Effect of hydrogen bonding on ligand substitution and its implication for the Heck reaction

Jiwu Ruan, Jonathan A. Iggo,* and Jianliang Xiao*

Department of Chemsitry, University of Liverpool, Liverpool, UK

iggo@liverpool.ac.uk; j.xiao@liverpool.ac.uk

Dedicated to Professor Dick Puddephatt on the occusion of his 75th birthday

Highlights

- Hydrogen bond-donating ammonium cations interact with aryl-Pd-Br species, a key intermediate in the Heck and other coupling reactions.
- The hydrogen bond donors (HBDs) promote substitution of the bromide ligand by phosphines.
- The reaction of aryl-Pd-Br with butyl vinyl ether is made possible by the HBD.
- The HBD accelerates the Heck reaction of electron-rich olefins by way of promoting the ionic pathway.

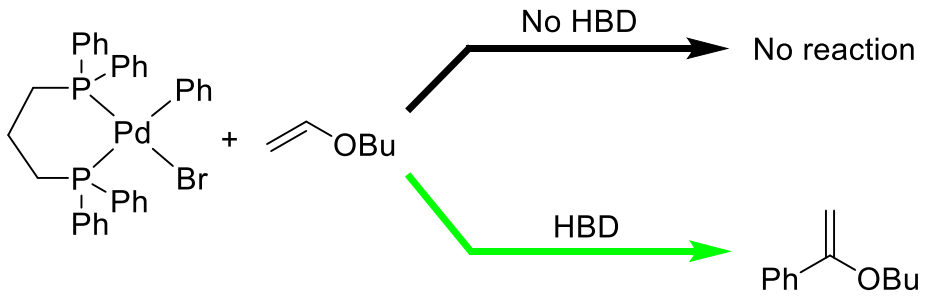
Abstract

Simple hydrogen-bond donating ammonium cations are found to hydrogen-bond with the halide ligand of a key intermediate in the Heck reaction, [Pd(diphosphine)PhBr], and promote the substitution of the halide by a phosphine ligand. Furthermore, upon introduction of an HBD, the palladium intermediate reacts with an electron-rich olefin to afford the expected Heck product, whereas no reaction was observed without the HBD. These observations support the hypothesis that HBDs accelerate the Heck α-arylation via facilitating halide dissociation from palladium and thereby the ionic pathway.

Keywords

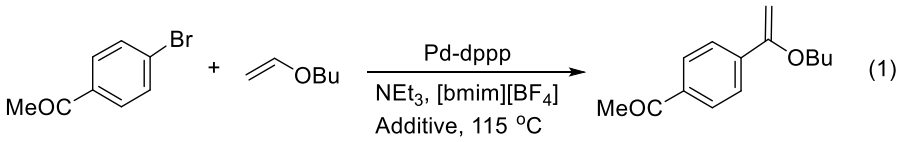
Hydrogen bonding, ligand substitution, hydrogen bond donors, Heck reaction, palladium catalysis

Graphic abstract



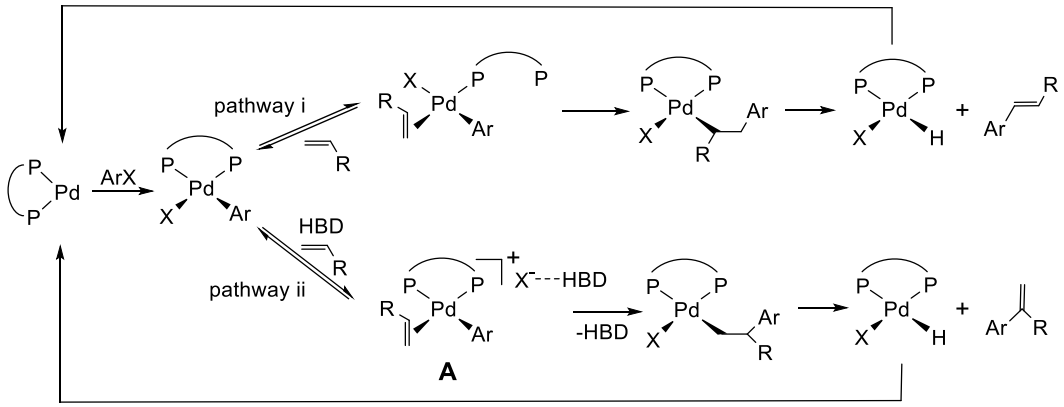
1. Introduction

Ligand substitution is perhaps the most fundamental reaction in transition-metal coordination chemistry and is central to most reactions catalysed by transition-metal complexes in which one or more of the substrates must become coordinated to the metal.[1, 2] As such, ligand substitution has been, and continues to be, widely studied. The general mechanisms of ligand substitution at square planar d^8 transition metal centres are now widely understood, as is the influence of factors such as solvent intervention, solvation, neighbouring group participation, etc. Many excellent reviews have been published.[3-7]



(1)

Our interest in ligand substitution at catalytic reaction centres was aroused by the observation that the addition of hydrogen bond donors (HBDs), such as dialkylammonium tetrafluoroborates or ethylene glycol, to Heck reactions accelerates the reaction and enables the highly regioselective α-arylation of electron-rich olefins with various aryl halides including deactivated aryl chlorides.[8-12] For example, the rate of α-arylation of olefins, catalysed by Pd-dppp (dppp = 1,3-bis(diphenylphosphino)propane) in 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), is considerably accelerated by addition of [H_nNR_{3-n}][BF_4] (n = 1, 2) but strongly inhibited by increasing the concentration of bromide ions (Eq. 1).[9, 11] Thus, in the presence of [$HNEt_3$][BF_4], 78% conversion of bromoacetophenone was observed after only 1 h, whilst only 2% conversion was observed in the presence of 1.5 equiv. [NBu_4][Br] after 12 h reaction.[9] Addition of [NBu_4][BF_4], which cannot act as a HBD, to the reaction brought about no significant effect on the rate. The last two observations preclude a salt effect[13] as the origin of the rate acceleration. We therefore suggested that this promotional effect might be due to hydrogen bonding between the hydrogen-bonding dialkylammonium cation and a halide ligand of the Pd catalyst and that this interaction diverted the Heck arylation into an ionic pathway (Scheme 1, pathway ii) rather than the neutral pathway generally followed in Heck reactions (Scheme 1, pathway i).[14, 15]



Scheme 1. Pathways in the Heck reaction and the hypothetic promoting effect of an HBD on the ionic pathway.

In this scenario, the coordination equilibrium involving displacement of the halide from the metal centre by olefin before the olefin insertion step could be rate controlling or prior to it. The overall reaction rate would then be directly proportional to the equilibrium constant *K* for substitution of the halide. Hydrogen bonding of the HBD to the halide X^- could drive this equilibrium to the right, thus enhancing the concentration of the cationic Pd(II)-olefin intermediate **A** and affording a faster arylation rate (Scheme 1). We note that Romeo has reported that hydrogen bonding by solvent to the coordinated chloride is important in promoting scission of the Pt-Cl bond in the *cis-trans* isomerization of *cis*-$[Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl]$,[16] and theoretically, studies of aquation of $[PtCl_4]^{2-}$ have suggested a role for hydrogen bonding in assisting dissociation of a chloride ligands[17] and in assisting cleavage of the Pd-F bond in $[(Ph_3P)_2Pd(F)R]$ in CH_2Cl_2 saturated with water.[18]

Hydrogen bonding is central to enzymatic catalysis and organocatalysis, and is important in crystal engineering[19] and host-guest chemistry.[20, 21] The involvement of hydrogen bonding in organometallic catalysis has also been observed, for example H-bonding between "specific" solvent molecules has been identified by DFT studies in, e.g. Pd catalysed alkene methoxycarbonylation[22-25] and Ru catalysed transfer hydrogenation,[26, 27] and H-bonding type interactions between incoming and metal bound substrates have been implicated in organometallic catalysed reactions.[28, 29] The addition of halide abstractors to enhance reactions involving substitution of a halide substituent is well known in organic chemistry. Examples of the addition of Lewis acids as halide acceptors to enhance the activity of organometallic catalysts have also been reported, e.g. in the carbonylation of MeOH to acetic acid, the BP CATIVA Process,[30-32] and in hydrovinylation.[33] However, the potential to accelerate a ligand substitution step in the catalytic cycle, and to accelerate organometallic catalysis more generally, afforded by the *deliberate* introduction of a hydrogen bond donor into the catalytic system, is only now being recognized.

We report here our studies on the influence of HBDs on ligand substitution reactions at Pd(II) centres of direct relevance to the Heck reaction, and show that the interaction between the HBD and a halide ligand results in labilization of the ligand coordinated to the metal centre, altering the position, and probably rate of attainment, of equilibrium in ligand substitution reactions at metal complexes. It is this effect that makes the ionic pathway in Heck catalysis favourable, resulting in preferential α-arylation of electron-rich olefins and accelerating the overall catalytic reaction rate.

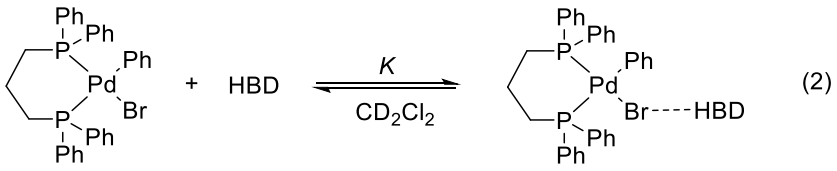
2. Results and Discussion

The Heck arylation of olefins by aryl halides is one of the most important tools for constructing sp^2 C-C bonds in synthetic chemistry. In the majority of reported Heck reactions, activated olefins, such as acrylates, are usually the substrates.[14] When used for arylation of electron-rich or deactivated olefins,

such as enol ethers, the Heck reaction often gives rise to a mixture of α and β-arylated products. The origin of the regioselectivity may be accounted for by two competing reaction pathways, as illustrated in Scheme 1.[11, 34-36] The neutral pathway (Pathway i, Scheme 1) affords the β-product, and features the displacement of a neutral ligand from Pd^{II}. In contrast, the ionic pathway (Pathway ii), involving halide displacement, yields the α product. Considering the electrophilic nature of cationic Pd^{II}, pathway ii is expected to favour electron-rich olefins. The ionic pathway can be favoured by employing aryl triflates – the lability of the Pd-Otf bond facilitates the formation of the cationic Pd^{II}-olefin species, or by adding stoichiometric silver or thallium salts when aryl iodides and bromides are chosen. For example, Hallberg, Larhed, Cabri and their coworkers reported that high α/β regioselectivity can be obtained using Pd-dppp catalysis with these additives.[34-36]

We showed that the Heck α-arylation of electron-rich olefins can be promoted by HBDs and attributed the promotion to HBD facilitating the dissociation of halide from Pd(II) and hence the ionic pathway ii (Scheme 1).[11] Our results suggested to us, although not conclusively, that HBDs are able to activate the organometallic centre toward substitution of the halide ligand by the olefin substrate, enhancing the concentration of the cationic Pd(II)-olefin species and hence the turnover rate of the ionic pathway. Therefore, we synthesised the neutral [Pd(dppp)PhBr] complex, precusor to the Pd(II)-olefin species, and investigated whether the neutral complex would engage in hydrogen bonding interactions with a HBD.

Hydrogen bonding. The existence of hydrogen bonding between an HBD, such as a dialkylammonium cation, and an acceptor, such as a halide ligand coordinated to a Pd(II) centre, results in a shift of the ^{1}H NMR resonances of the donor and is thus easily followed by NMR titration. We first examined whether the HBD $[H_2N(i\text{-}Pr)_2][BF_4]$ would interact with [Pd(dppp)PhBr] (Eq. 2), the key intermediate in the Heck reaction before the divergence of the reaction pathway (Scheme 1). Figure 1 shows a series of ^{1}H NMR spectra of solutions of [Pd(dppp)PhBr], to which increasing amounts of the HBD have been added. Progressive downfield shifting of the resonances of the HBD around 3.3 and 1.2 ppm are seen, as is a much smaller downfield shift of the methylene protons of the dppp ligand, suggesting hydrogen bonding between the dialkylammonium cation and the palladium complex (Eq. 2).



(2)

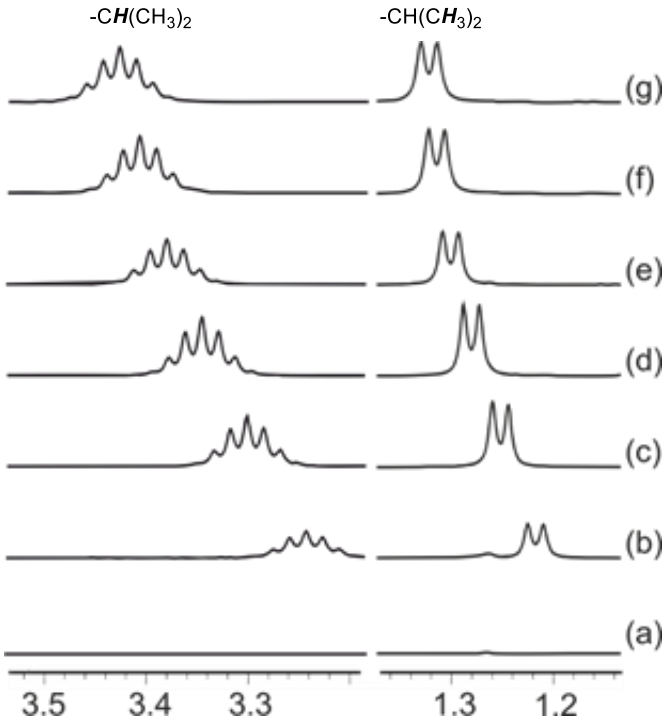
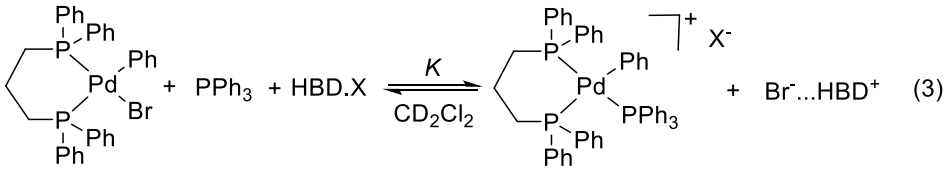


Figure 1. ^{1}H NMR spectra of CD_2Cl_2 solutions of [Pd(dppp)PhBr] and a HBD $[H_2N(i\text{-}Pr)_2][BF_4]$. Pd/HBD (molar) = (a) 10:0; (b) 10:1; (c) 10:3; (d) 10:7; (e) 10:15; (f) 10:30; (g) 10:50. See the Experimental for more details.

Promotion of ligand substitution. Having gained evidence on the hydrogen bonding interactions between [Pd(dppp)PhBr] and the ammonium HBD, we next investigated the effect of the HBD on ligand substitution reactions of the same species. In accord with the hypothesis that hydrogen bonding promotes ligand substitution, we found that addition of the HBD $[H_2N(i\text{-}Pr)_2][BF_4]$ to dichloromethane solutions of [Pd(dppp)PhBr] and PPh_3 dramatically promotes the bromide substitution by PPh_3 (Eq. 3), altering the equilibrium position and probably accelerating the rate of substitution as well (Figure 3 a vs b). *In the absence of the HBD, substitution of the bromide by PPh_3 is barely observable*. These observations indicate strongly that HBDs promotes the formation of and shift the equilibrium to favour the cationic palladium species, such as **A** (Scheme 1).



(3)

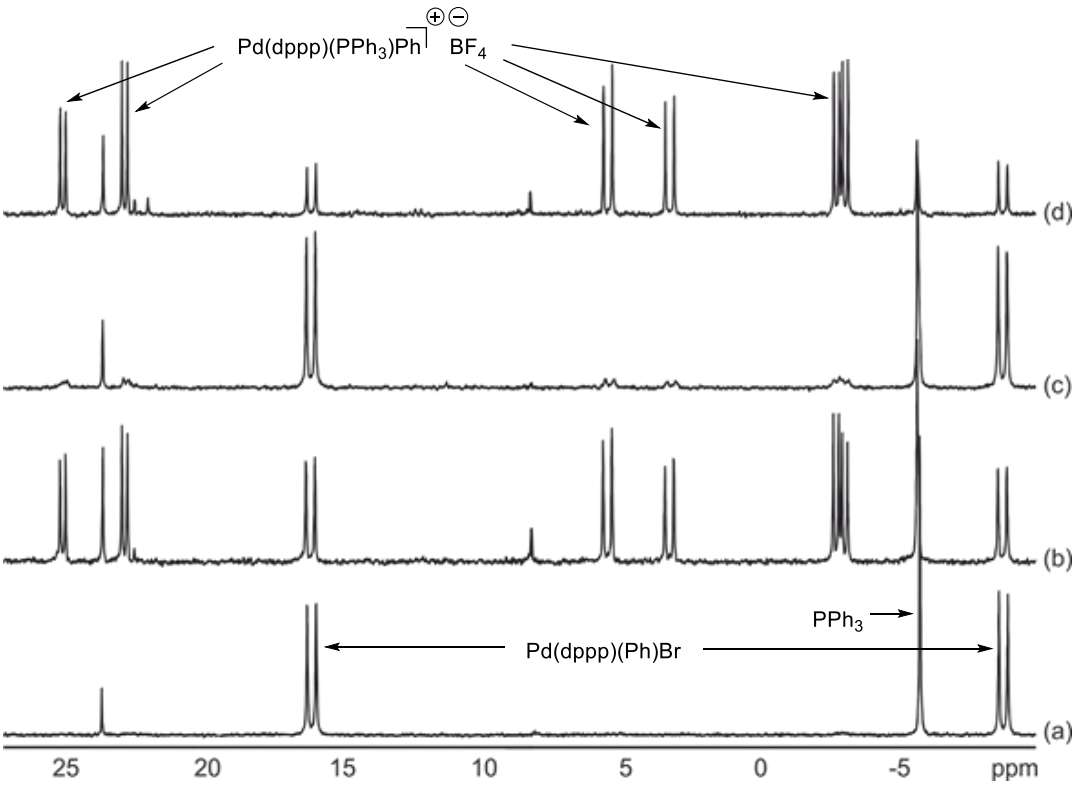


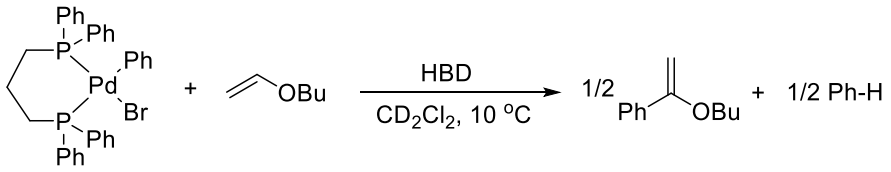
Figure 3. $^{31}P\{^{1}H\}$ NMR spectra of solutions of a 1:1 mixture of [Pd(dppp)PhBr], an alkylammonium salt and PPh_3 in CD_2Cl_2: salt = (a) none; (b) $[H_2N(i\text{-}Pr)_2][BF_4]$; (c) $[NEt_4][BF_4]$; (d) $[H_2N(CH(Me)Ph)_2][BF_4]$. See the Experimental for more details.

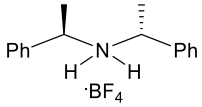
However, as we observed in our earlier study of the Heck reaction, addition of $[NEt_4][BF_4]$ has only an insignificant effect on the reaction (Figure 3 c), excluding a salt effect.[13, 37] Not all HBDs are equally effective; a clear difference can be seen in the position of equilibrium (Figure 3, b vs d) when comparing the HDBs $[H_2N(i\text{-}Pr)_2]BF_4$ and $[H_2N(CH(Me)Ph)_2]BF_4$, with the latter inducing significantly more substitution of bromide by PPh_3 (80% vs 62% conversion of the neutral Pd species to the ionic one). This difference in effect of the HBD might reflect differences in the steric hindrance of the two HBDs or differences in the pKa. Jutand has previously reported that treatment of *trans*-$[Pd(PPh_3)_2(Ar)X]$ with secondary amines results in substitution of a PPh_3 ligand rather than the expected substitution of the halide and found no clear correlation between the amine basicity and *K* and suggested that a combination of factors including amine basicity and steric effects influenced the magnitude of *K*.[38]

Promotion of Heck arylation of olefins. The results above suggest that halide substitution at metal centres can be promoted by the addition of an HBD to the reaction. We were particularly interested to verify if this acceleration of halide ligand displacement by the presence of an HDB, and presumably subsequent facilitation of coordination of the olefin substrate, was responsible for the increase in the Heck α-arylation of electro-rich olefins, as we had hypothesized in the past.[11] We therefore studied

the effect of various additives on the reaction of butyl vinyl ether with [Pd(dppp)(Ph)Br], the intermediate that, upon dissociation of the bromide ligand, leads to the ionic pathway ii in the Heck reaction to afford the branch olefin product (Scheme 1). The results are found in Table 1.

Table 1. The effect of HBDs on the reaction of a vinyl ether with [Pd(dppp)(Ph)Br]



HBD	Conversion / % [a]	b / l [b]
/	0	/
Ethylene glycol	0	/
$[NEt_4][BF_4]$	0	/
$[HNEt_3][BF_4]$	15	> 99/1
$[H_2N(i\text{-}Pr)_2][BF_4]$	19	> 99/1
	32	> 99/1

[a] Measured after 20 mins at 10 °C in CD_2Cl_2. [b] Molar ratio of branched vs linear olefin product with >99/1 indicating no linear product being detected by ^1H NMR. See the Experimental for more details.

Somewhat surprisingly, the vinyl ether does not react at all with the Pd-phenyl complex in the absence of an HBD, indicating that no bromide dissociation occurs under the conditions examined. Whilst the inability of $[NEt_4][BF_4]$ in promoting the reaction is expected, that of ethylene glycol is unexpected, given its established effect on the overall Heck reaction.[10, 39, 40] This is probably due to the much lower temperature employed than that of the normal Heck reaction. In stark contrast, *alkylammonium salts capable of hydrogen bonding to the bromide ligand on palladium all result in rapid reaction to afford the Heck arylation product* and the required equivalent of benzene. W note that the conversions achieved with $[H_2N(i\text{-}Pr)_2]BF_4$ and $[H_2N(CH(Me)Ph)_2]BF_4$ are in line with their ability in shifting the equilibrium shown in Eq. 3. These observations lend strong support to our hypothesis that such hydrogen bonding promotes the ionic pathway in the Heck reaction and is responsible for the acceleration we observed [11].

Brown and Hii have previously investigated the reactivity of the η^2-alkene complex 1,1-bis-(diphenylphosphino)ferrocenepalladium(η^2-methyl acrylate) ([(dppf)Pd(MeA)]) towards aryl iodides and triflates[41] and reported an accelerating effect of $Eu(OTf)_3$ on the oxidative addition rate of either PhI or PhOTf to [(dppf)Pd(MeA)], which was attributed to association of Eu^{3+} to the carbonyl oxygen of coordinated acrylate facilitating its dissociation, providing a significant concentration of the 14-electron (dppf)Pd[0] species, which then becomes the main channel for the oxidative addition. Although Brown and Hii's work focused on the oxidative addition to Pd(0), their conclusions parallel ours, that is creation of a reaction site at the metal centre being facilitated by a Lewis acid-Lewis base interaction between a "co-factor" and a ligand already coordinated to the metal and that must be removed to enable reaction to proceed efficiently.

3. Conclusion

The study reported in this paper shows that HBDs hydrogen-bond with the halide ligand of a key intermediate in the Heck reaction and promotes the substitution of the halide by a phosphine ligand. In line with this finding, the reaction of the palladium intermediate with an electron-rich olefin is made possible upon introduction of an HBD. Thus, as we have hypothesised before [11], HBDs accelerate the Heck α-arylation via facilitating the halide dissociation from palladium and thereby the ionic pathway. There are other transformations that are fundamental to catalysis, which may also be accelerated by HBDs. The oxidation addition of ArCl to Pd(0) is one such example, where HDBs have been shown to participate in the transition state, facilitating the departure of the chloride and thereby accelerating the oxidative addition reaction.[10] Thus, exploiting simple HBDs could have a large impact on both organometallic chemistry and catalysis.

4. Experimental Section

4.1. General methods and procedures

All manipulations involving solutions or solids were performed under an atmosphere of nitrogen using standard Schlenk techniques. All solvents were dried and distilled under nitrogen following standard literature methods. Deuterated solvents were degassed by 3 freeze – pump – thaw cycles under vacuum in a liquid nitrogen bath, then nitrogen saturated and stored over activated 4 Å molecular sieves under nitrogen for at least 24 hours prior to use. $^{31}P\{^1H\}$, ^{31}P, $^{13}C\{^1H\}$, ^{13}C and ^1H NMR measurements were performed on Bruker DPX400, or Avance2-400 instruments using commercial probes. Chemical shifts were referenced to internal TMS following IUPAC guidelines. Spectra of samples dissolved in non-deuterated solvents were referenced to the solvent resonance. Chemical shift errors are as follows; $^{31}P \pm 0.2$ ppm, $^1H \pm 0.05$ ppm. Coupling constant errors are as follows $^{31}P \pm 1.0$ Hz and $^1H \pm 0.1$ Hz.

4.2. ^1H NMR titration of [Pd(dppp)PhBr] with $[H_2N^iPr_2][BF_4]$

To a J Young NMR tube 35.8 mg (0.053 mmol) of [Pd(dppp)PhBr] was charged under argon. 0.7 mL of degassed CD_2Cl_2 was then introduced and shaken till all the [Pd(dppp)PhBr] dissolved (about half minute). The ^1H and ^{31}P NMR of the solution were recorded at 20 ^oC. Then 1 mg (0.0053 mmol) of $[H_2N^iPr_2][BF_4]$ was added to the NMR tube, which was shaken till all the $[H_2N^iPr_2][BF_4]$ was dissolved (ca. 1 minute). The ^1H and ^{31}P NMR of this solution with the molar ratio of [Pd(dppp)PhBr]/$[H_2N^iPr_2][BF_4]$ = 10:1 were recorded at 20 ^oC.

The ^1H and ^{31}P NMR of other molar ratios of the [Pd(dppp)PhBr]/$[H_2N^iPr_2][BF_4]$ solutions were obtained by simply increasing the quantity of $[H_2N^iPr_2][BF_4]$.

4.3. Procedure for ligand substitution in presence of an HBD

To a Young NMR tube 6.8 mg (0.01mmol) of [Pd(dppp)PhBr] and 1.9 mg (0.01mmol) of $[H_2N^iPr_2][BF_4]$ were charged under argon. 0.5 mL of degassed CD_2Cl_2 was introduced and shaken till all the solids dissolved (ca. 1 minute). Then 2.6 mg (0.01mmol) of PPh_3 was added and the tube was shaken for 2 minutes. The ^1H and ^{31}P NMR of this solution were recorded at 20 ^oC. The procedure was the same with other additives.

4.4. Procedure for the Heck reaction in presence of an HBD

To a Young NMR tube 6.8 mg (0.01mmol) of [Pd(dppp)PhBr] and 1.9 mg (0.01mmol) $[H_2N^iPr_2][BF_4]$ were charged under argon. 0.5 mL of degassed CD_2Cl_2 was introduced and shaken till all the solids dissolved (ca. 1 minute). The solution was cooled to 10 ^oC, to which was added 1.0 mg (0.01 mmol) of butyl vinyl ether. The NMR tube was shaken for 20 minutes at 10 ^oC and then the ^1H and ^{31}P NMR were recorded at the same temperature. The procedure was the same with other additives.

Acknowledgements

We thank the EPSRC for financial support, Grants EP/F000316/1 and EP/C005643/1.

References

[1] G. Salas, J.A. Casares, P. Espinet, Dalton Trans. (2009) 8413-8420.

[2] M. Kalek, J. Stawinski, Organometallics 27 (2008) 5876-5888.

[3] R.J. Cross. in: A.G. Sykes (Ed), Adv. Inorg. Chem. Academic Press, 1989, Vol. 34, pp. 219-292.

[4] R.J. Cross. Chem. Soc. Rev. 14 (1985) 197-223.

[5] R. Romeo, Comments Inorg. Chem. 11 (1990) 21 - 57.

[6] R. Romeo, L.M. Scolaro, in: C.G. Screttas and B.R. Steele (Eds), Perspectives in Organometallic Chemistry, Royal Society of Chemistry, 2003, pp. 208-221.

[7] C.D. Hubbard, R. van Eldik, J. Coord. Chem. 60 (2007) 1-51.

[8] J. Mo, L.J. Xu, J. Xiao, J. Am. Chem. Soc. 127 (2005) 751-760.

[9] J. Mo, J. Xiao, Angew. Chem., Int. Ed. Engl. 45 (2006) 4152-4157.

[10] J. Ruan, J.A. Iggo, N.G. Berry, J. Xiao, J. Am. Chem. Soc. 132 (2010) 16689-16699.

[11] J. Ruan, J. Xiao, Acc. Chem. Res. 44 (2011) 614-626.

[12] C. Wu, J. Zhou, J. Am. Chem. Soc. 136 (2014) 650-652.

[13] A.D. Ryabov, A.K. Yatsimirsky, Tetrahedron Lett. 21 (1980) 2757-2760.

[14] M. Beller, A. Zapf, T.H. Riermeier, in: M. Beller and C. Bolm (Eds), Transition Metals for Organic Synthesis (2nd Ed), 2004, Vol 1, pp. 271-306.

[15] C. Bäcktorp, P.-O. Norrby, Dalton Trans. 40 (2011) 11308-11314.

[16] R. Romeo, D. Minniti, S. Lanza, Inorg. Chem. 19 (1980) 3663-3668.

[17] J.K. Park, B.G. Kim, Bull. Korean Chem. Soc. 27 (2006) 1405-1417.

[18] M.C. Pilon, V.V. Grushin, Organometallics 17 (1998) 1774-1781.

[19] L. Brammer, Dalton Trans. (2003) 3145-3157.

[20] R. Bertani, P. Sgarbossa, A. Venzo, F. Lelj, M. Amati, G. Resnati, T. Pilati, P. Metrangolo, G. Terraneo, Coord. Chem. Rev. 254 (2010) 677-695.

[21] J.W. Steed, Chem. Soc. Rev. 38 (2009) 506-519.

[22] S.M.A. Donald, S.A. Macgregor, V. Settels, D.J. Cole-Hamilton, G.R. Eastham, Chem. Commun. (2007) 562-564.

[23] E. Zuidema, C. Bo, P. van Leeuwen, J. Am. Chem. Soc. 129 (2007) 3989-4000.

[24] P. Roesle, L. Caporaso, M. Schnitte, V. Goldbach, L. Cavallo, S. Mecking, J. Am. Chem. Soc. 136 (2014) 16871-16881.

[25] P. Roesle, C.J. Durr, H.M. Moller, L. Cavallo, L. Caporaso, S. Mecking, J. Am. Chem. Soc. 134 (2012) 17696-17703.

[26] J.W. Handgraaf, E.J. Meijer, J. Am. Chem. Soc. 129 (2007) 3099-3103.

[27] X. Wu, J. Liu, D. Di Tommaso, J. A. Iggo, C. R. A. Catlow, J. Bacsa, J. Xiao, Chem. Eur. J. 14 (2008) 7699-7715.

[28] F. Ragaini, M. Gasperini, S. Cenini, L. Arnera, A. Caselli, P. Macchi, N. Casati, Chem. Eur. J. 15 (2009) 8064-8077.

[29] Y.D. Lu, T.C. Johnstone, B.A. Arndtsen, J. Am. Chem. Soc. 131 (2009) 11284-11285.

[30] A. Haynes, P.M. Maitlis, G.E. Morris, G.J. Sunley, H. Adams, P.W. Badger, C.M. Bowers, D.B. Cook, P.I.P. Elliott, T. Ghaffar, H. Green, T.R. Griffin, M. Payne, J.M. Pearson, M.J. Taylor, P.W. Vickers, R.J. Watt, J. Am. Chem. Soc. 126 (2004) 2847-2861.

[31] S. Gautron, N. Lassauque, C. Le Berre, L. Azam, R. Giordano, P. Serp, G. Laurenczy, J.C. Daran, C. Duhayon, D. Thiebaut, P. Kalck, Organometallics 26 (2007) 1116-1116.

[32] R. Whyman, A.P. Wright, J.A. Iggo,B. T. Heaton, Dalton Trans. (2002) 771-777.

[33] N. Lassauque, G. Francio,W. Leitner, Eur. J. Org. Chem. (2009) 3199-3202.

[34] A. Arefalk, M. Larhed, A. Hallberg, J. Org. Chem. 70 (2005) 938-942.

[35] K.S.A. Vallin, Q.S. Zhang, M. Larhed, D.P. Curran, A. Hallberg, J. Org. Chem. 68 (2003) 6639-6645.

[36] W. Cabri, I. Candiani, Acc. Chem. Res. 28 (1995) 2-7.

[37] W.A. Herrmann, C. Brossmer, K. Ofele, C.P. Reisinger, T. Priermeier, M. Beller, H. Fischer, Angew. Chem., Int. Ed. Engl. 34 (1995) 1844-1848.

[38] A. Jutand, S. Negri, A. Principaud, Eur. J. Inorg. Chem. (2005) 631-635.

[39] Z. Hyder, J. Ruan, J. Xiao, Chem. Eur. J. 14 (2008) 5555-5566.

[40] M.C. Liu, Z. Hyder, Y.W. Sun, W.J. Tang, L.J. Xu, J. Xiao, Org. Biomol. Chem. 8 (2010) 2012-2105.

[41] A. Jutand, K.K.M. Hii, M. Thornton-Pett, J.M. Brown, Organometallics 18 (1999) 5367-5374.