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Mechanism of the Palladium-Catalyzed Metal−Carbon Bond Formation. A Dual Pathway for the Transmetalation Step

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Abstract: The mechanism of the transmetalation step in the metal−carbon bond-formation process catalyzed by palladium complexes has been studied by spectroscopic and kinetic methods. The reaction of properly designed model complexes [η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2](CO)$_3$MoPd(PR_3)I (**3**, R = Ph; **15**, R = Bu; **16**, R = Me), resulting from oxidative addition of a Mo−I moiety to a palladium center, with aryltributyltinacetylides $Bu_3Sn-C\equiv C-(p\text{-}XC_6H_4)$ (**11a**, X = H; **11b**, X = Cl) yields the products of transmetalation [η^5-(1-Ph_2-P-2,4-Ph_2)C_5H_2](CO)$_3$MoPd(PR_3)-C≡C−(p-XC_6H_4) (**5a,b**). The reaction, which shows a strong dependence on the nature of the phosphine ligand PR_3 (Ph > Bu > Me) and less so on the nature of the *p*-substituent X group, proceeds through two competing pathways, depending on the initial concentration of substrate. At high [**3**] ($\cong 10^{-2}$ M), the transmetalation proceeds through an intermediate species (**12**) formed by the interaction of complex **3** with **11a**. This associative complex accumulates in the presence of added PPh_3 and has been characterized spectroscopically. At low [**3**] ($\cong 10^{-4}$ M), the reaction rate shows an inverse dependence on the concentration of the complex. This is due to the formation of a solvent-coordinate species (**13**), in which PPh_3 has been substituted by a dimethylformamide (DMF) molecule, as shown by UV−vis and ^{31}P NMR spectroscopy. Values of k_{obs} depend on the concentration and nature of the aryltributyltinacetylides, in agreement with the existence of a kinetically detectable intermediate. A dimeric iodide bridged complex [{η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2}(CO)$_3$MoPdI]$_2$ (**14**) has been obtained during attempts at isolating **13**, which changes quantitatively into **13** upon dissolution in DMF and reacts with **11a** to give the transmetalation product.

Introduction

In the past few years most of our activity has been devoted to the study of the palladium-catalyzed metal−carbon (acetylide) bond formation.[1] This is an unprecedented feature of palladium that we discovered serendipitously while using the Stille reaction[2] to assemble bis(cyclopentadienyl)ethynyl-framed bimetallic complexes.[3] This new transformation consists of the zerovalent palladium-promoted coupling of metal halide (M−I) complexes (M = Fe, Ru, W, Mo) with trialkyltinacetylide compounds ($R_3Sn-C\equiv C-R'$) (R = Me, Bu; R′ = H, alkyl, aryl) to form metal acetylide derivatives ($M-C\equiv C-R'$).[4] The mild reaction conditions, the effectiveness of the transformation, and the considerable importance of the products have made this new procedure a useful synthetic tool. Following our seminal work,[4] other authors have used this procedure to obtain simple metal acetylide complexes,[5] metallaacetylide dimers,[6] oligomers, and polymers[4,7] (Scheme 1).

With regard to the mechanistic features of the overall process, we have looked for analogies with the palladium-catalyzed carbon−carbon (C−C) coupling reaction between organic electrophiles and organostannanes. This is known as the Stille reaction and is an extremely valuable tool in organic chemistry.[2] It is characterized by a sequence of *oxidative addition/transmetalation/trans-to-cis isomerization/reductive elimination* steps which are represented in Figure 1.[8] The detailed mechanism of this process has been studied for long time and is still a matter of intense debate,[2b] due to its intrinsic complexity.

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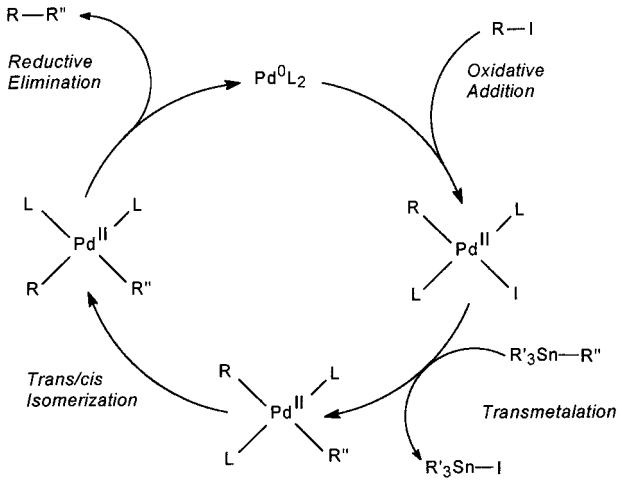
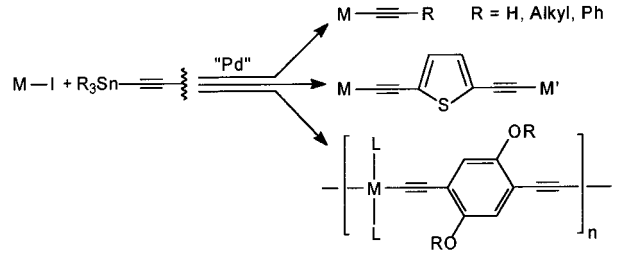


Figure 1. Catalytic cycle of the Pd-promoted carbon−carbon (C−C) bond-formation process.

Scheme 1



With the use of properly designed model substrates [η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2](CO)$_3$MI (**1**, M = Mo; **2**, M = W), bearing a chelating diphenylphosphine sidearm on a cyclopentadienyl ring, it has been possible to isolate and characterize the products of the stoichiometric reaction between the metal−iodide complexes **1** and **2** and zerovalent palladium[9] (Figure 2). The complexes [η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2](CO)$_3$MPd(PPh_3)I (**3**, M = Mo; **4**, M = W) are the product of oxidative addition of the M−I moiety of **1** or **2** to the palladium center. The subsequent reaction of **3** and **4** with trialkyltinacetylides Bu_3Sn−C≡C−R affords the corresponding transmetalated complexes [η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2](CO)$_3$MPd(PPh_3)(C≡CR) (**5**, M = Mo; **6**, M = W), which are further converted into complexes **7** and **8**, respectively, by *trans-to-cis isomerization*. The final products of the catalytic metal−carbon coupling process [η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2](CO)$_3$M(C≡CR) (**9**, M = Mo; **10**, M = W) are then generated by *reductive elimination* on palladium (Figure 2).[9c] Therefore, an entire catalytic cycle, from metal halides **1** and **2** to metal acetylides **9** and **10**, has been examined by analysis of each of the consecutive reaction steps, which are closely related to the typical sequence of the Pd-catalyzed C−C bond-formation process.[2,8]

During these studies, it has been possible to detect the existence of transient species in the various steps of the catalytic cycle by ^{31}P NMR, due to the presence of the two phosphorus centers in complexes **3**−**8**.[9b,c] These analyses have indicated that each step of the catalytic cycle outlined in Figure 2 is indeed composed by different elementary processes.

We report here a detailed mechanistic investigation of the transmetalation step of the metal−carbon bond-formation process. In Pd-catalyzed carbon−carbon coupling (Figure 1), the rate-determining event of the cycle has been proposed to be either the oxidative addition, the transmetalation, or the reductive elimination reaction,[8b,10,11] depending on the substrate and reaction conditions. While a number of accurate studies have been dedicated to the oxidative addition and reductive elimination processes,[12] the transmetalation step has received much less attention and is not well understood.[8c] On the basis of spectroscopic and kinetic studies, Farina[13] and Hartwig[14] have independently postulated that the transmetalation process is regulated by the rate of ligand dissociation (-L) from the intermediate **b** of Scheme 2. Upon screening the effect of a large variety of ligands of different donicity[13] and stannanes of different nucleophilicity[14] on the rate of transmetalation, they have ruled out that the reaction proceeds via a classical associative process.[15,19] In particular, it was shown that the reactions of complexes containing ligands of poor donicity, such as $AsPh_3$ which dissociates easily from the Pd(II) intermediate **b**, are much faster ($>10^3$) than those of complexes with good donor ligands (i.e., PPh_3).[13] Following ligand dissociation, the solvent-coordinated complex **c** interacts with the olefinic stannane to form an intermediate π-complex (**d**), which then evolves into the coupled product **e**. It was presumed that couplings involving alkynylstannanes proceed through formation of analogous intermediate π-complexes.

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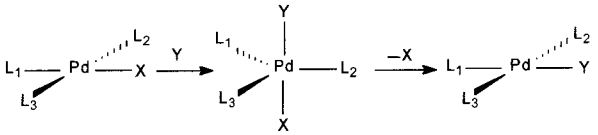
(15) If occurring through a classic substitution process, transmetalation should proceed via an associative mechanism in which the stannane (incoming group) and the halide (leaving group) are simultaneously bound at the apical positions of a penta-coordinate intermediate.[16,17] Recent studies also provided a theoretical background for this transformation.[18]



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(19) In a more recent study about the accelerating effect of Cu(I) salts in the Stille coupling, while remarking about the previously proposed "predissociation" mechanism, Farina postulates that the transmetalation of a newly formed organocopper derivative, after a Sn/Cu exchange, with the oxidative addition intermediate may occur through an associative mechanism (via a penta-coordinate intermediate).[15,20]

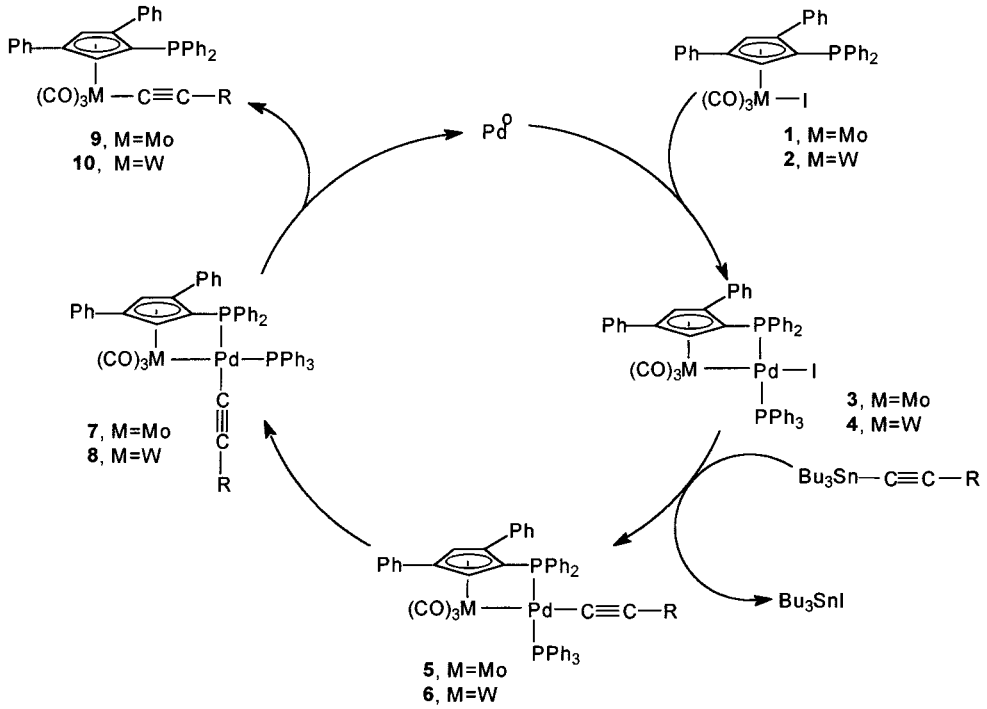
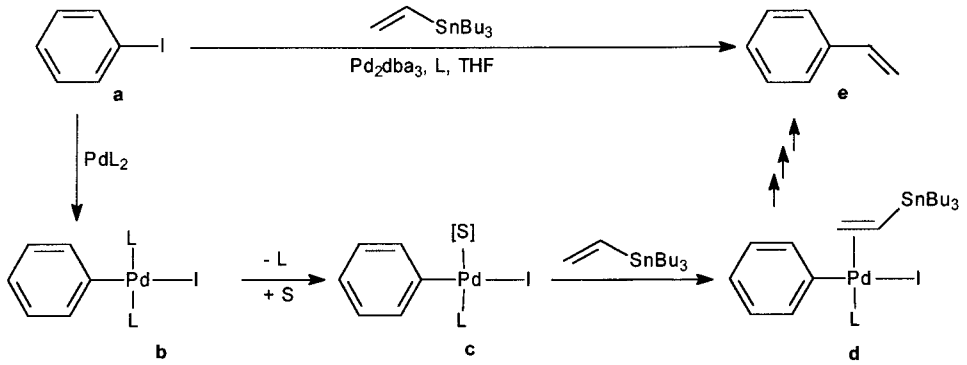


Figure 2. Catalytic cycle of the Pd-promoted metal−carbon (M−C) bond-formation process.

Scheme 2



In a series of recent papers,[11,21,22] Espinet has proposed that the transmetalation reaction in Pd-catalyzed coupling of aryl electrophiles R^1-X (X = halides, triflates) with organotin reagents R^2SnBu_3 (R^2 = vinyl) occurs via two different associative pathways, named "S_E2 cyclic" and "S_E2 open" (Scheme 3).[23]

The S_E2 cyclic mechanism, in solvents of moderate polarity and weakly coordinating, is characterized by the presence of a bridging leaving group X (halide), which assists the R^2-for-L substitution on palladium (path a). This process leads to the three-coordinate T-shaped intermediate **i**, from which the coupling product R^1-R^2 is rapidly formed without need of further dissociation or isomerization steps. The coupling is strongly retarded by free L, and the straightforward formation of the product R^1-R^2 does not allow the detection of intermediates after transmetalation.

When the cyclic mechanism cannot operate, because a coordinating solvent or the absence of halide prevents formation of the Pd−X−Sn bridge, transmetalation occurs via a "S_E2 open" mechanism. This proceeds through either neutral (**f**, path b) or cationic species (**l**, path c, S = L or solvent), which are involved in dynamic equilibria affected by the nature of X, L, the solvent, the temperature, or the presence of added LiCl (in the case of X = OTf). The process is an associative substitution reaction, in which the α carbon of R^2 is the entering ligand, and the Pd complex is the electrophile. Depending on the trans effect of R^1 and on the other ligands, the open transition state may form by a X-for-R^2 or a L-for-R^2 replacement at the Pd center, which leads either to the *cis* (**n**) or the *trans* (**o**) transmetalated intermediates. When the *trans*-to-*cis* isomerization is slow, the intermediate **o** may be observed before evolution toward the final product of coupling R^1-R^2. These studies, based on kinetic, spectroscopic, and stereochemical evidences, offer a comprehensive view of the Stille reaction and support an *associative* model based on an L-for-R^2 substitution as the rate-determining step of the transmetalation reaction (in contrast with the proposal of a *dissociative* rate-determining step).[13,14]

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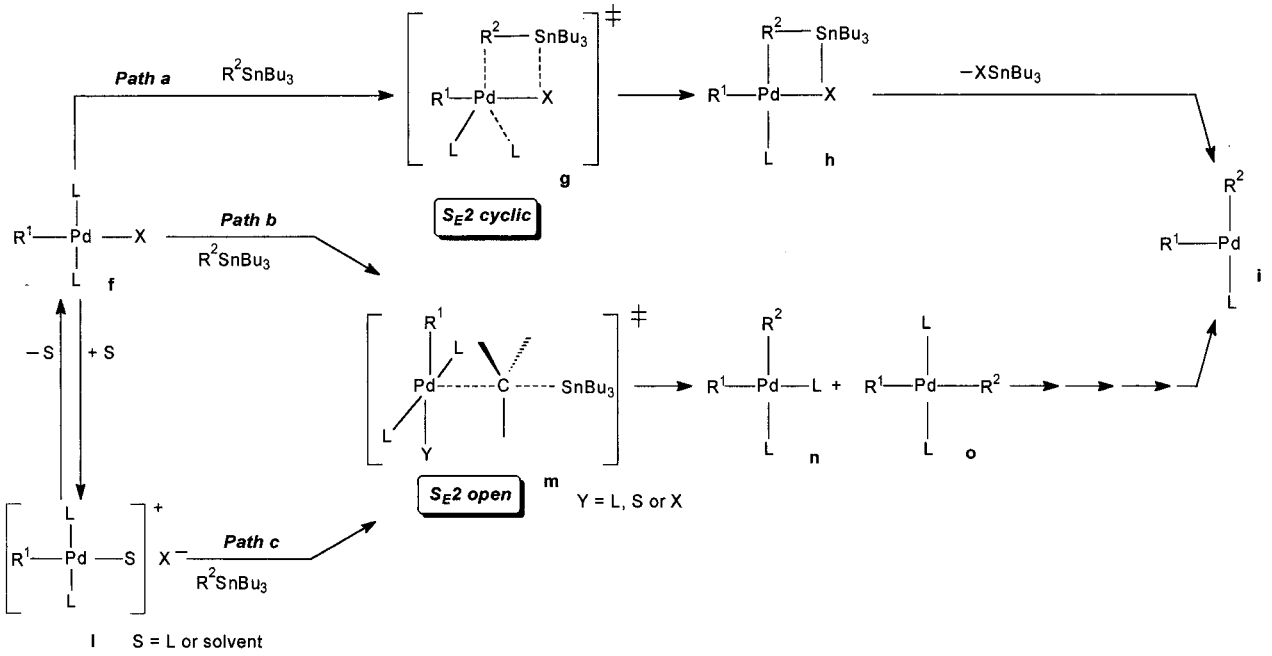
(22) Casado, A. L.; Espinet, P.; Gallego, A. M.; Martinez-Ilarduya, J. M. *Chem. Commun*. **2001**, 339.
(23) The possibility of a transmetalation process proceeding via a cyclic and/or an open transition state was first envisaged by Stille.[24]

Scheme 3 [a]



[a] Path a: X = halide, nonpolar, noncoordinating solvents. Paths b, c: X = halide, OTf; S = THF, PhCl, CH_2Cl_2, HMPA, NMP.

In this paper, we report the results of our studies on the transmetalation step in the palladium-catalyzed metal−carbon (M−C) coupling process. On the basis of (i) the spectroscopic observation of an adduct formed between the organostannane and the oxidative addition complex, (ii) the isolation (in a halobridged dimeric form) of an intermediate species resulting from ligand dissociation, and (iii) the analysis of consistent kinetic data, it is shown that the transmetalation reaction proceeds by two different mechanisms, which operate depending on the initial concentration of the oxidative addition complex.

Close analogies between the catalytic cycles of Pd-catalyzed carbon−carbon bond (Figure 1) and metal−carbon bond (Figure 2) formation become evident from comparison of our results with those reported in Farina's,[13] Hartwig's,[14] and Espinet's[11,21,22] studies.

Results and Discussion

The transmetalation reaction of this study is a transformation by which an arylethynyl group is transferred from tin to palladium.[25] The molybdenum complex **3**, that is, the product of the oxidative addition step of the catalytic cycle in Figure 2, has been used as substrate to study in detail the transmetalation process. The transformation of **3** into product **5** has been monitored by ^{31}P NMR spectroscopy, since both complexes bear two nonequivalent phosphorus moieties bound to palladium which exhibits two doublets ($J \cong 450$ Hz) characteristic of *trans* configuration around a square-planar metal center (Figure 3).

Different features were observed depending on the relative molar ratio between **3** and the tinacetylides **11a,b**. Upon treatment of **3** with a 3-fold excess of (phenylethynyl)tributyltin (**11a**), in DMF at 25 °C, a sequence of spectra shows the progressive decrease of the signals of the starting material and the simultaneous increase of the signals of the product (Figure 3, path a, red and blue, respectively).[29] In the reaction of **3** with a 10-fold excess of **11a**, two new narrow doublets ($J \cong 10$ Hz) appear along with the peaks of substrate and product, indicating the formation of a transient species (Figure 3, path b, green). The fact that this intermediate complex is observed only in the presence of a large excess of the reagent suggests that it is an adduct between complex **3** and the tinacetylide. This species appears during the time of conversion of **3** into **5** and is not detected at the end of the reaction. The strong variation of the ^{31}P NMR coupling constants, from ca. 450 Hz of complexes **3** or **5** to 10 Hz (see expansion in path b), indicates that the phosphorus ligands are still bound to the palladium center in the intermediate, while a severe change of the coordination geometry occurs during the transmetalation. On the basis of these facts, a tentative description of the intermediate complex is shown in Figure 3 as the five-coordinate structure **12**.

The proposal that the species **12** is an associative complex is supported by various considerations. (i) The tinacetylide compounds exhibit Lewis acid character and are prone to become five-coordinate, as in the case of intramolecular coordination of heteroligands.[30] (ii) The iodine atom of **3** offers an unshared electron pair to the Lewis acid center and may contribute to the association via a bridging halide.[31] (iii) π-Complexation between Pd and the acetylenic group is well known.[32] (iv) Finally, the palladium center of complex **3** suffers a severe distortion from the ideal square-planar geometry, as it was

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(25) The driving force of this metathesis reaction is provided by the difference in electronegativity of the two metals (Sn more electropositive than Pd)[26] as well as by the formation of the stable Bu_3SnI.[27,28]
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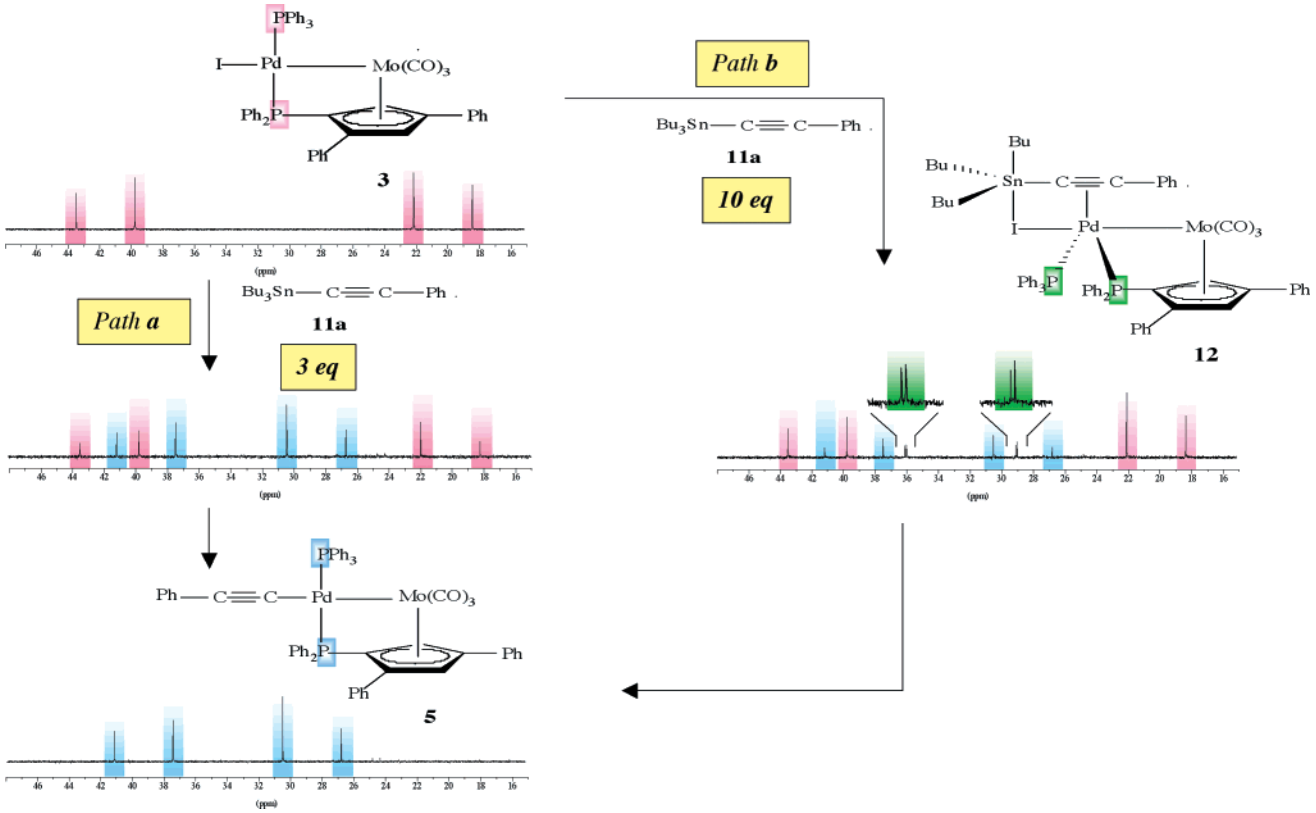

Figure 3. Transmetalation of complex **3** with tributyl(phenylethylnyl)tin (**11a**) followed by ^{31}P NMR spectroscopy. Path a: reaction of **3** with 3 equiv of **11a**. Path b: reaction of **3** with 10 equiv of **11a**.

determined by X-ray structural analysis,[9b] which makes pentacoordination a favorable process. Further support to our proposal comes from the structural analogy between **12** and the activated complex **g** of Scheme 3,[11,21] as well as from the structure of an associative intermediate observed by Cotter[33] in the course of a transmetalation reaction.

Kinetic and Spectroscopic Investigation of the Transmetalation Reaction by ^{31}P NMR: The Observation of Two Alternative Mechanisms. Reactions were carried out in DMF at 25 °C using complex **3** in the concentration range (1.5−4.5) × 10^{-2} M and at least a 10-fold excess of (phenylethynyl)tributyltin (**11a**), as to work under *pseudo* first-order conditions.[29] Disappearance of the substrate **3**, formation of the transmetalated product **5**, as well as of the intermediate **12** versus time are shown in Figure 4. The concentration of the intermediate species has already reached the highest value in the first spectrum after mixing. This indicates that the rate of formation of **12** is higher than the eventual back reaction or its transformation into **5**. Consumption of starting material was complete within 30 min and followed a first-order behavior. The analysis according to eq 1 yields a value of observed rate constant k_{obs} = 0.0021 s^{-1} ([**3**] = 0.045 M, [**11a**] = 0.47 M), and the corresponding plot of ln[**3**] versus time is linear. Values of k_{obs}

$$c_t = c_\infty + (c_0 - c_\infty)\exp(-k_{obs}t) \qquad (1)$$

for the disappearance of **3** under different conditions are reported in Table 1. At constant [**3**] = 0.023 M, k_{obs} increases upon increasing the concentration of (phenylethynyl)tributyltin, from 0.0026 s^{-1} (0.19 M) to 0.0042 s^{-1} (0.72 M), indicating rate

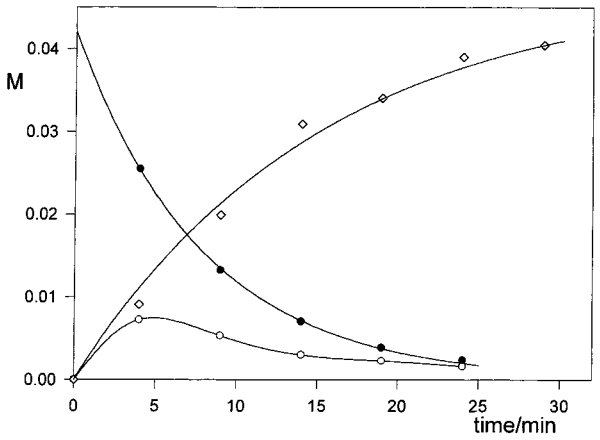

Figure 4. Reaction profile for the transmetalation step of complex **3** (0.045 M) with **11a** (0.47 M) in DMF-d_7 at 25 °C, obtained from the ^{31}P NMR signals of **3** (●, δ 22.0 ppm), **12** (○, δ 29.0 ppm), and **5** (◇, δ 30.5 ppm). The concentration values of the intermediate species **12** are only an estimate judged from peak intensities.

dependence on the concentration of the organostannane (entries 2−6, Table 1).

To evaluate the role of the triphenylphosphine ligand in the formation of the associative complex **12** and in the overall transmetalation process, measurements were performed in the presence of added PPh_3 (entry 9). The addition of PPh_3 (0.13 M) to the reaction of **3** (0.016 M) with **11a** (0.36 M) retards the consumption of the substrate and, to a greater extent, the

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(33) Cotter, W. D.; Barbour, L.; McNamara, K. L.; Hechter, R.; Lachicotte, R. J. *J. Am. Chem. Soc.* **1998**, *120*, 11016.

Table 1. Values of k_{obs} for the Reaction of Complex **3** with $Bu_3SnC{\equiv}CPh$ (**11a**), Obtained by ^{31}P NMR in DMF/DMF-d_7 at 25 °C

entry	**3** (M)	**11a** (M)	k_{obs} (s^{-1})
1	0.45	0.47	0.0021
2	0.023	0.19	0.0026
3	0.023	0.23	0.0026
4	0.023	0.33	0.0036
5	0.023	0.68	0.0041
6	0.023	0.72	0.0042
7	0.015	0.72	too fast
8	0.015	0.16	too fast
9	0.016	0.36 (+PPh_3 0.13 M)	very slow

conversion of the intermediate **12** into **5**. As a consequence, the species **12** accumulates in solution, where it is observed as the main component (Figure 5).

This experiment suggests that triphenylphosphine must temporarily dissociate from complex **12** (and re-enter in a subsequent step) to allow formation of **5** (vide infra). The dissociation step becomes rate limiting in the overall transmetalation reaction.

A rate dependence was observed on the initial concentration of complex **3**. At the same concentration of (phenylethynyl)-tributyltin (0.72 M) used in the experiment of entry 6, or lower (0.16 M), and [**3**] = 0.015 M, rather than 0.023 M, the reaction becomes too fast to be followed by ^{31}P NMR spectroscopy (entries 7, 8). This inverse dependence of the reaction rate on the initial concentration of **3** is also evident from comparison of the k_{obs} value of entry 1 with those of entries 4 and 5, where higher rates correspond to lower [**3**]. These results suggest that the true species which undergoes transmetalation is generated from **3** upon dilution. ^{31}P NMR spectra obtained upon increased dilution of **3**, in DMF, are shown in Figure 6, where traces a, b, and c correspond to different concentrations of the complex (a = 0.029 M, b = 0.0019 M, c = 0.0010 M). The clean doublet of doublets of the two nonequivalent phosphorus atoms in a *trans* configuration around palladium is displayed in trace a. In the more dilute sample b, a new peak appears at δ 51.9 ppm. This becomes the main species in solution c. The change from the doublet of doublets, relative to structure **3**, into a singlet accounts for the formation of a new species in which the two phosphorus atoms are no longer interacting. These experimental observations are in agreement with an equilibrium, described by eq 2,

$$K = \frac{c\alpha^2}{1-\alpha} \qquad (2)$$

which involves a substitution of ligand (PPh_3) by solvent (DMF) to form the species **13**, as represented in Scheme 4. The signal of free triphenylphosphine is not detectable under these conditions.[34]

Trace d is the spectrum obtained upon addition of an excess of triphenylphosphine to the solution of trace c (Figure 6). Disappearance of the signal at δ 51.9 ppm and formation of the original doublet of doublets of complex **3** account for the reverse reaction of Scheme 4. The formation of **13** accounts

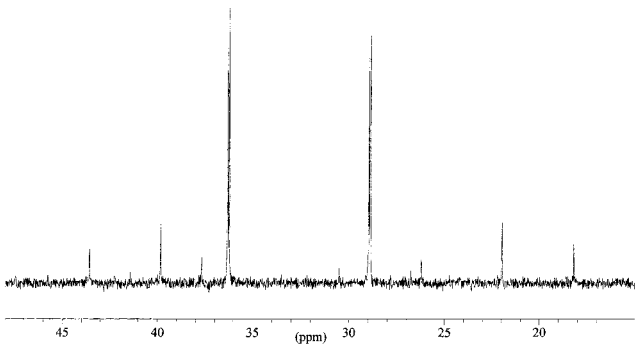


Figure 5. ^{31}P NMR spectrum recorded during transmetalation of **3** with **11a** in the presence of a 10-fold excess of PPh_3. Accumulation of the intermediate **12**.

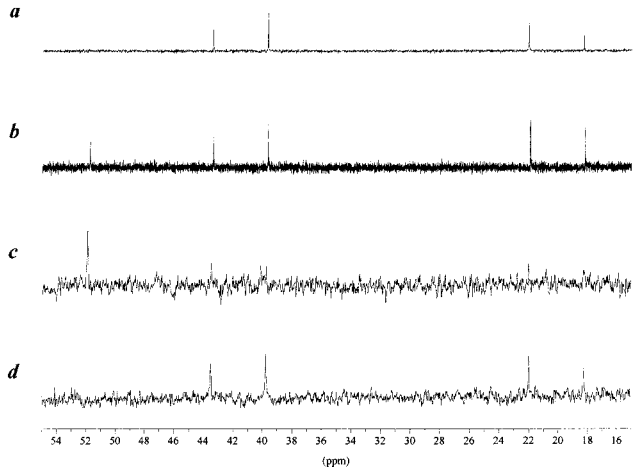
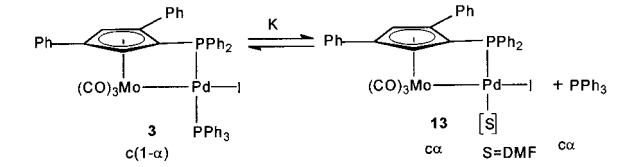


Figure 6. ^{31}P NMR spectra of complex **3** at different concentrations in DMF/DMF-d_7. Trace a, [**3**] = 0.029 M; trace b, [**3**] = 0.0019 M; trace c, [**3**] = 0.0010 M; trace d, solution of trace c after addition of excess PPh_3.

Scheme 4



for the inverse dependence of k_{obs} on the initial concentration of **3**. In diluted solutions, complex **13** is the main species and may react faster than **3** with the tin reagent, because of its higher electrophilic character.[35] The reactivity of the solvent-coordinate species **13** was investigated by addition of (phenylethynyl)-tributyltin (**11a**) to the solution of trace b. The signal at δ 51.9 ppm immediately disappears upon addition, and this is followed by a slower change of **3** into **5**.

The lability of the triphenylphosphine ligand in complex **3** was confirmed by its fast and complete replacement upon treatment of **3** with tributylphosphine.[36]The course of the transmetalation reactions of complexes bearing different L, with

(34) According to the dissociative equilibrium presented in Scheme 4, the ^{31}P NMR spectra a–c of Figure 7 should reveal the presence of free triphenylphosphine. It is possible that the rate of exchange of triphenylphosphine with the solvent on palladium is too fast with respect to the NMR time scale. Occasionally, a peak at δ 26.1 ppm, along with that at δ 51.9 ppm, appeared in progressively diluted samples of **3**. By comparison with an authentic sample, this new peak was identified as being due to triphenylphosphine oxide, which formed by adventitious oxidation of free PPh_3 released from **3**.

(35) Substitution of a good donor ligand such as PPh_3 by a solvent molecule is expected to increase the electrophilic character of palladium and hence to increase its reactivity.

(36) The ^{31}P NMR spectrum of a solution of **3** in DMF/DMF-d_7 in the presence of PBu_3 showed immediate and complete exchange of the phosphine ligand, as indicated by the replacement of the signals of **3** (trace a of Figure 7) with a new doublet of doublets (δ 35.1, d; −0.45, d; J = 468 Hz).

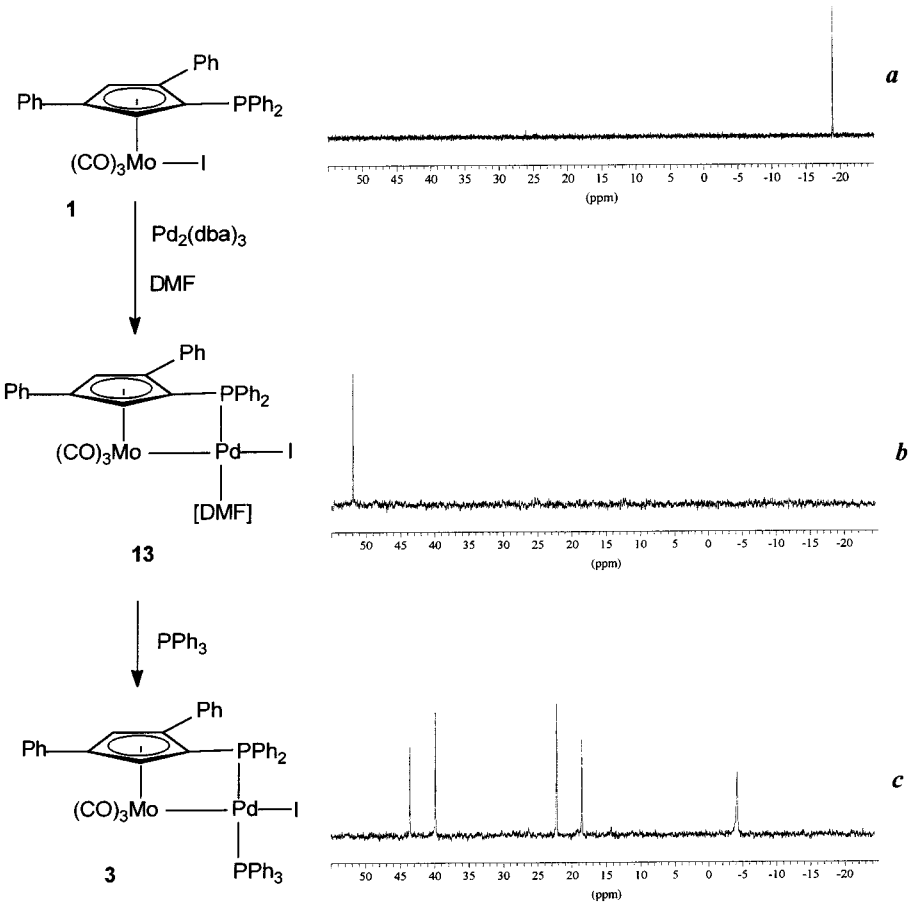


Figure 7. ^{31}P NMR evidence of the formation of the solvent-coordinate species **13** by reaction of complex **1** with $Pd_2(dba)_3$, and subsequent conversion of **13** into the oxidative addition intermediate **3** by reaction with PPh_3.

respect to **3**, gave further information on the role of the phosphine ligand.[37] At room temperature, both the tributyl- and trimethyl-phosphine derivatives **15** and **16** remain inert in the presence of an excess of (phenylethynyl)tributyltin. The onset of the transmetalation reaction is observed only at 65 °C, and several hours are required for completion. PBu_3 and PMe_3 are good donor ligands which have a smaller cone angle and a higher dissociation energy than does PPh_3.[37]

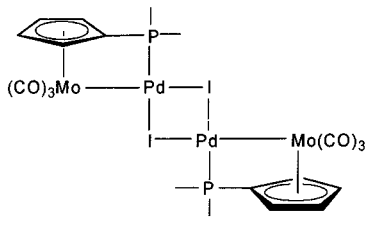
We attempted the direct synthesis of the solvent-coordinate species **13**. A preliminary investigation was carried out by following the ^{31}P NMR spectra of the reaction of **1** with 1 equiv of $Pd_2(dba)_3$ (dba = 1,5-diphenyl-1,4-pentadiene-3-one) in DMF (Figure 7). The singlet peak of **1** at δ −18.9 ppm (trace a) is replaced by a new peak at δ 51.9 ppm (trace b). By addition of PPh_3 to this mixture, the latter is immediately and completely converted into the doublet of doublets characteristic of **3** (trace c). This experiment shows that the solvent-coordinate species **13** (δ 51.9 ppm) can be either obtained from **3** by loss of PPh_3 (Scheme 4) or prepared independently by reaction of **1** with a zerovalent palladium complex in a coordinating solvent, *in the absence* of phosphorus ligands. The synthesis of **13** was then attempted on a preparative scale. Despite the complete formation of **13** observed by ^{31}P NMR, the workup of the reaction afforded instead the dimeric halobridged complex [η^5-(1-Ph_2P-2,4-Ph_2)-C_5H_2]$(CO)_3$MoPd(μ-I)$_2$PdMo$(CO)_3$[η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2] (**14**).[38]

The identification of the associative complex **12** and the existence of the solvent-coordinate species **13** (isolated in the halobridged dimeric form **14**) in diluted solutions indicate that the transmetalation reaction of complex **3** occurs by two distinct pathways. In this respect, the system of this study shows a close analogy with the dual pathway scheme found by Espinet for the transmetalation step of the Pd-catalyzed C−C bond-formation process (Scheme 3).

Kinetic and Spectroscopic Measurements by UV−Vis Spectrophotometry. UV−vis spectrophotometry has been used as a complementary technique to obtain more information on this complex phenomenon, in particular to observe the process in the low concentration range of substrate, where **13** is most likely the dominant or only species in solution. A series of UV−vis spectra of complex **3** in DMF were obtained in the concentration range $2.9 \times 10^{-5} - 1.0 \times 10^{-2}$ M. The intensity of a shoulder absorption with λ_{max} = 470 nm increases linearly

(37) Luo, L.; Nolan, S. P. *Organometallics* **1994**, *13*, 4781.

(38) During the preparation of this manuscript, a complex closely related to **14** was characterized by X-ray structural analysis.[39] The structure shows the existence of a halo-bridged dimeric form of two coordinatively unsaturated palladium moieties.



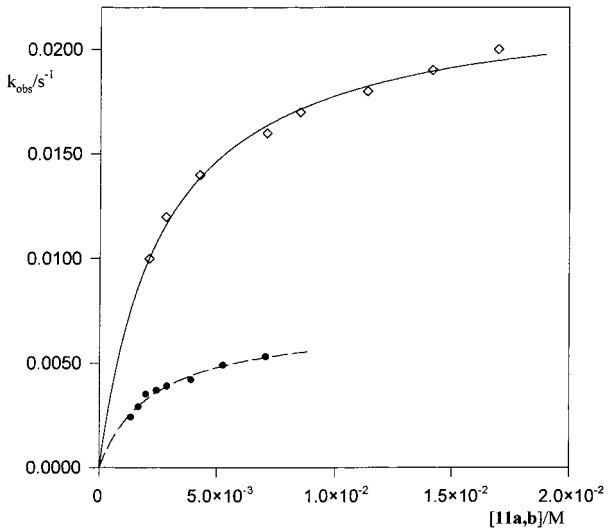


Figure 8. Plot of k_{obs} vs alkynylstannane concentration for the reactions of **3** (1.67×10^{-4} M) with **11a** (◇) and **11b** (●).

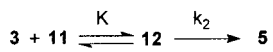
with concentration only up to [**3**] ≅ 1×10^{-3} M, while a downward deviation occurs at higher concentrations. This is indicative of a change in the nature of **3** with concentration, in analogy with the ^{31}P NMR studies.

The UV−vis spectra of the starting material **3** and of product **5** were recorded in DMF solutions at identical concentrations (1.7×10^{-4} M) to find the optimal conditions for kinetic measurements. Complex **3** is characterized by an intense band with $\lambda_{max} = 400$ nm ($\epsilon = 15\,117$ M^{-1} cm^{-1}), and complex **5** is characterized by a shoulder of smaller intensity ($\epsilon = 4\,586$ M^{-1} cm^{-1}) at the same wavelength.

The reaction of **3** (1.67×10^{-4} M) with $Bu_3SnC{\equiv}CPh$ (2.14×10^{-3} M) in DMF was monitored at 400 nm (25 °C). The process is characterized by a rapid decay of absorbance, which follows a first-order behavior ($k_{obs} = 0.010$ s^{-1}). This is followed by a slower increase, which is due to the reductive elimination reaction of complex **5**, favored by the excess of tinacetylide.[9c,40]

Effect of Concentration and Nature of the Organostannane. Kinetic measurements were obtained at different concentrations of $Bu_3SnC{\equiv}CPh$, and [**3**] = 1.67×10^{-4} M, using at least a 10-fold molar excess of stannane to ensure *pseudo* first-order conditions. A plot of k_{obs} values versus [**11a**] shows a saturation behavior (Figure 8) where the rate constants tend toward a limiting value ($k = 0.023$ s^{-1}). This is typical of a reaction proceeding through formation of kinetically detectable intermediates. Among the possible mechanisms which describe this phenomenon, one involves the formation of a molecular complex of substrate and reagent followed by rate-determining coupling between the two species,[42] and one involves rearrangement of the substrate in the first step followed by attack of the reagent.[43] Discrimination between the two alternative mechanisms is possible by varying the nature of the tinacetylide, which is expected to influence the limiting value of k_{obs} in case of rate-determining transformation of a molecular complex.

Scheme 5



A series of kinetic measurements performed using $Bu_3SnC{\equiv}C$ (*p*-Cl−C_6H_4) (**11b**) as the transmetalating agent also exhibit a saturation behavior, as observed for $Bu_3SnC{\equiv}CPh$, and yield a different extrapolated value of k_{obs} (0.0070 s^{-1}) (Figure 8). These data are therefore described by eq 3,

$$k_{obs} = \frac{K k_2 [\mathbf{11}]}{1 + K[\mathbf{11}]} \qquad (3)$$

in which K represents the equilibrium constant for formation of an associative complex between **3** and the tin reagent and k_2 is the rate constant of the transmetalation step, according to Scheme 5. The fitting between eq 3 and the experimental points is also shown in Figure 8. These results indicate that the transmetalation reaction occurs through a multistep mechanism characterized by a fast pre-equilibrium between substrate and tinacetylide to form an associative intermediate species, which slowly evolves toward the product. The kinetic analysis yields the values of the equilibrium constant between complex **3** and each of the tinacetylide species, which are K = 376 M^{-1} for $Bu_3SnC{\equiv}CPh$ and K = 430 M^{-1} for $Bu_3SnC{\equiv}C$(*p*-Cl−C_6H_4). The *p*-substituent in the aryl ring of the tinacetylide affects the rate of the transmetalation step (k_2) but does not influence the pre-equilibrium (K).

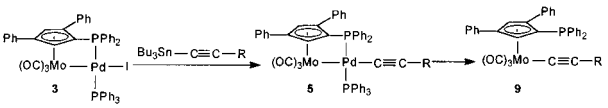
Rate Dependence on the Concentration of Complex 3. Rate measurements of the reaction with $Bu_3SnC{\equiv}CPh$ (1.14×10^{-2} M) were obtained using different solutions of complex **3** in DMF (in the range $10^{-5} - 10^{-3}$ M). A plot of k_{obs} versus [**3**] shows the inverse dependence of the rate constant on the initial concentration of the complex.

These results, in analogy with the ^{31}P NMR experiments, suggest that the transmetalation reaction proceeds via the solvent-coordinated species **13** of Scheme 4. The higher reactivity of complex **13** with respect to the phosphine-substituted complex **3** may be due to the higher electrophilic character of the palladium center when coordinated by a poor donor ligand such as DMF. As a consequence, the transmetalation rate increases with increasing dilution of **3**, which shifts the equilibrium of Scheme 4 versus **13**.

The halobridged dimeric complex **14**, which was obtained in the attempt to synthesize and isolate complex **13**, represents a useful precursor of the DMF-substituted reactive species.[44] A simple ^{31}P NMR experiment showed the connection between complexes **14** and **13**. The addition of DMF to a solution of pure **14** in $CDCl_3$ (δ 50.1 ppm) causes the appearance of a new signal at δ 50.8 ppm, which increases in intensity, with respect

(39) Ricci, A.; Angelucci, F.; Masi, D.; Bianchini, C.; Lo Sterzo, C., manuscript in preparation.

(40) To confirm this sequence, the reaction of **3** (0.015 M) with $Bu_3SnC{\equiv}CPh$ (0.17 M) in DMF was monitored by ^{31}P NMR spectroscopy. Following the fast disappearance of the doublet of doublets due to **3** and its replacement by the signals of **5**, a new peak at δ −20.2 ppm due to the reductive elimination product **9** appears and slowly rises in intensity with time.[41]



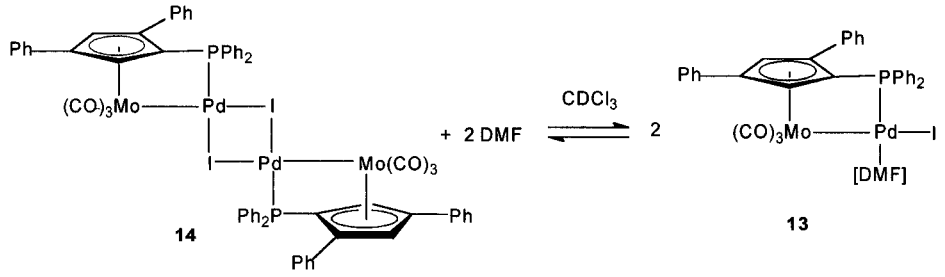
(41) In our former ^{31}P NMR studies, forcing conditions (80 °C) were necessary to induce the reductive elimination process ([**3**] = ∼0.1 M).[9c] In the present work, complex **3** (0.015 M) spontaneously evolves toward reductive elimination. This is also an indication that the rate of reductive elimination may show an inverse dependence on the initial concentration of **3**.

(42) Jenks, W. P. *Catalysis in Chemistry and Enzimology*; McGraw-Hill: New York, 1969; p 572.

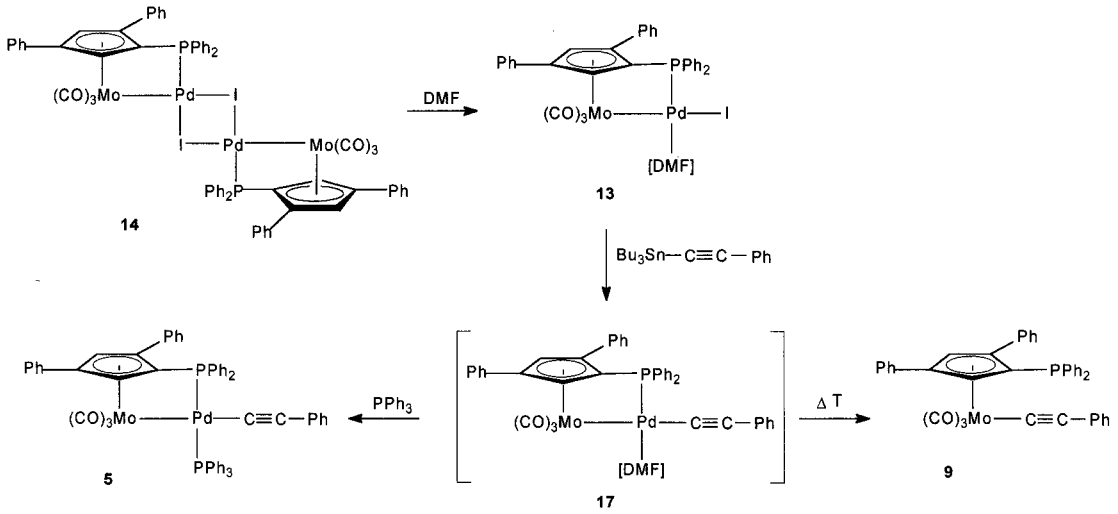
(43) Butler, I. S.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1967**, *6*, 2074.

(44) The structure and the reactive behavior of species **13** and **14** are similar to those of a dimeric halobridged oxidative addition intermediate previously described by Hartwig,[14b] which was isolated as a dimer, but found to react in the catalytic cycle as a monomer.

Scheme 6



Scheme 7



to that of the halobridged dimeric complex, upon further addition of DMF.[45] This new peak is due to the formation of the solvent-coordinated species **13**, which forms by attack of DMF to the halobridged dimer **14** (Scheme 6).

The interaction of DMF with complex **14** was studied further by UV−vis spectroscopy. Figure 9 shows the spectra of solutions of **14** at identical concentrations (3.1×10^{-5} M) in CH_2Cl_2 and in DMF. The different patterns of the two spectra indicate that different species exist in the two solvents, in particular that the dimeric complex **14** exists as such in the noncoordinating solvent CH_2Cl_2, while the solvent-coordinate species **13** forms in the donor solvent DMF.[46]

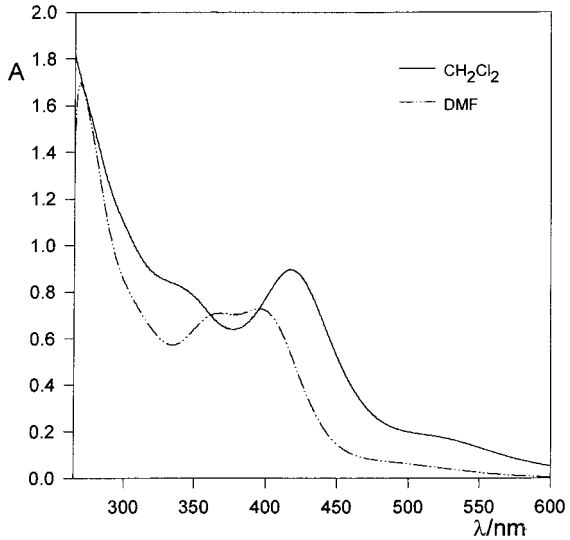


Figure 9. UV−vis spectra (250−600 nm) of complex **14** (3.1×10^{-5} M) in CH_2Cl_2 (−EnDash) and in DMF (−••−••).

Further ^{31}P NMR experiments have shown the involvement of complex **13** in the catalytic cycle of the palladium catalyzed metal−carbon bond-formation process. After dissolving complex **14** in DMF, the appearance of the ^{31}P NMR signal at 51.9 ppm indicates the immediate formation of the solvent-coordinated species **13**. This signal disappears upon addition of an 8-fold excess of $Bu_3SnC{\equiv}CPh$, while two peaks of equal intensity are found at δ 1.1 and 2.2 ppm. Subsequent addition of PPh_3 produced a slow conversion of these signals into the typical doublet of doublets of the transmetalated product **5**. This experiment indicates that the PPh_3-deficient species **13** undergoes transmetalation upon treatment with tinacetylides as well as it does with the corresponding PPh_3-coordinate complex **3**. In fact, the new species characterized by the signals at δ 1.1 and 2.2 ppm can be envisaged as the transmetalated intermediate **17**, which converts into the PPh_3-coordinate complex **5** upon addition of the phosphine (Scheme 7). When the PPh_3-deficient species **17** is warmed overnight at 60 °C, the total conversion into the reductive elimination product **9** is achieved.[47] Therefore, the intermediate complex **17** can transform directly into the reductive elimination product, also in the absence of PPh_3.

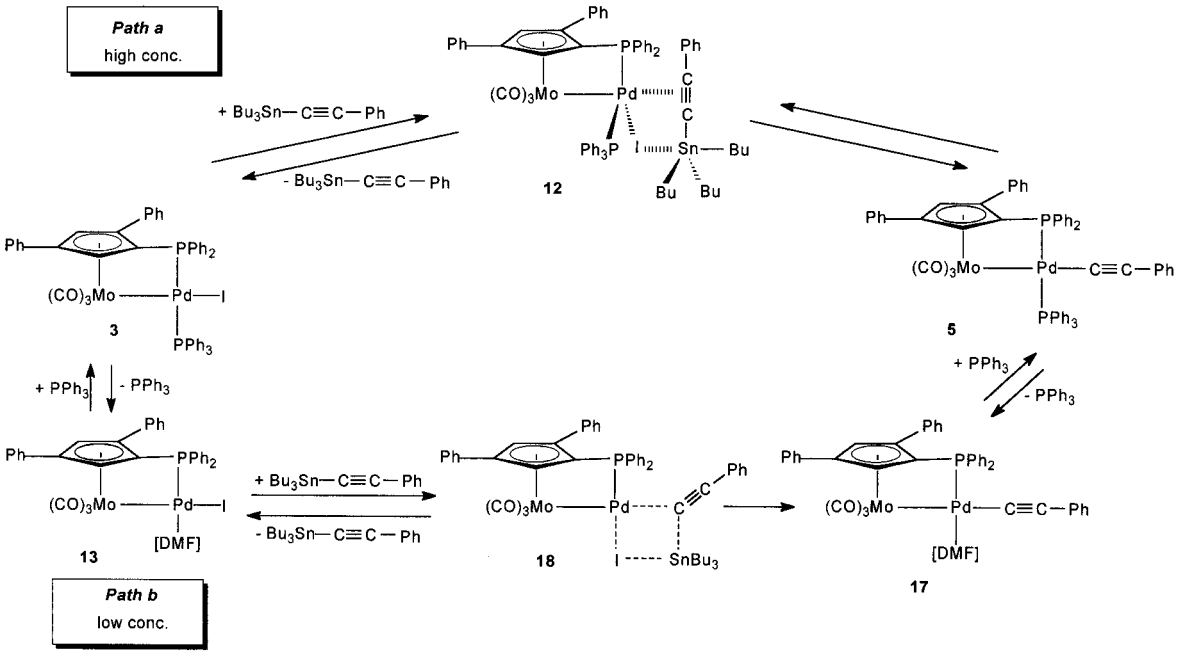
Kinetic experiments were performed on the reaction of $Bu_3SnC{\equiv}CPh$ with complex **14** in DMF, which generates **13** in situ. Values of k_{obs} identical within experimental error were

(45) Complex **14** dissolved in pure DMF is converted quantitatively into **13**, which shows a peak at δ 51.9 ppm in the ^{31}P NMR spectrum. The slight difference found for the chemical shift of **13** generated by addition of DMF into a $CDCl_3$ solution of **14** may be due to a solvent effect.

(46) The intense color of the CH_2Cl_2 solution with respect to the DMF solution and the band at $\lambda_{max} = 420$ nm might be due to a higher conjugation in **14** than that in **13**. Moreover, the spectrum profile of **13** obtained by dissolving **14** in DMF is the same as the spectra of **13** generated by increased dilution of **3** in DMF.

(47) Angelucci, F.; Ricci, A.; Lo Sterzo, C.; Masi, D.; Bianchini, C.; Bocelli, G., manuscript in preparation.

Scheme 8. Full Reaction Scheme for the Transmetalation of **3** with **11a**[a]



[a] Path a: reaction via the metallacycle intermediate **12**. Path b: reaction via the solvent-coordinate species **13**.

Table 2. Values of k_{obs} for the Reaction of **14** with **11a**, Obtained by UV−Vis Spectroscopy in DMF at 25 °C

entry	**14** (M)	**11a** (M)	k_{obs} (s^{-1})
1	3.4×10^{-5}	2.7×10^{-3}	0.034
2	1.7×10^{-5}	2.7×10^{-3}	0.036
3	3.4×10^{-5}	6.8×10^{-3}	0.057
4	1.7×10^{-5}	6.8×10^{-3}	0.056

obtained using two DMF solutions of **14** (3.4×10^{-5} and 1.7×10^{-5} M; [$Bu_3SnC{\equiv}CPh$] = 2.7×10^{-3} M; Table 2, entries 1 and 2). The reaction rate constants increased upon increasing the concentration of $Bu_3SnC{\equiv}CPh$ (6.8×10^{-3} M)[48] and were again identical at two different concentrations of **14** (entries 3 and 4). Therefore, the transmetalation rate is independent of the initial concentration of **14**, in contrast with the behavior of the PPh_3-substituted complex **3**. In this case, de-coordination of PPh_3 to form complex **13** precedes the transmetalation process.

Conclusions

The overall mechanistic picture which comes out of this work is described in Scheme 8. We have shown that the transmetalation reaction of the oxidative addition complex [η^5-(1-Ph_2-P-2,4-Ph_2)C_5H_2]$(CO)_3$MoPd(PPh_3)I (**3**) with tributyltinarylacetylides proceeds by two pathways (paths a and b), depending on the initial concentration of **3**.

In concentrated solutions of complex **3** ($\cong 10^{-2}$ M), transmetalation occurs through the formation of the intermediate species **12**, which is an associative complex between **3** and the organostannane (path a of Scheme 8). The essential feature of **12** is the cyclic structure resulting from the simultaneous interaction of the palladium and iodine atoms of **3** with the tin atom and the acetylenic moiety of the organostannane. Evolution of complex **12** toward the product of transmetalation **5** is strongly retarded by addition of an excess of PPh_3, which favors the accumulation of **12**.[49]

When transmetalation is performed using **3** in lower concentrations ($\cong 10^{-4}$ M) (path b of Scheme 8), the reaction proceeds through formation of a highly reactive solvent-coordinate species (**13**), in which the palladium center has gained a stronger electrophilic character, due to the substitution of a good donor ligand (PPh_3) by DMF. Since a competing exchange between PPh_3 and DMF accounts for the equilibrium between **3** and **13**, formation of the latter species is favored in dilute solutions, and, as a consequence, the reaction rate is inversely dependent on the initial concentration of complex **3**. In contrast, when the PPh_3-deficient halobridged dimeric complex [{η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2}$(CO)_3$MoPdI]$_2$ (**14**) is dissolved in DMF, it is converted immediately and quantitatively into the solvent-coordinated species **13**. Under these conditions, the transmetalation rate is independent of the initial concentration of **14**, due to the absence of PPh_3.

The transmetalation in the reaction of **13** occurs through an association complex with the organostannane (**18**), which has been kinetically detected. It is evident that path a, involving the formation of the metallacycle complex **12**, closely resembles the "S_E2 cyclic" mechanism proposed by Espinet[11,21,22] for the transmetalation step in the coupling of aryl halides with organostannanes (path a of Scheme 3). However, it should be taken into account that the key species **g** of the "S_E2 cyclic" mechanism of Scheme 3 is an activated complex, while the metallacycle complex **12** of this work is a true intermediate

(48) In entry 1, the [$Bu_3SnC{\equiv}CPh$]/[**13**] ratio is ca. 80, while in entry 3 the relative ratio is 200.

(49) Although a significant amount of **12** is formed in solution (path b in Figure 3) and, in the presence of an excess of PPh_3 (~8:1) and $Bu_3SnC{\equiv}CPh$ (~20:1), **12** represents the main component in solution (Figure 7), its characterization is mainly based on ^{31}P NMR evidence. Attempts to obtain ^{13}C NMR and ^1H NMR data of **12** are frustrated by the overwhelming intensities of signals of PPh_3 and $Bu_3SnC{\equiv}CPh$ that must be used in large excess to maximize its formation. However, a FT-IR analysis of the reaction mixture under similar conditions shows a band at $\nu = 2105$ cm^{-1}, which may account for π-coordination of the alkyne at Pd (ν ($Bu_3SnC{\equiv}CPh$) = 2132 cm^{-1}).

which can accumulate in solution as the main reaction component. However, the transmetalation mechanism of path b in Scheme 8, involving the formation of the highly reactive solvent-coordinate species **13**, is related to Espinet's "S_E2 open" mechanism, which occurs when the cyclic mechanism is disfavored by reaction conditions (paths b and c of Scheme 3). In this respect, it is worth mentioning that the intermediate **13** is an analogous species of the solvent-coordinate complex **c** proposed by Farina (Scheme 2).[20] In fact, a preliminary L-for-S (PPh_3 vs DMF) exchange occurs in complex **3** to form **13**, followed by an I-for-R^2 exchange, most likely preceded by an initial π-coordination of the alkynyl stannane on palladium. This sequence of events follows closely the one proposed by Farina (paths a−d, Scheme 2). Therefore, the results found in this work are characterized by clear analogies with mechanistic studies of the carbon−carbon coupling process and offer a unifying view of previous contradictory interpretations,[11,13,14,21,22] with the understanding that different systems have been investigated.

In conclusion, this work confirms our early supposition of similar mechanistic features between the palladium-catalyzed metal−carbon (M−C) bond-formation and the carbon−carbon (C−C) bond-formation processes.[9,50] In this respect, because of the fortunate design of the model substrates **1** and **2**, and the easy access to the stable, but still reactive, oxidative addition and transmetalated derivatives **3**−**6**, further investigations on this palladium-catalyzed process can be foreseen. Such studies may clarify the factors affecting the metal−carbon bond-formation reaction, as well as shed light on unclear aspects of the carbon−carbon coupling itself, a phenomenon of paramount importance in synthetic organic chemistry.

Experimental Section

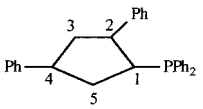
General Procedures. Elemental analyses were performed by the Servizio Microanalisi of the Dipartimento di Chimica, Università di Roma "La Sapienza". IR spectra were recorded on a FT-IR Nicolet 510 instrument in the solvent subtraction mode, using a 0.1 mm CaF_2 cell. UV−visible spectra were measured on a Perkin-Elmer Lambda 18 spectrophotometer. The kinetic measurements were performed on a Hewlett-Packard Vectra XM spectrophotometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC300P spectrometer at 300, 75, and 121 MHz, respectively. Chemical shifts (ppm) are reported in δ values relative to Me_4Si; for ^{1}H NMR, $CHCl_3$ (δ 7.24) or DMF (δ 2.90), and for ^{13}C NMR, $CDCl_3$ (δ 77.0) were used as internal standards. The ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. Mass spectra were obtained on a Fisons Instruments VG-Platform Benchtop LC-MS (positive ion electrospray, ESP^+) spectrometer. Solvents, including those used for chromatography, were thoroughly degassed before use. Chromatographic separations were performed with 70−230 mesh silica gel (Merck).

All manipulations were carried out under an atmosphere of argon with Schlenk type equipment on a dual manifold/argon vacuum system. Liquids were transferred by syringe or cannula. THF and Et_2O were distilled from sodium−potassium alloy; DMF was distilled from CaH_2 under reduced pressure.

Bu_3SnNEt_2[51] [η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2](CO)$_3$MoI (**1**),[9b] [η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2](CO)$_3$MoPd(PPh_3)I (**3**),[9b] and HC≡C(*p*-Cl−C_6H_4)[52] were prepared according to published procedures. [η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2](CO)$_3$MoPd(PPh_3)C≡CPh (**5**) was prepared by adapting our previously described procedure for the *p*-NO_2 derivative.[9b]

$Pd_2(dba)_3$ (Aldrich), PPh_3 (Aldrich), PBu_3 (Aldrich), PMe_3 (1 M in THF, Aldrich), and Bu_3Sn−C≡C−Ph (Aldrich) were used as received.

Legend for ^{13}C NMR spectra:



[η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2](CO)$_3$MoPd(PBu_3)I (15). A 100 mL Schlenk flask was loaded with [η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2](CO)$_3$MoI (**1**)·0.4CH_2Cl_2 (0.50 g, 0.67 mmol) and $Pd_2(dba)_3$ (0.34 g, 0.37 mmol). After three cycles of vacuum/argon, THF (20 mL) and PBu_3 (0.17 mL, 0.68 mmol) were added, causing the formation of a deep red solution. After stirring (1 h, room temperature), approximately 20 g of Celite was added to the reaction mixture, and the solvent was removed under vacuum. The residue was chromatographed on a silica column (40 cm × 3 cm). Elution with hexane/dichloromethane 7/3 allowed the separation of a pale yellow band, which was discarded. Further elution with hexane/dichloromethane 6/4 yielded a red band, which was collected to give, after removal of the solvent, 0.56 g (82%) of (**15**) as a red solid. A sample suitable for microanalysis was obtained by crystallization from THF/pentane (vapor diffusion) at room temperature. ^{1}H NMR ($CDCl_3$): δ_H 8.42−8.36 (m), 7.68−7.61 (m), 7.55−7.51 (m), 7.26−7.24 (m), 7.21−7.17 (m), 7.02−6.90 (m), 6.82−6.75 (m), 6.15 (t, 1H, J = 2.1 Hz, Cp−*H*), 4.57 (t, 1H, J = 2.1 Hz, Cp−*H*), 2.22−2.16 (m, 6H, P(C*H*$_2$CH$_2$CH$_2$CH$_3$)$_3$), 1.59−1.52 (m, 6H, P(CH$_2$C*H*$_2$-CH$_2$CH$_3$)$_3$), 1.47−1.40 (m, 6H, P(CH$_2$CH$_2$C*H*$_2$CH$_3$)$_3$), 0.93 (t, 9H, J = 7.1 Hz, P(CH$_2$CH$_2$CH$_2$C*H*$_3$)$_3$). ^{31}P NMR ($CDCl_3$): δ_P 35.13 (d, J = 469 Hz, −*P*Ph$_2$), −1.93 (d, J = 469 Hz, *P*Bu$_3$). ^{13}C NMR ($CDCl_3$): δ_C 236.2, 225.5, 225.3 (*C*O), 137.4−125.6 (*Ph*), 120.0 (d, J_{C-P} = 9.8 Hz, *C*$_2$), 110.9 (d, J_{C-P} = 7.3 Hz, *C*$_4$), 95.1 (d, J_{C-P} = 6.1 Hz, *C*$_3$), 90.2 (d, J_{C-P} = 7.3 Hz, *C*$_5$), 58.8 (d, J_{C-P} = 36.6 Hz, *C*$_1$), 26.7 (−CH$_2$-CH$_2$CH$_2$CH$_3$), 24.7 (d, J_{C-P} = 12.2 Hz, −*C*H$_2$CH$_2$CH$_2$CH$_3$), 24.4 (d, J_{C-P} = 2.4 Hz, −CH$_2$*C*H$_2$CH$_2$CH$_3$), 13.8 (−CH$_2$CH$_2$CH$_2$*C*H$_3$). FT-IR (CH_2Cl_2, cm^{-1}): 1959.8 (s), 1868.5 (s) (ν_{CO}). Anal. Calcd for $C_{44}H_{49}IMoO_3P_2Pd$: C, 51.96; H, 4.86. Found: C, 52.02; H, 4.88. MS (15 V, ESP^+) = *932* (M^+ − 3CO).

[η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2](CO)$_3$MoPd(PMe_3)I (16). A Schlenk flask was loaded with [η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2](CO)$_3$MoI (**1**)·0.4CH_2Cl_2 (0.31 g, 0.41 mmol) and $Pd_2(dba)_3$ (0.21 g, 0.23 mmol). After three cycles of vacuum/argon, the addition of THF (20 mL) and PMe_3 (1 M in THF, 0.4 mL, 0.82 mmol) produced a dark solution with yellow reflections. The mixture was stirred for 30 min, and then solvent and excess PMe_3 were removed by vacuum transfer. The resulting solid was dissolved in CH_2Cl_2, adsorbed on Celite, and chromatographed on a silica column (40 cm × 3 cm). Elution with hexane/dichloromethane 7/3 separated a pale yellow band, which was discarded. Further elution with hexane/dichloromethane 1/1 gave an orange band, which was eluted and collected. Evaporation to dryness left 0.32 g (88%) of (**16**) as an orange solid. The product was crystallized from THF/pentane (vapor diffusion) at room temperature. ^{1}H NMR ($CDCl_3$): δ_H 8.36−8.30 (m), 7.76−7.70 (m), 7.58−7.48 (m), 7.27−7.24 (m), 7.22−7.15 (m), 7.02−6.96 (m), 6.93−6.89 (m), 6.79−6.77 (m), 6.18 (t, 1H, J = 2.1 Hz, Cp−*H*), 4.60 (t, 1H, J = 2.1 Hz, Cp−*H*), 1.73 (dd, 9H, J^1_{P-H} = 9.5 Hz, J^2_{P-H} = 3.0 Hz, P(C*H*$_3$)$_3$). ^{31}P NMR ($CDCl_3$): δ_P 33.96 (d, J = 502 Hz, −*P*Ph$_2$), −15.19 (d, J = 502 Hz, *P*(CH$_3$)$_3$). ^{13}C NMR ($CDCl_3$): δ_C 235.9, 225.6, 224.9 (*C*O), 137.0−125.6 (*Ph*), 119.8 (d, J_{C-P} = 9.0 Hz, *C*$_2$), 111.0 (s, *C*$_4$), 94.7 (d, J_{C-P} = 5.4 Hz, *C*$_3$), 90.0 (d, J_{C-P} = 12.6 Hz, *C*$_5$), 59.9 (d, J_{C-P} = 37.7 Hz, *C*$_1$), 16.1 (d, J_{C-P} = 23.3 Hz, −*C*H$_3$). FT-IR (CH_2Cl_2, cm^{-1}): 1959.1

(50) Because the analogy between the two Pd-catalyzed processes is legitimate, it is worth mentioning that our early reports on the preparation of the transmetalated complex **5** and other similar derivatives[9b,c] indeed represent the first examples of observation and characterization of a transmetalated intermediate in a Stille-like catalytic cycle. Overlooking these papers, other authors have later claimed their reports as unprecedented.[11,12f,32]

(51) Jones, K.; Lappert, M. F. *J. Chem. Soc.* **1965**, 1944.
(52) Jacobs, T. L. *Organic Reactions*; John Wiley: New York, 1949; Vol. 5.

(s), 1865.1 (s) (ν_{CO}). Anal. Calcd for $C_{35}H_{31}IMoO_3P_2Pd$: C, 47.19; H, 3.51. Found: C, 47.31; H, 3.53. MS (15 V, ESP^+) = *806* ($M^+ - 3CO$).

[η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2](CO)$_3$MoPd(PPh_3)C≡CPh (5). A Schlenk flask was loaded with [η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2](CO)$_3$MoPd(PPh_3)I (**3**) (0.52 g, 0.48 mmol), and three cycles of vacuum/argon were performed. Upon addition of DMF (10 mL), a bright red solution was obtained. Following dropwise addition of tributyl(phenylethynyl)tin (0.56 g, 1.36 mmol), the color changed to dark brown, and the mixture was stirred for 1 h. The reaction mixture was transferred into a separatory funnel, diluted with 50 mL of THF, and extracted with brine (6 × 50 mL). The organic phase was dried over sodium sulfate, filtered, and concentrated. Pentane was added to the solution, which was left overnight at −28 °C, to allow the formation of a precipitate. This was washed with pentane and dried in a vacuum, yielding 0.50 g (92%) of product (**5**) as a brown solid. An analytical sample was obtained by recrystallization from THF/pentane (vapor diffusion) at room temperature. ^{1}H NMR ($CDCl_3$): δ_H 8.67−8.59 (m), 7.90−7.62 (m), 7.60−7.48 (m), 7.45−7.29 (m), 7.27−7.22 (m), 7.21−7.07 (m), 7.05−6.97 (m), 6.94−6.72 (m), 6.31−6.25 (m), 6.12 (t, 1H, J = 2.1 Hz, Cp−*H*), 4.74 (t, 1H, J = 2.1 Hz, Cp−*H*). ^{31}P NMR ($CDCl_3$): δ_P 39.72 (d, J = 455 Hz, −*P*Ph_2), 28.22 (d, J = 455 Hz, *P*Ph_3). ^{13}C NMR (DMF-d_7): δ_C 234.1, 226.5, 225.4 (*C*O), 138.1−124.9 (*Ph*), 118.7 (d, J_{C-P} = 9.8 Hz, C_2), 115.2 (d, J_{C-P} = 8.6 Hz, −C≡*C*−Ph), 109.6 (d, J_{C-P} = 7.3 Hz, C_4), 107.2 (dd, J^1_{C-P} = 6.1 Hz, J^2_{C-P} = 28.5 Hz, −*C*≡C−Ph), 94.4 (d, J_{C-P} = 6.1 Hz, C_3), 89.4 (d, J_{C-P} = 11.2 Hz, C_5), 55.1 (d, J_{C-P} = 43.3 Hz, C_1). FT-IR (CH_2Cl_2, cm^{-1}): 2106 (w) ($\nu_{C\equiv C}$), 1949.8 (s), 1869.0 (m), 1842.1 (s) (ν_{CO}). Anal. Calcd for $C_{58}H_{42}MoO_3P_2Pd$: C, 66.27; H, 4.03. Found: C, 66.54; H, 4.12. MS (15 V, ESP^+) = *967* ($M^+ - 3CO$).

Bu_3Sn−C≡C−(C_6H_4)*p*-Cl (11b). A mixture of (diethylamino)-tributylstannane (7.96 g, 0.022 mol) and *p*-clorophenylacetylene (2.50 g, 0.018 mol) was stirred at room temperature for 1 h. Following removal in vacuo of the diethylamine formed during the reaction, a pure product (6.90 g, 94%) was isolated, as a pale yellow oil, by Kugelrohr distillation at 200 °C/10^{-4} mm Hg. ^{1}H NMR ($CDCl_3$): δ_H 7.35 (d, 2H, J = 8.9 Hz, *meta* Ph), 7.23 (d, 2H, J = 8.9 Hz, *ortho* Ph), 1.61 (p, 6H, J = 8.6 Hz, $CH_3-CH_2-CH_2-CH_2-Sn$), 1.37 (s, 6H, J = 7.7 Hz, $CH_3-CH_2-CH_2-CH_2-Sn$), 1.05 (t, 6H, J = 8.3 Hz, $CH_3-CH_2-CH_2-CH_2-Sn$), 0.92 (t, 9H, J = 7.1 Hz, $CH_3-CH_2-CH_2-CH_2-Sn$). ^{13}C NMR ($CDCl_3$): δ_C 133.69, 133.07, 128.37, 122.51 (*Ph*), 108.71 (Ph−*C*≡C−Sn), 94.63 (Ph−C≡*C*−Sn), 28.87 (t, J_{CSn} = 11.3 Hz, $CH_3-CH_2-CH_2-CH_2-Sn$), 26.93 (t, J_{CSn} = 29.4 Hz, $CH_3-CH_2-CH_2-CH_2-Sn$), 13.65 ($CH_3-CH_2-CH_2-CH_2-Sn$), 11.12 ($CH_3-CH_2-CH_2-CH_2-Sn$). FT-IR (CH_2Cl_2, cm^{-1}): 2959 (s), 2924 (br), 2872 (m), 2854 (m), 2134 (w), 1848 (s), 1466 (m), 1377 (w), 1207 (w), 1094 (m). MS (15 V, ESP^+) = *449* ($M + Na)^+$. HRMS (*m*/*e*): calcd for $C_{20}H_{31}ClSn$ (M^+): 426.1136; found, 426.1084; calcd for $C_{20}H_{30}ClSn$ ($M - H$): 425.1058; found, 425.1060.

[η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2](CO)$_3$MoPd(μ-I)$_2$PdMo(CO)$_3$[η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2] (14). A Schlenk flask was loaded with [η^5-(1-Ph_2P-2,4-Ph_2)C_5H_2](CO)$_3$MoI (**1**)·0.4CH_2Cl_2 (0.20 g, 0.28 mmol) and Pd_2(dba)$_3$ (0.14 g, 0.15 mmol). After three cycles of vacuum/argon, 20 mL of THF was added to the flask, and the resulting dark solution was stirred for 30 min at room temperature. Celite (10 g) was added to the reaction mixture, the solvent was removed under vacuum, and the residue was placed on a silica column (30 cm × 3 cm). Elution with hexane/dichloromethane 4/6 produced a dark red band, which was eluted and collected. After removal of the solvent, l0.11 g (48%) of (**14**) as a dark brown solid was obtained. An analytical sample was obtained by crystallization from THF/pentane (vapor diffusion) at room temperature. ^{1}H NMR ($CDCl_3$): δ_H 8.57−8.45 (m), 7.73−7.48 (m), 7.22 (s), 7.22−7.14 (m), 7.00−6.89 (m), 6.83−6.75 (m), 6.06 (q, 1H, J_{HH} = 2.4 Hz, J_{HP} = 3.3 Hz, Cp−*H*), 4.59 (t, 1H, J = 2.4 Hz, Cp−*H*). ^{31}P NMR ($CDCl_3$): δ_P 50.16. ^{13}C NMR ($CDCl_3$): δ_C 237.7, 224.7, 223.7 (*C*O), 136.9−125.1 (*Ph*), 119.4 (d, J_{C-P} = 9.0 Hz, C_2), 110.5 (d, J_{C-P} = 9.0 Hz, C_4), 95.2 (d, J_{C-P} = 5.4 Hz, C_3), 89.2 (d, J_{C-P} = 12.6 Hz, C_5), 57.7 (d, J_{C-P} = 46.7 Hz, C_1). FT-IR (DMF, cm^{-1}): 1966 (s), 1895 (sh), 1876 (s) (ν_{CO}). Anal. Calcd for $C_{32}H_{22}IMoO_3PPd$: C, 47.17; H, 2.72. Found: C, 46.97; H, 2.74. MS (15 V, ESP^+) = *818* ($M + H)^+$.

Kinetic Measurements. Manipulations were carried out under argon. DMF was degassed and distilled from CaH_2 under reduced pressure. The kinetic experiments were performed by NMR spectroscopy and UV−visible spectrophotometry, under *pseudo* first-order conditions, using at least a 10-fold excess of tributyltinacetylides with respect to complexes **3** or **14**. The temperature in the NMR probe was determined from the chemical shift difference between the OH and CH_2 signals of a solution of ethylene glycol containing 20% DMSO-d_6. The NMR tube (5 mm) was charged with complex **3** (10−30 mg), 400 μL of DMF, and 100 μL of DMF-d_7, and Bu_3Sn−C≡C−Ph was added by syringe. Spectra were collected immediately, using a macro sequence. The rate of disappearance of the complex **3** was followed by recording the intensity value of the signal at δ 22.0 ppm. First-order rate constants (k_{obs}) were obtained by exponential fitting of [**3**] versus time, using a nonlinear least-squares regression program. The kinetic runs were reproducible to within 10%.

UV−Visible Kinetics. A series of stock solutions were prepared by dissolving complex **3** (4.4 mg) or complex **14** (3.5 mg) in dry degassed DMF in a 25 mL volumetric flask. In a typical run, a quartz cuvette (1 cm path length) was loaded with 2 mL of a stock solution and allowed to equilibrate at the appropriate temperature, before addition of tributyltinacetylide. Bu_3SnC≡CPh was added (2−15 μL) as neat liquid, while appropriate amounts (80−500 μL) of a solution of Bu_3SnC≡C(*p*-ClC_6H_4) in DMF (70.9 mg in 5 mL) were used. The decrease in absorbance associated with the reaction was followed with time. First-order rate constants (k_{obs}) were obtained by fitting the exponential dependence of absorbance versus time data using a nonlinear least-squares regression program, which provides values of k_{obs} and A_∞. Fittings of k_{obs} to eq 3 to give K and k_2 values were obtained with nonlinear least-squares calculations carried out by the program Sigma Plot. The reaction of **3** with Bu_3SnC≡CPh was followed at 400 nm for [**3**] < 2.0×10^{-4} M, and at 490 nm for higher concentrations. The reaction of **3** with Bu_3SnC≡C(*p*-Cl−C_6H_4) was followed at 420 nm, and that of **14** with Bu_3SnC≡CPh at 410 nm. Single kinetic runs were reproducible to within 5%, and the parameters K and k_2 were reproducible to within 12% on duplication of a full kinetic set.

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Supporting Information Available: Figure showing plot of ln[**3**] versus time for the reaction with **11a**, figure showing [**3**] versus time in the reaction with **11a** in the presence and absence of PPh_3, figure showing UV−vis spectra of complexes **3** and **5** in DMF, figure showing plot of k_{obs} versus [**3**] for the reaction with **11a**, figures showing ^{1}H and ^{13}C NMR spectra accounting purity of **11b** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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