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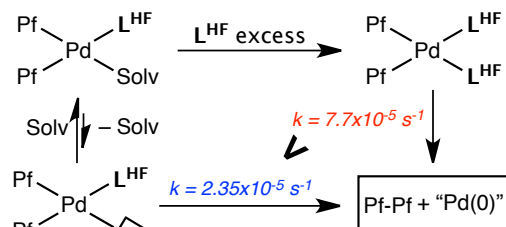
The Intriguing Behavior of an Apparently Simple Coupling Promoter Ligand, $\text{PPh}_2(p\text{-C}_6\text{H}_4\text{-C}_6\text{F}_5)$, in Their Pd Complexes

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ABSTRACT: Ligand $\text{PPh}_2(p\text{-C}_6\text{H}_4\text{-C}_6\text{F}_5)$, L^{HF} , is an example of monodentate biphenyl phosphine that allows for cis coordination of two phosphines to Pd, as in complex *cis*- $[\text{Pd}(\text{C}_6\text{F}_5)_2\text{Pd}(\text{L}^{\text{HF}})_2]$ (**A**). At 25 °C complex **A** undergoes easy reductive elimination to decafluorobiphenyl and, competitively, isomerizes to *trans*- $[\text{Pd}(\text{C}_6\text{F}_5)_2\text{Pd}(\text{L}^{\text{HF}})_2]$ via a 3-coordinated intermediate $[\text{Pd}(\text{C}_6\text{F}_5)_2\text{Pd}(\text{L}^{\text{HF}})]$. Unexpectedly the direct reductive $\text{C}_6\text{F}_5\text{-C}_6\text{F}_5$ elimination is faster from the 4-coordinated complex **A** than from the 3-coordinated intermediate. The reason of this is that two cis L^{HF} ligands play the role of a chelate with a large bite angle with tetrahedral distortion. As a matter of fact, using L^{HF} in excess gives $\Delta\text{G}_{\text{PF-PF}}^\ddagger = 23.1 \text{ kcal.mol}^{-1}$, which ranks its efficiency for coupling and formation of the corresponding Pd catalyst as better than XantPhos or PhPEWO-F, and about the same as ^tBuBrettPhos. On the other hand, complex $(\mu\text{-Cl})_2[\text{Pd}_2(\text{C}_6\text{F}_5)_2(\text{L}^{\text{HF}})_2]$ (**B**), obtained by reaction of $(\mu\text{-Cl})_2[\text{Pd}_2(\text{C}_6\text{F}_5)_2(\text{tht})_2]$ with L^{HF} , presents in the ¹⁹F NMR COSY spectrum a very intriguing *through space* coupling pattern of the F_{ortho} atoms of the C_6F_5 group in L^{HF} and the $\text{C}_6\text{F}_5\text{Cl}_2\text{-3,5}$ group on Pd. The intermitent coupling mechanism proposed is based on the switching of $\pi\text{-}\pi$ stacking of C_6F_5 with one or another Ph group of L^{HF} , which gives rise to enantiomers at the chiral P atom. Rotation around the P–biphenyl bond under hindrance of rotation around the C– C_6F_5 bond produces the intriguing selective coupling observed.



Introduction

Recently we reported a procedure to evaluate the ability of different ligands to facilitate difficult C–C couplings in Pd. It uses the so called *couplimeter* complex *cis*- $[\text{PdPF}_2(\text{THF})_2]$ (**1**) ($\text{PF} = \text{C}_6\text{F}_5$; THF = tetrahydrofuran), which allows to measure experimentally $\Delta\text{G}_{\text{PF-PF}}^\ddagger$, the activation energy of the coupling step producing Pf–Pf upon addition of the ligand. This leads to ranking the ligands according to their corresponding $\Delta\text{G}_{\text{PF-PF}}^\ddagger$ values.¹ Ligands ^tBuXPhos ($\Delta\text{G}_{\text{PF-PF}}^\ddagger = 21.8 \text{ kcal.mol}^{-1}$ at 0 °C) and PhPEWO-F ($\Delta\text{G}_{\text{PF-PF}}^\ddagger = 22.3 \text{ kcal.mol}^{-1}$ at 25 °C) are amongst the most active ligands for coupling at 0–25 °C, certainly more efficient than the typical large bite angle ligand Xantphos ($\Delta\text{G}_{\text{PF-PF}}^\ddagger = 24.2 \text{ kcal.mol}^{-1}$ at 25 °C). The byproduct of the reaction, Pf–Pf, is only hardly reactive, hence complex **1** can be used as convenient precursor to generate $[\text{Pd}^0\text{L}_n]$ catalysts *in situ*.¹

The coupling ability of PEWO-F ligands to induce C–C coupling, is due to the presence of a strongly electron-withdrawing double bond: it lowers the coupling activation energy by withdrawing the increasing electron density on Pd as the reduction from Pd^{II} to Pd^0 progresses.^{2–6} In fact the ligand PhPEWO-F, shown in Figure 1 left, induces much faster coupling than the related non-fluorinated PhPEWO-H, with H atoms instead of F atoms, because its olefin function is a stronger EWO group.¹

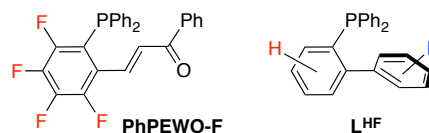


Figure 1. Partially fluorinated PEWO (PhPEWO-F) and $\text{PPh}_2(p\text{-C}_6\text{H}_4\text{-C}_6\text{F}_5)$, L^{HF} .

The double bond of Pd complexes of PEWO-F ligands, and the distal aryl of $\text{PdPR}_2(\text{biaryl})$ ligands show some similar features. For instance, the former undergo Pd–aryl insertion (1,2-addition of the Pd–aryl bond),² and the later undergo dearomative rearrangement that also starts by 1,2-addition of a Pd–aryl bond to the distal aryl.⁷ In X-ray diffraction structures of 3-coordinated palladium complexes with biphenyl phosphines one carbon atom of the distal aryl group is located at a short distance of the Pd atom; similarly, in some PEWO-F complexes one carbon atom of the olefin group is at a short distance of the Pd atom.⁸ These common features, suggestive of similarity of the respective EWO or biphenyl interactions with the Pd center, call for more detailed examination.

The electron density on the biphenyl of $\text{PR}_2(\text{biaryl})$ ligands has been reported to strongly affect the rate of reductive elimination from palladium(II) complexes. The presence of electron

donating groups on the distal arene is detrimental for the reductive elimination rate.⁹ Conversely, by similarity with our PEWO-F ligands, fluorination of the distal aryl of the biphenyl to make it a better π -acceptor fragment might enhance the coupling ability of the biaryl phosphine ligand. Although some partially fluorinated biaryl phosphines have already been reported, their catalytic performance was not particularly good when compared with non-fluorinated analogs.¹⁰⁻¹⁴ These results are not necessarily against our expectations for their coupling ability, since overall catalytic results are not informative of how a ligand behaves in the different steps of the cycle.

In this context of activity we decided to synthesize and examine the behavior of a new $\text{PR}_2(\text{biaryl})$ ligand fluorinated at the biaryl, L^{HF} (Figure 1, right). In the standard protocol to measure their coupling potential as $\Delta G_{\text{PF-PF}}^\ddagger$, we found that using 2:1 $\text{L}^{\text{HF}}:\text{Pd}$ ratio the initial coupling rate was $k = 2.35 \times 10^{-5} \text{ s}^{-1}$ ($\Delta G_{\text{PF-PF}}^\ddagger = 23.8 \text{ kcal.mol}^{-1}$) whereas, contrary to our expectations, the rate unexpectedly increased to $k = 7.7 \times 10^{-5} \text{ s}^{-1}$ ($\Delta G_{\text{PF-PF}}^\ddagger = 23.1 \text{ kcal.mol}^{-1}$) upon addition of further L^{HF} . The simple idea that biarylphosphines produce complexes with only one ligand and facilitate access to 3-coordinate Pd species, although probably substantially correct in many occasions, is too schematic, and just few (although excellent) studies on the avatar of these Pd complexes in solution are available.⁷ This work searches for the factors responsible for this odd ligand dependence of the Pf-Pf reductive elimination rate induced by L^{HF} addition on *cis*-[PdPf₂(THF)₂].

Results and discussion

Synthesis of the ligand. L^{HF} was synthesized from 2'-lithium-2,3,4,5,6-pentafluoro-1,1'-biphenyl and PPh_2Cl , and was chemically characterized in solution by ¹H, ¹⁹F, ³¹P and ¹³C NMR, as well as computationally. Its ¹⁹F NMR spectrum shows the typical AA'XX'Z spin system found for symmetrical C₆F₅ groups. The ³¹P{¹H} NMR signal is a triplet by coupling to the F¹ and F⁵ ortho atoms ($J_{\text{F-P}} = 27 \text{ Hz}$) as shown by a ¹⁹F-³¹P HSQC correlation. This supports that a fast rotation of the fluoraryl group around the C-C bond is taking place in solution at 25 °C. Values about 30 Hz are typical for ³J(F_{ortho}-P) couplings (e.g. P(C₆F₅)₃ or P(C₆F₅)₂Ph),^{15,16} and smaller values are found in other fluoroaryl phosphines such as PhPEWO-F (³J_{F-P} ≈ 15 Hz),¹⁷ and in fluoroalkylphosphines.¹⁸ Coupling constants ⁵J(¹⁹F-³¹P) are usually very small or unobservable, but exceptions are dicyclohexyl(2',6'-difluoro[1,1'-biphenyl]-2-yl)-phosphine ($J_{\text{F-P}} = 24 \text{ Hz}$) and L^{HF} .¹² The simplest explanation for these anomalous values is that there is some "through space" coupling contribution to coupling, strongly dependent on the distance between nuclei,^{19,20,21} in addition to the ⁵J scalar coupling contribution. In the palladium complexes of L^{HF} (see below) this ¹⁹F-³¹P coupling is not observed.}

The structure of L^{HF} in gas phase has been calculated by DFT (B3LYP/6-31G//B3LYP/SDD, details in SI). The most stable atropisomer is shown in Figure 2 and shows that the biphenyl group is oriented opposite to the lone electron pair of the phosphorus atom. In this conformation the P...F_{ortho} distances are 4.210 and 4.227 Å, close enough expect some through-space contribution to coupling. Note also in Figure 2 the existence of Pf-Ph stacking, with a C_{ipso}Pf-C_{ipso}Ph distance of 3.091 Å, which makes the P atom transiently chiral.

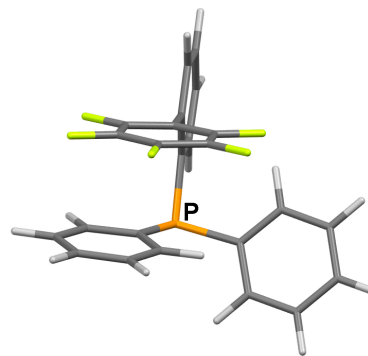
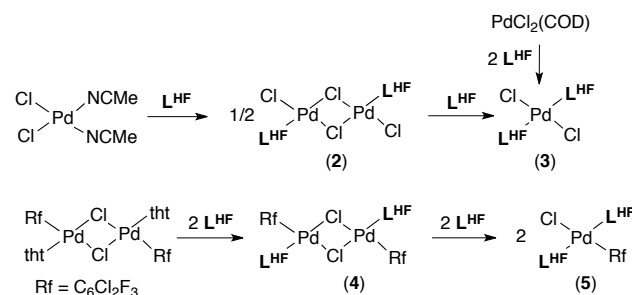


Figure 2. View of the most stable conformation of L^{HF} .

Coordination of L^{HF} to palladium(II). Scheme 1 shows the syntheses of complexes 2-5, prepared initially on purpose for the study. Other complexes appearing or being formed are discussed later, as they are required.



Scheme 1. Synthesis of complexes 2-4.

Ligand L^{HF} (one equivalent per palladium) reacts with $\text{PdCl}_2(\text{NCMe})_2$ to produce the dimer $(\mu\text{-Cl})_2[\text{PdCl}(\text{L}^{\text{HF}})]_2$ (**2**). The use of excess of L^{HF} yields the monomer $[\text{PdCl}_2(\text{L}^{\text{HF}})_2]$ (**3**), which is better obtained by reaction of $[\text{PdCl}_2(1,5\text{-COD})]$ with two equivalents of L^{HF} . Both complexes show in the IR spectrum the typical $\nu(\text{Pd}-^{35}\text{Cl})$ stretching band of terminal bonds close to 360 cm^{-1} , and the $\nu(\text{Pd}-^{37}\text{Cl})$ shoulder at 353 cm^{-1} . The dimer shows additionally absorptions for the bridging chlorides, at lower wavenumbers ($304, 294$ and $272, 264 \text{ cm}^{-1}$).

The X-ray structure of dimer **2** shows a co-planar arrangement of their two square-planar halves.²² The L^{HF} conformation is different than for the free phosphine, at least in the solid state: the modest out-of-the-plane steric hindrance of the chloro ligands allows for the distal pentafluorophenyl group of the biphenyl to occupy the space above and below the Pd coordination planes, lying almost parallel to them (Figure 3). Bond distances and angles are conventional, but it is worth noting the short distance from the Pd atom to the C_{ipso}(Cl) of Pf (3.142 Å). This kind of biphenyl arrangement is well known and has been studied for linear Au^I complexes.²³ Note that Au^I and Pd^{II} have almost identical radii.²⁴ A similar arrangement is found for the olefin group of PhPEWO-F in $[\text{Pd}(\text{C}_6\text{H}_4\text{CF}_3\text{-}p)(\text{PhPEWO-F})(\text{AsPh}_3)]$, where the shortest Pd...C_{olefin} distance is 3.321(5) Å, and corresponds to the carbon connected to the fluorinated aryl.² The molecular orbitals of the two complexes being compared, $[\text{Pd}(\text{C}_6\text{H}_4\text{CF}_3\text{-}p)(\text{PhPEWO-F})(\text{AsPh}_3)]$ and **2** feature an image suggestive of incipient polarization of electron density from Pd towards the π^* orbitals of the olefin or distal pentafluorophenyl C atom closest to Pd, more evident for the former complex than for **2** (see Figure S4 in SI).

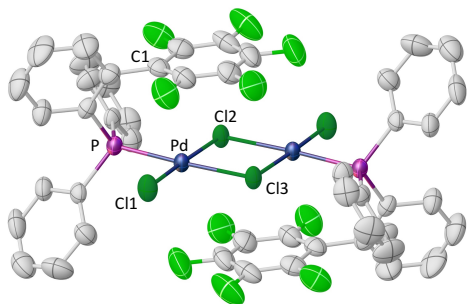


Figure 3. ORTEP diagram (50%) of $(\mu\text{-Cl})_2[\text{Pd}_2\text{Cl}_2(\text{L}^{\text{HF}})_2]$. Bond distances (Å): Pd–P = 2.226; Pd–Cl1 = 3.141; Pd–Cl2 = 2.272; Pd–Cl3 = 2.411; Pd–Cl4 = 2.320.

The $^31\text{P}\{^1\text{H}\}$ NMR spectrum of **2** at 25 °C displays one singlet ($\nu_{1/2} = 5$ Hz), where no $^5J_{\text{F-P}}$ is observed. In the ^{19}F NMR spectrum the two F_{ortho} nuclei and the two F_{meta} nuclei are equivalent, meaning that there is fast rotation of the C_6F_5 group about the C–C bond. Obviously this requires that the Pd coordination plane and the distal Pf group, observed in close parallel arrangement in the X-ray structure, separate in solution in order to allow for rotation around the P–C and C–Pf bonds. The coalescence temperature is not still reached down to –30 °C, suggesting that the rotational barriers in **2** must be very small.

Similar ^{19}F NMR behavior is found for the monomeric *trans*- $[\text{PdCl}_2(\text{L}^{\text{HF}})_2]$ (**3**). The *trans* structure of **3** is assigned based on the observation in the IR spectrum of two bands corresponding to $\nu(\text{Pd}-^{35}\text{Cl})$ and $\nu(\text{Pd}-^{37}\text{Cl})$ at 360 and 351 cm^{-1} , respectively.

The dimeric complex $(\mu\text{-Cl})_2[\text{PdRf}(\text{L}^{\text{HF}})_2]$ (**4**) (Rf = $\text{C}_6\text{F}_3\text{Cl}_2$, 3,5-dichloro2,4,6-trifluorophenyl) is easily prepared reacting the precursor $(\mu\text{-Cl})_2[\text{PdRf}(\text{THT})_2]$, (THT = tetrahydrothiophene) with L^{HF} (Pd: L^{HF} = 1:1). It shows IR bridging chloride bands at lower wavenumbers, at 306, 296 and 284, 271 cm^{-1} . The X-Ray structure of **4**·CHCl₃ is shown in Figure 4.

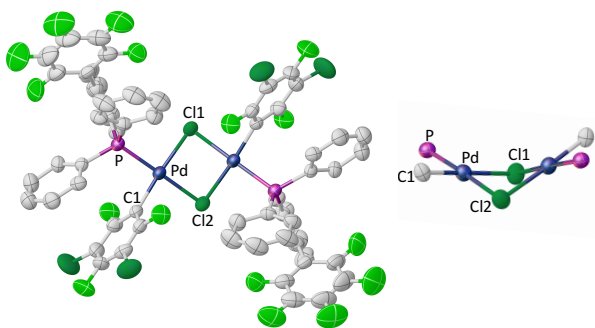


Figure 4. Left: ORTEP diagram (50%) of $(\mu\text{-Cl})_2[\text{PdRf}(\text{L}^{\text{HF}})_2]$ (**4**)·CHCl₃, CHCl₃ omitted for clarity) Bond distances (Å): Pd–Cl1 = 1.994; Pd–P = 2.260; Pd–Cl11 = 2.407; Pd–Cl12 = 2.390; Ph–Ph stacking = 3.117; Ph–Pf stacking = 3.212. Right: angular arrangement of the two coordination square planes.

The complex displays two square-planar units making a 135.8° dihedral angle at the $(\mu\text{-Cl})_2$ edge. Each square planar complex has conventional Pd–Cl, (238.8 Å) Pd–P, (226.2 Å) and Pd–C (199.5 Å) distances and angles, and no significant distortion from planarity.²⁵ The Rf group imposes steric constraints at the coordination plane zone, which force a conformational change on L^{HF} pushing the pentafluorophenyl ring away from the palladium coordination plane. This different rearrangement from **2** does not alter significantly the bond distances and

angles at the coordination plane, but the L^{HF} coordinated ligand is involved in two relatively strong π -stacking interactions: one *intra*-ligand Ph–Pd at 3.117 Å, reminiscent of what happens in the free ligand, and one *extra*-ligand Ph–Rf at 3.212 Å.

The ^{19}F NMR spectrum of compound **4** (see Figure 5 for spectra and F labeling) is surprising and intriguing. It shows the expected number of signals for an Rf group with chemically equivalent halves (two signals in ratio 2:1 for F^1 and F^2) and for a Pf group with chemically equivalent halves (three signals in 2:2:1 ratio for $F^3:F^4:F^5$). Even assuming that the two Pd coordination planes of the dimer will fast average to coplanar in the NMR timescale, the chemical equivalence of the two F^1 atoms in the Rf group is something unusual: It is very well established that the rotation of Rf groups about the C–Pd bond is severely restricted in complexes with non easily dissociable and non flat ligands (e.g. PPh_3) coordinated in *cis* relative to Rf.²⁶ Hence, since the Pd coordination plane of **4** is not a symmetry plane for the molecule, the two F^1 should be anisochronous. The $^31\text{P}\{^1\text{H}\}$ NMR spectrum of **4** shows a triplet ($^4J_{(19\text{F}-31\text{P})} = 11$ Hz), as expected for a phosphine *cis* to Rf, provided that the two F^1 were equivalent. Consequently, a mechanism different from the hindered rotation about the Rf–Pd bond must exist

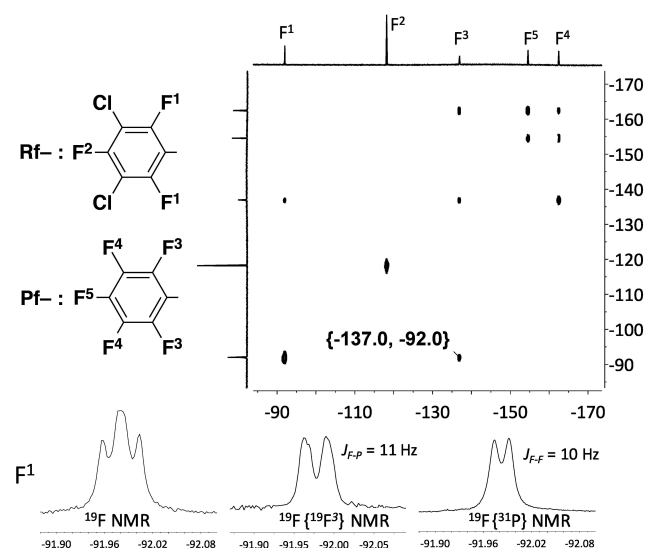


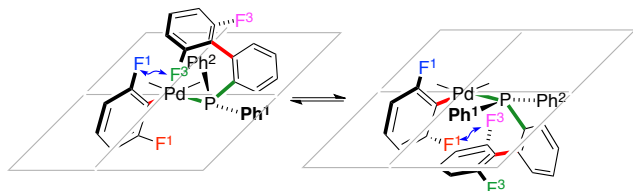
Figure 5. Above: ^{19}F -COSY of **4** in CDCl_3 at 25 °C. Below: Effect of selective irradiations on the deceptive F^1 triplet.

The ^{19}F -COSY of **4** in CDCl_3 at 25 °C (Figure 5) confirms the internal F–F coupling between the fluorine nuclei of Pf and the absence of internal F–F coupling in Rf. Additionally, it reveals the existence of unexpected (looking at the X-ray structure in Figure 3) through space $J_{\text{F-F}}$ coupling ($J \approx 10$ Hz) between F^1 and F^3 .²¹ This produces a deceptive triplet for the F^1 signal. Double irradiation experiments ($^{19}\text{F}\{^{31}\text{P}\}$ and $^{19}\text{F}\{^{19}\text{F}^3\}$), reveal that this deceptive multiplicity is due to coupling to the phosphorus ($^4J_{\text{F-P}} = 11$ Hz) and to only one F^3 atom ($J \approx 10$ Hz) of the Pf group ($J_{\text{F-F}} = 10$ Hz) (note that paradoxically both F^3 atoms are spectroscopically equivalent). Thus the equivalence mechanism has to be able to explain the through space F^1 - F^3 involving only one pair of atoms at a time, and still justify the chemical equivalence of the two halves of the Pf and Rf groups. In other words: what kind of fluxional process produces chemical

equivalence of the two F^3 and still does not produce coupling of each F^1 to both F^3 ? This suggests that the process must be explained under restricted rotation of Pf around the Pf–C bond, or at least a higher rotational barrier than the fluxionality leading to the through space couplings observed.

A closer inspection of the X-ray structure of complex **4** shows that the π -stacking interactions commented above make the P atom a chiral center. The choice of one or the other Ph ring to interact with the Pf group, determines the P conformation. This is already seen in the free L^{HF} , where the lone pair plays the role of Pd in the complex (Figure 2).

In the complex, the hindrance produced by the π - π stacked chiral conformation allows that only one F^3 can get close to the F^1 at that side of the coordination plane. The NMR behavior observed ^{19}F can then be explained as associated to the switching between enantiomers. The slippage of the Pf group from Ph^1 to Ph^2 , involving progressive weakening of the π - π stacking with Ph^1 and strengthening of the π - π stacking with Ph^2 occurs along a crowded pathway were rotation around the Pf–C bond is restricted. In the new isomer the Pf group is at the other side of the coordination plane (rotation around the Pd–P bond is forced in the same movement) and it is the other F^1/F^3 pair the one that can get close to produce through space coupling. It is interesting to note the facts that the rotation around the P–C(biphenyl) bond occurs with the restriction that the Pf–C rotation cannot occur, while the rotation of the phosphine around the P–Pd bond maintains the hindrance to rotation of the Rf group around the Rf–Pd bond (Scheme 2). Since the spin-spin connection is not lost along the fluxional movement because there is no phosphine dissociation, the observed $J \approx 10$ Hz is the time averaged value varying along the fluxional process from a non-determined maximum value to zero. As far as we are aware, nothing like this racemization mechanism associated to π - π stacking slippage has been reported before, although it must be taking place in many related systems, being unobservable or passing unnoticed.



Scheme 2. Fluxional process observed for complexes **4** and **5**. For simplicity only the F_{ortho} atoms (F^1 and F^3) are represented. Green bonds indicate allowed rotations and red bonds restricted rotations.

Complex **4** reacts with excess of L^{HF} to produce *trans*-[PdRfCl(L^{HF})₂] (**5**). The NMR spectra of **5** behave as just discussed for **4**, following the same clockwork fluxional behavior observed in, with a small variation due to the presence of two L^{HF} ligands: The ^{31}P NMR shows a triplet due to the coupling with two F^1 atoms, and the F^1 signals appear as a deceptive quintuplets in the ^{19}F NMR spectrum, due to coupling of two P atoms and coincidence of J_{F-P} and J_{F-F} values.

The reductive elimination reaction. The reductive elimination of [PdPf₂(THF)₂] (**1**) was studied in toluene, adding different proportions of L^{HF} and monitoring the formation of Pf–Pf by ^{19}F NMR. The behavior was anomalous compared to the case

of $tBuXPhos$, where the coupling rate was independent on the Pd:L used.¹ This led us to study the case in more detail.

The addition of two or more equivalents of L^{HF} per palladium to complex **1** produces immediately *cis*-[PdPf₂(L^{HF})₂] (**6**). This complex is unstable at room temperature and undergoes reductive elimination of Pf–Pf, but it can be crystallized from toluene at -35 °C as a colorless solid. The poor quality of the crystals obtained affects the reliability of the X-ray diffraction data and the reliability of the structure of **6**·toluene obtained. This defective structure (suppressing the toluene molecule) was DFT optimized in gas phase and the valuable geometrical information obtained (coincident with the X-ray data except for moderate variations in bond distances and angles) is shown in Figure 6. The complex has *cis* square-planar tetrahedrally distorted (the two *trans* Pf–Pd–P angles are 164.0°) geometry. A C_2 axis makes the two Pf groups, and the two L^{HF} phosphines symmetry equivalent. The conformation of L^{HF} shows the biphenyl with its Pf ring away from the palladium plane, as expected. The repulsion between the two bulky phosphine ligands forces a P–Pd–P angle of 104.8° , a bit larger than the same angle in [PdRf₂(Xantphos)]·2CH₂Cl₂ (103.5°).²⁷ Thus, the effect of the two voluminous phosphines forcing a large P–Pd–P angle is higher than that of Xantphos (a typical chelate with large bite angle). Consistently the C–Pd–C angle in **6** (81.21°) is smaller than 90° , but a bit larger than in the rigid complex with Xantphos (79.6°) because in the case of Xantphos the planar square plane is less distorted. The coupling promoter effect of ligands with large bite angles is well known. Moreover, not only the reduction of the C–Pd–C angle but also a tetrahedral distortion of the square plane are features observed in the structural evolution during C–C coupling in case that the four ligands are conserved during the reaction.²⁸ Both features are incipiently observed for *cis*-[PdPf₂(L^{HF})₂]. The tetrahedral distortion effect is not observed in the complex with Xantphos and perhaps this explains the significantly higher coupling efficiency of 2 L^{HF} ($\Delta G_{Pf-Pf}^\ddagger = 23.1$ kcal.mol⁻¹ at 25 °C, see later) compared to Xantphos ($\Delta G_{Pf-Pf}^\ddagger = 24.2$ kcal.mol⁻¹ at 25 °C), in spite of the smaller C–Pd–C angle defined by Xantphos in the ground state structure.

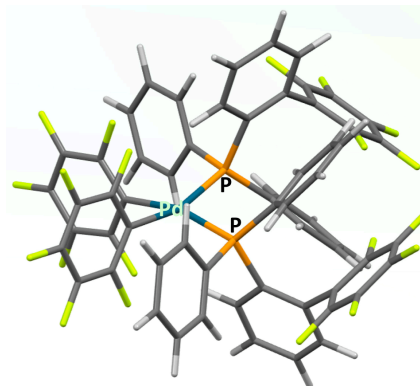
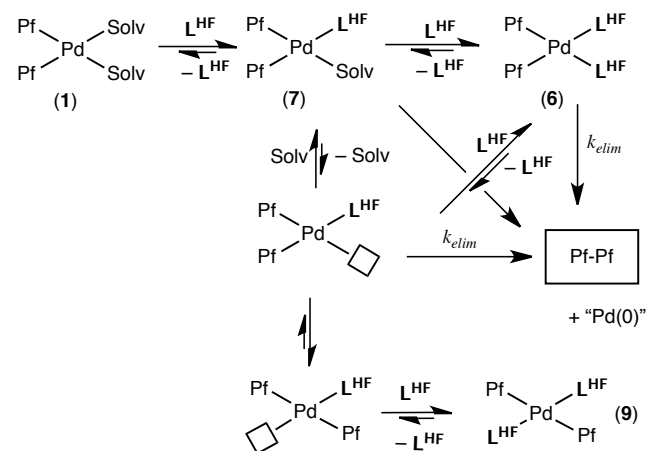


Figure 6. DFT capped-stick structure of *cis*-[PdPf₂(L^{HF})₂], optimized from a defective X-ray solution of **6**·toluene (see ESI). It shows some tetrahedral distortion of the square planar structure induced by the biaryl substituents on P. Pd: blue; P: orange; F: yellow-green.

The NMR spectra of mixtures of **1** and L^{HF} in different proportions, prepared and recorded at -20 °C in order to prevent coupling, reveal the existence of the complexes and equilibria shown in Scheme 3. Above 0 °C two processes are observed: the reductive elimination to Pf–Pf, and the isomerization of **6**

to *trans*-[PdPf₂(L^{HF})₂] (**9**). The reductive elimination behavior at 25 °C can be analyzed based on the existence of these equilibria and the kinetic monitoring of the processes in different L^{HF}:Pd ratios. Data related to the characterization of these equilibria at different temperatures are discussed in the SI.



Scheme 3. Equilibria observed in toluene solution at -20 °C, and evolution to **9** at 0 °C. Note that "dry" toluene contains a small amount of residual water (about 5 ppm).²⁹ For simplicity the possible contribution of complex **1** to the formation of Pf-Pf is not shown.

1) With a large excess of L^{HF} ([L^{HF}]:[PdPf₂(THF)₂] ≥ 4:1) the solution contains initially *cis*-[PdPf₂(L^{HF})₂] (**6**) plus two or more equivalents of free L^{HF} and two equivalents of THF) the reductive elimination is the only process observed at 25 °C. The concentration/time plots (Figure 8) fit very well a first order kinetics ($k_{\text{elim}} = 7.7 \cdot 10^{-5} \text{ s}^{-1}$, $\Delta G_{\text{PF-Pf}}^{\ddagger} = 23.1 \text{ kcal.mol}^{-1}$ at 25 °C), and the observed rate does not change increasing the concentration of L^{HF}, confirming that the coupling is taking place on the 4-coordinated complex, induces by the large bite angle defined by the two phosphines in *cis*.

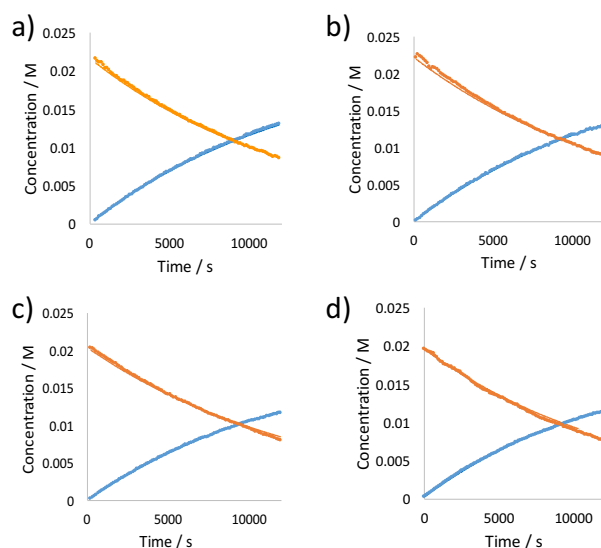


Figure 7. Concentration/time plots and best least square fitting (continuous line) for reductive elimination of **6** in toluene under selected concentrations of L^{HF} at 298K. Red dots: *cis*-[PdPf₂(L^{HF})₂] (**6**); Blue dots: Pf-Pf. Starting conditions: a) [1] = 0.02 M + [L^{HF}] = 0.08 M (**1:4**), $k_{\text{obs}} = 7.7 \cdot 10^{-5} \text{ s}^{-1} \pm 8 \cdot 10^{-8} \text{ s}^{-1}$; b) [1] = 0.018 M + [L^{HF}] = 0.14 M (**1:8**), $k_{\text{obs}} = 7.44 \cdot 10^{-5} \text{ s}^{-1} \pm 1 \cdot 10^{-7} \text{ s}^{-1}$; c) [1] = 0.018 M + [L^{HF}] = 0.22 M (**1:12**), $k_{\text{obs}} = 7.36 \cdot 10^{-5} \text{ s}^{-1} \pm 4$

10^{-7} s^{-1} ; d) [1] = 0.018 M + [L^{HF}] = 0.22 M (**1:12**) and [FC₆H₄] = 0.054 M (**1:3**), $k_{\text{obs}} = 7.38 \cdot 10^{-5} \text{ s}^{-1} \pm 1.69 \cdot 10^{-7} \text{ s}^{-1}$.

An experiment in the presence of 4-fluoriodobenzene as re-oxidant gave also the same k_{elim} . Thus in this proportion L^{HF} performs better to form the corresponding Pd⁰ catalyst than XantPhos or PhPEWO-F, and about the same as ^tBuBrettPhos.² The ³¹P spectra in toluene at 25 °C show independent signals for L^{HF} free ($\delta = -11.1 \text{ ppm}$) or coordinated to Pd⁰ ($\delta = 45.6 \text{ ppm}$), and integration supports the composition Pd(L^{HF})₃ regardless of the excess of L^{HF} (≥ 3) used. It is also worth noting that competing formation of PfH, observed for some other ligands,¹ was not detected.

2) For [L^{HF}]:[PdPf₂(THF)₂] = 2:1, or with the isolated complex *cis*-[PdPf₂(L^{HF})₂] (**6**), the evolution shows a more complex kinetics. In addition to the coupling product, Pf-Pf, the reaction produces also: *i*) isomerization to *trans*-[PdPf₂(L^{HF})₂] (**9**) by a dissociative mechanism,³⁰ more easily accessible for crowded complexes; and, *ii*) if **6** has been made *in situ* from **1**, and THF is present in the solution, regenerates some complex [PdPf₂(THF)₂] (**1**). The latter is as a consequence of the capability of palladium(0) complex Pd(L^{HF})₂ to sequester L^{HF} forming Pd(L^{HF})₃, so that some **1** is formed from **6** (Scheme 3). The values obtained from the ¹⁹F integrals corresponding to the Pd⁰ complex with respect to the internal standard suggest that the number of coordinated phosphines is between 2 and 3. In the presence of 4-fluoriodobenzene as re-oxidant, the fast formation of *trans*-[Pd(C₆H₄F-*p*)](L^{HF})₂ precludes formation of Pd(L^{HF})₃ and also prevents formation of **1** from **6**.

3) Finally, for ([L^{HF}]:[PdPf₂(THF)₂]) in the range 1-2, a mixture of complexes is formed in solution, that evolve as shown in Figure 8: *cis*-[PdPf₂(L^{HF})₂] (**6**) is consumed relatively fast, during the first 30 minutes in which Pf-Pf is formed slowly. Also, *cis*-[PdPf₂(L^{HF})(THF)] (**7**), in equilibrium with **6** and L^{HF}, is consumed at slower rate (Figure 8).

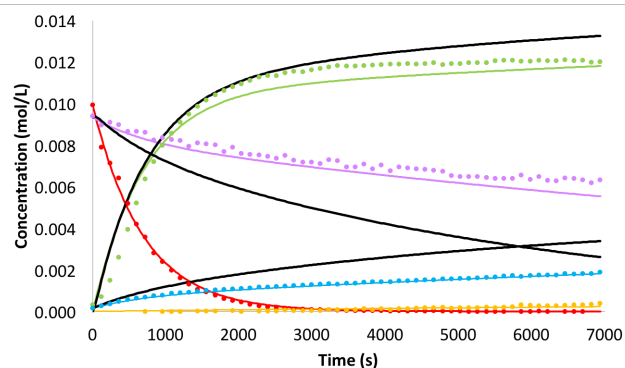


Figure 8. Concentration/time plots (dots) and best least square fitting (continuous lines) for the reductive elimination in toluene (0.5 mL) from (**1**) (0.019 M) + L^{HF} (0.030 M) (**1:1.5**) at 298K, monitored by ¹⁹F NMR. Red dots: *cis*-[PdPf₂(L^{HF})₂] (**6**); Purple dots: *cis*-[PdPf₂(L^{HF})(THF)] (**7**); green dots: *trans*-[PdPf₂(L^{HF})₂] (**9**); blue dots: Pf-Pf; orange dots: [PdPf₂(THF)₂] (**1**). Black lines represent the kinetic simulation obtained by fixing the same rate for the reductive elimination from complexes **6** and **7**. Colored lines represent the kinetic simulation obtained by fitting the equations optimized with different values for k_{obs} from **6** and from **7**.

The main product of the reaction is *trans*-[PdPf₂(L^{HF})₂] (**9**), and, during the experiment, *cis*-[PdPf₂(THF)₂] (**1**) is also formed. Knowing the rate constants for the formation of Pf-Pf

from **6** and from **1**, it is possible to calculate k_{obs} for the reductive elimination from **7**, (no assumption about the pathway was made); a value $k_{obs} = 2.3 \cdot 10^{-5} \text{ s}^{-1}$ was obtained. A kinetic simulation visualizes how fast Pf–Pf would be formed if the rates of the reductive elimination were the approximately identical for **6** and for **7** (black lines in Figure 8). The rate of formation of Pf–Pf would be noticeably faster than observed experimentally.

In summary, the experimental results fit very well the mechanistic proposal in Scheme 3, and show that: a) in the absence of excess \mathbf{L}^{HF} to prevent phosphine dissociation, the isomerization of **6** to **9** is faster than the reductive elimination process. Since the most plausible mechanism of isomerization is through a T-shaped tricoordinate intermediate, that means that this intermediate is energetically accessible and that the reductive elimination from it is not very fast; and b) the reductive elimination takes place faster from the crowded **6** than from the less crowded **7** or from the related 3-coordinated putative intermediate.

Conclusions

Ligand \mathbf{L}^{HF} is an example of monodentate biphenyl phosphine with a size that allows coordination to Pd of two phosphines in a cis arrangement, although in the absence of extra \mathbf{L}^{HF} one \mathbf{L}^{HF} is easily dissociated, or displaced by a weak smaller ligand such as THF or OH_2 . When the two phosphines \mathbf{L}^{HF} are coordinated in cis positions, the inter-ligand repulsions close the Pf–Pf angle to about 81.21° and induce a tetrahedral distortion of the square-planar coordination. These two distortions make the reductive elimination transition state more accessible from this tetracoordinated species than from a tricoordinated one, and much more than from square planar complexes with regular ligands. As a matter of fact, the use of \mathbf{L}^{HF} in excess reduces the coupling barrier to $\Delta G_{\text{PF-PF}}^\ddagger = 23.1 \text{ kcal.mol}^{-1}$, which ranks its efficiency for coupling and formation of the corresponding Pd^0 catalyst as better than XantPhos or PhPEWO-F, and about the same as ^tBuBrettPhos. The contribution of the bulkiness of the two ligands to push the structure towards tetrahedral distortion seems to help for an easier coupling. This suggests that the design of chelating ligands forcing tetrahedral distortions at Pd might be catalytically productive.

The studies on \mathbf{L}^{HF} in this paper uncover some unusual chemical aspects of their Pd complexes that could be interesting to take into account as they might have been overlooked in some related cases. Other studies on structurally related ligands are in progress.

ASSOCIATED CONTENTS

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

General methods. Synthesis of new compounds. Determination of rate constants. Other studies in solution. Computational section. Experimental procedure for X-ray Crystallography. NMR spectra. IR spectra. References. 47 pages

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