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Synthesis and Characterization of Trimetallic Complexes Containing M−Pd−M Arrays (M = Mo, W) and Their Relevance in Palladium-Catalyzed Metal−Carbon Bond Formation

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The heterobimetallic complexes [MPd(PPh$_3$)(C≡C−Ph)(CO)$_3$(η^5-C_5−C$_5$H$_2$Ph$_2$(PPh$_2$)] (**5a**, M = Mo; **5b**, M = W) convert under chromatography to diastereomeric mixtures of the new trimetallic clusters [Pd{M(CO)$_3$(η^5-C$_5$H$_2$Ph$_2$(PPh$_2$)}$_2$] (M = Mo, **9a**; W, **9b**), which contain a linear M−Pd−M array clamped between two (diphenyl)cyclopentadienyl-diphenylphosphino ligands. Diastereomeric pure forms of both trimetallic clusters **9a**,**b** were obtained by fractional crystallization procedures, and the molecular structures of *rac*-**9a** and *rac*-**9b** were determined by single-crystal X-ray diffraction analyses. The trimetallic complexes **9a**,**b** have been found to be intermediates in coupling reactions between M−I moieties and Bu$_3$Sn−C≡C−Ph, to form metallacetylides M−C≡C−Ph. Independent high-yield synthetic routes to **9a**,**b** have been developed.

Introduction

The ability to promote metal−carbon bond formation by coupling metal halides M−X (M = Fe, Ru, Mo, W; X = I) and trialkyltin acetylide moieties R$_3$Sn−C≡C−R′ (R′ = H, alkyl, aryl) is a peculiar property of zerovalent palladium catalysts that has been discovered by some of us[1] and has been successfully applied to form (i) simple transition metal σ-acetylides (M−C≡C−R′);[2] (ii) elaborated homo- and hetero-bimetallic μ-acetylene complexes (M−C≡C−Ar−C≡C−M′);[3] and (iii) highly ethynylated organometallic oligomers and polymers [−M−C≡C−Ar−C≡C−]$_n$.[4]

In view of the importance of conjugated carbon-rich materials for advanced technological applications,[5] this Pd-catalyzed coupling reaction has received attention by other research groups, which have reported successful coupling of the Ru−Cl as well as various M−Br (M = Mn, Re) moieties with trialkyltin acetylides.[6]

With the use of properly designed tungsten or molybdenum models such as [MI(CO)$_3$(η^5-C$_5$H$_2$Ph$_2$(PPh$_2$)] (**1a**, M = Mo; **1b**, M = W) (Scheme 1), it has been possible to establish that the principal steps of this Pd-catalyzed M−C bond formation process[7] are closely related to the *oxidative addition/transmetalation/trans-to-cis isomerization/reductive elimination* sequence, which is commonly used to describe the Stille reaction, i.e. the palladium-catalyzed coupling of organic electrophiles and organostannanes.[8]

The diphenylphosphino sidearm on the cyclopentadienyl ring of complexes **1a**,**b** efficiently stabilizes and allows isolation of crucial intermediates such as [MPd(PPh$_3$)I(CO)$_3$(η^5-C$_5$H$_2$Ph$_2$(PPh$_2$)] **2a**,**b** and [MPd(PPh$_3$)(C≡C−Ph)(CO)$_3$(η^5-C$_5$H$_2$Ph$_2$(PPh$_2$)] **5a**,**b** (Scheme 1),

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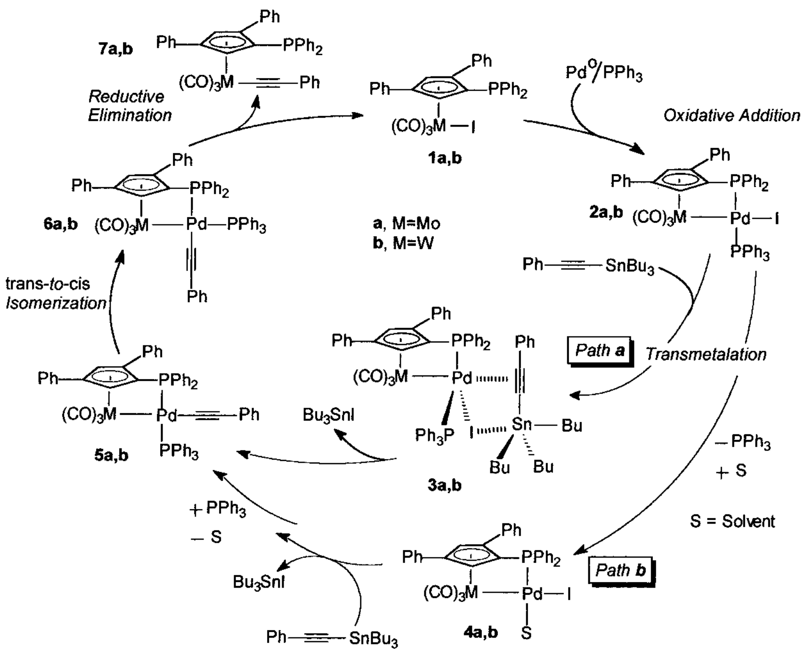
Scheme 1



without depressing further reactivity. Other steps of the catalytic cycle are therefore amenable to in-depth studies. For example, on the basis of accurate kinetic and spectroscopic work[7d] it has been possible to establish that the transmetalation process occurs by two different pathways (paths a and b of Scheme 1), depending on the initial concentration of the oxidative-addition intermediate **2a**. In concentrated solutions of [**2a**] ($\cong 10^{-2}$ M), the transmetalation reaction proceeds via the formation of the intermediate species $[\mathrm{MoPd(PPh_3)I(CO)_3(\eta^5\text{-}C_5H_2Ph_2(PPh_2)\cdot Bu_3Sn{-}C{\equiv}C{-}Ph}]$ **3a** formed by association between **2a** and the organostannane (path a). When the transmetalation is performed at lower concentration of **2a** ($\cong 10^{-4}$ M) (path b), the reaction proceeds through the highly reactive solvento-coordinate species $[\mathrm{MoPd(S)I(CO)_3(\eta^5\text{-}C_5H_2Ph_2(PPh_2)}]$ **4a** (S = *N*,*N*-dimethylformamide).

In this work we report on the characterization of two new trimetallic complexes, $[\mathrm{Pd\{M(CO)_3(\eta^5\text{-}C_5H_2Ph_2(PPh_2)\}_2}]$, featuring an unprecedented M−Pd−M array (M = Mo, **9a**; W, **9b**). Although these compounds have been originally obtained by degradation under chromatographic conditions of the transmetalated intermediates **5a**,**b**, they revealed a surprising reactivity toward phenyltributyltin acetylides, leading through a unique pathway to the reductive-elimination products $[\mathrm{M(C{\equiv}C{-}Ph)(CO)_3(\eta^5\text{-}C_5H_2Ph_2(PPh_2)}]$ **7a**,**b**. Independent high-yield synthetic routes to **9a**,**b** have therefore been developed.

Results and Discussion

Monitoring the reactions between the oxidative-addition products **2a**,**b** and phenyltributyltin acetylide, $\mathrm{Bu_3Sn{-}C{\equiv}C{-}Ph}$, by ^{31}P{^{1}H} NMR spectroscopy showed the quantitative formation of the expected transmetalation products **5a**,**b** (Scheme 1). Isolation of the latter compounds was troublesome. In fact, the chromatographic separation[8a,9] of the reaction mixture yielded three different products, none of which, surprisingly, was either **5a** or **5b**. For simplicity, only the reaction between **2a** and phenyltributyltin acetylide is described in detail, that of **2b** being identical.

The spectroscopic characterization of the product eluted as the first deep-red band is strongly consistent with formation of the palladium(I) complex $[\mathrm{Pd_2\mu\text{-}I(PPh_3)_2(\eta^3\text{-}C_5H_2Ph_2(PPh_2)}]$ (**8**).[10,11] The third band (red) was due to starting material **2a**, whose formation during the workup accounts for the reverse process between **5a** and $\mathrm{Bu_3SnI}$.

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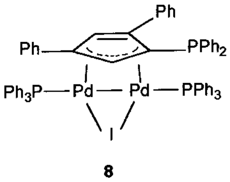
(9) The isolation of pure transmetalated products **5a**,**b** was achieved by precipitation and recrystallization.[7b]

(10) ^{1}H NMR (CDCl$_3$): δ 7.68 (m), 7.61−7.54 (m), 7.39−6.77 (m), 6.64−6.59 (m), 6.55−6.49 (m), 6.11 (m, *Cp*). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz): AMX pattern, δ_A 32.9 (dd, J_{AM} = 147 Hz, J_{AX} = 25 Hz), δ_M 24.0 (dd, J_{AM} = 147 Hz, J_{MX} = 135 Hz), δ_X −3.3 (dd, J_{AX} = 25 Hz, J_{MX} = 135 Hz). FT-IR (CH$_2$Cl$_2$, cm^{-1}): 3055 (s), 2988 (m), 2306 (m), 1423 (m). MS (15 V, ESP$^+$): 1266 (M + H)$^+$, 1140 (M − I)$^+$, 1003 (M − PPh$_3$ + H)$^+$. Anal. Calcd for $\mathrm{C_{65}H_{42}P_3IPd_2}$: C, 61.68; H, 4.14. Found: C, 63.20; H, 4.02. Consistent with the proposed structure, this product was isolated also by chromatographic separation of the products of transmetalation obtained by reaction of **2a**,**b** with different tin acetylides $[\mathrm{Bu_3Sn{-}C{\equiv}C{-}C_6H_4}(p\text{-X})]$ (X = H, Cl, NO$_2$)].



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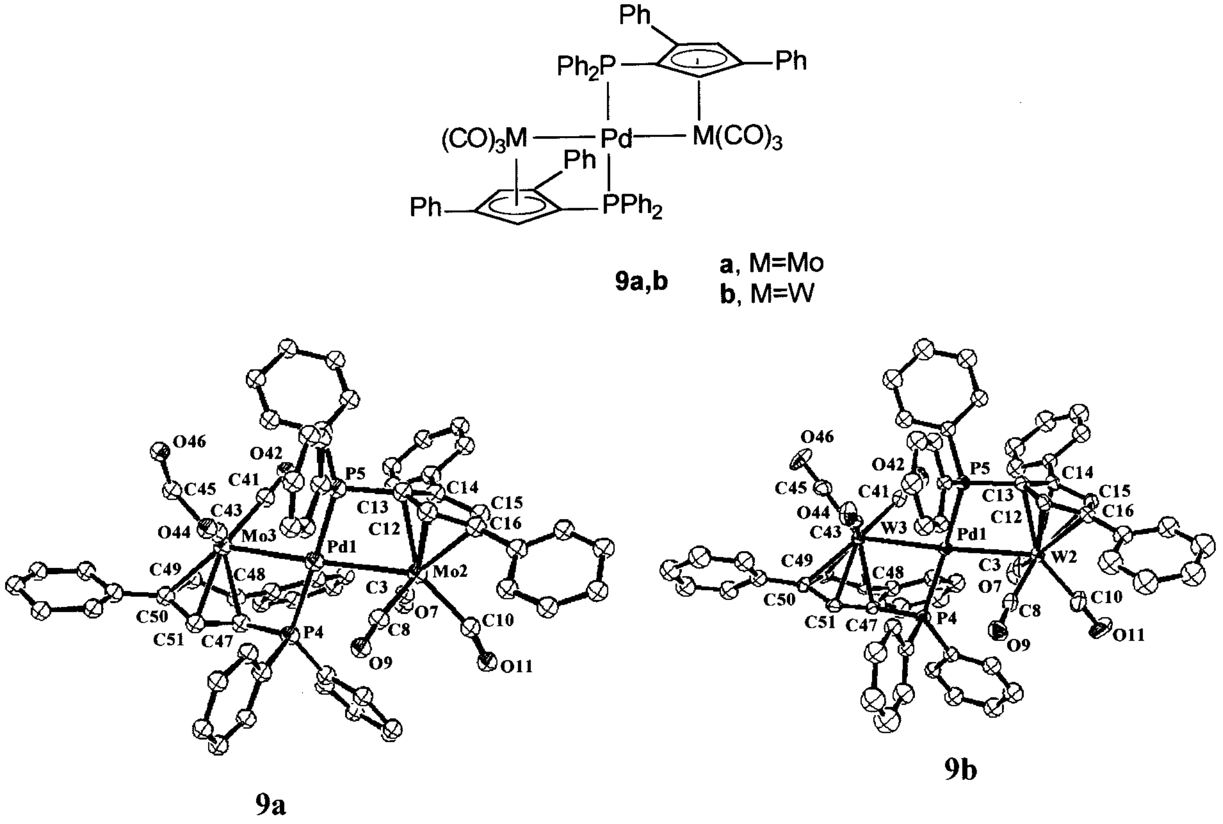


Figure 1. Sketches and ORTEP drawings of **9a** and **9b**.

The red-purple solid isolated from the second band of the chromatographic column gave a ^{31}P NMR spectrum containing two broad signals of slightly different intensity at δ 35.0 and 34.3 ppm. Initially, the presence of two noncorrelated ^{31}P NMR signals was interpreted in terms of the formation of two different products, but accurately repeated chromatographic separations gave invariably a single spot elution. Fortunately, well-shaped crystals of the material eluted as the second fraction were obtained starting from either **5a** or **5b**, which allowed us to carry out single-crystal X-ray analyses.

X-ray Structure Analysis of Complexes 9a and 9b. The molecular structures of complexes *rac*-**9a**,**b** are shown in Figure 1 (together with a sketch of the complexes), while crystal and structural refinement data are listed in Table 1.

In both compounds, the most relevant feature is a linear M−Pd−M array in which a palladium center in a square-planar environment is bound to two *trans* molybdenum or tungsten atoms. This trimetallic assembling is framed by two η^5-cyclopentadienyl-η^1-diphenylphosphino chelating ligands. Each cyclopentadienyl moiety coordinates either molybdenum or tungsten in η^5 fashion, while two *trans* diphenylphosphino groups complete the square-planar coordination geometry about palladium. In turn, three terminal carbonyl ligands complete the piano-stool coordination of each molybdenum or tungsten center.

In both isostructural compounds, the chelating cyclopentadienyl-diphenylphosphino ligands cause a severe deformation of the octahedral and square-planar geometries around the molybdenum (or tungsten) and palladium centers, respectively. The most relevant deformation is experienced by palladium, whose coordination array deviates remarkably from an ideal square-planar geometry.

Table 1. Crystal Data and Structural Refinements Details for 9a and 9b

	9a	9b
formula	$C_{64}H_{52}Mo_2O_{10}P_2Pd$	$C_{74}H_{72}O_6P_2PdW_2$
fw	1341.35	1593.44
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	32.413(3)	13.691(7)
b (Å)	11.466(2)	21.324(9)
c (Å)	16.818(3)	21.714(2)
β (deg)	103.01(4)	97.72(2)
V (Å^3)	6089.9	6281.9
Z	4	4
D_x (g/cm^3)	1.46	1.67
μ (cm^{-1})	7.89	4.04
no. of reflns collcd	13216	8698
no. of reflns with $I_o > 2\sigma(I_o)$	6535	8698
no. of variables	735	380
GOF	1.64	0.991
R	0.077	0.046
R_w	0.154	0.1069

In view of the better quality of the refinement data for the W−Pd−W derivative, a detailed structural description is presented only for *rac*-**9b** (vide infra).

The axes P4−Pd−P5 and W2−Pd−W3, which should be orthogonal, are instead heavily bent, with the W2−Pd−P5 and W3−Pd−P4 angles measuring 75.4° and 76.2°, respectively, while the W3−Pd−P5 and W2−Pd−P4 angles are 104.6° and 105.7°, respectively (Table 2); all values diverge remarkably from those of an orthogonal geometry that would require 90° for all angles.

The P4−Pd−P5 and W2−Pd−W3 axes, which, at first glance, seem to contain the three atoms aligned in a

Table 2. Summary of Selected Distances (Å) and Angles (deg) for Complexes 9a and 9b

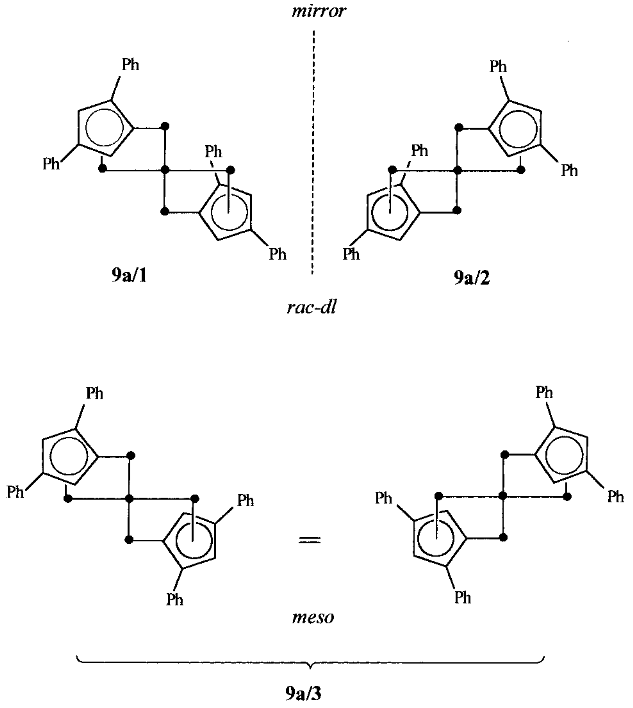
	9a	**9b**
M =	Mo	W
Pd−M2	2.941(2)	2.912(1)
Pd−M3	2.932(2)	2.920(1)
Pd−P4	2.325(5)	2.326(3)
Pd−P5	2.333(5)	2.321(3)
M2−Cp1(centrd)	2.019(4)	2.003(1)
M3−Cp2(centrd)	1.935(3)	1.992(1)
|M2−Pd−M3|	169.2(1)	172.0(3)
P4−Pd−P5	171.4(3)	166.6(1)
M2−Pd−P4	104.6(1)	105.7(8)
M2−Pd−P5	75.8(1)	75.4(8)
M3−Pd−P4	75.6(1)	76.2(8)
M3−Pd−P5	105.7(1)	104.5(8)
Cp1(centrd)−M2−Pd	107.2(1)	108.3(3)
Cp1(centrd)−M2−C6	125.7(2)	125.4(3)
Cp1(centrd)−M2−C8	127.8(1)	126.7(4)
Cp1(centrd)−M2−C10	112.5(1)	120.5(3)
Cp2(centrd)−M3−Pd	107.5(2)	107.3(5)
Cp2(centrd)−M3−C41	123.5(1)	127.0(3)
Cp2(centrd)−M3−C43	129.1(1)	123.4(4)
Cp2(centrd)−M3−C45	114.5(1)	120.4(4)

straight line, are significantly bent, forming a broken line with angles of 166.6° and 172.0°, respectively. In addition, both tungsten centers suffer a severe distortion from an ideal octahedral geometry. In the two four-membered rings Cp1−W2−Pd−P5 and Cp2−W3−Pd−P4 (each Cp is assumed to act as a single unit of this ring), the $\mathrm{Cp1}_{\mathrm{centroid}}$−W2−Pd angle and $\mathrm{Cp2}_{\mathrm{centroid}}$−W3−Pd angle measure only 108.3° and 107.3°. This heavy distortion reflects also the deformation of the angles of the carbonyls *trans* to the W2−Pd and W3−Pd bonds; the $\mathrm{Cp1}_{\mathrm{centroid}}$−W2−C10 (120.5°) and $\mathrm{Cp2}_{\mathrm{centroid}}$−W3−C45 (120.3°) angles are quite different from the values found for all the other $\mathrm{Cp}_{\mathrm{centroid}}$−W−CO angles (123.4−127.0°). Further evidence of the ring strain affecting the two $\mathrm{Cp}_{\mathrm{centroid}}$−W−Pd−P four-membered rings is seen in the pronounced out-of-plane bending of both phosphorus (P4 = 0.54 Å, P5 = 0.59 Å) with respect to the corresponding cyclopentadienyl planes. About the central core of the complex not only is the square arrangement heavily deformed, but also the expected planarity around palladium is not observed. The palladium atom is in fact found approximately 0.18 Å out of the mean plane formed by the coordinated W2, W3, P4, and P5 atoms (their out-of-plane deviation is 0.02, 0.02, −0.45, and 0.46 Å, respectively).

Being unsymmetrically substituted and conformationally blocked by the chelating action of the diphenylphosphine groups anchored to palladium, the cyclopentadienyl moieties of **9a**,**b** constitute two elements of chirality.[12] Consequently both complexes **9a**,**b** exist as a mixture of two diastereisomers (*rac-dl* and *meso*) (Scheme 2). Therefore, the presence of two distinct singlets in the ^{31}P NMR spectra of crude **9a**,**b** as obtained by in-column degradation of **5a**,**b** can be attributed to the formation of both *rac* (sketches **9a/1−2** of Scheme 2) and *meso* forms (structure **9a/3**) in a 1:1 ratio.[13]

Alternative Synthesis of the Trimetallic Complexes 9a,b. Complexes **9a**,**b** with their unusual M−Pd−M array represent unique structures with potential applications in catalytic processes promoted by combinations of early and late transition metals.[14] However, any study of the reactivity of **9a**,**b** requires the development of a convenient high-yield synthesis, in contrast to the chromatographic degradation of the transmetalation products **5a**,**b**. In search of more efficient routes to the trimetallic compounds, we have found that the μ-I binuclear complexes $[\mathrm{Pd}(\mu\text{-I})\{\mathrm{M(CO)_3}\text{-}(\eta^5\text{-}\mathrm{C_5H_2Ph_2(PPh_2)})\}]_2$[7d] (**10a**,**b**) shown in Scheme 3 are excellent starting materials to obtain complexes **9a**,**b**. The synthetic strategy involves the selective removal of a $\mathrm{PdI_2}$ group from **10a**,**b** by a chelating diphosphine ligand such as dppe (dppe = 1,2-diphenylphosphinoethane) (Scheme 3). Using this procedure both complexes **9a**,**b** were obtained as a mixture of the **9a**,**b/1−3** stereoisomers.

Scheme 2



Reactivity of 9a toward Organostannanes. In previous mechanistic studies of the palladium-catalyzed M−C bond formation reaction, the transmetalation complexes **5a**,**b** have been shown to be crucial intermediates in the catalytic cycle leading to the cross-coupling products **7a**,**b** (Scheme 1). Indeed, both the metal center M and the acetylide moiety in complexes **5a**,**b** join in a single molecular unit, and completion of the coupling process only needs the *trans*-to-*cis* isomerization and the reductive elimination steps. It was found that the

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[12] Haltermann, R. L. *Chem. Rev.* **1992**, *92*, 965.

[13] From a comparison of the X-ray structures of **9a** reported in Figure 1 with the sketches **9a/1−3** (Scheme 2), it is evident that the crystalline material obtained upon recrystallization of chromatographically pure **9a** is the *rac* mixture **9a/1−2**. Consequently, the mother liquor from which these crystals were obtained should result enriched in the *meso* form **9a-3**. According to this, the ^{31}P NMR spectra of a sample of the crystalline material (**9a/1−2**) used for the X-ray analysis show a single peak at 34.3 ppm, while that of the material recovered from the mother liquor shows a major peak at 35.0 ppm, due to the *meso* form **9a-3**, accompanied by a little signal due to a residual amount of the *rac* form. An identical NMR behavior was displayed by the W−Pd−W derivatives *rac*-**9b** and *meso*-**9b** (see the Experimental Section).

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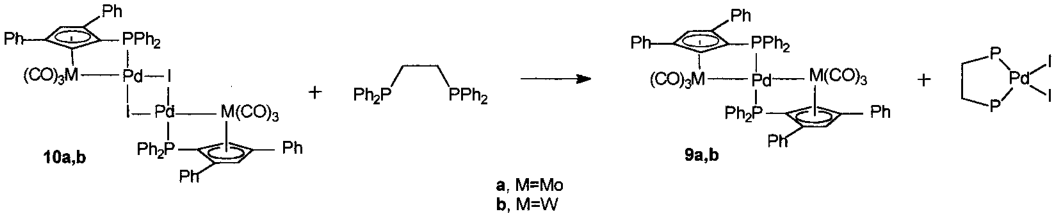
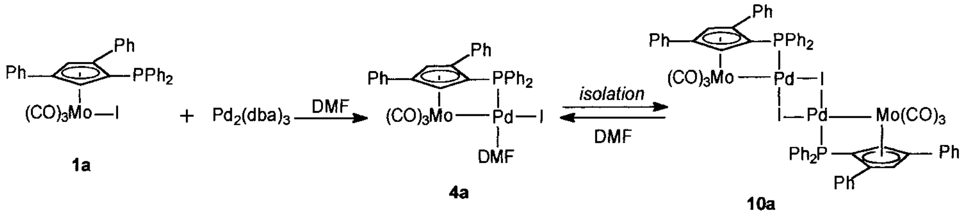
Scheme 3



Scheme 4



transmetalation reaction proceeds under dilute conditions ([**2a**] ≅ 10^{-4} M) with the intermediacy of the solvento complex **4a** generated by substitution of PPh_3 with DMF (path b of Scheme 1).[7d] Unambiguous identification of the solvento complex **4a** was obtained from its independent synthesis by reaction of **1a** with a phosphine-free zerovalent palladium complex, $Pd_2(dba)_3$ (dba = dibenzylideneacetone) (Scheme 4). Although all our attempts to isolate **4a** invariably ended with the isolation of the binuclear μ-I complex $[Pd(\mu\text{-}I)\{Mo(CO)_3(\eta^5\text{-}C_5H_2Ph_2(PPh_2)\}]_2$ (**10a**), the latter dissolved in DMF converted immediately and quantitatively into **4a**, which was studied in the reaction toward organostannanes.

The solvento complex **4a**, generated in DMF from **10a**, was treated with $Bu_3Sn{-}C{\equiv}C{-}Ph$ in a 5 mm NMR tube, and the reaction was followed by ^{31}P NMR spectroscopy (Figure 2). Upon addition of a 10-fold excess of the tin acetylide at room temperature, the singlet of **4a** at 51.9 ppm (trace a) disappeared immediately to give two signals at 1.2 and 2.2 ppm. A signal at −20.2 ppm appeared later (trace b taken after 15 min), which was attributed to the reductive-elimination product **7a**. On warming the sample at 60 °C, the concentration of **7a** increased and two new signals at 34.7 and 34.1 ppm due to **9a**/**1**−**3** (*meso*/*rac*) appeared in the spectrum (trace c). After 20 h at 60 °C, while the signals at 1.2 and 2.2 ppm had disappeared, the main product **7a** was accompanied by a residual amount of **9a** (trace d). Further in time only **7a** was visible in the spectrum.

The intermediacy of **9a** along the way from **4a** to **7a** was initially quite surprising. In fact, it was hard to conceive that this trimetallic complex, previously isolated after chromatographic degradation of **5a**, could still be reactive toward an organostannane yielding **7a**. This is indeed what happened, as shown by an independent NMR experiment in which pure **9a** in DMF reacted with a 10-fold excess of phenyltributyltin acetylide to selectively give **7a** after 20 h at 60 °C.

^{31}P NMR spectroscopy gave valuable information on the structure of the intermediate along the conversion of **4a** to **9a**. PPh_3 was added into the NMR tube when the spectrum contained the two singlets at 1.2 and 2.2 ppm (trace b in Figure 2). Immediately, the two peaks disappeared and were replaced by a doublet of doublets with $J(PP) = 454$ Hz, which was attributed to the formation of complex **5a** bearing *trans* PPh_3 and $Cp{-}PPh_2$ groups.[7b] Therefore, it is likely that the precursor PPh_3-deficient complex is the DMF adduct $[Pd(C{\equiv}C{-}Ph)(DMF)\{Mo(CO)_3(\eta^5\text{-}C_5H_2Ph_2(PPh_2)\}]$ quoted as **11a** in Figure 2. This figure incorporates all the experimental evidence obtained and summarizes the stepwise transformation of **10a** into **7a**, as well as the reaction with PPh_3 used to intercept the reactive solvento intermediate **11a**.

Conclusions

The complexes of transmetalation **5a**,**b**, which are key intermediates in the Pd-catalyzed coupling of a metal halide with trialkyltin acetylide moieties, are unstable under chromatographic separation and degrade to two new products: a trimetallic cluster containing a linear M−Pd−M array (**9a**, M = Mo; **9b**, M = W) and a dimeric palladium(I) complex **8** with a Pd−Pd bond.[11] In this formally Pd(I) complex, the two metal centers are bridged by an iodide atom and by a η^3-pseudoallylic cyclopentadienyl ligand. The formation of both products is difficoult to explain given the complexity of the intra- and intermolecular rearrangements involved as well as the absence of detected intermediates.

An independent high-yield synthesis of **9a**,**b** has been developed. It will allow us to study in depth the chemistry of these unique compounds in which the bridging palladium atom still mediates the formation of $M{-}C{\equiv}C{-}R$ moieties from trialkyltin acetylenes. It is very likely that other reactions at molybdenum or tungsten may be assisted by the bridging palladium center that may behave as either a leaving group or an active promoter. One of the many possible reactions is the hydrodesulfurization (HDS) of thiophenes, carried out in the industrial practice with catalysts containing either molybdenum or tungsten in conjunction with late transition metals (like palladium) as activators.[14,15]

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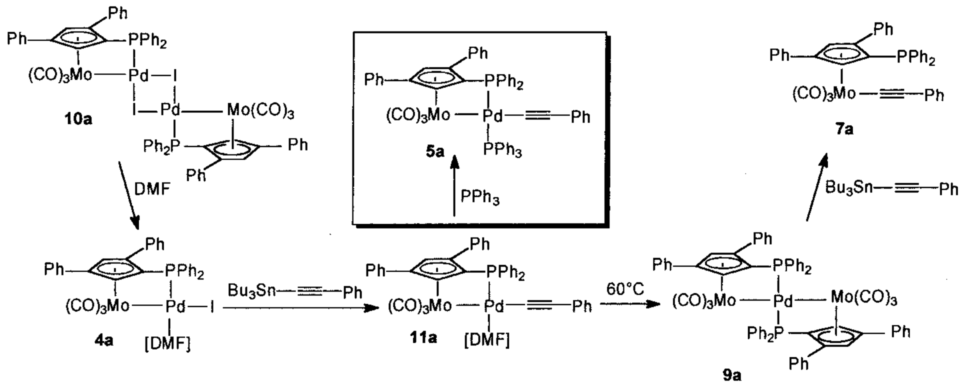
(15) (a) Kabe, T.; Ishihara, A.; Qian, W. *Hydrodesulfurization and Hydrodenitrogenation*; Wiley-VCH: Weinheim, 1999. (b) Vasudevan, P. T.; Fierro, J. L. G. *Catal. Rev. Sci. Eng.* **1996**, *38*, 161.



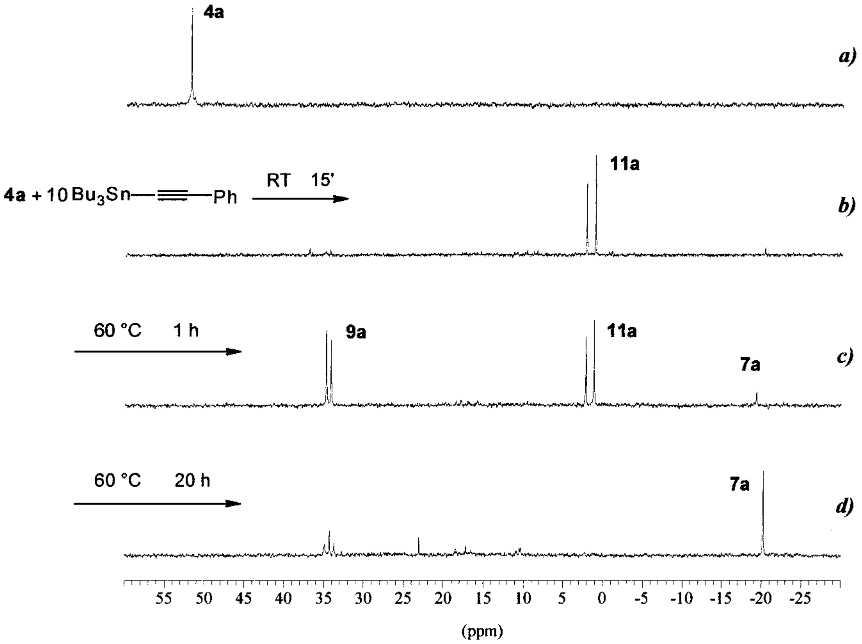
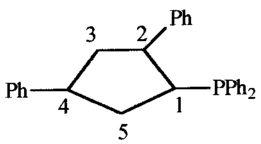


Figure 2. In situ $^{31}P\{^1H\}$ NMR study of the reaction between **4a** and $Bu_3SnC{\equiv}C{-}Ph$ in DMF-d_7.

Experimental Section

General Procedures. Elemental analyses were performed by the Servizio Microanalisi of the Dipartimento di Chimica, Università di Roma "La Sapienza". FT-IR spectra were recorded on a Nicolet 510 instrument in the solvent subtraction mode, using a 0.1 mm CaF_2 cell. ^1H, ^{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 ^1H NMR, $CHCl_3$ (δ 7.24) or DMF (δ 2.90) and for ^{13}C NMR $CDCl_3$ (δ 77.0) or DMF-d_7 (δ 161.7) 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 using 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 was distilled from sodium−potassium alloy. $[W(I)(CO)_3(\eta^5\text{-}C_5{-}C_5H_2Ph_2(PPh_2)]$ (**1b**)[7b] and $[Pd(\mu\text{-}I)\{Mo(CO)_3(\eta^5\text{-}C_5{-}C_5H_2Ph_2(PPh_2)\}]_2$ (**10a**)[7d] were prepared according to published procedures. $Ph_2PCH_2CH_2PPh_2$ (dppe), $Pd_2(dba)_3$, $Bu_3Sn{-}C{\equiv}C{-}Ph$, and PPh_3 (Aldrich) were used as received.

Legend for ^{13}C NMR assignments:



$[Pd\{Mo(CO)_3(\eta^5\text{-}C_5\text{-}C_5H_2Ph_2(PPh_2)\}_2]$ (9a). This compound was isolated as a product of decomposition, under chromatographic conditions (*n*-hexane/dichloromethane, 7:3), of the product of transmetalation **5a**. Subsequently, the following direct synthesis has been developed. In a Schlenk tube **10a** (0.195 g, 0.12 mmol) and dppe (0.049 g, 0.12 mmol) were dissolved in THF (20 mL) to give a deep brown solution. Upon warming to 50 °C for 16 h, the reaction mixture turned deep purple. After cooling at room temperature, deep yellow crystals of $PdI_2(dppe)$[16] separated from the solution, which were filtered off, washed with THF, and dried under vacuum. Celite was added to the filtered solution and the solvent removed under vacuum. The coated residue was chromatographed on a silica column (30 cm × 2 cm). Elution with *n*-hexane/dichloromethane, 7:3, produced a purple band, which

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[16] (a) Ito, T.; Tsuchiya, H.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1977**, *50* (5), 1319. (b) Oberhauser, W.; Bachmann, C.; Stampfl, T.; Haid, R.; Brüggeller, P. *Polyhedron* **1997**, *16*, 2827.

was eluted and collected to give, after removal of the solvent, 0.097 g (64%) of **9a**. ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic data showed this product to be a ca. 1:1 mixture of the *rac* and *meso* diastereoisomers. Anal. Calcd for $C_{64}H_{44}Mo_2O_6P_2Pd$: C, 60.56; H, 3.49. Found: C, 60.87; H, 3.47.

Subsequent recrystallization of this mixture (CH_2Cl_2/*n*-pentane, vapor diffusion) at −20 °C afforded a crystalline material, whose X-ray structural determination showed it to be the *rac* diastereoisomer (**9a/1−2**). By evaporation of the solvent from the mother liquor a residue consisting in the *meso* diastereoisomer (**9a/3**), slightly contaminated by a residual amount of the *rac* diastereoisomer, was obtained.

Characterization of 9a/1−2 (*rac* diastereoisomer). ^{1}H NMR ($CDCl_3$): δ 7.67 (br), 7.46−7.07 (m), 6.99−6.85 (m), 6.30 (m, *Cp*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.3 (bs). ^{13}C NMR ($CDCl_3$): δ 234.5, 222.4, 213.7 (*CO*), 134.5−125.7 (*Ph*), 116.1 (s, C_2), 111.0 (br, C_4), 93.0 (s, C_3), 90.1 (s, C_5), 57.8 (d, J_{C-P} = 44.9 Hz, C_1). FT-IR (CH_2Cl_2, cm^{-1}): 1939 (s), 1875 (s) (ν_{CO}).

Characterization of 9a/3 (*meso* diastereoisomer). ^{1}H NMR ($CDCl_3$): δ 7.60 (br), 7.29−7.01 (m), 6.81−6.63 (m), 6.26 (m, *Cp*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 35.0 (bs). ^{13}C NMR ($CDCl_3$): δ 237.8, 226.6, 213.7 (*CO*), 134.5−125.4 (*Ph*), 116.2 (s, C_2), 110.9 (br, C_4), 94.0 (s, C_3), 90.8 (s, C_5), 58.1 (d, J_{C-P} = 48.5 Hz, C_1). FT-IR (CH_2Cl_2, cm^{-1}): 1938 (s), 1873 (s) (ν_{CO}).

Characterization of PdI_2(dppe). ^{1}H NMR ($CDCl_3$): δ 7.84−7.74 (m), 7.55−7.43 (m), 2.35 (s), 2.23 (s). $^{31}P\{^1H\}$ NMR (DMF-d_7): δ 66.7 (s). Anal. Calcd for $C_{26}H_{24}I_2P_2Pd$: C, 41.2; H, 3.2. Found: C, 41.3; H, 3.4. MS (15 V, ESP$^+$): *781* (M + Na)$^+$, *633* (M − I)$^+$. Analytical and spectroscopic properties are in agreement with reported data.[16]

[Pd(μ-I){W(CO)$_3$(η^5-C$_5$H$_2$Ph$_2$(PPh$_2$)}]$_2$ (10b). A Schlenk flask was loaded with [W(I)(CO)$_3${η^5-(1-Ph$_2$P-2,4-Ph$_2$)C$_5$H$_2$}] (**1b**)[7b] (0.58 g 0.73 mmol) and $Pd_2(dba)_3$ (0.33 g, 0.36 mmol). After three cycles of vacuum/argon, 15 mL of THF was added to the flask and the resulting dark solution was stirred for 30 min at room temperature. Upon addition of *n*-pentane, a brown powder precipitated, which was collected by filtration, washed repeatedly with pentane to eliminate the residual dba ligand, and dried under vacuum. Then 0.42 g (64%) of pure **10b** was obtained. ^{1}H NMR ($CDCl_3$): δ 8.49 (m), 7.75−7.51 (m), 7.30−7.15 (m), 7.00−6.75 (m), 6.00 (m, 1H, Cp-*H*), 4.68 (m, 1H, Cp-*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 39.0. ^{13}C NMR ($CDCl_3$): δ 228.4, 214.4, 212.5 (*CO*), 136.8−125.4 (*Ph*), 116.7 (d, J_{C-P} = 7.2 Hz, C_2), 108.0 (d, J_{C-P} = 7.2 Hz, C_4), 92.6 (d, J_{C-P} = 7.2 Hz, C_3), 87.0 (d, J_{C-P} = 12.6 Hz, C_5), 58.7 (d, J_{C-P} = 46.7 Hz, C_1). FT-IR (CH_2Cl_2, cm^{-1}): 1965 (s), 1889 (s), 1869 (sh) (ν_{CO}). Anal. Calcd for $C_{32}H_{22}IMoO_3PPd$: C, 47.17; H, 2.72. Found: C, 46.97; H, 2.74.

[Pd{W(CO)$_3$(η^5-*C$_5$*-C$_5$H$_2$Ph$_2$(PPh$_2$)}$_2$] (9b). Like **9a**, this compound was first isolated as a product of decomposition, under chromatographic conditions (silica gel, *n*-hexane/dichloromethane, 1:1), of the product of transmetalation **5b**. Subsequently, the direct synthesis was accomplished with a procedure similar to that used for **9a**. In a Schlenk tube **10b** (0.257 g, 0.14 mmol) and dppe (0.063 g, 0.15 mmol) were dissolved in THF (10 mL), and the resulting deep brown solution was warmed at 70 °C for 17 h. After cooling at room temperature, Celite was added to the crude mixture and the solvent was removed under vacuum. The coated residue was then chromatographed on a silica column (30 cm × 2 cm). Elution with *n*-hexane/dichloromethane, 1:1, produced a dark purple band, which was eluted and collected to give, after removal of the solvent, 0.097 g (63%) of **9b** as a bordeaux crystalline solid. ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic data showed this product to be a 1:1 mixture of the *rac* and *meso* diastereoisomers. These were easily separated due to their different solubility in acetone. Treating the mixture with acetone, a solution of the *rac* diastereoisomer was obtained, while the solid residue was the *meso* diastereoisomer, slightly contaminated by a residual amount of the *rac* form. Anal. Calcd for $C_{64}H_{44}W_2O_6P_2Pd$: C, 53.19; H, 3.07. Found: C, 54.17; H, 3.28.

Characterization of 9b/1−2 (*meso* diastereoisomer, insoluble in acetone). ^{1}H NMR ($CDCl_3$): δ 7.68 (br), 7.45−7.06 (m), 6.97−6.85 (m), 6.23 (m, *Cp*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 28.1 (bs). ^{13}C NMR ($CDCl_3$): δ 227.6, 222.6, 213.9 (*CO*), 134.6−125.6 (*Ph*), 113.9 (s, C_2), 106.0 (br, C_4), 88.4 (s, C_3), 91.2 (s, C_5), 58.7 (s, C_1). FT-IR (CH_2Cl_2, cm^{-1}): 1932 (s), 1862 (s) (ν_{CO}).

Characterization of 9b/3 (*rac-dl* diastereoisomer, soluble in acetone). ^{1}H NMR ($CDCl_3$): δ 7.61 (br), 7.26−7.01 (m), 6.86−6.63 (m), 6.18 (m, *Cp*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 28.4 (bs). ^{13}C NMR ($CDCl_3$): δ 227.0, 223.1, 214.0 (*CO*), 134.6−126.0 (*Ph*), 113.5 (s, C_2), 88.1 (s, C_3), 90.7 (s, C_5), 59.0 (br, C_1). FT-IR (CH_2Cl_2, cm^{-1}): 1926 (s), 1859 (s) (ν_{CO}).

X-ray Diffraction Studies. A summary of crystal and intensity data is presented in Table 2 for both compounds.

Complex 9a. A prismatic specimen of the complex, with dimensions 0.3 × 0.6 × 0.9 mm, was mounted on a Philips PW1100 single-crystal diffractometer.[17] Data collection was carried out at room temperature with Mo Kα radiation (λ = 0.71069 Å) in the θ range 3−25° ($-41 \le h \le 40$, $0 \le k \le 14$, $0 \le l \le 21$). Cell parameters were obtained from least-squares of 32 reflections (θ range 4.9−13.0°) automatically well centered on the diffractometer.

One check reflection was monitored every 100: a decomposition of about 21% was observed during the data collection time. A total of 6535 reflections were with $I \ge 2\sigma(I)$ out of a total of 13216 independent measured (R_{int} = 0.043). Only 3831 are those with $I \ge 3\sigma(I)$; however corrections for the decay and for Lorentz and polarization effects were applied. The absorption correction was performed with the program DIFABS.[18] The structure was obtained with the SIR97[19] program using all the measured reflections and was refined with the CRYSRULER package[20] using SHELX97.[21] Four water molecules were detected in the lattice structure and successfully refined. The low quality of the experimental data stopped the refinement to R = 0.154.

Complex 9b. A parallelepiped crystal with dimension 0.55 × 0.125 × 0.175 mm was used for the data collection. Experimental data were recorded at room temperature (20 °C) on an Enraf-Nonius CAD4. A set of 25 carefully centered reflections in the range 7° ≤ θ ≥ 9.5° was used for determining the lattice constants. As a general procedure, the intensities of three standard reflections were measured periodically every 200 reflections for orientation and intensity control. This procedure did not reveal decay of intensities. The data were corrected for Lorentz and polarization effects. Atomic scattering factors were those tabulated by Cromer and Waber[22] with anomalous dispersion corrections taken from ref 23. An empirical absorption correction was applied via Ψ scan with correction factors in the range 0.996−0.863. The computational work was carried out by using the program SHELX97.[21] Final atomic coordinates of all atoms and structure factors are available on request from the authors and are provided as Supporting Information. The structure was solved by direct methods using the SIR92 program.[19] The refinement was done

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by full-matrix least-squares calculations, initially with isotropic thermal parameters, then with anisotropic thermal parameters for Pd, W, O, P, and all C atoms but the phenyls. The phenyl rings were treated as rigid bodies with D_{6h} symmetry, and the hydrogen atoms were allowed to ride on the attached carbon atoms. Two solvent crystallization molecules, pentane and cyclopentadiene, were detected and successfully refined.

Supporting Information Available: Figures showing ^{1}H, ^{31}P NMR and MS spectra of **8**. Full tables of crystal data, atomic coordinates, thermal parameters, and bond lengths and angles for **9a** and **9b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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