Phosphine–Borane Ligands Induce Chemoselective Activation and Catalytic Coupling of Acyl Chlorides at Palladium

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Maxime Boudjelel,[a] Sonia Mallet-Ladeira,[b] Yago García-Rodeja,[c] E. Daiann Sosa-Carrizo,[c] Karinne Miqueu,*[c] Ghenwa Bouhadir[a] and Didier Bourissou*[a]

[a] Dr. M. Boudjelel, Dr. G. Bouhadir, Dr. D. Bourissou, CNRS/Université Toulouse III Paul Sabatier, Laboratoire Hétérochimie Fondamentale et Appliquée (LHFA, UMR 5069) 118 Route de Narbonne, 31062 Toulouse Cedex 09 (France). E-Mail: dbouriss@chimie.ups-tlse.fr, Homepage: http://lhfa.cnrs.fr/index.php/equipes/lbpb/accueil-lbpb

[b] Dr. S. Mallet-Ladeira, Institut de Chimie de Toulouse, Université Toulouse III Paul Sabatier (FR2599) 118 Route de Narbonne, 31062 Toulouse Cedex 09 (France)

[c] Dr. Y. García-Rodeja, Dr. E. D. Sosa-Carrizo, Dr. K. Miqueu, Institut Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux (UMR 5254), Equipe Chimie Physique Université de Pau et des Pays de l'Adour, Hélioparc, 2 Avenue du Président Angot, 64053 Pau cedex 09 (France). E-mail: karinne.miqueu@univ-pau.fr

Abstract: Acyl chlorides are highly reactive and widely used substrates in catalytic cross-coupling reactions, but so far, chemoselectivity has remained an issue. In this work, Pd complexes deriving from the phosphine-boranes $[iPr_2P(o\text{-}C_6H_4)]_2BFXyl$ and $iPr_2P(o\text{-}C_6H_4)BFXyl_2$ (Fxyl = 3,5-$(F_3C)_2C_6H_3$) were found to preferentially activate acyl chlorides over C–I, C–Br, C–OTf… bonds. The system is amenable to catalysis (Stille and Negishi couplings), providing a simple and efficient mean to forge C(=O)–C bonds in a site-selective manner and readily access functionalized ketones. To gain insight into the role and influence of the ambiphilic ligands, key Pd complexes have been authenticated and the reaction profiles have been analyzed by DFT calculations.

Introduction

Pd-catalyzed cross-couplings occupy a forefront position in homogeneous catalysis both in academia and in industry.[1] Over the years, tremendous progress has been achieved in efficiency and scope, and nowadays Pd catalysts are ubiquitously used in organic synthesis and materials science. One of the remaining challenge and current focus is to find ways to achieve site-selective coupling when several competing reactive sites are present such as in polyfunctional substrates (Figure 1). This is highly desirable to access and extend chemical complexity. However, contributions on chemoselective Pd-catalyzed cross-couplings remain sparse and empirical. There is still no general method and site-selectivity is most often substrate-driven. A noteworthy example was reported early on by G. Fu.[2] Fine tuning of the reaction conditions and ancillary ligand, P*t*Bu_3 *vs* PCy_3, induced Ar–Cl over Ar–OTf chemoselectivity in Suzuki-Miyaura and Stille couplings.[3] In the same vein, while developing a catalytic C–$TeCF_3$ coupling, Schoenebeck recently showed that C(sp^2)–I bonds were selectively functionalized over C(sp^2)–Br/Cl/OTf bonds when using Xantphos as ligand.[4]

Furthermore, spectacular advances have been made varying the “metal form”: Pd(I) dimers and cationic Pd trimers have been found to enable chemoselective C–C and C–X couplings with activation of C–I over C–Br bonds, and C–Br over C–OTf/C–Cl bonds.[5]

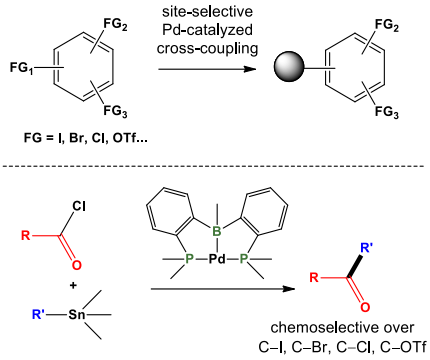


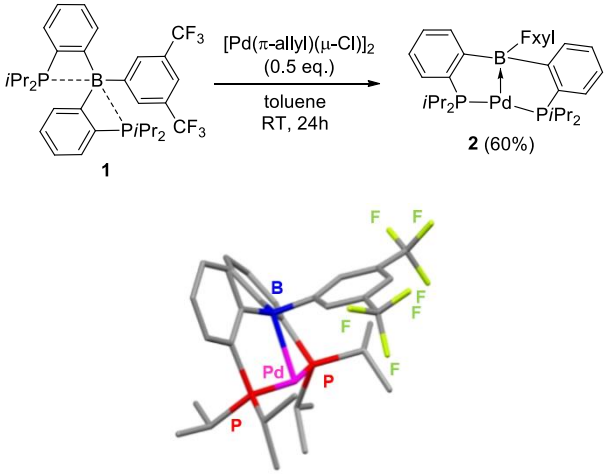
Figure 1. Chemoselective Pd-catalyzed cross-coupling: general scheme (top) and this work (bottom).

In the course of our investigations of transition metal / Lewis acid cooperativity arising from ambiphilic ligands, we discovered the faculty of phosphine-borane ligands to elicit chemoselectivity to Pd in the activation of acyl chlorides over other functional groups typically used in cross-coupling reactions. This provides a simple and general mean to forge functionalized ketones with complete site-selectivity. Here we report these results including stoichiometric reactivity studies and catalytic application in the Stille coupling. To understand the origin of chemoselectivity, key Pd complexes have been authenticated and the reaction profiles have been analyzed by DFT calculations. On the one hand, ambiphilic ligands are an emerging and promising class of ligands, with unique features. Our knowledge about their coordination properties has significantly progressed,[6] but their application in transition metal catalysis is still in its infancy.[7] Strikingly, ambiphilic ligands have been rarely employed in Pd catalysis so far, with only scant studies in allylation reactions (C–N and C–C coupling),[8] addition reactions to enynes,[9] Suzuki coupling[10] and hydro-dechlorination.[11] On the other hand, acyl chlorides attract for some time renewed interest in Pd catalysis on several grounds: (*i*) their preparation by carbonylation of aryl halides[12] or shuttle catalysis,[13] (*ii*) their use as substrates in cross-couplings, without or with decarbonylation, to form RCO–C or R–C bonds,[14] (*iii*) their functional group metathesis with aryl iodides.[15]

Results & discussion

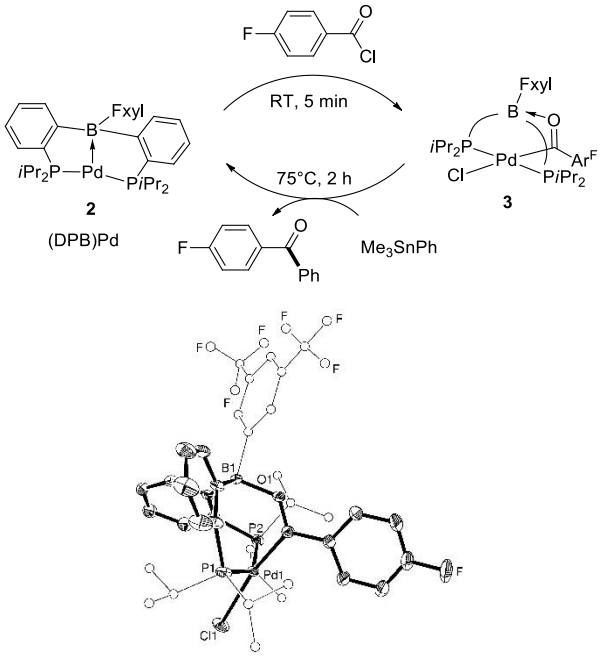
Building on our recent work on *i*Pr$_2$P(*o*-C$_6$H$_4$)BFXyl$_2$ (Fxyl = 3,5-(F$_3$C)$_2$C$_6$H$_3$),[16] we targeted the diphosphine-borane **1** (DPB). The Fxyl group was expected to confer high Lewis acidity to boron without stringent steric shielding, and in contrast to C$_6$F$_5$,[17] it can be easily introduced by ionic coupling.[18] The reaction proceeded smoothly and efficiently with FxylBCl$_2$ as electrophile, giving access to **1** as a viscous oil in gram quantity. The corresponding Pd

complex **2** was most conveniently synthesized using [Pd(π-allyl)(μ-Cl)]$_2$ as precursor (Scheme 1). It was isolated as a yellow fluffy powder. No crystals suitable for X-ray analysis could be obtained, despite our efforts, but its molecular structure was unequivocally ascertained by high-resolution mass spectrometry (HRMS), multi-nuclear NMR spectroscopy and DFT calculations.[19,20] Most diagnostic is the ^{11}B NMR signal at δ 18.7 ppm, indicative of noticeable Pd→B interaction. This is consistent with the optimized geometry which displays a short Pd···B distance (2.294 Å) and a pyramidalized environment around B (Σ(CBC) bond angles = 348.2°). A significant Pd→B donor-acceptor interaction is also found in the NBO analysis [ΔE(2) = 30.0 kcal/mol].



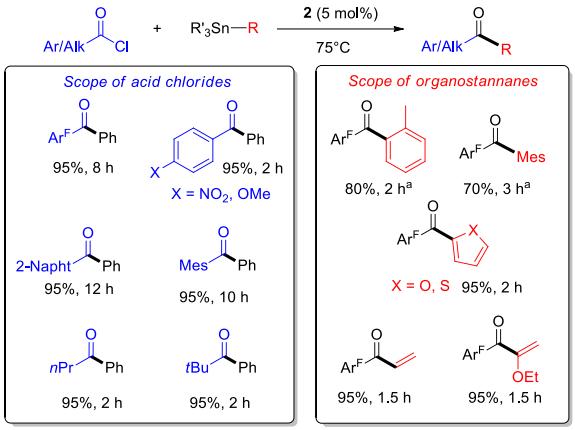
Scheme 1. Synthesis and optimized structure of the diphosphine-borane Pd complex **2**.

Complex **2** was then reacted with *p*-fluoro benzoyl chloride. ^{19}F NMR monitoring indicated immediate and complete conversion at room temperature, with formation of a unique species **3**. Surprisingly, no distinct ^{31}P NMR signal was observed at room temperature, but cooling the NMR tube down to 213 K resulted in a well-resolved AB pattern, with a large J_{PP} coupling constant (290.8 Hz) indicative of *trans* arrangement. To gain more insight into the structure of complex **3**, crystals were grown by slow evaporation of a pentane solution at room temperature. The X-ray diffraction analysis (Scheme 2) revealed a distorted square-planar Pd(II) complex (τ_4 = 0.31)[21] resulting from *trans* addition of the acyl chloride to Pd. The boron center is engaged in strong acyl→B interaction, as apparent from the short O–B distance (1.593(2) Å), the strong pyramidalization around B (335.2°) and the elongation of the C=O double bond (1.2616(19) Å).[22] The DFT-optimized geometry of complex **3** nicely reproduces that determined crystallographically.[19] The O→B interaction is found as a covalent bond in the NBO analysis [ΔE(2) = 243.7 kcal/mol]. Of note, the alternative structure with the borane moiety *trans* to the acyl group and engaged in Cl→B interaction is located 6.0 kcal/mol higher in energy.[23]



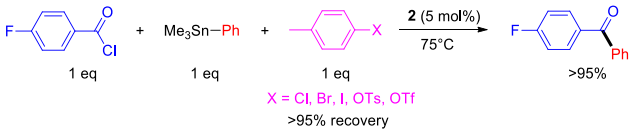
Scheme 2. Reaction of the Pd complex **2** with *p*F-C_6H_4-COCl, then $PhSnMe_3$. Molecular structure of the acyl-Pd(II) complex **3** showing the strong O→B interaction (thermal ellipsoids at 50% probability, *i*Pr and Fxyl groups simplified for clarity).

The possibility to achieve transmetalation and ultimately cross-coupling was then investigated. To this end, complex **3** was reacted with $PhSnMe_3$. Complete conversion was achieved within 2 h at 75°C. The diaryl ketone *p*F-C_6H_4-C(O)–Ph was formed quantitatively, as shown by NMR spectroscopy and GC/MS spectrometry. No sign of biaryl product deriving from a decarbonylative coupling was detected. The acyl−Ph coupling is accompanied by regeneration of the (DPB)Pd complex **2**, suggesting the possibility to perform the reaction catalytically. To our delight, using 5 mol% of (DPB)Pd complex **2** and a 1:1 ratio of *p*F-C_6H_4-COCl and $PhSnMe_3$, the transformation indeed proceeded well (95% yield in coupling product after 8 h at 75°C). The scope of substrates was then studied and the transformation proved general (Scheme 3). Aroyl chlorides featuring electron-withdrawing as well as electron-donating substituents were efficiently coupled. The reaction worked with aliphatic acid chlorides (*n*Pr) and sterically hindered substrates (Mes, *t*Bu). Note that the preparation of sterically hindered ketones by catalytic cross-coupling is challenging.[24-26] As far as the stannane partner is concerned, aryl and heteroaryl groups, including the bulky Mes groups can be transferred, as well as vinyl groups.



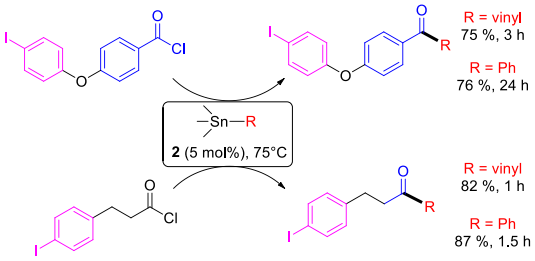
Scheme 3. Stille couplings from acyl chlorides catalyzed by the diphosphine-borane Pd complex **2**. ArF = *p*F-C_6H_4; R' = Me for R = Ph, otherwise R' = *n*Bu; [a]120°C instead of 75°C.

The preference of the diphosphine-borane Pd complex for acyl chlorides over other functional groups typical used in catalytic cross-coupling reactions was then assessed. As pointed out in the introduction, site-selectivity is very appealing to access complex polyfunctionalized compounds and shortcut multi-step syntheses. While effective solutions have recently emerged for halides and pseudo-halides, selective coupling of acyl chlorides has been so far only scarcely studied and is limited to a few specific examples.[27-29] Competitive experiments were carried out.[30,31] The catalytic coupling of *p*F-C_6H_4-COCl and $PhSnMe_3$ was performed as previously (5 mol% of Pd complex **2**, 75°C) but in the presence of one equivalent of *p*Tol–X derivative (X = Cl, Br, I, OTs, OTf). The diaryl ketone *p*F-C_6H_4-C(O)–Ph was obtained in >95% yield whatever the *p*Tol–X additive, including the most reactive iodo and triflate derivatives (Scheme 4). In all cases, the *p*Tol–X additive remained inert (>95% recovery after the reaction). Similar results were obtained using the aliphatic acyl chloride *n*PrCOCl (instead of *p*F-C_6H_4-COCl) or the stannane H_2C=CHSn(*n*Bu)$_3$ (instead of $PhSnMe_3$).[19] The diphosphine-borane Pd complex is thus highly chemoselective for the activation and coupling of acyl chlorides.



Scheme 4. Competitive Stille couplings between acyl chlorides and *p*Tol–X derivatives under (DPB)Pd catalysis.

To illustrate the synthetic interest of such as catalytic system, it was applied to the chemical derivatization of two substrates combining acid chloride and iodo-arene moieties. Stille cross-couplings proceeded in a site-selective manner to afford the iodo-functionalized ketones in 75-87 % yield (Scheme 5).



Scheme 5. Site-selective Stille couplings of difunctionalized substrates under (DPB)Pd catalysis.

To gain more insight into the preference of the (DPB)Pd complex for acyl chlorides, DFT calculations were performed.[19] The most favoured pathway for the oxidative addition of *p*F-C_6H_4-COCl and PhI are displayed in Figure 2. Accordingly, chemoselectivity is not due to thermodynamics (both reaction are favoured by 9.0-9.2 kcal/mol) but is rather kinetic in origin. The activation barrier to activate the C(O)−Cl bond is about 3 kcal/mol smaller than that of Ph−I. In both transition states, the halogen atom approaches Pd *trans* to the boron center and the Lewis acid slightly moves away from Pd compared to the starting (DPB)Pd complex [the Pd−B distance increases from 2.294 Å to 2.366 Å (PhI) and 2.392 Å (*p*F-C_6H_4-COCl)]. In the case of the acyl chloride, the Lewis acid rolls-over from Pd to O and engages in strong O→B interaction. According to Activation Strain Model calculations and Energy Decomposition Analyses,[19] the difference in the activation barrier of oxidative addition is not due to the strain energy required to deform the fragments to reach the transition state ($\Delta\Delta E_{strain}$ ~ 1 kcal/mol between *p*F-C_6H_4-COCl and PhI) but rather to the interaction energy between the two fragments ($\Delta\Delta E_{int}$ ~ 8 kcal/mol). In particular, the orbital interaction energy term (ΔE_{orb}) was found to be more stabilizing by ~ 12 kcal/mol for the acyl chloride.

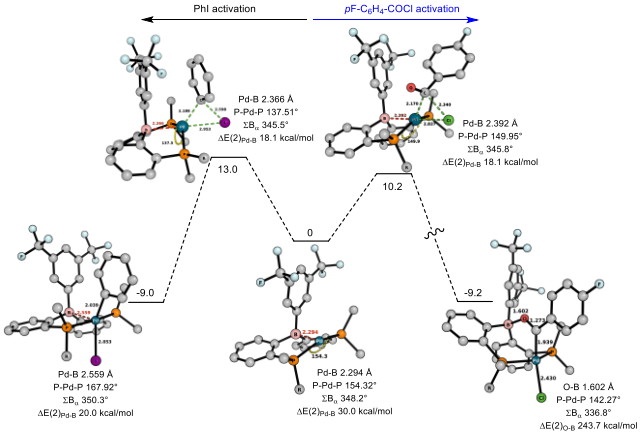
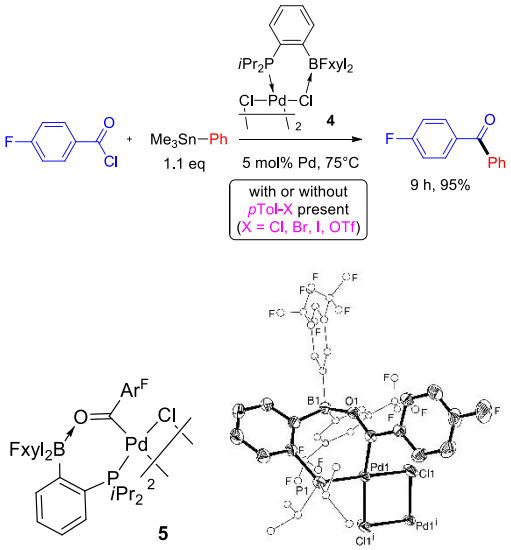


Figure 2. Comparison of the oxidative addition of *p*F-C_6H_4-COCl and PhI to the (DPB)Pd complex **2**, with key geometric and NBO [stabilizing energy ΔE(2) associated to Pd→B or O→B interactions] data. Computations performed at the B97D/SDD+f(Pd)/6-31G**(other atoms) level of theory. Free energies in kcal/mol.

The chemoselectivity observed with the Pd complex **2** in the Stille coupling of acyl chlorides raises the question of the uniqueness of DPB in such a behaviour. To assess the generality of phosphine-boranes to display such a preference for the activation and catalytic coupling of acyl chlorides, we turned to the monophosphine-borane *i*Pr_2P(o-C_6H_4)BFXyl$_2$ (MPB).[16] The corresponding $PdCl_2$ complex **4** was isolated as a P→Pd−Cl→B bridged μ-Cl dimer. Stille coupling between *p*F-C_6H_4-COCl and $PhSnMe_3$ (used in slight excess to reduce *in situ* the Pd(II) precursor into the catalytic active Pd(0) species) worked smoothly to give the diaryl ketone in 95% yield after 9 h (Scheme 6). The resting state of the catalyst was identified thanks to ^{31}P NMR spectroscopy. It is the MPB acyl complex **5** which was independently synthesized and fully characterized, including by X-ray diffraction.[19] As in the related DPB complex **3**, the O atom strongly interacts with the B center (O–B 1.588(4) Å) and the C=O bond is noticeably elongated (1.262(4) Å). Notably, MPB imparts to Pd complete selectivity towards acyl chlorides, similarly to DPB. This is apparent from competitive experiments using *p*Tol-X additives (X = Cl, Br, I, OTf) and site-selective derivatization of difunctionalized substrates. Preliminary tests have also been performed to extend the scope of the cross-coupling to organozinc derivatives. Promisingly, Negishi coupling between *p*F-C_6H_4-COCl and PhZnCl proceeded very efficiently and selectively (no interference noticed in the presence of one equivalent of *p*Tol–I).[32] The diaryl ketone was obtained in >95% yield within 10 minutes at room temperature using only 0.25 mol% of the (MPB)Pd complex **4**.[19]



Scheme 5. Stille coupling catalyzed by the monophosphine-borane Pd complex **4**. Molecular structure of the resting state, *ie* the acyl complex **5** (thermal ellipsoids at 50% probability, *i*Pr and Fxyl groups simplified for clarity).

Conclusion

Their high reactivity make acyl chlorides interesting and useful substrates in catalytic cross-coupling reactions, but so far, site-selectivity over other functional groups (C–I, C–Br, C–OTf

bonds) has remained an issue. As reported above, the use of phosphine-borane ligands offer a convenient solution. They impart to Pd strong preference for the activation of acyl-chlorides so that Stille couplings can be achieved with high chemoselectivity. This ligand-induced behavior was observed with both diphosphine- and monophosphine-boranes, and also in Negishi cross-coupling, suggesting this approach has some generality in terms of ambiphilic ligand as well as catalytic transformation.

Besides its synthetic interest in terms of catalytic C(=O)–C bond formation and preparation of functionalized ketones, these results advance the chemistry of ambiphilic ligands. They substantiate the compatibility and synthetic utility of ambiphilic ligands in Pd-catalyzed cross-coupling reactions. The structure of the key Pd complexes involved in these processes were authenticated, showing the boron centers interacting with either the Pd center or a co-ligand (a chloride or the oxygen of the acyl moiety). On this basis, we surmise that the versatile and adaptative coordination properties of the ambiphilic ligands play a major role in the observed chemoselectivity. It is also noteworthy that previous examples of transition metal / Lewis acid cooperativity involved either the increase of the TM electrophilicity (*via* TM→LA interaction or internal abstraction of an X-type ligand) or the activation of σ-bonds by addition across TM→LA interactions. A new facet of ambiphilic ligands is unveiled here, their faculty to impart chemoselectivity. Future work will aim to explore further this approach and apply ambiphilic ligands to other catalytic transformations, with a special interest for site-selective C–C and C–X couplings from polyfunctional substrates.

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Keywords: acyl chlorides • chemoselectivity • cross-coupling • phosphine-boranes • Pd catalysis

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[22] According to a CCDC search, the Pd–C(O) bond length in **3** is at the lower limit of those found in structurally characterized acyl Pd(II) complexes (1.964–2.071 Å, 10 compounds) while the C=O bond is at the upper limit (1.181–1.214 Å). According to a CCDC search, the B–O and C=O bond lengths found in **3** fall in the average of those found in structurally characterized adducts between carbonyl compounds and triaryl-borane (23 compounds).