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Full Picture of the Catalytic Cycle Underlying Palladium-Catalyzed Metal−Carbon Bond Formation

Simona Tollis, Valentina Narducci, Paola Cianfriglia, Claudio Lo Sterzo,* and Egidio Viola

Centro CNR di Studio sui Meccanismi di Reazione, Dipartimento di Chimica, Università "La Sapienza", Piazzale Aldo Moro, 5-00185 Roma, Italy

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*Summary: A catalytic cycle of reaction between [η^5-1-(diphenylphosphino)-2,4-diphenylcyclopentadienyl]tricarbonylmetal iodides, [η^5-1-Ph_2P-2,4-$Ph_2C_5H_2$]$M(CO)_3I$ (**1a**, M = Mo; **1b**, M = W), with zerovalent palladium and tributyltin acetylides affords the final acetylide products [η^5-1-Ph_2P-2,4-$Ph_2C_5H_2$]$M(CO)_3C{\equiv}CPh$ (**5a**, M = Mo; **5b**, M = W). This communication describes the main processes and intermediates involved in this palladium-catalyzed metal−carbon bond formation.*

We have recently discovered that zerovalent palladium catalysts allow the formation of transition-metal−carbon bonds by promoting the coupling of transition-metal iodides and trialkyltin acetylides.[1] This procedure has been employed successfully in the preparation of a range of mono and bis σ-metal acetylides,[2,3] thus revealing good potential in the application of this novel property of palladium catalysts (eq 1).

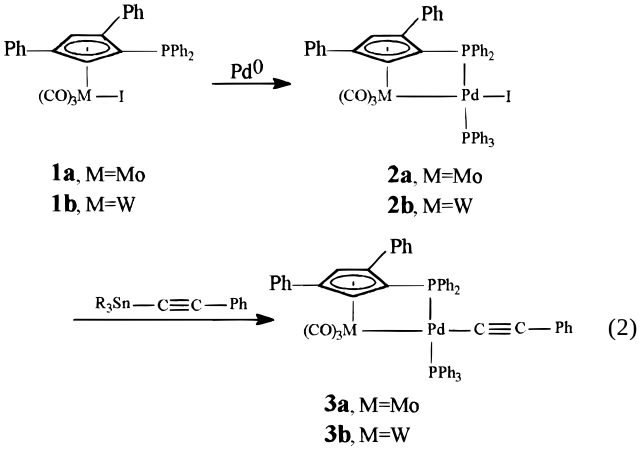
$$\mathrm{Cp(CO)_nM{-}I + R_3Sn{-}C{\equiv}C{-}R \xrightarrow{Pd^0} Cp(CO)_nM{-}C{\equiv}C{-}R} \quad (1)$$

$$\mathrm{M = Fe, Ru, Mo, W}$$

Along with the development of this synthetic manifold, we also investigated the intimate role played by palladium in promoting these transformations.[4] Analogies to the oxidative-addition/transmetalation/*trans* to *cis* isomerization/reductive-elimination sequence, used to describe the palladium-catalyzed coupling of organic electrophiles and organostannanes—*i.e.* the Stille reaction[5]—were sought.

Following preliminary evidence that coupling of metal iodides and tin acetylides occurs only in the presence of zerovalent palladium,[2a] we have recently reported that the investigation of the reaction mechanism requires the design of suitable models since the intermediates involved are too labile to be detected.[4]

Reaction between the [η^5-1-(diphenylphosphino)-2,4-diphenylcyclopentadienyl]tricarbonylmetal iodide complexes **1a,b** and a stoichiometric amount of zerovalent palladium (eq 2) gives the products of oxidative addition **2a,b** which, after treatment with trialkyltin acetylides, yield **3a,b** by a transmetalation process. These transformations demonstrated that transition-metal iodides undergo a sequence of oxidative addition and transmetalation, in analogy to the first two processes of the palladium-promoted carbon−carbon bond formation.[5]



In this paper the conversion of **3a,b** into the final corresponding acetylide products via a *trans* to *cis* isomerization followed by reductive elimination is reported. The results of ^{31}P NMR studies provide strong supporting evidence for the overall process hypothesized herein.

Preliminary studies concerning the evolution of complexes **3a,b** toward the cis isomers and the products from reductive elimination were carried out by ^{31}P NMR spectroscopy. A pure sample of **3a** in DMF-d_7 displays, at room temperature, a ^{31}P NMR spectrum consisting of two doublets at 40.9 and 30.8 ppm (J = 453.4 Hz) (Figure 1c). When the temperature is raised to 323 K, a new set of doublets at 36.5 and 26.3 ppm, of smaller coupling constant (J = 66 Hz), appears in the spectrum (see doublets marked with two asterisks in Figure 1d), suggesting the occurrence of a *trans* to *cis* isomerization process[6] (eq 3). However, shortly after, the spectrum

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[1] Lo Sterzo, C. *J. Chem. Soc., Dalton Trans.* **1992**, 1989.

[2] (a) Crescenzi, R.; Lo Sterzo, C. *Organometallics* **1992**, *11*, 4301. (b) Viola, E.; Lo Sterzo, C.; Crescenzi, R.; Frachey, G. *J. Organomet. Chem.* **1995**, *493*, 55. (c) Viola, E.; Lo Sterzo, C.; Crescenzi, R.; Frachey, G. *J. Organomet. Chem.* **1995**, *493*, C9. (d) Viola, E.; Lo Sterzo, C.; Trezzi, F. *Organometallics* **1996**, *15*, 4352. (e) Buttinelli, A.; Viola, E.; Lo Sterzo, C. *Organometallics*, in press.

[3] (a) Hartbaum, C.; Roth, G.; Fischer, H. *Chem. Ber./Rec.* **1997**, *130*, 479. (b) Hartbaum, C.; Fischer, H. *Chem. Ber./Rec.* **1997**, *130*, 1063.

[4] (a)Spadoni, L.; Lo Sterzo, C.; Crescenzi, R.; Frachey, G. *Organometallics* **1995**, *14*, 3149. (b) Cianfriglia, P.; Narducci, V.; Lo Sterzo, C.; Viola, E.; Bocelli, G.; Kodenkandath, T. A. *Organometallics* **1996**, *15*, 5220.

[5] (a) Heck, R. F. *Palladium in Organic Synthesis*; Academic Press: New York, 1985. (b) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (d) Saá, J. M.; Martorell, G.; Garcia-Raso, A. *J. Org. Chem.* **1992**, *57*, 678. (e) Mitchell, T. N. *Synthesis* **1992**, 803. (f) Farina, V.; Krishnan, B.; Marshall, D. R.; Roth, G. P. *J. Org. Chem.* **1993**, *58*, 5434. (g) Schlosser, M., Ed. *Organometallics in Synthesis*; Wiley: Chichester, England, **1994**.

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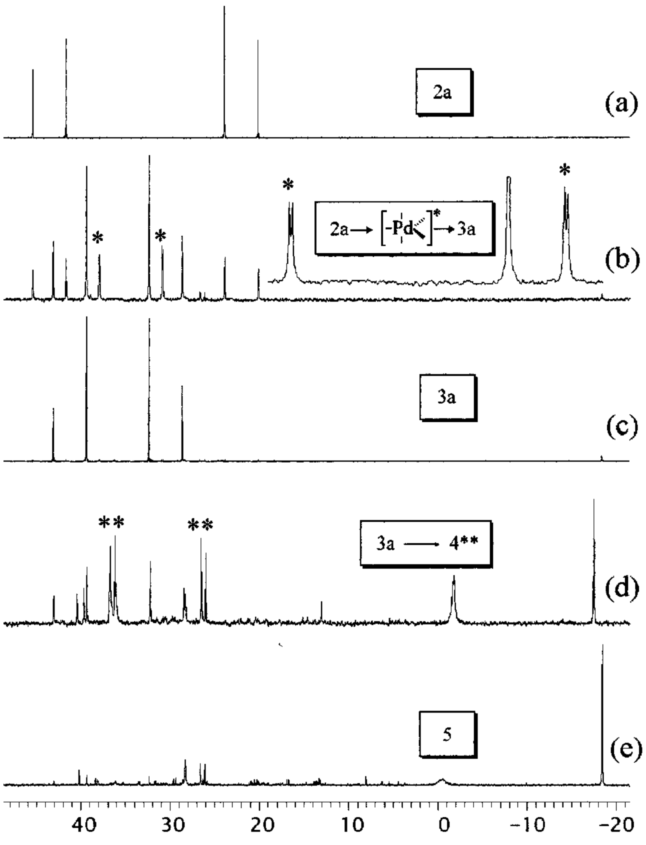
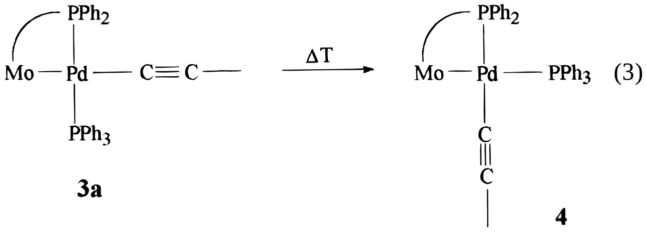


Figure 1. ${}^{31}P$ NMR (121 MHz) study of the sequence of transformations occurring in the Pd-catalyzed metal–carbon bond formation in DMF-d_7: (a) pure **2a**; (b) 1 equiv of **2a** + **6** equiv of $Bu_3SnC{\equiv}CPh$ (after 30 min at room temperature; peaks marked with an asterisk are expanded in the insert); (c) complete formation of **3a** (after 1 h at room temperature); (d) *trans* to *cis* isomerization (peaks marked with two asterisks are attributed to the *cis* isomer **4**; spectrum recorded at 353 K); (e) formation of **5**. In (d) and (e) free triphenylphospine, which is formed during reductive elimination, appears as a broad peak at −1.8 ppm.

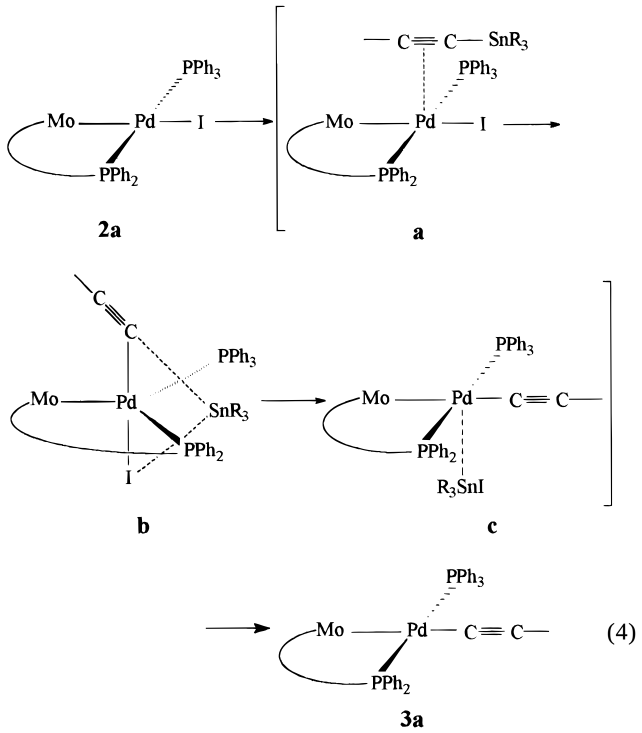


evolved in a more complicated pattern, clearly indicating dispersion of material through different processes which cannot be attributed to reductive elimination.[7]

The aim of inducing reductive elimination led our search for conditions that would favor the release of palladium from **4**. Considering that the transmetalation reaction usually requires an excess of tin acetylide[4b]—which does not cause undesired side effects—we decided to carry out the preparation of **3a** using a strong excess of tin acetylide. The expectation was that, following the transmetalation and the thermally induced *trans* to *cis* isomerization, the exceeding alkyne might favor—through coordination-release of palladium from **4**.[8] The reaction of **2a** with a 6-fold excess of (phenylethynyl)tributyltin was then carried out in a NMR tube in DMF-d_7 at room temperature, followed by ${}^{31}P$ NMR (Figure 1).

When the reagents were mixed—during the transmetalation process—the presence of a transient species was unexpectedly detected by the appearance of two doublets at 38.0 and 30.9 ppm ($J = 9.9$ Hz), respectively, which persisted until complete conversion of **2a** into **3a** occurred (Figure 1b). These signals therefore suggest the presence of a five-coordinate intermediate formed during the substitution reaction.[9–11]

Although at this point it is not possible to offer a precise description of the transient species which forms during the transmetalation process, we believe that one of the structures **a**–**c**, shown in brackets in eq 4, or a combination of them might reasonably account for experimental evidence. This interpretation is consistent with two facts: (i) The transient species appears only in the presence of a strong excess of ethynylstannane, thus, under conditions in which an association between ethynylstannane and the Mo–Pd–I complex is likely to occur. (ii) The two narrow doublets appearing in the



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[6] (a) Pregosin, P. S. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; Chapter 14. (b) Bampos, N.; Field, L. D.; Messerle, B. A. *Organometallics* **1993**, *12*, 2529 and references therein.

[7] We retain that in the absence of extra ligands or a suitable partner that would assist the release of palladium—and thus the occurrence of reductive elimination—compound **4** might collapse toward the formation of polymetallic aggregates.

[8] (a) Gillie, A.; Stille, J. K *J. Am. Chem. Soc.* **1980**, *102*, 4933. (b) Davies, J. A. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, England, 1995; Vol. 9, Chapter 6. (c) Schager, F.; Bonrath, W.; Porschke, K.-R.; Kessler, M.; Kruger, C.; Seevogel, K. *Organometallics* **1997**, *16*, 4276. (d) Trost, B. M.; Sorum, M. T.; Chan, C.; Harms, A. E.; Ruhter, G. *J. Am. Chem. Soc.* **1997**, *119*, 698. (e) Besides the scavenging effect that acetylides might exert through coordination on palladium, it should be also taken into account the fact that organostannanes can efficiently perform reduction of Pd: Pugh, C.; Percec, V. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1990**, *28*, 1101.

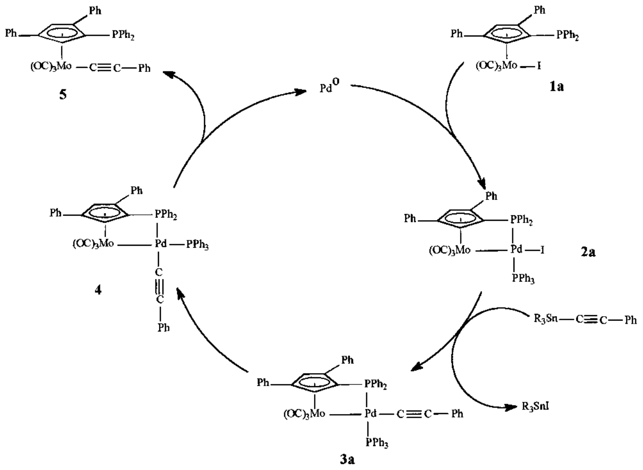

Figure 2.

^{31}P NMR spectrum indicate that during the substitution process both phosphorus atoms remain attached to the palladium center while this center is undergoing a severe variation of the coordination geometry.

When the transmetalation process was complete (30 min), the temperature was raised to 353 K and in a few minutes the *trans* to *cis* isomerization process was detected by the appearance of two doublets at 36.5 and 26.3 ppm ($J = 66$ Hz) (Figure 1d). At the same time, a singlet at −18.4 ppm due to **5** started to rise and, after 4 h, remained the only prominent signal (Figure 1e).

The critical need for a reagent able to assist the release of palladium from **4** in the reductive-elimination process was confirmed by the smooth formation of **5**, which occurred in the presence of dppe[12] (eq 5).

$$\mathbf{3a} + 2\ \mathrm{dppe} \rightarrow \mathbf{5} + \mathrm{Pd(dppe)_2} + \mathrm{PPh_3} \qquad (5)$$

Significant proof of the important role played by **1a**, **2a**, and **3a** in the catalytic process leading to **5** was obtained by reacting **3a** with an equivalent amount of **1a**. The existence of two simultaneous processes was detected by ^{31}P NMR spectroscopy (eq 6).

$$\mathbf{3a} + \mathbf{1a} \rightarrow \mathbf{5} + \mathbf{2a} \qquad (6)$$

Palladium was extracted from **3a** to give **5** by reductive elimination. Simultaneously, the Mo−I moiety of **1a** captured the palladium released from **3a**, forming the oxidative-addition product **2a**. *The core of the catalytic turnover consists of these combined processes, as depicted in Figure 2.*

If the coupling reaction of **1a** with (phenylethynyl)-tributyltin is carried out in the presence of only a catalytic amount (5%) of $(CH_3CN)PdCl_2$, the coupled product **5** is isolated in 23% yield. This scant efficiency of the coupling reaction in the presence of a catalytic amount of palladium may be ascribed to the effect of the diphenylphosphine sidearm on the Cp ring. Not only does this functionality allow stabilization—and thus detection and/or characterization of intermediates—but also it settles palladium in a chelating environment and makes more difficult the catalytic turnover.[14]

In conclusion, the processes described in Figure 2 strongly suggest very close analogies between the Pd-catalyzed *carbon−carbon* and *metal−carbon* bond formation mechanisms. This parallelism might give helpful hints in the understanding of the mechanism of the former process that, despite its widespread use, is currently still under much debate.[15] To our knowledge this is the first example of straightforward identification of all intermediates involved in the overall sequence of transformations constituting this catalytic cycle.

Supporting Information Available: Text giving the experimental details and characterization data for new compounds (5 pages). Ordering information is given on any current masthead page.

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[9] Transmetalation is a substitution process expected to 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 pentacoordinate intermediate.[10] Recent studies also provided a theoretical background for this transformation.[11]

[10] Cattalini, L. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: Chichester, England, 1970; Vol. 13, pp 263−327.

[11] Frankcombe, K. E.; Cavell, K. J.; Yates, B. F.; Knott, R. B. *Organometallics* **1997**, *16*, 3199 and references therein.

[12] The ^{31}P NMR spectrum recorded 2 h after **3a** was mixed with 2 equiv of the chelating phosphine, at room temperature, showed a signal at −18.4 ppm due to **5** and a signal at 32.5 ppm due to $\mathrm{Pd(dppe)_2}$.[13,15d]

[13] Mason, M. R.; Verkade, J. G. *Organometallics* **1992**, *11*, 2212.

[14] In contrast, the same coupling reaction carried out with $[\eta^5$-2,4-diphenylcyclopentadienyl]tricarbonylmetal iodides, $[\eta^5\text{-}(2,4\text{-}Ph_2)\text{-}C_5H_2]M(CO)_3I$, which do not carry the chelating sidearm, and $Bu_3SnC{\equiv}CPh$ in the presence of 5% of $(CH_3CN)PdCl_2$, occurs with the usual efficiency, and the coupled product $[\eta^5\text{-}2,4\text{-}Ph_2C_5H_2]M(CO)_3C{\equiv}CPh$ is isolated in 87% yield.

[15] (a) Farina, V.; Krishnan, B.; Marshall, D. R.; Roth, G. P. *J. Am. Chem. Soc.* **1991**, *113*, 9585. (b) Amatore, C.; Jutand, A.; Suarez, A. *J. Am. Chem. Soc.* **1993**, *115*, 9531. (c) Mateo, C.; Fernandez-Rivas, C.; Echavarren, A.; Cardenas, D. J. *Organometallics* **1997**, *16*, 1997 and references therein. (d) Amatore, C.; Broeker, G.; Jutand, A.; Khalil, F. *J. Am. Chem. Soc.* **1997**, *119*, 5176.