Formation of Mo−Pd and W−Pd Complexes. Insight into the Mechanism of Palladium-Catalyzed Metal−Carbon Bond Formation

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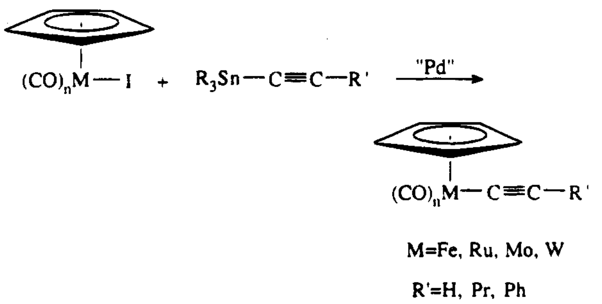
Summary: The oxidative addition of M−I moieties (M = Mo, W) at Pd^0 was investigated in order to elucidate the mechanism of palladium-catalyzed metal−carbon bond formation. By the use of metal phosphine-substituted cyclopentadienyl iodo complexes of formula $[\eta^5\text{-}(Ph_2P)C_5H_4](CO)_3MI$ (M = Mo, W) it was possible to isolate and characterize a product of oxidative addition to zerovalent palladium, $[\eta^5\text{-}(Ph_2P)C_5H_4](CO)_3MPd(PPh_3)I$ (M = Mo, W).

The use of zerovalent palladium catalysts in organic synthesis to form carbon−carbon bonds is a well-established procedure,[1] and the Stille coupling reaction itself represents one of the most important synthetic methodologies for transition-metal-mediated cross-coupling reactions.[2] We recently disclosed an unprecedented feature of palladium, showing that this metal can also promote *metal−carbon bond formation.* In the presence of a catalytic amount of Pd^0 a σ-acetylide complex is formed by coupling of an iron−iodide complex and a trimethyltin acetylide.[3a] Subsequently, we have shown that this coupling can be successfully carried out on a variety of tin acetylides and transition metals[3b,4] (eq 1). These reactions occur under the same reaction conditions, leading to the formation of carbon−carbon bonds by palladium catalysis.



(1)

This new reaction gives easy access to an important class of compounds, the σ-metallaacetylides, and has revealed an unexpected and fascinating feature of palladium chemistry, a thus far unknown ability to catalyze the formation of metal−carbon bonds. In addition to the synthetic utility of this new reaction, an intriguing aspect of the phenomenon is the understanding of the intimate role of palladium in these transformations.

The present work deals with the attempt of obtaining insight into the plausible working mechanism of these reactions. The first approach was to seek for a parallel to the well-known mechanism operating in the Stille coupling reaction[5] initiated by the oxidative addition of an electrophile to a palladium(0) complex.[6] If this parallel is true, in the present case the zerovalent palladium complex should insert, thus undergoing oxidative addition into the M−I bond, with formation of an M−Pd−I moiety (eq 2).

$$M{-}I + Pd^0 \rightarrow M{-}Pd{-}I \qquad (2)$$

$$M = Fe, Ru, Mo, W$$

The electrophilicity of the M−I functionality in $CpM(CO)_nI$ (Cp = η^5-cyclopentadienyl; M = Fe, Mo, W) complexes has been previously demonstrated[7] by its ability to oxidatively add zerovalent mercury with formation of the M−Hg−I array. On the other hand, several literature reports account for the insertion of palladium, and more generally zerovalent group 10 metals, into organomercurials and organometallic derivatives of group 14 elements.[3b] Complexes such as M−Pd−X, containing Pd inserted between a transition metal and a halide (M = transition metal; X = Cl, Br, I), have been reported,[8] and in some cases their formation has been rationalized as an oxidative addition of M−X moieties to Pd^0.

In a series of preliminary experiments, we reacted $CpFe(CO)_2I$ and a stoichiometric amount of the complex

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[8] M−Pd−X complexes: (a) M = Mn: Hoskins, B. F.; Steen, R. J.; Turney, T. W. *J. Chem. Soc., Dalton Trans.,* **1984,** 1831. Hoskins, B. F.; Steen, R. J.; Turney, T. W. *Inorg. Chim. Acta* **1983,** *77,* L69. (b) M = W: Engel, P. F.; Pfeffer, M.; Fischer, J.; Dedieu, A. *J. Chem. Soc., Chem. Commun.* **1991,** 1274. (c) M = Fe: Braunstein, P.; Knorr, M.; Tiripicchio, A.; Tiripicchio Carmellini, M. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 1361. (d) M = Rh: Arena, C. G.; Rotondo, E.; Faraone, F. Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1991,** *10,* 3877 and references therein. Bailey, D. A.; Balch, A. L.; Fossett, L. A.; Olmstead, M. M.; Reedy, P. E., Jr. *Inorg. Chem.* **1987,** *26,* 2413 and references therein. (e) M = Mo: Zhang, Z. Z.; Wang, H. K.; Wang, H. G.; Wang, R. J. *J. Organomet. Chem.* **1986,** *314,* 357. Klaui, W.; Hamers, H.; Pfeffer, M.; de Cian, A.; Fischer, J. *J. Organomet. Chem.* **1990,** *394,* 213. Mashima, K.; Nakano, H.; Nakamura, A. *J. Am. Chem. Soc.* **1993,** *115,* 11632. (f) M = Pd: Rutherford, N. M.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1984,** *23,* 2833 and references therein. Bender, R.; Braunstein, P.; Tiripicchio, A.; Tiripicchio-Carmellini, M. *J. Chem. Soc., Chem. Comm.* **1984,** 42. (g) M = Ru: Maisonnet, A.; Farr, J. P.; Olmstead, M. M.; Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1982,** *21,* 3961 and references therein.

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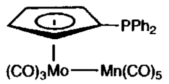
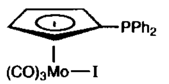
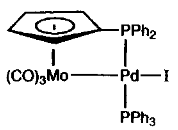
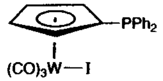
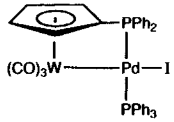
Table 1. ^{1}H, ^{13}C, and ^{31}P NMR and IR Data for Complexes 2, 3, and 6

	^{1}H NMR[a]			^{13}C NMR[b]					
	Cp	PPh$_2$	PPh$_3$	Cp	PPh$_2$	PPh$_3$	CO	^{31}P NMR[c]	IR[d]
	4.49, q, 2H, $J = 2.1$ Hz (β,β') 5.43, q, 2H, $J = 2.1$ Hz (α,α')	7.46–7.43, m, 6H (*m*, *p*) 7.97–7.90, m, 4H (*o*)		56.68, d, $J = 50.6$ Hz (*ipso*) 87.89, d, $J = 10.3$ Hz (α,α') 89.15, d, $J = 6.2$ Hz (β,β')	129.27, d, $J = 10.6$ Hz 131.42, d, $J = 12.4$ Hz 131.65, s 133.32, d, $J = 42.5$ Hz		231.03 225.73 215.34 (br)	58.74	2057.5 (s) 1988.0 (sh) 1971.8 (s) 1938.2 (m) 1908.7 (m) 1881.7 (m)
	5.56, q, 2H, $J = 2.1$ Hz (β,β') 5.75, m, 2H (α,α')	7.55–7.52, m, 6H (*m*,*p*) 7.97–7.90, m, 4H (*o*)		108.47, d, $J = 28.5$ Hz (*ipso*) 102.99, d, $J = 8.4$ Hz (α,α') 93.97, d, $J = 5.7$ Hz (β,β')	129.05, d, $J = 9.8$ Hz 131.95, d, $J = 43.8$ Hz 132.23 s 133.15, d, $J = 10.1$ Hz		232.86 218.10	32.39	2085.9 (m) 2044.4 (s) 2017.8 (sh) 2004.7 (s) 1968.5 (s)
	4.45, q, 2H, $J = 2.1$ Hz (β,β') 5.47, q, 2H, $J = 2.1$ Hz (α,α')	7.45–7.55, m, 6H (*m*,*p*) 8.09–8.16, m, 4H (*o*)	7.35–7.45, m, 9H (*m*,*p*) 7.58–7.90, m, 6H (*o*)	60.24, d, $J = 41.3$ Hz (*ipso*) 93.33, d, $J = 11.7$ Hz (α,α') 92.46, d, $J = 6.9$ Hz (β,β')	131.76, s 132.20, d, $J = 38.6$ Hz 135.58, d, $J = 11.7$ Hz	127.92, d, $J = 9.5$ Hz 128.53, d, $J = 11.5$ Hz 130.00, s	235.75 224.93	33.50, d, $J = 459$ Hz 17.00, d, $J = 459$ Hz	1966.1 (s) 1891.4 (m) 1867.7 (s)

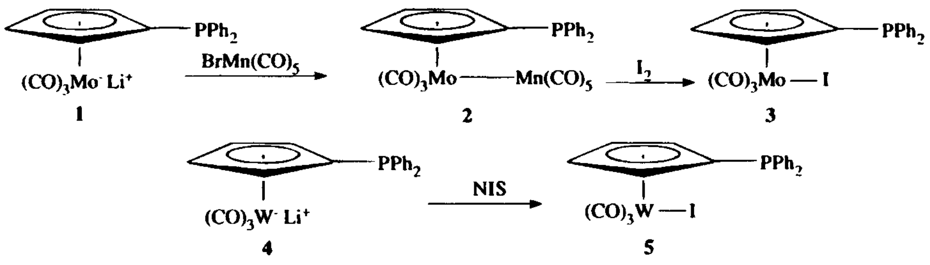
[a] CDCl$_3$, ppm, 298 K, 300 MHz, TMS reference. [b] CDCl$_3$, ppm, 298 K, 75.46 MHz, TMS reference. [c] CDCl$_3$, ppm, 298 K, 121.49 MHz, 85% H$_3$PO$_4$ reference. [d] CH$_2$Cl$_2$, cm^{-1}, s = strong, sh = shoulder, m = medium, w = weak.

Table 2. ^{1}H, ^{13}C, and ^{31}P NMR and IR Data for Complexes 5 and 7

	^{1}H NMR[a]			^{13}C NMR[b]					
	Cp	PPh$_2$	PPh$_3$	Cp	PPh$_2$	PPh$_3$	CO	^{31}P NMR[c]	IR[d]
	5.43, dt, 2H, $J_{H-H} = 2.2$ Hz, $J_{P-H} = 0.7$ Hz (α,α') 5.92, t, 2H, $J = 2.2$ Hz (β,β')	7.34–7.44, m, 10H		104.34, d, $J = 23.0$ Hz (*ipso*) 95.90, d, $J = 11.1$ Hz (α,α') 97.75, s (β,β')	128.87, d, $J = 6.8$ Hz 129.78, s 133.45, d, $J = 20.1$ Hz 135.87, d, $J = 11.0$ Hz		208.43 223.15, d, $J = 5.6$ Hz	-17.24	2036.9 (s) 1950.1 (s) 1892.8 (w)
	4.54, m, 2H (β,β') 5.38, m, 2H (α,α')	7.36–7.72, m, 20H 8.08–8.18, m, 5H		61.86, d, $J = 40.2$ Hz (*ipso*) 91.19, d, $J = 10.6$ Hz (α,α') 89.73, d, $J = 5.9$ Hz (β,β')		125.40–140.36, m	214.00 224.81, d, $J = 5.0$ Hz	24.68, d, $J = 461$ Hz 15.24, d, $J = 461$ Hz	1961.7 (s) 1940.1 (sh) 1882.0 (s) 1862.2 (s)

[a] CDCl$_3$, ppm, 298 K, 300 MHz, TMS reference. [b] CDCl$_3$, ppm, 298 K, 75.46 MHz, TMS reference. [c] CDCl$_3$, ppm, 298 K, 121.49 MHz, 85% H$_3$PO$_4$ reference. [d] CH$_2$Cl$_2$, cm^{-1}, s = strong, sh = shoulder, w = weak.

Scheme 1

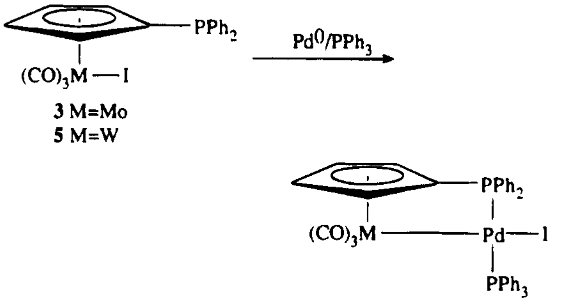


$Pd[P(Ph_3)]_4$ under standard coupling conditions,[3c] but we observed only formation of $CpFe(CO)(PPh_3)I$ and $CpFe(PPh_3)_2I$, generated by phosphine replacement of the CO ligand on the starting iron complex. We have therefore used the bis(dibenzylideneacetone) complex $Pd(dba)_2$ in order to avoid the inconvenience caused by PPh_3, but it was only possible to monitor the consumption of starting materials without detection and/or isolation of intermediates or products.

A more suitable substrate to achieve our purpose was a cyclopentadienylmetal iodide complex having a diphenylphosphino group linked to the Cp ring. The (diphenylphosphino)cyclopentadienyl moiety has been widely used to hold two metal centers within the same molecular unit, one linked in an η^5 fashion to the Cp ring and the other coordinated in an η^1 mode to the phosphorus atom.[9] Scheme 1 illustrates the reaction pathways for the preparation of the ((diphenylphosphino)cyclopentadienyl)tricarbonylmetal iodide complexes $[\eta^5\text{-}(Ph_2P)C_6H_5]M(CO)_3I$ (**3**, M = Mo; **6**, M = W).

The reaction of **1**[10] with $BrMn(CO)_5$ formed the Mo–Mn complex **2** in 46% yield; then the subsequent reaction with iodine quantitatively afforded complex **3**. In contrast, the tungsten complex **5** was formed by the direct reaction of anion **4**[11] with NIS (*N*-iodosuccinimide). However, the direct reaction of **1** with a source of I^+ such as NIS or 1,2-diiodoethane was unsuccessful.

Both complexes **3** and **5** reacted with a stoichiometric amount of zerovalent palladium complex, $Pd^0[(PPh_3)]_4$ or $Pd(dba)_2$, in THF at room temperature within minutes[12] (eq 3). In the case of the reaction with $Pd(dba)_2$, 1 equiv of PPh_3 was added to the reaction mixture in order to stabilize the product. Although ^1H NMR spectra of the crude reaction mixtures showed complete conversion of starting material into product **6** or **7**, the following workup and chromatographic separation afforded a variable amount of pure material from run to run. The best results were 32% for the Mo–Pd complex **6** and 29% for the W–Pd complex **7**. Proof of identity of complexes **6** and **7** has been obtained by elemental analysis, IR, and ^1H, ^{13}C, and ^{31}P NMR. Very impressive are the NMR spectroscopic variations observed by comparing the spectra of compounds **3** and **5** with those of the corresponding products **6** and **7** obtained upon reaction with Pd^0. The spectroscopic data for molybdenum complexes **2**, **3**, and **6** are reported in Table 1, while data for the tungsten complexes **5** and **7** are listed in Table 2. In the ^1H NMR spectrum of **3** the deshielding effect of the phosphorus atom imposes a marked downfield shift in the α,α′-protons of the Cp and in the ortho protons of the phenyl rings with respect to the Cp β,β'-protons and the meta and para phenyl protons.[10,13] In **6**, due to the rigidity of the metallacycle formed and to the presence of the second phosphorus group, these differences became even larger. The ^{13}C NMR spectrum shows that the insertion of Pd^0 into the Mo–I bond of **3** produces heavy variations on the chemical shift of the Cp carbons. In **6** the C_{ipso} signal is shifted 48 ppm upfield with respect to that for **3**! The comparison of the ^{31}P NMR spectra of **3** and **6** clearly confirms the structural variations occurring around the Mo center of **3** upon reaction with Pd. The ^{31}P NMR spectrum of **3** appears as a broad singlet at 32.40 ppm, while in the spectrum of **6** the two nonequivalent phosphorus atoms bonded to palladium give rise to a simple first-order AB splitting pattern that produces two sets of doublets, centered respectively at 33.50 and 17.00 ppm, with a coupling constant of 459 Hz. This large value is characteristic of two different phosphorus atoms lying trans to each other, one of which is engaged in a four-membered metallo ring.[14] Similar variations are observed for the tungsten pair **5**, **7**.



3 M=Mo
5 M=W

6 M=Mo
7 M=W

(3)

On the basis of these preliminary findings we have shown that Mo–I and W–I moieties can oxidatively add to zerovalent palladium to form the corresponding M–Pd–I species. These transformations can be viewed at as an oxidation of Pd^0 to Pd^I by Mo^{II} and W^{II}. In our opinion, complexes **6** and **7** afford a reasonable entry in the attempt to give a rational design to the mechanism of Pd-catalyzed metal–carbon coupling.[15] Work is in progress to map other steps of the catalytic process.

Supporting Information Available: Text giving detailed synthetic procedures and analytical data and a figure giving ^1H, ^{13}C, and ^{31}P NMR spectra for complexes **3** and **6** (5 pages). Ordering information is given on any current masthead page.

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(11) **4** was prepared analogously to **1** from $[(Ph_2P)C_5H_4]^-Li^+$ and $(CH_3CN)_3W(CO)_3$.

(12) Complex **3** (0.72 g, 1.3 mmol) was dissolved in THF (40 mL), and to this solution were added $Pd(dba)_2$ (0.74 g, 1.3 mmol) and $P(C_5H_6)_3$ (0.35 g, 1.3 mmol). After it was stirred for 2 h at room temperature, the reaction mixture was reduced to a minimum volume under vacuum and the residue chromatographed on silica gel by a gradient elution with a mixture of CH_2Cl_2 and hexane. Complex **6** (0.38 g, 32%) was obtained as a red solid. The same result was obtained by reacting an equivalent amount of **3** and $Pd[P(C_6H_5)_3]_4$ in THF under the same reaction conditions. Complex **7** (29%) was obtained in an identical procedure by reacting **5** with a stoichiometric amount of $Pd(dba)_2/P(C_5H_6)_3$ or $Pd[P(C_6H_5)_3]_4$.

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(15) One reviewer raised the point that complexes **6** and **7** would be stabilized too much by the cyclopentadienylphosphine bridging ligand to act as true intermediates in the catalytic process. We recently found that these complexes smoothly undergo all the catalytic steps leading to metal–carbon bond formation. Narducci, V.; Cianfriglia, P.; Lo Sterzo, C.; Bocelli, G., manuscript in preparation.