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Phosphines with Tethered Electron-Withdrawing Olefins as Ligands for Efficient Pd-Catalyzed Aryl-Alkyl Coupling

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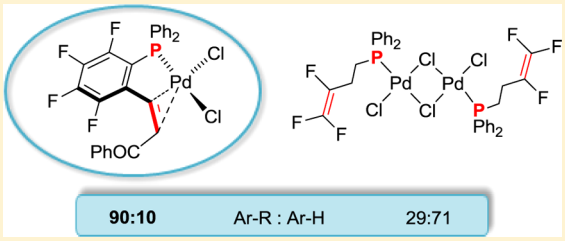
Supporting Information

ABSTRACT: A group of phosphine/alkene ligands L = $Ph_2P(2\text{-}RC_6F_4)$ (R = CH═CHMe, CH═CHPh, CH═CHCOPh) or $Ph_2P(CH_2)_2CF{=}CF_2$ and their $[PdCl_2L]$ complexes have been prepared. These phosphines are easy to prepare and fairly stable toward oxidation. Their palladium complexes feature chelated L structures with the double bond coordinated as the *Z* isomer, except for $Ph_2P(CH_2)_2CF{=}CF_2$, where the double bond is not coordinated and the complex is a dimer with Cl bridges. The ligands have been tested for their activity in the Negishi palladium-catalyzed aryl-alkyl coupling, where there is a competition of coupling and reduction products. Only the ligands forming chelated Pd^{II} complexes rise the coupling/reduction ratio to values 42/58 or higher. Of these, it is the ligand bearing the more electron-withdrawing substituent (R = CH═CHCOPh) that is the one producing remarkably high selectivity toward coupling: 90/10 under the usual Negishi conditions, and noticeably higher (97/3) if the proportion of $ZnEt_2$ in the reaction is lowered. These results fit well with the hypothesis that chelating phosphines with tethered electron-acceptor olefins improve the selectivity toward coupling products mostly because they reduce the activation barrier for C−C coupling, and not because they protect the complex from *β*-H elimination.



INTRODUCTION

In the field of metal-catalyzed reactions, olefins are looked at as reagents more often than as ligands. However, the presence of a double bond function in the reaction mixture, whether in an additive, as a part of the structure of a reagent, or included in the catalyst molecule, can dramatically influence the outcome of the process and determine the rate and selectivity of the transformation.[1,2] Olefins with electron-withdrawing groups (electron-withdrawing olefins, EWO) are particularly important additives in metal-catalyzed cross-coupling reactions. Although their importance is well-known and they are present in the panoply of the synthetic chemist, it is acknowledged that "there is a current lack of understanding of their mode of action in transition metal catalysis".[1] A particularly useful effect of EWO is that they facilitate the C−C coupling (so-called reductive elimination) step. Moreover, they do this when alkyl groups are involved, thus preventing or diminishing the undesired *β*-hydride elimination processes that lead to C−H rather than C−C coupled products (this process is often confusingly named "reduction" because of the product formed). The EWO effect has been traditionally attributed to two plausible but not fully demonstrated reasons: (i) coordination of an electron-withdrawing olefin results in reduced electron density at the metal center, which facilitates the reductive elimination step; and (ii) coordination of the olefin fills the vacant coordination sites required for *β*-H elimination to occur, thus inhibiting this process.[3]

A few years ago we showed experimentally and calculated theoretically why and how much olefins can reduce the activation energy of the C−C coupling step in Pd-catalyzed processes.[4] For instance, it was calculated that the Me−Me coupling activation barriers are about 20−23 kcal/mol in regular square-planar tetracoordinated complexes *cis*-$[PdMe_2(PMe_3)L]$ (L = conventional ligand). This value goes down to 13 kcal/mol in a three-coordinated intermediate *cis*-$[PdMe_2(PMe_3)]$. Impressively, it further falls down to values as low as 6 kcal/mol in tetracoordinated complexes *cis*-$[PdMe_2(PMe_3)(EWO)]$, increasing several orders of magnitude the coupling rate. It is not easy to conceive that an electron-withdrawing olefin will reduce the electron density on the metal more than the lack of one ligand, particularly in a Pd^{II} system, where back-donation is moderate because of the high stabilization of the d orbitals.[5] In effect, our theoretical analysis showed that the extraordinary effect of EWO, at least in Pd, goes beyond a simple variation in electron density on Pd^{II} and has its origin in how the EWO−Pd orbital interactions change as the coupling rearrangement progresses, thus leading to a large reduction of the activation energy of the process.[4,6]

The suggested protecting effect of EWO against *β*-H elimination by blocking the coordination vacant is also an unsatisfactory explanation for improvement of the coupling/reduction ratio in a conflicting synthesis, because often the

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addition of better coordinating ligands than olefins does not suppress nor reduce β-H elimination in systems where EWO do produce that effect.

Besides the above-mentioned synthetic advantages toward coupling, there are some drawbacks when using EWO as *external* coupling additives. Thus, if a substitution reaction of a stronger conventional ligand for an external EWO is needed, the latter has to be used in fairly high concentration in order to produce small but kinetically significant amounts of the EWO complex undergoing coupling. On the other hand, EWO can produce, after coupling, highly stable Pd^0 intermediates $[PdL_n(EWO)]$, which could slow down or even preclude the oxidative addition needed for Pd to reenter the catalytic cycle.[7,8] The use of hybrid $PR_2(EWO)$ ligands, favoring the intramolecular chelating coordination of the olefin group, should skip the need of a large amount of EWO for its coordination to Pd^{II}, and perhaps the structural constrains of an appropriate ligand might contribute to diminish the stability of the Pd^0 intermediate, thus reducing its undesired reluctance to oxidation. Thus, a $PR_2(EWO)$ ligand might offer a good trade-off between the pros and cons of external EWO additives. In fact, $PR_2(EWO)$ ligands in Chart 1 have led to dramatic

Chart 1

R^1 = Ph, Cy
R^2 = H, COPh, CO_2Me, $CO_2{}^tBu$ R = Me, Et, ^{i}Pr, ^{t}Bu

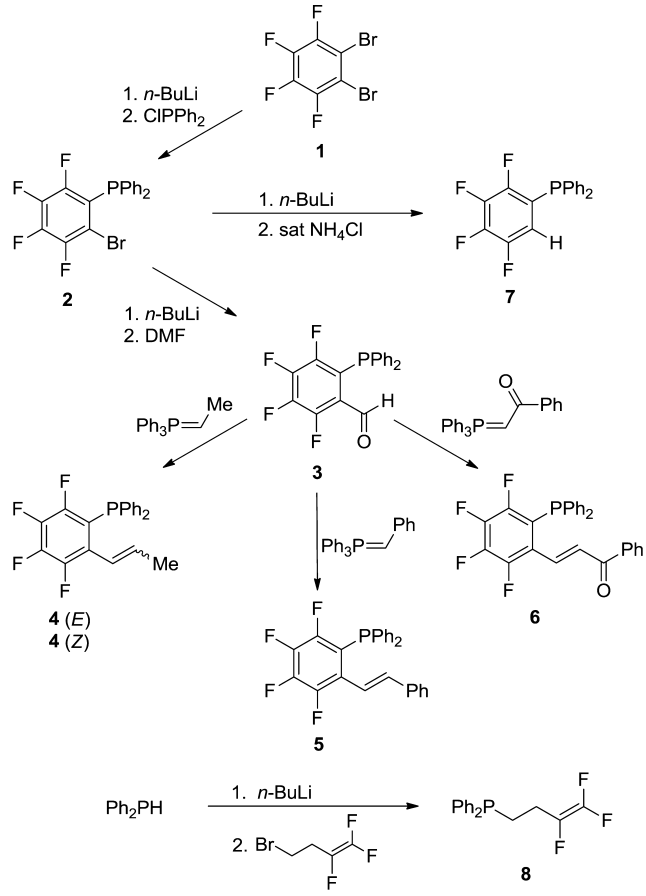
improvement in the efficiency of $C(sp^2)-C(sp^2)$ and $C(sp^3)-C(sp^2)$ couplings in Suzuki,[9] and Negishi reactions,[10] enhancing the selectivity of processes involving $C(sp^3)$ atoms toward C−C coupling instead of β-hydride elimination and C−H coupling (reduction). It was argued that coordination of the olefin slowed down the undesired β-H elimination.

In this study we are trying to get additional information about the behavior of $PR_2(olefin)$ systems as experimental support for future mechanistic and catalytic studies. The structure of the efficient ligands in Chart 1 with R^1 = Ph was chosen, but we designed a set of related phosphines, polyfluorinated in the functionalyzed aryl ring, which have some practical advantages for our purposes. First, the phosphines in this work are easier to synthesize and handle, as the fluorinated ring makes them less sensitive to oxidation than those in Chart 1. Second, they provide improved solubility, which has allowed us to obtain and characterize the corresponding Pd^{II} complexes by ^{1}H, ^{19}F and ^{31}P NMR, and by X-ray diffraction.[11] Third, the presence of F atoms in the molecule facilitates monitoring of the reactions by ^{19}F NMR. A potential disadvantage of our phosphines for the stabilization of Pd^{II}, and at the Pd^0/Pd^{II} oxidation step, is that they are expectedly somewhat less donor and more π-acceptor at the phosphorus, but in practice this has turned out not to be a problem, and some of them have shown to be very efficient in catalysis. It is interesting to note that the fluorinated aryl ring is already an electron-withdrawing olefin substituent itself.

RESULTS AND DISCUSSION

Synthesis of the Phosphines. The syntheses of the phosphines are summarized in Scheme 1. Monolithiation of the

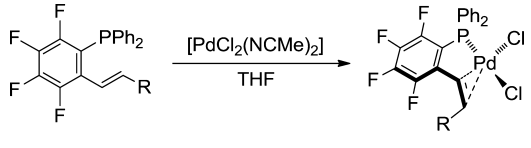
Scheme 1. Synthesis of the Phosphines



commercially available **1**, followed by reaction with $ClPPh_2$ gave phosphine **2**. A second lithiation, followed by quenching with DMF, afforded the crude phosphine-aldehyde **3**, which could be used without further purification. Wittig olefination of **3** with $Ph_3P{=}CH_2R$ afforded ligands **4**−**6** (with R = Me, Ph, and COPh, respectively). Phosphine **4** is formed as a mixture of *E*- and *Z*-isomers, which can be separated by column chromatography. Additionally, a phosphine without the alkene functionalization but containing the tetrafluorinated ring (**7**) was synthesized from **2** by lithiation and quenching with a water solution saturated with NH_4Cl. Finally, a related phosphine (**8**), with an aliphatic chain with the same number of carbons linking P to the double bond, as the others, and a fluorinated double bond, was synthesized by alkylation of PPh_2H.

Synthesis and Characterization of the Palladium(II) Complexes. Addition of phosphine **4**−**6** to a solution of $[PdCl_2(NCMe)_2]$ in THF (phosphine:Pd = 1:1), at room temperature, yielded the corresponding complexes **9**−**11** (Scheme 2). Their NMR spectra suggest that the ligand is

Scheme 2. Synthesis of the Pd^{II} Complexes



4-6 R = Me (**9**), Ph (**10**), COPh (**11**)

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bonded to Pd^{II} as a chelate:[12] upon coordination, the $^{31}P\{^1H\}$ NMR signal (multiplet, due to coupling to ^{19}F) shows a clear downfield shift in all cases, and the ^1H NMR spectra also show a clear shift of the olefinic protons. The IR spectra also display a clear shift of the C=C frequency (from ca. 1600 cm^{-1} in the free ligands to ca. 1500 cm^{-1} in the complexes),[13] revealing a weakening of the double bond that is consistent with alkene coordination. Interestingly, for R = Me, both isomers **4**(*Z*) and **4**(*E*) formed the same palladium complex **9**, as seen by ^1H NMR. The X-ray structure of **9**, discussed below, reveals that the olefin group coordinates in the *Z* conformation, hence **4**(*Z*) coordinates directly but **4**(*E*) needs isomerization to afford **9**. The isomerization of olefins is known to be catalyzed by Pd^{II} and by Pd^0 complexes.[14,15] Interestingly, when the coordinated phosphine **4**(*Z*) is displaced from **9** by addition of excess of PPh_3, **4** is liberated as a mixture of *E* and *Z* isomers that, in the presence of Pd, slowly isomerize to the most stable *E* isomer.

The proposed structures, containing chelated PPh_2(olefin) ligands, were unambiguously confirmed by X-ray diffraction for **9** (Figure 1) and **11** (Figure 2). Both structures feature square-

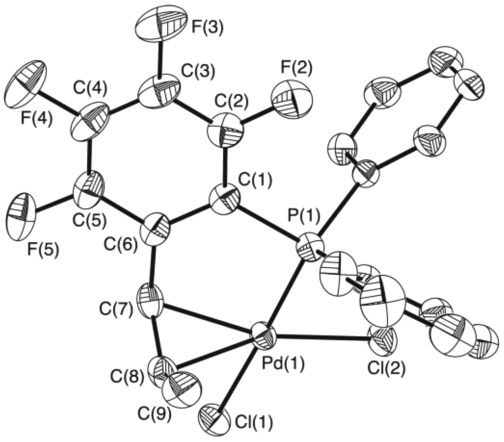

Figure 1. ORTEP of the crystal structure of complex **9**. The ellipsoids are shown at 30% probability (H atoms are omitted for clarity). Selected distances (Å): Pd(1)−C(7) 2.193(3); Pd(1)−C(8) 2.263(3); Pd(1)−P(1) 2.2370(7); Pd(1)−Cl(1) 2.3587(7); Pd(1)−Cl(2) 2.2951(7); C(7)−C(8) 1.383(4). Selected angles (°): C(7)−Pd(1)−P(1) 85.62(8); C(7)−Pd(1)−C(8) 36.11(9); P(1)−Pd(1)−C(8) 97.23(8); C(7)−Pd(1)−Cl(2) 164.57(7); P(1)−Pd(1)−Cl(2) 87.12(3); C(8)−Pd(1)−Cl(2) 158.99(8); C(7)−Pd(1)−Cl(1) 95.05(8); P(1)−Pd(1)−Cl(1) 174.07(2); C(8)−Pd(1)−Cl(1) 86.68(8); Cl(2)−Pd(1)−Cl(1) 90.80(3).

planar coordination of Pd. Taking the midpoint of the double bond for the olefin as the coordination position, the angles defined by adjacent ligands in the plane are close to 90° in the two complexes. The C7−C8 double bond lengths are longer than the typical distances in free olefins, as expected from the effect of coordination of the olefin to the metal. The most remarkable feature is that the *Z* isomer is found in both cases, confirming the structure suggested by their ^1H NMR spectra.

These structures are important because in the previous work with the phosphines in Chart 1, the structure of this kind of catalyst could not be demonstrated, because of the poor solubility of those dichloropalladium complexes. In fact, the structure of the Pd^{II} complexes was proposed as a polymeric one, with monodentate phosphines and uncoordinated double bonds.[10b] Here, the higher solubility of our complexes has

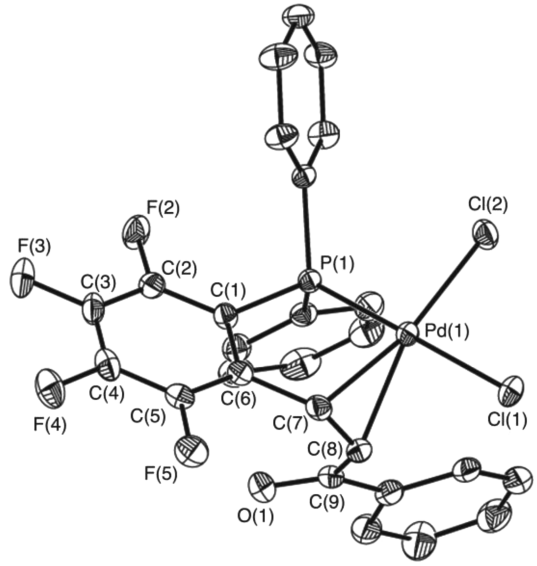

Figure 2. ORTEP of the crystal structure of complex **11**. The ellipsoids are shown at 30% probability (H atoms are omitted for clarity). Selected distances (Å): Pd(1)−C(7) 2.189(3); Pd(1)−C(8) 2.178(3); Pd(1)−P(1) 2.2489(8); Pd(1)−Cl(1) 2.3857(8); Pd(1)−Cl(2) 2.3107(9); C(7)−C(8) 1.381(5); C(9)−O(1) 1.222(4). Selected angles (°): C(8)−Pd(1)−C(7) 36.87(12); C(8)−Pd(1)−P(1) 94.72(9); C(7)−Pd(1)−P(1) 85.82(9); C(8)−Pd(1)−Cl(2) 154.81(9); C(7)−Pd(1)−Cl(2) 167.57(9); P(1)−Pd(1)−Cl(2) 87.87(3); C(8)−Pd(1)−Cl(1) 84.80(9); C(7)−Pd(1)−Cl(1) 93.93(9); P(1)−Pd(1)−Cl(1) 179.46(3); Cl(2)−Pd(1)−Cl(1) 92.46(3).

allowed us to prove unambiguously that the Pd^{II} complexes are monomeric and the double bond is coordinated to palladium.

Some structural differences between **9** (R = Me) and **11** (R = COPh) are noteworthy. In complex **9** the double bond shows a nonsymmetrical coordination (Pd−C7 = 2.193(3) Å; Pd−C8 = 2.263(3) Å), whereas in complex **11**, with a second electron-withdrawing substituent in the olefin, the alkene coordination is almost symmetrical (Pd−C7 = 2.189(3) Å; Pd−C8 = 2.178(3) Å). Curiously the bond lengths of the coordinated double bond are almost identical in both complexes (C7−C8 = 1.383(4) Å for **9**; C7−C8 = 1.381(5) Å for **11**), in spite of their expectedly different electronic properties. Both distances are longer than the typical bond length of C=C bonds not involved in coordination (1.34 Å), as expected.[16] A theoretical study of different olefins coordinated to Pd suggested that nonsymmetrical coordination,[17] typically found in Pd^{II} complexes, indicates olefins behaving on coordination as a mostly σ-electron donor ligand from its π olefin full orbital, with negligible back-donation from the metal to the π^* olefin empty orbital; in contrast, symmetric coordination is found in systems involving more π-back-donation, typically in Pd^0 complexes.[18] Using this criterion our data would suggest that the double bond of ligand **4** in complex **9** is a somewhat better σ donor and worse π acceptor than the double bond of ligand **6** in complex **11**. Both components of the olefin-Pd bond, σ-donation and π-back-donation, contribute to elongate the C=C bond and, by chance, have led in this case to similar double bond distances in **9** and **11**. It is worth reminding that electron π-back-donation is expectedly small for Pd^{II} [5] compared to Pd^0 complexes.[19] This predicts that the coupling accelerating effects arising from π-back-donation, which become more important as the system is evolving from Pd^{II} toward Pd^0, will show at that

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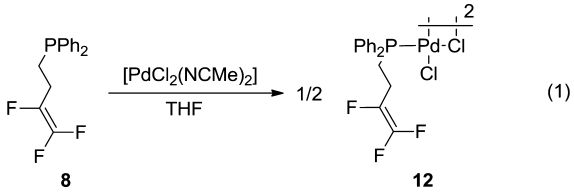
point stronger for **11**. This is consistent with the results of catalysis discussed below.

In contrast with ligands **4**–**6**, which form chelates when coordinated to Pd^{II} in 1:1 ratio, **8** coordinates only through the phosphorus atom, affording a dimeric complex (**12**) with bridging Cl atoms, whether in THF or in the crystal (eq 1).



8 **12** (1)

This is supported in solution by the only very small modification of the ^{19}F NMR chemical shifts of the olefinic F atoms upon coordination of the phosphine. The structure in the solid state could be confirmed by X-ray diffraction (Figure 3). The molecule is centrosymmetric, so the atoms generated by inversion are labeled with A.

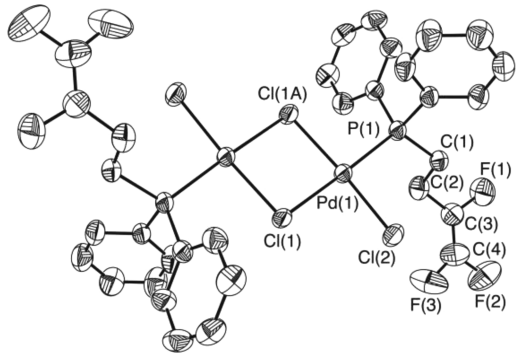


Figure 3. ORTEP of the crystal structure of complex **12**. The ellipsoids are shown at 30% probability (H atoms are omitted for clarity). Selected distances (Å): Pd(1)–P(1) 2.2202(15); Pd(1)–Cl(1) 2.4149(15); Pd(1)– Cl(1A) 2.3098(15); Pd(1)–Cl(2) 2.2636(16); Pd(1)–Cl(2) 2.3107(9); C(3)–C(4) 1.257(11). Selected angles (°): P(1)–Pd(1)–Cl(2) 90.61(6); P(1)–Pd(1)–Cl(1A) 93.53(6); P(1)–Pd(1)–Cl(1) 174.30(7); Cl(2)–Pd(1)–Cl(1A) 175.85(6).

The structure of **12** features, as expected, a dinuclear Pd complex with monodentate phosphines and chloro bridges. The bond distances and angles are within normal values. No other interactions with the metal are observed, so the double bonds of the fluorinated olefin are uncoordinated. Since ligand **8** could form, upon coordination of the double bond, a palladacycle with the same number of links as **4**–**6**, its different behavior is probably due not to geometrical restrictions, but to the fact that the double bond in **8** is a much worse σ donor than those in **4**–**6**, and this is not compensated by its higher π^*-acceptor nature because of the poor back-donation from Pd^{II} in all cases. In other words, it is the σ donation that determines the coordination ability of the double bond in Pd^{II} complexes. This is in keeping with previous observations by Brookhart and calculations by Ziegler.[20,21]

Finally, the reaction of phosphine **6** with $[PdCl_2(NCMe)_2]$ in 2:1 ratio in chloroform produces *trans*-$[PdCl_2((E)\text{-}\mathbf{6})_2]$ (**13**). The X-ray diffraction structure of **13** is shown in Figure 4. The Pd atom displays a trans square-planar geometry defined by two P and two Cl atoms, with bond angles close to 90°. As the most

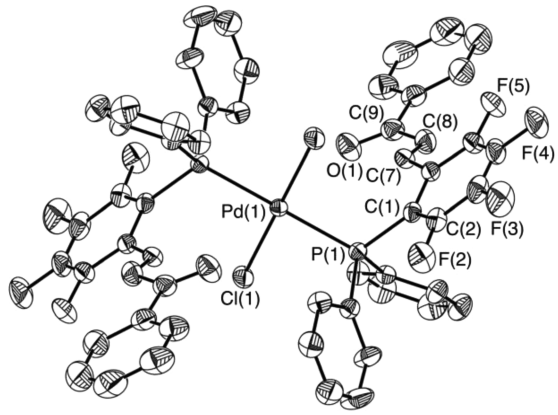
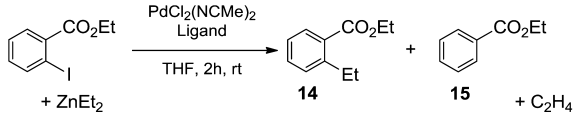


Figure 4. ORTEP of the crystal structures of complex **13**. The ellipsoids are shown at 30% probability (H atoms are omitted for clarity). Selected distances (Å): Pd(1)–Cl(1) 2.2903(7); Pd(1)–P(1) 2.3231(7); C(7)–C(8) 1.314(4); C(9)–O(1) 1.212(4). Selected angles (°): Cl(1)–Pd(1)–P(1) 87.89(3); Cl(1A)–Pd(1)–P(1) 92.11(3).

prominent feature, the two phosphine ligands are acting as monodentate, and the double bond of the EWO is not bonded to Pd and shows an *E* conformation, as in the free phosphine. The C7–C8 distance is 1.314(4) Å, within the typical range of C=C bonds, in contrast with the longer distances (ca. 1.38 Å) observed in the structures of **9** and **11**, where the double bond is coordinated to Pd^{II}. This structure shows that, in the presence of excess phosphine, the formation of a second Pd–P bond is preferred to the Pd-(EWO) chelation, in spite of the favorable entropic contribution for the latter.

Catalytic Activity. The catalytic performance of the ligands was tested in the model reaction in eq 2. The reactions were



(2)

carried out in THF for 2 h affording, after hydrolysis, coupling (**14**) and reduction (**15**) products, with only traces of other compounds. All the conversions were quantified by GC analysis. The results are given in Table 1.

By far the best performance was found for ligand **6**, and in general, the ligands able to coordinate to Pd^{II} in a chelating mode (entries 1–5) gave better selectivity toward the coupling product than the ligands that do not coordinate as chelates (entries 6–9). This suggests that coordination of the double

Table 1. Catalytic Results for the Et-Ar Coupling

entry	Et_2Zn:ArI	phosphine	**14**:**15**
1	2.5	**4**(*Z*) (0.05)	63:37
2	2.5	**4**(*E*) (0.05)	49:51
3	2.5	**5** (0.05)	42:58
4	2.5	**6** (0.05)	90:10
5	0.65	**6** (0.05)	97:3
6[a]	2.5	**7** (0.05)	0:100
7	2.5	**7** (0.10)	15:85
8[b]	2.5	**7** (0.05)	29:71
9	2.5	**8** (0.05)	15:85

[a]20% of starting material. [b]5 equiv of chalcone were added as external olefin.

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bond has to occur at the stage of Pd^{II} in order to favor coupling versus reduction. In fact ligands **7** (lacking a double bond substituent) and **8** (with a poor donor double bond, as discussed) gave only very modest enhancement of the **14**/**15** ratio.

The addition of chalcone (large excess) to the monodentate phosphine **7** was tested (chalcone would provide the olefinic fragment missing in ligand **7** as compared to **6**, but as external cocatalyst). The use of chalcone produced some improvement (entry 8 vs. 6 and 7), but as expected, the **14**/**15** ratio was still far from the results obtained with ligand **6**, or even with other ligands containing more conventional double bonds.[4,5] The catalytic results with **4**(*Z*) and **4**(*E*) (entries 1 and 2) are significantly different, in spite of the fact that the complex they eventually form is the same, **9**. This is probably due to the need of isomerization when **4**(*E*) is used for catalysis. It seems that the presence of the fluorinated aryl core of the phosphines is enough to provide some EWO character to the double bonds in **4** and **5**. In fact, the selectivity toward coupling of **4** and **5** is much better than with a simple phosphine **7** lacking olefin (entries 5 and 6).

In addition to the results in Table 1, if the catalysis is carried out using complex *trans*-[$PdCl_2$((*E*)-**6**)$_2$] (**13**), the **14**/**15** ratio obtained is 19/81 (cf. the result reported by Lei for PPh_3, 39/61).[10a] These bad results confirm that chelation via double bond is not operating in solution when the Pd center has two P donor atoms available to coordination.

Although in detail interpretation of the catalytic activity of the different ligands is not possible in these systems, as it depends on a combination of electronic and steric factors further complicated by possible double bond isomerizations, in general it seems that a prerequisite for a ligand to induce good coupling/reduction ratios is a sufficiently efficient coordination of the olefin to Pd^{II}, which mostly depends on the σ donor ability of the double bond and on sterics. On the other hand, as the molecule evolves toward the coupling transition state (hence toward the precursor of the Pd^0 and R−R′ coupling products), it is the growing π-back-donation from Pd that matters and takes the main control of the coupling barrier.[4]

Finally, a synthetically interesting finding was that diminishing the proportion of zinc reagent from 2.5 to 0.65 (Table 1, entry 5) produced a notable increase of selectivity toward the coupling product. Total conversion of the reagents was observed, indicating that the second ethyl group of $ZnEt_2$ had also been transferred to Pd and used in the reaction. Besides that, the coupling/reduction ratio went up to 97/3, instead of 90/10, although with formation of a small amount of the homocoupling biaryl product.[22] This is, no doubt, an interesting improvement in atom economy of the process, with a bonus in the selectivity of the reaction.

In conclusion, we have synthesized a group of phosphine/alkene ligands and have tested their activity in the Negishi Pd-catalyzed aryl-alkyl coupling. The ligands acting as monodentate P-donors give poor coupling/reduction ratios, about 15/85. Only the ligands able to coordinate in a chelating mode to Pd^{II} increase this ratio to values 42/58 or higher. Among the latter, it is the ligand bearing the more electron-withdrawing substituent, **6**, the one that produces the best coupling/reduction selectivity: 90/10, or higher (97/3) if the proportion of $ZnEt_2$ in the reaction is lowered. These results fit well in the hypothesis that the selectivity toward the coupling product increases using PR_2(EWO) ligands because the coordination of the EWO fragment reduces the activation energy of the coupling step. There is no indication in favor of the proposal that PR_2(EWO) protects the complexes against β-H elimination followed by reduction. In fact, one should expect higher protection against β-H elimination in palladium complexes with two strong PR_3 ligands (such as **13**) than with one hemilabile PR_2(EWO) ligand (such as **11**), but the opposite effect (more reduction) is observed. It looks more logic to think that, from a common intermediate, when the coupling pathway becomes faster with the help of a coordinated EWO the β-hydride elimination pathway simply becomes kinetically less competitive.

EXPERIMENTAL SECTION

General Methods. All the manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques unless otherwise stated. Solvents were dried using a solvent purification system SPS PS-MD-5 or distilled from appropriate drying agents under nitrogen, prior to use. The compounds [$PdCl_2(NCMe)_2$][23] and 2-$BrC_6F_4PPh_2$ (**2**)[24] were prepared by literature methods; all other reagents were commercially available and used as received.

^1H, $^{13}C\{^1H\}$, ^{19}F, and $^{31}P\{^1H\}$ spectra were recorded on a Bruker AV-400 or a Varian Inova 500 spectrometer. Chemicals shifts (in δ units, parts per million) were referenced to the residual solvent signal, to $CFCl_3$ and to 85% H_3PO_4, respectively. The spectral data were recorded at 293 K unless otherwise noted. GC−mass spectra were recorded on a Thermo Scientific Focus DSQII system. Elemental analyses were performed on a Perkin-Elmer 2400B CHN analyzer.

2-(Diphenylphosphino)-3,4,5,6-tetrafluorobenzaldehyde (3). ^{n}BuLi 1.6 M in hexanes (1.51 mL, 2.42 mmol) was added to a solution of **2** (1.00 g, 2.42 mmol) in dry ether (35 mL) at −78 °C. The solution was stirred for 15 min, and then dry DMF (376 μL, 4.84 mmol) was added, and the resulting solution was further stirred for 1 h at the same temperature. The solution was allowed to warm up to −50 °C, and a deoxygenated saturated NH_4Cl solution in water was added (50 mL). The mixture was extracted with ether (2 × 50 mL), and the organic layer was dried over $MgSO_4$. The volatiles were removed, and the resulting oily yellow residue **3** (0.72 g, 82%) was used in the next steps without further purification. ^1H NMR (400.13 MHz, δ, $CDCl_3$): 10.69 (d, J = 6.0 Hz, 1H), 7.46−7.31 (m, 10H). ^{19}F NMR (376.46 MHz, δ, $CDCl_3$): −121.42 (m, 1F), −143.22 (m, 1F), −145.13 (m, 1F), −150.89 (m, 1F). $^{31}P\{^1H\}$ NMR (161.97 MHz, δ, $CDCl_3$): −17.02 (ddd, J = 12.1, 3.6, 1.7 Hz, 1P). Anal. Calcd for $C_{19}H_{11}F_4OP$: C, 62.99; H, 3.06. Found: C, 61.65; H, 3.11.

(*E*)- and (*Z*)-Diphenyl(2,3,4,5-tetrafluoro-6-(prop-1-enyl)-phenyl)phosphine (4(*E*) and 4(*Z*)). ^{n}BuLi 1.6 M in hexanes (0.45 mL, 0.72 mmol) was added to a suspension of ethyltriphenylphosphonium iodide (0.30 g, 0.72 mmol) in dry THF (20 mL) at 0 °C and was allowed to warm up to room temperature. The resulting solution was added over a solution of **3** (0.24 g, 0.66 mmol) in dry THF (10 mL), and stirred for 2 h. A deoxygenated NH_4Cl saturated aqueous solution was added (20 mL), and the mixture was extracted with ether (2 × 20 mL). The organic layer was dried over $MgSO_4$, and the volatiles were removed. The residue was purified by chromatography (SiO_2, hexane) giving two fractions as white solids. The first fraction was **4**(*E*): 39.4 mg, 16% overall yield from **3**. ^1H NMR (400.13 MHz, δ, $CDCl_3$): 7.40−7.33 (m, 10H), 6.80 (dm, J = 16.1 Hz, 1H), 6.12 (dqm, J = 16.1, 6.8 Hz, 1H), 1.89 (d, J = 6.8 Hz, 3H). ^{19}F NMR (376.46 MHz, δ, $CDCl_3$): −122.81 (m, 1F), −141.12 (m, 1F), −152.83 (m, 1F), −157.16 (m, 1F). $^{31}P\{^1H\}$ NMR (161.97 MHz, δ, $CDCl_3$): −17.86 (ddd, J = 14.3, 6.7, 3.8 Hz, 1P). Anal. Calcd for $C_{21}H_{15}F_4P$: C, 67.38; H, 4.04. Found: C, 67.12; H, 4.13. The second fraction was **4**(*Z*): 49.6 mg, 20% overall yield from **3**. ^1H NMR (400.13 MHz, δ, $CDCl_3$): 7.42−7.32 (m, 10H), 6.41 (dm, J = 11.2 Hz, 1H), 6.01 (dqt, J = 11.2, 7.0, 1.8 Hz, 1H), 1.44 (dm, J = 7.0 Hz, 3H). ^{19}F NMR (376.46 MHz, δ, $CDCl_3$): −124.34 (m, 1F), −137.91 (m, 1F), −152.83 (m, 1F), −156.15 (m, 1F). $^{31}P\{^1H\}$ NMR (161.97 MHz, δ, $CDCl_3$): −16.88 (ddd, J = 15.0, 7.5, 3.9 Hz, 1P). Anal. Calcd for $C_{21}H_{15}F_4P$: C, 67.38; H, 4.04. Found: C, 67.21; H, 3.90.

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(*E*)-Diphenyl(2,3,4,5-tetrafluoro-6-styrylphenyl)phosphine (5). Following the procedure for the Wittig reaction described for **4**, and using benzyltriphenylphosphonium bromide (0.243 g, 0.56 mmol) and **3** (0.185 g, 0.51 mmol), **5** was obtained, after column chromatography (SiO_2, hexane), as a white solid (105 mg, 47%). ^{1}H NMR (400.13 MHz, δ, $CDCl_3$): 7.74 (dd, J = 16.6, 4.6 Hz, 1H), 7.55−7.30 (m, 15H), 7.11 (d, J = 16.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 137.4 (ddd, J = 11.2, 4.2, 1.6 Hz), 119.9 (dm, J = 28.8 Hz) (olefinic carbons). ^{19}F NMR (376.46 MHz, δ, $CDCl_3$): −122.10 (m, 1F), −139.75 (m, 1F), −152.41 (m, 1F), −155.95 (m, 1F). $^{31}P\{^1H\}$ NMR (161.97 MHz, δ, $CDCl_3$): −18.06 (ddd, J = 14.0, 5.7, 3.6 Hz, 1P). Anal. Calcd for $C_{26}H_{17}F_4P$: C, 71.56; H, 3.93. Found: C, 71.70; H, 3.80.

(*E*)-3-(2-(Diphenylphosphino)-3,4,5,6-tetrafluorophenyl)-1-phenylprop-2-en-1-one (6). (2-Oxo-2-phenylethyl)-triphenylphosphonium ylide (0.205 g, 0.54 mmol) was added to a solution of **3** (0.149 g, 0.41 mmol) in dry THF (25 mL), and the resulting mixture was stirred 2 h. A deoxygenated saturated NH_4Cl aqueous solution was added (20 mL), and the mixture was extracted with ether (2 × 20 mL). The organic layer was dried over $MgSO_4$, and the volatiles were removed. The residue was purified by column chromatography (SiO_2, hexane/ether, 9.6/0.4) to give **6** as a white solid (102 mg, 53%). ^{1}H NMR (400.13 MHz, δ, $CDCl_3$): 8.36 (dd, J = 16.1, 4.8 Hz, 1H), 7.95−7.92 (m, 2H), 7.59 (m, 1H), 7.50−7.40 (m, 3H), 7.38−7.33 (m, 10H). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 134.9 (dm, J = 28.0 Hz), 130.2 (ddd, J = 11.0, 4.4, 1.1 Hz) (olefinic carbons). ^{19}F NMR (376.46 MHz, δ, $CDCl_3$): −121.31 (m, 1F), −136.96 (m, 1F), −151.58 (m, 1F), −151.97 (m, 1F). $^{31}P\{^1H\}$ NMR (161.97 MHz, δ, $CDCl_3$): −17.42 (ddd, J = 12.4, 5.0, 3.9 Hz, 1P). Anal. Calcd for $C_{27}H_{17}F_4OP$: C, 69.83; H, 3.69. Found: C, 69.65; H, 3.49.

Diphenyl(2,3,4,5-tetrafluorophenyl)phosphine (7). ^{n}BuLi 1.6 M in hexanes (185 μL, 0.30 mmol) was added to a solution of **2** (122 mg, 0.30 mmol) in dry ether (8 mL) at −78 °C. The solution was stirred for 15 min at that temperature, and then a deoxygenated saturated NH_4Cl aqueous solution was added (5 mL). The resulting mixture was allowed to warm up to room temperature and then was extracted with ether (2 × 8 mL). The organic layer was dried over $MgSO_4$. The volatiles were removed to give a white solid (70 mg, 71%). ^{1}H NMR (400.13 MHz, δ, $CDCl_3$): 7.44−7.30 (m, 10H), 6.41 (m, 1H). ^{19}F NMR (376.46 MHz, δ, $CDCl_3$): −129.89 (m, 1F), −138.63 (m, 1F), −154.06 (m, 1F), −155.21 (m, 1F). $^{31}P\{^1H\}$ NMR (161.97 MHz, δ, $CDCl_3$): −17.74 (d, J = 48.0 Hz, 1P). Anal. Calcd for $C_{18}H_{11}F_4P$: C, 64.68; H, 3.32. Found: C, 64.79; H, 3.53.

Diphenyl(3,4,4-trifluorobut-3-enyl)phosphine (8). ^{n}BuLi 1.6 M in hexanes (838 μL, 1.34 mmol) was added to a solution of diphenylphosphine (232 μL, 1.34 mmol) in dry THF (7 mL) at −35 °C. The resulting solution was stirred for 1 h at that temperature and then allowed to warm up to 0 °C. Then the reaction mixture was cooled down to −35 °C, and a solution of 4-bromo-1,1,2-trifluorobut-1-ene (253 mg, 154 μL, 1.34 mmol) in dry THF (7 mL) was added. The resulting mixture was allowed to warm up to room temperature. A deoxygenated saturated NH_4Cl aqueous solution was added (10 mL), and the mixture was extracted with ether (2 × 15 mL). The organic layer was dried over $MgSO_4$. The volatiles were removed, and the crude residue was purified by column chromatography (SiO_2, hexane/ether, 9/1) to give **8** as a white solid (177 mg, 45%). ^{1}H NMR (400.13 MHz, δ, $CDCl_3$): 7.46−7.34 (m, 10H), 2.47−2.24 (m, 4H). ^{19}F NMR (376.46 MHz, δ, $CDCl_3$): −105.66 (dd, J = 87.2, 32.1 Hz, 1F), −124.03 (dd, J = 114.2, 87.2 Hz, 1F), −175.20 (ddtd, J = 114.2, 32.1, 21.3, 3.5 Hz, 1F). $^{31}P\{^1H\}$ NMR (161.97 MHz, δ, $CDCl_3$): −16.90 (s, 1P). Anal. Calcd for $C_{16}H_{14}F_3P$: C, 65.31; H, 4.80. Found: C, 65.48; H, 4.62.

General Procedure for the Synthesis of the Complexes 9−11. The corresponding phosphine was added to a 0.035 M solution of $[PdCl_2(NCMe)_2]$ in THF (phosphine:Pd molar ratio = 1:1). The reaction mixture was stirred for 5 h. The volatiles were evaporated, and hexane was added. The precipitate was filtered and washed with hexane and pentane.

[$PdCl_2$((*Z*)-4)] (9). $[PdCl_2(NCMe)_2]$ (7.0 mg, 0.027 mmol) and **4** (Z or E) (10.1 mg, 0.027 mmol) reacted to give **9** as a yellow solid (10.0 mg, 76%). ^{1}H NMR (400.13 MHz, δ, $CDCl_3$): 8.06 (m, 2H), 7.72 (m, 1H), 7.62 (m, 2H), 7.58−7.33 (m, 6H), 7.00 (dm, J = 8.6 Hz, 1H), 1.47 (ddd, J = 6.6, 2.5. 1.0 Hz, 3H). ^{19}F NMR (376.46 MHz, δ, $CDCl_3$): −122.70 (m, 1F), −135.11 (m, 1F), −142.37 (m, 1F), −147.88 (m, 1F). $^{31}P\{^1H\}$ NMR (161.97 MHz, δ, $CDCl_3$): 44.13 (m, 1P). Anal. Calcd for $C_{21}H_{15}Cl_2F_4PPd$: C, 45.72; H, 2.74. Found: C, 45.89; H, 2.48.

[$PdCl_2$((*Z*)-5)] (10). $[PdCl_2(NCMe)_2]$ (8.0 mg, 0.031 mmol) and **5** (13.4 mg, 0.031 mmol) reacted to give **10** as a yellow solid (12.0 mg, 72%). ^{1}H NMR (400.13 MHz, δ, $CDCl_3$): 8.33 (d, J = 9.2 Hz, 1H), 7.51−7.30 (m, 8H), 7.21 (m, 2H), 7.12 (m, 1H), 7.06 (d, J = 9.2 Hz, 1H), 7.02 (m, 2H), 6.94 (m, 2H). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 115.2 (s), 94.3 (s) (olefinic carbons). ^{19}F NMR (376.46 MHz, δ, $CDCl_3$): −121.78 (m, 1F), −135.20 (m, 1F), −142.49 (m, 1F), −147.39 (m, 1F). $^{31}P\{^1H\}$ NMR (161.97 MHz, δ, $CDCl_3$): 43.73 (m, 1P). Anal. Calcd for $C_{26}H_{17}Cl_2F_4PPd$: C, 50.88; H, 2.79. Found: C, 50.63; H, 3.32.

[$PdCl_2$((*Z*)-6)] (11). $[PdCl_2(NCMe)_2]$ (40.0 mg, 0.154 mmol) and **6** (74.3 mg, 0.160 mmol) reacted to give **11** as a yellow solid (80.0 mg, 81%). ^{1}H NMR (400.13 MHz, δ, $CDCl_3$): 7.98 (m, 2H), 7.81 (d, J = 9.6 Hz, 1H), 7.65 (m, 2H), 7.58−7.46 (m, 3H), 7.44−7.18 (m, 9H). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 100.9 (bs), 98.5 (s) (olefinic carbons). ^{19}F NMR (376.46 MHz, δ, $CDCl_3$): −124.03 (m, 1F), −135.79 (m, 1F), −143.78 (m, 1F), −148.68 (m, 1F). $^{31}P\{^1H\}$ NMR (161.97 MHz, δ, $CDCl_3$): 44.30 (bs, 1P). Anal. Calcd for $C_{27}H_{17}Cl_2F_4OPPd$: C, 50.53; H, 2.67. Found: C, 50.70; H, 2.53.

[$PdCl_2$(8)]$_2$ (12). $[PdCl_2(NCMe)_2]$ (11.0 mg, 0.042 mmol) and **8** (12.5 mg, 0.042 mmol) reacted to give **12** as an orange solid (15.0 mg, 75%). ^{1}H NMR (400.13 MHz, δ, $CDCl_3$): 7.75 (m, 8H), 7.58 (m, 4H), 7.48 (m, 8H), 2.68−2.42 (m, 8H). ^{19}F NMR (376.46 MHz, δ, $CDCl_3$): −103.87 (dd, J = 83.1, 32.8 Hz, 1F), −122.13 (ddm, J = 114.4, 83.1 Hz, 1F), −175.73 (ddt, J = 114.4, 32.8, 24.4 Hz, 1F). $^{31}P\{^1H\}$ NMR (161.97 MHz, δ, $CDCl_3$): 29.28 (bs, 1P). Anal. Calcd for $C_{32}H_{28}Cl_4F_6P_2Pd_2$: C, 40.75; H, 2.99. Found: C, 40.43; H, 3.32.

***trans*-[$PdCl_2$((*E*)-6)$_2$] (13).** To a solution of $[PdCl_2(NCMe)_2]$ (19.5 mg, 0.075 mmol) in $CHCl_3$ (25 mL), **6** (69.8 mg, 0.15 mmol) was added, and the mixture was stirred for 2 h. The solvent was evaporated, and cold MeCN was added. The precipitate was filtered and washed with ether giving a yellow solid (66.5 mg, 80%). ^{1}H NMR (400.13 MHz, δ, $CDCl_3$): 7.96 (m, 8H), 7.75 (m, 4H), 7.68 (d, J = 15.9 Hz, 2H), 7.53 (m, 2H), 7.44−7.31 (m, 16H), 7.07 (dd, J = 15.9, 1.9 Hz, 2H). ^{19}F NMR (376.46 MHz, δ, $CDCl_3$): −121.26 (m, 1F), −136.35 (m, 1F), −149.63 (m, 1F), −152.37 (m, 1F). $^{31}P\{^1H\}$ NMR (161.97 MHz, δ, $CDCl_3$): 16.35 (s, 1P). Anal. Calcd for $C_{54}H_{34}Cl_2F_8O_2P_2Pd$: C, 58.64; H, 3.10. Found: C, 58.75; H, 3.45.

General Procedure for the Catalysis. $[PdCl_2(NCMe)_2]$ (3.89 mg, 0.015 mmol), the phosphine ligand (0.015 mmol) and dry THF (1 mL) were introduced in a "flame-dried" Schlenk tube under argon and stirred for 5 min. Then ethyl-2-iodobenzoate (51.2 μL, 0.300 mmol) and 1 M solution of $ZnEt_2$ in hexane (0.75 mL, 0.75 mmol) were added, and the resulting mixture was further stirred for 2 h. The mixture was carefully hydrolyzed with a 2 M HCl solution and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered through a short pad of silica and analyzed with GC. As an example the isolated yield of **14** in entry 4 was 72%.

X-ray Crystal Structure Analysis. Single crystals of **9**·CH_2Cl_2, **11** and **12** suitable for X-ray diffraction studies were obtained from slow diffusion of diethyl ether or hexane into a dichloromethane solution of the products. Crystals from **13** were grown from slow diffusion of hexane into a THF solution of the product at −20 °C. Data collection was performed in an Oxford Diffraction Super Nova diffractometer with a Mo microfocus source with multilayer optics. Data integration, scaling and empirical absorption correction were carried out using the CrysAlisPro program package.[25] The structure was solved using direct methods and refined by Full-Matrix-Least-Squares against F^2 with SHELXTL.[26] The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at idealized positions and refined using the riding model. Crystallographic data (excluding structure

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factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications with the deposition numbers CCDC-937789 for **9**, CCDC-937791 for **11**, CCDC-937792 for **12**, and CCDC-937792 for **13**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. A table with the crystal data and structure refinements is provided in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

Tables and CIF files giving complete characterization data are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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