Ranking ligands by their ability to ease \((\text{C}_6\text{F}_5)_2\text{Ni}^\text{II}L \rightarrow \text{Ni}^0\text{L} + (\text{C}_6\text{F}_5)_2\) coupling vs. hydrolysis: Outstanding activity of PEWO ligands

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Supporting Information Placeholder

ABSTRACT: The Ni^II literature complex \(\text{cis}^\text{-}[\text{Ni}(\text{C}_6\text{F}_5)_2](\text{THF})_2\) is a synthon of \(\text{cis}^\text{-}\text{Ni}(\text{C}_6\text{F}_5)_2\) that allows us to establish a protocol to measure and compare the ligand effect on the Ni^II \(\rightarrow\) Ni^0 reductive elimination step (coupling), often critical in catalytic processes. Several ligands of different types were submitted to this Ni-meter comparison: bipyridines, chelating diphosphines, monodentate phosphines, PR\(_2\) (biaryl) phosphines, and PEWO ligands (phosphines with one potentially chelate electron attractor moieties such as electron-withdrawing olefins). Extremely different \(\text{C}_6\text{F}_5\text{-C}_6\text{F}_5\) coupling rates, ranging from those totally inactive (producing stable complexes at room temperature) to those inducing almost instantaneous coupling at 25 °C, were found for the different ligands tested. The PR\(_2\) (biaryl) ligands, very efficient for coupling in Pd, are slow and inefficient in Ni, and the reason for this difference is examined. In contrast, PEWO type ligands are amazingly efficient and provide the lowest coupling barriers ever observed for Ni^II complexes: they yield up to 96% \(\text{C}_6\text{F}_5\text{-C}_6\text{F}_5\) coupling in 5 minutes at 25 °C (the rest is \(\text{C}_6\text{F}_5\text{H}\)) and 100% coupling with no hydrolysis in 8 h, at -22 to -53 °C.

INTRODUCTION

The interest in Ni-catalyzed cross-coupling reactions has boomed in the last two decades.\(^1\) Compared to the deeply studied Pd processes, the available information to select appropriate ligands for Ni-catalyzed C–C couplings is still scarce. For identical structures of group 10 metals, the activation energy of C–C reductive elimination follows the trend Ni < Pd < Pt.\(^2\) It looks, however, that often the efficiencies of identical ligands do not run parallel for Pd and Ni. For instance, bulky PR\(_2\) ligands and Buchwald type biaryl phosphines are very efficient in Pd-catalyzed processes, but there are few examples of their successful use in Ni catalysis.\(^3,4\) In general, ligand extrapolation from Pd to Ni is likely to fail due to different factors. One reason analyzed by Doyle is that, due to the smaller radius of Ni, the cone angle \(^\theta\) increases, reduced long ago by Tolman,\(^5\) is smaller for the same ancillary ligand on Pd than on Ni.\(^6\) This reduces the volume available to accommodate the reacting groups coordinated to Ni.\(^7\) If the groups defining the cone angle are remote from the small Ni center, some percentage of the cone angle in the spatial neighborhood of the Ni atom is not buried, and it is still available to be accessed when required by the transformations in a catalytic cycle. In fact, ligands designed with large \(\theta\) but low \(\%V_{\text{bur}}\) make operative some Ni catalyzed couplings that fail with ligands such as PBU₃ or JohnPhos.\(^7\)

The non-buried volume requirement is a necessary but not sufficient condition throughout a catalytic process. Additionally, for a catalytic cycle to work it has to have accessible activation barriers at each catalytic step. Our specific interest here is how to get information on the rate of reductive elimination (coupling) step, which closes the cross-coupling catalytic processes, in competence with detrimental hydrolysis. C–C Pd coupling, and presumably in Ni too, the reductive elimination gets more difficult in the order aryl-aryl < aryl-alkyl < alkyl-aryl < < CF₃-CF₃ < CF₃-CF₂ < CF₂-CF₃.\(^8\) In the early 1970’s, seminal studies of A. Yamamoto’s group had already found that butane formation from \([\text{Ni}^\text{II}(\text{Et})_2\text{bipy}])\) was induced by addition of electron-attractor moieties such as electron-withdrawing olefins (EWOs),\(^9\) aromatic compounds, and phosphines.\(^10\) They proposed that coordination of an EWO to the complex and reduced the elimination barrier from 68 kcal mol\(^{-1}\) in \([\text{Ni}^\text{II}(\text{Et})_2\text{bipy}])\) to 20 kcal mol\(^{-1}\) in \([\text{Ni}^\text{II}(\text{Et})_2\text{bipy}])\). For perfluoroaryl groups the coupling barriers turned inaccessible, and EWO addition failed to promote coupling in \([\text{Ni}^\text{II}(\text{C}_6\text{F}_5)_2\text{bipy}])\) at any temperature.\(^11\) In this line, the group of Doyle has reported an electron-deficient olefin \(\text{Fro-DO}\) (with \(\text{E}-\text{R}(\text{O})-\text{CH} = \text{CH}(\text{O})-\text{R}\) structure) that enables for efficient nickel-catalyzed cross-coupling of 1,1-disubstituted aziridines with organozinc reagents to generate quaternary centers at room temperature.\(^12\)

There are not many computational studies so far. One comparing the effect of 42 diphosphines on the reductive elimination barrier of \(\text{Ph-CF}_3\) from \([\text{Ni}(\text{CF}_3)\text{Ph(P-P)})\) is available, but access to parallel experimental data was limited to two cases because of synthetic problems.\(^13\) There is also a theoretical study showing that, dimethyl furamate facilitates the nickel-catalyzed conjunctive cross-coupling of alkenyl amides with aryl iodides and aryl boronic esters because lowers the aryl-alkyl coupling activation energy from \(\Delta G \equiv 14.6\) kcal mol\(^{-1}\) with ethylene to only \(\Delta G \equiv 2.6\) kcal mol\(^{-1}\) with dimethyl furamate.\(^14\) Much earlier, using Me–Me coupling as a model, our studies on Pd had confirmed experimentally and explained theoretically the dramatic facilitation of coupling by coordination of electron withdrawing olefins (EWOs).\(^15\)
More recently, we proposed the use of complex cis-[Pd(C₆F₅)₂(THF)] as a Pd-meter to rank experimentally the different ligand according to their ability to facilitate the difficult C₆F₅-C₆F₅ coupling. The procedure consists in measuring the activation energy for C₆F₅-C₆F₅ formation (ΔG°C₆F₅-C₆F₅) upon addition of the ligand being tested to cis-[Pd(C₆F₅)₂(THF)]. Although the C₆F₅-C₆F₅ coupling barrier from Pd is difficult, the percentages of competing hydrolysis are moderate in Pd, which is not oxophilic. The work here aims at extending this idea to a Ni²⁺-meter that might provide information to compare the coupling barriers in Ni¹⁺ (ΔG°C₆F₅-C₆F₅) with different ligands in similar conditions. We expect hydrolysis to be more competitive with coupling in Ni than it was in Pd, which may prevent to quantify this coupling barrier, except for the most active ligands. Yet, valuable semiquantitative information on the ligand ability of coupling should be obtained for all the cases.

RESULTS AND DISCUSSION

The Ni²⁺-meter complex should be a fairly stable synthon of cis-[Ni²⁺(C₆F₅)₂] easy to prepare and handle, where addition of the examined ligand at low temperature should lead to fast coordination before any significant coupling occurs, in order to avoid deceptive interferences when measuring coupling and hydrolysis rates. After a few trials with more stable complexes that did not facilitate fast ligand substitution (cis-[Ni¹⁺(C₆F₅)₂(NCPh)₃])¹⁸ or trans-[Ni¹⁺(C₆F₅)₂(SbPh₃)₃])¹⁹, we found cis-[Ni(C₆F₅)₂(THF)] (I) as the one fulfilling reasonably our requirements. Based on the two reported syntheses of I,²⁰ we have developed a more direct procedure: Commercially available [NiX₂(DME)] (X = Br, Cl; DME = 1,2-dimethoxyethane) reacts with Ag(C₆F₅)₂ in THF (1 hour at -40 °C) to produce I (Eq. 1). Evaporation, extraction with Et₂O, and filtration to remove the insoluble silver salts, followed by evaporation to dryness affords I as an orange solid with > 97% purity.²²

\[
\text{[NiX₂(DME)] + 2 Ag(C₆F₅) \rightarrow \text{THF} \rightarrow -40 °C \rightarrow \text{THF} \rightarrow \text{C₆F₅} + 2 \text{AgX} + \text{DME}}
\]

Complex I is stable for several months in the fridge under inert atmosphere, but it is somewhat sensitive to atmospheric oxygen and water at room temperature.²¹ Solutions of I in freshly distilled dry THF are stable enough for comfortable quick handling at room temperature, and can be stored in the freezer for a few hours, although decomposition (turbidity) is eventually observed. In non-coordinating solvents, complex I decomposes noticeably fast to a mixture of the coupling product (C₆F₅-C₆F₅) and the hydrolysis byproduct (C₆F₅H), presumably due to easy THF dissociation to the three-coordinate [Ni¹⁺(C₆F₅)₂(THF)] that undergoes faster reductive elimination than the four-coordinate I, and competitive substitution to [Ni¹⁺(C₆F₅)₂(THF)(OH₂)] followed by hydrolysis (Scheme 1).²⁴

![Scheme 1. Coupling vs. hydrolysis from the Ni⁺-meter.](image)

The protocol for the coupling/hydrolysis measurements shown in Eq. 2 (where each L stands for one potentially bidentate ligand or for two monodentate ligands) is as follows: The reactions are monitored by ¹⁹F NMR. The addition of L is made at lower temperature and the NMR tube is brought to the coupling temperature once the ligand coordination has reached equilibrium. Excess ligand (L: Ni molar ratio: 2:1 for chelating ligands, 4:1 for monodentate ligands) is used to stabilize the reduction product as [Ni²⁺L₃] (n = 2-4 depending on L), in order to prevent that initially formed Ni²⁺ could sequester part of the L needed for completion of Ni³⁺ complex. We confirmed for L chelates that using L:Ni = 1:1 or 2:1 does not change the initial coupling rate. The CH₃Cl solvent in all the experiments reported was as supplied by our solvent purification system (SPS) PS-MD-5. In the experimental reagent concentrations used (limited by its solubility), the I: H₂O molar ratio was approximately 1:0.7. In toluene, used occasionally, it was approximately 1:0.3 (see SI).

\[
\text{THF} \rightarrow \text{Ni} \rightarrow \text{C₆F₅} \rightarrow \text{+ 2 L} \rightarrow \text{CH₃Cl} \text{+ THF} \rightarrow \text{C₆F₅-C₆F₅} \text{+ Ni²⁺L₃-n} \text{+ Lₙ}}
\]

The Ni-meter I itself undergoes coupling and hydrolysis (Scheme 1) and can be taken as reference. It reveals immediately much higher hydrolysis:coupling ratio (53:47 mol%) at 25 °C than observed for the equivalent Pd-meter.²⁶ In general, higher participation of hydrolysis is found in Ni compared to Pd for all the tested ligands, consistent with the more favorable coordination of water and its higher acidity on the harder Ni³⁺ center than on the softer Pd⁶⁺. In the presence of D₂O the hydrolysis product was enriched in C₆F₅-D, as expected (see SI for details).

The ligands tested are grouped into five types (Scheme 2): a) bipyridines; b) chelating diphosphines; c) monodentate phosphines; d) dialkyliaryl (Buchwald type) phosphines; e) PEWO type ligands (phosphine-electron-withdrawing olefin ligands). Upon addition of these ligands to I, results spanning from formation of totally inert complexes to instantaneous C₆F₅-C₆F₅ coupling, as well as diverse C₆F₅-C₆F₅:C₆F₅H ratios, were observed at 25 °C. X-ray diffraction structures were solved when the stable complexes allowed for crystallization.
The reaction of 1 with Xantphos in CH₂Cl₂ at 25 °C produced the trans chelate complex 22. Its X-ray diffraction structure confirmed the expectations from the NMR studies, and is shown in Figure 2. Monitoring of the reaction of 1 with Xantphos at -40 °C showed that cis-[Ni(C₅F₅)₂(Xantphos)] (23) was initially formed (Scheme 3) and then it isomerized to the thermodynamically favored trans-[Ni(C₅F₅)₂(Xantphos)] (22). This supports that isomerization of the initially formed cis complex at 25 °C is considerably faster than coupling at the same temperature. The cis- and trans-chelation ability of XantPhos is well known,23 but only trans coordination of XantPhos to Ni has been reported so far.24,25

![Figure 2](image-url)

**Figure 2.** X-ray diffraction structure of trans-[Ni(C₅F₅)₂(XantPhos)]·toluene (22). Solvent molecule and H atoms omitted for clarity.

**Scheme 3.** Reaction sequence observed at -40 °C in the formation of trans-[Ni(C₅F₅)₂(XantPhos)] (22).

In contrast to the stability of the precedent complexes, coupling (C₅F₅-C₅F₅) and hydrolysis (C₅F₅H) was observed at 25 °C for all the other ligands in Scheme 2. These two evolutions are comparatively slow for most ligands of groups c and d, but extremely fast for ligands of group e. Table 1 summarizes all the results, including information on: i) The complexes formed in solution by reaction of 1 with L, when they are stable; or NMR data on the complex formed in solution, before coupling/hydrolysis occurs (column 2); ii) the conversion produced in the time specified; and iii) the C₅F₅-C₅F₅:C₅F₅H ratio formed, as percentage of products. Some specific reactions with addition of p-benzoquinone (bqz), a strongly electron deficient olefin (EDO) with strong electron-withdrawing effect upon coordination (EWO) are also included, as specified in the 1st column of Table 1.15

For complex 1, the reactions in Scheme 1 are sensitive to 2:1 addition of bqz (entry 2 vs. 1). Presumably the coupling occurs on Ni²⁺ species with at least one coordinated bqz in equilibrium with free bqz, which accelerates the coupling reaction and noticeably improves the coupling/hydrolysis ratio. Consistently, increasing the bqz concentration (entry 3 in Table 1) has a larger positive effect on the percentage of substitution and on the coupling rate, as well as on the coupling/hydrolysis ratio. Obviously, neither THF nor bqz are hoped to maintain the Ni center active throughout a catalytic cycle, but these initial entries of Table 1 are interesting to illustrate the potential positive coupling effect of an EWO ligand at the coupling step when facing non-easy couplings.

**Scheme 2.** Ligand types tested with the Ni⁺⁺-meter

(a) N-type ligands

(b) Chelating diporphine ligands

(c) Monodentate phosphine ligands

(d) Buchwald type phosphine ligands

(e) PEWO type ligands

The bipy ligands (2, 3) form immediately the X-ray characterized [Ni(C₅F₅)₂(L)] chelated complexes (18, 19) (Figure 1, above). The symmetrical diporphine ligands 4 and 5 also lead to stable [Ni(C₅F₅)₂(L)] chelated complexes 20 and 21, respectively, which were isolated and X-ray characterized (Figure 1, below). As reported by Yamamoto for the [Ni(C₅F₅)₂(2,2'-bipy)] complexes,11 coupling on 18-21 does not occur at 25 °C. Moreover, all these complexes are stable not only at 25 °C in CH₂Cl₂, but also at 80 °C in dioxane.

![Figure 1](image-url)

**Figure 1.** Above: Left: Ni(C₅F₅)₂(CO₂Et-bipy) (18); Right: Ni(C₅F₅)₂(Bu-bipy) (19). Below: Left: Ni(C₅F₅)₂(dppe)-1/2 CH₂Cl₂ (20); Right: Ni(C₅F₅)₂(dppe) n-pentane (21). All solvent molecules and H atoms omitted for clarity.
using Pdination and subsequent hydrolysis. This result discourages solution. Since two non showed that only one molecule of Pdation and subsequent hydrolysis. This result discourages solution. Since two non

stable

Table 1. Conversion (%) of 1 (eq. 2), and coupling:hydrolysis ratio with ligands in Scheme 2 (in CH2Cl2; T = 25 °C). L: Ni molar ratio: a 2:1; b 20:1; c 4:1; d 1:1; e in toluene.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compounds in solution and NMR signals</th>
<th>t</th>
<th>Conv. (%)</th>
<th>(C6F3)-: C6F3H molar ratio</th>
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<tr>
<td>1</td>
<td>THF Complex 1</td>
<td>2h</td>
<td>85</td>
<td>49:51</td>
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<td>2</td>
<td>bzq² equilibrium mixture (text)</td>
<td>4h</td>
<td>100</td>
<td>47:53</td>
</tr>
<tr>
<td>3</td>
<td>bzq² equilibrium mixture (text)</td>
<td>1.5h</td>
<td>100</td>
<td>66:34</td>
</tr>
<tr>
<td>4</td>
<td>7c Complex 24 + 2 free L</td>
<td>24h</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>8c Complex 25 + 2 free L</td>
<td>24h</td>
<td>–</td>
<td>–</td>
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<tr>
<td>6</td>
<td>9c Complex 26 + 3 free L</td>
<td>2h</td>
<td>100</td>
<td>11:89</td>
</tr>
<tr>
<td>7</td>
<td>10a Cis-1:1 complex, 2 nonequiv. C6F3 1L</td>
<td>6h</td>
<td>78</td>
<td>20:80</td>
</tr>
<tr>
<td>8</td>
<td>11a Cis-1:1 complex, 1 free L</td>
<td>6h</td>
<td>77</td>
<td>29:71</td>
</tr>
<tr>
<td>9</td>
<td>11e Cis-1:1 complex, 2 nonequiv. C6F3 1L</td>
<td>6h</td>
<td>45</td>
<td>42:58</td>
</tr>
<tr>
<td>10</td>
<td>11a+bzq Complex 1:1 complex, 2 nonequiv. C6F3 1L</td>
<td>18h</td>
<td>76</td>
<td>20:80</td>
</tr>
<tr>
<td>11</td>
<td>12a Cis-1:1 complex, 2 nonequiv. C6F3 1L</td>
<td>6h</td>
<td>83</td>
<td>23:77</td>
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<tr>
<td>12</td>
<td>13a Cis-1:1 + trans-1:2 complexes + 1L</td>
<td>28h</td>
<td>100</td>
<td>40:60</td>
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<tr>
<td>13</td>
<td>13d Cis-1:1 + trans-1:2 complexes + 1</td>
<td>28h</td>
<td>100</td>
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<td>15</td>
<td>15a Complex 28 + 1 free L</td>
<td>&lt;5 min</td>
<td>100</td>
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<tr>
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<tr>
<td>17</td>
<td>17a Complex 30 + 1 free L</td>
<td>&lt;5 min</td>
<td>100</td>
<td>96:4</td>
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Monodentate phosphines with different molecular sizes totally replace THF. The small PPh3 (7) and PCy3 (8) form the stable trans-[Ni(C6F3)2(PCy3)] complexes 24 and 25 (entries 4 and 5, Table 1). The trans arrangement of the two C6F3 groups prevents reductive elimination. Figure 3 shows the structure of trans-[Ni(C6F3)2(PCy3)]. On the other hand, the NMR spectra show that only one molecule of PBU4 (9) can coordinate to the Ni² center, producing the reactive cis-[Ni(C6F3)2(PCy3)] (26), and leaving the other three PBU4 uncoordinated (entry 6).

Complex 26 undergoes fast evolution at 25 °C, predominantly to C6F3H. The reaction was complete in less than 2h, which precluded to obtain single crystals of the complex in solution. Since two non-equivalent C6F3 groups are observed in the ¹⁹F NMR spectrum, it is not excluded that complex 26 in THF solution could be [Ni(C6F3)2(PBU4)](THF)]. The efficient hydrolysis shows that complex 26 is allowing for water coordination and subsequent hydrolysis. This result discourages using PBU4 for difficult couplings on Ni, in contrast with its successful utilization in Pd-catalyzed processes.

Figure 3. X-ray diffraction structure of trans-[Ni(C6F3)2(PCy3)] (25). Solvent molecule and H atoms omitted for clarity.

Biaryl phosphines 10–12 (group d) are very efficient in Pd-catalyzed processes, but there are only scarce examples of good performance in Ni catalysis. In the reaction with the Pd-met, they were very fast for coupling, or at least very efficient to hinder undesired hydrolysis. With the Ni-met, however, they are very inefficient (entries 7–12, Table 1): it took 6–9.5 h at 25 °C to reach 47–83% conversion in CH2Cl2, showing slower coupling than hydrolysis with only 20–23% of coupling product (entry 8). The reaction in toluene instead of dichloromethane (entry 9) was not any faster, but it produced a better (still bad) coupling:hydrolysis ratio: 42:58 in 6h and 59:41 in 9.5 h, possibly due to the lower water content in the toluene. The late improvement of this ratio possibly occurs when the initial H2O content in toluene has been practically exhausted. Thus, in sharp contrast with their good behavior on Pd², not only these PR3(biaryl) phosphines are quite inefficient for C6F3-C6F3 coupling on Ni, but are also unable to protect the Ni² center and prevent hydrolysis. The slowness of the coupling reactions and the double dependence of water and L prevented to measure (AG°(C6F3-C6F3)) for these ligands, although some qualitative information can be surmised from the conversion time and products time evolution. The possible cooperative effect of addition of p-benzoquinone (L:bzq = 1:1) was checked with ligand 11, hoping for a higher rate of the coupling reaction and better protection against hydrolysis, but no improvement was observed (entry 10).

The recently reported fluorinated biaryl ligand 13, where the fluorinated aryl might somehow resemble an electron withdrawing olefin (see later), was also tested. Its reactivity was slow and produced somewhat better but still very unsatisfactory coupling:hydrolysis ratio (entries 12–13).

Finally, concerning the PEWO ligands 14–17 of group e in Scheme 2, they produce complexes 27–30 in CD2Cl2 (entries 14–17). Single crystals for X-ray diffraction of these complexes could not be obtained due to very fast conversion to C6F3—P=olefin chelate coordination in solution is unambiguously confirmed by observation of four non-equivalent F ortho signals in their ¹⁹F NMR spectrum. In a square planar Ni² complex the P-olefin chelate coordination leads to two non-equivalent C6F3 groups. The Ni coordination plane is not a symmetry plane, and the restriction to rotation of the C6F3 groups produces non-equivalence of their two F ortho atoms affording four F ortho signals. The upfield shifts of the olefinic protons (e.g. δ = 7.32 and 5.97 ppm in 29 compared to δ = 8.35 and 7.17 ppm in the free PhPEWO-H phosphine 16) further support the coordination of the C=C group and the proposed geometry. These PEWO ligands 14–17 show an exceptional power to induce C6F3—C6F3 coupling due to the effect
of coordination of the EWO olefin group. All of them beat any other ligand in this respect: total conversion of complex at 25 °C occurs in a scale of seconds, rather than hours! Furthermore, the conversion at this temperature affords very predominantly coupling product (82-96%). To the best of our knowledge, these coupling ratios are the fastest ever observed in Ni\(^{II}\)→Ni\(^{II}\) reductive elimination processes. In fact, they are too fast to be measured by NMR at 25 °C applying the initial rates method.

The dramatically different behavior of PR\(_2\)(biaryl) and PEWO ligands in the Ni-meter, in contrast with to their similar behavior in the Pd-meter, must probably have a structural origin. In Pd, both types of ligand behave as chelating: For PEWO ligands several X-ray diffraction Pd\(^{II}\) and Pd\(^{0}\) structures of chelated complexes with E- or Z-coordinated olefin have been reported, and many Pd\(^{II}\) and Pd\(^{0}\) complexes with PR\(_2\)(biaryl) ligands show Pd-C\(_{\text{o}}\)\(_{\text{olefin}}\) chelating interactions with the distal aryl (Pd-C\(_{\text{ipso}}\) distances in the range 2.19-2.60 Å). These interactions help to stabilize [Pd(aryl)XL] or [Pd(aryl)RL] intermediates in the catalytic cycles and support their chelating coordination along the C-C coupling process for both kinds of ligand.

There is no similar structural X-ray information available for Ni complexes with these ligands, and we also have failed to obtain single crystals in this work, but the NMR spectra for these complexes in CH\(_2\)Cl\(_2\), in NiL = 1:2 solutions, show always one free L and one coordinated (entries 7-17). For the PEWO complexes (entries 14-17) coordination of the olefin group is clearly seen in the \(^1\)H NMR spectra, but the PR\(_2\)(biaryl) complexes with ligands 10-12 (entries 7-11) show ill-defined broad \(^1\)H spectra perhaps associated to slow conformational changes. The fact is that their chemical behavior is very similar to that of PBU\(_5\): formation of Ni:P = 1:1 complexes in solution; NMR observation of 2 chemically non-equivalent C\(_6\)F\(_5\) groups: slow conversion; and much less coupling than hydrosylation. This suggests that the PR\(_2\)(biaryl) Ni complexes are behaving in cis-[Ni(C\(_6\)F\(_5\))\(_2\)]\(\{\text{PR}_{2}\text{(biaryl)}\}\) or cis-[Ni(C\(_6\)F\(_5\))\(_2\)]\{PR\(_2\text{(biaryl)}\}\{(THF)\}] as bulky monodentate ligands, allowing for easy coordination of water and hydrosylation. As an exception, the fluorinated biaryl phosphate 13 forms in solution a mixture of cis-[Ni(C\(_6\)F\(_5\))\(_2\)]\{PR\(_2\text{(biaryl)}\}\}(THF) and some trans-[Ni(C\(_6\)F\(_5\))\(_2\)]\{PR\(_2\text{(biaryl)}\}\}(2) (entries 12-13), the later with two P-coordinated phosphines.

In the lack of access to other experimental information, we performed DFT calculations on the stabilization of the potential Pd and Ni complexes formed by reaction of one molecule of the ligand JohnPhos (10) to complex [M(C\(_6\)F\(_5\))\(_2\)](THF)\(_2\) (M = Pd, Ni), taking as zero energy the starting complex in each case. The results in Table 2 show that, in dichloromethane, the replacement of one or the two THF ligands in Pd produces more stable complexes, supporting plausibility of chelation along the coupling evolution. On the contrary, for Ni in dichloromethane the calculations show that displacement of one THF is clearly favorable, but displacement of the second is very disfavored, supporting a monodentate coordination of JohnP, like PBU\(_5\), along the process.

### Table 2. DFT calculations for the thermodynamic effect of displacing one or two THF upon addition of ligand 10, in CH\(_2\)Cl\(_2\) solution. L = JohnP. \(\Delta G^\circ\) in kcal/mol\(^{-1}\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\Delta G^\circ)</th>
<th>Compound</th>
<th>(\Delta G^\circ)</th>
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<tr>
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<td>0.0</td>
<td><a href="THF">Ni(C(_6)F(_5))(_2)</a>(_2)</td>
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<tr>
<td><a href="THF">Pd(C(_6)F(_5))(_2)</a>(L)</td>
<td>-11.8</td>
<td><a href="THF">Ni(C(_6)F(_5))(_2)</a>(L)</td>
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<tr>
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<td>-6.6</td>
<td><a href="L">Ni(C(_6)F(_5))(_2)</a></td>
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</tbody>
</table>

Consistent with the overall evidence and these computational results, it is reasonable to propose the structures in solution depicted in Figure 4. For Pd, the structure in CH\(_2\)Cl\(_2\) solution of the complex with JohnP must be A, as observed in the solid state by X-ray diffraction studies. For Ni and the cis-(C\(_6\)F\(_5\))\(_2\) structures in entries 10-17 (Table 2), the distal aryl would be unable to chelate Ni in competence with the smaller and harder THF (or eventually water), and structure B is preferred, even in the presence of only low concentration of THF or water. The lack of coordination of the distal aryl is very detrimental for coupling, which becomes slow, and allows for faster hydrosylation. Finally, the chelate coordination of PEWO (Table 2, entries 14-17) affords structure C for the complexes in solution.

![Figure 4. Proposed structures in CH\(_2\)Cl\(_2\) solution for [Pd(C\(_6\)F\(_5\))\(_2\)]\{PR\(_2\text{(biaryl)}\}\} (A), [Ni(C\(_6\)F\(_5\))\(_2\)]\{PR\(_2\text{(biaryl)}\}\} (THF)] (B), and [Ni(C\(_6\)F\(_5\))\(_2\)] (R-PEWO) (C).](image)

It is worth noting that the coupling power of the PEWO ligands is much higher in Ni than in Pd, to the point that the quantitative kinetic studies required the use of very low temperatures (-22 to -53 °C, instead of 0 °C in Pd). This is due to the gain in stability of the EWO olefin as the coupling evolution starts, which is higher for a hard Ni\(^{II}\) → soft Ni\(^{II}\) process than for a soft Pd\(^{II}\) → soft Pd\(^{0}\) coupling. The measured \(\Delta G^\circ\)(C\(_6\)F\(_5\))\(_2\)-C\(_6\)F\(_5\))\(_2\)-(C\(_6\)F\(_5\))\(_2\)) barriers at the corresponding experimental temperature used in each case (Table 3, column 2), are collected in Table 3, column 4. Additionally, we determined \(\Delta H^\circ\)(C\(_6\)F\(_5\))\(_2\)-C\(_6\)F\(_5\))\(_2\)) and \(\Delta S^\circ\)(C\(_6\)F\(_5\))\(_2\)-C\(_6\)F\(_5\))\(_2\)) for ligand 16 in an experimental variable temperature study. Assuming that the \(\Delta S^\circ\)(C\(_6\)F\(_5\))\(_2\)-C\(_6\)F\(_5\))\(_2\)) contribution is unlikely to change much from one PEWO ligand to another, we could work out a unified comparative scale at 0 °C (Table 3, column 5).

### Table 3. Experimental \(\Delta G^\circ\)(C\(_6\)F\(_5\))\(_2\)-C\(_6\)F\(_5\))\(_2\) (kcal/mol\(^{-1}\)) for reductive elimination of cis-[Ni(C\(_6\)F\(_5\))\(_2\)](THF)] (I) promoted by PEWO ligands in Scheme 2, at the indicated temperature.

<table>
<thead>
<tr>
<th></th>
<th>(T) (°C)</th>
<th>[C(_6)F(_5))(_2]-C(_6)F(_5))(_2)] (%</th>
<th>(\Delta G^\circ) at (T) °C</th>
<th>(\Delta G^\circ) at 0 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>10</td>
<td>61:39</td>
<td>21.9</td>
<td>–</td>
</tr>
<tr>
<td>14</td>
<td>-53</td>
<td>100:0</td>
<td>16.7</td>
<td>17.7</td>
</tr>
<tr>
<td>15</td>
<td>-52</td>
<td>100:0</td>
<td>17.0</td>
<td>18.1</td>
</tr>
<tr>
<td>16</td>
<td>-22</td>
<td>100:0</td>
<td>19.5</td>
<td>19.9</td>
</tr>
<tr>
<td>17</td>
<td>-36</td>
<td>100:0</td>
<td>18.1</td>
<td>18.8</td>
</tr>
</tbody>
</table>
Comparing the data in Table 3 with those at 25 °C in Table 1, it is clear that lower temperatures increase the conversion times but favor higher C₆F₅-C₆F₃-C₆F₃-H ratios. The reference complex 1 already shows this cooling effect, and lowering the work temperature from 25 to 10 °C improves this ratio from 47:53 (in 4 h) in Table 1 to 61:39 (in 6 h) in Table 3. For the PEWO ligands their reactions, carried out at temperatures below -22 °C, are complete in about 8 h and do not show any sign of hydrolysis.

The temperature-unified column in Table 3 shows that the couplings are clearly faster the more electron deficient the olefin group is: i) PEWO-F ligands (14, 15), are faster than PEWO-H ligands (16, 17); ii) the PEWO-F ligand 14 is faster than its PEWO-H homologous 16; and iii) the PEWO-H ligand 17 (with two CO₂Me substituents) is faster than the PEWO-H ligand 16 (with only one CO₂Ph group). However, contrary to Pd, for Ni PhPEWO-F (14) is faster than o-TolPEWO-F (15), suggesting that bulkier R groups on phosphorus can be beneficial in Pd but are detrimental in Ni. Although this fits well the steric expectations, it should be taken with caution until more cases are available for comparison.

Figure 5 summarizes graphically, for representative ligands, the most significant experimental results of this study.

**EXPERIMENTAL SECTION**

Experimental details are given in Supporting Information.

**ASSOCIATED CONTENT**

Supporting Information

General Methods, Synthesis, Experimental Coupling/hydrolysis Studies, Kinetic and Variable Temperature NMR studies, Computational Methods and Results, X-ray Crystallographic Data, NMR Spectra, SI references (30 pages, PDF).

The Supporting Information is available free of charge on the ACS Publications website.

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Notes
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Since the early estimations in physical models (by the way, using Ni as the metal center), other methods have been incorporated, including the modern application of computational methods to different coordination geometries and metal centers: Jover, J.; Cirera, J. Computational assessment on the Tolman cone angles for P-ligands. Dalton Trans., 2019, 48, 15036–15048.


EWO or EDO applies to the same kind of olefin, electron-defficient (EDO) as free, or electron-withdrawing (EWO) as metal-coordinated.


The purity of complex 1 was evaluated by NMR (see S1).

Complex 1 should be handled in a glove box or under N2 or Ar atmosphere. Prolonged vacuum evacuation should be avoided.
due to elimination of the weakly coordinated THF ligand. The solid product should be kept at -20 °C.


