CHEMISTRY
A EUROPEAN JOURNAL

Dimeric Palladium Complexes with Bridging Aryl Groups: When are they Stable?

Ana C. Albéniz,* Pablo Espinet,* Oscar López-Cimas, and Blanca Martín-Ruiz[a]

Dedicated to the memory of Dr. Juan Carlos del Amo, a Spanish chemist and innocent victim of the terrorist attack in Madrid

Abstract: Stable dimeric palladium(II) complexes of general formula $[Pd_2(\mu\text{-}R)_2(\eta^3\text{-allyl})_2]$ (R = haloaryl, mesityl) have been prepared. Their X-ray crystal structures, determined for some of the complexes, show that the two coordination square planes are usually coplanar. The haloaryl complexes are fluxional in solution, showing exchange between *cis* and *trans* isomers (relative to the orientation of the two allyl groups in the dimer) through solvent-assisted associative bridge splitting. A number of other ancillary ligands (O,O, S,S, or C,N donors) failed to stabilize the bridging situation. Also, bridging phenyls were unstable. The reasons for this behavior and the formation of alternative compounds in attempts at synthesizing them are fully analyzed and explained. Stable aryl bridges seem to be favored by a combination of factors: the use of ancillary ligands of small size and lacking electron lone pairs, and the use of aryl ligands reluctant to homo and hetero C–C coupling. These seem to be more important factors in the stabilization of bridging aryl complexes than the strength of the bridges themselves.

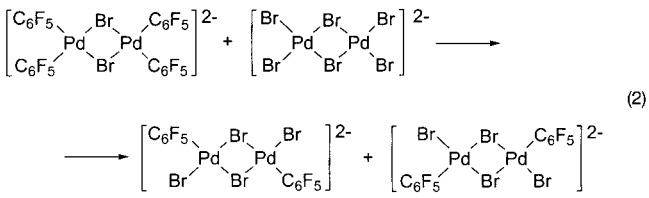
Keywords: allyl ligands · associative bridging ligand splitting · electron-deficient compounds · palladium

Introduction

Bridging aryl groups are common in the chemistry of main-group elements and Group 11 transition metals. They are far less common for palladium and platinum complexes, and only a few examples of stable derivatives have been reported.[1] Nonetheless, they are proposed to be involved in the transfer of aryl groups between palladium centers,[2,3] and in the transmetalation of aryl groups in some Pd-catalyzed cross-coupling reactions [Eq. (1)], such as the Stille and the Hiyama reactions.[4,5]

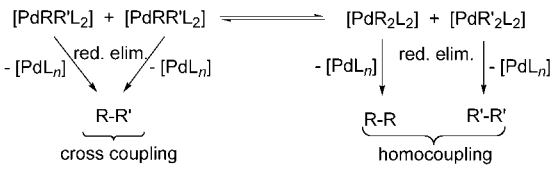
$$RX + R'M \xrightarrow{[Pd]} R\text{-}R' + MX \qquad (1)$$

The transfer of aryl groups between palladium atoms has been used to synthesize monoaryl palladium derivatives,[6] as in the process shown in Equation (2).[6a] Again, intermediates with bridging aryl groups should be involved.



(2)

This aryl rearrangement is also relevant in Pd-mediated cross-coupling reactions [Eq. (1)], since, provided it is fast enough relative to the reductive elimination step leading to the final cross coupling products, it opens a pathway to undesired homocoupling products (Scheme 1).



Scheme 1. Formation of homocoupling products in Pd-catalyzed cross-coupling reactions.

[a] Dr. A. C. Albéniz, Prof. Dr. P. Espinet, O. López-Cimas, B. Martín-Ruiz
Química Inorgánica, Facultad de Ciencias
Universidad de Valladolid, 47005 Valladolid (Spain)
Fax: (+34) 983-423-013
E-mail: albeniz@qi.uva.es
espinet@qi.uva.es

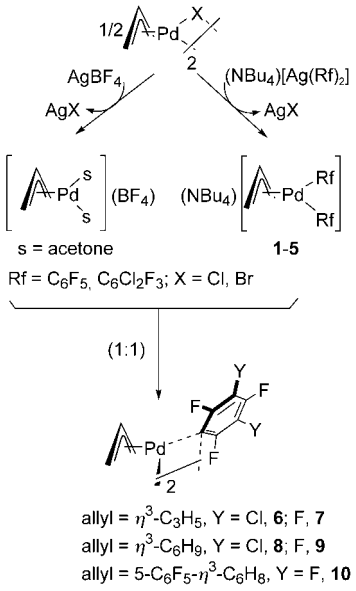
Supporting Information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

DOI: 10.1002/chem.200400612

In the course of a study of the Stille reaction with allyl halides we found that, in the absence of other ligands, η^3-allyl complexes of palladium with bridging aryl groups were very stable.[1a] This remarkable stability prompted us to explore the synthesis of other complexes of this type and to look into the factors that contribute to the stabilization of these electron-deficient bridges. Only one other Pd complex with aryl bridges, $(NBu_4)_2[Pd_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$, and one mixed Pd/Pt complex, $(NBu_4)_2[PdPt(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$, have been reported to date,[1b] but these were not characterized by X-ray diffraction and were reported to decompose slowly in solution at room temperature.

Results

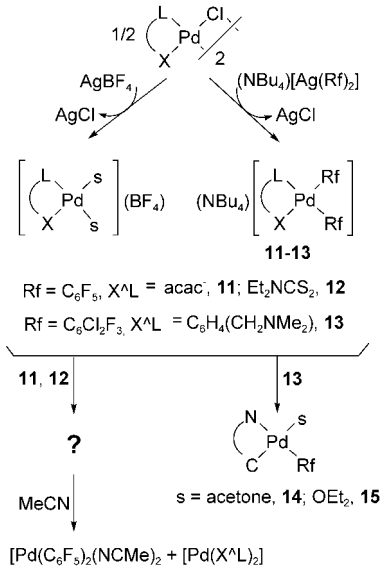
Synthesis of complexes: Several allyl–palladium complexes with bridging perhalophenyl ligands were synthesized following the route described in Scheme 2. The cationic acetone complexes were prepared and used "in situ". The synthesis and isolation of a cationic 5-C_6F_5-1,3-η^3-cyclohexenylpalladium·solvato derivative has been reported in detail.[1a] The bis-aryl anionic complexes $(NBu_4)[Pd(\eta^3\text{-allyl})(Rf)_2]$, {$\eta^3$-allyl = η^3-C_3H_5, Rf = $C_6Cl_2F_3$ (**1**), C_6F_5 (**2**); η^3-allyl = η^3-cyclohexenyl, Rf = $C_6Cl_2F_3$ (**3**), C_6F_5 (**4**); η^3-allyl = 5-C_6F_5-1,3-η^3-cyclohexenyl, Rf = C_6F_5 (**5**)} were prepared by arylation of the allyl, halo-bridged dimers with $(NBu_4)[Ag(Rf)_2]$. They displace acetone from the cationic complexes, affording the dimeric compounds **6**–**10** as orange solids.



Scheme 2. Synthesis of haloaryl-bridged dimeric allylic palladium complexes.

The bridging nature of the fluorinated aryl ligands in **6**–**10** is shown by the characteristic downfield shift of the F_{ortho} signals in their ^{19}F NMR spectra. They display chemical shifts close to −100 ppm for C_6F_5 or −75 ppm for 3,5-$C_6Cl_2F_3$ (in $CDCl_3$, reference $CFCl_3$). These shifts are about 10–15 ppm downfield from the corresponding signals in terminal perhaloarylpalladium complexes. In $CDCl_3$ each complex appears as a mixture of two isomers (ca. 1:1 ratio) arising from the mutual *cis* and *trans* arrangement of the two allyl ligands in the dimer (see later). Coordinating solvents, such as acetonitrile, cleave the aryl bridges to form monomeric solvato complexes. In less coordinating solvents, such as Et_2O or acetone, equilibria of dimeric aryl-bridged complexes with monomeric solvent complexes are observed.

A similar synthetic route was attempted with other auxiliary chelating X^L ligands different from allyl groups (Scheme 3). For this purpose the bis-aryl derivatives **11**–**13** were synthesized by transmetalation with the appropriate diarylsilver reagents and were fully characterized. It is worth noting that the rotation of the dichlorotrifluorophenyl rings around the Rf–Pd bond in the complex with the orthometallated dimethylbenzylamine ligand (**13**) falls well in the slow exchange limit at room temperature. This rotation is fast in analogous allylic derivatives **1**–**5**, which are less sterically demanding. The coordination plane of palladium is a symmetry plane in **13**, due to the presence of the planar κ^2-*C*,*N*-dimethylbenzylamine ligand; this results in the equivalence of the two F_{ortho} atoms in a perhaloaryl ring. The hindrance to rotation of the perhaloaryl groups in **13** was detected by analysis of the through-space coupling constants between F_{ortho} atoms of different inequivalent rings: the values of J for these *syn* (relative to the coordination square plane, i.e., $^{ts}J(F^1_o{-}F^2_o) = {}^{ts}J(F^{1\prime}_o{-}F^{2\prime}_o)$) and *anti* ($^{ts}J(F^1_o{-}F^{2\prime}_o) = {}^{ts}J(F^{1\prime}_o{-}F^2_o)$) F_{ortho}–F_{ortho} couplings (Figure 1) are unequal (7.1 and 4.2 Hz), as determined by computer simulation of the observed AA′XX′ spin system, whereas they should average in value in a fast rotation process of the haloaryl group around



Scheme 3. Attempted synthesis of aryl-bridged palladium complexes with auxiliary ligands different from allyl groups.

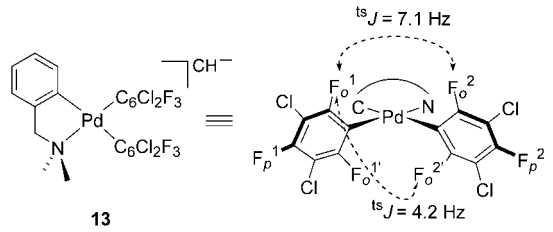
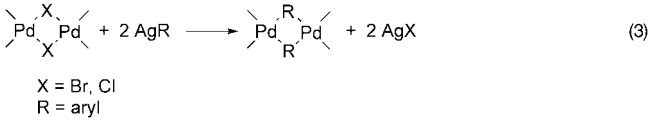


Figure 1. Through-space ^{19}F–^{19}F coupling constants for complex **13**.

the aryl–Pd bond. In complexes **1–5** the two aryl rings are equivalent by symmetry, but the two F_{ortho} at each side of the coordination plane should be inequivalent. However, equivalence of all the F_{ortho} atoms is observed and indicates fast rotation of the perhaloaryl rings. This different hindrance to aryl rotation for **1–5** relative to **13** is steric in origin, and the phenomenon has been discussed in detail in previous papers.[7]

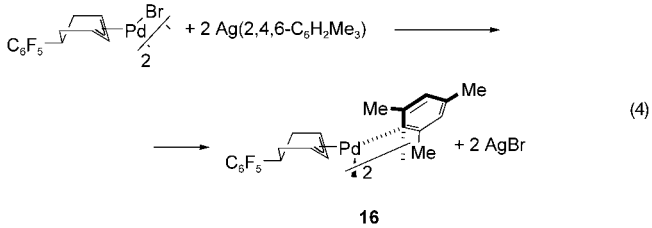
Attempts at synthesizing aryl-bridged dimeric complexes by using **11–13** as starting materials (Scheme 3), following a route similar to that in Scheme 2, were unsuccessful. For X^L = acac or diethyldithiocarbamate the product isolated from the reaction showed only broad signals in the ^{19}F NMR spectrum in $CDCl_3$; these signals appeared in the chemical shift range of terminal fluoroaryl groups, with no indication of bridging aryl groups. Upon addition of a small amount of acetonitrile to these ill-identified complexes, they slowly rearranged to $[Pd(Rf)_2(NCMe)_2]$ and $[Pd(X^L)_2]$. However, for X^L = κ^2-*C*,*N*-$C_6H_4CH_2NMe_2$ the products of the reaction were monomeric solvato complexes $[Pd\{\kappa^2\text{-}C,N\text{-}C_6H_4CH_2NMe_2\}(Rf)(s)]$ (Rf = 3,5-$C_6Cl_2F_3$; s = acetone (**14**) or OEt_2 (**15**) depending on the reaction solvent and the isolation procedure).

The reaction of AgR with halobridged dimers [Eq. (3)] might be an alternative method to synthesize aryl-bridged complexes. Indeed this is a suitable route to compounds **6–10**, although it usually produces somewhat lower yields than the process in Scheme 2.



Solutions of $Ag(C_6F_5)$ in $CDCl_3$ can be generated, as described in the literature,[8] by mixing $(NBu_4)[Ag(C_6F_5)_2]$ and $Ag(BF_4)$ in Et_2O, filtering the $(NBu_4)BF_4$ formed, evaporating the solvent, and dissolving the residue in $CDCl_3$. These solutions were used for testing, by NMR monitoring, the possible formation of other aryl-bridged compounds, but it is necessary to consider that it is extremely unlikely that these solutions are strictly free of Et_2O and H_2O, which can act as bridge-splitting ligands. The reaction with the cationic complex $[Pd_2(\mu\text{-}Cl)_2(PEt_3)_4](BF_4)_2$ produced *cis*-$[Pd(C_6F_5)_2(PEt_3)_2]$ and $[Pd_2(\mu\text{-}OH)_2(PEt_3)_4](BF_4)_2$, along with some unreacted material.[9] Similarly, the reaction of $[Pd_2(\mu\text{-}Cl)_2(py)_4](BF_4)_2$ with $Ag(C_6Cl_2F_3)$ (prepared by mixing $(NBu_4)[Ag(C_6Cl_2F_3)_2]$ and $Ag(BF_4)$, as described for the pentafluorophenyl derivative) showed no indication of bridging aryl groups in the ^{19}F NMR spectra of reaction mixtures, in chloroform or acetone.

The synthesis of dimeric complexes with bridging aryl groups other than fluoroaryl groups was also attempted. The reaction of $[Pd_2(\mu\text{-}Br)_2(5\text{-}C_6F_5\text{-}1,3\text{-}\eta^3\text{-cyclohexenyl})_2]$ with $Ag(2,4,6\text{-}C_6H_2Me_3)$ in Et_2O, gave the purple complex $[Pd_2(\mu\text{-}(2,4,6\text{-}C_6H_2Me_3))_2(5\text{-}C_6F_5\text{-}1,3\text{-}\eta^3\text{-cyclohexenyl})_2]$ (**16**) in moderate yield (51%, [Eq. (4)]).



This is the most convenient preparation procedure, since the reaction of $[Pd_2(\mu\text{-}Br)_2(5\text{-}C_6F_5\text{-}1,3\text{-}\eta^3\text{-cyclohexenyl})_2]$ with $(2,4,6\text{-}C_6H_2Me_3)MgBr$ (Pd:Mg = 1:1), leads to a mixture of **16** and starting material. The use of a higher amount of $MgBr(2,4,6\text{-}C_6H_2Me_3)$ did not lead to **16** as a pure complex. An equilibrium between **16** and $[Pd_2(\mu\text{-}Br)_2(5\text{-}C_6F_5\text{-}1,3\text{-}\eta^3\text{-cyclohexenyl})_2]$ was reached because of the presence of bromide salts in solution. Complex **16** is a mixture of *cis* and *trans* isomers (*cis*:*trans* = 1:1.3) as a result of the two possible mutual allyl arrangements in the dimer, as observed for **6–10**. Low temperature reactions of $[Pd_2(\mu\text{-}Br)_2(5\text{-}C_6F_5\text{-}1,3\text{-}\eta^3\text{-cyclohexenyl})_2]$ and LiPh (Pd:LiPh = 1:1) in Et_2O were also carried out. Deep red solutions were obtained upon mixing, but the characterization in solution and the isolation of solid complexes were prevented by rapid decomposition. Biphenyl and benzene were observed as decomposition products.

A rough estimation of the strength of the electron-deficient aryl bridges can be obtained from the extent of bridge splitting in coordinating solvents to give [Pd(aryl)(allyl)(solvent)]. In acetone, the mesityl bridges in **16** remain unaltered, whereas about 20% of **10** is split. The previously reported complex $[Pd_2(\mu\text{-}C_6Cl_2F_3)_2(5\text{-}C_6F_5\text{-}1,3\text{-}\eta^3\text{-cyclohexenyl})_2]$ (**17**) behaves like **10**. Compound **16** is not soluble in acetonitrile, whereas **10** and **17** are fully converted to the monomeric solvato complex. The decomposition of **16** at 50°C in $CDCl_3$ is analogous to that observed for **17**;[1a] it does not lead to the homocoupling product bimesityl, but to β-H elimination in the allylic moiety and formation of 1,3,5-$C_6H_3Me_3$.

Crystal structures of some aryl-bridged complexes: X-ray crystal-structure determinations were carried out for com-

plexes **6**, **7**, **9**, and **16**. The four complexes show very similar features, also in common with the complex $[Pd_2(\mu\text{-}C_6Cl_2F_3)_2(5\text{-}C_6F_5\text{-}1,3\text{-}\eta^3\text{-cyclohexenyl})_2]$ (**17**) previously reported.[1a] Selected bond lengths and angles are given in Table 1 for two representative complexes, **6** and **16**. Figure 2 shows the corresponding ORTEP drawings. Complex **16** crystallized with a molecule of solvent (Et_2O), which is not shown in Figure 2. Bond lengths, angles, and ORTEP drawings for **7** and **9** are given as Supporting Information.

Table 1. Selected bond lengths [Å] and angles [°] for complexes **6** and **16**.

Complex **6**		Complex **16**	
Pd1–C1	2.172(14)	Pd1A–C13	2.198(4)
Pd1A–C1	2.191(12)	Pd1–C13	2.267(5)
Pd1–Pd1A	2.681(2)	Pd1–Pd1A	2.6310(12)
Pd1–C7	2.133(13)	Pd1–C1	2.146(6)
Pd1–C8	2.119(19)	Pd1–C2	2.099(5)
Pd1–C9	2.080(18)	Pd1–C3	2.175(4)
C1-Pd1-C1A	104.2(4)	C13-Pd1-C13A	107.83(14)
Pd1-C1-Pd1A	75.8(4)	Pd1-C13-Pd1A	72.17(14)
C6-C1-C2	115.4(12)	C14-C13-C18	116.3(4)
C7-C8-C9	131.0(2)	C1-C2-C3	116.4(5)
C7-Pd1-C9	66.6(7)	C1-Pd1-C3	66.6(2)

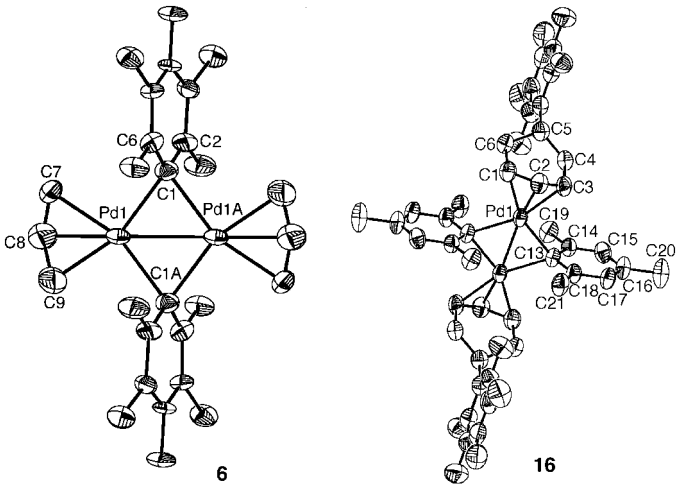


Figure 2. ORTEP drawings of the molecular structures for complexes **6** and **16**.

The bridging aryl rings lie perpendicular to the Pd–Pd axis (Figure 2) and are coplanar. The Pd–Pd distance is short in all cases: it ranges from 2.681(2) to 2.6310(12) Å, indicating a Pd–Pd bonding interaction consistent with the presence of electron-deficient aryl bridges. The aryl groups bridge the palladium centers in a symmetrical way for **6** (we consider a bridge to be symmetrical when both Pd–C_{ipso} distances are equal within $\pm 3\sigma$), but more often they are slightly asymmetrical (**16**, **17**). The two Pd and two C_{ipso} atoms are coplanar.

The Pd–allyl bond lengths and angles are within the normal ranges.[10,11] Only the *trans* isomer was found in the solid state for **6** and **16**, as was also the case for **17**. The cyclohexenyl ring in **16** shows a pseudoboat conformation. Substituted η^3-cyclohexenylpalladium complexes can be found in the literature in either the pseudoboat or pseudochair conformations, depending on whether the substituents are placed in an equatorial, less sterically demanding arrangement.[11,12]

The X-ray crystal structure of complex **18** (its anion is shown in Figure 3) was determined to make a comparison between terminal and bridged aryl groups. The synthesis has

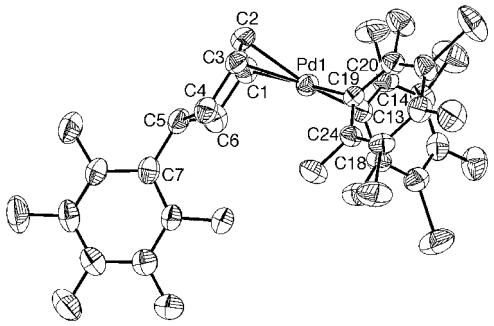


Figure 3. ORTEP drawing for the structure of the anion in complex **18**.

been reported previously.[1a] Selected bond lengths and angles are given in Table 2. The allyl moiety is symmetrically coordinated, with very similar Pd–C1 and Pd–C3 bond

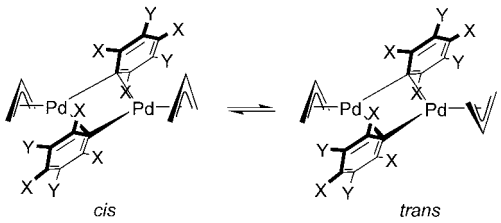
Table 2. Selected bond lengths [Å] and angles [°] for complex **18**.

Pd1–C13	2.070(4)	C19–Pd1–C13	92.73(13)
Pd1–C19	2.068(3)	C1–Pd1–C3	66.53(15)
Pd1–C1	2.170(3)	C13–Pd1–C1	99.58(14)
Pd1–C2	2.106(4)	C19–Pd1–C3	100.99(13)
Pd1–C3	2.187(3)	C3–C2–C1	117.5(4)
C1–C2	1.405(5)	C14–C13–C18	112.6(3)
C2–C3	1.390(5)	C24–C19–C20	112.1(3)

lengths (2.170(3) and 2.187(3) Å). The fluoroaryl rings are not perpendicular to the palladium coordination plane, but tilted in the same direction 24.2° (C13 fluoroaryl) and 12.5° (C19 fluoroaryl) from the ideal perpendicular position. The Pd–C(aryl) bond lengths are 2.070(4) and 2.068(3) Å, noticeably shorter than those of Pd–fluoroaryl in the dimeric complexes.

***The cis/trans* exchange**: In $CDCl_3$ complexes **6–10** exist as approximate 1:1 mixtures of *cis* and *trans* isomers, whereas a 1:1.3 mixture was found for complex **16** [Eq. (5)]. This mixture was seen clearly at room temperature for all the complexes in the ^{19}F NMR spectra in $CDCl_3$, but only for **10** and **16** in the ^1H NMR spectra. The *cis*/*trans* exchange was observed for the haloaryl complexes as the temperature was raised.

A variable-temperature study was undertaken for complex **6**, which provides a simple NMR pattern. The low-tempera-



(5)

ture spectrum of **6** corresponds to the slow exchange limit (213 K, Figure 4) and shows distinct signals for each isomer. Two singlets are observed for the F_{para} resonance in the

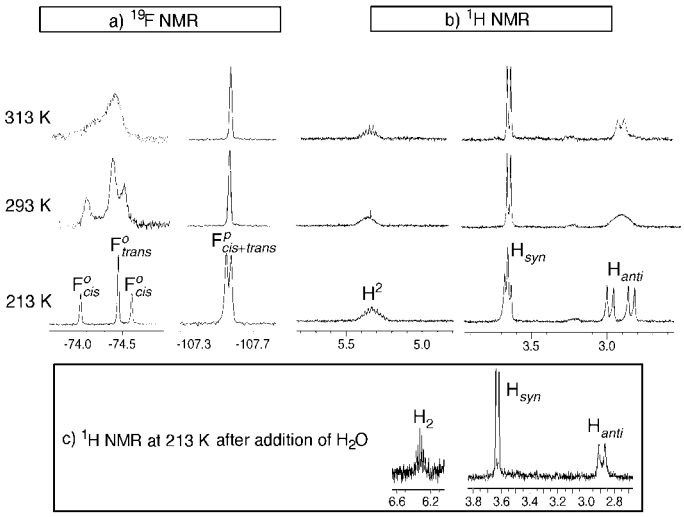
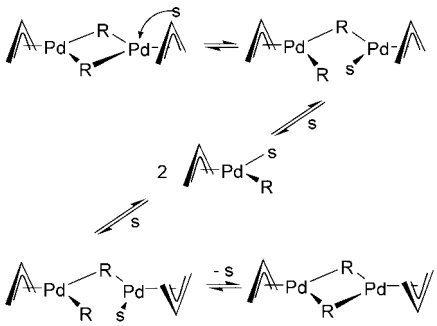


Figure 4. The *cis*/*trans* isomerization and ^{19}F and ^{1}H NMR spectra of complex **6** in $CDCl_3$ in different conditions.

^{19}F NMR spectrum. The symmetry of each isomer determines that the F_{ortho} resonances appear as one singlet for the four equivalent atoms in the *trans* isomer, and as two singlets for the two nonequivalent F_{ortho} atoms of each of the two equivalent aryl groups in the *cis* isomer (Figure 4a). Two sets of allylic protons are observed in the ^{1}H NMR spectrum (Figure 4b). At higher temperature coalescence of the signals of both isomers occurs and only one set of allylic resonances is observed in the ^{1}H NMR spectrum at 313 K (Figure 4b). Coalescence is also seen for the corresponding signals in the ^{19}F NMR spectrum (Figure 4a). The exchange does not operate through the frequent $\pi\rightleftarrows\sigma\rightleftarrows\pi$ rearrangement in this case, since it should lead to exchange of the *syn* and *anti* protons in the allyl moiety; this type of exchange is not observed (Figure 4b).[13] Line-shape analysis of the ^{1}H NMR spectra in $CDCl_3$ in the range 213–313 K afforded the exchange rates,[14] and an Eyring plot led to the following activation parameters for the process: $\Delta H^{\neq} = 43 \pm 3\ kJ\,mol^{-1}$, $\Delta S^{\neq} = -73 \pm 9\ J\,mol^{-1}\,K^{-1}$ ($\Delta G^{\neq}_{298} = 65 \pm 4\ kJ\,mol^{-1}$). The exchange was faster in acetone and was also accelerated when a small amount of H_2O was added to a solution of **6** in $CDCl_3$ (Figure 4c, note the similarity of this spectrum at 213 K with the spectrum at 313 K in $CDCl_3$ without added water).

Bridge cleavage and statistical rearrangement of dimers is commonly observed for electron-precise halogen-, carboxylate-, or aryloxide-bridged allylic compounds.[15] In the case of the electron-deficient bridges discussed here, our observations suggest a solvent-assisted cleavage of the aryl bridges (adventitious water in the case of $CDCl_3$, the exchange rate increasing when water is added on purpose). The highly negative value of $\Delta S^{\neq}$ rules out a dissociative mechanism for bridge cleavage, and further supports the intervention of the solvent (or the water in the case of $CDCl_3$) in an associative mechanism. The *cis*/*trans* conversion cannot be achieved in a monobridged intermediate. It requires the complete cleavage of the dimer into monomeric species, even if these are formed only in undetected concentration (Scheme 4). In fact an equimolar mixture of complexes **6** and **8** in $CDCl_3$ produces a statistical mixture of **6**, **8**, and [Pd(η^3-cyclohexenyl)(μ-$C_6Cl_2F_3$)$_2$Pd(η^3-C_3H_5)] (**19**).

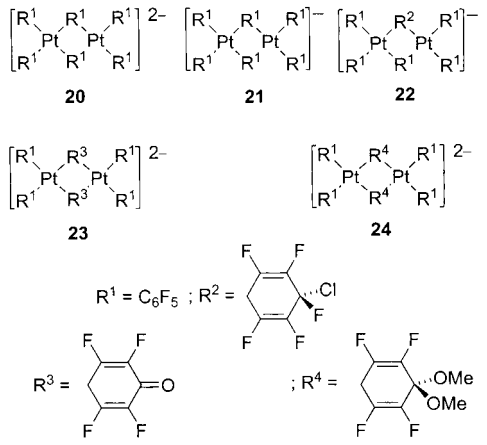


Scheme 4. Proposed mechanism for the *cis/trans* exchange in aryl-bridged dimeric palladium complexes.

Discussion

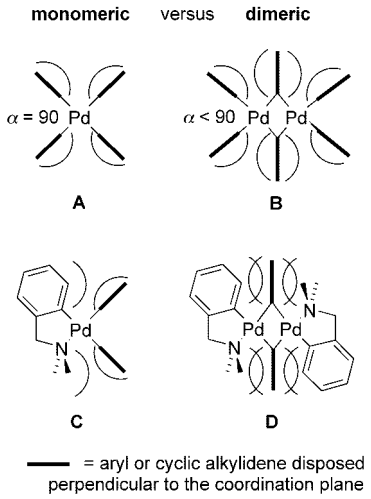
Judging by the frequent observations of processes requiring aryl transmetalation between Pd atoms, or between Pd and other metals not very dissimilar in electronegativity (Sn, Si, B, etc.), aryl bridges must pervade palladium chemistry as transient intermediates and in transition states, but they are extremely elusive to observation in isolated compounds. These two facts are not in contradiction, since palladium compounds are very efficient catalysts and a stable intermediate should make the overall reaction slow.

Only two kinds of Pd complexes featuring electron-deficient aryl bridges have been unambiguously observed so far: The anionic complexes $(NBu_4)_2[PdM(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (M = Pd, Pt), which were not studied by X-ray diffraction and decompose slowly in solution; and the series of complexes $[Pd_2(\mu\text{-}Ar)_2(allyl)_2]$ discussed here, which are fairly stable in solution. There are a number of closely related complexes in the literature that have been structurally characterized, for example, compounds with Pt^{II} or Pt^{III} and bridging perhaloaryl groups or bridging halogenated alkylidene ligands derived from them (Scheme 5).[1e,f,g]



Scheme 5. Dimeric platinum complexes with halogenated hydrocarbyl bridges.

All these systems with bridging aryl or alkylidene groups have a planar or nearly planar "$M_2(C_{ipso})_2$" fragment. The molecular orbitals pertinent to the bridge "$M_2(\mu\text{-}R)_2$" in several geometries, including square-planar complexes and sp^2- and sp^3-hybridized bridging atoms, have been thoroughly analyzed on model compounds using DFT and ab initio calculations, in order to find a rationale for the planar or bent structure of the bridge.[16] In the bridged systems containing terminal aryl groups (**20**–**24**) the angles at the metal determined by the terminal aryl groups are below 85.1° and can be as low as 82.5°.[1e,f,g] These values are in the lower range of angles found for *cis*-$(C_6F_5)_2M$ fragments in electron-precise square-planar complexes (82.7–91.8°,[10,17] 92.73° for *cis*-$(C_6Cl_2F_3)_2Pd$ in **18**) and suggest that the bridging aryl groups or alkylidenes are exerting some repulsion on the terminal aryl groups (the thickness of an aryl ring is estimated to be about 3.50 Å).[18] Scheme 6 clearly shows that the separation between terminal aryl groups in a conventional square-planar structure (**A**) is larger (they make angles of 90° in an ideal geometry) than the separation between terminal and bridging aryl groups (**B**) (they make angles of 45° in an ideal square-planar coordination geometry). Consequently the angle between terminal aryl groups (α) needs to be reduced in order to minimize the overall steric repulsive interactions in the molecule, whether the bridge is electron deficient (**20**, **21**, **22**) or not (**23**, **24**) (see the C_t–M–C_t angle 84.8° found for **20**,[1g] compared to 89.90° for the related complex with a small bridging group $(NBu_4)_2[Pd_2(\mu\text{-}OH)_2(C_6F_5)_4]$[19]). This suggests that favorable sterics is a factor for the special stability of aryl-bridged complexes with allyl groups as ancillary terminal ligands. Since allyl groups have small bite (66°) and cone angles, the repulsive bridge–terminal ligand interactions are basically absent and the complexes gain stability relative to complexes with other terminal ligands. At the other extreme, if we consider terminal ligands extended in the coordination plane (model structures **C** and **D** in Scheme 6), the bridged structure **D** can be discarded as a low-energy one, simply on the grounds of the severe steric hindrance. This suffices to explain why aryl-bridged complexes could not be obtained when X^L = κ^2-*C*,*N*-$C_6H_4CH_2NMe_2$ as terminal ligand, and the formation of monomeric solvato complexes [Pd{κ^2-*C*,*N*-$C_6H_4CH_2NMe_2$}(Rf)(s)] was preferred. For the same reason one should not expect $[Pd_2(\mu\text{-haloaryl})_2(PEt_3)_4](BF_4)_2$ to be a favored species due to the steric requirement of PEt_3.[20] In fact, this kind of structure could not be prepared.



Scheme 6. Steric constraints in monomeric and dimeric arylpalladium complexes.

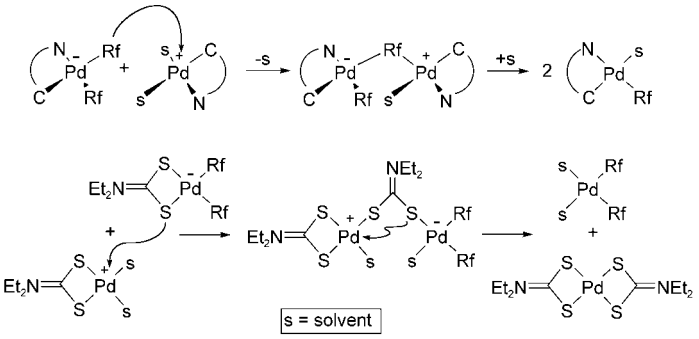
However, steric hindrance cannot be argued as an important factor of instability in other attempted cases such as $[Pd_2(\mu\text{-haloaryl})_2(py)_4](BF_4)_2$ or $[Pd_2(\mu\text{-Ph})_2(allyl)_2]$, since py, disposed perpendicularly to the coordination plane as terminal ligand, is sterically similar to the haloaryl groups as terminal ligands, for which anionic, bridged complexes are known. Other factors need to be considered that should make the bridged system unstable versus other alternative outcomes, such as the intrinsic stability of the bridges, the susceptibility to attack by external ligands, and the ease of decomposition by intramolecular coupling.

It is difficult to extract fine conclusions on the intrinsic stability of the bridges from inspection of the structural data (see complexes **6** and **16**), but an experimental assessment of the relative strength of the bridges for the bridging aryl groups used in this work can be obtained from the extent of bridge splitting by coordinating solvents to give monomeric solvato complexes in acetone. The dimer/monomer ratios found (see Results) lead to the following stability trend: mesityl > $C_6F_5 \approx C_6Cl_2F_3$. Thus, although the dimeric complexes are the major species in every case, the electron-deficient bridges are more stable the higher the electron density available in the aryl group, as indicated by the sum of Hammet parameters for the substituents in the ring ($\Sigma\sigma$: mesityl < $C_6F_5 \approx C_6Cl_2F_3$).[21]

When the compounds are made cationic by replacing the allyl group by two neutral ligands (py or PEt_3) the metal center becomes harder and more electrophilic. Whether this should stabilize or destabilize the bridges cannot be experimentally assessed, because in practice the metal center be-

comes too reactive towards hard nucleophiles in solution (OEt_2, adventitious H_2O), which will split the electron deficient bridges. In fact, cationic, bridged complexes are not detected. This reactivity explains the different behavior of py versus C_6F_5 as terminal ligands, in spite of its steric similarity.

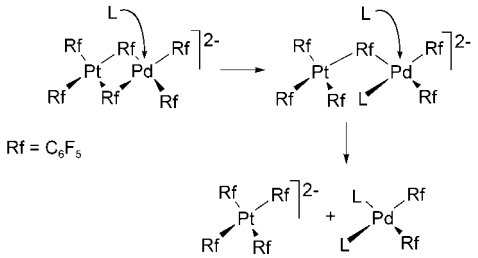
The ligands acetylacetonate or diethyl dithiocarbamate, particularly the latter with a bite angle of about 75°,[22] should not offer unbearable steric hindrance to aryl-bridge formation. Hence the failure to produce aryl-bridged complexes using these groups as terminal ligands should be imputed to them possessing lone pairs, which facilitates their transfer through electron-precise (3c, 4e) bridges (Scheme 7). It is interesting to note that the orthometallated terminal ligand, which lacks lone pairs, behaves quite differently and it is the perhaloaryl ring that is transferred.



Scheme 7. Reaction pathways observed for aryl palladium complexes with orthometallated or dithiocarbamate auxiliary ligands.

The combination of allylic ligands and haloaryl groups or mesityl is well suited to prevent the occurrence of fast coupling/decomposition reactions. Allyl–aryl coupling is not an easy process according to our previous studies on the decomposition of complex **17** in the context of a Stille coupling.[1a] Cyclohexenylhaloaryl and -mesityl derivatives eventually decompose by β-H elimination from the cyclohexenyl and aryl–H formation by reductive elimination. This decomposition takes place most probably on monomeric electron poor solvato complexes [Pd(allyl)(Ar)(s)] in solution. On the other hand, aryl–aryl homocoupling reactions might occur from minute amounts of $[Pd(allyl)(Ar)_2]^-$ complexes in equilibrium with the aryl-bridged and the cationic monomeric solvato complexes (the reversal of Scheme 2). These are kinetically disfavored for Ar = haloaryl groups,[23] and also for the sterically hindered mesityl group.[24] This homocoupling is, however, a decomposition process that is observed for Ar = Ph in competition with β-H elimination and C_6H_6 formation, and the deep red solutions formed at low temperature from $[Pd_2(\mu\text{-}Br)_2(5\text{-}C_6F_5\text{-}1,3\text{-}\eta^3\text{-cyclohexenyl})_2]$ and LiPh (which probably contain the corresponding phenyl-bridged derivative) undergo fast decomposition to biphenyl and benzene as the temperature is raised, or during workup. Easy homocoupling and formation of biaryl moieties has been reported in the decomposition of monoarylpalladium derivatives both for phenyl and for *meta*- or *para*-substituted aryl groups in which the C_{ipso} atoms are not hindered.[25] Since the strength of phenyl bridges should be intermediate between those of mesityl and C_6F_5, it is clear that the instability of Ph bridges is not due to an intrinsic weakness, but to a higher efficiency of the undesired decomposition pathways.

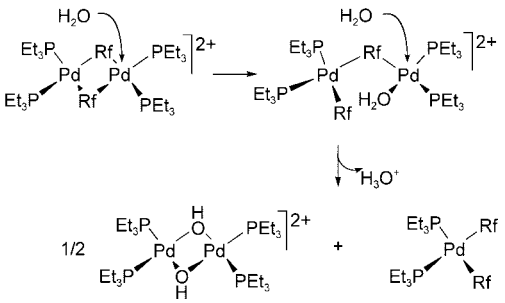
Finally it is worth commenting on the reaction mechanisms operating in these perhaloaryl-bridged palladium systems. In the preceding paragraphs we have proposed associative mechanisms both for the NMR fluxionality and for the reactivity observed (involving ligand substitution and transmetalation processes). Dissociative mechanisms might alternatively be invoked, involving splitting of the electron-deficient bridges to give three-coordinate intermediates. However, we have discussed elsewhere the unlikeness of kinetically relevant 14e intermediates in ligand-substitution processes.[26] There are indications in some of the reactions observed here or reported in the literature that in our opinion are clear hints for associative pathways. Thus, in contrast to the symmetric splitting by PPh_3 of the bridges in $[M_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]^{2-}$ (M = Pd, Pt), which affords only $[M(C_6F_5)_3(PPh_3)]^-$, the splitting of $[PdPt(\mu\text{-}C_6F_5)_2(C_6F_5)_4]^{2-}$ gives *cis*-$[Pd(C_6F_5)_2(PPh_3)_2]$ and $[Pt(C_6F_5)_4]^{2-}$. This remarkable difference, which was not discussed in the original paper,[1b] can be understood only taking into account that associative reactions for Pd are much faster than for Pt.[27] Hence the asymmetric bridge splitting is the logical result of a double associative substitution on Pd of the bridging Rf ligand (Rf = C_6F_5) by the incoming ligand (Scheme 8). The



Scheme 8. Bridge splitting by associative substitution on palladium.

kinetic products are sufficiently stable and do not rearrange easily to the expected thermodynamic products (those of symmetric splitting). We have shown previously that the *cis*/*trans* isomerization of complexes $[Pd(Rf)_2(PR_3)_2]$ (Rf = C_6F_5, $C_6Cl_2F_3$) is extremely slow.[2a]

Similarly, the formation of *cis*-$[Pd(C_6F_5)_2(PEt_3)_2]$ in our attempts to prepare $[Pd_2(\mu\text{-}C_6F_5)_2(PEt_3)_4]^{2+}$ can be explained assuming that this dimer is formed as an unstable (because of steric hindrance) and very reactive (because of the high electrophilicity and hard character of the Pd centers) intermediate, which immediately reacts with water in the solvent according to Scheme 9.



Scheme 9. Final products obtained by evolution of a putative cationic haloaryl-bridged palladium complex.

Conclusion

The formation of stable aryl bridges is favored by a combination of factors, which should mainly avoid other evolution pathways of the reaction. The use of small ancillary ligands to reduce steric crowding in the bridged complex, and the use of aryl ligands and ancillary ligands reluctant to homo or hetero C–C coupling, seem to be determinant. Donor atoms in the molecule or in the solvents are to be avoided, as they can induce bridge splitting. The tolerance to hard, weakly coordinating solvents can be fairly good in the less electrophilic, anionic or neutral, bridged complexes. The reactivity of the aryl-bridged complexes is often connected to an initial homolytic or heterolytic cleavage of the aryl bridges, which for Pd^{II} usually follows a fast associative mechanism. Electron-poor bridges seem to be slightly weaker and, in addition, this increases the electrophilicity of the metal. This makes these complexes particularly susceptible to cleavage, initiated by associative attack of an external nucleophile (e.g., solvent or adventitious water). The higher inertia of Pt towards associative processes can be a reason for the higher stability of aryl-bridged Pt complexes reported in the literature.

Experimental Section

General: ^{1}H, ^{19}F, and ^{31}P NMR spectra were recorded on Bruker AC-300 and ARX-300 spectrometers. Chemical shifts (in δ units, ppm) were referenced to TMS for ^{1}H, to $CFCl_3$ for ^{19}F, and to H_3PO_4 for ^{31}P. The spectral data were recorded at 293 K unless otherwise noted. C, H, and N elemental analyses were performed on a Perkin–Elmer 240 microanalyzer. Solvents were dried following standard procedures and distilled before use. Complexes $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$,[28] $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-cyclohexenyl})_2]$,[29] $[Pd_2(\mu\text{-}Br)_2(5\text{-}C_6F_5\text{-}1,3\text{-}\eta^3\text{-cyclohexenyl})_2]$,[11d] $[Pd_2(\mu\text{-}Cl)_2(acac)_2]$,[30] $[Pd_2(\mu\text{-}Cl)_2(Et_2NCS_2)_2]$,[31] $[Pd_2(\mu\text{-}Cl)_2\{\kappa^2\text{-}C,N\text{-}C_6H_4CH_2N(CH_3)_2\}]$,[32] $[Pd_2(\mu\text{-}Cl)_2(PEt_3)_4](BF_4)_2$,[33] $(NBu_4)[Ag(C_6F_5)_2]$,[8] $(NBu_4)[Ag(C_6Cl_2F_3)_2]$,[1a] and $Ag(2,4,6\text{-}C_6H_2Me_3)$[34] were prepared as described elsewhere.

Synthesis of bisarylpalladium derivatives

Complex 2: $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ (0.1260 g, 0.344 mmol) and $(NBu_4)[Ag(C_6F_5)_2]$ (0.4710 g, 0.688 mmol) were dissolved in CH_2Cl_2 (10 mL). The mixture was stirred for 30 min in the dark. The grayish suspension that formed was filtered, and the filtrate evaporated to dryness. Isopropanol (5 mL) and *n*-hexane (20 mL) were added to the residue. The white solid formed was filtered, washed with hexane, and air-dried (0.4292 g, 86% yield). Elemental analysis calcd (%) for $C_{31}H_{41}F_{10}NPd$: C 51.42, H 5.71, N 1.93; found: C 51.71, H 5.42, N 1.93; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -165.32$ (m; F_{meta}, F_{para}), -109.75 ppm (m; F_{ortho}); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.13$ (tt, $J = 12.6$ Hz, 6.3 Hz, 1H; H^2), 3.58 (d, $J = 6.3$ Hz, 2H; H^1_{syn}, H^3_{syn}), 3.02 (m, 8H; CH_2-α NBu_4), 2.58 (d, $J = 12.6$ Hz, 2H; H^1_{anti}, H^3_{anti}), 1.60 (m, 8H; CH_2-β NBu_4), 1.31 (m, 8H; CH_2-γ NBu_4), 0.95 ppm (m, 12H; CH_3 NBu_4).

Complexes **1**, **3**–**5**, and **11**–**13** were prepared in a similar way, starting from the corresponding dimeric chloro (bromo for complex **5**) and $(NBu_4)[Ag(Rf)_2]$ derivatives. *n*-Hexane, instead of a mixture of isopropanol/*n*-hexane, was used to obtain complexes **5**, **11** and **12**.

Complex 1: Yield, 81%; elemental analysis calcd (%) for $C_{31}H_{41}Cl_4F_6NPd$: C 47.14, H 5.23, N 1.77; found: C 46.69, H 4.89, N 1.81; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -123.70$ (s; F_{para}), -83.90 ppm (s; F_{ortho}); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.11$ (tt, $J = 13.2$, 6.6 Hz, 1H; H^2), 3.53 (d, $J = 6.6$ Hz, 2H; H^1_{syn}, H^3_{syn}), 3.02 (m, 8H; CH_2-α NBu_4), 2.57 (d, $J = 13.2$ Hz, 2H; H^1_{anti}, H^3_{anti}), 1.60 (m, 8H; CH_2-β NBu_4), 1.31 (m, 8H; CH_2-γ NBu_4), 0.95 ppm (t, 12H; CH_3 NBu_4).

Complex 3: Yield, 62%; elemental analysis calcd (%) for $C_{34}H_{45}Cl_4F_6NPd$: C 49.21, H 5.47, N 1.69; found: C 48.79, H 5.05, N 1.47; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -124.04$ (s; F_{para}), -84.76 ppm (s; F_{ortho}); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.16$ (t, $J = 6.0$ Hz, 1H; H^2), 4.62 (m, 2H; H^1, H^3), 3.02 (m, 8H; CH_2-α NBu_4), 2.06 (m, 1H; H^5), 1.89 (m, 4H; H^4, H^6), 1.60 (m, 8H; CH_2-β NBu_4), 1.31 (m, 8H; CH_2-γ, NBu_4), 1.08 (m, 1H; $H^{5'}$), 0.95 ppm (t, 12H; CH_3 NBu_4).

Complex 4: Yield, 79%; elemental analysis calcd (%) for $C_{34}H_{45}F_{10}NPd$: C 53.44, H 5.94, N 1.83; found: C 52.99, H 5.38, N 1.85; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -165.60$ (t; F_{para}), -165.20 (m; F_{meta}), -110.60 ppm (m; F_{ortho}); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.15$ (t, $J = 6.6$ Hz, 1H; H^2), 4.65 (br m, 2H; H^1, H^3), 3.02 (m, 8H; CH_2-α NBu_4), 2.07 (m, 1H; H^5), 1.92 (m, 4H; H^4, H^6), 1.60 (m, 8H; CH_2-β NBu_4), 1.31 (m, 8H; CH_2-γ NBu_4), 1.10 (m, 1H; $H^{5'}$), 0.95 ppm (t, $J = 6.6$ Hz, 12H; CH_3 NBu_4).

Complex 5: Yield, 79%; elemental analysis calcd (%) for $C_{40}H_{44}F_{15}NPd$: C 51.65, H 4.77, N 1.50; found: C 51.08, H 4.55, N 1.63; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = 165.43$ (t, 2F; $F_{para\ Rf\text{-}Pd}$), -165.13 (m, 4F; $F_{meta\ Rf\text{-}Pd}$), -163.96 (m, 2F; $F_{meta\ Rf\text{-}C}$), -159.27 (t, 1F; $F_{para\ Rf\text{-}C}$), -141.73 (m, 2F; $F_{ortho\ Rf\text{-}C}$), -110.37 ppm (m, 4F, $F_{ortho\ Rf\text{-}Pd}$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.47$ (t, $J = 6.0$ Hz, 1H; H^2), 4.83 (t, $J = 6.0$ Hz, 2H; H^1, H^3), 3.03 (m, 8H; CH_2-α NBu_4), 2.70 (m, 1H; H^5), 2.49 (m, 2H; H^4, H^6), 2.16 (m, 2H; $H^{4'}$, $H^{6'}$), 1.55 (m, 8H; CH_2-β NBu_4), 1.32 (m, 8H; CH_2-γ NBu_4), 0.94 ppm (t, $J = 7.0$ Hz, 12H; CH_3 NBu_4).

Complex 11:[35] Yield, 91%; elemental analysis calcd (%) for $C_{33}H_{43}F_{10}NO_2Pd$: C 50.68, H 5.54, N 1.79; found: C 49.94, H 5.48, N 1.83; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -167.81$ (t; F_{para}), -167.18 (m; F_{meta}), -111.28 ppm (m; F_{ortho}); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.42$ (s, 1H; CH acac), 3.02 (m, 8H; CH_2-α NBu_4), 2.08 (s, 6H; CH_3 acac), 1.60 (m, 8H; CH_2-β NBu_4), 1.31 (m, 8H; CH_2-γ NBu_4), 0.95 ppm (t, 12H; CH_3 NBu_4).

Complex 12: Yield, 90%; elemental analysis calcd (%) for $C_{34}H_{46}F_{10}N_2PdS_2$: C 47.68, H 5.58, N 3.37; found: C 47.22, H 5.40, N 3.49; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -165.40$ (m; F_{meta}), -164.60 (t; F_{para}), -112.20 ppm (m; F_{ortho}); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.75$ (q, 4H; $J = 9.0$ Hz, CH_2 Et_2NCS_2), 3.20 (t, 6H; $J = 9.0$ Hz, CH_3 Et_2NCS_2), 3.02 (m, 8H; CH_2-α NBu_4), 1.60 (m, 8H; CH_2-β NBu_4), 1.31 (m, 8H; CH_2-γ NBu_4), 0.95 ppm (t, 12H; CH_3 NBu_4).

Complex 13: Yield, 65%; elemental analysis calcd (%) for $C_{37}H_{48}Cl_4F_6N_2Pd$: C 50.33, H 5.48, N 3.17; found: C 49.28, H 5.05, N 3.17; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -125.10$ (t, $J = 2.0$ Hz, 1F; F^1_{para}), -123.20 (s, 1F; F^2_{para}), -87.12 (m, AA′XX′ spin system $J = 7.0$, 4.2 Hz, 2F; F^2_{ortho}), -84.33 (m, AA′XX′ spin system, $J = 7.0$, 4.2, 2.0 Hz, 2F; F^1_{ortho}); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.96$ (d, $J = 7.8$ Hz, 1H; C_6H_4), 6.82 (td, $J = 7.8$, 0.9 Hz, 1H; C_6H_4), 6.70 (td, $J = 7.0$, 0.9 Hz, 1H; C_6H_4), 6.49 (d, $J = 7$ Hz, 1H; C_6H_4), 3.88 (s, 2H; CH_2), 2.88 (m, 8H; CH_2-α

NBu_4), 2.52 (s, 6H; CH_3), 1.45 (m, 8H; CH_2-β NBu_4), 1.29 (m, 8H; CH_2-γ NBu_4), 0.92 ppm (t, J=6.6 Hz, 12H; CH_3 NBu_4).

Synthesis of dimeric palladium derivatives with aryl bridges

Method A [$Pd_2(\mu\text{-}C_6F_5)_2(\eta^3\text{-}C_3H_5)_2$] (7): [$Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2$] (0.0438 g, 0.120 mmol) was added to a solution of $AgBF_4$ (0.0466 g, 0.239 mmol) in acetone (15 mL). The mixture was stirred for 15 min in the dark and the suspension was filtered. Upon addition of complex **2** (0.1891 g, 0.239 mmol) to the filtrate the solution immediately changed from yellow to orange. The solvent was evaporated to dryness and *i*PrOH (5 mL) was added to the residue. The orange solid formed was filtered, washed with *i*PrOH, and air-dried (0.1197 g, 72% yield). The solid obtained is a 1:1 mixture of *cis* and *trans* isomers. Elemental analysis calcd (%) for $C_{18}H_{10}F_{10}Pd_2$: C 34.37, H 1.60; found: C 34.00, H 1.52; ^{19}F NMR (282 MHz, $CDCl_3$): δ=−163.90 (m, 1F; $F_{meta,cis}$), −163.48 (m, 2F; $F_{meta,trans}$), −163.04 (m, 1F; $F_{meta,cis}$), −148.02 (t, 2F; $F_{para,cis-trans}$), −99.37 ppm (m, 4F; $F_{ortho,cis-trans}$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.32 (br m, 2H; $H^2_{cis-trans}$), 3.64 (d, J=7.0 Hz, 4H; $H_{syn,cis+trans}$), 2.91 ppm (br m, 4H; $H_{anti,cis-trans}$); ^{1}H NMR (300 MHz, $CDCl_3$, 213 K): δ=5.33 (br m, 2H; $H^2_{cis-trans}$), 3.62 (d, J=6.6 Hz, 2H; $H_{syn,cis}$)*, 3.65 (d, J=6.6 Hz, 2H; $H_{syn,trans}$)*, 3.02 (d, J=13.2 Hz, 2H; $H^3_{anti,trans}$)*, 2.87 ppm (d, J=13.2 Hz, 2H; $H_{anti,cis}$)*; *: *cis* and *trans* assignments for these signals are only tentative.

Complexes **6**, **8**–**10** can be prepared in a similar way.

Method B [$Pd_2(\mu\text{-}C_6F_5)_2(\eta^3\text{-}C_6H_9)_2$] (9): A solution of $Ag(C_6F_5)$ was previously prepared by mixing $AgBF_4$ (0.0511 g, 0.262 mmol) and $(NBu_4)[Ag(C_6F_5)_2]$ (0.1797 g, 0.262 mmol) in Et_2O (20 mL). The suspension was stirred at 0°C for 10 min in the dark and the insoluble $(NBu_4)BF_4$ was filtered. [$Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_6H_9)_2$] (0.1064 g, 0.239 mmol) was added to the filtrate and a deep orange solution was immediately formed. The solvent was evaporated to dryness and *n*-hexane (10 mL) was added to the residue. An orange solid was obtained which was filtered, washed with *n*-hexane and air-dried (0.091 g, 55% yield). The solid obtained is a 1:1 mixture of *cis* and *trans* isomers. Elemental analysis calcd (%) for $C_{24}H_{18}F_{10}Pd_2$: C 40.65, H 2.37; found: C 40.66, H 2.37; ^{19}F NMR (282 MHz, $CDCl_3$): δ=−164.40 (m, 1F; $F_{meta,cis}$), −164.00 (m, 2F; $F_{meta,trans}$), −163.80 (m, 1F; $F_{meta,cis}$), −150.40 (t, 2F; F_{para}), −103.20 (m, 1F; $F_{ortho,cis}$), −101.60 (m, 2F; $F_{ortho,trans}$), −100.00 ppm (m, 1F $F_{ortho,cis}$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.40 (br m, 2H; H^2), 4.65 (m, 4H; H^1, H^3), 1.96 (m, 2H; H^5), 1.50 (m, 8H; H^4, H^6), 1.20 ppm (m, 2H; H^5).

Complexes **6**, **8**–**10** can also be prepared by using method B, but yields are generally lower than when method A is used.

Complex 6: Yield 66% (method A); elemental analysis calcd (%) for $C_{18}H_{10}Cl_4F_6Pd_2$: C 31.11, H 1.45; found: C 31.02, H 1.61; ^{19}F NMR (282 MHz, $CDCl_3$): δ=−107.50 (s, 4F; $F_{para,cis-trans}$), −74.04 (s, 2F; $F_{ortho,cis}$), −73.91 (s, 4F; $F_{ortho,trans}$), −73.64 ppm (s, 2F; $F_{ortho,cis}$); ^{19}F NMR (282 MHz, $CDCl_3$, 213 K): δ=−107.50 (s, 1F; $F_{para,cis}$), −107.53 (s, 1F; $F_{para,trans}$), −74.60 (s, 1F; $F_{ortho,cis}$), −74.45 (s, 2F; $F_{ortho,trans}$), −74.03 ppm, (s, 1F; $F_{ortho,cis}$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.32 (br m, 2H; H^2), 3.62 (d, J=7.0 Hz, 4H; H_{syn}), 2.88 (br m, 4H; H_{anti}); ^{1}H NMR (300 MHz, $CDCl_3$, 213 K): δ=5.36 (tt, J=12.6, 6.6 Hz, 1H; H^2, *cis*)*, 5.30 (tt, J=12.9, 6.4 Hz, 1H; H^2, *trans*)*, 3.67 (d, J=6.6 Hz, 2H; $H_{syn,cis}$)*, 3.64 (d, J=6.4 Hz, 2H; $H_{syn,trans}$)*, 2.98 (d, J=12.9 Hz, 2H; $H_{anti,trans}$)*, 2.84 (d, J=12.6 Hz, 2H; $H_{anti,cis}$)*; *: *cis* and *trans* assignments for these signals are only tentative.

Complex 8: Yield 76% (method A); elemental analysis calcd (%) for $C_{24}H_{18}Cl_4F_6Pd_2$: C 37.20, H 2.34; found: C 33.87, H 2.29; ^{19}F NMR (282 MHz, $CDCl_3$): δ=−110.11 (s, 2F; F_{para}), −77.87 (s, 1F; $F_{ortho,cis}$), −76.40 (s, 2F; $F_{ortho,trans}$), −74.96 ppm (s, 1F; $F_{ortho,cis}$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.34 (m, 2H; H^2), 4.60 (m, 4H; H^1, H^3), 1.98 (m, 2H; H^5), 1.46 (m, 8H; H^4, H^6), 1.20 ppm (m, 2H; H^5).

Complex 10: Yield 64% (method A); elemental analysis calcd (%) for $C_{36}H_{16}F_{20}Pd_2$: C 41.52, H 1.55; found: C 41.58, H 1.76. ^{19}F NMR (282 MHz, $CDCl_3$): δ=−163.73 (m, 1F; $F_{meta,cis}$), −163.18 (m, 2F; $F_{meta,trans}$), −162.92 (m, 1F; $F_{meta,cis}$), −162.11 (m, 4F; $F_{meta,Rf\text{-}C}$), −156.58 (t, 1F; $F_{para,Rf\text{-}C,cis}$)*, 156.52 (t, 1F; $F_{para,Rf\text{-}C,trans}$)*, −149.26 (t, 1F; $F_{para,cis}$)*, −149.15 (t, 1F; $F_{para,trans}$)*, −141.80 (m, 4F; $F_{ortho,Rf\text{-}C}$), −100.50 (m, 1F; $F_{ortho,cis}$), −100.03 (m, 2F; $F_{ortho,trans}$), −99.40 ppm (m, 1F; $F_{ortho,cis}$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.61 (t, J=5.7 Hz, 1H; H^2, *cis*)*, 5.50 (t, J=5.7 Hz, 1H; H^2_{trans})*, 4.78 (t, J=5.7 Hz, 2H; H^1, H^3_{cis})*, 4.76 (t, J=5.7 Hz, 2H; H^1, H^3_{trans})*, 2.63 (m, 2H; $H^5_{cis-trans}$), 2.20–1.80 ppm (m, 8H; H^4, $H^{4'}$, H^6, $H^6_{cis-trans}$ *: *cis* and *trans* assignments for these signals are only tentative.

[$Pd_2(\mu\text{-}(2,4,6\text{-}C_6H_2Me_3))_2(5\text{-}C_6F_5\text{-}1,3\text{-}\eta^3\text{-}C_6H_8)_2$] (16): A solution of $Ag(2,4,6\text{-}C_6H_2Me_3)$ (0.1309 g, 0.5767 mmol) and [$Pd_2(\mu\text{-}Br)_2(5\text{-}C_6F_5\text{-}1,3\text{-}\eta^3\text{-}C_6H_8)_2$] (0.2000 g, 0.2307 mmol) in Et_2O (10 mL) was stirred at 0°C for 30 min in the dark and the insoluble AgBr was filtered. The solvent was evaporated under reduced pressure to about 5 mL and cooled. A purple solid was obtained which was filtered and air-dried (0.1107 g, 51% yield). The solid obtained was a 1:1.3 mixture of *cis* and *trans* isomers. Elemental analysis calcd (%) for $C_{42}H_{38}F_{10}Pd_2$: C 53.35, H 4.05; found: C 52.66, H 3.60. ^{19}F NMR (282 MHz, $CDCl_3$): δ=−162.75 (m, 4F; $F_{meta,cis-trans}$), −157.75 (t, 1F; $F_{para,cis}$), −157.67 (t, 1F; $F_{para,trans}$), −142.69 (m, 2F; $F_{ortho,cis}$), −142.60 ppm (m, 2F; $F_{ortho,trans}$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.77 (s, 1H; $H_{ortho,Mes,cis}$), 6.71 (s, 2H; $H_{ortho,Mes,trans}$), 6.63 (s, 1H; $H_{ortho,Mes,cis}$), 5.26 (t, J=5.7 Hz, 1H; H^2_{trans}), 5.18 (t, J=5.7 Hz, 1H; H^2_{cis}), 3.98 (m, 4H; H^1, $H^3_{cis-trans}$), 2.83 (s, 3H; $Me_{ortho,cis}$), 2.57 (s, 6H; $Me_{ortho,trans}$), 2.28 (s, 3H; $Me_{ortho,cis}$), 2.24 (s, 6H; $Me_{para,cis-trans}$), 2.52 (m, 2H; $H^5_{cis-trans}$), 1.90–1.78 ppm (m, 8H; H^4, $H^{4'}$, H^6, $H^6_{cis-trans}$).

Formation of [$Pd(\eta^3\text{-}C_6H_9)(\mu\text{-}C_6Cl_2F_3)_2Pd(\eta^3\text{-}C_3H_5)$] (19) in solution: Complexes **6** (0.0069 g, 0.010 mmol) and **8** (0.0077 g, 0.010 mmol) were dissolved of $CDCl_3$ (0.6 mL) and the mixture was analyzed by NMR spectroscopy after 5 min. Complexes **6**, **8**, and **19** were detected.

Complex **19**: ^{19}F NMR (282 MHz, $CDCl_3$): δ=−74.62 (s, 2F; F_{ortho}), −75.72 (s, 2F; F_{ortho}), −108.99 ppm (s, 2F; F_{para}).

Synthesis of [$Pd(C_6Cl_2F_3)\{\kappa^2\text{-}C,N\text{-}C_6H_4CH_2N(CH_3)_2\}$(acetone)] (14): A solution of $Ag(C_6Cl_2F_3)$ was previously prepared by mixing $AgBF_4$ (0.0723 g, 0.371 mmol) and $(NBu_4)[Ag(C_6Cl_2F_3)_2]$ (0.2786 g, 0.371 mmol) in Et_2O (20 mL). The suspension was stirred at 0°C for 10 min in the dark and the insoluble $(NBu_4)BF_4$ was filtered. The filtrate was evaporated to dryness and acetone was added (30 mL). [$Pd_2(\mu\text{-}Cl)_2\{\kappa^2\text{-}C,N\text{-}PhCH_2N(CH_3)_2\}$] (0.2050 g, 0.371 mmol) was added to this solution and the mixture was stirred for 20 min. The AgCl formed was filtered, the solution was evaporated to about 5 mL, and *n*-hexane (10 mL) was added. The yellow solid that formed was filtered, washed with *n*-hexane, and vacuum-dried (0.1655 g, 46% yield). Elemental analysis calcd (%) for $C_{18}H_{18}Cl_2F_3NOPd$: C 43.34, H 3.63, N 2.81; found: C 43.00, H 3.48, N 2.65; ^{19}F NMR (282 MHz, $CDCl_3$): δ=−120.06 (s, 1F; F_{para}), −87.29 ppm (s, 2F; F_{ortho}); ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.94 (m, 2H; C_6H_4), 6.75 (m, 1H; C_6H_4), 6.35 (d, J=7.6 Hz, 1H; C_6H_4), 3.92 (s, 2H; CH_2), 2.74 (s, 6H; CH_3, NMe_2), 2.28 ppm (s, 6H; CH_3, acetone).

Preparation of 15: Complex **15** can be prepared in a similar way but using an Et_2O solution of $Ag(C_6F_5)$. ^{19}F NMR (282 MHz, $CDCl_3$): δ=−119.39 (s, 1F; F_{para}), −87.40 ppm (s, 2F; F_{ortho}); ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.92 (m, 2H; C_6H_4), 6.72 (m, 1H; C_6H_4), 6.30 (m, 1H; C_6H_4), 3.90 (s, 2H; CH_2), 3.51 (q, 4H; CH_2 Et_2O), 2.72 (s, 6H; CH_3, -NMe_2), 1.38 ppm (t, 6H; CH_3 Et_2O).

The analogous reactions with **11** and **12** led to unidentified products showing broad signals in the NMR spectra (see Results).

Determination of the activation parameters for the *cis–trans* exchange: Variable-temperature NMR spectra were recorded using a VT-100 temperature control unit on Bruker AC300 and ARX300 spectrometers. The temperature was calibrated by measuring the difference between the chemical shifts of MeOH signals at each temperature.[36] First-order rate constants for exchange (k_{exch}) were obtained from line-shape analysis by matching the observed variable-temperature ^{1}H NMR spectra of complex **6** in $CDCl_3$ with those simulated using the computer program gNMRV3.6.5.[14] An Eyring plot of $\ln(k_{exch}/T)$ versus $1/T$ afforded the activation parameters, ΔH^{+} and ΔS^{+}, as the slope and the intercept respectively of the best fit line drawn by a least-squares analysis. Uncertainties in the activation parameters were calculated from the uncertainties of the slope and the intercept of the best fit line, as reported previously.[2a,37]

X-ray crystal-structure determinations: Crystals of **6** and **18** were obtained by slow diffusion of *n*-hexane in solutions of the complexes in dichloromethane at −20°C. Crystals of complex **16** were obtained from Et_2O at −20°C. A colorless prism of dimensions 0.05×0.11×0.14 mm^3

(**18**), a purple prism of dimensions $0.07\times0.29\times0.29\ mm^3$ (**16**), and an orange prism of dimensions $0.02\times0.12\times0.16\ mm^3$ (**6**) were mounted on the tip of glass fibers. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å). Reflections were collected, intensities integrated, and the structure was solved by direct-methods procedure.[38] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. CCDC-209044 (**6**), CCDC-209043 (**16**) and CCDC-209040 (**18**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223 336033; or deposit@ccdc.cam.uk). Relevant crystallographic data for the three complexes are given below. Data and comments for the crystal structure determination of complexes **7** (CCDC-209042) and **9** (CCDC-209041) are included as Supporting Information.

Complex 6: Crystal data: triclinic $P\bar{1}$: $a=7.305(3)$, $b=7.368(3)$, $c=10.291(4)$ Å; $\alpha=74.914(8)°$, $\beta=70.111(8)°$, $\gamma=84.992(9)°$; $V=502.8(4)$ Å^3; formula unit: $C_{18}H_{10}Cl_4F_6Pd_2$ with $Z=1$; formula weight = 694.86; $\rho_{calcd}=2.295\ g\,cm^{-3}$; $F(000)=332$; $\mu(Mo_{K\alpha})=2.377\ mm^{-1}$. 2315 reflections were collected ($1.65° > \theta > 23.31°$). Full-matrix least-squares refinement (on F^2) based on 1431 independent reflections converged with 136 variable parameters and no restraints. $R1=0.0758$, for $F^2 > 2\sigma(F^2)$; $wR2=0.1921$.[39] GoF (F^2) = 1.020. $\Delta\rho_{max}=2.256$ (close to Pd) $\Delta\rho_{min}=-1.721$ e Å^3.

Complex 16: Crystal data: monoclinic P-1: $a=9.254$ (5), $b=9.352$ (5), $c=13.109$ (5) Å; $\alpha=103.654$ (5)°, $\beta=97.362$ (5)°, $\gamma=91.872$ (5)°; $V=1091.0$ (9) Å^3; formula: $C_{23}H_{19}F_5O_{0.5}Pd$, $Z=2$; $M_r=504.78$; $\rho_{calcd}=1.537\ g\,cm^{-3}$; $F(000)=504$; $\mu(Mo_{K\alpha})=0.900\ mm^{-1}$. 2711 reflections were collected ($1.61° > \theta > 23.25°$). Full-matrix least-squares refinement (on F^2) based on 2277 independent reflections converged with 274 variable parameters and no restraints. $R1=0.0292$ for $F^2>2\sigma(F^2)$; $wR2=0.0807$.[39] GoF (F^2) = 1.102. $\Delta\rho_{max}=0.298$ e Å^3, $\Delta\rho_{min}=-0.263$ e Å^3.

Complex 18: Crystal data: monoclinic $P2_1/n$: $a=15.0723(15)$, $b=14.6622(15)$, $c=19.657(2)$ Å; $\alpha=90.00°$, $\beta=93.290(2)°$, $\gamma=90.00°$; $V=4336.9(8)$ Å^3; formula: $C_{40}H_{44}Cl_4F_{11}NPd$, $Z=4$; $M_r=995.96$; $\rho_{calcd}=1.525\ g\,cm^{-3}$; $F(000)=2016$; $\mu(Mo_{K\alpha})=0.751\ mm^{-1}$. 20345 reflections were collected ($1.66° > \theta > 23.28°$). Full-matrix least-squares refinement (on F^2) based on 6249 independent reflections converged with 518 variable parameters and no restraints. $R1=0.0310$, for $F^2>2\sigma(F^2)$; $wR2=0.0727$.[39] GoF (F^2) = 0.914. $\Delta\rho_{max}=0.433$ e Å^3, $\Delta\rho_{min}=-0.323$ e Å^3.

Acknowledgements

This work was supported by the Dirección General de Investigación (Grant no. BQU2001–2015) and the Junta de Castilla y León (Projects VA057/03 and VA058/03). We also thank Iberdrola for a fellowships to B.M.-R.

[1] Some examples: Palladium: a) A. C. Albéniz, P. Espinet, B. Martín-Ruiz, *Chem. Eur. J.* **2001**, *7*, 2481–2489; b) R. Usón, J. Forniés, M. Tomás, J. M. Casas, R. Navarro, *J. Chem. Soc. Dalton Trans.* **1989**, 169–172; Platinum: c) L. R. Falvello, J. Forniés, C. Fortuño, F. Durán, A. Martín, *Organometallics*, **2002**, *21*, 2226–2234; d) I. Ara, L. R. Falvello, J. Forniés, E. Lalinde, A. Martín, F. Martínez, M. T. Moreno, *Organometallics* **1997**, *16*, 5392–5405; e) R. Usón, J. Forniés, L. R. Falvello, M. Tomás, J. M. Casas, A. Martín, F. A. Cotton, *J. Am. Chem. Soc.* **1994**, *116*, 7160–7165; f) R. Usón, J. Forniés, M. Tomás, J. M. Casas, F. A. Cotton, L. R. Falvello, X. Feng, *J. Am. Chem. Soc.* **1993**, *115*, 4145–4154; g) R. Usón, J. Forniés, M. Tomás, J. M. Casas, F. A. Cotton, L. R. Falvello, R. Llusar, *Organometallics* **1988**, *7*, 2279–2285; h) D. G. Evans, G. R. Hughes, D. M. P. Mingos, J. M. Bassett, A. J. Welch, *J. Chem. Soc. Chem. Commun.* **1980**, 1255–1257; Nickel: i) T. R. Belderraín, E. Gutiérrez, A. Monge, M. C. Nicasio, M. Paneque, M. L. Poveda, E. Carmona, *Organometallics* **1993**, *12*, 4431–4442; j) M. A. Bennett, K. D. Griffiths, T. Okano, V. Parthasararhi, G. B. Robertson, *J. Am. Chem. Soc.* **1990**, *112*, 7047–7048; interaction between Pd and the C_{ipso} of aryl phosphines in Pd^I complexes has been described and could be considered as an aryl bridge between Pd and P: k) T. Murahashi, T. Otani, T. Okuno, H. Kurosawa, *Angew. Chem.* **2000**, *112*, 547–550; *Angew Chem. Int. Ed.* **2000**, *39*, 537–540; l) P. H. M. Budzelaar, P. W. N. M. van Leeuwen, C. F. Roobeek, A. G. Orpen, *Organometallics* **1992**, *11*, 23–25.

[2] a) A. L. Casado, J. Casares, P. Espinet, *Organometallics* **1997**, *16*, 5730–5736, and references therein; b) A. L. Casado, P. Espinet, *Organometallics* **1998**, *17*, 3677–3683.

[3] a) F. Ozawa, T. Hidaka, T. Yamamoto, A. Yamamoto, *J. Organomet. Chem.* **1987**, *330*, 253–263; b) F. Ozawa, M. Fujimoto, T. Yamamoto, A. Yamamoto, *Organometallics* **1986**, *5*, 2144–2149; c) F. Ozawa, K. Kurihara, M. Fujimori, T. Hidaka, T. Toyoshima, A. Yamamoto, *Organometallics* **1989**, *8*, 180–188.

[4] a) *Metal-catalyzed Cross-coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, **1998**; b) V. Farina, in *Comprenhensive Organometallic Chemistry II, Vol. 12* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, **1995**, Chapter 3.4.

[5] a) A. L. Casado, P. Espinet, *J. Am. Chem. Soc.* **1998**, *120*, 8978–8985; b) A. L. Casado, P. Espinet, A. M. Gallego, *J. Am. Chem. Soc.* **2000**, *122*, 11771–11782; c) Y. Hatanaka, T. Hiyama, *J. Am. Chem. Soc.* **1990**, *112*, 7794–7796.

[6] a) R. Usón, J. Forniés, J. A. Nalda, M. J. Lozano, P. Espinet, A. C. Albéniz, *Inorg. Chim. Acta* **1989**, *156*, 251–256; b) R. Usón, J. Forniés, P. Espinet, E. Lalinde, P. G. Jones, G. M. Sheldrick, *J. Chem. Soc. Dalton Trans.* **1982**, 2389–2395; c) R. Usón, J. Forniés, R. Navarro, M. P. García, B. Bergareche, *Inorg. Chim. Acta* **1977**, *25*, 269–271; d) P. Espinet, J. Martínez-Ilarduya, C. Pérez-Briso, A. L. Casado, M. A. Alonso, *J. Organomet. Chem.* **1998**, *551*, 9–20.

[7] a) A. C. Albéniz, A. L. Casado, P. Espinet, *Organometallics* **1997**, *16*, 5416–5423; b) M. A. Alonso, J. Casares, P. Espinet, J. M. Martínez-Ilarduya, C. Pérez-Briso, *Eur. J. Inorg. Chem.* **1998**, 1745–1753; c) J. A. Casares, S. Coco, P. Espinet, Y-S. Lin, *Organometallics* **1995**, *14*, 3058–3067; d) A. L. Casado, P. Espinet, *Organometallics* **1997**, *16*, 770–779; e) A. C. Albéniz, A. L. Casado, P. Espinet, *Inorg. Chem.* **1999**, *38*, 2510–2515.

[8] R. Usón, A. Laguna, J. A. Abad, *J. Organomet. Chem.* **1983**, *246*, 341–345.

[9] NMR signals were compared with independently prepared samples of *cis*-$[Pd(C_6F_5)_2(PEt_3)_2]$ (R. Usón, J. Forniés, P. Espinet, F. Martínez, M. Tomás, *J. Chem. Soc. Dalton Trans.* **1981**, 463–465) and $[Pd_2(\mu\text{-}OH)_2(PEt_3)_4](BF4)_2$ (prepared by addition of $AgBF_4$ to a wet solution of $[PdCl_2(PEt_3)_2]$ in acetone following the procedure described by S. Ganguly, J. T. Mague, D. M. Roundhill, *Inorg. Chem.* **1992**, *31*, 3831–3835; $^{31}P\{^1H\}$ NMR, $CDCl_3$, $\delta=48.8$ ppm).

[10] Cambridge Structural Database, CCDC, 12 Union Road, Cambridge CB2 1EZ (UK).

[11] Some reported X-ray structures of η^3-cyclohexenyl derivatives: a) C. Jonasson, M. Kritikos, J. -E. Backvall, K. J. Szabo, *Chem. Eur. J.* **2000**, *6*, 432–436; b) Y. Tsuji, T. Kusui, T. Kojima, Y. Sugiura, N. Yamada, S. Tanaka, M. Ebihara, T. Kawamura, *Organometallics* **1998**, *17*, 4835–4841; c) H. Grennberg, V. Langer, J. -E. Backvall, *J. Chem. Soc. Chem. Commun.* **1991**, 1190–1192; d) A. C. Albéniz, P. Espinet, C. Foces-Foces, F. H. Cano, *Organometallics* **1990**, *9*, 1079–1085;

[12] B. Akermark, J. D. Oslob, P. -O. Norrby, *Organometallics* **1995**, *14*, 1688–1693.

[13] a) J. W. Faller, M. E. Thompsen, M. J. Mattina, *J. Am. Chem. Soc.* **1971**, *93*, 2642–2653; b) K. Vrieze in *Dynamic Nuclear Magnetic Resonance Spectroscopy* (Eds.: L. M. Jackman, F. A. Cotton), Academic Press, London, **1975**, pp. 441–487; c) S. Hansson, P.-O. Norrby, M. P. T. Sjögren, B. Akermark, M. E. Cucciolito, F. Giordano, A. Vitagliano, *Organometallics* **1993**, *12*, 4940–4948; d) P. S. Pregosin, R. Salzmann, A. Togni, *Organometallics* **1995**, *14*, 842–847.

[14] gNMR v3.6.5, IvorySoft; Cherwell Scientific Publishing Ltd. Oxford.

[15] a) J.-M. Rosset, M. P. Glenn, J. D. Cotton, A. C. Willis, C. H. L. Kennard, K. A. Byriel, B. H. Riches, W. Kitching, *Organometallics* **1998**, *17*, 1968–1983; b) A. C. Albéniz, P. Espinet, C. Foces-Foces, F. H. Cano, *Organometallics* **1990**, *9*, 1079–1085; c) P. W. N. M. Van Leeuwen, J. Lukas, A. P. Praat, M. Appelman, *J. Organomet. Chem.* **1972**, *38*, 199–207; d) D. L. Tibbetts, T. L. Brown, *J. Am. Chem. Soc.* **1969**, *91*, 1108–1112; e) J. Powell, *J. Am. Chem. Soc.* **1969**, *91*, 4311–4313; f) P. D. Hampton, S. Wu, T. M. Alam, J. P. Claverie, *Organometallics* **1994**, *13*, 2066–2074.

[16] a) S. Álvarez, A. A. Palacios, G. Aullón, *Coord. Chem. Rev.* **1999**, *185–186*, 431–450; b) G. Aullón, P. Alemany, S. Álvarez, *J. Organomet. Chem.* **1994**, *478*, 75–82; c) G. Aullón, S. Álvarez, *Organometallics* **2002**, *21*, 2627–2634; d) G. Aullón, S. Álvarez, *Inorg. Chem.* **2001**, *40*, 4937–4946; e) G. Aullón, A. Lledós, S. Álvarez, *Inorg. Chem.* **2000**, *39*, 906–916; f) G. Aullón, G. Ujaque, A. Lledós, S. Álvarez, P. Alemany, *Inorg. Chem.* **1998**, *37*, 804–813; g) A. A. Palacios, G. Aullón, P. Alemany, S. Álvarez, *Inorg. Chem.* **2000**, *39*, 3166–3175; h) G. Aullón, G. Ujaque, A. Lledós, S. Álvarez, *Chem. Eur. J.* **1999**, *5*, 1391–1410; i) P. Alemany, S. Álvarez, *Inorg. Chem.* **1992**, *31*, 4266–4275; j) A. A. Palacios, P. Alemany, S. Álvarez, *J. Chem. Soc. Dalton Trans.* **2002**, 2235–2243; k) R. H. Simons, K. J. Galat, J. D. Bradshaw, W. J. Youngs, C. A. Tessier, G. Aullón, S. Álvarez, *J. Organomet. Chem.* **2001**, *628*, 241–254.

[17] The few values in this search below 85° are always associated with special steric hindrance with the other ligands in the coordination sphere: a) I. Ara, J. R. Berenguer, E. Eguizabal, J. Forniés, E. Lalinde, A. Martín, F. Martínez. *Organometallics* **1998**, *17*, 4578–4596; b) I. Ara, L. R. Falvello, S. Fernández, J. Forniés, E. Lalinde, A. Martín, M. T. Moreno, *Organometallics* **1997**, *16*, 5923–5937.

[18] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, **1960**.

[19] G. López, J. Ruiz, G. García, C. Vicente, J. Casabó, E. Molins, C. Miravilles, *Inorg. Chem.* **1991**, *30*, 2605–2610.

[20] As an example, the angle formed by the two aryl groups in *cis*-$[Pd(C_6F_5)_2(PPh_3)_2]$ is 84.745° (K. Miki, N. Nasaki, H. Kurosawa, *Acta Crystallogr. Sect. C* **1988**, *44*, 1132–1134) showing that the two PPh_3 ligands are exerting some repulsion on the C_6F_5 groups in a structure of type **A**. It seems likely that PEt_3 should exert a high steric hindrance in a structure of type **B**.

[21] a) C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165–195; b) P. Segura, *J. Org. Chem.* **1985**, *50*, 1045–1053.

[22] D.-L. Long, W.-T. Wong, S. Shi, X.-Q. Xin, J.-S. Huang, *J. Chem. Soc. Dalton Trans.* **1997**, 4361–4365.

[23] R. Usón, J. Forniés, *Adv. Organomet. Chem.* **1988**, *28*, 219–297.

[24] J. Yin, M. P. Rainka, X.-X. Zhang, S. L. Buchwald, *J. Am. Chem. Soc.* **2002**, *124*, 1162–1163.

[25] a) T. Yagyu, M. Hamada, K. Osakada, T. Yamamoto, *Organometallics* **2001**, *20*, 1087–1101; b) V. V. Grushin, *Organometallics* **2000**, *19*, 1888–1900.

[26] J. A. Casares, P. Espinet, G. Salas, *Chem. Eur. J.* **2002**, *8*, 2–11.

[27] a) F. Basolo, R. G. Pearson, *Mechanisms of Inorganic Reactions: A Study of Metal Complexes in Solution*, 2nd ed., Wiley, New York, **1967**, p. 414; b) J. A. Casares, P. Espinet, J. M. Martínez de Ilarduya, Y.-S. Lin, *Organometallics* **1997**, *16*, 770–779.

[28] W. T. Dent, R. Long, A. J. Wilkinson, *J. Chem. Soc.* **1964**, 1585–1588.

[29] S. Imaizumi, T. Matsuhisa, Y. Senda, *J. Organomet. Chem.* **1985**, *280*, 441–448.

[30] Z. Kanda, Y. Nakamura, S. Kawaguchi, *Inorg. Chem.* **1978**, *17*, 910–914.

[31] M. C. Cornock, T. A. Stepehnson, *J. Chem. Soc. Dalton Trans.* **1977**, 683–688.

[32] A. C. Cope, E. C. Friedrich, *J. Am. Chem. Soc.* **1968**, *90*, 909–913.

[33] C. Eaborn, N. Farrell, J. L. Murphy, A. Pidcock, *J. Chem. Soc. Dalton Trans.* **1976**, 58–67.

[34] E. M. Meyer, S. Gambarotta, C. Floriani, Chiesi-A. Villa, C. Guastini, *Organometallics* **1989**, *8*, 1067–1079.

[35] This complex has been prepared before by a different synthetic route: a) J. Forniés, R. Navarro, E. P. Urriolabeitia, *J. Organomet. Chem.* **1990**, *390*, 257–265; b) J. Forniés, F. Martínez, R. Navarro, E. P. Urriolabeitia, *Polyhedron* **1990**, *9*, 2181–2183.

[36] A. L. Van Geet, *Anal. Chem.* **1970**, *42*, 679–6800.

[37] L. Kirkup, *Experimental Methods*, Wiley, Brisbane, **1994**.

[38] The data analysis and the drawing were performed with the programs: SMART V5.051, 1998; SAINT V6.02, 1999; Sheldrick, G. M. SHELXTL V5.1, 1998; Bruker AXS, Inc. Madison, Wi. SIR 92; A. Altomare, G. Cascarano, C. Giacovazzo, A. Gualardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350.

[39] $R1 = \Sigma\,(||F_0| - |F_c||)/\Sigma|F_0|)$; $wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$.

Received: June 17, 2004
Published online: November 17, 2004