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Transmetalation reactions. The role of the stabilizing olefin in determining the overall reaction rate

Luciano Canovese *, Fabiano Visentin, Carlo Levi, Claudio Santo

Dipartimento di Chimica, Università Ca' Foscari, Calle Larga S. Marta 2137, 30123 Venezia, Italy

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ABSTRACT

A systematic study concerning the transmetalation reaction between the palladium butadienyl complexes [PdCl((ZC=CZ)$_2$Me)(L-L')] (Z = COOMe; L-L' = MeN-SPh (**1A**), N-SPh (**1B**), DPPQ-Me (**1C**), BiPy (**1D**), DPPE (**1E**)) and tributyl-phenylethynyl-stannane in the presence of some stabilizing olefins (ma, fn, nq, dmfu, and tmetc) was undertaken. The dependence of the reaction rate on the nature of the ancillary ligand was discussed in terms of the donor capability and steric characteristics of the ligand. It has been noticed that, other things being equal, the joined distorted MeN-SPh ligand imparts the highest reactivity to its derivative (complex **1A**). The most surprising issue was however represented by the olefin which seems to affect heavily the reactivity of the starting substrate thereby increasing the overall reaction rate. The most active olefins were ma and fn. In the case of the reaction between the complex **1A** and tributyl-phenylethynyl-stannane in the presence of fn an exhaustive kinetic study was carried out and a mechanistic hypothesis was advanced.

1. Introduction

The Stille reaction consisting in the palladium catalyzed cross coupling between carbon electrophiles and organo-stannanes is an important and attractive method in modern synthetic organic chemistry [1]. It is usually represented by a catalytic cycle in which the Pd(0) catalyst is firstly oxidized by the organic electrophile to the corresponding Pd(II) derivative which undergoes the transmetalation reaction followed by the reductive elimination of the coupled organic derivative and the subsequent restoration of the Pd(0) catalyst [1f,2]. The complexity of the entire mechanism is testified by the number of papers dealing with the different steps of the cycle and by the fact that the nature of the solvent, the electronic and steric properties of the ancillary ligand, the stannane and the organic electrophile heavily affect the reactivity of every single step [3a]. The rate-determining step of the whole process can be therefore represented by the oxidative addition, by the transmetalation and even by the reductive elimination [1a,1i,2,4].

However, the transmetalation reaction seems to be the most complex and therefore the less granted process even though its associative character (apart from few exceptions [4g]) is recognized on the basis of the work of Espinet [3a–c and refs. therein]. In particular, two different associative pathways which are strongly dependent on the nature of the solvent and the reactant are possible. Thus, poorly coordinating solvents with low dielectric constant and strongly coordinating ligands favour the S_E2 cyclic step whereas the S_E2 open path is preferred when the solvents display remarkable polarity and coordinating capability and the ligands are weak as coordinating and bridging species [5]. Consequently, the general catalytic cycle for the Stille reaction can be represented by Scheme 1.

In order to optimize the efficiency of the transmetalation step two different approaches are available *i.e.* the enhancement of the nucleophilic character of the organo-stannanes and the enhancement of the electrophilic character of the palladium complex. The former can be achieved by the use of suitable additives as fluoride [6] and hydroxide ions [7] whereas the electrophilicity of the palladium complex can be generally obtained by decreasing the basicity of the ancillary ligands (*i.e.* arsine complexes are more reactive than their phosphine analogues [1e,4e,4f] and the reactivity order induced by coordinated halide is I < Br < Cl [3a, p. 4720]). In this respect, it is well known that coordinated electron-poor olefins are effective in removing electron density from the metal centre. Such an effect was widely utilized to facilitate reductive elimination in palladium(II) substrates [8], and for that reason when the reductive elimination step becomes the rate determining step in a palladium catalyzed C–C coupling the addition of an exogenous olefin was particularly advantageous. Thus, Schwartz and co-workers have shown that the coupling of allyl halides with allyl tin [9a] reagents (and with other allyl organometallic substrates [9b,9c]) does not proceed unless an electron-withdrawing olefin such as maleic anhydride was added. This is confirmed by the detailed kinetics and theoretical studies of Kurosawa et al. on allyl

* Corresponding author. Tel.: +39 041 2348655; fax: +39 041 2348517.
E-mail address: cano@unive.it (L. Canovese).

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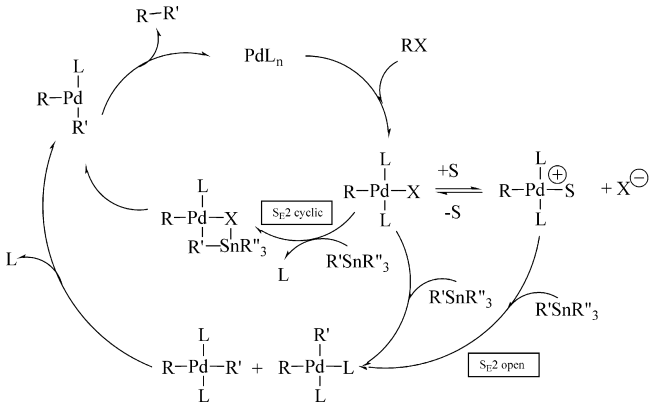


Scheme 1.

aryl palladium complex which showed that the reductive elimination occurs from an η^3-allyl palladium complexes with a coordinated olefin [10].

In a preliminary study concerning the synthesis of some poly-unsaturated compounds by transmetalation we noticed that the nature and the concentration of the olefin employed heavily interferes with the overall rate of the stoichiometric reaction, thereby showing that its role was not simply confined to the stabilisation of the palladium(0) reaction product [11]. Moreover, in this case the rate determining step was better represented by the transmetalation step than by of the reductive elimination which was proved to be fast [12]. Since the mechanism governing the palladium catalyzed synthesis of poly-unsaturated compounds is a widely investigated topics [13] and therefore its comprehension would represent a very important task, we decided to undertake an exhaustive study of the kinetics of the reactions between some butadienyl palladium(II) complexes bearing differently designed bidentate ancillary ligands (prepared according to published methods [14]) and tributyl-phenylethynyl-stannane.

The reaction and the compounds involved in the present paper are reported in Scheme 2.

2. Results and discussion

2.1. Synthesis of palladium butadienyl and palladium(0) olefin derivatives

The complex [PdCl((MeOOC–C=C–COOMe)$_2$Me)(MeN-SPh)] (**1A**) was obtained by reacting an excess of dmbd (dimethyl-2-butynedioate) with the complex [PdCl(Me)(MeN-SPh)] (dmbd: complex = 3:1) for 22 h in CH_2Cl_2 at RT [14a]. The palladium butadienyl derivatives [PdCl((ZC=CZ)$_2$Me)(L-L′)] (Z = COOMe; L-L′ = N-SPh (**1B**), DPPQ-Me (**1C**), BiPy (**1D**), DPPE (**1E**)) were obtained according to published methods [14] by adding an equimolar amount of the appropriate ligand (**B**, **C**, **D**, **E**) to a solution of the complex (**1A**) in freshly distilled anhydrous CH_2Cl_2. All the complexes bearing mixed chelating ligands (N–S or N–P) display the butadienyl group in *trans* position to the pyridine nitrogen atom [14a].

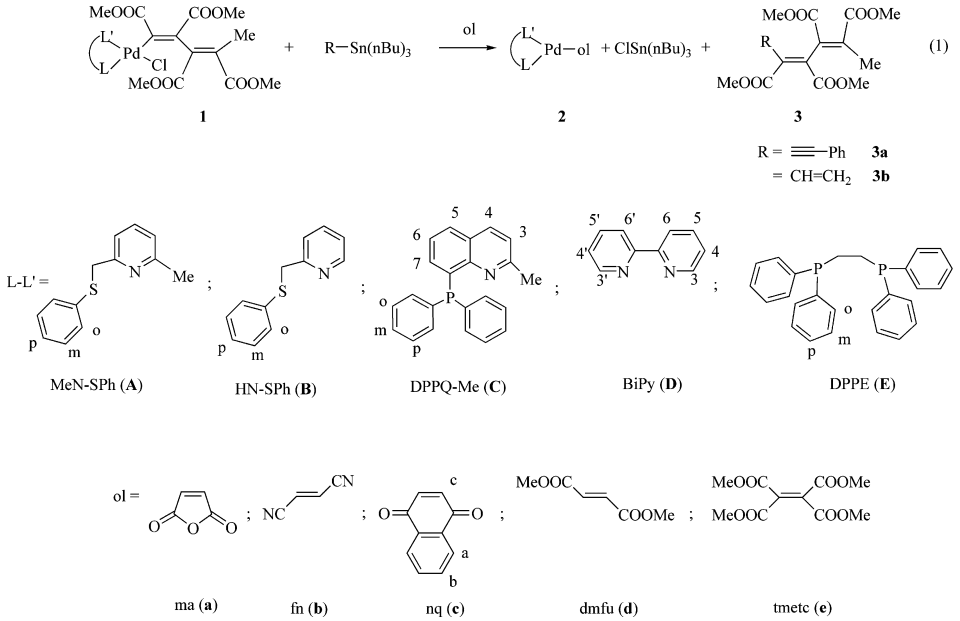
The organic poly-unsaturated products **3** were easily separated from the dried mixture of the transmetalation reaction (1) by extraction with diethyl ether. The solid residue yields the complexes [Pd(η^2-ol)(L-L′)] (L-L′ = **A**, **B**, **C**, **D**, **E**; ol = **a**, **b**, **c**, **d**, **e**). As a check of consistency we also prepared the complexes independently by reacting $Pd_2DBA_3 \cdot CHCl_3$ with the corresponding ligand L-L′ and olefin ol in anhydrous acetone under inert atmosphere (N_2) according to published procedures [15,16]. The complex **2Cb** was obtained through direct olefin exchange by reacting the substrate **2Cd** with fumaronitrile.

2.2. Kinetic and mechanistic study

The reactions between the type **1** complexes and tributyl-phenylethynyl-stannane yielding (2*Z*,4*Z*)-tetramethyl-7-phenylhepta-2,4-dien-6-yne-2,3,4,5-tetracarboxylate (**3a**) and the palladium(0) olefin derivatives **2** went smoothly to completion and were followed by ^{1}H NMR technique in $CDCl_3$ at RT and studied in detail by UV–Vis spectrophotometric technique in $CHCl_3$ at RT.

2.3. The role of the olefin

The most surprising result arising from this study is represented by the role of the olefin in determining the rate of reaction (1). As a



Scheme 2.

matter of fact, addition of maleic anhydride to the slowly reacting equimolar solution of complex **1A** and tributyl-phenylethynyl-stannane drives the reaction to completion in few minutes. Thus, we decided to study the dependence on the olefin in the case of complex **1A** (which displays the highest reactivity among all the other complexes synthesized) and **1C**. We therefore determined a qualitative order of reactivity when reaction (1) was carried out using different olefins but maintaining constant the temperature (298 K), the solvent ($CDCl_3$), the concentration of the complex, stannane and the concentration of the olefin under study by means of ^1H NMR technique.

The efficiency of the olefin in promoting the reaction (1) is summarized in the following reactivity order and in Table 1 [17]:

ma > fn ≈ nq > dmfu > tmetc

In order to shed light on the overall mechanism we undertook an exhaustive investigation on the reactivity of complex **1A** as a function of the concentration of stannane and fumaronitrile [18] in $CHCl_3$ at 298 K using the UV–Vis spectrophotometric technique which allows higher and therefore favourable concentration ratios among reactants and the complex under study.

Each kinetic run, carried out in the presence of an excess of stannane and fumaronitrile (*i.e. pseudo*-first order conditions with respect to the complex concentration, $[\text{Stannane}]_0 \geqslant 10 \cdot [\mathbf{1A}]_0$; $[\text{fn}]_0 \geqslant 10 \cdot [\mathbf{1A}]_0$), went smoothly to completion according to the mono-exponential rate law

$$D_t = D_\infty + (D_0 - D_\infty)e^{-k_{obs} * t} \quad (2)$$

where D_0, D_∞ and k_{obs} (parameters to be optimized) represent the initial, the final absorbance and the observed rate constant. Each set of rate constants obtained at various stannane concentrations and at fixed fn concentration fits the expression:

$$k_{obs} = \delta \frac{[\text{R}'\text{Sn}(n\text{-Bu}_3)]}{(1 + \gamma[\text{R}'\text{Sn}(n\text{-Bu}_3)])} \quad (3)$$

From the analysis of the whole set of kinetic data it appears that the concentration of fn determines the asymptotic value of each curve (see Fig. 1).

Therefore, the following expression will appropriately describe the family of curves:

$$k_{obs} = \frac{(\alpha + \beta[\text{fn}])[\text{R}'\text{Sn}(n\text{-Bu}_3)]}{(1 + \gamma[\text{R}'\text{Sn}(n\text{-Bu}_3)])} \quad (4)$$

The values for δ and γ for each k_{obs} set at different fn concentrations are listed in Table 2.

From the linear regression of δ vs. [fn] reported in Fig. 2 we obtained the following values: $\alpha = 0.12 \pm 0.01$ mol^{-1} dm^3 s^{-1}; $\beta = 44 \pm 5$ mol^{-2} dm^6 s^{-1}.

In analogy with the observations of other authors, we also noticed that addition of free bidentate ligand L-L′ to the reaction mixture markedly slowed down the reaction rate. Therefore a plausible reaction scheme which takes into account the kinetic evidence might be the following Scheme 3 [19]:

Path 1 represents the preferred process since the electrophilic character of the metal centre is significantly enhanced by coordination of the electron-withdrawing olefin which favours the efficiency of the stannane attack on intermediate **I** ($k_2[\text{R}'\text{Sn}(n\text{-Bu}_3)]$). [21] As can be deduced from Table 1, it is apparent that ma is the most effective promoter, probably because it combines a high electron-withdrawing character with a modest *Z*-symmetry modulated steric demand which would drive the attack through the unsubstituted side of the olefin [15].

Path 2 represents the process occurring without added olefin and takes place by π pre-coordination of the alkynyl stannane [22].

The observed rate constant for the reaction in Scheme 3 is described by the following expression (5) when the steady state approximation is applied to the monodentate intermediate species **I** and **I*** in path 1 and 2, respectively:

Table 1
Reaction time (95% conversion) in minutes for complexes **1A** and **1C** reacting with tributyl-phenylethynyl-stannane in the presence of different olefins

Complex	ma	fn	nq	dmfu	No olefin
1A	<7[a]	15	40	90	150
1C	<7[a]	60	60	240	Days[b]

[a] Time required for recording the NMR spectrum.
[b] With decomposition.

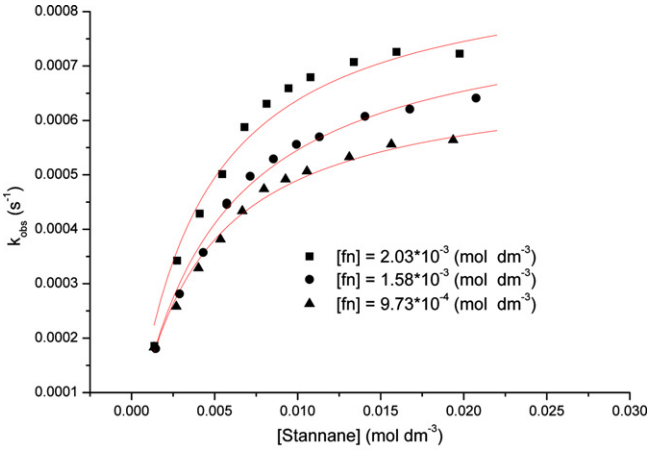


Fig. 1. Plot of k_{obs} vs. [Stannane] with the corresponding best-fits for the reaction of complex **1A** with tributyl-phenylethynyl-stannane in $CHCl_3$ at 298 K. For the sake of clarity k_{obs} values are reported for only three different concentrations of fn.

Table 2
Kinetic parameters δ and γ determined from non linear regression of Eq. (3) carried out at each fumaronitrile concentration

[fn] (mol dm^{-3})	δ (mol^{-1} dm^3 s^{-1})	γ (mol^{-1} dm^3)
0.97×10^{-3}	0.171 ± 0.009	248 ± 18
1.29×10^{-3}	0.174 ± 0.010	249 ± 20
1.58×10^{-3}	0.189 ± 0.002	247 ± 8
2.03×10^{-3}	0.220 ± 0.020	246 ± 31
2.51×10^{-3}	0.232 ± 0.003	247 ± 11

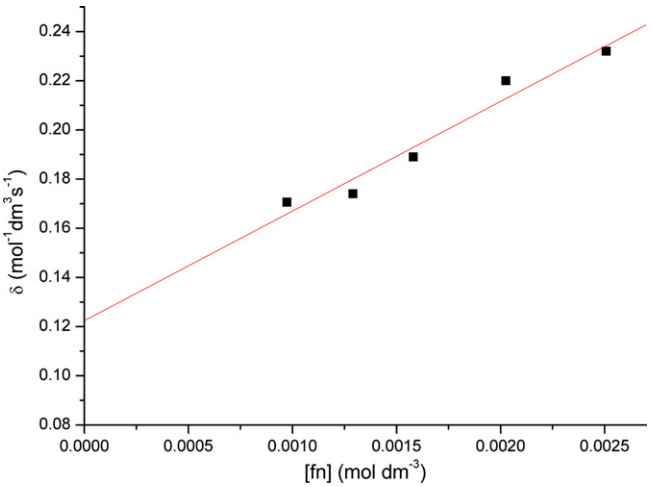


Fig. 2. Linear fit of δ vs. [fn].

$$k_{obs} = \frac{k_2 k_1 (k^*_{-1} + k^*_2)[\text{fn}][\text{R}'\text{Sn}(n\text{-Bu}_3)] + k_{-1} k^*_1 k^*_2 [\text{R}'\text{Sn}(n\text{-Bu}_3)] + k_2 k^*_1 k^*_2 [\text{R}'\text{Sn}(n\text{-Bu}_3)]^2}{(k^*_{-1} + k^*_2) k_{-1} + (k^*_{-1} + k^*_2) k_2 [\text{R}'\text{Sn}(n\text{-Bu}_3)]} \quad (5)$$

Eq. (5) reduces to Eq. (6) upon some rearrangement and under the hypothesis that the term $k_2 k^*_1 k^*_2[\text{R}'\text{Sn}(n\text{-Bu}_3)]^2$ is negligible with respect to the other addends.

$$k_{obs} = \frac{\left(\frac{k_1 k_2}{k_{-1}}[\text{fn}] + \frac{k^*_1 k^*_2}{k^*_{-1} + k^*_2}\right)[\text{R}'\text{Sn}(n\text{-Bu}_3)_3]}{1 + \frac{k_2}{k_{-1}}[\text{R}'\text{Sn}(n\text{-Bu}_3)]} \quad (6)$$

Eq. (4) and Eq. (6) are coincident with $\alpha = k^*_1 k^*_2/(k^*_{-1} + k^*_2)$, $\beta = k_1 k_2/k_{-1}$ and $\gamma = k_2/k_{-1}$.

Owing to the complexity of Eq. (6), only some qualitative considerations can be made. As a matter of fact the ratio $k_2/k_{-1} = 247 \pm 30$ suggests that the attack of the stannane to the monodentate species **I** is very efficient even when compared with the entropically favoured ring closure since the coordinated olefin would enhance the electrophilicity of the metal centre. The k_1 value is given by the ratio $\beta/\gamma = 0.18 \pm 0.03$ and can presumably be traced back to the entering of the olefin into a complex which displays a high tendency to ring opening; according to the steady state approximation, it is remarkably smaller than the rate constants consuming the intermediate **I**. The value of $\alpha = 0.12 \pm 0.01$ which is related to Path 2 is not easily interpreted. It probably reflects the high value of the entropically favoured k^*_{-1} with respect to the other rate constants when Path 2 is taken into account.

2.4. The role of the ancillary ligand

The soundness of Scheme 3 strongly relies on the lability of the pyridine nitrogen of the chelating MeN-SPh ligand (**A**) which is well documented in several papers [15]. As a matter of fact, the distortion of the MeN-SPh ligand coupled with the marked *trans* influence of the butadienyl group in complex **1A** induces a remarkable emilability of the pyridine nitrogen and therefore a marked fluxionality of the ligand, thereby favouring the attack of even adventitious nucleophiles at the metal centre. Thus, the overall reaction rate would slow down when a complex bearing ligands with lower lability is employed. Such hypothesis was clearly confirmed by comparison of the reactivity data of all the complexes reported in Scheme 2. The ensuing reactivity order for the complexes, determined in $CDCl_3$ at RT using fumaronitrile (or maleic anhydride) as stabilizing olefin, is the following [23]:

1A > **1B** >> **1C** >> **1D** >> **1E**

This order is governed by the electrophilicity of the palladium(II) centre which in turn is modulated by the donor capability and by the steric characteristics of the ligands. An increase in the Lewis basicity of the chelating atom (from N, S to P) and in the rigidity of the ancillary ligand itself disfavours the reactivity of the related complexes owing to the enhanced electronic density of the palladium and to the lack of necessary flexibility of the ancillary ligand in forming the substrate with an uncoordinated wing. The difference in reactivity between the distorted complex **1C** and the complex **1D** again emphasizes that the most important role in this sort of reactions is played by the distortion and the consequent ligand emilability. As a matter of fact, substrate **1C** is more reactive than **1D** despite the fact that the better donor ability of the phosphorus atom in **1C** would decrease its nucleophilicity. Eventually, the low reactivity of complex **1E** can directly be traced back to the coordinating capability of the phosphine which probably renders the ring opening pathway negligible.

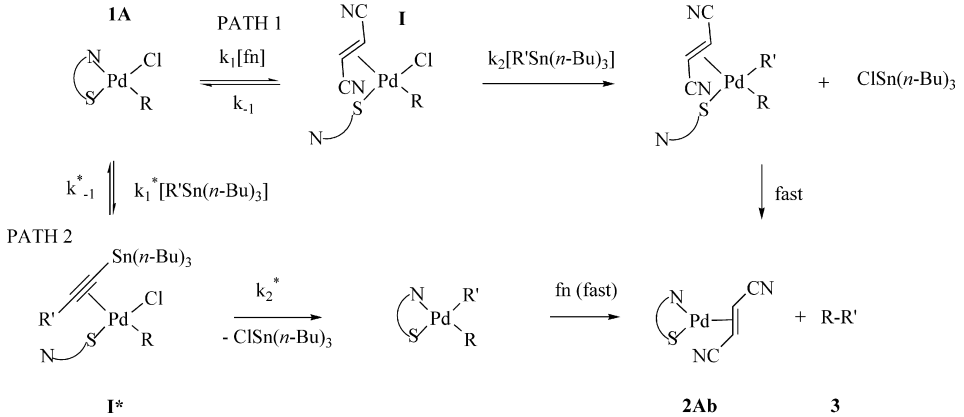
2.5. Activation of a less reactive stannane

The most obvious extension of the enhanced overall reactivity of the coupling processes promoted by the presence of the olefin in excess is the transmetalation reaction with poorly reactive stannanes. We therefore tested the reaction between the complex **1A** and tributyl-vinyl-stannane (CH_2=CH–Sn(n-Bu)$_3$) which is less prone to electrophilic attack than tributyl-phenylethynyl-stannane. As a matter of fact, the presence of a slight excess of maleic anhydride in the reaction between the complex **1A** and the vinyl stannane ([**1A**]:[vinyl stannane]:[ma] = 1:1.1:1.2; [**1A**] $\approx 3 \times 10^{-2}$ mol dm^{-3}) in $CDCl_3$ at 298 K drives the reaction to completion in ~120′ with the formation of the (2*Z*,4*Z*)-tetramethylhepta-2,4,6-triene-2,3,4,5-tetracarboxylate derivative (CH_2=CH(MeOOC=CCOOMe)$_2$Me) (**3b**). The same reaction carried out in the absence of maleic anhydride takes more than several days.

3. Conclusions

From the experimental results of the present work it is possible to conclude that:

(a) The olefin heavily interferes in the mechanism of transmetalation step in the C–C coupling between the palladium-butadienyl complexes and alkynyl-stannane and its nature is of primary importance in determining the overall reaction rate.
(b) The most efficient olefin is maleic anhydride, probably thanks to its high electron-withdrawing character and reduced steric requirements which favour its pre-coordination.



Scheme 3.

(c) In the reaction between the complex **1A** and tributyl-phenylethynyl-stannane in the presence of fumaronitrile, the kinetics indicate a mechanism involving an associative attack of both stannane and olefin on the starting complex.
(d) The reaction rate of the transmetalation reactions of butadienyl chloro palladium complexes bearing bidentate ligands is influenced by the ligand emilability which depends on the ground state distortion of the complex itself and on the mutual *trans* labilization of the butadienyl fragment and the opposite atom.
(e) Maleic anhydride displays its efficiency in promoting the transmetalation reaction also when the less activated vinyl-stannanes are used.
(f) In the possible application of the results described in the present paper to a catalytic approach to the Stille reaction, it might be anticipated that the use of dmfu as olefin could be useful since it could display its accelerating effect on the transmetalation reaction while allowing a sufficient reactivity to the ensuing palladium(0) dmfu derivative which can be quite easily oxidized by the organic halide [4k].

4. Experimental

4.1. Solvents and reagents

Acetone and CH_2Cl_2 were distilled over 4 Å molecular sieves and CaH_2, respectively. $CHCl_3$ was distilled over silver foil under inert atmosphere. All the other chemicals were commercially available grade products and were used as purchased.

4.2. Data analysis

Mathematical and statistical analysis of data was carried out by locally adapted non linear regression algorithms written under SCIENTIST™ environment.

4.3. IR, NMR, and UV–Vis measurements

The IR and the ^1H and ^{13}C NMR spectra were recorded on a Perkin–Elmer Spectrum One spectrophotometer and on a Bruker 300 Avance spectrometer, respectively. UV–Vis spectra were taken on a Perkin–Elmer Lambda 40 spectrophotometer equipped with a Perkin–Elmer PTP6 (Peltier temperature programmer) apparatus.

4.4. GC-MS spectrometry measurements

The GC–MS spectra were recorded on a Thermo Quest Finnigan Trace 2000 Series gas chromatograph-mass spectrometer using a Mega Fused Silica capillary column (stationary phase: SE52, 30 m × 0.25 mm i.d.).

4.5. Preliminary studies and kinetic measurements

All the transmetalation reactions were preliminarily studied by ^1H NMR technique by dissolving the complex under study in 0.6 ml of $CDCl_3$ ($[Complex]_0$ 1–3 × 10^{-2} mol dm^{-3}) and adding microaliquots of a concentrated $CDCl_3$ solution of tributyl-phenylethynyl-stannane (or tributyl-vinyl-stannane) and olefin. The reaction progress was followed by monitoring the signal for the disappearance of the starting complex and the contemporary appearance of the final products **2** and **3**.

The UV–Vis preliminary study was carried out by placing 3 ml of freshly prepared solution of the complex **1A** ($[\mathbf{1A}]_0 = 1 \times 10^{-4}$ mol dm^{-3}) in a thermostatted (298 K) cell compartment of the UV–Vis spectrophotometer. Microaliquots of solution containing tributyl-phenylethynyl-stannane and fumaronitrile at adequate concentrations were added and the absorbance changes were monitored in the 250–400 nm wavelength interval or at fixed wavelength (320 nm).

4.6. Synthesis of the butadienyl complexes [PdCl((MeOOC═CCOOMe)$_2$Me)(HN-SPh)] (*1B*)

To a suspension of 0.64 g (0.0975 mmol) of **1A** in 6 ml of freshly distilled anhydrous CH_2Cl_2 0.0604 g (0.3 mmol) of the ligand HN-SPh (**B**) was added and the reaction mixture was stirred for 60 min. The solution was concentrated under reduced pressure and the complex was precipitated as pale creamy solid by addition of diethyl ether. The product was filtered off, washed with small aliquots of diethyl ether and dried under vacuum (0.576 g, yield 92%).

^1H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 9.21 (d, 1H, H^6, J = 5.3 Hz), 7.65 (t, 1H, H^4, J = 7.7 Hz), 7.62–7.69 (m, 2H, phenyl H^{ortho}), 7.39–7.28 (m, 5H, H^3, H^5, phenyl H^{meta}, H^{para}), 5.11 (d, 2H, J = 16.5 Hz Pyr–CH_2–S), 4.19 (d, 2H, J = 16.5 Hz Pyr–CH_2–S), 3.81, (s, 3H, $COOCH_3$), 3.77, (bs, 3H, $COOCH_3$), 3.67, (s, 3H, $COOCH_3$), 3.64 (bs, 3H, $COOCH_3$), 2.19 (s, 3H, ═CCH_3).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm), δ: 171.3 (CO, $COOCH_3$), 170.3 (CO, $COOCH_3$), 168.1 (broad CO, $COOCH_3$), 161.0 (CO, $COOCH_3$), 157.2 (C, C^2), 150.7 (CH, C^6), 139.0 (CH, C^4), 132.0 (CH, phenyl C^{meta}), 130.4 (CH, phenyl C^{para}), 129.7 (C, phenyl C^{ipso}), 129.6 (CH, phenyl C^{ortho}), 123.9 (CH, C^5), 122.8 (CH, C^3), 52.4, 52.2, 52.0, 51.6 (CH_3, $COOCH_3$), 49.1 (broad CH_2, CH_2–S), 26.4 (CH_3, Pyr–CH_3), 19.0 (CH_3, ═CCH_3).

IR (KBr pellet): ν = 1711 cm^{-1} (C═0), 1602.6 cm^{-1} (C═N).

Anal. Calc. for $C_{25}H_{26}ClNO_8PPdS$: C, 46.74; H, 4.08; N, 2.18. Found: C, 46.82; H, 4.12; N, 2.27%.

The complexes **1A**, **1C**, **1D**, **1E** were prepared according to published procedures [14a].

4.7. [Pd(η^2-dmfu)(MeN-SPh)] (*2Ad*)

Owing to solubility reasons and to its intrinsic instability the title complex is hardly separable in pure form from $Pd_2DBA_3 \cdot CHCl_3$ which represents the most useful starting substrate for obtaining [Pd(η^2-ol)(L-L′)] derivatives. Therefore, we have identified it directly from the NMR tube as the product of the reaction of complex **1B** with stannane in the presence of dmfu by comparison with the spectra of analogous species. No further purification was carried out.

^1H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 7.56 (t, 1H, H^4, J = 7.7 Hz), 7.47–7.44 (m, 2H, phenyl H^{ortho}), 7.29–7.25 (m, 4H, H^3, phenyl H^{meta}, H^{para}), 7.13 (d, 1H, H^5, J = 7.7 Hz); 4.38 (bs, 2H, Pyr–CH_2–S), 3.08 (bs, 2H, CH═CH); 2.84 (bs, 3H, Pyr–CH_3).

4.8. Synthesis of the Pd(0) olefin complexes [Pd(η^2-nq)(DPPQ-Me)] (*2Cc*)

To a solution of 0.1035 g (0.1 mmol) of $Pd_2DBA_3 \cdot CHCl_3$ in 10 ml of freshly distilled anhydrous acetone, 0.072 g (0.22 mmol) of DPPQ-Me (**C**) and 0.791 g (0.5 mmol) of naphthoquinone (nq) were added. The solution was stirred under inert atmosphere (Ar) for 3 h at RT. The solvent was removed under reduced pressure and the dry residue was dissolved in CH_2Cl_2. The resulting solution was filtered on a celite filter, concentrated and the complex was precipitated as an orange solid by addition of diethyl ether. The complex was filtered off, washed with small aliquots of diethyl ether and dried under vacuum (0.077 g, yield 65%).

^1H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 8.19 (d; 1H, J = 8.4 Hz; H^4); 8.04 (d; 1H, J = 7.7 Hz; H^a); 7.90 (d; H, J = 7.9 Hz; H^5); 7.79 (t; 1H, $J_{HP} = J_{HH}$ 7.7 Hz; H^7); 7.69 (d; 1H, J = 7.7 Hz;

H^a); 7.58–7.62 (m, 2H, PPh_2); 7.51–7.56 (m; 2H; H^6, H^3); 7.38–7.47 (m; 6H; H^b, PPh_2); 7.29–7.35 (m; 2H; PPh_2); 7.06–7.13 (m, 2H, PPh_2); 5.01 (m, 2H, CH=CH); 3.14 (s, 3H, quinoline-CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 185.1 (CO, CO *trans*-P); 184.0 (d, CO, J_{CP} = 6.2 Hz CO *trans*-N); 165.6 (C, C^2); 151.5 (C, C^{10}); 151.2 (C, C^9); 138.3 (CH, C^4); 137.8 (CH, C^7); 134.3 (d, C, J_{CP} = 35.1 Hz, C^8); 131.2 (CH, C^b); 131.0 (CH, C^5); 130.5 (CH, C^b); 126.3 (d, CH, J_{CP} = 4.8 Hz, C^6); 125.4 (CH, C^a); 125.0 (CH, C^a); 123.8 (CH, C^3); 66.2 (d, CH, J_{CP} = 21.0 Hz CH=CH *trans*-P); 62.6 (CH, CH=CH *trans*-N); 30.2 (CH_3, quinoline-CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 25.3. IR(KBr pellet) ν = 1636, 1622 cm^{-1} (C=O); 1588 cm^{-1} (C=N). Anal. Calc. for $C_{32}H_{24}NO_2PPd$: C, 64.93; H, 4.09; N, 2.37. Found: C, 64.64; H, 4.27; N, 2.39%.

The complexes **2Aa**, **2Ab**, **2Ac**, **2Ae**, **2Bb** [16a], **2Ca** [16b], **2Cd** [24], **2Db**, **2Eb** [25], **2Ea** [26] were prepared according to published procedures.

4.9. [Pd(η^2-fn)(DPPQ-Me)] (**2Cb**)

To a solution of 0.10 g (0.17 mmol) of [Pd(η^2-dmfu)(DPPQ-Me)] (**2Cd**) in 20 ml of freshly distilled CH_2Cl_2, 0.0162 g (0.21 mmol) of fumaronitrile was added. The reaction mixture was stirred under inert atmosphere for 30 min. The solvent was removed under reduced pressure and the creamy residue was washed several times with diethyl ether. The suspension was eventually filtered off and dried under vacuum (0.0829 g, yield 93.6%).

^1H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 8.30 (d; 1H, J = 8.4 Hz; H^4); 8.00 (d; H, J = 7.8 Hz; H^5); 7.84 (t; 1H, J_{HP} = J_{HH} 7.4 Hz; H^7); 7.64 (t; 1H, J = 7.4 Hz; H^6); 7.63 (d; 1H; J = 8.4 Hz; H^3); 7.58–7.43 (m; 10H; PPh_2); 3.45 (dd, 1H, J_{HH} = 9.5 Hz, J_{PH} = 3.2 Hz, CH=CH *trans*-N); 3.24 (s, 3H, quinoline-CH_3); 2.96 (t, 1H, J_{HH} = J_{PH} = 9.5 Hz, CH=CH *trans*-P).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 163.8 (C, C^2); 151.6 (C, C^{10}); 151.3 (C, C^9); 138.7 (CH, C^4); 137.7 (CH, C^7); 134.1 (d, C, J_{CP} = 33.5 Hz, C^8); 131.1 (CH, C^5); 126.5 (d, CH, J_{CP} = 4.8 Hz, C^6); 124.0 (CN, J_{CP} = 8.9 Hz, CN *trans*-N); 123.8 (CH, C^3); 122.1 (CN, CN *trans*-P); 31.7 (CH_3, quinoline-CH_3); 23.7 (CH, CH=CH *trans*-N); 22.9 (d, CH, J_{CP} = 45.4 Hz CH=CH *trans*-P). $^{31}P\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 20.3. IR(KBr pellet) ν = 2190 cm^{-1} (C≡N); ν = 1603 cm^{-1} (C=N).

Anal. Calc. for $C_{26}H_{20}N_3PPd$: C, 61.01; H, 3.94; N, 8.21. Found: C, 61.12; H, 3.82; N, 8.27%.

4.10. PhC≡C(MeOOCC=CCOOMe)$_2$Me (**3a**) and CH$_2$=CH(MeOOCC=CCOOMe)$_2$Me (**3b**)

These products were obtained by extraction with diethyl ether from their reaction mixtures which were preliminarily taken to dryness. The ethereal fractions containing **3a** or **3b** together with the compound Sn(*n*-Bu)$_3$Cl were dried under reduced pressure and washed with hexane in order to remove the stannane. Both the oily residues (yield > 50%) were characterized by ^1H, ^{13}C NMR and GC–MS spectrometry.

4.11. (2Z,4Z)-Tetramethyl 7-phenylhepta-2,4-dien-6-yne-2,3,4,5-tetracarboxylate (**3a**)

^1H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 7.51–7.56 (m, 2H, Ph); 7.32–7.40 (m, 3H, Ph); 3.94 (s, 3H, $COOCH_3$); 3.90 (s, 3H, $COOCH_3$); 3.80 (s, 3H, $COOCH_3$); 3.75 (s, 3H, $COOCH_3$); 2.10 (s, 3H, CH_3).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 169.8 (CO); 164.7 (CO); 164.6 (CO); 164.5 (CO); 146.2 (C, C=C); 133.9 (C, C=C); 132.3 (CH; Ph); 130.0 (CH; Ph); 128.9 (C, C=C); 128.4 (CH; Ph); 125.7 (C, C=C); 121.2 (C; Ph); 103.9 (C, C≡C); 83.4 (C, C≡C); 53.2 (CH_3, $COOCH_3$); 52.8 (CH_3, $COOCH_3$); 52.6 (CH_3, $COOCH_3$); 52.5 (CH_3, $COOCH_3$); 18.7 (CH_3, =CCH_3);

MS (m/z, %): 400 (29) [M^+], 368 (39), 341 (100), 336 (43), 309 (28), 165 (28), 152 (29), 105 (64), 77 (39), 59 (42).

4.12. (2Z,4Z)-Tetramethyl hepta-2,4,6-triene-2,3,4,5-tetracarboxylate (**3b**)

^1H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 6.42 (dd, 1H, J = 17.6, 11.7 Hz, H^c); 5.66 (d, 1H, J = 11.7, H^a); 5.61 (d, 1H, J = 17.6, H^b); 3.93 (s, 3H, $COOCH_3$); 3.87 (s, 3H, $COOCH_3$); 3.76 (s, 3H, $COOCH_3$); 3.73 (s, 3H, $COOCH_3$); 1.93 (s, 3H, CH_3).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 169.5 (CO); 167.4 (CO); 164.9 (CO); 164.8 (CO); 145.3 (C, C=C); 144.7 (C, C=C); 130.0 (CH_2; CH_2=CH); 125.9 (C, C=C); 125.8 (CH; CH_2=CH); 124.2 (C, C=C); 52.7 (CH_3, $COOCH_3$); 52.6 (2CH_3, $COOCH_3$); 52.5 (CH_3, $COOCH_3$); 18.1 (CH_3, =CCH_3).

MS (m/z, %): 326 (11) [M^+], 267 (37), 235 (91), 336 (43), 309 (28), 165 (28), 152 (29), 105 (64), 77 (39), 59 (42).

Appendix A. Supplementary material

Summary of the observed rate constants at different concentrations of fumaronitrile and stannane. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.07.028.

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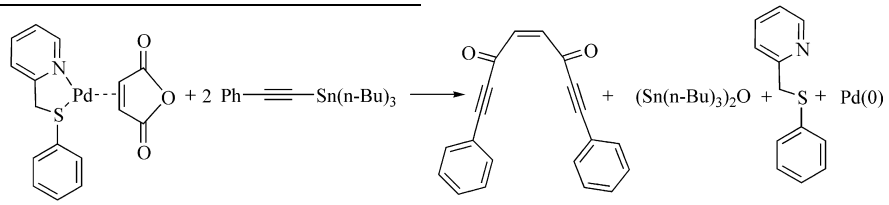

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[17] The reactions of complexes **1A** and **1C** with tributyl-phenylethynyl-stannane were carried out under equal experimental conditions ($[Complex]_0$:$[Stannane]_0$:$[ol]_0$ = 1:1.1:1.2; $[Complex]_0 \approx 3 \times 10^{-2}$ mol dm^{-3}) in $CDCl_3$ at 298 K. In the case of complex 1A we have also studied the reaction in the presence of but-2-ynedioic acid dimethyl ester (dma) yielding the palladacyclopentadiene derivative. The reactivity induced by dma lies between those of nq and dmfu.
[18] We chose fumaronitrile as the target olefin since the ensuing reactivity rates were within reasonable time intervals and because the reactions carried out in the presence of ma underwent a further slow attack of the stannane to the carbonyl groups of the coordinated maleic anhydride to give 1,8-diphenyl-oct-4-ene-1,7-diyne-3,6-dione, di(*n*-butyl-stannane)oxide, the free ligand MeN-SPh and palladium metal according to the reaction in the following scheme 4. It is noteworthy that the reaction between free ma and stannane carried out in the presence of complex **1A** is remarkably slower than that reported above. Apparently, the side reaction noticed during the kinetic investigation is the attack of the stannane to the coordinated ma in the Pd(0) derivative.
[19] Several different approaches were taken into account but among all the equation rates we entertained only the schemes based on pre-equilibrium or steady state were consistent with the shape of Eq. (4). However, in the pre-equilibrium cases considered the ensuing equilibrium constant values were not consistent with the fact that no monosubstituted monodentate species were ever detected by ^{1}H NMR technique under our experimental conditions. We therefore took into consideration the steady state approach following the associative attack which was suggested by other authors [20].
Moreover, the ring opening is somehow confirmed by the slowing down of the overall reaction rate upon addition of the free ligand MeN-SPh. Apparently, the free ligand strongly competes with the stannane and the olefin in solution owing to its capability in saturating the vacant coordination sites. Furthermore, the complete displacement of the ligand was also ruled out since in this case the ensuing kinetic law did not agree with the experimentally observed one.
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