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Article

Ranking Ligands by Their Ability to Ease $(C_6F_5)_2Ni^{II}L \rightarrow Ni^0L + (C_6F_5)_2$ Coupling versus Hydrolysis: Outstanding Activity of PEWO Ligands

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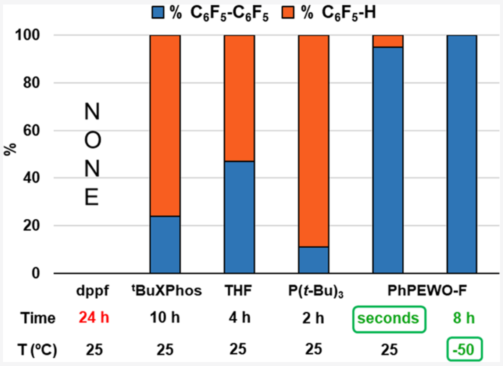
ABSTRACT: The Ni^{II} literature complex *cis*-$[Ni(C_6F_5)_2(THF)_2]$ is a synthon of *cis*-$Ni(C_6F_5)_2$ that allows us to establish a protocol to measure and compare the ligand effect on the $Ni^{II} \rightarrow Ni^0$ reductive elimination step (coupling), often critical in catalytic processes. Several 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-withdrawing olefin). Extremely different $C_6F_5-C_6F_5$ coupling rates, ranging from 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% $C_6F_5-C_6F_5$ coupling in 5 min at 25 °C (the rest is C_6F_5H) 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_3 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 θ, proposed long ago by Tolman,[5] for the same ancillary ligand is smaller on Pd than that 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, then 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 θ but low $\%V_{bur}$ make operative some Ni catalyzed couplings that fail with ligands such as P^tBu_3 or JohnPhos.[7]

The nonburied 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.

In C−C Pd coupling, and presumably in Ni as well, the reductive elimination gets more difficult in the order aryl−aryl < aryl−alkyl < alkyl−alkyl < $C_6F_5-C_6F_5$ < aryl−CF_3 ≪ CF_3-CF_3.[8] In the early 1970s, seminal studies of A. Yamamoto's group had already found that butane formation from $[Ni^{II}(Et)_2(bipy)]$ 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 molecule formed a 5-coordinate Ni^{II} complex and reduced the Et−Et coupling barrier from 68 kcal × mol^{-1} in $[Ni^{II}(Et)_2(bipy)]$ to 20 kcal × mol^{-1} in $[Ni^{II}(Et)_2(bipy)(EWO)]$. For perfluoroaryl groups, the coupling barriers turned inaccessible, and EWO addition failed to promote coupling in $[Ni^{II}(C_6F_5)_2(bipy)]$ at any temperature.[11] 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.[12]

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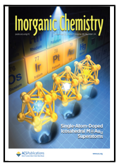

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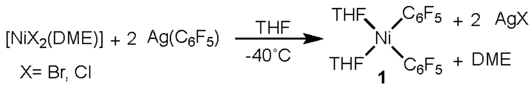
There are not many computational studies so far. One comparing the effects of 42 diphosphines on the reductive elimination barrier of Ph−CF_3 from [Ni(CF_3)Ph(P−P)] is available, but access to parallel experimental data was limited to two cases because of synthetic problems.[13] There is also a theoretical study showing that dimethyl 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^{-1} with ethylene to only $\Delta G^{\ddagger}$ = 2.6 kcal × mol^{-1} with dimethyl fumarate.[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 EWOs.[15]

More recently, we proposed the use of complex *cis*-[$Pd(C_6F_5)_2(THF)_2$] as a Pd^{II}-meter to rank experimentally the different ligands according to their ability to facilitate the difficult C_6F_5−C_6F_5 coupling. The procedure consists of measuring the activation energy for C_6F_5−C_6F_5 formation ($\Delta G^{\ddagger}(C_6F_5{-}C_6F_5)_{Pd}$) upon addition of the ligand being tested to *cis*-[$Pd(C_6F_5)_2(THF)_2$].[16] Although the C_6F_5−C_6F_5 coupling barrier from Pd is difficult,[17] the percentages of competing hydrolysis are moderate in Pd, which is not oxophilic. The work here aims at extending this idea to a Ni^{II}-meter that might provide information to compare the coupling barriers in Ni^{II} ($\Delta G^{\ddagger}(C_6F_5{-}C_6F_5)_{Ni}$) 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^{II}-meter complex should be a fairly stable synthon of *cis*-[$Ni^{II}(C_6F_5)_2$] that is 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*-[$Ni^{II}(C_6F_5)_2(NCPh)_2$][18] or *trans*-[$Ni^{II}(C_6F_5)_2(SbPh_3)_2$]),[19] we found *cis*-[$Ni(C_6F_5)_2(THF)_2$] (**1**) as the one fulfilling reasonably our requirements. On the basis of the two reported syntheses of **1**,[20] we have developed a more direct procedure: Commercially available [NiX_2(DME)] (X = Br and Cl; DME = 1,2-dimethoxyethane) reacts with $Ag(C_6F_5)$[21] in THF (1 h at −40 °C) to produce **1**:

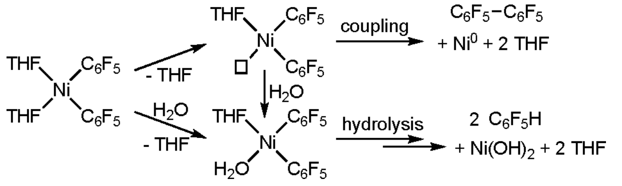


(1)

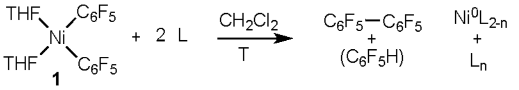
Evaporation, extraction with Et_2O, and filtration to remove the insoluble silver salts, followed by evaporation to dryness affords **1** as an orange solid with >97% purity.[22]

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.[23] 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 noncoordinating solvents, complex **1** decomposes noticeably quickly to a mixture of the coupling product (C_6F_5−C_6F_5) and the hydrolysis byproduct (C_6F_5H),[16] presumably due to easy THF dissociation to the three-coordinate [$Ni^{II}(C_6F_5)_2(THF)$] that undergoes reductive elimination more quickly than the four-coordinate **1** and competitive substitution to [$Ni^{II}(C_6F_5)_2(THF)(OH_2)$] followed by hydrolysis (Scheme 1).[24]

Scheme 1. Coupling versus Hydrolysis from the Ni^{II}-Meter



The protocol for the coupling/hydrolysis measurements shown in eq 2



(2)

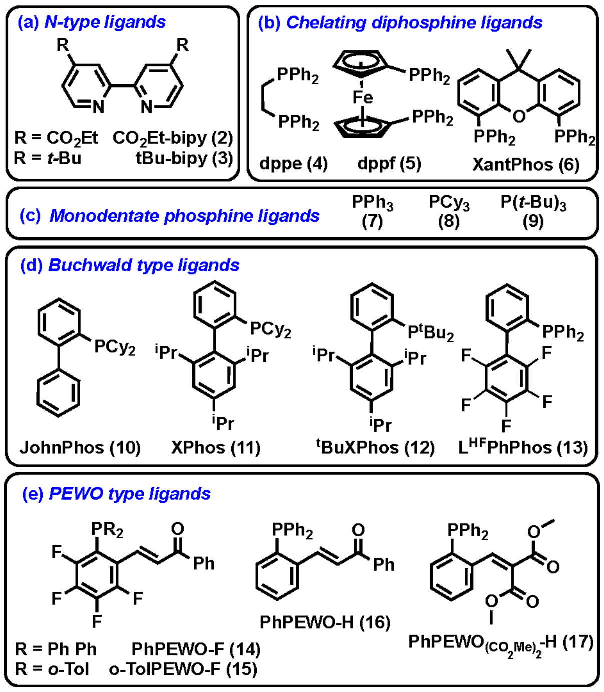
(where each L stands for one potentially bidentate ligand or for two monodentate ligands) is as follows: The reactions are monitored by ^{19}F NMR. The addition of L is made at lower temperature, and the NMR tube is brought to the coupling temperature once the ligand coordination has reached equilibrium. 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^0L_n] (n = 2−4 depending on L), in order to prevent initially formed Ni^0 from sequestering a portion of the L needed for completion of Ni^0 complex. We confirmed for L chelates that using L/Ni = 1:1 or 2:1 does not change the initial coupling rate. The CH_2Cl_2 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_2O molar ratio was approximately 1:0.7. In toluene, used occasionally, it was approximately 1:0.3 (see the Supporting Information).

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.[16] In general, higher participation of hydrolysis is found in Ni compared to Pd for all the quested ligands, consistent with the more favorable coordination of water and its higher acidity on the harder Ni^{II} center than on the softer Pd^{II}. In the presence of D_2O the hydrolysis product was enriched in C_6F_5−D, as expected (see the Supporting Information 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; and (e) PEWO type ligands (phosphine-EWO ligands). Upon addition of these ligands to **1**, results spanning from formation of totally inert complexes to instantaneous C_6F_5−C_6F_5 coupling, as well as diverse C_6F_5−C_6F_5:C_6F_5H ratios, were observed at 25 °C. X-ray diffraction structures were solved when the stable complexes allowed for crystallization.

The bipy ligands (**2** and **3**) immediately form the X-ray characterized [$Ni^{II}(C_6F_5)_2L$] chelated complexes (**18** and **19**) (Figure 1, above). Symmetrical diphosphine ligands **4** and **5** also lead to stable [$Ni^{II}(C_6F_5)_2L$] chelated complexes **20** and

Scheme 2. Ligand Types Tested with the Ni^{II}-Meter



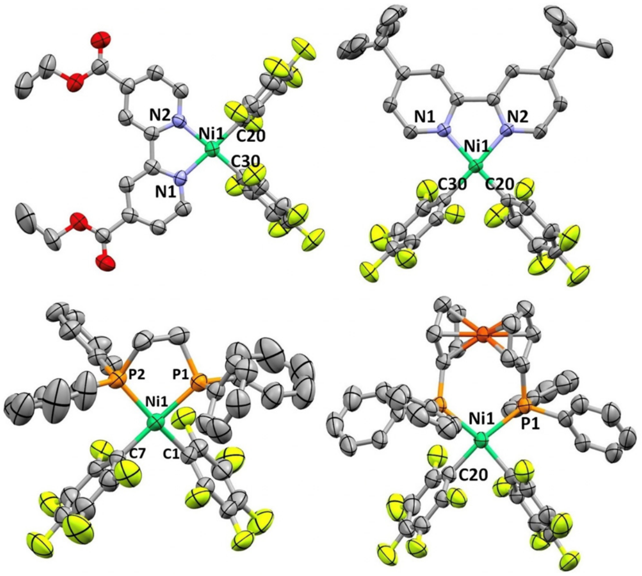


Figure 1. Top left: $[Ni(C_6F_5)_2(CO_2Et\text{-}bipy)]$ (**18**). Top right: $[Ni(C_6F_5)_2({}^tBu\text{-}bipy)]$ (**19**). Bottom left: $[Ni(C_6F_5)_2(dppe)]\cdot 1/2\ CH_2Cl_2$ (**20·1/2 CH₂Cl**). Bottom right: $[Ni(C_6F_5)_2(dppf)]\cdot$*n*-pentane (**21**·*n*-pentane). All solvent molecules and H atoms omitted for clarity.

21, respectively, which were isolated and X-ray characterized (Figure 1, below). As reported by Yamamoto for the $[Ni^{II}(C_6F_5)_2(2,2'\text{-}bipy)]$ complexes,[11] coupling on **18**−**21** does not occur at 25 °C. Moreover, all these complexes are stable not only at 25 °C in CH_2Cl_2 but also at 80 °C in dioxane.

The reaction of **1** with Xantphos in CH_2Cl_2 at 25 °C produced *trans*-chelate complex **22**. Its X-ray diffraction structure confirmed the expectations from the NMR studies, and it is shown in Figure 2. Monitoring of the reaction of **1** with Xantphos at −40 °C showed that *cis*-$[Ni(C_6F_5)_2(Xantphos)]$ (**23**) was initially formed (Scheme 3) and then isomerized to the thermodynamically favored *trans*-$[Ni(C_6F_5)_2(Xantphos)]$ (**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,[25] but only trans coordination of XantPhos to Ni^{II} had been reported so far.[26,27]

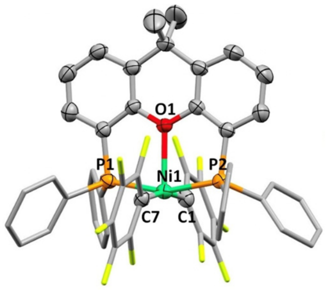
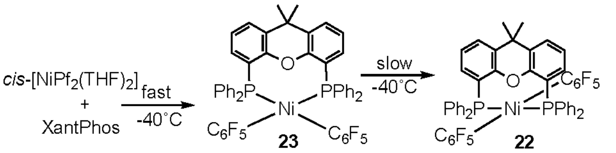


Figure 2. X-ray diffraction structure of *trans*-$[Ni(C_6F_5)_2(XantPhos)]\cdot$toluene (**22**·toluene). Solvent molecule and H atoms omitted for clarity.

Scheme 3. Reaction Sequence Observed at −40 °C in the Formation of *trans*-$[Ni(C_6F_5)_2(XantPhos)]$ (22)



In contrast to the stability of the precedent complexes, coupling (C_6F_5−C_6F_5) and hydrolysis (C_6F_5H) 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 the following: (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_6F_5−C_6F_5/C_6F_5H ratio formed, as percentage of products. Some specific reactions with addition of *p*-benzoquinone (bzq), a strongly electron-deficient olefin (EDO) with a strong electron-withdrawing effect upon coordination (EWO) are also included, as specified in the first column of Table 1.[15]

For complex **1**, the reactions in Scheme 1 are sensitive to 2:1 addition of bzq (entry 2 versus 1). Presumably the coupling occurs on Ni^{II} 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 difficult couplings.

Monodentate phosphines with different molecular sizes totally replace THF. The small PPh_3 (**7**) and PCy_3 (**8**) form stable *trans*-$[Ni(C_6F_5)_2(PR_3)_2]$ complexes **24** and **25** (entries

Table 1. Conversion (%) of 1 (Equation 2) and Coupling/Hydrolysis Ratio with Ligands in Scheme 2[a]

entry/L	compounds in solution and NMR signals	*t*	conv. %	$(C_6F_5)_2$/C_6F_5H (mol %)
1. THF	complex **1**	2 h	85	49:51
		4 h	100	47:53
2. bzq[b]	equilibrium mixture (text)	4 h	100	66:34
3. bzq[c]	equilibrium mixture (text)	1.5 h	100	89:11
4. **7**[d]	complex **24** + 2 free L	24 h		
5. **8**[d]	complex **25** + 2 free L	24 h		
6. **9**[d,f]	complex **26** + 3 free L	2 h	100	11:89
7. **10**[b]	*cis*-1:1 complex, 2 nonequiv C_6F_5, 1 L	6 h	78	20:80
8. **11**[b]	*cis*-1:1 complex, 2 nonequiv. C_6F_5, 1 free L	6 h	47	29:71
		9.5 h	77	24:76
9. **11**[f]	*cis*-1:1 complex, 2 nonequiv C_6F_5, 1 L	6 h	45	42:58
		9.5 h	68	59:41
10. **11** + bzq[b]	*cis*-1:1 complex, 2 nonequiv C_6F_5, 1 L	18 h	76	20:80
11. **12**[b]	*cis*-1:1 complex, 2 nonequiv C_6F_5, 1 L	6 h	83	23:77
12. **13**[b]	*cis*-1:1 + *trans*-1:2 complexes + free L	28 h	100	40:60
13. **13**[e]	*cis*-1:1 + *trans*-1:2 complexes + **1**	28 h	100	43:57
14. **14**[b]	complex **27** + 1 free L	<5 min	100	95:5
15. **15**[b]	complex **28** + 1 free L	<5 min	100	82:18
16. **16**[b]	complex **29** + 1 free L	<5 min	100	89:11
17. **17**[b]	complex **30** + 1 free L	<5 min	100	96:4

[a] In CH_2Cl_2; $T = 25$ °C. [b] L/Ni molar ratio = 2:1. [c] L/Ni molar ratio = 20:1. [d] L/Ni molar ratio = 4:1. [e] L/Ni molar ratio = 1:1. [f] In toluene.

4 and 5, Table 1). The trans arrangement of the two C_6F_5 groups prevents reductive elimination. Figure 3 shows the structure of *trans*-$[Ni(C_6F_5)_2(PCy_3)_2]$. In contrast, the NMR spectra show that only one molecule of P^tBu_3 (**9**) can coordinate to the Ni^{II} center, producing the reactive *cis*-$[Ni(C_6F_5)_2(P^tBu_3)]$ (**26**), and leaving the other three P^tBu_3 uncoordinated (entry 6).

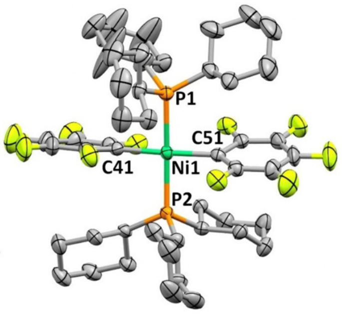


Figure 3. X-ray diffraction structure of *trans*-$[Ni(C_6F_5)_2(PCy_3)_2]$ (**25**). H atoms omitted for clarity.

Complex **26** undergoes fast evolution at 25 °C, predominantly to C_6F_5H. The reaction was complete in less than 2 h, which precluded obtaining single crystals of the complex in solution. Since two nonequivalent C_6F_5 groups are observed in the ^{19}F NMR spectrum, it is not excluded that complex **26** in THF solution could be $[Ni(C_6F_5)_2(P^tBu_3)(THF)]$. The efficient hydrolysis shows that complex **26** allows for water coordination and subsequent hydrolysis. This result discourages using P^tBu_3 for difficult couplings on Ni, in contrast with its successful utilization in Pd-catalyzed processes.

Biaryl phosphines **10**−**12** (group (d)) are very efficient in Pd-catalyzed processes, but there are few examples of good performance in Ni catalysis.[3,4] In the reaction with the Pd-meter, they were very fast for coupling, or at least very efficient to hinder undesired hydrolysis.[16] 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 47−77% conversion in CH_2Cl_2, showing slower coupling than hydrolysis with only 20−24% 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 of 42:58 in 6 h 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_2O content in toluene has been practically exhausted. Thus, in sharp contrast with their good behavior on Pd^{II}, these PR_2(biaryl) phosphines not only are quite inefficient for C_6F_5−C_6F_5 coupling on Ni but are also unable to protect the Ni^{II} center and prevent hydrolysis. The slowness of the coupling reactions and the double dependence of water and L prevented to measure $(\Delta G^{\ddagger}(C_6F_5{-}C_6F_5)_{Ni})$ 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).

Recently reported fluorinated biaryl ligand **13**,[28] where the fluorinated aryl might somehow resemble an EWO (see later), was also tested. Its reactivity was slow and produced somewhat better but still very unsatisfactory coupling/hydrolysis ratio (entries 12 and 13).

Finally, concerning PEWO ligands **14**−**17** of group (e) in Scheme 2, they produce complexes **27**−**30** in CD_2Cl_2 (entries 14−17). Single crystals for X-ray diffraction of these complexes could not be obtained due to very fast conversion to C_6F_5−C_6F_5, but their P−olefin chelate coordination in solution is unambiguously confirmed by observation of four nonequivalent F_{ortho} signals in their ^{19}F NMR spectra.[29] In a square planar Ni^{II} complex the P−olefin chelate coordination leads to two nonequivalent C_6F_5 groups. The Ni coordination plane is not a symmetry plane, and the restriction to rotation of the C_6F_5 groups produces nonequivalence of their two F_{ortho} atoms affording four F_{ortho} signals. The upfield shifts of the olefinic protons (e.g., $\delta = 7.32$ and 5.97 ppm in **29** compared to $\delta = 8.35$ and 7.17 ppm in free PhPEWO-H phosphine **16**)[30] further support the coordination of the C═C group and the proposed geometry. PEWO ligands **14**−**17** show an exceptional power to induce C_6F_5−C_6F_5 coupling due to the effect of coordination of the EWO olefin group.[15] 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 $Ni^{II} \rightarrow Ni^{0}$ reductive elimination processes.[31] In fact, they are too fast to be measured by NMR at 25 °C by applying the initial rates method.

The dramatically different behavior of PR_2(biaryl) and PEWO ligands in the Ni-meter, in contrast 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,[32] and many Pd^{II} and Pd^{0} complexes with PR_2(biaryl) ligands show Pd−C_{ipso} chelating interactions with the distal aryl (Pd−C_{ipso} distances in the range of 2.19−2.60 Å).[33] 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.[15]

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. The NMR spectra for these complexes in CH_2Cl_2, in Ni/L = 1:2 solutions, always show one free L and one coordinated L (entries 7−17). For the PEWO complexes (entries 14−17) coordination of the olefin group is clearly seen in the ^1H NMR spectra, but the PR_2(biaryl) complexes with ligands **10**−**12** (entries 7−11) show ill-defined broad ^1H spectra perhaps associated to slow conformational changes. The fact is that their chemical behavior is very similar to that of P^tBu_3: formation of Ni/P = 1:1 complexes in solution, NMR observation of 2 chemically nonequivalent C_6F_5 groups, slow conversion, and much less coupling than hydrolysis. This suggests that the PR_2(biaryl) Ni complexes are behaving in *cis*-[Ni$(C_6F_5)_2$\{PR_2(biaryl)\}] or *cis*-[Ni$(C_6F_5)_2$\{PR_2(biaryl)\}(THF)] as bulky monodentate ligands, allowing for easy coordination of water and hydrolysis. As an exception, fluorinated biaryl phosphine **13** in solution forms a mixture of *cis*-[Ni$(C_6F_5)_2$\{PR_2(biaryl)\}(THF)] and some *trans*-[Ni$(C_6F_5)_2$\{PR_2(biaryl)\}$_2$] (entries 12 and 13), the latter with two P-coordinated phosphines.[28]

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$(C_6F_5)_2(THF)_2$] (M = Pd and Ni), taking as the starting complex in each case zero energy. 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 JohnPhos, like P^tBu_3, along the process.

Table 2. DFT Calculations for the Thermodynamic Effect of Displacing 1 or 2 THF upon Addition of Ligand 10[a]

compound	$\Delta\Delta G^0$	compound	$\Delta\Delta G^0$
[Pd$(C_6F_5)_2(THF)_2$]	0.0	[Ni$(C_6F_5)_2(THF)_2$]	0.0
[Pd$(C_6F_5)_2$(THF)(L)]	−11.8	[Ni$(C_6F_5)_2$(THF)(L)]	−6.7
[Pd$(C_6F_5)_2$(L)]	−6.6	[Ni$(C_6F_5)_2$(L)]	4.5

[a] In CH_2Cl_2 solution. L = JohnPhos. $\Delta\Delta G^0$ in kcal × mol^{-1}.

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_2Cl_2 solution of the complex with JohnPhos must be **A**, as observed in the solid state by X-ray diffraction studies. For Ni and the *cis*-$(C_6F_5)_2$ 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 hydrolysis. Finally, the chelate coordination of PEWO (Table 2, entries 14−17) affords structure **C** for the complexes in solution.

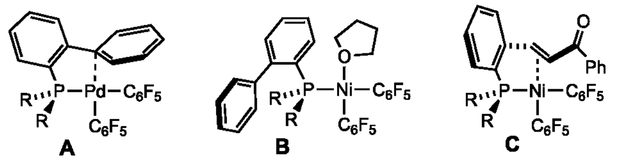


Figure 4. Proposed structures in CH_2Cl_2 solution for [**Pd**$(C_6F_5)_2$\{PR_2(biaryl)\}] (**A**), [**Ni**$(C_6F_5)_2$\{PR_2(biaryl)\}(THF)] (**B**), and [**Ni**$(C_6F_5)_2$(R-PEWO)] (**C**).

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 $Ni^{II} \rightarrow$ soft Ni^{0} process than for a soft $Pd^{II} \rightarrow$ soft Pd^{0} coupling. The measured $\Delta G^{\ddagger}(C_6F_5{-}C_6F_5)_{Ni}$ barriers at the corresponding experimental temperature used in each case (Table 3, column 2), are collected in Table 3, column 4. Additionally, we determined $\Delta H^{\ddagger}(C_6F_5{-}C_6F_5)_{Ni}$ and $\Delta S^{\ddagger}(C_6F_5{-}C_6F_5)_{Ni}$ for ligand **16** in an experimental variable-temperature study. Assuming that the $\Delta S^{\ddagger}(C_6F_5{-}C_6F_5)_{Ni}$ 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 $\Delta G^{\ddagger}(C_6F_5{-}C_6F_5)_{Ni}$ (kcal × mol^{-1}) for Reductive Elimination of *cis*-[$Ni^{II}(C_6F_5)_2(THF)_2$] (1)[a]

L	*T* (°C)	$(C_6F_5)_2/C_6F_5H$ (%)	$\Delta G^{\ddagger}$ at *T*	$\Delta G^{\ddagger}$ at 0 °C
THF	10	61:39	21.9	
14	−53	100:0	16.7	17.7
15	−52	100:0	17.0	18.1
16	−22	100:0	19.5	19.9
17	−36	100:0	18.1	18.8

[a] Promoted by PEWO ligands in Scheme 2, at the indicated temperature.

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 $C_6F_5{-}C_6F_5$:C_6F_5H 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 clearly that the more electron deficient the olefin group, the faster the couplings: (i) PEWO-F ligands (**14** and **15**) are faster than PEWO-H ligands (**16** and **17**). (ii) PEWO-F ligand **14** is faster than its PEWO-H homologue **16**. (iii) PEWO-H ligand **17** (with two CO_2Me substituents) is faster than PEWO-H ligand **16** (with only one CO_2Ph 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.

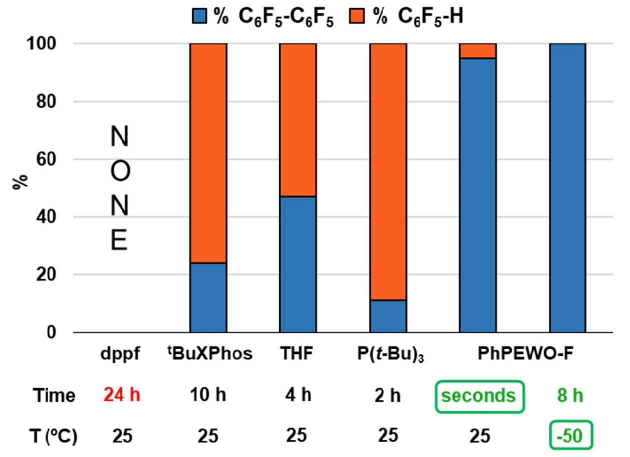


Figure 5. L and *T* dependence of coupling versus hydrolysis.

CONCLUSIONS

In conclusion, we have established a protocol to evaluate qualitatively, and quantitatively when possible, ligand effects on the $Ni^{II} \rightarrow Ni^0$ reductive elimination rate and the competitive hydrolysis, using *cis*-$[Ni(C_6F_5)_2(THF)_2]$ (**1**) as Ni-meter at room or lower temperatures. Experimental determination of $\Delta G^{\ddagger}(C_6F_5{-}C_6F_5)_{Ni}$ 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_2(biaryl) ligands in Ni.

Competitive hydrolysis on the hard Ni^{II} center can be a serious problem for survival of the Ni^{II} catalysts, unless strict dryness conditions are used or the high activity of the nucleophile (e.g., LiR, ZnR_2, 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_2(biaryl) ligands, this undesired hydrolysis competence is due in part to the small nonburied volume in the *cis*-$Ni(C_6F_5)_2$ 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 very negatively affects the performance of PR_2(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 coupling results of Ni and Pd with PEWO versus PR_2(biaryl) ligands show the reasons behind the scarce success in Ni catalysis of some structurally sophisticated ligands efficient in Pd catalysis. For structurally simple ligands, $\Delta G^{\ddagger}$ trends in group 10 metals run often parallel to $\Delta H^{\ddagger}$ trends because they give rise to similar structures along the reaction pathway.[2] However, this structural match becomes particularly unlikely when combining metals of unequal radii and volumes, such as Ni and Pd, with structurally sophisticated ligands tailored for one of them. This is the case for the direct (one-step) coupling process studied here and the PR_2(biaryl) ligands. The complexes of Ni and Pd with the flexible and adaptable PEWO ligands have identical ground-state structures, and Ni shows, as expected from the enthalpy trends, lower $\Delta G^{\ddagger}(C_6F_5{-}C_6F_5)_M$ activation energy. In contrast, the PR_2(biaryl) complexes of Ni and Pd have different ground-state structures, and Ni happens to show (against the enthalpy trend in this case) noticeably higher $\Delta G^{\ddagger}(C_6F_5{-}C_6F_5)_M$ activation energy than Pd for reductive elimination.

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 $[Ni^{II}(C_6F_5)_2(bipy)]$ at any temperature[10] occurs from $[Ni^{II}(C_6F_5)_2(PEWO)]$ 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 the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications Web site. The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02831.

General methods, synthesis, experimental coupling/hydrolysis studies, kinetic and variable-temperature NMR studies, computational methods and results, X-ray crystallographic data, NMR spectra, additional references (PDF)

Optimized gas phase structures of the Ni–Pd species in Table 2 (XYZ)

Accession Codes

CCDC 1907218, 1907224, 1907226, 1907227, 1907229, and 1963893 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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