845(6)	Si1–C1–Pd1	104.5(3)
C1–Pd1	2.067(6)	N1–C14–Si1	110.3(4)
C14–N1	1.503(7)	Si2–C20–Pd2	103.5(3)
C14–Si1	1.897(7)	N2–C33–Si2	110.3(4)
C20–Si2	1.845(6)	C14–N1–Pd1	104.0(3)
C20–Pd2	2.065(6)	C33–N2–Pd2	104.4(3)
C33–N2	1.501(7)	N4–N3–Pd2	118.7(3)
C33–Si2	1.916(6)	N3–N4–Pd1	115.6(3)
C39–N3	1.344(7)	N6–N5–Pd2	117.0(3)
C39–C40	1.382(8)	N5–N6–Pd1	117.6(3)
C40–C41	1.378(8)	N4–Pd1–C1	89.9(2)
C41–N4	1.361(7)	N4–Pd1–N6	86.5(2)
C44–N5	1.357(7)	C1–Pd1–N6	175.4(2)
C44–C45	1.381(8)	N4–Pd1–N1	176.4(2)
C45–C46	1.374(8)	C1–Pd1–N1	87.1(2)
C46–N6	1.347(7)	N6–Pd1–N1	96.6(2)
N1–Pd1	2.155(5)	N5–Pd2–C20	90.5(2)
N2–Pd2	2.164(5)	N5–Pd2–N3	84.5(2)
N3–N4	1.383(6)	C20–Pd2–N3	174.7(2)
N3–Pd2	2.113(5)	N5–Pd2–N2	177.7(2)
N4–Pd1	2.014(5)	C20–Pd2–N2	87.2(2)
N5–N6	1.378(6)	N3–Pd2–N2	97.7(2)
N5–Pd2	2.002(5)	C1–Si1–C14	103.5(3)
N6–Pd1	2.131(5)		

Complex **4**, which crystallises with 0.5 equiv. of hexane, displays pseudo-C_2 symmetry and consists of two Pd atoms bridged by two dmpz ligands with the usual boat-like conformation of the Pd_2N_4 six-membered metallacycle.[17] The distance between the two palladium atoms is 3.275(1) Å, indicating no metal–metal bond interaction, and similar to those found in other diazolato-bridged Pd complexes.[17] The two remaining coordination sites surrounding each Pd atom are occupied by the cyclopalladated ligands mutually coordinated in a *transoid* position, thus minimising the interactions between the piperidine groups, which tend to fill the space between both coordination planes. The angle between the normals of both planes containing the pyrazolato ligands is 82.6(2)° (the rms deviation of fitted atoms is 0.04 Å and 0.05 Å). Both Pd centres display the usual square-planar coordination environment, and the angle between the normals of these planes is 78.0(1)° (the rms deviation of fitted atoms is 0.04 Å and 0.02 Å).

The distances between the palladium atoms and the nitrogen atoms of the bridging pyrazolato groups reflect the different *trans* influences of the donor atoms of the palladacycle: As expected, bonds *trans* to the carbon donor atoms are longer [2.113(5) Å and 2.131(5) Å] than bonds *trans* to the piperidine moiety [2.014(5) Å and 2.002(5) Å]. This difference in bond length is quite large in comparison to other pyrazolato-bridged complexes with different donor atoms coordinated in *trans* position.[17a,17b]

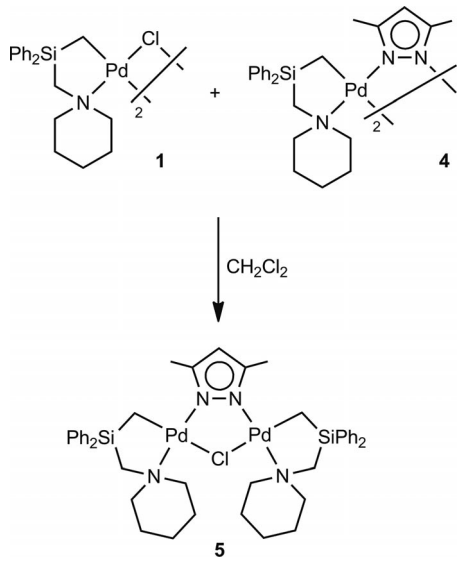
The five-membered [diphenyl(piperidinomethyl)silyl]methyl metallacycles adopt the typical envelope conformation.[9b] The palladium atoms are bent by 46.9(2)° and 48.4(2)° out of the pseudoplanes defined by the other four atoms in the metallacycle (the rms deviation of fitted atoms is 0.09 Å and 0.06 Å). This conformation allows for minimised repulsion between the substituents in the cyclometallated ligand. The distance between Pd and C, as well as the other bond lengths and angles found in the palladacycles are similar to those reported previously.[9b]

The ^{1}H NMR spectrum of the first batch of crystals, which were also subjected to the X-ray diffraction analysis, reveals the presence of only the *transoid* isomer in solution. However, a small amount of a second minor isomer, which has been assigned to the *cisoid* structure, is always detected in the solid obtained in a second batch after concentration of the mother liquor. The solutions of either the pure *transoid* isomer or the mixture of isomers show no isomerisation even after prolonged heating. Therefore, it can be assumed that the isomers detected in solution are formed during the reaction, but no exchange equilibrium is established between them once they are formed. Conversely, the consistency of the spectra even upon heating indicates that both isomers are rigid in solution. This is what is usually observed for dimethylpyrazolato-bridged dimetallic complexes, in opposition to the less-hindered pyrazolato-bridged dinuclear species, where inversion of the central $M(N–N)_2M$ ring is often detected on the NMR time scale.[17e,17f]

In summary, the three complexes **1**, **3** and **4** with different bridging ligands described above show different structures and different behaviour in solution. The parent chlorido-bridged complex **1** is planar and shows a slow equilibrium between the *transoid* and *cisoid* isomers,[9b] whereas complexes **3** and **4** are bent: the acetato-bridged complex appears only as the *transoid* isomer but undergoes a dynamic process forming two enantiomers. The dimethylpyrazolato-bridged complex **4** is rigid, and no equilibrium is detected between the *transoid* and *cisoid* isomers.[19]

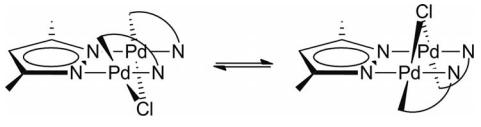
To complete this study, we used the complexes **1**, **3** and **4** to synthesise new mixed dimetallic complexes containing two different bridging ligands. The interest of these dinuclear complexes lies in the isolation of only *cisoid* geometries, in accordance with the anti-symbiotic effect of the soft

palladium(II) centre,[20] also redefined as *transphobia*.[21] No mixed chlorido/acetato-bridged complex could be obtained, as heating equimolar amounts of **1** and **3** in $CDCl_3$ or thf led to the deposition of metallic Pd. This is not surprising as we have no knowledge of any report on this type of complex, although many reports describe dichlorido- or diacetato-bridged complexes. However, the reaction between **1** and **4** yields the new, pure chlorido/dimethylpyrazolato-bridged complex [$Pd_2\{CH_2SiPh_2(CH_2NC_5H_{10})$-$\kappa^2C,N\}_2$(μ-Cl)(μ-dmpz-$\kappa N$:$\kappa' N$)] (**5**) (Scheme 3).



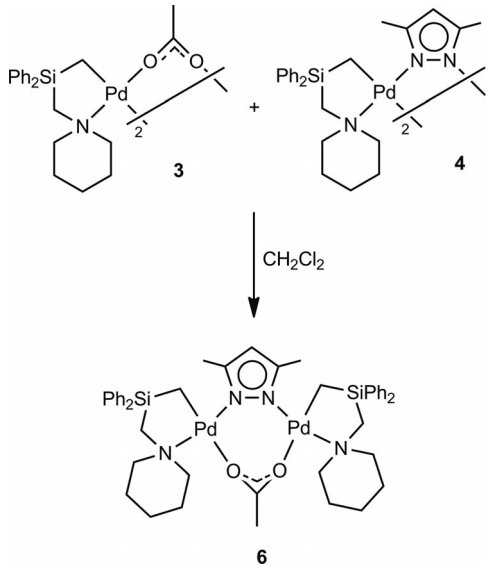
Scheme 3. Synthesis of the mixed chlorido/dimethylpyrazolato-bridged dimetallic complex **5**.

The *cisoid* geometry is confirmed by the NMR spectra, which show the equivalence of the two methyl groups of the bridging dimethylpyrazolato ligand. This *cisoid* geometry is expected considering the anti-symbiotic or *transphobia* effect.[20,21] As observed for **3**, some signals in the ^{1}H NMR spectrum at room temperature are broad, and sharpen in the ^{1}H NMR spectrum at 333 K. This spectrum is expected for an averaged planar structure. This data points to a dynamic process in solution similar to that observed for **3**. In solution, the five-membered ring formed by the metal atoms and the bridging ligands of complex **5** invert as shown in Scheme 4. Upon lowering the temperature, most of the signals start to duplicate, although they still remain broad at –80 °C, making their assignment impossible.



Scheme 4. Dynamic behaviour of compound **5**, [(piperidinomethyl)silyl]methyl groups have been omitted for clarity.

Equimolar amounts of the two dimetallic complexes described in this work, **3** and **4**, were mixed and heated to 40 °C in order to obtain a mixed acetato/pyrazolato-bridged dinuclear complex. Only chlorinated solvents, such as CH_2Cl_2 or $CHCl_3$ allowed the isolation of the expected product, [$Pd_2\{CH_2SiPh_2(CH_2NC_5H_{10})$-$\kappa^2C,N\}_2$(μ-$O_2CCH_3$-$\kappa O$:$\kappa' O$)(μ-dmpz-$\kappa N$:$\kappa' N$)] (**6**), (Scheme 5), although only in low yields. Other solvents, such as toluene, acetone, or thf, led to rapid decomposition of the reaction mixture.[22,23]



Scheme 5. Synthesis of the mixed acetato/dimethylpyrazolato-bridged dimetallic complex **6**.

The bridging coordination of the acetato group is confirmed by the IR spectrum, given the large difference between both CO stretching absorptions (142 cm^{-1}).[12] The equivalence of the methyl groups of the bridging dimethylpyrazolato ligand in the ^{1}H NMR spectrum also supports the *cisoid* geometry proposed by the anti-symbiotic or *transphobia* effect.[20,21] The protons of the methylene group in the $PdCH_2Si$ and $SiCH_2N$ moieties are diastereotopic, which indicates that complex **6** is not planar in solution. In fact a boat-type conformation is expected for this complex, since both the acetato- and pyrazolato-bridged complexes present non-planar structures. This conformation of complex **6** is rigid, since the ^{1}H NMR spectrum remains unchanged upon heating. A similar rigid structure was also observed for complex **4**.

In summary, the replacement of a dimethylpyrazolato group by an acetato ligand in **4** gives rise to another rigid dimetallic complex, whereas the replacement of a dimethylpyrazolato group by a chlorido ligand lowers the barrier of this inversion process (Scheme 3).

Computational Studies

To support our experimental findings of the preferred *transoid* or *cisoid* structure in the Pd dinuclear complexes **3**–**6** quantum chemical calculations were applied. Possible *cisoid* and *transoid* geometries were optimised for the aforementioned compounds by using the B3LYP hybrid functional and the 6-31+G(d) basis set for all atoms except palladium, for which the Stuttgart basis set and pseudopotential ECP28MWB[24] was applied. In the chlorido-bridged

complex, which was used as a starting material, both the *cisoid* and *transoid* geometries coexist in solution,[9b] and therefore no energy difference between the possible calculated isomers was found (see Supporting Information). However, in solution, both the pure acetato- and dimethylpyrazolato-bridged complexes **3** and **4** form a *transoid* structure. This was supported by an energy difference of 11 kJ mol^{-1} (**3**, Figure 2) and 10 kJ mol^{-1} (**4**) between the preferred *transoid* and the energetically less stable *cisoid* structure. Both bridging ligands, the acetato as well as the dimethylpyrazolato group, give rise to bent structures; therefore, the preference of the *transoid* forms may be due to steric reasons.

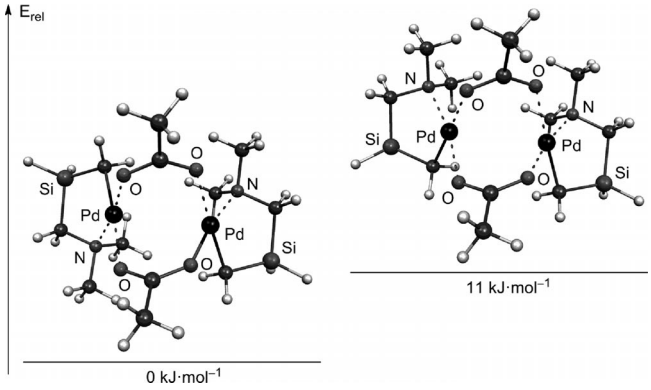


Figure 2. Calculated energy difference between the *transoid* and *cisoid* acetato-bridged complex **3** [B3LYP; Pd: ECP28MWB,[25] others: 6-31+G(d)].

For the complexes with mixed bridging ligands, a chlorido/dimethylpyrazolato (**5**) and acetato/dimethylpyrazolato (**6**) bridge, the preferred structure in solution is *cisoid*. This behaviour was also simulated in the calculations of these compounds, resulting in an energy difference of 22 kJ mol^{-1} between the preferred one of two possible *cisoid* geometries and the *transoid* structure for complex **5**. A similar difference in energy of 18 kJ mol^{-1} was found for the acetato/dimethylpyrazolato-bridged complex **6** (Figure 3).[25] In the case of these complexes, the preference of the *cisoid* form may be due to the *transphobia* effect.

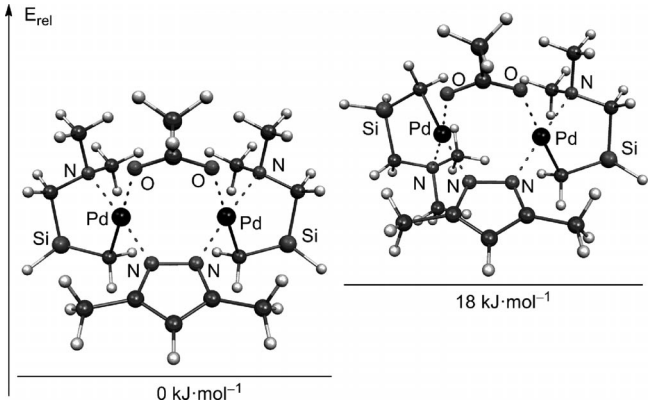


Figure 3. Calculated energy difference between the *transoid* and the most stable *cisoid* mixed acetato/dimethylpyrazolato-bridged complex **6** [B3LYP; Pd: ECP28MWB,[25] others: 6-31+G(d)].

Conclusions

Several dimetallic complexes containing palladacycles with the [(piperidinomethyl)silyl]methyl ligand have been synthesised and characterised. The nature of the bridging ligands determines both the presence of *transoid* or *cisoid* isomers and the rigidity of the complex in solution. The latter is especially demonstrated by the examples of mixed bridged dimetallic compounds. As previously reported, small and non-directional bridging chlorido groups give rise to a planar arrangement and to a slow equilibrium in solution due to the presence of *transoid* and *cisoid* isomers.[9b] If the bridging ligand is larger and more directional, the *transoid* isomer is preferred, and the complex is more rigid. Thus, bridging acetato ligands result in the *transoid* isomer only, and a dynamic process is detected in solution due to the formation of two enantiomers. However, the complex with bridging pyrazolato groups is rigid, and only a small amount of *cisoid* isomer is detected. No exchange process with the major *transoid* isomer is observed. The behaviour of the mixed bridged dimetallic compounds in solution also depends on the size and directionality of the bridging ligands, since the presence of small and non-directional chlorido groups in the chlorido/pyrazolato-bridged complex results in a ring inversion process. In contrast, the combination of both an acetato and pyrazolato ligand, directional and larger, results in a rigid structure. As expected from the anti-symbiotic effect, only the *cisoid* isomer is detected for these mixed bridged dimetallic complexes.

Experimental Section

General Remarks: IR (KBr pellets, 4000–450 cm^{-1}): Perkin–Elmer Spectrum RX I FT-IR. ^{1}H NMR [solvent $CDCl_3$; internal standard $CHCl_3$ (δ = 7.20 ppm); recorded at room temperature unless otherwise indicated]: Bruker AC-300 or ARX-300 (300.13 MHz). ^{13}C NMR [solvent and internal standard $CDCl_3$ (δ = 77.00 ppm); recorded at room temperature]: Bruker ARX-300 (75.78 MHz). Assignment of the ^{13}C NMR spectroscopic data was supported by DEPT experiments and relative intensities of the resonance signals. Microanalyses: Perkin–Elmer 2400B microanalyzer, Departamento de Química Inorgánica, Facultad de Ciencias, Valladolid (Spain). All reactions were carried out under oxygen-free and dried N_2 by conventional Schlenk techniques. Filtrations were carried out on dry Celite under N_2. The solvents were dried according to common procedures. Complex **1** was obtained as described previously.[7b]

[Pd{*C*H$_2$SiPh$_2$(CH$_2$*N*C$_5$H$_{10}$)-κ^2*C*,*N*}(NCMe)$_2$]BF$_4$ (2): MeCN (1 mL) and $TlBF_4$ (0.058 g) (***Caution:*** Tl^{I} derivatives are toxic and should be handled with care) were added to a solution of **1** (0.087 g, 0.1 mmol) in thf (10 mL). The mixture was stirred at room temperature for 3 h, during which time TlCl precipitated as a white solid. This mixture was used without further purification to obtain **3** or **4**. In order to obtain **2**, the mixture was filtered, and the filtrate was concentrated to dryness. The greenish-yellow solid obtained was washed with hexane (4 × 3 mL) and dried in vacuo, yielding 0.087 g (76%) of spectroscopically pure **2**. ^{1}H NMR: δ = 1.19 (m, 1 H, NCH$_2$CH$_2$C*H*$_2$), 1.53 (s, 2 H, PdC*H*$_2$Si), 1.54 (m, 1 H, NCH$_2$CH$_2$C*H*$_2$), 1.67 (m, 4 H, NCH$_2$C*H*$_2$), 2.24 (s, 3 H, NCC*H*$_3$), 2.29 (m, 2 H, NC*H*$_2$CH$_2$), 2.35 (s, 3 H, NCC*H*$_3$), 2.97 (s, 2 H, SiC*H*$_2$N), 3.15 (m, 2 H, NC*H*$_2$CH$_2$), 7.36 (m, 6 H, C$_6$*H*$_5$), 7.58 (m,

4 H, C_6H_5) ppm. IR: ṽ = 3067 (w), 3047 (w), 2941 (m), 2863 (w), 1826 (w), 1485 (w), 1452 (w), 1428 (m), 1378 (w), 1284 (w), 1262 (w), 1231 (w), 1084 (br. vs), 910 (w), 864 (w), 806 (w), 768 (m), 735 (s), 700 (s), 620 (w), 519 (w), 492 (m), 472 (m) cm^{-1}.

[Pd{*C*H$_2$SiPh$_2$(CH$_2$*N*C$_5$H$_{10}$)-κ^2*C*,*N*}(μ-*O*$_2$CCH$_3$-κ*O*:κ′*O*)]$_2$ (3): KO_2CCH_3 (0.022 g, 0.22 mmol) was added to the mixture obtained after **1** (0.087 g, 0.1 mmol), thf (10 mL), MeCN (1 mL), and $TlBF_4$ (0.058 g, 0.02 mmol) had been stirred at room temperature for 3 h. The mixture was stirred at room temperature for an additional 1 h and then evaporated to dryness, yielding a dark residue, which was extracted with toluene (3 × 5 mL). The yellow solution thus obtained was concentrated to dryness, and the yellow solid obtained was washed with hexane (3 × 5 mL) and dried in vacuo, yielding 0.089 g (97%) of **3**. ^{1}H NMR (333 K): δ = 1.40 (br. m, 6 H, NC_5H_{10} and 4 H, PdCH_2Si), 1.64 (br. m, 4 H, NC_5H_{10}), 1.86 br (m, 2 H, NC_5H_{10}), 1.88 (s, 6 H, CH_3CO$_2$), 2.46 (br. m, 4 H, NC_5H_{10}), 3.04 (s, 4 H, SiCH_2N), 3.31 (br. m, 4 H, NC_5H_{10}), 7.30 (m, 12 H, C_6H_5), 7.65 (m, 8 H, C_6H_5) ppm. ^{1}H NMR (293 K): δ = 1.28 (br. m, 6 H, NC_5H_{10} and 4 H, PdCH_2Si), 1.62 (br. m, 6 H, NC_5H_{10}), 1.87 (s, 6 H, CH_3CO$_2$), 2.27 (br. m, 2 H, NC_5H_{10}), 2.72 (br. m, 4 H, SiCH_2N and 2 H, NC_5H_{10}), 3.52 (br. m, 4 H, NC_5H_{10}), 7.31 (m, 12 H, C_6H_5), 7.65 (br. m, 8 H, C_6H_5) ppm. ^{1}H NMR (253 K): δ = 1.07 (d, J = 11.6 Hz, 2 H, PdCH_2Si), 1.18 (br. m, 4 H, NC_5H_{10}), 1.27 (d, J = 11.6 Hz, 2 H, PdCH_2Si), 1.41 (br., 2 H, NC_5H_{10}), 1.60 (br., 6 H, NC_5H_{10}), 1.87 (s, 6 H, CH_3CO$_2$), 2.67 (d, J = 12.2 Hz, 2 H, SiCH_2N), 2.84 (br., 2 H, NC_5H_{10}), 3.04 (br. m, 2 H, NC_5H_{10}), 3.26 (br. m, 2 H, NC_5H_{10}), 3.36 (overlapped with the following signal, 2 H, NC_5H_{10}), 3.36 (d, J = 12.2 Hz, 2 H, SiCH_2N), 7.29 (m, 10 H, C_6H_5), 7.44 (m, 4 H, C_6H_5), 7.62 (m, 2 H, C_6H_5), 7.82 (m, 4 H, C_6H_5) ppm. ^{13}C{^{1}H} NMR: δ = –3.3 (br., Pd*C*H$_2$Si), 1.0 (s, *C*H$_3$CO$_2$), 22.2 (s, NCH$_2$CH$_2$*C*H$_2$), 23.4 (s, NCH$_2$*C*H$_2$CH$_2$), 53.5 (br. s, Si*C*H$_2$N), 61.3 (s, N*C*H$_2$CH$_2$), 127.9 (s, Si-*m*-C_6H_5), 129.2 (s, Si-*p*-C_6H_5), 134.7 (s, Si-*o*-C_6H_5), 136.8 (s, Si-*i*-C_6H_5), 180.0 (br. s, CH$_3$*C*O$_2$) ppm. IR: ṽ = 3066 (w), 3010 (w), 2944 (m), 2854 (m), 1590 (vs), 1441 (m), 1413 (vs), 1260 (w), 1192 (w), 1106 (m), 1042 (w), 959 (w), 866 (w), 765 (s), 735 (s), 703 (s), 556 (w), 504 (w), 488 (m) cm^{-1}. $C_{42}H_{54}N_2O_4Pd_2Si_2$ (919.87): calcd. C 54.84, H 5.92, N 3.05; found C 54.54, H 5.93, N 3.07.

[Pd{*C*H$_2$SiPh$_2$(CH$_2$*N*C$_5$H$_{10}$)-κ^2*C*,*N*}(μ-dmpz-κ*N*:κ′*N*)]$_2$ (4): A solution of Kdmpz (0.20 mmol) in MeOH, previously prepared from dmpzH (0.020 g) and KOH in MeOH (0.078 M, 2.6 mL), was added to the mixture obtained after **1** (0.087 g, 0.1 mmol), thf (10 mL), MeCN (1 mL), and $TlBF_4$ (0.058 g, 0.02 mmol) had been stirred at room temperature for 3 h. The mixture was stirred at room temperature for an additional 1 h and then concentrated to dryness, yielding a dark residue that was extracted with CH_2Cl_2 (3 × 5 mL). Hexane (ca. 10 mL) was added to the colourless solution thus obtained, which was concentrated in vacuo and cooled to –20 °C. The colourless microcrystalline solid thus obtained was washed with hexane (3 × 5 mL) and dried in vacuo, yielding 0.082 g (83%) of **4**. The first crystals obtained are usually only the *transoid* isomer, whereas concentration of the mother liquor usually gives a mixture with the minor *cisoid* isomer (ca. 90:10). ^{1}H NMR: *transoid* isomer: δ = 0.84 (AB system, J = 9.5 Hz, 4 H, PdCH_2Si), 1.28 (m, NC_5H_{10}, 4 H), 1.62 (m, NC_5H_{10}, 6 H), 1.81 (s, CH_3 dmpz, 6 H), 2.28 (m, NC_5H_{10}, 4 H), 2.41 (s, CH$_3$ dmpz, 6 H), 2.82 (d, J = 14.0 Hz, SiCH_2N, 2 H), 2.84 (m, NC_5H_{10}, 2 H), 3.24 (m, NC_5H_{10}, 2 H), 3.56 (m, NC_5H_{10}, 2 H), 3.65 (d, J = 14.0 Hz, SiCH_2N, 2 H), 5.41 (s, C*H* dmpz, 2 H), 7.34 (m, C_6H_5, 12 H), 7.62 (m, C_6H_5, 4 H), 7.80 (m, C_6H_5, 4 H); *cisoid* isomer (detected signals): δ = 2.01 (s, 6 H, CH_3 dmpz), 2.47 (s, 6 H, CH_3 dmpz), 3.07 (m, 2 H, SiCH_2N), 5.57 (s, 2 H, C*H* dmpz), 7.34 (m, 12 H, C_6H_5), 7.73 (m, 8 H, C_6H_5) ppm; the lowest ratio *transoid*/*cisoid* detected for the different samples studied was 85:15. ^{13}C{^{1}H} NMR: δ = –7.4 (s, Pd*C*H$_2$Si, *transoid*), –6.7 (s, Pd*C*H$_2$Si, *cisoid*), 14.1 (s, *C*H$_3$ dmpz, *transoid*), 14.2 (s, *C*H$_3$ dmpz, *transoid*), 14.3 (s, *C*H$_3$ dmpz, *cisoid*), 14.4 (s, *C*H$_3$ dmpz, *cisoid*), 21.6 (s, NCH$_2$*C*H$_2$, *cisoid*), 22.6 (s, NCH$_2$*C*H$_2$, *transoid*), 23.7 (s, NCH$_2$CH$_2$*C*H$_2$, *cisoid* and *transoid*), 56.5 (br., Si*C*H$_2$N, *cisoid*), 61.8 (s, N*C*H$_2$CH$_2$, *cisoid*), 62.5 (s, N*C*H$_2$CH$_2$, *transoid*), 64.2 (s, Si*C*H$_2$N, *transoid*), 102.6 (s, *C*H dmpz, *transoid*), 102.7 (s, *C*H dmpz, *cisoid*), 102.8 (s, *C*H dmpz, *cisoid*), 127.8 (s, Si-*m*-C_6H_5, *cisoid* and *transoid*), 128.7 (s, Si-*p*-C_6H_5, *cisoid*), 128.7 (s, Si-*p*-C_6H_5, *cisoid*), 128.8 (s, Si-*p*-C_6H_5, *transoid*), 134.4 (s, Si-*o*-C_6H_5, *transoid*), 134.6 (s, Si-*o*-C_6H_5, *cisoid*), 134.8 (s, Si-*o*-C_6H_5, *transoid*), 138.3 (s, Si-*i*-C_6H_5, *cisoid*), 138.7 (s, Si-*i*-C_6H_5, *cisoid*), 138.9 (s, Si-*i*-C_6H_5, *cisoid*), 139.4 (s, Si-*i*-C_6H_5, *transoid*), 145.4 (s, *C*CH$_3$ dmpz, *transoid*), 146.7 (s, *C*CH$_3$ dmpz, *cisoid*), 146.9 (s, *C*CH$_3$ dmpz, *cisoid*), 147.0 (s, *C*CH$_3$ dmpz, *transoid*) ppm. IR: ṽ = 3065 (w), 3046 (w), 2925 (s), 2855 (s), 1526 (w), 1485 (w), 1441 (w), 1426 (s), 1358 (w), 1304 (w), 1262 (w), 1230 (w), 1177 (w), 1143 (w), 1102 (s), 1067 (w), 1041 (m), 944 (w), 863 (m), 766 (s), 732 (vs), 698 (vs), 649 (w), 544 (m), 502 (w), 489 (m) cm^{-1}. $C_{48}H_{62}N_6Pd_2Si_2$ (992.03): calcd. C 58.12, H 6.31, N 8.47; found C 58.32, H 6.57, N 8.13.

[Pd$_2${*C*H$_2$SiPh$_2$(CH$_2$*N*C$_5$H$_{10}$)-κ^2*C*,*N*}$_2$(μ-Cl)(μ-dmpz-κ*N*:κ′*N*)] (5): CH_2Cl_2 (10 mL) was added to a mixture of **4** (0.050 g, 0.05 mmol) and **1** (0.044 g, 0.05 mmol), and the solution was heated in a closed Schlenk flask at 40 °C for 24 h. The solution was filtered, and hexane (ca. 20 mL) was added to the resulting yellow solution, which was then concentrated in vacuo and cooled to –20 °C. The yellow crystals thus obtained were washed with hexane (3 × 3 mL) and dried in vacuo, yielding 0.073 g (80%) of **5**. ^{1}H NMR (333 K): δ = 1.45 (br. m, 4 H, NC_5H_{10} and 4 H, PdCH_2Si), 1.69 (br. m, 8 H, NC_5H_{10}), 2.50 (s, 6 H, CH_3 dmpz), 2.53 (m, 4 H, NC_5H_{10}), 2.99 (s, 4 H, SiCH_2N), 3.65 (m, 4 H, NC_5H_{10}), 5.67 (s, 1 H, C*H* dmpz), 7.26 (m, 12 H, C_6H_5), 7.72 (m, 8 H, C_6H_5) ppm. ^{1}H NMR (293 K): δ = 1.20 (d, J = 9 Hz, 2 H, PdCH_2Si), 1.36 (m, 2 H, NC_5H_{10} and 2 H, PdCH_2Si), 1.56 (br., 6 H, NC_5H_{10}), 1.67 (br., 4 H, NC_5H_{10}), 2.18 (s, 6 H, CH_3 dmpz), 2.37 (br., 4 H, NC_5H_{10}), 2.93 (s, 4 H, SiCH_2N), 3.54 (br., 4 H, NC_5H_{10}), 5.66 (s, 1 H, C*H* dmpz), 7.30 (br. m, 12 H, C_6H_5), 7.69 (br. m, 8 H, C_6H_5) ppm. ^{13}C{^{1}H} NMR: δ = –1.4 (s, Pd*C*H$_2$Si), 15.1 (s, *C*H$_3$ dmpz), 21.8 (s, NCH$_2$*C*H$_2$), 23.4 (s, Si*C*H$_2$N), 53.2 (br., NCH$_2$CH$_2$*C*H$_2$), 61.4 (br., N*C*H$_2$CH$_2$), 62.7 (br., N*C*H$_2$CH$_2$), 105.2 (s, *C*H dmpz), 127.8 (s, Si-*m*-C_6H_5), 129.1 (s, Si-*p*-C_6H_5), 134.7 (s, Si-*o*-C_6H_5), 137.4 (s, Si-*i*-C_6H_5), 148.7 (s, *C*CH$_3$ dmpz) ppm. IR: ṽ = 3064 (w), 3018 (w), 2956 (m), 2921 (s), 2850 (s), 2807 (w), 2056 (w), 1992 (w), 1586 (w), 1528 (w), 1484 (w), 1427 (s), 1374 (w), 1354 (w), 1302 (w), 1258 (w), 1177 (w), 1156 (w), 1110 (s), 1034 (w), 998 (w), 966 (w), 910 (w), 883 (w), 862 (m), 796 (w), 768 (s), 760 (s), 732 (vs), 718 (s), 699 (vs), 650 (w), 618 (w), 576 (w), 549 (w), 503 (w), 490 (m), 478 (w), 460 (w) cm^{-1}. $C_{43}H_{55}ClN_4Pd_2Si_2$ (932.36): calcd. C 55.39, H 5.95, N 6.01; found C 55.05, H 5.96, N 5.83.

[Pd$_2${*C*H$_2$SiPh$_2$(CH$_2$*N*C$_5$H$_{10}$)-κ^2*C*,*N*}$_2$(μ-*O*$_2$CCH$_3$-κ*O*:κ′*O*)(μ-dmpz-κ*N*:κ′*N*)] (6): CH_2Cl_2 (10 mL) was added to a mixture of **3** (0.046 g, 0.05 mmol) and **4** (0.050 g, 0.05 mmol), and the solution was heated in a closed Schlenk flask at 40 °C for 24 h. The solution was filtered, and hexane (ca. 15 mL) was added to the resulting yellow solution, which was then concentrated in vacuo and cooled to –20 °C. After some crops of crystals of the starting materials had been collected, concentration of the mother liquor yielded 0.022 g of **6** (23%) as pale yellow crystals, which were washed with hexane (3 × 3 mL) and dried in vacuo. ^{1}H NMR: δ = 0.91 (d, J = 13.4 Hz, 2 H, PdCH_2Si), 1.16 (d, J = 13.4 Hz, 2 H, PdCH_2Si), 1.45 (m, 6 H, NC_5H_{10}), 1.75 (s, 3 H, CH_3CO$_2$), 1.78 (m, 6 H, NC_5H_{10}), 2.26 (s, 3 H, CH_3 dmpz), 2.67 (br. d, J = 12.0 Hz, 2 H, NC_5H_{10}),

2.82 (d, J = 14.3 Hz, 2 H, SiCH_2N), 2.95 (d, J = 13.5 Hz, 2 H, NC$_5H_{10}$), 3.24 (d, J = 14.3 Hz, 2 H, SiCH_2N), 3.33 (t, J = 11.3 Hz, 2 H, NC$_5H_{10}$), 3.58 (t, J = 11.3 Hz, 2 H, NC$_5H_{10}$), 5.70 (s, 1 H, CH dmpz), 7.19 (m, 4 H, C$_6H_5$), 7.33 (m, 8 H, C$_6H_5$), 7.60 (m, 4 H, C$_6H_5$) ppm. IR: $\tilde{\nu}$ = 3065 (w), 2932 (m), 2854 (m), 1560 (vs), 1540 (m), 1522 (w), 1507 (w), 1456 (m), 1418 (s), 1374 (w), 1339 (w), 1260 (w), 1108 (m), 1032 (w), 998 (w), 967 (w), 866 (w), 804 (w), 777 (w), 728 (m), 700 (m), 668 (w), 617 (w), 556 (w), 504 (m), 492 (m), 472 (m) cm^{-1}. $C_{45}H_{58}N_4O_2Pd_2Si_2$ (955.95): calcd. C 56.54, H 6.12, N 5.86; found C 56.23, H 5.95, N 5.93.

Crystal Structure Determination of Complex 4: Crystals were grown by slow diffusion of hexane into a concentrated solution of the complex in CH_2Cl_2 at –20 °C. Crystallographic details are given in Table 2. Measurements were carried out with a Bruker Apex CCD diffractometer; programs used for data collection, cell determination and refinement: Smart V. 5622 (Bruker AXS, 2001), integration: SaintPlus V. 6.02 (Bruker AXS, 1999), empirical absorption correction: Sadabs V. 2.01 (Bruker AXS, 1999). The structure was solved by using direct and Fourier methods. Refinement was performed by full-matrix least-squares methods (based on F_o^2, SHELXL-97). Anisotropic thermal parameters for all non-hydrogen atoms were included in the final cycles. Hydrogen atoms were refined by using a riding model in their ideal geometric positions. The SHELXS-86 and SHELXL-97 computer programs were used for solving the structure.[26] CCDC-865034 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystal data and refinement details for **4**.

Empirical formula	$C_{51}H_{69}N_6Pd_2Si_2$
M	1035.10
T	173(2) K
λ (Mo-K_α)	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
a	13.268(5) Å
b	14.863(4) Å
c	15.112(4) Å
α	92.95(3)°
β	106.60(3)°
γ	110.75(4)°
V	2631.5(13) Å^3
Z	2
$\rho_{calcd.}$	1.306 g cm^{-3}
μ	0.767 mm^{-1}
F(000)	1074
Crystal size	0.20 × 0.10 × 0.10 mm
Scan range	2.48° ≤ θ ≤ 25.00°
Index ranges	–15 ≤ h ≤ 15
	–17 ≤ k ≤ 17
	–17 ≤ l ≤ 17
Reflections collected	22886
Independent reflections	8707 [R(int) = 0.0642]
Completeness to θ = 25.00°	94.0%
Max. and min. transmission	0.9273 and 0.8618
Refinement method	full-matrix least squares on F^2
Data/restraints/parameters	8707/0/553
Goodness-of-fit on F^2	0.993
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.0535, $wR2$ = 0.1493
R indices (all data)	$R1$ = 0.0697, $wR2$ = 0.1621
Largest diff. peak and hole	1.686 and –1.244 e Å^{-3}

Supporting Information (see footnote on the first page of this article): Total energies and Cartesian coordinates for all computed structures.

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[1] a) J. Dupont, M. Pfeffer (Eds.), *Palladacycles: Synthesis Characterization and Applications*, 1st ed., Wiley-VCH, Weinheim, **2008**; b) M. Albrecht, *Chem. Rev.* **2010**, *110*, 576–623; c) J. Dupont, C. S. Consorti, J. Spencer, *Chem. Rev.* **2005**, *105*, 2527–2571; d) G. R. Newkome, W. E. Puckett, V. K. Gupta, G. E. Kiefer, *Chem. Rev.* **1986**, *86*, 451–489.

[2] a) A. D. Ryabov, *Synthesis* **1985**, 233–252; b) M. Pfeffer, *Pure Appl. Chem.* **1992**, *64*, 335–342; c) I. Omae, *Coord. Chem. Rev.* **2004**, *248*, 995–1023.

[3] a) P. Espinet, M. A. Esteruelas, L. A. Oro, J. L. Serrano, E. Sola, *Coord. Chem. Rev.* **1992**, *117*, 215–274; b) M. Ghedini, I. Aiello, A. Crispini, A. Golemme, M. La Deda, D. Pucci, *Coord. Chem. Rev.* **2006**, *250*, 1373–1390.

[4] C. Navarro-Ranninger, I. López-Solera, J. M. Pérez, J. R. Masaguer, C. Alonso, *Appl. Organomet. Chem.* **1993**, *7*, 57–61.

[5] a) S. B. Wild, *Coord. Chem. Rev.* **1997**, *166*, 291–311; b) J. Albert, J. Granell, G. Muller, *J. Organomet. Chem.* **2006**, *691*, 2101–2106.

[6] a) W. A. Herrmann, V. P. W. Böhm, C.-P. Reisinger, *J. Organomet. Chem.* **1999**, *576*, 23–41; b) I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009–3066; c) N. J. Whitcombe, K. K. Hii, S. E. Gibson, *Tetrahedron* **2001**, *57*, 7449–7476; d) A. F. Littke, G. C. Fu, *Angew. Chem.* **2002**, *114*, 4350; *Angew. Chem. Int. Ed.* **2002**, *41*, 4176–4211; e) R. B. Bedford, *Chem. Commun.* **2003**, 1787–1796; f) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731–1770; g) A. Zapf, M. Beller, *Chem. Commun.* **2005**, 431–440.

[7] a) I. P. Beletskaya, A. V. Cheprakov, *J. Organomet. Chem.* **2004**, *689*, 4055–4082; b) C. S. Consorti, F. R. Flores, J. Dupont, *J. Am. Chem. Soc.* **2005**, *127*, 12054–12065; c) N. T. S. Phan, M. Van Der Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609–679; d) M. Weck, C. W. Jones, *Inorg. Chem.* **2007**, *46*, 1876–1883; e) K. Köhler, W. Kleist, S. S. Pröckl, *Inorg. Chem.* **2007**, *46*, 1865–1875; f) J. P. Knowles, A. Whiting, *Org. Biomol. Chem.* **2007**, *5*, 31–44; g) A. M. Trzeciak, J. J. Ziółkowski, *Coord. Chem. Rev.* **2007**, *251*, 1281–1293.

[8] a) C. Strohmann, B. C. Abele, D. Schildbach, K. Strohfeldt, *Chem. Commun.* **2000**, 865–866; b) C. Strohmann, O. Ulbrich, D. Auer, *Eur. J. Inorg. Chem.* **2001**, 1013–1018; c) C. Strohmann, K. Lehmen, A. Ludwig, D. Schildbach, *Organometallics* **2001**, *20*, 4138–4140; d) C. Strohmann, K. Lehmen, K. Wild, D. Schildbach, *Organometallics* **2002**, *21*, 3079–3081.

[9] a) C. Strohmann, B. C. Abele, K. Lehmen, F. Villafañe, L. Sierra, S. Martín-Barrios, D. Schildbach, *J. Organomet. Chem.* **2002**, *661*, 149–158; b) D. Schildbach, L. Sierra, S. Martín-Barrios, K. Lehmen, F. Villafañe, C. Strohmann, *Organometallics* **2004**, *23*, 3228–3238.

[10] a) T. H. Chan, P. Pellon, *J. Am. Chem. Soc.* **1989**, *111*, 8737–8738; b) G. Fraenkel, J. H. Duncan, K. Martin, J. Wang, *J. Am. Chem. Soc.* **1999**, *121*, 10538–10544; c) C. Strohmann, D. H. M. Buchold, T. Seibel, K. Wild, D. Schildbach, *Eur. J. Inorg. Chem.* **2003**, 3453–3463; d) C. Strohmann, B. C. Abele, K. Lehmen, D. Schildbach, *Angew. Chem.* **2005**, *117*, 3196; *Angew. Chem. Int. Ed.* **2005**, *44*, 3136–3139; e) C. Unkelbach, B. C. Abele, K. Lehmen, D. Schildbach, B. Waerder, K. Wild, C. Strohmann, *Chem. Commun.* **2012**, *48*, 2492.

[11] a) S. Paavola, K. Zetterberg, T. Privalov, I. Csöregh, C. Moberg, *Adv. Synth. Catal.* **2004**, *346*, 237–244; b) C. López, A. González, C. Moya, R. Bosque, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* **2008**, *693*, 2877–2886; c) S. Z. Vatsadze,

A. V. Medved′ko, N. V. Zyk, A. L. Maximov, S. A. Kurzeev, G. M. Kazankov, K. A. Lyssenko, *Organometallics* **2009**, *28*, 1027–1031.

[12] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed., John Wiley & Sons, New York, **1978**, p. 232.

[13] a) J. Powell, *J. Am. Chem. Soc.* **1969**, *91*, 4311–4316; b) J. Powell, T. Jack, *Inorg. Chem.* **1972**, *11*, 1039–1048; c) A. J. Deeming, I. P. Rothwell, *J. Organomet. Chem.* **1981**, *205*, 117–131; d) A. D. Ryabov, *Inorg. Chem.* **1987**, *26*, 1252–1260.

[14] Some examples of non-rigid cyclopalladated acetato-bridged complexes at room temp.: a) G. Balavoine, J. C. Clinet, P. Zerbib, K. Boubekeur, *J. Organomet. Chem.* **1990**, *389*, 259–275; b) Y. Fuchita, K. Yoshinaga, H. Kusaba, M. Mori, K. Hiraki, K. Takehara, *Inorg. Chim. Acta* **1995**, *239*, 125–132; c) P. G. Evans, N. A. Brown, G. J. Clarkson, C. P. Newman, J. P. Rourke, *J. Organomet. Chem.* **2006**, *691*, 1251–1256.

[15] See, for example: a) K. Hiraki, Y. Fuchita, K. Takechi, *Inorg. Chem.* **1981**, *20*, 4316–4320; b) E. Wehman, G. van Koten, J. T. B. H. Jastrzebski, H. Ossor, M. Pfeffer, *J. Chem. Soc., Dalton Trans.* **1988**, 2975–2981; c) M. T. Alonso, O. Juanes, J. de Mendoza, J. C. Rodríguez-Ubis, *J. Organomet. Chem.* **1992**, *430*, 335–347; d) J. Vicente, I. Saura-Llamas, M. G. Palin, P. G. Jones, M. C. R. de Arellano, *Organometallics* **1997**, *16*, 826–833; e) J. Vicente, M. C. Lagunas, E. Bleuel, M. C. R. de Arellano, *J. Organomet. Chem.* **2002**, *648*, 62–71.

[16] See, for example: a) Y. Fuchita, K. Hiraki, T. Uchiyama, *J. Chem. Soc., Dalton Trans.* **1983**, 897–899; b) K. Hiraki, M. Nakashima, T. Uchiyama, Y. Fuchita, *J. Organomet. Chem.* **1992**, *428*, 249–258; c) M. T. Alonso, O. Juanes, J. de Mendoza, J. C. Rodríguez-Ubis, *J. Organomet. Chem.* **1992**, *430*, 349–355; d) J. Buey, P. Espinet, *J. Organomet. Chem.* **1996**, *507*, 137–145; e) J. L. Serrano, L. García, J. Pérez, E. Pérez, J. M. Galiana, J. García, M. Martínez, G. Sánchez, I. da Silva, *Dalton Trans.* **2011**, *40*, 156–168.

[17] See, for example: a) V. K. Jain, S. Kannan, E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.* **1992**, 2231–2234; b) L. R. Falvello, J. Forniés, A. Martín, R. Navarro, V. Sicilia, P. Villarroya, *Chem. Commun.* **1998**, 2429–2430; c) J. Ruiz, F. Florenciano, M. A. Sánchez, G. López, M. C. Ramírez de Arellano, J. Pérez, *Eur. J. Inorg. Chem.* **2000**, 943–949; d) J. Pons, A. Chadghan, J. Casabó, A. Alvarez-Larena, J. F. Piniella, J. Ros, *Inorg. Chem. Commun.* **2000**, *3*, 296–299; e) R. de la Cruz, P. Espinet, A. M. Gallego, J. M. Martín-Alvarez, J. M. Martínez-Ilarduya, *J. Organomet. Chem.* **2002**, *663*, 108–117; f) L. R. Falvello, J. Forniés, A. Martín, V. Sicilia, P. Villarroya, *Organometallics* **2002**, *21*, 4604–4610; g) P. Baran, C. M. Marrero, S. Pérez, R. G. Raptis, *Chem. Commun.* **2002**, 1012–1013; h) A. Singhal, R. Mishra, S. K. Kulshreshtha, P. V. Bernhardt, E. R. T. Tiekink, *J. Organomet. Chem.* **2006**, *691*, 1402–1410; i) A. M. Santana, J. G. Ferreira, A. C. Moro, S. C. Lemos, A. E. Mauro, A. V. G. Netto, R. C. G. Frem, R. H. A. Santos, *Inorg. Chem. Commun.* **2011**, *14*, 83–86.

[18] E. Keller, *SCHAKAL 92*, University of Freiburg, Freiburg, **1992**.

[19] The higher flexibility of bridging acetato groups compared to bridging pyrazolato ligands in palladium complexes can also be extended to their solid-state structures, as has been reported after examining the crystalline structures of different acetato- and pyrazolato-bridged complexes: K. Umakoshi, Y. Yamauchi, K. Nakamiya, T. Kojima, M. Yamasaki, H. Kawano, M. Onishi, *Inorg. Chem.* **2003**, *42*, 3907–3916.

[20] R. G. Pearson, *Inorg. Chem.* **1973**, *12*, 712–713.

[21] a) J. Vicente, A. Arcas, D. Bautista, P. G. Jones, *Organometallics* **1997**, *16*, 2127–2138; b) J. Vicente, J. A. Abad, A. D. Frankland, M. C. Ramírez de Arellano, *Chem. Eur. J.* **1999**, *5*, 3066–3075.

[22] The mixed chlorido/pyrazolato-bridged complex **5** was also detected and isolated when $CHCl_3$ was used as a solvent. The origin of the chlorido ligand is undoubtedly the HCl produced during extended heating, even though oxygen and light were excluded: D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon Press, Oxford, **1988**. This chlorination should be favoured during the formation of the complex, since a sample of **6** maintained in $CDCl_3$ for 24 h did not show signals of **5**.

[23] Chlorido-bridged complexes are readily obtained by treating acetato-bridged complexes with HCl, see for example ref.[16c] or: a) M. J. Baena, J. Buey, P. Espinet, H.-S. Kitzerow, G. Heppke, *Angew. Chem.* **1993**, *105*, 1238; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1201–1203; b) M. J. Baena, P. Espinet, M. B. Ros, J. L. Serrano, A. Ezcurra, *Angew. Chem.* **1993**, *105*, 1260; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1203–1205. The traditional method uses alkaline chlorides, see for example ref.[1d,2c] or: c) H. Onoue, I. Moritani, *J. Organomet. Chem.* **1972**, *43*, 431–436.

[24] a) D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123–141; b) J. M. L. Martin, A. Sundermann, *J. Chem. Phys.* **2001**, *114*, 3408–3420.

[25] Additional information and graphics on these calculations are included in the Supporting Information.

[26] G. M. Sheldrick, *SHELXS-86, Structure Solving Program for Crystal Structure Determination*, University of Göttingen, Göttingen, **1986**; G. M. Sheldrick, *SHELXL-97, A Computer Program for Refinement of Crystal Structures*, University of Göttingen, Göttingen, **1997**.

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