

Kinetic Studies of the Oxidative Addition and Transmetallation Steps Involved in the Cross-Coupling of Alkynyl Stannanes with Aryl Iodides Catalysed by η^2 -(Dimethyl fumarate)(iminophosphane)palladium(0) Complexes

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The complexes $[\text{Pd}(\eta^2\text{-dmfu})(\text{P-N})]$ {dmfu = dimethyl fumarate; P-N = 2-(PPh₂)C₆H₄-1-CH=NR, R = C₆H₄OMe-4 (**1a**), CHMe₂ (**2a**), C₆H₃Me₂-2,6 (**3a**), C₆H₃(CHMe₂)₂-2,6 (**4a**)} undergo dynamic processes in solution which consist of a P-N ligand site exchange through initial rupture of the Pd-N bond at lower energy and an olefin dissociation-association at higher energy. According to equilibrium constant values for olefin replacement, the complex $[\text{Pd}(\eta^2\text{-fn})(\text{P-N})]$ (fn = fumaronitrile, **1b**) has a greater thermodynamic stability than its dmfu analogue **1a**. The kinetics of the oxidative addition of ArI (Ar = C₆H₄CF₃-4) to **1a** and **2a** lead to the products $[\text{PdI}(\text{Ar})(\text{P-N})]$ (**1c**, **2c**) and obey the rate law, $k_{\text{obs}} = k_{1\text{A}} + k_{2\text{A}}[\text{ArI}]$. The $k_{1\text{A}}$ step involves oxidative addition to a reactive species $[\text{Pd}(\text{solvent})(\text{P-N})]$ formed from dmfu dissociation. The $k_{2\text{A}}$ step is better interpreted in terms of oxidative addition to a species $[\text{Pd}(\eta^2\text{-dmfu})(\text{solvent})(\kappa^1\text{-P-N})]$ formed in a pre-equilibrium step from Pd-N bond breaking. The

complexes **1c** and **2c** react with PhC≡CSnBu₃ in the presence of an activated olefin (ol = dmfu, fn) to yield the palladium(0) derivatives $[\text{Pd}(\eta^2\text{-ol})(\text{P-N})]$ along with ISnBu₃ and PhC≡CAr. The kinetics of the transmetallation step, which is rate-determining for the overall reaction, obey the rate law: $k_{\text{obs}} = k_{2\text{T}}[\text{PhC}\equiv\text{CSnBu}_3]$. The $k_{2\text{T}}$ values are markedly enhanced in more polar solvents such as CH₃CN and DMF. The solvent effect and the activation parameters suggest an associative S_E2 mechanism with substantial charge separation in the transition state. The kinetic data of the above reactions in various solvents indicate that, for the cross-coupling of PhC≡CSnBu₃ with ArI catalysed by **1a** or **2a**, the rate-determining step is represented by the oxidative addition and that CH₃CN is the solvent in which the highest rates are observed.

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Introduction

The cross-coupling of organo-stannanes with carbon electrophiles catalysed by palladium complexes (Stille reaction) is a powerful synthetic method in organic chemistry.^[1] The generally accepted catalytic cycle involves an initial oxidative addition of the organic electrophile to a palladium(0) species followed by transmetallation, *trans*-to-*cis* isomerisation if *trans*-diorganopalladium(II) intermediates are formed, and eventually reductive elimination of the coupled product.^[1,2] As shown in previous studies,^[3] for the complexity of the reactions involved the mechanism of the process can be variously affected by the nature of the ligand, the solvent, the reacting stannane and organic electrophile, and by the presence of additives such as LiCl or the free

ligand. In fact, the rate-determining step of the cycle can either be the oxidative addition or the transmetallation or even the reductive elimination.^[1c,2,4]

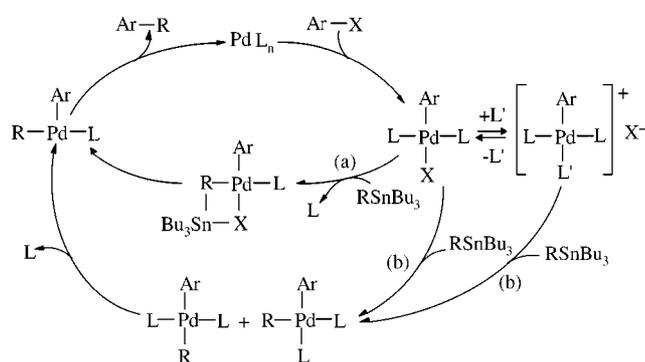
The mechanism described in Scheme 1 for the coupling of ArX (Ar = pentahalophenyl; X = halide, triflate) with RSnBu₃ (R = vinyl) has been recently proposed.^[5]

In this mechanism, two transmetallation pathways may be present without any prior dissociation (or solvent displacement) of the ligand L in the intermediates *trans*- $[\text{PdXArL}_2]$. The associative S_E2 cyclic step (a) is favoured in weakly coordinating solvents of low polarity when X is a good bridging ligand such as a halide. It leads to a highly reactive *cis* species which undergoes an immediate reductive elimination and is strongly retarded by the presence of the free ligand L. The associative S_E2 open step (b) is favoured when L' is a ligand or a polar coordinating solvent both of which lack bridging capability and when X is a good-leaving and poorly coordinating anionic ligand without bridging ability.

In contrast, the transmetallation of $[\{\eta^5\text{-(1-Ph}_2\text{P)(2,4-Ph}_2\text{)C}_5\text{H}_2\}(\text{CO})_3\text{MoPdI(PPh}_3)]$ by PhC≡CSnBu₃, leading to $[\{\eta^5\text{-(1-Ph}_2\text{P)(2,4-Ph}_2\text{)C}_5\text{H}_2\}(\text{CO})_3\text{MoPd(C}\equiv\text{CPh)-}$

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(L = PPh₃, AsPh₃; L' = ligand or solvent)

Scheme 1. Catalytic cycle for the cross-coupling reaction with palladium complexes containing monodentate ligands L

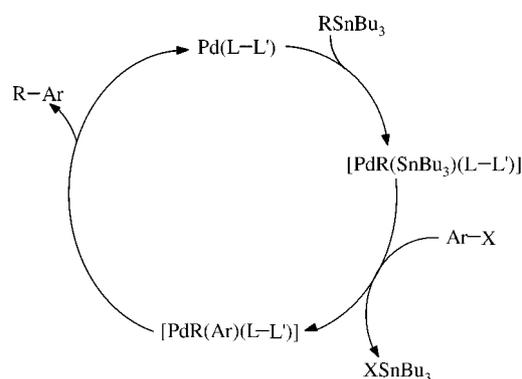
(PPh₃) in dimethylformamide (DMF), was reported to proceed through a reactive species [$\{\eta^5\text{-}(1\text{-Ph}_2\text{P})(2,4\text{-Ph}_2)\text{C}_5\text{H}_2\}(\text{CO})_3\text{MoPdI}(\text{DMF})\}$], formed in a displacement equilibrium of the ligand PPh₃ by the solvent when a low initial concentration of the starting complex was used.^[6]

On the other hand, the complex *trans*-[PdIPh(AsPh₃)₂] was also found to be in equilibrium with the species [PdIPh(solvent)(AsPh₃)₂] (solvent = DMF) upon release of AsPh₃ in dimethylformamide,^[7] in agreement with previous kinetic studies.^{[1b][3e]} In a recent report, however, the concentration of [PdXR(solvent)(AsPh₃)₂] (X = Cl, I; R = Ph, C₆Cl₂F₃) was found to be negligible in the presence of free arsane, indicating that under catalytic conditions the predominant transmetalation step involves the associative reaction of the stannane with the complex [PdXR(AsPh₃)₂].^[8]

In the coupling of pentahaloaryl triflates (ArX) with CH₂=CHSnBu₃ catalysed by [PdXAr(dppe)] [dppe = 1,2-bis(diphenylphosphanyl)ethane] the main intermediates, [PdAr(CH=CH₂)(dppe)] and [Pd($\eta^2\text{-CH}_2\text{=CHAr}$)(dppe)], have been spectroscopically detected and characterised.^[9]

The system [PdCl($\eta^3\text{-C}_3\text{H}_5$)₂/L-L'] (1:2 molar ratio) {L-L' = 2-(PPh₂)C₆H₄-1-CH=NC₂H₄Ph}, was found to have a high catalytic efficiency in the coupling of 4-(trifluoromethyl)iodobenzene with PhC≡CSnBu₃.^[10] From the detection of the labile complexes [PdI(SnBu₃)(L-L')] and [Pd(C≡CPh)(SnBu₃)(L-L')] in the ³¹P NMR spectra of the reaction mixture, an alternative catalytic cycle was proposed involving the initial oxidative addition of PhC≡CSnBu₃ to an in situ generated palladium(0) species, Pd(L-L') (Scheme 2).

The zero-valent complexes [Pd($\eta^2\text{-dmfu}$)(P-N)] {dmfu = dimethyl fumarate; P-N = 2-(PPh₂)C₆H₄-1-CH=NR, R = alkyl and aryl group},^[11] are quite active catalysts (or catalyst precursors) in the coupling of organostannanes with aryl halides.^[12] The catalytic efficiency is retained for a prolonged period of time and increases considerably on going from alkyl to aryl *N*-substituents, and also in the presence of the free iminophosphane for a P-N/



[L-L' = 2-(PPh₂)C₆H₄-1-CH=NC₂H₄Ph]

Scheme 2. Alternative catalytic cycle for the cross-coupling reaction with the system [PdCl($\eta^3\text{-C}_3\text{H}_5$)₂/L-L'] (1:2 molar ratio)

[Pd($\eta^2\text{-dmfu}$)(P-N)] molar ratio ≥ 1 . In a mechanistic investigation based mainly on IR and NMR spectroscopic data,^[13] we have reported that the cross-coupling of PhC≡CSnBu₃ with IC₆H₄CF₃-4 proceeds through the classical cycle involving initial oxidative addition of the aryl iodide to [Pd($\eta^2\text{-dmfu}$)(P-N)] {P-N = 2-(PPh₂)C₆H₄-1-CH=NR, R = C₆H₄OMe-4, CHMe₂}, or [Pd($\eta^2\text{-dmfu}$)(P-N)₂] formed from the reaction of [Pd($\eta^2\text{-dmfu}$)(P-N)] with one equivalent of the iminophosphane P-N, followed by *trans*-metalation of the product [PdI(C₆H₄CF₃-4)(P-N)] and by fast reductive elimination of the alkyne PhC≡CC₆H₄CF₃-4 to regenerate the starting palladium(0) compound. With [Pd($\eta^2\text{-dmfu}$)(P-N)] as the catalyst, the oxidative addition is the rate-determining step, while for [Pd($\eta^2\text{-dmfu}$)(P-N)₂] the oxidative addition and transmetalation steps proceed at comparable rates.

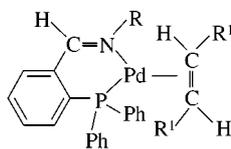
We report herein the results of a kinetic investigation of the oxidative addition of IC₆H₄CF₃-4 to [Pd($\eta^2\text{-dmfu}$)(P-N)] and the transmetalation of [PdI(C₆H₄CF₃-4)(P-N)] by PhC≡CSnBu₃. The studies have been carried out using UV/Vis spectroscopic techniques in order to get a better understanding of the mechanism and of the factors which affect these fundamental steps of the catalytic cycle.

Results and Discussion

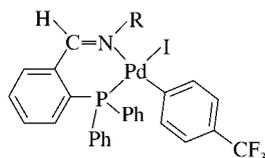
The structures of the palladium complexes used in the kinetic study are shown in Scheme 3.

According to the X-ray structural analyses of the iminophosphane derivatives [Pd($\eta^2\text{-fn}$)(P-N)] (fn = fumaronitrile, **1b**)^[14] and [PdI(Ph)(P-N)] {P-N = 2-(PPh₂)C₆H₄-1-CH=NR; R = Me, Et},^[15] the olefin carbons are almost coplanar with the N-Pd-P coordination plane for the palladium(0) complexes, while in the palladium(II) complexes the iodide ligand is *trans* to the phosphorus atom.

In order to clarify the intimate mechanism governing the cross-coupling reaction between IC₆H₄CF₃-4 and PhC≡CSnBu₃ catalysed by the complexes **1a** and **2a**,^[12,13]



	1a	1b	2a	2b	3a	4a	5b
R	C ₆ H ₄ OMe-4	C ₆ H ₄ OMe-4	CHMe ₂	CHMe ₂	C ₆ H ₃ Me ₂ -2,6	C ₆ H ₃ (CHMe ₂) ₂ -2,6	bornyl
R'	CO ₂ Me	CN	CO ₂ Me	CN	CO ₂ Me	CO ₂ Me	CN



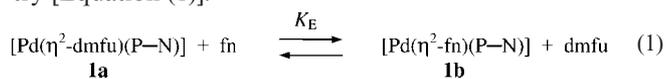
	1c	2c
R	C ₆ H ₄ OMe-4	CHMe ₂

Scheme 3. Structures of the (iminophosphane)palladium complexes [bornyl = *endo*-(1*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]

we have chosen to break the problem down into separate studies, i.e. the oxidative addition and the transmetalation/reductive elimination reactions. Preliminary studies on the relative stability of the palladium(0) olefin complexes **1a** and **1b**, and on the solution behaviour of the palladium(0) and the palladium(II) complexes of Scheme 3 have been also carried out.

Relative Stability of Palladium(0) Olefin Complexes from Olefin Exchange Equilibria

Previous results on the oxidative addition of IC₆H₄CF₃-4 to [Pd(η²-ol)(P-N)] (ol = dmfu, fn) involved in the catalytic cycle of the cross-coupling reaction^[12,13] have shown that only the dmfu complexes display appreciable reactivity. Thus, we have tried to attribute this feature to a lower thermodynamic stability of such species with respect to their fn analogues by studying the equilibrium 1 of olefin exchange in THF and CHCl₃ by UV/Vis spectrophotometry [Equation (1)].



The resultant K_E values of 8520 ± 300 in CHCl₃ and 640 ± 20 in THF indicate that the position of equilibrium is strongly shifted to the right. The much greater stability of complex **1b** is largely due to the greater π -accepting properties of fumaronitrile which increase the strength of the palladium-olefin bond as already observed for the olefin exchange equilibria in similar zero-valent complexes [Pd(η²-ol)(L-L')] {L-L' = 2-(iminomethyl)pyridine^[16] or 2-(methylthio)pyridine^[17]}. A reduced electron density on the metal in **1b** will render the complex less susceptible to oxi-

dative addition by the organic halide, thereby explaining its lack of reactivity.

The equilibrium constant in CHCl₃ is one-order of magnitude higher than in THF. We have confirmed the observed solvent effect by comparing the corresponding K_E values for the 2-(iminomethyl)pyridine complex [Pd(η²-dmfu)(C₅H₄N-2-CH=NC₆H₄OMe-4)]. In THF, a value of 731 ± 32 was obtained whereas in CHCl₃ a value of 4000 ± 400 was previously determined.^[16] We surmise that such an effect predominantly stems from a different stabilisation, by solvation, of the olefins in the two solvents examined even though they have comparable dielectric constants.

Solution Behaviour of the Palladium(0) and Palladium(II) Complexes

It is known that palladium(0) olefin complexes with *P,N*-chelating ligands undergo various dynamic processes in solution such as olefin rotation around its bond axis to the central metal, olefin dissociation, Pd-N bond rupture and exchange between the free and coordinated olefin.^[11,18] The dissociative processes lead to unsaturated (or solvent-coordinated) species which may be of importance in the mechanism of the oxidative addition.^[19] For instance, olefin dissociation leads to a species of the type Pd(P-N), which can be generated in situ also from the reaction of a mixture of [PdCl(η³-C₃H₅)₂]/L-L' (1:2 molar ratio) {L-L' = 2-(PPh₂)C₆H₄-1-CH=NC₂H₄Ph} with NaCH(CO₂Me)₂.^[10] Such a species undergoes oxidative addition with PhC≡CSnBu₃ or IC₆H₄CF₃-4 to give the products [Pd(C≡CPh)(SnBu₃)(P-N)] or [PdI(SnBu₃)(P-N)]. We have therefore examined the ¹H NMR spectra of the complexes **1a** and **2a** at 25 °C in CDCl₃ and [D₈]toluene and at variable-temperatures in [D₈]toluene (Table 1).

As can be seen, the signals of the imino proton appear at lower frequencies ($\delta = 0.6\text{--}0.7$ ppm) in the aromatic solvent whereas those of the olefin protons appear at higher frequencies ($\delta = 0.4\text{--}0.7$ ppm) relative to the corresponding signals in CDCl₃. The proton resonances of **1a** are fairly sharp in CD₃Cl but broader in [D₈]toluene indicating the occurrence of dynamic processes at increasing rates in the latter solvent. At higher temperatures in [D₈]toluene, the olefin H_{cis} and H_{trans} resonances ($\Delta\nu = 260$ Hz) coalesce at 56 °C, from which a ΔG^\ddagger value of $63.4 \text{ kJ}\cdot\text{mol}^{-1}$ can be evaluated.^[20] The olefin methyl signals also coalesce at ca. 35 °C but in this case, however, a more precise measurement of the coalescence temperature was prevented by overlapping with the iminophosphane OCH₃ singlet (at $\delta = 3.31$ ppm in the spectrum at 25 °C). The ¹H NMR spectra of **2a** at 25 °C are characterised by sharp olefin signals in the solvents examined. Upon heating the [D₈]toluene solution, the H_{cis} and H_{trans} signals ($\Delta\nu = 129$ Hz) coalesce at 75 °C ($\Delta G^\ddagger = 69.3 \text{ kJ}\cdot\text{mol}^{-1}$). At approximately the same temperature the olefin methyl resonances are also in coalescence but overlap largely with the CHMe₂ septet (at $\delta = 3.22$ ppm in the spectrum at 25 °C) of the iminophosphane. It is interesting to point out that the isopropyl Me groups remain diastereotopic at the various temperatures exam-

Table 1. Selected ^1H NMR spectroscopic data of the palladium complexes

Complex	Solvent	Iminophosphane protons ^[a]		CH ₃	Olefin protons ^[a]		CH ₃
		N=CH	N-CH		CH _{cis} ^[b]	CH _{trans} ^[c]	
1a	[D ₈]toluene	7.54 d [2.8]		3.31 s	4.85 br. s	4.20 br. s	3.30 br. s, 3.20 br. s
	CDCl ₃ ^[11]	8.11 d [4.0]		3.81 s	4.23 d (9.9)	3.55 dd (9.9)[9.9]	3.32 s, 3.14 s
2a	[D ₈]toluene	7.54 d [3.6]	3.22 spt (6.4)	1.31 d, 1.28 d (6.4) (6.4)	4.65 dd (10.0) [2.8]	4.32 dd (10.0) [10.0]	3.52 s, 3.12 s
	CDCl ₃	8.24 [3.2]	3.65 spt ^[d]	1.30 d, 1.29 d (6.3) (6.3)	4.13 dd (10.4) [2.4]	3.88 dd (10.4) [10.4]	3.65 s, 3.14 s
3a	[D ₈]toluene	7.42 d [3.0]		2.14 s, 1.91 s	4.82 dd (10.2) [2.6]	3.94 dd (10.4) [10.4]	3.23 s, 3.17 s
	CDCl ₃	8.06 d [3.2]		2.16 s, 1.90 s	4.24 dd (10.0) [2.4]	3.37 dd (10.2) [10.2]	3.18 s
4a	[D ₈]toluene	7.73 d [3.2]		1.45 d, 1.19 d, (6.8) (6.8) 0.92 d, 0.59 d (6.8) (6.8)	4.82 dd (10.0) [3.0]	4.05 dd (10.0) [10.0]	3.15 s, 2.97 s
	CDCl ₃	8.06 d [2.1]		1.45 d, 1.09 d, (6.8) (6.8) 0.98 d, 0.56 d (6.8) (6.8)	4.25 dd (10.4) [2.5]	3.49 dd (10.4) [10.4]	3.24 s, 2.93 s
5b ^[e]	[D ₈]toluene	7.92 s	3.63 m	0.92 s, 0.72 s, 0.21 s	3.16 dd (9.5) [3.8]	2.82 dd (9.5) [9.5]	
5b ^[f]	[D ₈]toluene	8.12 s	4.41 m	mk	mk	2.66 dd (9.7) [9.7]	
1c	CD ₃ CN	8.31 s		3.80 s			
2c	[D ₈]toluene	7.54 s	5.93 spt (6.8)	1.05 d (6.8)			

^[a] At 25 °C. Coupling constants $J_{\text{H,H}}$ in round brackets, $J_{\text{P,H}}$ in square brackets. br = broad, mk = masked. ^[b] *cis* to phosphorus. ^[c] *trans* to phosphorus. ^[d] Overlapping with the olefin CH₃ signal. ^[e] Major diastereoisomer, see text. ^[f] Minor diastereoisomer.

ined. Even at 75 °C, they are detected as two sharp doublets at $\delta = 1.27$ and 1.24 ppm, respectively.

The fluxional behaviour of complexes **1a** and **2a** may be explained either by olefin rotation, by olefin dissociation-association or by P–N ligand site exchange through initial rupture of the Pd–N bond. In order to ascertain which is the actual process operating in solution, we have examined the variable-temperature ^1H NMR spectra of the complexes **3a** and **4a** which contain *N*-aryl substituents with increasing steric requirements, as well as those of complex **5b** which contains a chiral iminophosphane ligand. We have also compared the olefin ^{13}C NMR signals of **1a** and **2a** with those of **3a** and **4a** (Table 2).

The ^1H NMR spectrum of **5b** at 25 °C shows the presence of two diastereoisomers in a molar ratio of 6.0:1. The olefin H_{cis} and H_{trans} signals of the major diastereoisomer ($\Delta\nu = 138$ Hz) coalesce at 73 °C ($\Delta G^\ddagger = 68.7$ kJ·mol⁻¹). At this temperature, the other resonances of the two dia-

stereoisomers are distinct and sharp, although the molar ratio between the major and minor isomer decreases to 3.6:1. These findings indicate that the observed dynamic process does not involve olefin dissociation-association (which would cause interconversion of the diastereoisomers and eventually coalescence of their signals). However, the olefin dissociation-association process does occur at a lower rate (on the NMR time-scale) as indicated by the change in the isomer molar ratio when the temperature is increased.

The ^1H NMR spectra of **3a** and **4a** at 25 °C are characterised by the non-equivalence of the 2,6 groups on the *N*-aryl moieties: for **3a**, two singlets can be detected for the protons of the 2,6-Me groups (the singlet at $\delta = 2.14$ ppm partially overlapping with the solvent signals) whereas for **4a**, four doublets can be detected for the Me protons and two septets (at $\delta = 3.38$ and 2.83 ppm, respectively) for the CH protons of the 2,6-CHMe₂ groups. This is clearly a consequence of the asymmetric nature of the complexes and

Table 2. Selected ^{13}C NMR spectroscopic data of the palladium(0) complexes

Complex	Iminophosphane carbons ^[a]		CH_3	Olefin carbons ^[a]		CH_3	$\text{HC}=\text{CH}$
	$\text{N}=\text{CH}$	$\text{N}-\text{C}$		$\text{C}=\text{O}$			
1a ^[11]	164.6	148.7	55.5	173.8, 173.5		50.4–50.0 ^[b]	50.4–50.0 ^[b]
2a	161.8	137.5	23.4, 22.1	174.2, 174.0		50.4, 50.3	48.2 ^[c] , 48.0 d ^[d] (32)
3a	167.3	151.9	18.6, 18.1	173.8, 173.3		50.6	50.2 ^[c] , 49.6 d ^[d] (30)
4a	166.9	150.5	24.2, 23.1, 22.6, 22.0	174.0, 172.6		50.5, 50.4	50.3 ^[c] , 49.8 d ^[d] (31)

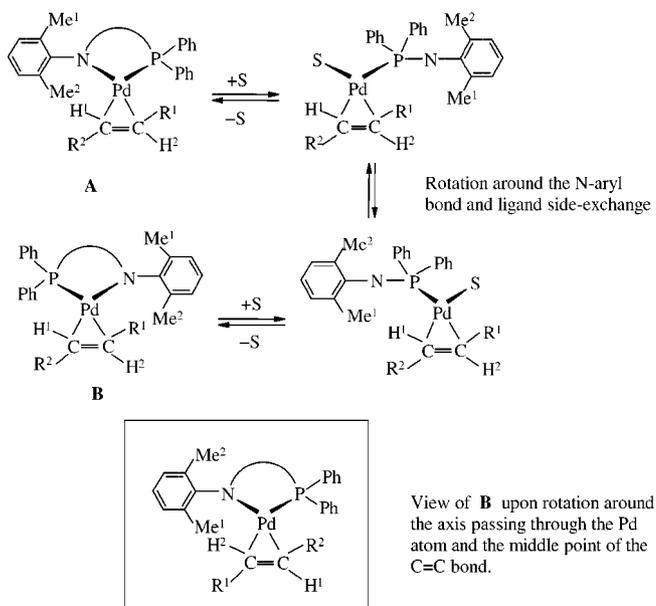
^[a] In CDCl_3 at 25 °C. Coupling constants $J_{\text{P,H}}$ in round brackets. ^[b] Overlapping signals. ^[c] *cis* to phosphorus. ^[d] *trans* to phosphorus.

of the restricted rotation around the N–aryl bond. When the $[\text{D}_8]$ toluene solution of **4a** is warmed up, all the olefin and the CHMe_2 signals progressively broaden but at 95 °C (the highest temperature explored) only the coalescence of the olefin methyl signals ($\Delta\nu = 70$ Hz) can be observed ($\Delta G^\ddagger = 75.3$ kJ·mol⁻¹). In contrast, for the solution of **3a**, the olefin methyl signals ($\Delta\nu = 23$ Hz) coalesce at 53 °C ($\Delta G^\ddagger = 69.4$ kJ·mol⁻¹), the methyl signals of the $N\text{-C}_6\text{H}_3\text{Me}_2\text{-2,6}$ substituent ($\Delta\nu = 91$ Hz) coalesce at 72 °C ($\Delta G^\ddagger = 69.7$ kJ·mol⁻¹) and eventually the olefin H_{cis} and H_{trans} signals ($\Delta\nu = 351$ Hz) coalesce at 93 °C ($\Delta G^\ddagger = 70.0$ kJ·mol⁻¹). The close values of the activation free energies indicate that the same dynamic process is operating which interconverts simultaneously the two olefin methyl groups, the two methyl groups of the $N\text{-C}_6\text{H}_3\text{Me}_2\text{-2,6}$ substituent and the olefin H_{cis} and H_{trans} protons. Such a process cannot be the olefin rotation because it would lead to interconversion of only the olefin protons. The dynamic behaviour of **3a**, as well as that of the other complexes examined, is better rationalised by a process involving an initial solvent-assisted rupture of the Pd–N bond, followed by rotation around the N–aryl bond in the *P*-monodentate iminophosphane and ligand site exchange, as depicted in Scheme 4.

As can be seen by comparing structure **A** and the (rotated) structure **B**, this process brings about the simultaneous interconversions $\text{R}^1 \rightleftharpoons \text{R}^2$, $\text{Me}^1 \rightleftharpoons \text{Me}^2$, and $\text{H}^1 \rightleftharpoons \text{H}^2$.

It is worth noting that the same mechanism applied to complex **2a** leads to the observed interconversions $\text{R}^1 \rightleftharpoons \text{R}^2$ and $\text{H}^1 \rightleftharpoons \text{H}^2$, but not to $\text{Me}^1 \rightleftharpoons \text{Me}^2$ because the Me groups of the $N\text{-CHMe}_2$ substituent cannot interconvert by a simple rotation around the N–C bond in the *P*-monodentate iminophosphane. For such an interconversion, an inversion of configuration at the $N\text{-C}_{\text{isopropyl}}$ carbon atom would also be required.

According to this mechanism, the decreasing rate of the dynamic process in the complexes with *N*-aryl groups (**1a** > **3a** > **4a**) can be explained by the increasing steric hindrance exerted by the 2,6-substituents on the *N*-aryl group towards the incoming solvent molecule. Inspection of the ^{13}C NMR spectroscopic data in Table 2 shows that the olefin C=C carbons have comparable electron density in the complexes



Scheme 4. Proposed mechanism for the dynamic behaviour of complex **3a** ($\text{R}^1 = \text{R}^2 = \text{CO}_2\text{Me}$; S = solvent)

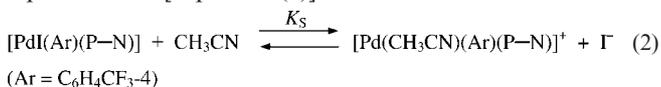
1a, **3a**, and **4a** since they resonate in the narrow range of 50.4–49.6 ppm. In other words, this means that the extent of π back-donation in the Pd– η^2 -dmfu bond and the electron donor properties of the P–N ligands (in essence, their bond strengths to the central metal) are comparable in this closely related series of complexes.

The different rate of the dynamic process observed for the complexes **1a** and **2a** (**1a** > **2a**) is essentially due to electronic factors since the $N\text{-C}_6\text{H}_4\text{OMe-4}$ and $N\text{-CHMe}_2$ groupings of the P–N ligands have similar steric requirements. From the data in Table 2 it appears that the olefin C=C carbons of **2a** are shielded by ca. 2 ppm relative to the corresponding carbons of **1a**, indicating a certain increase of π back-donation in the Pd– η^2 -dmfu bond. This is clearly related to the electron-releasing isopropyl group which increases the σ donor properties of the imino nitrogen and, therefore, the strength of the Pd–N bond in **2a**. The imino ligands have been found to act more as σ -donors than as π -acceptors to palladium.^[21] Conversely, the for-

mally zero-valent complexes $[\text{Pd}(\eta^2\text{-ol})(\text{N}-\text{N}')]]$ (ol = activated olefin, $\text{N}-\text{N}' = \alpha$ -diimine) and $[\text{Pd}(\eta^2\text{-ol})(\text{P}-\text{N})]$ are better described as Pd^{II} -cyclopropane complexes on the basis of spectroscopic and crystallographic data.^[11,14,21]

The ^1H spectra of **1c** (in CD_3CN) and **2c** (in $[\text{D}_8]\text{toluene}$) at 25 °C show that these palladium(II) complexes exist as single geometrical isomers in solution. No isomerisation or other dynamic process was observed in the variable-temperature ^1H NMR spectra of **2c** in $[\text{D}_8]\text{toluene}$ in the range 25–90 °C.

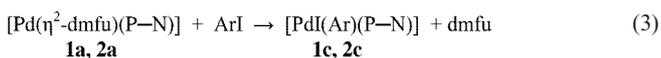
As suggested by electrical conductivity measurements in acetonitrile, the complexes **1c** and **2c** undergo the solvolytic equilibrium 2 [Equation (2)].



The cationic complexes $[\text{Pd}(\text{CH}_3\text{CN})(\text{Ar})(\text{P}-\text{N})]^+$ have been isolated as BF_4^- or CF_3SO_3^- salts upon addition of AgBF_4 or AgCF_3SO_3 to the solution (see Exp. Sect.). The equilibrium constants K_S were determined by conductivity and checked by UV/Vis experiments at 25 °C (see Exp. Sect.). From the measured values [$K_S = (6.9 \pm 0.9) \times 10^{-6}$ for **1c**; $K_S = (2.1 \pm 0.5) \times 10^{-5}$ for **2c**] it appears that more than 20% and 35% of the cationic species $[\text{Pd}(\text{CH}_3\text{CN})(\text{Ar})\{2\text{-}(\text{PPh}_2)\text{C}_6\text{H}_4\text{-1-CH=NC}_6\text{H}_4\text{OMe-4}\}]^+$ and $[\text{Pd}(\text{CH}_3\text{CN})(\text{Ar})\{2\text{-}(\text{PPh}_2)\text{C}_6\text{H}_4\text{-1-CH=NCHMe}_2\}]^+$, respectively, are present in acetonitrile solution at 25 °C under kinetic conditions ($[\mathbf{1c}]_0$ and $[\mathbf{2c}]_0 = 1 \cdot 10^{-4}$ M). Conductivity measurements in other solvents (CHCl_3 , THF, toluene, DMF) suggest that only in CH_3CN does the solvolytic equilibrium (2) take place.

Oxidative Addition Reactions

The oxidative addition of $\text{IC}_6\text{H}_4\text{CF}_3$ -4 (ArI) to the complexes **1a** or **2a** proceeds according to Equation (3).



The progress of the reaction was monitored by ^1H and ^{31}P NMR spectroscopy at 25 °C in various solvents (CDCl_3 , $[\text{D}_8]\text{THF}$, $[\text{D}_7]\text{DMF}$, and CD_3CN) using **1a** or **2a**/ArI molar ratios in the range of 1:5–1:10. The spectra at different times showed the presence of the reactants and products of Equation (3). No signal attributable to intermediates or side-products was detected. Under the same experimental conditions, no reaction was observed to occur between the fumaronitrile derivative **1b** and ArI.

For kinetic measurements, the oxidative addition to **1a** was monitored in different solvents and at different temperatures (in the range 15–45 °C) in the presence of an excess of ArI ($[\text{ArI}] \geq 10 \times [\mathbf{1a}]_0$). The rate of any single reaction obeys the mono-exponential law:

$$D_t = D_\infty + (D_0 - D_\infty) \exp(-k_{\text{obs}} t)$$

where D_t , D_0 , and D_∞ represent the absorbance of the system at time t , at time $t = 0$ and at the end of the reaction respectively, and k_{obs} is the pseudo-first-order rate constant.

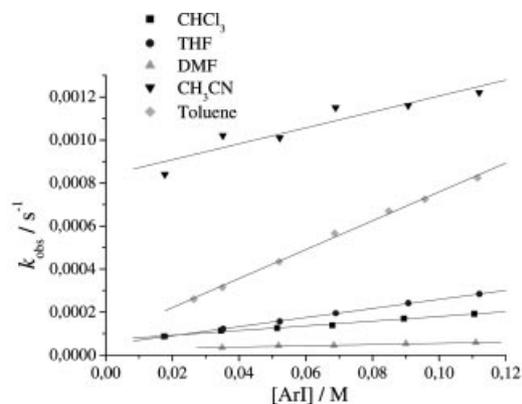


Figure 1. Plots of k_{obs} versus the aryl iodide concentration for the oxidative addition of ArI to complex **1a** in different solvents at 25 °C in the presence of dmfu ($[\mathbf{1a}]_0 = 1 \cdot 10^{-4}$ M; $[\text{dmfu}] = 3 \cdot 10^{-3}$ M)

The ensuing k_{obs} values display a linear dependence on $[\text{ArI}]$ in any solvent. As can be seen in Figure 1, a concentration independent (k_{1A}) and a concentration dependent (k_{2A}) path can always be detected so that the observed rate constants are represented by the following relationship:

$$k_{\text{obs}} = k_{1A} + k_{2A}[\text{ArI}]$$

The values of k_{1A} and k_{2A} in the solvents examined are reported in Table 3.

Table 3. Kinetic constants for the oxidative addition of ArI to **1a** in different solvents at 25 °C in the presence of dmfu ($[\mathbf{1a}]_0 = 1 \cdot 10^{-4}$ M; $[\text{dmfu}] = 3 \cdot 10^{-3}$ M)

Solvent	k_{1A}/s^{-1}	$k_{2A}/\text{M}^{-1}\text{s}^{-1}$
DMF	$(2.6 \pm 0.2) \times 10^{-5}$	$(2.9 \pm 0.3) \times 10^{-4}$
THF	$(4.81 \pm 0.12) \times 10^{-5}$	$(2.11 \pm 0.02) \times 10^{-3}$
CHCl_3	$(7.1 \pm 0.4) \times 10^{-5}$	$(1.09 \pm 0.06) \times 10^{-3}$
Toluene	$(8.7 \pm 1.1) \times 10^{-5}$	$(6.7 \pm 0.2) \times 10^{-3}$
CH_3CN	$(8.3 \pm 0.5) \times 10^{-4}$	$(3.8 \pm 0.7) \times 10^{-3}$

The lowest k_{1A} and k_{2A} values were observed in DMF, while the highest k_{1A} value was observed in CH_3CN and the highest k_{2A} value in toluene. Such a reactivity clearly does not depend on the difference in dielectric constants, indicating that the transition states for both steps do not involve a substantial separation of electric charge. Furthermore, a radical mechanism can be ruled out since no diiodo derivative, which represents a typical by-product in the radical reactions, could be detected.

The kinetic constants were not appreciably influenced by different concentrations of free dmfu, as reported in Table 4.

From the kinetic data at different temperatures (Table 5), the activation parameters were determined using a re-parameterised Eyring equation.^[22]

The negative activation entropies for the k_{1A} step suggest an essentially associative process. Negative ΔS^\ddagger values were also obtained for the k_{2A} step, but these data should be regarded with caution (see further discussion).

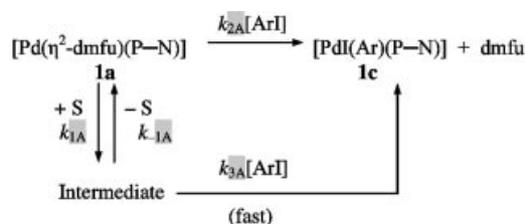
Table 4. Kinetic constants for the oxidative addition of ArI to **1a** in CHCl₃ at 25 °C in the presence of variable concentrations of added dmfu (**1a**)₀ = 1·10⁻⁴ M)

[dmfu]/M	k _{1A} /s ⁻¹	k _{2A} /M ⁻¹ s ⁻¹
0	(5.4±0.3)×10 ⁻⁵	(1.24±0.05)×10 ⁻³
1·10 ⁻³	(5.9±0.1)×10 ⁻⁵	(1.20±0.02)×10 ⁻³
3·10 ⁻³	(7.1±0.4)×10 ⁻⁵	(1.09±0.06)×10 ⁻³
5·10 ⁻³	(7.4±0.2)×10 ⁻⁵	(1.08±0.04)×10 ⁻³

Table 5. Kinetic constants and activation parameters (ΔH[‡]/kJ·mol⁻¹; ΔS[‡]/J·mol⁻¹K⁻¹) for the oxidative addition of ArI to **1a** at variable temperature in different solvents in the presence of dmfu (**1a**)₀ = 1·10⁻⁴ M; [dmfu] = 3·10⁻³ M)

Solvent	T / °C	k _{1A} /s ⁻¹	k _{2A} /M ⁻¹ s ⁻¹
CH ₃ CN	15	(3.0±0.1) × 10 ⁻⁴	(9±1) × 10 ⁻⁴
	25	(8.3±0.5) × 10 ⁻⁴	(3.8±0.7) × 10 ⁻³
	35	(2.34±0.04) × 10 ⁻³	(4.8±0.5) × 10 ⁻³
	45	(5.2±0.2) × 10 ⁻³	(1.6±0.4) × 10 ⁻²
			ΔH [‡] = 71±21 ΔS [‡] = -63±8
Toluene	15	(5.2±0.4) × 10 ⁻⁵	(2.26±0.05) × 10 ⁻³
	25	(1.57±0.04) × 10 ⁻⁴	(5.97±0.05) × 10 ⁻³
	35	(8.3±0.8) × 10 ⁻⁴	(1.06±0.09) × 10 ⁻²
	45	(1.39±0.03) × 10 ⁻³	(3.87±0.17) × 10 ⁻²
			ΔH [‡] = 83±11 ΔS [‡] = -38±4

On the basis of the above experimental data, the following mechanism can be proposed in which the reaction proceeds through two parallel pathways to yield the final product **1c**.



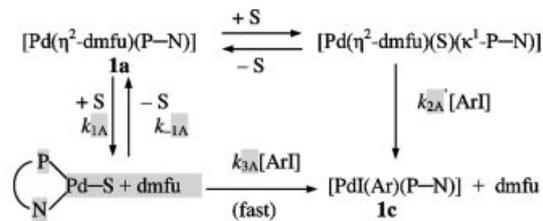
In the step k_{1A}, the interaction with the solvent produces a highly reactive intermediate which rapidly reacts with ArI to give **1c**. To a first approximation, step k_{2A} may be conceived as a bimolecular attack by the electrophile ArI on the starting complex **1a**. According to the solution behaviour of the complexes [Pd(η²-dmfu)(P-N)] and to literature data on the mechanism of oxidative addition of iodobenzene to [Pd(η²-dba)(L-L')] (dba = dibenzylideneacetone; L-L' = N, P ligand of the type aminophosphane or oxazolinophosphane),^[19] the reactive intermediate may be formulated as a [Pd(solvent)(P-N)] species, resulting from the dissociation of the η²-bound dmfu, or as a [Pd(η²-dmfu)(solvent)(κ¹-P-N)] species, containing a P-monodentate iminophosphane and resulting from the Pd-N bond rupture (see Scheme 4). Under the steady state

approach and with reasonable approximations,^[23] the rate law:

$$d[\mathbf{1a}]/dt = -[\mathbf{1a}](k_{1A} + k_{2A}[\text{ArI}])$$

can be obtained which is identical to the experimental results irrespective of the nature of the reactive intermediate. However, a comparison of the ΔG[‡] value of 63.4 kJ·mol⁻¹ {calculated at the coalescence temperature of 56 °C for the dynamic process of **1a** in [D₈]toluene, in which the intermediate [Pd(η²-dmfu)(solvent)(κ¹-P-N)] is formed} and the ΔG[‡] value of 95.5 kJ·mol⁻¹ (calculated at the same temperature from the activation parameters in Table 5 for step k_{1A} in toluene) rules out any intermediacy of [Pd(η²-dmfu)(solvent)(κ¹-P-N)]. In the solvolytic pathway k_{1A}, a higher energy process is involved which is well represented by the solvent-assisted dissociation of the η²-bound dmfu to form the intermediate [Pd(solvent)(P-N)] whose enhanced reactivity toward oxidative additions^[10,13] is essentially due to the increased electron density on the central metal.

In order to get a better understanding of the second-order step k_{2A}, a kinetic study of the oxidative addition of ArI to the *N*-CHMe₂ complex **2a** was carried out in CH₃CN at 45 °C in the presence of dmfu (**2a**)₀ = 1·10⁻⁴ M; [dmfu] = 3·10⁻³ M). The observed rate law is identical to that found for **1a**, with k_{1A} = (2.71±0.03)×10⁻⁴ s⁻¹ and k_{2A} = (6.3±0.4)×10⁻⁴ M⁻¹s⁻¹. If compared with the corresponding rate constants for the reaction of **1a** under the same experimental conditions [k_{1A} = (5.2±0.2)×10⁻³ s⁻¹ and k_{2A} = (1.6±0.4)×10⁻² M⁻¹s⁻¹] one can see that for **2a** the k_{1A} value has decreased by one order of magnitude, while the k_{2A} value has decreased by two orders of magnitude. These changes are mainly related to electronic factors since the steric requirements of the *N*-substituents in these complexes are comparable. Thus, the decrease in k_{1A} can be explained by the presence of a stronger Pd-η²-dmfu bond in **2a** due to the greater extent of π back-donation (see the ¹³C NMR spectroscopic data in Table 2) which makes the olefin dissociation step more difficult. However, the marked decrease in k_{2A} is in contrast with the k_{2A} step, being a direct electrophilic attack on the palladium center of the complexes [Pd(η²-dmfu)(P-N)]. The presence of a more electron-donating iminophosphane in **2a** increases the electron density on the central metal and, therefore, would favour such attack as reported for other palladium(0) complexes when the donor properties of the ancillary ligands are increased.^[3f,24] The changes in the k_{2A} values can be rationalised if the oxidative addition of ArI in the path k_{2A} does not occur on the complexes [Pd(η²-dmfu)(P-N)] but on the intermediates [Pd(η²-dmfu)(solvent)(κ¹-P-N)] formed in a pre-equilibrium step (K).



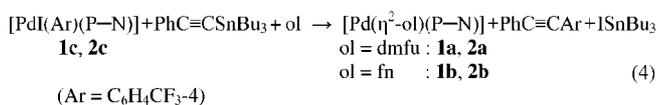
In this case, the observed rate law becomes:

$$k_{\text{obs}} = k_{1A} + k_{2A}' \cdot K[\text{ArI}]$$

The measured k_{2A} term can now be represented by the product $k_{2A}' \cdot K$. Although the K constant cannot be experimentally determined due to the low, undetectable concentration of $[\text{Pd}(\eta^2\text{-dmfu})(\text{solvent})(\kappa^1\text{-P-N})]$ in the NMR solutions, its value is expected to decrease on going from **1a** to **2a** due to the presence of a stronger Pd–N bond in the latter complex. In contrast, it is reasonable to assume that the kinetic constants k_{2A}' are not particularly affected by the different electronic properties of the N -substituents in the intermediates with a P -monodentate iminophosphane.

Transmetalation and Reductive Elimination Reactions

The complexes **1c** and **2c** react with the stannane $\text{PhC}\equiv\text{CSnBu}_3$ in the presence of an activated olefin according to Equation (4).



As reported for palladium complexes with chelating bidentate ligands,^[3d,9,10] the transmetalation of $[\text{PdI}(\text{Ar})(\text{P-N})]$ by $\text{PhC}\equiv\text{CSnBu}_3$ leads to a labile intermediate $[\text{Pd}(\text{C}\equiv\text{CPh})(\text{Ar})(\text{P-N})]$ which undergoes reductive elimination of $\text{PhC}\equiv\text{CAr}$ and η^2 -coordination of the olefin to give the product $[\text{Pd}(\eta^2\text{-ol})(\text{P-N})]$. In the IR spectra (in THF) and in the ¹H, ¹¹⁹Sn and ³¹P spectra (in [D₈]THF) of the reaction mixtures at different times, only the starting materials and the final products were observed.^[13] No side-product or intermediate of the type $[\text{Pd}(\text{C}\equiv\text{CPh})(\text{Ar})(\text{P-N})]$ was detected during the course of the reaction, indicating that the reductive elimination and η^2 -coordination of the olefin are faster than the initial transmetalation step.

A kinetic study of reaction (4) was carried out under pseudo-first-order conditions using UV/Vis spectroscopy in different solvents and at different temperatures with an initial concentration $[\mathbf{1c}]_0$ or $[\mathbf{2c}]_0 = 1 \cdot 10^{-4}$ M. Preliminary investigations in which the nature and the concentration of the activated olefin were changed (ol = dmfu, fn; [ol] in the range $2 \cdot 10^{-4}$ to $6 \cdot 10^{-4}$ M) led to the conclusion that the reaction rates are influenced neither by the different π -accepting properties nor by the concentration of the olefin. These findings along with the previous spectroscopic results^[13] imply that i) transmetalation is the rate-determining step of the overall reaction (4) and ii) it is possible to choose the more π -accepting olefin fn that will impart a higher stability to the zero-valent products $[\text{Pd}(\eta^2\text{-fn})(\text{P-N})]$ in order to assess unequivocally the mechanistic path without interference from side-reactions involving decomposition.

Irrespective of solvent and temperature, each reaction obeys the mono-exponential law:

$$D_t = D_\infty + (D_0 - D_\infty) \cdot \exp(-k_{\text{obs}} \cdot t)$$

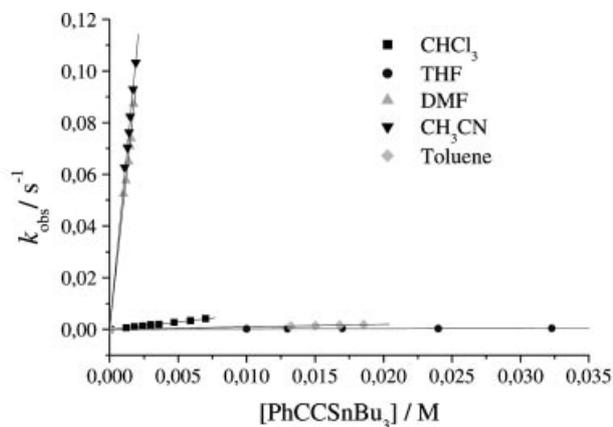
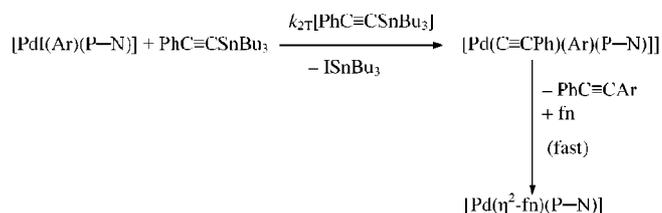


Figure 2. Plots of k_{obs} versus the stannane concentration for the transmetalation of **1c** with $\text{PhC}\equiv\text{CSnBu}_3$ in different solvents at 25 °C in the presence of fn ($[\mathbf{1c}]_0 = 1 \cdot 10^{-4}$ M; $[\text{fn}] = 2 \cdot 10^{-4}$ M)

As reported in Figure 2 for the reactions of **1c**, the k_{obs} values at 25 °C depend on the stannane concentration in a linear manner so that the observed rate law can be represented by the relationship:

$$k_{\text{obs}} = k_{2T}[\text{PhC}\equiv\text{CSnBu}_3]$$

and the corresponding mechanism may be formulated as follows:



In all the solvents examined, the rate law does not display a solvolytic path, no intercept being detected in the plots in Figure 2. The measured k_{2T} values are listed in Table 6.

Table 6. Kinetic constants k_{2T} for the transmetalation of **1c** with $\text{PhC}\equiv\text{CSnBu}_3$ in different solvents at 25 °C in the presence of fn ($[\mathbf{1c}]_0 = 1 \cdot 10^{-4}$ M; $[\text{fn}] = 2 \cdot 10^{-4}$ M)

Solvent	$k_{2T} / \text{M}^{-1}\text{s}^{-1}$
THF	0.0107 ± 0.0006
Toluene	0.10 ± 0.01
CHCl_3	0.59 ± 0.01
$\text{CH}_3\text{CN}^{\text{[a]}}$	31 ± 1
DMF	48 ± 2

^[a] In the presence of an excess of NEt_4I ($[\text{NEt}_4\text{I}] = 1 \cdot 10^{-3}$ M).

As can be seen, a marked solvent effect is present with the highest k_{2T} values being observed in the more polar solvents CH_3CN and DMF. The kinetic measurements in CH_3CN were carried out in the presence of a large excess of NEt_4I in order to shift the position of equilibrium (2) completely to the left. In the absence of NEt_4I and with all other things being equal, the reaction in CH_3CN proceeds at a higher rate indicating that the cationic complex $[\text{Pd}(\text{Ar})(\text{CH}_3\text{CN})\{2\text{-}(\text{PPh}_2)\text{C}_6\text{H}_4\text{-1-CH=NC}_6\text{H}_4\text{OMe-4}\}]^+$

is a more reactive species than the neutral complex **1c**. Unfortunately, the reactivity of $[\text{Pd}(\text{Ar})(\text{CH}_3\text{CN})\{\text{2}-(\text{PPh}_2)\text{C}_6\text{H}_4-1-\text{CH}=\text{NC}_6\text{H}_4\text{OMe}-4\}]^+$ (as CF_3SO_3^- salt) could not be determined because extensive decomposition occurred in the reaction mixture in the absence of the I^- ions.

From kinetic measurements at variable temperature, the activation parameters shown in Table 7 were evaluated.

Table 7. Kinetic constants k_{2T} and activation parameters for the transmetallation of **1c** with $\text{PhC}\equiv\text{CSnBu}_3$ in different solvents

Solvent	$T / ^\circ\text{C}$	$k_{2T} / \text{M}^{-1}\text{s}^{-1}$	$\Delta H^\ddagger / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta S^\ddagger / \text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$
CHCl_3 ^[a]	15	0.334 ± 0.006	31 ± 3	-146 ± 12
	25	0.59 ± 0.01		
	35	0.80 ± 0.02		
	45	1.00 ± 0.03		
CH_3CN ^{[a][b]}	15	27 ± 1	23 ± 1	-139 ± 9
	25	55 ± 1		
	35	68 ± 4		
	45	108 ± 4		

^[a] In each kinetic run: $[\text{1c}]_0 = 1 \cdot 10^{-4} \text{ M}$; $[\text{fn}] = 2 \cdot 10^{-4} \text{ M}$. ^[b] In each kinetic run: $[\text{NEt}_4\text{I}] = 1 \cdot 10^{-3} \text{ M}$.

The markedly negative ΔS^\ddagger values clearly point to an associative $\text{S}_{\text{E}2}$ mechanism for the transmetallation step in both solvents. Because complex **1c** has an iodide ligand of good bridging ability, a cyclic four-center transition state may be operative in solvents of low polarity (toluene, THF, CHCl_3).^[5] However, the strong acceleration observed in highly polar solvents (CH_3CN , DMF) is very much in favour of an open transition state with substantial charge separation.^[5]

In the case of complex **2c**, the kinetic study of reaction (4) was carried out at 25 °C in CHCl_3 and CH_3CN under the same experimental conditions as for **1c**. In CH_3CN , an excess of NEt_4I was added ($[\text{NEt}_4\text{I}] = 1 \cdot 10^{-3} \text{ M}$). The observed kinetic law is identical to that found for **1c**, with $k_{2T} = 0.32 \pm 0.01 \text{ M}^{-1}\text{s}^{-1}$ in CHCl_3 and $k_{2T} = 27 \pm 4 \text{ M}^{-1}\text{s}^{-1}$ in CH_3CN . When compared with the corresponding values of **1c** in Table 6, one can see that the transmetallation step proceeds at comparable rates for both complexes. Presumably, the lower electrophilic character of the palladium center in **2c**, due to the greater electron-donating properties of the *N*-CHMe₂ substituent, is compensated for by the increased lability of the iodide ligand as can be inferred from the difference in the K_{S} constants of the equilibrium 2 for these complexes.

Conclusion

From the solution behaviour of the complexes $[\text{Pd}(\eta^2\text{-dmfu})(\text{P}-\text{N})]$ and kinetic data for the oxidative addition of ArI ($\text{Ar} = \text{C}_6\text{H}_4\text{CF}_3-4$), a mechanism can be proposed consisting of (i) a solvolytic path the rate of which is zero-order with respect to ArI and involves the reactive species $[\text{Pd}(\text{solvent})(\text{P}-\text{N})]$ formed in the olefin dissociation and

(ii) a parallel path the rate of which is first-order with respect to ArI and involves the species $[\text{Pd}(\eta^2\text{-dmfu})(\text{solvent})(\kappa_1\text{-P}-\text{N})]$ formed in a pre-equilibrium dissociation of the $\text{Pd}-\text{N}$ bond.

The reaction of $[\text{PdI}(\text{Ar})(\text{P}-\text{N})]$ with $\text{PhC}\equiv\text{CSnBu}_3$ in the presence of activated olefins yields the complexes $[\text{Pd}(\eta^2\text{-ol})(\text{P}-\text{N})]$. For this reaction, the rate-determining transmetallation step obeys a rate law which is first-order with respect to the stannane. The kinetic data suggest an associative $\text{S}_{\text{E}2}$ mechanism via an open transition state with substantial charge separation in highly polar solvents such as CH_3CN and DMF (path b of Scheme 1).

From the present study it clearly emerges that the oxidative addition represents the rate-determining step in the cross-coupling of $\text{PhC}\equiv\text{CSnBu}_3$ with ArI catalysed by $[\text{Pd}(\eta^2\text{-dmfu})(\text{P}-\text{N})]$. The nature of the solvent is of great importance for increasing the overall rate of the catalysed reaction. In this respect, CH_3CN (a solvent with good coordinating properties and a high dielectric constant) proves to be the best suited medium since it enhances the rates of both the oxidative addition and transmetallation steps involved in the Stille process. Moreover, in the case of transmetallation in CH_3CN , the absence of added iodide allows the formation of a significant amount of the cationic species $[\text{Pd}(\text{CH}_3\text{CN})(\text{Ar})(\text{P}-\text{N})]^+$ which increases the apparent rate of the reaction without leading to secondary decomposition products.

Experimental Section

^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker AM400 spectrometer operating at 400.13, 100.61, and 161.98 MHz, respectively, using solutions of the palladium complexes with concentrations in the range of $1 \cdot 10^{-2}$ to $2 \cdot 10^{-2} \text{ M}$. Chemical shifts are reported in ppm relative to TMS (^1H , ^{13}C) or external 85% H_3PO_4 (^{31}P). For the ^1H NMR spectra at variable temperature, the probe temperature was controlled by a standard unit calibrated with a methanol reference. Coalescence temperatures were determined to within an accuracy of 3 K. The estimated error in the calculated ΔG^\ddagger values is $0.6-0.8 \text{ kJ}\cdot\text{mol}^{-1}$. IR spectra were carried out using a Perkin-Elmer 983 spectrophotometer. UV/Vis spectra at variable temperature were recorded on a Peltier equipped Perkin-Elmer lambda 40 spectrophotometer. Conductivities were measured with CDM83 and Metrohm 660 conductimeters at 25 °C. All solvents were purified and dried before use according to standard methods.^[25] The reactions were carried out under N_2 unless otherwise stated. The compounds $\text{PhC}\equiv\text{CSnBu}_3$, dimethyl fumarate, fumaronitrile, AgBF_4 , and AgCF_3SO_3 were commercial samples and were used without further purification. The aryl iodide $\text{IC}_6\text{H}_4\text{CF}_3-4$ was distilled at reduced pressure before use. The iminophosphane $2-(\text{PPh}_2)\text{C}_6\text{H}_4-1-\text{CH}=\text{NR}$ [$\text{R} = \text{CHMe}_2$, $\text{C}_6\text{H}_4\text{OMe}-4$, $\text{C}_6\text{H}_3\text{Me}_2-2,6$, $\text{C}_6\text{H}_3(\text{CHMe}_2)_2-2,6$, bornyl] and the complexes $[\text{Pd}(\eta^2\text{-dmfu})(\text{P}-\text{N})]$ (**1a**, **2a**), $[\text{Pd}(\eta^2\text{-fn})(\text{P}-\text{N})]$ (**1b**, **2b**, **5b**), $[\text{PdI}(\text{C}_6\text{H}_4\text{CF}_3-4)(\text{P}-\text{N})]$ (**1c**, **2c**) were prepared by published methods.^[11,13,26] The complex $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ was synthesised as described in the literature.^[27]

Preparations

$[\text{Pd}(\eta^2\text{-dmfu})(\text{P}-\text{N})]$ (3a**, **4a**):** The required iminophosphane (1.0 mmol) and dmfu (173 mg, 1.2 mmol) were added to a stirred

suspension of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (1.035 g, 1 mmol) in dry acetone (30 mL). Stirring was continued for 2 h and the solution was then evaporated to dryness at reduced pressure. The solid residue was extracted with CH_2Cl_2 (20 mL) in the presence of activated charcoal. After filtration through celite, the clear red-brown solution was concentrated to a small volume (ca. 3 mL) and diluted with Et_2O to precipitate the products as yellow-orange solids. The complexes were purified by further precipitation from a toluene/*n*-hexane mixture.

3a: Yield 83% (535 mg). $\text{C}_{33}\text{H}_{32}\text{NO}_4\text{PPd}$ (644.0): calcd. C 61.54, H 5.01, N 2.17; found C 61.56, H 5.10, N 2.12%. IR (Nujol): $\tilde{\nu} = 1670$ vs (C=O), 1615 ms (C=N) cm^{-1} . ^1H NMR (CDCl_3 , 25 °C): $\delta = 8.06$ (d, $J_{\text{P,H}} = 3.2$ Hz, 1 H, N=CH), 7.6–6.9 (m, 17 H, $\text{C}_6\text{H}_3 + \text{C}_6\text{H}_4 + \text{C}_6\text{H}_5$), 4.24 (dd, $J_{\text{H,H}} = 10.0$, $J_{\text{P,H}} = 2.4$ Hz, 1 H, =CH *cis* to P), 3.77 (dd, $J_{\text{H,H}} = J_{\text{P,H}} = 10.2$ Hz, 1 H, =CH *trans* to P), 3.18 (s, 6 H, OCH₃), 2.16 (s, 3 H, CH₃), 1.90 (s, 3 H, CH₃) ppm. ^{31}P NMR (CDCl_3 , 25 °C): $\delta = 19.69$ (s) ppm.

4a: Yield 80% (560 mg). $\text{C}_{37}\text{H}_{40}\text{NO}_4\text{PPd}$ (700.1): calcd. C 63.47, H 5.76, N 2.00; found C 63.20, H 5.85, N 1.95%. IR (Nujol): $\tilde{\nu} = 1685$ vs (C=O), 1622 ms (C=N) cm^{-1} . ^1H NMR (CDCl_3 , 25 °C): $\delta = 8.06$ (d, $J_{\text{P,H}} = 2.1$ Hz, 1 H, N=CH), 7.6–6.9 (m, 17 H, $\text{C}_6\text{H}_3 + \text{C}_6\text{H}_4 + \text{C}_6\text{H}_5$), 4.25 (dd, $J_{\text{H,H}} = 10.4$, $J_{\text{P,H}} = 2.5$ Hz, 1 H, =CH *cis* to P), 3.49 (dd, $J_{\text{H,H}} = J_{\text{P,H}} = 10.4$ Hz, 1 H, =CH *trans* to P), 3.37 (spt, $J_{\text{H,H}} = 6.8$ Hz, 1 H, CHMe₂), 3.24 (s, 3 H, OCH₃), 2.93 (s, 3 H, OCH₃), 2.64 (spt, $J_{\text{H,H}} = 6.8$ Hz, 1 H, CHMe₂), 1.45 (d, $J_{\text{H,H}} = 6.8$ Hz, 3 H, CH₃), 1.09 (d, $J_{\text{H,H}} = 6.8$ Hz, 3 H, CH₃), 0.98 (d, $J_{\text{H,H}} = 6.8$ Hz, 3 H, CH₃), 0.56 (d, $J_{\text{H,H}} = 6.8$ Hz, 3 H, CH₃) ppm. ^{31}P NMR (CDCl_3 , 25 °C): $\delta = 22.36$ (s) ppm.

[Pd(CH₃CN)(C₆H₄CF₃-4)]₂-(PPh₂)C₆H₄-1-CH=NC₆H₄OMe-4)]CF₃SO₃: AgCF₃SO₃ (31 mg, 0.12 mmol) dissolved in CH₃CN (1 mL) was added to a solution of **1c** (93 mg, 0.12 mmol) in a CH₂Cl₂/CH₃CN mixture (7:1 v/v, 8 mL). After standing for 2 h in the dark, the insoluble AgI was removed by filtration and the resultant solution was evaporated to dryness at reduced pressure. The solid residue was redissolved in CH₂Cl₂ (10 mL). Addition of activated charcoal and filtration gave a clear solution which was concentrated to small volume (ca. 2 mL), then diluted with Et₂O to precipitate the product as a yellow microcrystalline solid. Yield 69% (69 mg). Λ_{M} ($1 \cdot 10^{-3}$ M, CH₃CN) = 134.4 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. $\text{C}_{36}\text{H}_{29}\text{F}_6\text{N}_2\text{O}_4\text{PPdS}$ (837.0): calcd. C 51.65, H 3.49, N 3.35; found C 51.81, H 3.55, N 3.45%. IR (CHCl₃): $\tilde{\nu} = 2289$ ms (C≡N), 1636 m (C=N) cm^{-1} . ^1H NMR (CDCl_3 , 25 °C): $\delta = 8.33$ (s, 1 H, N=CH), 7.9–7.7 (m, 2 H, *o*-disubstituted C₆H₄), 7.59 (m, 1 H, *o*-disubstituted C₆H₄), 7.5–7.2 (m, 15 H, *o*-disubstituted C₆H₄ + *p*-disubstituted C₆H₄ + C₆H₅), 7.0–6.9 (m, 4 H, *meta* protons of *p*-disubstituted C₆H₄), 3.84 (s, 3 H, OCH₃), 2.30 (s, 3 H, CH₃CN) ppm. ^{31}P NMR (CDCl_3 , 25 °C): $\delta = 34.74$ (s) ppm.

[Pd(CH₃CN)(C₆H₄CF₃-4)]₂-(PPh₂)C₆H₄-1-CH=NCHMe₂)]BF₄: AgBF₄ (49 mg, 0.25 mmol) was added to a solution of **2c** (177 mg, 0.25 mmol) in CH₃CN (10 mL). The mixture was worked up as described above for the preparation of the analogous cationic complex to give the product as a yellow microcrystalline solid. Yield 73% (130 mg). Λ_{M} ($1 \cdot 10^{-3}$ M, CH₃CN) = 147.0 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. $\text{C}_{31}\text{H}_{29}\text{BF}_7\text{N}_2\text{PPd}$ (710.7): calcd. C 52.38, H 4.11, N 3.94; found C 52.15, H 4.02, N 3.86%. IR (CHCl₃): $\tilde{\nu} = 2316$ mw, 2289 mw (C≡N), 1634 ms (C=N) cm^{-1} . ^1H NMR (CDCl_3 , 25 °C): $\delta = 8.36$ (s, 1 H, N=CH), 7.90 (m, 1 H, *o*-disubstituted C₆H₄), 7.78 (m, 1 H, *o*-disubstituted C₆H₄), 7.56 (m, 1 H, *o*-disubstituted C₆H₄), 7.5–7.2 (m, 13 H, *o*-disubstituted C₆H₄ + *p*-disubstituted C₆H₄ + C₆H₅), 6.95 (m, 2 H, *meta* protons of C₆H₄CF₃-4), 4.52 (spt, $J_{\text{H,H}} = 6.4$ Hz, 1 H, CHMe₂), 2.30 (s, 3 H, CH₃CN), 1.37 (d,

$J_{\text{H,H}} = 6.4$ Hz, 6 H, CH₃) ppm. ^{31}P NMR (CDCl_3 , 25 °C): $\delta = 32.70$ (s) ppm.

Determination of the Equilibrium Constant K_E : To a thermostatically controlled (25 °C) solution of the complex under study (50 mL, ca. $1 \cdot 10^{-4}$ M) in the appropriate solvent were added successive micro-aliquots of the designated olefin and the absorbance changes were recorded in the range of 500–280 nm at 25 °C. The resultant array of absorbance data vs. the total concentration of added olefin was treated according to a published mathematical/statistical model.^[16,17]

Determination of the Equilibrium Constant K_S : Several solutions of the complexes **1c** and **2c** at different concentrations (concentration intervals: $2.3 \cdot 10^{-5}$ to $2.4 \cdot 10^{-3}$ M, **1c**; $2.5 \cdot 10^{-5}$ to $2.6 \cdot 10^{-3}$ M, **2c**) in freshly distilled CH₃CN were prepared and thermostatically controlled at 25 °C. The specific conductivities were determined for each solution and the related molar conductivities were treated according to the method of Fuoss and Shedlovsky.^[28]

A UV/Vis spectroscopic check was carried out as follows: the molar extinction coefficients (ϵ_k) of the starting complex (**1c** or **2c**) were determined from their solutions in the presence of a strong excess of NEt_4I , and those (ϵ_s) of the cationic species $[\text{Pd}(\text{CH}_3\text{CN})(\text{Ar})(\text{P}-\text{N})]^+$ were determined from the solutions of their CF_3SO_3^- or BF_4^- salts synthesised independently. The consistency of the conductivity determined K_S values and the reliability of the results was thus checked by a single spectrophotometric experiment by measuring the absorbance of a $1 \cdot 10^{-4}$ M solution of **1c** (or, **2c**) in CH₃CN. The ensuing absorbance values confirm, in both cases, the independently determined K_S constants.

Kinetic Measurements: The kinetics of the oxidative addition and transmetallation reactions were followed by UV/Vis spectroscopy upon addition of known micro-aliquots of a pre-thermostatically controlled solution of the appropriate reagent (ArI, or $\text{PhC}\equiv\text{CSnBu}_3$ and olefin) to a thermostatically controlled solution in the appropriate solvent of the complex under study $\{[\text{Pd}(\eta^2\text{-dmfu})(\text{P}-\text{N})]$ or $[\text{PdI}(\text{Ar})(\text{P}-\text{N})]\}$ at the suitable temperature. The concentration of the reactant ensured in any case pseudo-first-order conditions and the reactions were followed by recording spectral changes in the suitable wavelength range or at a fixed wavelength. Mathematical and statistical data analysis was carried out on a PC equipped with a locally adapted non-linear regression procedure.

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- $$[\text{Pd}(\eta^2\text{-dmfu})(\text{P-N})] \xrightleftharpoons[\text{-S}]{\text{+S}} \text{Intermediate}$$
- 1a**
- was never taken into account since for both intermediates it leads to rate laws which do not correspond to the experimental one. As an example, for $[\text{Pd}(\eta^2\text{-dmfu})(\text{solvent})(\kappa^1\text{-P-N})]$ as the intermediate the rate law should become: $k_{\text{obs}} = (k_{2A} + k_{3A}K_1)[\text{ArI}]/(1 + K_1)$.
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