

## Ranking ligands by their ability to ease $(C_6F_5)_2Ni^{II}L \rightarrow Ni^0L + (C_6F_5)_2$ coupling vs. hydrolysis: Outstanding activity of PEWO ligands

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**ABSTRACT:** The Ni<sup>II</sup> literature complex *cis*-[Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>2</sub>] is a synthon of *cis*-Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> that allows us to establish a protocol to measure and compare the ligand effect on the Ni<sup>II</sup> → Ni<sup>0</sup> 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<sub>2</sub>(biaryl) phosphines, and PEWO ligands (phosphines with one potentially chelate electron-withdrawing olefin). Extremely different C<sub>6</sub>F<sub>5</sub>–C<sub>6</sub>F<sub>5</sub> 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<sub>2</sub>(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<sup>II</sup> complexes: they yield up to 96% C<sub>6</sub>F<sub>5</sub>–C<sub>6</sub>F<sub>5</sub> coupling in 5 minutes at 25 °C (the rest is C<sub>6</sub>F<sub>5</sub>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.<sup>1</sup> 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.<sup>2</sup> It looks, however, that often the efficiencies of identical ligands do not run parallel for Pd and Ni. For instance, bulky PR<sub>3</sub> 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.<sup>3,4</sup> 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  $\theta$ , proposed long ago by Tolman,<sup>5</sup> is smaller for the same ancillary ligand on Pd than on Ni.<sup>6</sup> This reduces the volume available to accommodate the reacting groups coordinated to Ni.<sup>7</sup> 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<sub>bur</sub> make operative some Ni catalyzed couplings that fail with ligands such as P<sup>t</sup>Bu<sub>3</sub> or JohnPhos.<sup>7</sup>

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.

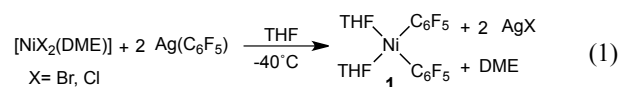
C–C Pd coupling, and presumably in Ni too, the reductive elimination gets more difficult in the order aryl-aryl < aryl-alkyl < alkyl-alkyl < C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub> < aryl-CF<sub>3</sub> << CF<sub>3</sub>-CF<sub>3</sub>.<sup>8</sup> In the early 1970's, seminal studies of A. Yamamoto's group had already found that butane formation from [Ni<sup>II</sup>(Et)<sub>2</sub>(bipy)] was induced by addition of electron-tractor moieties such as electron-withdrawing olefins (EWOs),<sup>9</sup> aromatic compounds, and phosphines.<sup>10</sup> They proposed that coordination of an EWO molecule formed a 5-coordinate Ni<sup>II</sup> complex and reduced the Et-Et coupling barrier from 68 kcal×mol<sup>-1</sup> in [Ni<sup>II</sup>(Et)<sub>2</sub>(bipy)] to 20 kcal×mol<sup>-1</sup> in [Ni<sup>II</sup>(Et)<sub>2</sub>(bipy)(EWO)]. For perfluoroaryl groups the coupling barriers turned inaccessible, and EWO addition failed to promote coupling in [Ni<sup>II</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(bipy)] at any temperature.<sup>11</sup> In this line, the group of Doyle has reported an electron-deficient olefin Fro-DO (with *E*-R-C(O)-CH=CH-C(O)-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.<sup>12</sup>

There are not many computational studies so far. One comparing the effect of 42 diphosphines on the reductive elimination barrier of Ph-CF<sub>3</sub> from [Ni(CF<sub>3</sub>)Ph(P-P)] is available, but access to parallel experimental data was limited to two cases because of synthetic problems.<sup>13</sup> There is also a theoretical study showing that, dimethyl fumarate facilitates the nickel-catalyzed conjunctive cross-coupling of alkenyl amides with aryl iodides and aryl boronic esters because it lowers the aryl-alkyl coupling activation energy from  $\Delta G^\ddagger = 14.6$  kcal×mol<sup>-1</sup> with ethylene to only  $\Delta G^\ddagger = 2.6$  kcal×mol<sup>-1</sup> with dimethyl fumarate.<sup>14</sup> 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).<sup>15</sup>

More recently, we proposed the use of complex *cis*-[Pd(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>2</sub>] as a Pd<sup>II</sup>-*meter* to rank experimentally the different ligand according to their ability to facilitate the difficult C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub> coupling. The procedure consists in measuring the activation energy for C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub> formation ( $\Delta G^\ddagger(\text{C}_6\text{F}_5\text{-C}_6\text{F}_5)_{\text{Pd}}$ ) upon addition of the ligand being tested to *cis*-[Pd(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>2</sub>].<sup>16</sup> Although the C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub> coupling barrier from Pd is difficult,<sup>17</sup> the percentages of competing hydrolysis are moderate in Pd, which is not oxophilic. The work here aims at extending this idea to a Ni<sup>II</sup>-*meter* that might provide information to compare the coupling barriers in Ni<sup>II</sup> ( $\Delta G^\ddagger(\text{C}_6\text{F}_5\text{-C}_6\text{F}_5)_{\text{Ni}}$ ) 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.

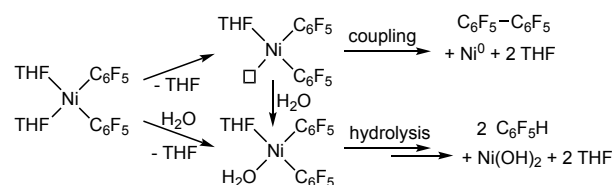
## RESULTS AND DISCUSSION

The Ni<sup>II</sup>-*meter* complex should be a fairly stable synthon of *cis*-[Ni<sup>II</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] 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*-[Ni<sup>II</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(NCPH)<sub>2</sub>],<sup>18</sup> or *trans*-[Ni<sup>II</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(SbPh<sub>3</sub>)<sub>2</sub>]<sup>19</sup>), we found *cis*-[Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>2</sub>] (**1**) as the one fulfilling reasonably our requirements. Based on the two reported syntheses of **1**,<sup>20</sup> we have developed a more direct procedure: Commercially available [NiX<sub>2</sub>(DME)] (X = Br, Cl; DME = 1,2-dimethoxyethane) reacts with Ag(C<sub>6</sub>F<sub>5</sub>),<sup>21</sup> in THF (1 hour at -40 °C), to produce **1** (Eq. 1). Evaporation, extraction with Et<sub>2</sub>O, and filtration to remove the insoluble silver salts, followed by evaporation to dryness affords **1** as an orange solid with > 97% purity.<sup>22</sup>

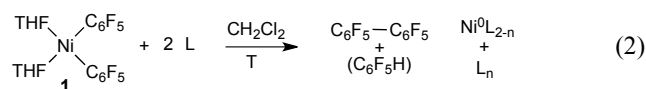


Complex **1** is stable for several months in the fridge under inert atmosphere, but it is somewhat sensitive to atmospheric oxygen and water at room temperature.<sup>23</sup> Solutions of **1** in freshly distilled dry THF are stable enough for comfortable quick handling at room temperature, and can be stored in the freezer for a few hours, although decomposition (turbidity) is eventually observed. In non-coordinating solvents, complex **1** decomposes noticeably fast to a mixture of the coupling product (C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub>) and the hydrolysis byproduct (C<sub>6</sub>F<sub>5</sub>H),<sup>16</sup> presumably due to easy THF dissociation to the three-coordinate [Ni<sup>II</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)] that undergoes faster reductive elimination than the four-coordinate **1**, and competitive substitution to [Ni<sup>II</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)(OH<sub>2</sub>)] followed by hydrolysis (Scheme 1).<sup>24</sup>

## Scheme 1. Coupling vs. hydrolysis from the Ni<sup>II</sup>-*meter*.



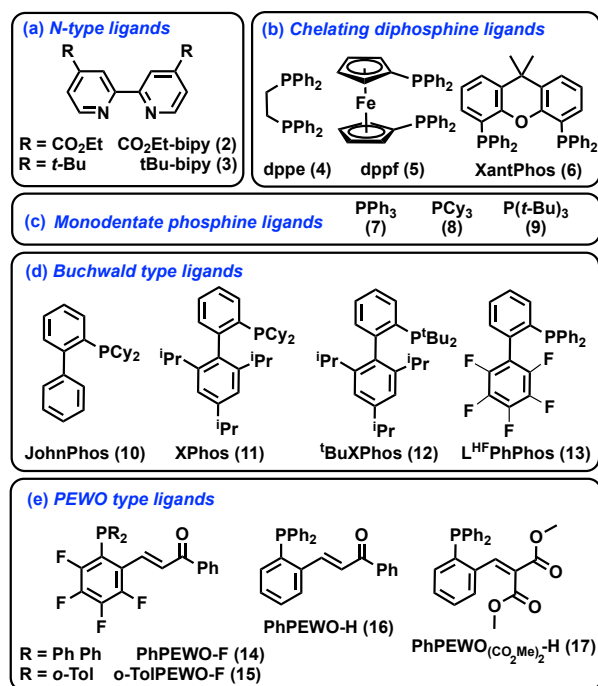
The protocol for the coupling/hydrolysis measurements shown in Eq. 2 (where each L stands for one potentially bidentate ligand or for two monodentate ligands) is as follows: The reactions are monitored by <sup>19</sup>F NMR. The addition of L is made at lower temperature and the NMR tube is brought to 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 [Ni<sup>0</sup>L<sub>n</sub>] (n = 2-4 depending on L), in order to prevent that initially formed Ni<sup>0</sup> could sequester part of the L needed for completion of Ni<sup>0</sup> complex. We confirmed for L chelates that using L:Ni = 1:1 or 2:1 does not change the initial coupling rate. The CH<sub>2</sub>Cl<sub>2</sub> 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 1:H<sub>2</sub>O molar ratio was approximately 1:0.7. In toluene, used occasionally, it was approximately 1:0.3 (see SI).



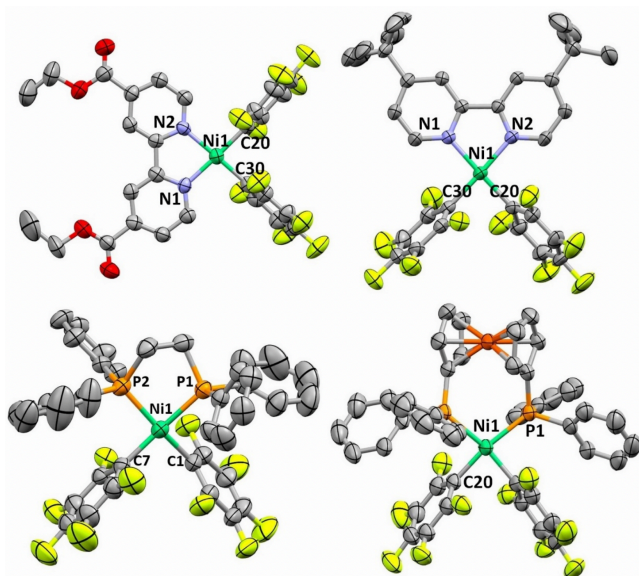
The Ni-*meter* **1** itself undergoes coupling and hydrolysis (Scheme 1) and can be taken as reference. It reveals immediately much higher hydrolysis:coupling ratio (53:47 mol%) at 25 °C than observed for the equivalent Pd-*meter*.<sup>16</sup> In general, higher participation of hydrolysis is found in Ni compared to Pd for all the queried ligands, consistent with the more favorable coordination of water and its higher acidity on the harder Ni<sup>II</sup> center than on the softer Pd<sup>II</sup>. In the presence of D<sub>2</sub>O the hydrolysis product was enriched in C<sub>6</sub>F<sub>5</sub>-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*) dialkylbiaryl (Buchwald type) phosphines; *e*) PEWO type ligands (phosphine-electron-withdrawing olefin ligands). Upon addition of these ligands to **1**, results spanning from formation of totally inert complexes to instantaneous C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub> coupling, as well as diverse C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub>:C<sub>6</sub>F<sub>5</sub>H ratios, were observed at 25 °C. X-ray diffraction structures were solved when the stable complexes allowed for crystallization.

## Scheme 2. Ligand types tested with the Ni<sup>II</sup>-meter



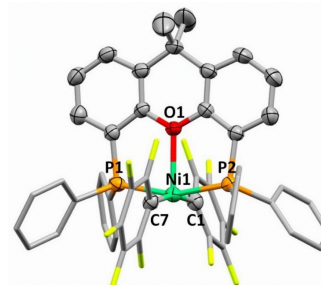
The bipy ligands (**2**, **3**) form immediately the X-ray characterized [Ni<sup>II</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>L] chelated complexes (**18**, **19**) (Figure 1, above). The symmetrical diphosphine ligands **4** and **5** also lead to stable [Ni<sup>II</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>L] chelated complexes **20** and **21**, respectively, which were isolated and X-ray characterized (Figure 1, below). As reported by Yamamoto for the [Ni<sup>II</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(2,2'-bipy)] complexes,<sup>11</sup> coupling on **18–21** does not occur at 25 °C. Moreover, all these complexes are stable not only at 25 °C in CH<sub>2</sub>Cl<sub>2</sub>, but also at 80 °C in dioxane.



**Figure 1.** Above: Left: Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(CO<sub>2</sub>Et-bipy) (**18**); Right: Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(*t*Bu-bipy) (**19**). Below: Left: Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(dppe)·1/2 CH<sub>2</sub>Cl<sub>2</sub> (**20**); Right: Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(dppf)·*n*-pentane (**21**). All solvent molecules and H atoms omitted for clarity.

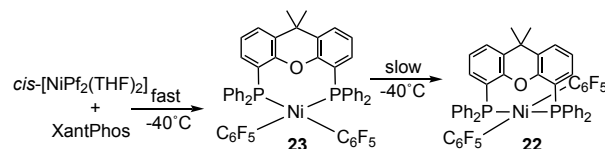
The reaction of **1** with Xantphos in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C produced the *trans* chelate complex **22**. Its X-ray diffraction structure confirmed the expectations from the NMR studies, and is

shown in Figure 2. Monitoring of the reaction of **1** with Xantphos at -40 °C showed that *cis*-[Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(Xantphos)] (**23**) was initially formed (Scheme 3) and then it isomerized to the thermodynamically favored *trans*-[Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(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,<sup>25</sup> but only *trans* coordination of XantPhos to Ni<sup>II</sup> had been reported so far.<sup>26,27</sup>



**Figure 2.** X-ray diffraction structure of *trans*-[Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(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(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(XantPhos)] (**22**).



In contrast to the stability of the precedent complexes, coupling (C<sub>6</sub>F<sub>5</sub>–C<sub>6</sub>F<sub>5</sub>) and hydrolysis (C<sub>6</sub>F<sub>5</sub>H) 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 C<sub>6</sub>F<sub>5</sub>–C<sub>6</sub>F<sub>5</sub>:C<sub>6</sub>F<sub>5</sub>H ratio formed, as percentage of products. Some specific reactions with addition of *p*-benzoquinone (bzq), 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.<sup>15</sup>

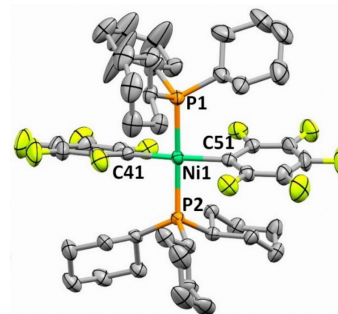
For complex **1**, the reactions in Scheme 1 are sensitive to 2:1 addition of bzq (entry 2 vs. 1). Presumably the coupling occurs on Ni<sup>II</sup> species with at least one coordinated bzq in equilibrium with free bzq, which accelerates the coupling reaction and noticeably improves the coupling/hydrolysis ratio. Consistently, increasing the bzq 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 bzq 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.

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

Entry. L	Compounds in solution and NMR signals	t	Conv. %	(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> :C <sub>6</sub> F <sub>5</sub> H mol%
1. THF	Complex 1	2h 4 h	85 100	49:51 47:53
2. bzq <sup>a</sup>	equilibrium mixture (text)	4 h	100	66:34
3. bzq <sup>b</sup>	equilibrium mixture (text)	1.5 h	100	89:11
4. 7 <sup>c</sup>	Complex 24 + 2 free L	24 h	–	–
5. 8 <sup>c</sup>	Complex 25 + 2 free L	24 h	–	–
6. 9 <sup>c,e</sup>	Complex 26 + 3 free L	2 h	100	11:89
7. 10 <sup>a</sup>	Cis-1:1 complex, 2 nonequiv. C <sub>6</sub> F <sub>5</sub> , 1 L	6 h	78	20:80
8. 11 <sup>a</sup>	Cis-1:1 complex, 2 nonequiv. C <sub>6</sub> F <sub>5</sub> , 1 free L	6 h 9.5 h	47 77	29:71 24:76
9. 11 <sup>e</sup>	Cis-1:1 complex, 2 nonequiv. C <sub>6</sub> F <sub>5</sub> , 1 L	6 h 9.5 h	45 68	42:58 59:41
10. 11+bzq <sup>a</sup>	Cis-1:1 complex, 2 nonequiv. C <sub>6</sub> F <sub>5</sub> , 1 L	18 h	76	20:80
11. 12 <sup>a</sup>	Cis-1:1 complex, 2 nonequiv. C <sub>6</sub> F <sub>5</sub> , 1 L	6 h	83	23:77
12. 13 <sup>a</sup>	Cis-1:1 + <i>trans</i> -1:2 complexes + free L	28h	100	40:60
13. 13 <sup>d</sup>	Cis-1:1 + <i>trans</i> -1:2 complexes + 1	28h	100	43:57
14. 14 <sup>a</sup>	Complex 27 + 1 free L	< 5 min	100	95:5
15. 15 <sup>a</sup>	Complex 28 + 1 free L	< 5 min	100	82:18
16. 16 <sup>a</sup>	Complex 29 + 1 free L	< 5 min	100	89:11
17. 17 <sup>a</sup>	Complex 30 + 1 free L	< 5 min	100	96:4

Monodentate phosphines with different molecular sizes totally replace THF. The small PPh<sub>3</sub> (**7**) and PCy<sub>3</sub> (**8**) form the stable *trans*-[Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] complexes **24** and **25** (entries 4 and 5, Table 1). The *trans* arrangement of the two C<sub>6</sub>F<sub>5</sub> groups prevents reductive elimination. Figure 3 shows the structure of *trans*-[Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>]. On the other hand, the NMR spectra show that only one molecule of P<sup>t</sup>Bu<sub>3</sub> (**9**) can coordinate to the Ni<sup>II</sup> center, producing the reactive *cis*-[Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(P<sup>t</sup>Bu<sub>3</sub>)] (**26**), and leaving the other three P<sup>t</sup>Bu<sub>3</sub> uncoordinated (entry 6).

Complex **26** undergoes fast evolution at 25 °C, predominantly to C<sub>6</sub>F<sub>5</sub>H. The reaction was complete in less than 2h, which precluded to obtain single crystals of the complex in solution. Since two non-equivalent C<sub>6</sub>F<sub>5</sub> groups are observed in the <sup>19</sup>F NMR spectrum, it is not excluded that complex **26** in THF solution could be [Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(P<sup>t</sup>Bu<sub>3</sub>)(THF)]. The efficient hydrolysis shows that complex **26** is allowing for water coordination and subsequent hydrolysis. This result discourages using P<sup>t</sup>Bu<sub>3</sub> for difficult couplings on Ni, in contrast with its successful utilization in Pd-catalyzed processes.



**Figure 3.** X-ray diffraction structure of *trans*-[Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(PCy<sub>3</sub>)] (**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.<sup>3,4</sup> In the reaction with the Pd-*meter*, they were very fast for coupling, or at least very efficient to hinder undesired hydrolysis.<sup>16</sup> With the Ni-*meter*, 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 CH<sub>2</sub>Cl<sub>2</sub>, 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 H<sub>2</sub>O content in toluene has been practically exhausted. Thus, in sharp contrast with their good behavior on Pd<sup>II</sup>, not only these PR<sub>2</sub>(biaryl) phosphines are quite inefficient for C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub> coupling on Ni, but are also unable to protect the Ni<sup>II</sup> center and prevent hydrolysis. The slowness of the coupling reactions and the double dependence of water and L prevented to measure (ΔG<sup>‡</sup>(C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub>)<sub>Ni</sub>) 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**,<sup>28</sup> 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 CD<sub>2</sub>Cl<sub>2</sub> (entries 14-17). Single crystals for X-ray diffraction of these complexes could not be obtained due to very fast conversion to C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub>, but their P-olefin chelate coordination in solution is unambiguously confirmed by observation of four non-equivalent F<sub>ortho</sub> signals in their <sup>19</sup>F NMR spectra.<sup>29</sup> In a square planar Ni<sup>II</sup> complex the P-olefin chelate coordination leads to two non-equivalent C<sub>6</sub>F<sub>5</sub> groups. The Ni coordination plane is not a symmetry plane, and the restriction to rotation of the C<sub>6</sub>F<sub>5</sub> groups produces non-equivalence of their two F<sub>ortho</sub> atoms affording four F<sub>ortho</sub> 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**),<sup>30</sup> further support the coordination of the C=C group and the proposed geometry. These PEWO ligands **14-17** show an exceptional power to induce C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub> coupling due to the effect

of coordination of the EWO olefin group.<sup>15</sup> 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 rates are the fastest ever observed in Ni<sup>II</sup>→Ni<sup>0</sup> reductive elimination processes.<sup>31</sup> 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<sub>2</sub>(biaryl) and PEWO ligands in the Ni-meter, in contrast with 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<sup>II</sup> and Pd<sup>0</sup> structures of chelated complexes with *E*- or *Z*-coordinated olefin have been reported,<sup>32</sup> and many Pd<sup>II</sup> and Pd<sup>0</sup> complexes with PR<sub>2</sub>(biaryl) ligands show Pd-C<sub>ipso</sub> chelating interactions with the distal aryl (Pd-C<sub>ipso</sub> distances in the range 2.19-2.60 Å).<sup>33</sup> These interactions help to stabilize [Pd(aryl)XL] or [Pd(aryl)R'L] intermediates in the catalytic cycles and support their chelating coordination along the C-C coupling process for both kinds of ligand.<sup>15</sup>

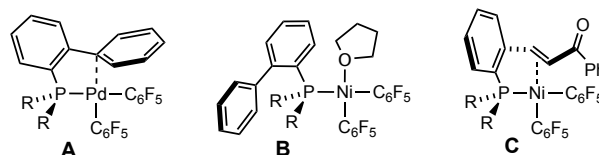
There is no similar structural X-ray information available for Ni complexes with these ligands, and we also have failed to obtain single crystals in this work, but the NMR spectra for these complexes in CH<sub>2</sub>Cl<sub>2</sub>, in Ni:L = 1:2 solutions, show always one free L and one coordinated (entries 7-17). For the PEWO complexes (entries 14-17) coordination of the olefin group is clearly seen in the <sup>1</sup>H NMR spectra, but the PR<sub>2</sub>(biaryl) complexes with ligands **10-12** (entries 7-11) show ill-defined broad <sup>1</sup>H spectra perhaps associated to slow conformational changes. The fact is that their chemical behavior is very similar to that of P<sup>t</sup>Bu<sub>3</sub>: formation of Ni:P = 1:1 complexes in solution; NMR observation of 2 chemically non-equivalent C<sub>6</sub>F<sub>5</sub> groups: slow conversion; and much less coupling than hydrolysis. This suggests that the PR<sub>2</sub>(biaryl) Ni complexes are behaving in *cis*-[Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>{PR<sub>2</sub>(biaryl)}] or *cis*-[Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>{PR<sub>2</sub>(biaryl)}(THF)] as bulky monodentate ligands, allowing for easy coordination of water and hydrolysis. As an exception, the fluorinated biaryl phosphine **13** forms in solution a mixture of *cis*-[Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>{PR<sub>2</sub>(biaryl)}(THF)] and some *trans*-[Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>{PR<sub>2</sub>(biaryl)}<sub>2</sub>] (entries 12-13), the later with two P-coordinated phosphines.<sup>28</sup>

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<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>2</sub>] (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 P<sup>t</sup>Bu<sub>3</sub>, along the process.

**Table 2.** DFT calculations for the thermodynamic effect of displacing one or two THF upon addition of ligand **10**, in CH<sub>2</sub>Cl<sub>2</sub> solution. L = JohnP. ΔΔG<sup>0</sup> in kcal×mol<sup>-1</sup>.

Compound	ΔΔG <sup>0</sup>	Compound	ΔΔG <sup>0</sup>
[Pd(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (THF) <sub>2</sub> ]	0.0	[Ni(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (THF) <sub>2</sub> ]	0.0
[Pd(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (THF)(L)]	-11.8	[Ni(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (THF)(L)]	-6.7
[Pd(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (L)]	-6.6	[Ni(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (L)]	4.5

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<sub>2</sub>Cl<sub>2</sub> 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<sub>6</sub>F<sub>5</sub>) structures in entries 10-17 (Table 2), the distal aryl would be unable to chelate Ni in competition 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 hydrolysis. 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<sub>2</sub>Cl<sub>2</sub> solution for [Pd(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>{PR<sub>2</sub>(biaryl)}] (**A**), [Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>{PR<sub>2</sub>(biaryl)}(THF)] (**B**), and [Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(R-PEWO)] (**C**).

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<sup>II</sup> → soft Ni<sup>0</sup> process than for a soft Pd<sup>II</sup> → soft Pd<sup>0</sup> coupling. The measured ΔG<sup>‡</sup>(C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub>)<sub>Ni</sub> barriers at the corresponding experimental temperature used in each case (Table 3, column 2), are collected in Table 3, column 4. Additionally, we determined ΔH<sup>‡</sup>(C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub>)<sub>Ni</sub> and ΔS<sup>‡</sup>(C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub>)<sub>Ni</sub> for ligand **16** in an experimental variable temperature study. Assuming that the ΔS<sup>‡</sup>(C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub>)<sub>Ni</sub> 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).

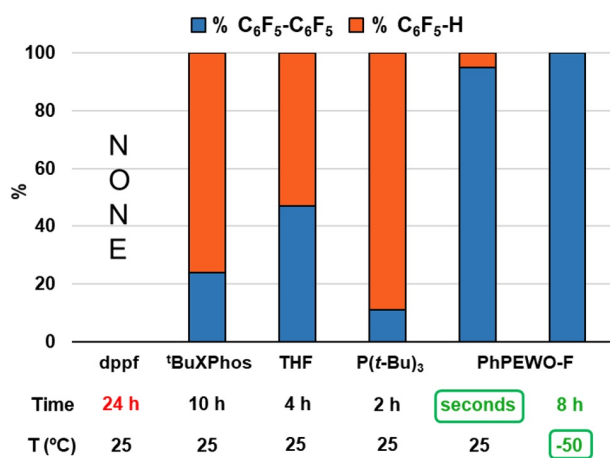
**Table 3.** Experimental ΔG<sup>‡</sup>(C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub>)<sub>Ni</sub> (kcal×mol<sup>-1</sup>) for reductive elimination of *cis*-[Ni<sup>II</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>2</sub>] (**1**) promoted by PEWO ligands in Scheme 2, at the indicated temperature.

L	T (°C)	(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> :C <sub>6</sub> F <sub>5</sub> H (%)	ΔG <sup>‡</sup> at T °C	ΔG <sup>‡</sup> at 0 °C
THF	10	61:39	21.9	–
<b>14</b>	-53	100:0	16.7	17.7
<b>15</b>	-52	100:0	17.0	18.1
<b>16</b>	-22	100:0	19.5	19.9
<b>17</b>	-36	100:0	18.1	18.8

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 C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub>:C<sub>6</sub>F<sub>5</sub>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 CO<sub>2</sub>Me substituents) is faster than the PEWO-H ligand **16** (with only one CO<sub>2</sub>Ph 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.



**Figure 5.** L and T dependence of coupling vs. hydrolysis.

## CONCLUSIONS

In conclusion, we have established a protocol to evaluate qualitatively, and quantitatively when possible, ligand effects on the Ni<sup>II</sup>→Ni<sup>0</sup> reductive elimination rate and the competitive hydrolysis, using *cis*-[Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>2</sub>] (**1**) as *Ni-meter* at room or lower temperatures. Experimental determination of ΔG<sup>‡</sup>(C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub>)<sub>Ni</sub> can be achieved easily for the more efficient ligands. An additional bonus is that NMR monitoring of the process can provide plausible clues to understand the unsatisfactory coupling performance of PR<sub>2</sub>(biaryl) ligands in Ni.

Competitive hydrolysis on the hard Ni<sup>II</sup> center can be a serious problem for survival of the Ni<sup>II</sup> catalysts, unless strict dryness conditions are used or the high activity of the nucleophile (*e.g.* LiR, ZnR<sub>2</sub>, etc.) guarantees solvent dryness. The hydrolysis/coupling ratio found in this work using SPS quality solvents shows that water contents acceptable for Pd, can be unacceptable for Ni. In the case of PR<sub>2</sub>(biaryl) ligands, this undesired hydrolysis competence is due in part to the small non-

buried volume in the *cis*-Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> fragment, which prevents their protecting chelate coordination, but allows coordination of small O-donor ligands such as water, with subsequent fast hydrolysis. In addition to the slowness of coupling, this affects very negatively, the performance of PR<sub>2</sub>(biaryl) phosphines in Ni. The different entropy dependence of the two processes (hydrolysis must be at least bimolecular) helps to reduce the percentage of hydrolysis at low temperatures.

The comparison of the Ni and Pd results with PEWO and PR<sub>2</sub>(biaryl) phosphines also warns against the risk of making ΔG<sup>‡</sup> extrapolations for the activity of ligands on 10 group metals based on the known variations of bond enthalpies,<sup>2</sup> unless there is absolute certainty that the structures are identical for the metal centers being compared. This can be often uncertain for metals with unequal radii and volumes. For instance, the PEWO complexes of Ni and Pd have identical structures and Ni shows, as expected, lower ΔG<sup>‡</sup>(C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub>)<sub>M</sub> activation energy. In contrast, PR<sub>2</sub>(biaryl) phosphines complexes of Ni and Pd have different structures and Ni shows noticeably higher ΔG<sup>‡</sup>(C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub>)<sub>M</sub> activation energy than Pd.

Last but not least, the family of PEWO ligands is impressively efficient in Ni, inducing hydrolysis protection and fast coupling even at very low temperatures. The coupling that was reported impossible from [Ni<sup>II</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(bipy)] at any temperature,<sup>11</sup> occurs from [Ni<sup>II</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(PEWO)] complexes in only 8 h at -50 °C, or *in seconds at room temperature!!* Investigation of the application of PEWO ligands in Ni catalysis is ongoing.

## 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

The authors declare no conflict of interest.

The authors declare no competing financial interests.

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### Ranking ligands by their ability to ease (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Ni<sup>II</sup>L → Ni<sup>0</sup>L + (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> coupling vs. hydrolysis: Outstanding activity of PEWO ligands

The ability of ligands to facilitate a difficult C–C coupling and protect from hydrolysis in Ni(II) is very different from their performance in Pd(II). Most remarkably, for ligands with comparable performance in Pd(II), PR<sub>2</sub>(bipy) and P(<sup>t</sup>Bu)<sub>3</sub> are not efficient in Ni(II) whereas PEWO ligands are amazingly efficient and induce C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub> coupling even at –50 °C.

