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Mechanistic study on the cross-coupling of alkynyl stannanes with aryl iodides catalyzed by η^2-(dimethyl fumarate)palladium(0) complexes with iminophosphine ligands

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The reactions of [Pd(η^2-dmfu)(P–N)] [dmfu = dimethyl fumarate; P–N = 2-(PPh_2)C_6H_4-1-CH=NR, R = C_6H_4OMe-4 (**1a**), $CHMe_2$ (**2a**)] and [Pd(η^2-dmfu)(P–N)$_2$] with $IC_6H_4CF_3$-4, $ISnBu_3$ and $PhC{\equiv}CSnBu_3$ have been studied under pseudo-first-order conditions. The oxidative addition of $IC_6H_4CF_3$-4 yields [PdI($C_6H_4CF_3$-4)(P–N)] (**1b** or **2b**). No reaction takes place with $PhC{\equiv}CSnBu_3$ and also with $ISnBu_3$ in the presence of an excess of $PhC{\equiv}CSnBu_3$. In the presence of fumaronitrile (fn), **1b** and **2b** undergo transmetalation by $PhC{\equiv}CSnBu_3$ followed by fast reductive elimination to yield [Pd(η^2-fn)(P–N)]. The same reaction sequence occurs for the system [PdI($C_6H_4CF_3$-4)(P–N)]/P–N (1 : 1 molar ratio) to give [Pd(η^2-fn)(P–N)$_2$]. The palladium(0) complexes are active catalysts in the cross-coupling of $PhC{\equiv}CSnBu_3$ with aryl iodides ArI (Ar = $C_6H_4CF_3$-4, Ph). The catalytic efficiency depends on the complex: [Pd(η^2-dmfu)(P–N)$_2$] > [Pd(η^2-dmfu)(P–N)], and on the substituent R: C_6H_4OMe-4 > $CHMe_2$. The reactivity and spectroscopic data suggest a catalytic cycle involving initial oxidative addition of ArI to a palladium(0) species, followed by transmetalation of the product and by fast reductive elimination to regenerate the starting palladium(0) compound. For [Pd(η^2-dmfu)(P–N)] as catalyst, the oxidative addition is the rate-determining step, while for [Pd(η^2-dmfu)(P–N)$_2$] the oxidative addition and the transmetalation steps occur at comparable rate.

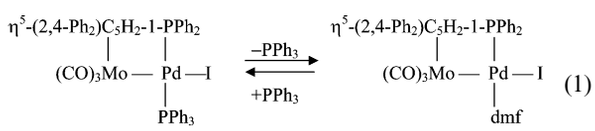
Introduction

The palladium-catalyzed cross-coupling of stannanes with organic electrophiles (Stille reaction) is a widely used synthetic method for the formation of carbon–carbon bonds.[1] The commonly accepted picture of the catalytic cycle involves an initial oxidative addition of the organic electrophile to a palladium(0) species followed by transmetalation, *trans*-to-*cis* isomerization if *trans*-diorganopalladium(II) intermediates are formed, and eventually by reductive elimination of the coupling product.[1,2] The rate-determining step of the cycle can be either the oxidative addition or the transmetalation or even the reductive elimination.[1c,2,3] Although detailed studies have been carried out for long time,[4] the mechanism of the process is still the subject of intense research for the complexity of the reactions involved, which can be variously influenced by the nature of the ligand, the solvent, the reacting organostannane and carbon electrophile, and by the presence of additives such as LiCl or the free ligand.

In recent papers,[5] Espinet has proposed the mechanism described in Scheme 1 for the coupling of ArX (Ar = pentahalophenyl; X = halide, triflate) with $RSnBu_3$ (R = vinyl).

Two transmetalation pathways may be present: step (a) through an associative S_E2 "cyclic" mechanism and step (b) through an associative "open" mechanism. The S_E2 cyclic step (a) is much favoured in weakly coordinating solvents of low polarity when X is a good bridging ligand such as a halide. It leads to a *cis* highly reactive species which undergoes an immediate reductive elimination, and is strongly retarded by the presence of free ligand L. The S_E2 open step (b) is favoured when L′ is a ligand or a polar coordinating solvent, both lacking bridging ability, and when X is a good-leaving and poorly coordinating anionic ligand without bridging ability.

In contrast to this mechanism where the transmetalation steps proceed without any prior dissociation (or solvent displacement) of the ligand L in the intermediates *trans*-[PdXArL$_2$], the transmetalation of [{η^5-(1-Ph_2P)(2,4-Ph_2)C_5H_2}$(CO)_3$MoPdI(PPh_3)] by $PhC{\equiv}CSnBu_3$, leading to [{η^5-(1-Ph_2P)(2,4-Ph_2)C_5H_2}$(CO)_3$MoPd(C≡CPh)(PPh_3)], was recently reported to proceed *via* formation of a reactive solvent-coordinate species at low initial concentration of the starting complex, according to eqn. (1):[6]



(1)

(dmf = dimethylformamide)

On the other hand, also the complex *trans*-[PdIPh($AsPh_3$)$_2$] was found by Amatore to be involved in a slow equilibrium with the species [PdIPh(solvent)($AsPh_3$)] (solvent = $CDCl_3$, dmf) upon release of $AsPh_3$,[7] in agreement with previous kinetic investigations by Farina.[1b,4e] In a very recent report, however, the concentration of [PdXR(solvent)($AsPh_3$)] (X = Cl, I; R = Ph, $C_6Cl_2F_3$) was found to be negligible in the presence of free arsine (for a mixture $AsPh_3$/[PdXR($AsPh_3$)$_2$] in a 2 : 1 molar ratio), indicating that under catalytic conditions the predominant pathway involves the associative reaction of the stannane with the complex [PdXR($AsPh_3$)$_2$].[8]

So far, mainly palladium complexes with monodentate phosphine or arsine ligands have been used in such catalytic reactions. Bidentate chelating diphosphines usually slow down the reaction rate,[4e,9] although improved rates have also been observed.[10] A few reports dealing with cross-coupling reactions catalyzed by palladium complexes with bidentate nitrogen ligands have been published.[11] More recently, the main intermediates, namely [PdAr(CH=CH_2)(dppe)] and [Pd(η^2-CH_2=CHAr)(dppe)], have been observed and characterized in the coupling of pentahaloaryl triflates (ArX) with CH_2=$CHSnBu_3$ catalyzed by [PdXAr(dppe)] [dppe = 1,2-bis(diphenylphosphino)ethane)].[12]

In a comparative study on the catalytic activity of the systems [PdCl(η^3-C_3H_5)]$_2$/L–L′ (1 : 2 molar ratio) [L–L′ = 2-(PPh_2)C_6H_4-1-CH=NC_2H_4Ph, 2-(PPh_2)C_6H_4-1-CH_2NMe_2,

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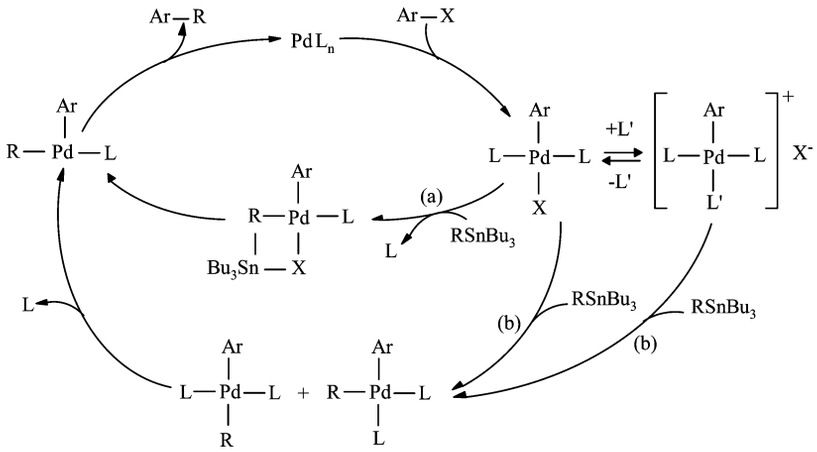
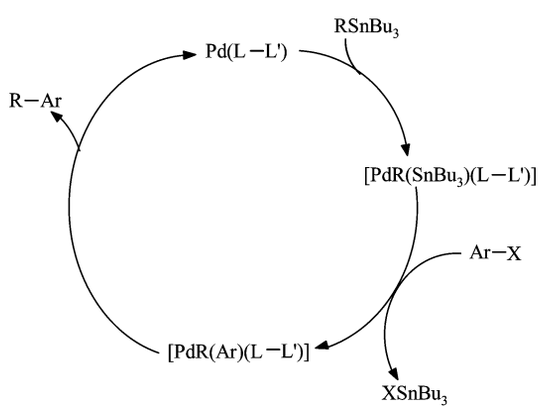


Scheme 1 L = PPh_3, $AsPh_3$; L′ = ligand or solvent.

1,3-$(PPh_2)_2C_3H_6$], Shirakawa noticed that the iminophosphine system has the higher catalytic efficiency in the coupling of 4-(trifluoromethyl)iodobenzene with $PhC{\equiv}CSnBu_3$.[13] From the detection of the complexes $[PdI(SnBu_3)(L–L')]$ and $[Pd(C{\equiv}CPh)(SnBu_3)(L–L')]$ [L–L′ = 2-$(PPh_2)C_6H_4$-1-CH=NC_2H_4Ph] in the ^{31}P NMR spectra of the reaction mixture, a new catalytic cycle was proposed involving the initial oxidative addition of $PhC{\equiv}CSnBu_3$ to a palladium(0) species Pd(L–L′) generated *in situ* (Scheme 2).



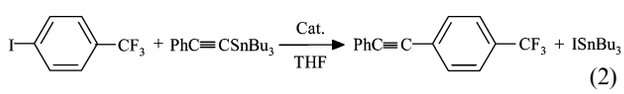
[L–L' = 2-$(PPh_2)C_6H_4$-1-CH=NC_2H_4Ph]

Scheme 2

Following our studies on the catalytic properties of the zerovalent complexes [Pd(η²-dmfu)(P–N)] [dmfu = dimethyl fumarate; P–N = 2-$(PPh_2)C_6H_4$-1-CH=NR, R = alkyl and aryl group],[14] which can be easily prepared and stored without appreciable decomposition in the presence of air,[15] we have recently reported that these complexes are quite active catalysts (or catalyst precursors) in the coupling of organostannanes with aryl halides.[16] The catalytic efficiency is retained for prolonged time and increases considerably on going from alkyl to aryl *N*–R substituents, and also in the presence of the free iminophosphine for a P–N/[Pd(η²-dmfu)(P–N)] molar ratio ≥ 1. These observations prompted us to carry out a mechanistic investigation in order to ascertain (*i*) the actual catalytic cycle of the reaction and (*ii*) the origin of the long life-time of the catalyst.

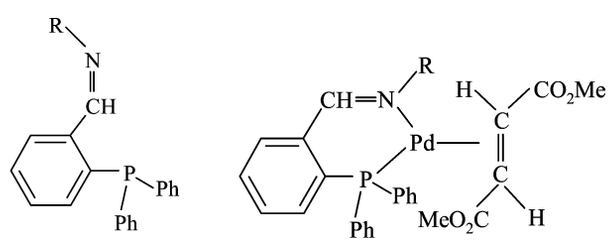
Results and discussion

The cross-coupling of 4-(trifluoromethyl)iodobenzene with tributyl(phenylethynyl)tin was chosen as a model reaction for the mechanistic study [eqn. (2)]:



(2)

The iminophosphine ligands and the zerovalent complexes [Pd(η²-dmfu)(P–N)] used as catalysts (or catalyst precursors) are shown in Scheme 3.



R = C_6H_4OMe-4 : **1** R = C_6H_4OMe-4 : **1a**

R = $CHMe_2$: **2** R = $CHMe_2$: **2a**

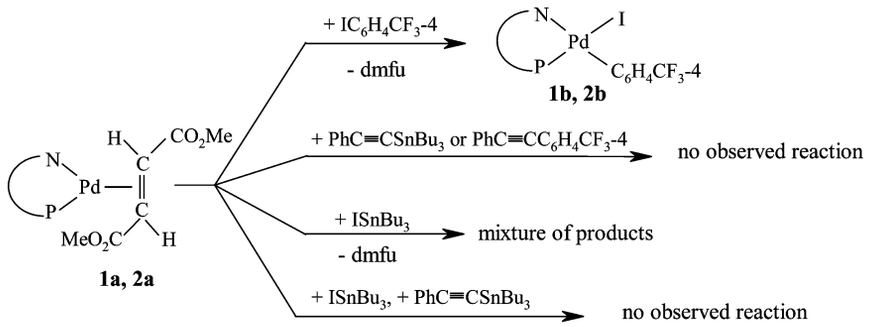
Scheme 3

The choice of these ligands stems from the fact that the imino nitrogen substituents R, a *para*-substituted aryl group in **1** and a secondary alkyl group in **2**, have comparable steric requirements but different electronic properties. Where possible, the reactions involved in the single steps of the cycles in Scheme 1 and Scheme 2 have been examined in thf (or thf-d_8) at 25 °C, under pseudo-first-order conditions generally using a palladium complex/reactant molar ratio of 1 : 10 either in the absence or in the presence of one equivalent of added iminophosphine. An initial palladium complex concentration of 2×10^{-2} mol dm^{-3} was used. The progress was monitored by IR spectroscopy in the range 2400–1500 cm^{-1}, and by ^1H and ^{31}P NMR spectroscopy.

Reactions in the absence of added iminophosphine

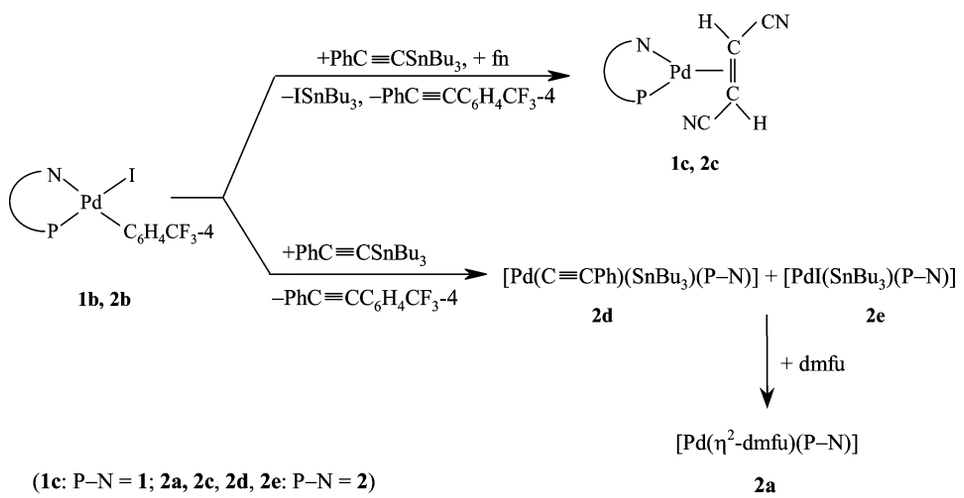
Since the complexes [Pd(η²-dmfu)(P–N)] undergo oxidative addition of organic halides and also olefin substitution by π-accepting unsaturated ligands,[15] we have examined the possible reactions of **1a** and **2a** with the reactants and products of the cross-coupling catalysis [eqn. (2)].

Oxidative additions and olefin substitutions. The occurrence of these reactions can be easily detected in the IR spectra as they involve the formation of free dmfu characterized by a *ν*(C=O) band at 1726 cm^{-1} (*cf.* the corresponding *ν*(C=O) band at 1687 cm^{-1} for **1a** and at 1688 cm^{-1} for **2a**). The reactions studied are summarized in Scheme 4.



(**1b**: P–N=**1**; **2b**:P–N= **2**)

Scheme 4



(**1c**: P–N = **1**; **2a**, **2c**, **2d**, **2e**: P–N = **2**)

Scheme 5

The reaction with a ten-fold excess of $IC_6H_4CF_3$-4 goes to completion in *ca.* 40 min for **1a**, whereas it is much slower for **2a** (*ca.* 15% progress in 40 min). The products **1b** and **2b** were isolated and characterized (see Experimental). Although their coordination geometry cannot be assessed from the ^{1}H and ^{31}P NMR data, we propose a configuration with the aryl ligand *trans* to the imino nitrogen on the basis of *trans* influence considerations, the aryl group and the phosphorus atom being the strongest donors,[17] and X-ray structural analyses of related complexes [PdX(R)(L–L′)] (X = Cl, I; R = alkyl or aryl group; L–L′ = aminophosphine or iminophosphine).[18]

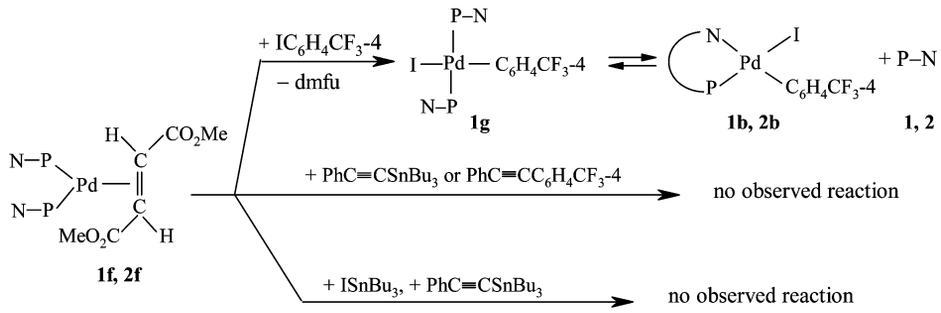
No reaction is observed to occur between **1a** or **2a** and a ten-fold excess of $PhC{\equiv}CSnBu_3$ or $PhC{\equiv}CC_6H_4CF_3$-4. In the case of **1a**, only a slight decomposition of the complex takes place after prolonged time (3–5 h). This result shows that these alkynes are unable to displace the η^2-bound olefin and also that the alkynylstannane does not oxidatively add to [Pd(η^2-dmfu)(P–N)].

The complex **1a** reacts with a ten-fold excess of $ISnBu_3$ at a lower rate than with $IC_6H_4CF_3$-4. After 2 h, the ^{31}P NMR spectrum of the reaction mixture shows the presence of at least four products [δ(P^{31}) signals as singlets at 40.5, 32.8, 31.1 and 15.1 ppm] which could not be isolated and characterized. The corresponding reaction with **2a** is much slower and leads to a mixture of several products. On the basis of the course of the oxidative addition of $ISnBu_3$ to palladium(0) substrates,[13] these reactions presumably involve the initial and slow formation of labile derivatives [PdI($SnBu_3$)(P–N)] which readily decompose in solution.

No reaction of **1a** or **2a** with $ISnBu_3$ is observed in the presence of an excess of $PhC{\equiv}CSnBu_3$ when the reactants [Pd(η^2-dmfu)(P–N)]/$ISnBu_3$/$PhC{\equiv}CSnBu_3$ are mixed together in a 1 : 5 : 10 molar ratio.

Transmetalation and reductive elimination. As is generally accepted for palladium complexes containing chelating bidentate ligands,[4d,12,13] the transmetalation of [PdI($C_6H_4CF_3$-4)(P–N)] (**1b** or **2b**) with $PhC{\equiv}CSnBu_3$ leads to a labile intermediate [Pd(C≡CPh)($C_6H_4CF_3$-4)(P–N)]. The subsequent reductive elimination of $PhC{\equiv}CC_6H_4CF_3$-4 generates a coordinatively unsaturated palladium(0) transient, Pd(P–N), which may undergo different reactions with the species present in solution, such as η^2-coordination of unsaturated ligands[4d,12] or oxidative addition of $ISnBu_3$ and/or $PhC{\equiv}CSnBu_3$.[13] We have therefore examined two different types of reactions as reported in Scheme 5.

The reaction of **1b** or **2b** with $PhC{\equiv}CSnBu_3$ was first studied in the presence of an activated olefin of enhanced π-accepting properties, such as fumaronitrile (fn), since the products [Pd(η^2-fn)(P–N)] (**1c**, **2c**), independently prepared,[15] do not react with either $ISnBu_3$ or $PhC{\equiv}CSnBu_3$. As indicated by the IR and the multinuclear (^{1}H, ^{31}P, ^{119}Sn) NMR spectra of the mixtures [PdI($C_6H_4CF_3$-4)(P–N)]/$PhC{\equiv}CSnBu_3$/fn (1 : 10 : 1.5 molar ratio), the reaction yields smoothly and quantitatively the products [Pd(η^2-fn)(P–N)] [**1c**: ν(C≡N) at 2202 cm^{-1} and δ(^{31}P) at 23.0 ppm; **2c**: ν(C≡N) at 2195 cm^{-1} and δ(^{31}P) at 22.3 ppm], $ISnBu_3$ [δ(^{119}Sn) at 79.5 ppm] and $PhC{\equiv}CC_6H_4CF_3$-4 [ν(C≡C) at 2220 cm^{-1}], no intermediate or side-product being detected. This implies that the reductive elimination of $PhC{\equiv}CC_6H_4CF_3$-4 from the proposed intermediate [Pd(C≡CPh)($C_6H_4CF_3$-4)(P–N)] is much faster than the initial transmetalation step. The overall rate depends also on the iminophosphine nitrogen substituent in the order R = C_6H_4OMe-4 > $CHMe_2$ as estimated by the completion times of *ca.* 15 min for **1b** and of *ca.* 70 min for **2b**. Quite similar results are obtained in the presence of a less π-accepting olefin such as dmfu. As an example, the reaction of **2b** with $PhC{\equiv}CSnBu_3$ and dmfu (1 : 10 : 1.5 molar ratio) goes to



(**1g**: P–N = **1**)

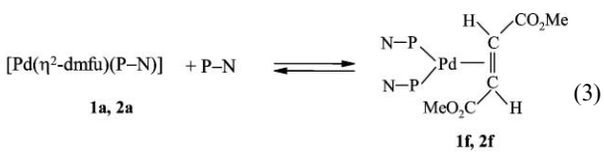
Scheme 6

completion in *ca.* 65 min and yields quantitatively the product **2a** [ν(C=O) at 1688 cm^{-1} and δ(^{31}P) at 22.9 ppm] along with $ISnBu_3$ and $PhC{\equiv}CC_6H_4CF_3$-4. No side-product or intermediate of the type [Pd(C≡CPh)($C_6H_4CF_3$-4)(P–N)] is observed during the course of the reaction, indicating that also in this case the reductive elimination is faster than the transmetalation step.

The complexes [PdI($C_6H_4CF_3$-4)(P–N)] were then reacted with an excess of $PhC{\equiv}CSnBu_3$ (Pd/Sn 1 : 11 molar ratio) without any added olefin. For **1b**, a fast reaction took place, followed by precipitation of a red–brown solid which prevented any spectroscopic analysis of the mixture. For **2b**, the reaction was somewhat slower but no precipitation was observed. After completion (*ca.* 70 min), two products were formed in a ratio of 3.2 : 1. The major product is characterized by the following NMR spectral data: a δ(N=CH) doublet at 8.45 ppm [J(PH) 2.7 Hz], a $\delta(CHMe_2)$ septet at 4.77 ppm, a δ(^{31}P) singlet at 33.2 ppm, and a δ(^{119}Sn) doublet at −7.8 ppm [J(PSn) 25 Hz]. For the minor product, the corresponding NMR signals consist of a δ(N=CH) doublet at 8.33 ppm [J(PH) 3.2 Hz], a $\delta(CHMe_2)$ septet at 5.32 ppm, a δ(^{31}P) singlet at 39.5 ppm, and a δ(^{119}Sn) doublet at 35.5 ppm [J(PSn) 123 Hz]. The ^{119}Sn NMR spectrum shows also a singlet at 79.5 ppm due to $ISnBu_3$. The observed NMR spectral data are very close to those reported for the labile derivatives [Pd(C≡CPh)($SnBu_3$)(P–N)] and [PdI($SnBu_3$)-(P–N)] [P–N = 2-(PPh_2)C_6H_4-1-CH=NC_2H_4Ph], obtained in solution from the oxidative addition of $PhC{\equiv}CSnBu_3$ and $ISnBu_3$, respectively, to a palladium(0) species generated *in situ* by reacting the mixture [PdCl(η^3-C_3H_5)]$_2$/P–N (1 : 2 molar ratio) with $NaCH(CO_2Me)_2$.[13] Accordingly, the major product is formulated as complex **2d** and the minor one as complex **2e**, which originate from the corresponding reactions of Pd(P–N) formed in the reductive elimination of the transmetalated intermediate [Pd(C≡CPh)($C_6H_4CF_3$-4)(P–N)] (P–N = **2**). Furthermore, the absorption at 2088 cm^{-1} in the IR spectrum of the reaction mixture is assigned to a C≡C stretching vibration of **2d** as it falls in the range typical of the ν(C≡C) bands for alkynylpalladium(II) complexes.[19] The complexes **2d** and **2e** are in equilibrium with each other as indicated by the dependence of the **2d/2e** molar ratio on the relative concentration of $PhC{\equiv}CSnBu_3$ and $ISnBu_3$. The equilibrium shifts in favour of **2d** when the concentration of $PhC{\equiv}CSnBu_3$ is increased: upon addition of five equivalents of $PhC{\equiv}CSnBu_3$ to the equilibrium mixture resulting from the reaction of **2b** with $PhC{\equiv}CSnBu_3$ (1 : 11), the molar ratio **2d/2e** changes from 3.2 : 1 to 5.0 : 1. Conversely, the equilibrium shifts in favour of **2e** when the concentration of $ISnBu_3$ is increased: upon addition of four equivalents of $ISnBu_3$ to the equilibrium mixture resulting from the reaction of **2b** with $PhC{\equiv}CSnBu_3$ (1 : 11), the molar ratio **2d/2e** changes from 3.2 : 1 to 0.16 : 1. When dimethyl fumarate is added to the reaction mixtures (Pd/dmfu = 1 : 1.5), both products **2d** and **2e** disappear with concomitant formation of the complex **2a**.[20] These results indicate that a complex equilibrium system is present in the above mixtures which shifts completely towards the more stable palladium(0) derivative **2a** upon addition of dmfu, in agreement with the observed lack of reaction of **1a** or **2a** with $ISnBu_3$ in the presence of an excess of $PhC{\equiv}CSnBu_3$.

Reactions in the presence of added iminophosphine

Like the analogous derivatives [Pd(η^2-fn)(P–N)],[15] the complexes **1a**, **2a** react with one equivalent of iminophosphine according to eqn. (3):



(3)

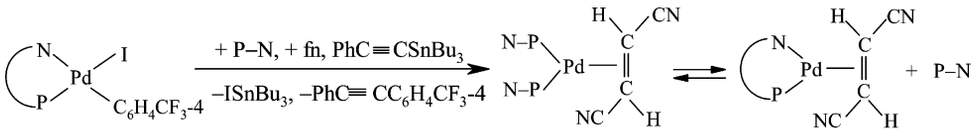
(**1f**: P–N = **1**; **2f**: P–N = **2**)

Although being slow (on the NMR time scale) and much shifted to the right (>95%), such an equilibrium prevents the isolation of **1f** and **2f** as pure compounds. However, these products can be conveniently characterized in solution by spectroscopic methods (see Experimental). Both complexes contain two P-monodentate iminophosphines as indicated by the close proximity of the imino proton signals to those of the free ligands [δ(N=CH) at 9.19 ppm in **1f** and at 9.32 ppm in **1**; δ(N=CH) at 9.34 ppm in **2f** and at 9.02 ppm in **2**], and an η^2-bound olefin as indicated by the low-frequency shift of 35–40 cm^{-1} (relative to free dmfu) for the ν(C=O) bands and by the considerable shielding of 2.8–3.0 ppm (relative to free dmfu) for the olefin protons, which are detected as an AA′ multiplet of an AA′XX′ spin system.

Oxidative additions and olefin substitutions. These reactions are carried out on complexes **1f** and **2f** prepared in solution [eqn. (3)] and are summarized in Scheme 6.

The oxidative addition of 4-(trifluoromethyl)iodobenzene to **1f** or **2f** occurs at higher rates than the corresponding reaction with **1a** or **2a** (Scheme 4). For an initial Pd/$IC_6H_4CF_3$-4 molar ratio of 1 : 10, the completion times are of *ca.* 20 min for **1f** and of *ca.* 50 min for **2f**. The reaction with **2f** yields the product **2b** along with the free iminophosphine **2**, whereas the reaction with **1f** yields an equilibrium mixture of **1g**, **1b** and the free iminophosphine **1**. The same equilibrium mixture can be obtained from the reaction of **1b** with one equivalent of the ligand **1**.

The complex **1g** was characterized in solution as containing two *trans* P-monodentate iminophosphine ligands from its NMR data: δ(^{31}P) as a rather broad singlet at 19.6 ppm and δ(N=CH) as a rather broad signal at 9.15 ppm (*cf.* the corresponding proton resonance at 9.32 ppm in the free ligand **1** and at 8.52 ppm in the complex **1b** where the iminophosphine is P,N-chelate to the central metal). The broadness of the NMR signals of **1g**, as compared to the sharpness of the related signals of **1b** and **1** in the equilibrium mixture, indicates that the



(**1h**: P–N = **1**; **2h**: P–N = **2**)

Scheme 7

equilibrium is slow on the NMR time scale, and that the complex **1g** has some fluxional behaviour in solution. It is to be noted that a similar equilibrium does not occur for complex **2b** under comparable experimental conditions, in agreement with the better ligating properties of the imino nitrogen carrying the electron-donating isopropyl substituent.

In the ^{31}P NMR spectra of the reaction mixtures, however, a weak singlet in the range 28.5–29.5 ppm is detected, which is assigned to a small amount of the phosphonium salt $[PPh_2(C_6H_4CF_3\text{-}4)(C_6H_4\text{-}2\text{-}CH{=}NR)]I$ formed in the reaction of $IC_6H_4CF_3$-4 with P–N and/or in the interaction of $[PdI(C_6H_4CF_3\text{-}4)(P–N)]$ with P–N.[21]

As in the case of complexes **1a** and **2a**, the η^2-bound dmfu in **1f** and **2f** is not displaced by alkynes such as $PhC{\equiv}CSnBu_3$ or $PhC{\equiv}CC_6H_4CF_3$-4. On the other hand, the lack of oxidative addition with $PhC{\equiv}CSnBu_3$ rules out the catalytic cycle of Scheme 2 for the cross-coupling reaction 2 when the systems $[Pd(\eta^2\text{-dmfu})(P–N)]$/P–N are used as catalysts.[16]

No reaction is observed to occur between **1f** or **2f** and $ISnBu_3$ if an excess of $PhC{\equiv}CSnBu_3$ is present (**1f** or **2f**/$ISnBu_3$/$PhC{\equiv}CSnBu_3$ molar ratio of 1 : 5 : 10) even though the complexes **1f** and **2f** react with $ISnBu_3$ at higher rates than **1a** and **2a**, yielding a mixture of unidentified products. It is likely that also in this case the initial oxidative addition of $ISnBu_3$ is followed by extensive decomposition which prevents the characterization of the products.

Transmetalation and reductive elimination. The complexes $[PdI(C_6H_4CF_3\text{-}4)(P–N)]$ (**1b** or **2b**) in the presence of 1 equivalent of the corresponding iminophosphine P–N (**1** or **2**) and 1.5 equivalents of fumaronitrile react with a ten-fold excess of $PhC{\equiv}CSnBu_3$ as shown in Scheme 7.

In addition to $ISnBu_3$ and $PhC{\equiv}CC_6H_4CF_3$-4, the products consist of an equilibrium mixture of the complexes $[Pd(\eta^2\text{-fn})(P–N)_2]$, $[Pd(\eta^2\text{-fn})(P–N)]$ and of the free ligand P–N. For P–N = **1**, the equilibrium is rather fast (on the ^{1}H NMR time scale) and almost completely shifted towards the product **1h**, as previously reported.[15] Thus, in thf-d_8 at 25 °C, the imino proton and the olefin protons resonate as broad signals at 9.0 and 3.0 ppm, respectively, while in the ^{31}P NMR spectrum only a singlet at 20.8 ppm is observed, no signals due to **1c** and **1** being detected. For P–N = **2**, the equilibrium is also rather fast (on the NMR time scale) but it involves comparable amounts of the three species **2h**, **2c** and **2**. In the ^{1}H NMR spectrum at 25 °C, broad resonances are present at 9.1 ppm for the imino protons, at 3.6 ppm for the isopropyl $CHMe_2$ protons, and at 2,9 ppm for the olefin protons, whereas, in the ^{31}P NMR spectrum, three broad singlets appear at 22.3 ppm (**2c**), 19.5 ppm (**2h**) and −11.9 ppm (**2**). At lower temperatures, however, the equilibrium shifts toward the left in favour of the complex **2h**.[22]

During the course of the reactions, the ^{31}P NMR spectra show also the presence of a weak singlet in the range 28.5–29.5 ppm (assigned to the phosphonium salt $[PPh_2(C_6H_4CF_3\text{-}4)(C_6H_4\text{-}2\text{-}CH{=}NR)]I$),[21] the intensity of which remains practically constant throughout, but give no evidence for transmetalated intermediates. This result indicates that also in the presence of added iminophosphine the initial transmetalation step is followed by a much faster reductive elimination to yield the palladium(0) products. The completion times are of *ca.* 30 min for **1b/1** and of *ca.* 75 min for **2b/2**. If compared with the corresponding reactions with **1b** and **2b** in the absence of added iminophosphine, one can see that the overall rate decreases for the **1b/1** system, whereas it remains almost unchanged for **2b/2**. Such a retarding effect is to be related to the occurrence of the equilibrium with the species **1g** in the initial mixture **1b/1** (1 : 1), as confirmed by the fact that when the reaction is carried out with a **1b/1** molar ratio of 1 : 2, other things being equal, the completion time increases to 40 min.

Table 1 Cross-coupling of iodobenzene with tributyl(phenylethynyl)tin: catalytic data at 50 °C[a]

Run	Catalyst	Conversion (%) at different times			
		1 h	2 h	4 h	24 h
1	**1a**	50	65	84	94
2	**2a**	31	50	59	82
3	**1a/1**[b]	89	91	95	99
4	**2a/2**[b]	46	72	79	90

[a] Solvent: thf (5 cm^3); PhI (1.35 mmol); $PhC{\equiv}CSnBu_3$ (1.35 mmol); palladium complex (0.0065 mmol); substrate/Pd = 200/1 (mol/mol). [b] Palladium complex/ligand = 1/1 (mol/mol).

Catalytic reactions

Two sets of catalytic experiments have been examined. In the first set, the reaction 2 was carried out with a catalytic amount (5%) of the palladium complex at 25 °C in thf (or thf-d_8). The reaction progress was monitored by IR spectroscopy. ^{31}P NMR spectra of the reaction mixtures were also run at different times in order to identify the palladium complexes involved in the rate-determining steps. In the second set, the cross-coupling of iodobenzene with $PhC{\equiv}CSnBu_3$ was carried out with a catalytic amount (0.5%) of the palladium complex at 50 °C in thf. The reaction progress was monitored by GLC analysis of the mixture at different times. The results of the latter experiments are listed in Table 1.

Cross-coupling reactions catalyzed by $[Pd(\eta^2\text{-dmfu})(P–N)]$. The rate of reaction 2 catalyzed by **1a** or **2a** depends markedly on the imino nitrogen substituent in the order R = C_6H_4OMe-4 > $CHMe_2$ as indicated by the different times required to reach a 50% conversion: 115 min for **1a** and 510 min for **2a**. The greater catalytic efficiency of **1a** is also evident from a comparison of the runs 1 and 2 in Table 1. On the basis of the reactivity results reported above, a catalytic cycle is proposed in which the initial oxidative addition of the aryl iodide to $[Pd(\eta^2\text{-dmfu})(P–N)]$ is the rate-determining step, as it is followed by a faster transmetalation of $[PdI(C_6H_4CF_3\text{-}4)(P–N)]$ and by an even faster reductive elimination of the transmetalated intermediate to yield the coupling product and regenerate the starting palladium(0) complex. This is confirmed by the spectral data of the reaction mixture. When reaction 2 is catalyzed by **2a**, the ^{31}P NMR spectra show that only complex **2a** is present in the mixture up to 50% conversion (Fig. 1b). When reaction 2 is catalyzed by **1a**, complex **1a** is the predominant species in the mixture up to 50% conversion (Fig. 1a) as it is accompanied by

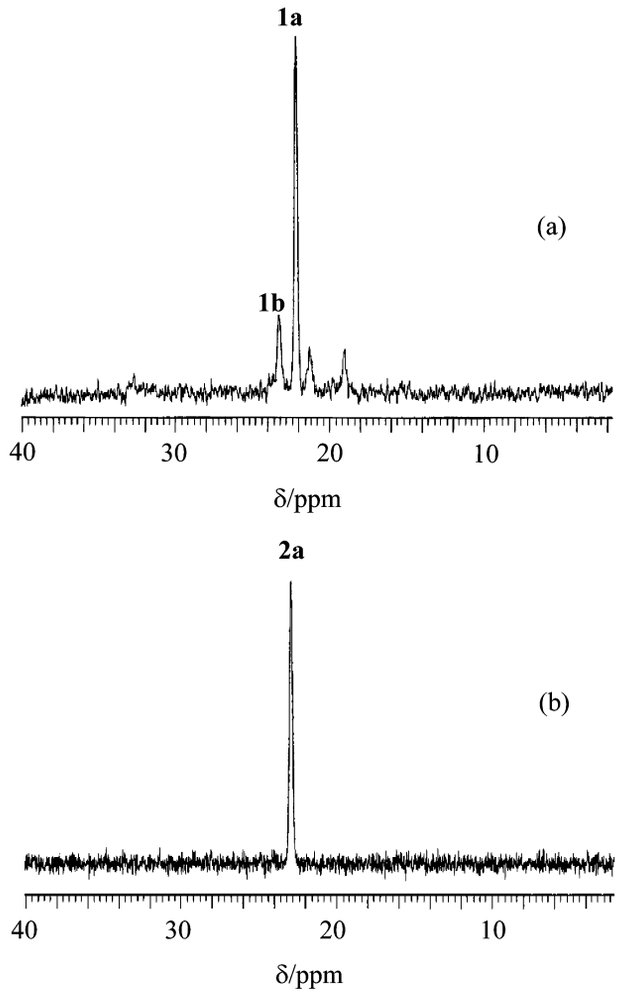


Fig. 1 ^{31}P NMR spectra of the reaction mixture (at *ca.* 40% conversion) of the coupling of $IC_6H_4CF_3$-4 with $PhC{\equiv}CSnBu_3$ in thf: (a) in the presence of complex **1a**; (b) in the presence of complex **2a**.

a small amount of **1b** and trace amounts of decomposition products.

Consistently, a weak ν(C=O) band of the free dmfu at 1726 cm^{-1} is detected in the IR spectra along with a strong ν(C=O) band of **1a** at 1687 cm^{-1}. The presence of **1b** is due to the fact that its transmetalation with $PhC{\equiv}CSnBu_3$ is not exceedingly faster than the oxidative addition of $IC_6H_4CF_3$-4 to **1a** (see the completion times for these reactions reported above).

The rate-determining oxidative addition accounts for the different catalytic activity of the complexes **1a** and **2a**, the oxidative addition of $IC_6H_4CF_3$-4 to **1a** being much faster than that to **2a**, and also for the solvent effect observed in the cross-coupling of iodobenzene with $PhC{\equiv}CSnBu_3$ catalyzed by **1a**.[16] The increasing rate in solvents of increasing polarity can be related to an increased rate of the oxidative addition step, as reported by Farina for similar reactions with $[Pd(AsPh_3)_4]$.[4f]

Cross-coupling reactions catalyzed by [Pd(η²-dmfu)(P–N)]/P–N (1 : 1 molar ratio). With the systems **1a/1** or **2a/2** the reaction 2 proceeds at a faster rate than with the complexes **1a** or **2a** alone. Also in this case, the rate depends on the imino nitrogen substituent (R = C_6H_4OMe-4 > $CHMe_2$). For **1a/1**, a 50% conversion is reached after 75 min from the mixing of the reactants, whereas for **2a/2** the time required is 290 min. The catalytic cycle proposed for the systems **1a/1** and **2a/2** is analogous to that proposed for the reaction 2 catalyzed by **1a** and **2a** (see the Results and discussion). In the case of the systems [Pd(η²-dmfu)(P–N)]/P–N, however, the oxidative addition of $IC_6H_4CF_3$-4 to [Pd η²-dmfu)$(P–N)_2$] and the transmetalation step involving the mixture [PdI($C_6H_4CF_3$-4)(P–N)]/P–N (1 : 1 molar ratio) occur at comparable rates, as suggested by the comparable completion times. As a matter of fact, in the ^{31}P NMR spectra of the reaction mixture with the catalytic system **2a/2** (up to 50% conversion) comparable amounts of the complex **2b** (24.1 ppm), **2f** (19.7 ppm) and of the free ligand **2** (−11.9 ppm) are detected, while in those with the catalytic system **1a/1** a small amount of the complex **1g** is also detected at 19.6 ppm (Fig. 2). In both cases, the ^{31}P NMR spectra show also the presence of a singlet in the range 28.5–29.5 ppm, assigned to the phosphonium salt [PPh_2($C_6H_4CF_3$-4)(C_6H_4-2-CH=NR)]I.[21]

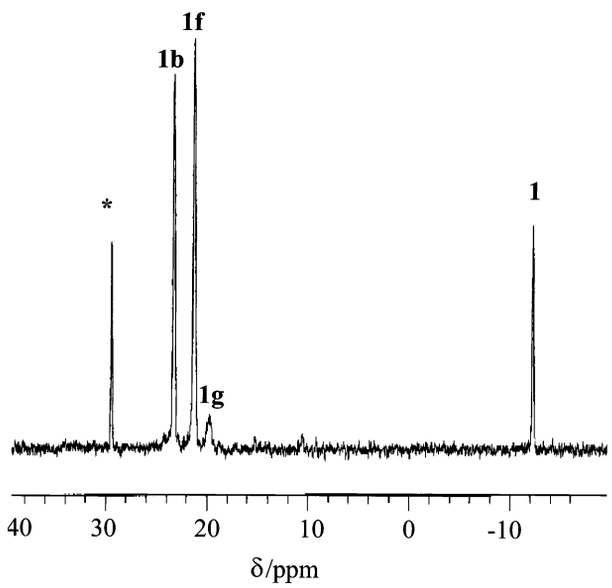


Fig. 2 ^{31}P NMR spectra of the reaction mixture (at *ca.* 30% conversion) of the coupling of $IC_6H_4CF_3$-4 with $PhC{\equiv}CSnBu_3$ in thf in the presence of the system **1a/1** (1 : 1 molar ratio). * signal assigned to the phosphonium salt [PPh_2($C_6H_4CF_3$-4)(C_6H_4-2-CH=$NC_6H_4OCH_3$-4]I.

Consistently, in the IR spectra a substantial amount of the free dmfu (liberated in the oxidative addition step leading to [PdI($C_6H_4CF_3$-4)(P–N)]) is present together with the complex [Pd(η²-dmfu)$(P–N)_2$]. Thus, the higher catalytic activity of the system **1a/1** results from the fact that both the oxidative addition and transmetalation steps are faster in **1a/1** than in **2a/2**.

The greater catalytic efficiency of the systems **1a/1** and **2a/2** compared to that of **1a** and **2a**, respectively, and the increasing reaction rate on going from **2a/2** to **1a/1** are also observed in the cross-coupling of iodobenzene with $PhC{\equiv}CSnBu_3$ at 50 °C (runs 3 and 4 of Table 1).

Conclusion

From the observed reactivity and catalytic data it can be concluded that the cross-coupling of aryl iodides with alkynyl stannanes in the presence of the zerovalent derivatives [Pd(η²-dmfu)(P–N)] or [Pd(η²-dmfu)$(P–N)_2$] proceeds through a catalytic cycle where the initial oxidative addition of the aryl iodide to the palladium(0) complex is followed by transmetalation of the product and by fast reductive elimination to regenerate the palladium(0) species. The increasing catalytic activity on going from [Pd(η²-dmfu)(P–N)] to [Pd(η²-dmfu)$(P–N)_2$] is due to the increasing rate of the oxidative addition step, which is rate-determining for [Pd(η²-dmfu)(P–N)]. For [Pd(η²-dmfu)$(P–N)_2$] the oxidative addition and the transmetalation steps proceed at comparable rates. The greater catalytic efficiency of the complexes with P–N = **1** (R = C_6H_4OMe-4) compared to that of the corresponding complexes

with P–N = **2** (R = $CHMe_2$) results from the fact that both the oxidative addition and transmetalation steps are faster for P–N = **1** than for P–N = **2**. A detailed kinetic investigation of these reactions is now in progress.

The prolonged catalytic activity of [Pd(η^2-dmfu)(P–N)] and [Pd(η^2-dmfu)(P–N)$_2$] can be explained by the lack of reaction of these zerovalent complexes with $ISnBu_3$ in the presence of $PhC{\equiv}CSnBu_3$.

Experimental

General

^{1}H, ^{31}P and ^{119}Sn NMR spectra were recorded on a Bruker AM400 spectrometer operating at 400.13, 161.98 and 149.21 MHz, respectively. Chemical shifts are reported in ppm downfield from $SiMe_4$ for ^{1}H, from H_3PO_4 as external standard for ^{31}P, and from $SnMe_4$ as external standard for ^{119}Sn. The spectra were recorded at 25 °C except when noted. IR spectra were carried out using a Perkin-Elmer 983G spectrophotometer. All the reactions and catalytic experiments were carried out under N_2. The solvent thf was distilled from sodium benzophenone. The compounds $PhC{\equiv}CSnBu_3$, $ISnBu_3$, dimethyl fumarate and fumaronitrile are commercially available and were used without further purification. The aryl iodides $IC_6H_4CF_3$-4 and PhI were distilled at reduced pressure before use. The iminophosphine **1** and the complexes **1a** and **1c** were prepared as reported in the literature.[15] The alkyne $PhC{\equiv}CC_6H_4CF_3$-4 was prepared by a published method.[13]

Synthesis of *N*-(2-(diphenylphosphino)benzylidene)(isopropyl)-amine (2). The 2-(diphenylphosphino)benzaldehyde[23] (4.35 g, 15 mmol) and isopropylamine (2.22 g, 37.5 mmol) were dissolved in 160 cm^3 of the solvent mixture $MeOH/CH_2Cl_2$ (3 : 1 v/v). When the condensation was complete (3 h at room temperature), the reaction mixture was worked up as described for the preparation of **1** [15] to give the product as a pale-yellow microcrystalline solid (4.13 g, 83%); found: C 79.92, H 6.60, N 4.26% – $C_{22}H_{22}NP$ requires C 79.73, H 6.69, N 4.23%; ν_{max}/cm^{-1} (C=N) 1629s (thf); δ_H (thf-d_8) 9.01 (1 H, d, ^4J(PH) 4.8 Hz, N=CH), 3.52 (1 H, spt, ^3J(HH) 6.3 Hz, $CHMe_2$), 1.20 (6 H, d, ^3J(HH) 6.3 Hz, CH_3); δ_P (thf-d_8) −11.9 (s).

Synthesis of [Pd(η^2-ol)(P–N)] [ol = dmfu (2a), fn (2c)]. The complexes **2a** and **2c** were prepared from the reaction of [Pd(η^3-C_3H_5)(P–N)]BF_4 (P–N = **2**, 1 mmol) with a moderate excess of diethylamine (0.266 g, 2.5 mmol) in the presence of the appropriate olefin (1.2 mmol) as described in the literature for related compounds.[15]

*Complex **2a*** (0.471 g, 81%): found: C 57.50, H 5.10, N 2.42% – $C_{28}H_{30}NO_4PPd$ requires C 57.79, H 5.20, N 2.41%; ν_{max}/cm^{-1} (C=O) 1688s, (C=N) 1622mw (thf); δ_H (thf-d_8) 8.57 (1 H, d, ^4J(PH) 3.4 Hz, N=CH), 4.18 (1 H, dd, ^3J(HH) 9.9 Hz, ^3J(PH) 2.7 Hz, olefin CH *trans* to N), 3.86–3.78 (overlapping signals, 2 H, dd, ^3J(HH) = ^3J(PH) 10.0 Hz; olefin CH *trans* to P, and spt, ^3J(HH) 6.5 Hz; $CHMe_2$), 3.65 (3 H, s, OCH_3), 3.24 (3 H, s, OCH_3), 1.46 (3 H, d, ^3J(HH) 6.5 Hz, CH_3), 1.44 (3 H, d, ^3J(HH) 6.5 Hz, CH_3); δ_P (thf-d_8) 22.9 (s).

*Complex **2c*** (0.480 g, 93%): found: C 60.62, H 4.75, N 8.10% – $C_{26}H_{24}N_3PPd$ requires C 60.53, H 4.70, N 8.15%; ν_{max}/cm^{-1} (C≡N) 2197s, (C=N) 1623m (Nujol); δ_H (thf-d_8) 8.66 (1 H, d, ^4J(PH) 3.3 Hz, N=CH), 3.88 (1 H, spt, ^3J(HH) 6.4 Hz, $CHMe_2$), 3.33 (1 H, dd, ^3J(HH) 9.5 Hz, ^3J(PH) 3.4 Hz, olefin CH *trans* to N), 2.90 (1 H, dd, ^3J(HH) = ^3J(PH) 9.6 Hz, olefin CH *trans* to P), 1.50 (3 H, d, ^3J(HH) 6.4 Hz, CH_3), 1.47 (3 H, d, ^3J(HH) 6.4 Hz, CH_3); δ_P (thf-d_8) 22.3 (s).

Synthesis of [PdI($C_6H_4CF_3$–4)(P–N)] (1b, 2b). The complex **1a** (0.646 g, 1 mmol) or **2a** (0.582 g, 1 mmol) and the aryl iodide $IC_6H_4CF_3$-4 (0.410 g, 1.5 mmol) were dissolved in toluene (80 cm^3). The mixture was heated at 70 °C (40 min for **1a**, or 90 min for **2a**). The solvent was then removed at reduced pressure, and the solid residue was exctracted with CH_2Cl_2 (2 × 20 cm^3). The solution was filtered and evaporated to about 3 cm^3. Upon addition of Et_2O, the product precipitated as a yellow (**1b**) or pale-yellow (**2b**) solid. Both compounds were further purified by recrystallization from CH_2Cl_2/Et_2O.

*Complex **1b*** (0.580 g, 75%): found: C 51.45, H 3.33, N 1.80% – $C_{33}H_{26}F_3INOPPd$ requires C 51.22, H 3.39, N 1.81%; ν_{max}/cm^{-1} (C=N) 1612mw (Nujol); δ_H (thf-d_8) 8.49 (1 H, d, ^4J(PH) 2.2 Hz, N=CH), 7.06–7.00 (2 H, m, *m*-H of C_6H_4OMe-4), 6.94–6.88 (2 H, m, *m*-H of $C_6H_4CF_3$-4), 3.95 (3 H, s, OCH_3); δ_P (thf-d_8) 23.2 (s).

*Complex **2b*** (0.504 g, 71%): found: C 49.30, H 3.60, N 2.00% – $C_{29}H_{26}F_3INPPd$ requires C 49.07, 3.69, N 1.97%; ν_{max}/cm^{-1} (C=N) 1620m (Nujol); δ_H (thf-d_8) 8.45 (1 H, s, N=CH), 6.95–6.89 (2 H, m, *m*-H of $C_6H_4CF_3$-4), 5.75 (1 H, spt, ^3J(HH) 6.6 Hz, $CHMe_2$), 1.36 (6 H, d, ^3J(HH) 6.6 Hz, CH_3); δ_P (thf-d_8) 24.1 (s).

Reactions of [PdI($C_6H_4CF_3$-4)(P–N)] (2b) with $PhC{\equiv}CSnBu_3$. *In the presence of fn.* For IR measurements, the stannane $PhC{\equiv}CSnBu_3$ (0.35 ml, 1 mmol) was added to a solution of **2b** (71.0 mg, 0.1 mmol) and fn (11.7 mg, 0.15 mmol) in thf (5 ml), in a round-bottom flask thermostatted at 25 °C. The progress of the reaction was monitored by IR spectra of the mixture at different times in the range 2400–2000 cm^{-1}, following the increase in intensity of the ν(C≡N) band of **2c** at 2195 cm^{-1}. For ^{31}P and ^{119}Sn NMR measurements, $PhC{\equiv}CSnBu_3$ (0.14 ml, 0.4 mmol) was added to a solution of **2b** (28.4 mg, 0.04 mmol) and fn (4.7 mg, 0.06 mmol) in 2 ml of a mixture of thf/thf-d_8 (3 : 1 v/v). The progress of the reaction was monitored by ^{31}P NMR spectra of the solution at different times, following the increase in intensity of the **2c** singlet at 22.3 ppm and the concomitant decrease in intensity of the **2b** singlet at 24.1 ppm. No other signal was detected during the course of the reaction. When the reaction was complete, the ^{119}Sn NMR spectrum showed a signal at 79.5 ppm due to $ISnBu_3$.

In the presence of dmfu. The reactions were carried out under the same experimental conditions as above, using dmfu (21.6 mg, 0.15 mmol, for IR measurements and 8.6 mg, 0.06 mmol, for ^{31}P NMR measurements). The reaction progress was monitored by IR spectra at different times in the range 2300–1600 cm^{-1}, following the increase in intensity of the ν(C=O) band of **2a** at 1688 cm^{-1} and of the ν(C≡C) band of $PhC{\equiv}CC_6H_4CF_3$-4 at 2220 cm^{-1}. The ^{31}P NMR spectra at different times showed the presence of only a singlet of increasing intensity at 22.9 ppm (**2a**) and a singlet of decreasing intensity at 24.1 ppm (**2b**).

In the absence of olefin. For IR measurements, the reaction was carried out under similar experimental conditions as described above, by adding $PhC{\equiv}CSnBu_3$ (0.385 ml, 1.1 mmol) to the solution of **2b** (71.0 mg, 0.1 mmol). For ^{31}P and ^{119}Sn NMR measurements, the stannane (58 μl, 0.165 mmol) was added to a solution of **2b** (10.6 mg, 0.015 mmol) in thf-d_8 (0.75 ml). In the IR spectra, we observed a weak band of increasing intensity at 2220 cm^{-1} [ν(C≡C) of $PhC{\equiv}CC_6H_4CF_3$-4] and a medium–weak band at 2088 cm^{-1} assigned to a ν(C≡C) vibration of **2d**, the intensity of which initially increased and then slowly decreased to a constant value. In the ^{31}P NMR spectra, only a singlet at 33.2 ppm (**2d**) and a singlet at 39.5 ppm (**2e**) were detected, along with a singlet at 24.1 ppm (**2b**) which decreased progressively in intensity and eventually disappeared. After completion (*ca.* 70 min), the ^{119}Sn NMR spectrum showed a singlet at 79.5 ppm ($ISnBu_3$), a doublet at − 7.8 ppm (**2d**) and a doublet at 35.5 ppm (**2e**). When the reactions were complete, addition of dmfu (21.6 mg, 0.15 mmol, to the IR solution and 3.3 mg, 0.023 mmol, to the ^{31}P NMR solution) caused the disappearance of the **2d** and **2e** signals and the concomitant appearance of the characteristic signals of **2a** [ν(C=O) at 1688 cm^{-1} and δ(^{31}P) at 22.9 ppm]. For ^{1}H NMR

measurements, $PhC{\equiv}CSnBu_3$ (77 μl, 0.22 mmol) was added to a solution of **2b** (14.2 mg, 0.02 mmol) in thf-d_8 (0.5 ml). After completion of the reaction, the **2d/2e** molar ratio was estimated by integration of the $CHMe_2$ septets at 4.77 ppm (**2d**) and at 5.32 ppm (**2e**).

Synthesis and characterization of [Pd(η²-dmfu)(P–N)₂] (1f, 2f) in solution. The complexes **1f** or **2f** are formed almost quantitatively in the reaction of [Pd(η²-dmfu)(P–N)] (**1a** or **2a**) with 1 equivalent of P–N (**1** or **2**) in thf. For NMR measurements, the complex **1a** (11.6 mg, 0.018 mmol) or **2a** (10.5 mg, 0.018 mmol) and the ligand **1** (7.1 mg, 0.018 mmol) or **2** (6.0 mg, 0.018 mmol) were dissolved in thf-d_8 (0.6 cm^3). For IR measurements, the complex **1a** (12.9 mg, 0.02 mmol) or **2a** (11.6 mg, 0.02 mmol) and the ligand **1** (7.9 mg, 0.02 mmol) or **2** (6.6 mg, 0.02 mmol) were dissolved in thf (1 cm^3).

Complex **1f**: ν_{max}/cm^{-1} (C=O) 1690s, (C=N) 1614mw; δ_H 9.19 (2 H, d, ^4J(PH) 3.0 Hz, N=CH), 4.21 (2 H, m, olefin CH), 3.90 (6 H, s, OCH_3); δ_P 21.3 (s).

Complex **2f**: ν_{max}/cm^{-1} (C=O) 1687s, (C=N) 1629m; δ_H 9.34 (2 H, d, ^4J(PH) Hz, N=CH), 3.98 (2 H, m, olefin CH), 3.51 (2 H, spt, ^3J(HH) 6.2 Hz, $CHMe_2$), 1.29 (6 H, d, ^3J(HH) 6.2 Hz, CH_3), 0.95 (6 H, d, ^3J(HH) 6.2 Hz, CH_3); δ_P 19.7 (s).

Catalytic experiments

Reaction 2 was carried out at 25 °C in thf under nitrogen, with a palladium complex concentration of 1×10^{-2} mol dm^{-3} and with an initial complex/$IC_6H_4CF_3$-4/$PhC{\equiv}CSnBu_3$ molar ratio of 1 : 20 : 20. The reaction progress was monitored by IR spectroscopy (in the absorbance mode), following the increasing intensity of the ν(C≡C) band of $PhC{\equiv}CC_6H_4CF_3$-4 at 2220 cm^{-1} and the concomitant decreasing intensity of the ν(C≡C) band of $PhC{\equiv}CSnBu_3$ at 2134 cm^{-1}, the conversion at different times being estimated from calibration curves. The details of reaction 2 catalyzed by **1a** are reported as an example. The reactants, $IC_6H_4CF_3$-4 (0.151 cm^3, 1.0 mmol) and $PhC{\equiv}CSnBu_3$ (0.370 cm^3, 1.0 mmol), and the complex **1a** (32.3 mg, 0.05 mmol) were dissolved in thf (5 cm^3) under nitrogen in a two-necked round-bottom flask, which was kept in a thermostat at 25 °C. Samples of the reaction mixture were taken at different times for IR spectra.

The cross-coupling of iodobenzene with $PhC{\equiv}CSnBu_3$ was carried out in a jacketed glass reactor equipped with a reflux condenser, a side arm with stopcock for freeze–thaw cycles and with a threaded side port with rubber septum and cap for syringe sampling. The details for run 1 of Table 1 are reported as an example. The reactor was charged under argon with thf (5 cm^3), $PhC{\equiv}CSnBu_3$ (0.510 g, 1.3 mmol), iodobenzene (0.270 g, 1.3 mmol) and the complex **1a** (4.2 mg, 6.5×10^{-3} mmol). The reactor was then heated at 50 °C by circulating a thermostatic fluid through the outer jacket. Samples of the reaction mixture were taken at different times, cooled to room temperature and analysed by GLC to determine substrate conversion and product yield.

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References and notes

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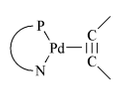
20 Alternatively, the products of the reaction of **2b** with an excess of $PhC{\equiv}CSnBu_3$ may be formulated either as an equilibrium mixture of the two isomers [Pd(η²-$PhC{\equiv}CSnBu_3$)(P–N)], resulting from different orientations of the asymmetric alkyne relative to the P–N ligand in an essentially planar structure of the type:



or as an equilibrium mixture of one isomer [Pd(η²-$PhC{\equiv}CSnBu_3$)-(P–N)] with the oxidative addition derivative **2d**. In both cases, the formation of **2a** upon addition of dmfu would occur by displacement of the coordinated alkyne. These equilibria, however, appear to be hardly influenced by the concentrations of $PhC{\equiv}CSnBu_3$ or $ISnBu_3$. On the other hand, the IR spectra of the reaction mixture show no absorption attributable to a ν(C≡C) vibration of the η²-bound alkyne in the range 2000–1700 cm^{-1}. For structural and IR data of palladium(0) complexes with η²-bound alkynes, see: P. M. Maitlis, P. Espinet and M. J. H. Russell, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 6, ch. 38.5.2, pp. 353–356.

21 A weak singlet in the range 28.5–29.5 ppm appears also in the ^{31}P NMR spectra of the mixtures **1** or **2**/$IC_6H_4CF_3$-4 (1 : 20 molar ratio) in thf-d_8 after 2–3 h at 25 °C. On the other hand, formation of phosphonium salts has been reported to occur in palladium-catalyzed reaction involving oxidative addition of aryl halides to palladium(0)–phosphine complexes, see: C. B. Ziegler, Jr and R. F. Heck, *J. Org. Chem.*, 1978, **43**, 2941–2946. A convenient preparation of tetraarylphosphonium iodides is based on the reaction of ArI with PAr_3 catalyzed by $[Pd(PPh_3)_4]$ or $Pd(OAc)_2$, see: T. Migita, T. Nagai, K. Kiughi and M. Kosugi, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 2869–2870 . However, any attempt to isolate the salt $[PPh_2(C_6H_4CF_3\text{-}4)(C_6H_4\text{-}2\text{-}CH{=}NR)]I$ from the reaction of $IC_6H_4CF_3$-4 with an equimolar amount of P–N, in the presence of a catalytic amount (1%) of [Pd(η^2-dmfu)(P–N)] or [PdI($C_6H_4CF_3$-4)-(P–N)], was unsuccessful even though for the reaction in refluxing thf the ^{31}P NMR spectra at different times showed a singlet of increasing intensity in the range 28.5–29.5 ppm.

22 At −35 °C, the equilibrium of Scheme 7 is almost completely shifted towards the complex **2h**, characterized by the following ^{1}H NMR spectrum: δ_H (thf-d_8) 9.13 (2 H, s, N=CH), 3.44 (2 H, spt, ^3J(HH) 5.8 Hz, $CHMe_2$), 2.94 (2 H, m, olefin CH), 1.25 (6 H, d, ^3J(HH) 5.8 Hz, CH_3), 1.00 (6 H, d, ^3J(HH) 5.8 Hz, CH_3).

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