# Isolation of Transmetalation Intermediates in the Stille Cross-Coupling Reaction of Stannanes: Synthesis of Palladacycles, Ligand Substitution, and Insertion Reactions

**Cristina Mateo, Diego J. Cárdenas, Carolina Fernández-Rivas, and Antonio M. Echavarren***

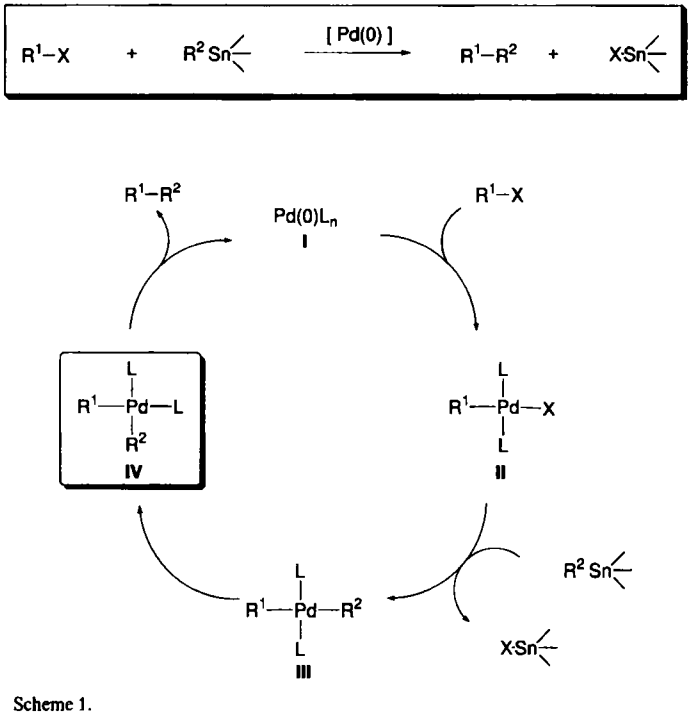
**Abstract:** A strategy based on a Stille cross-coupling reaction of organostannanes interrupted at the reductive elimination step has been applied to the synthesis of oxa- and azapalladacycles with the general formula *cis*-[PdArR(L)$_2$]. The synthesis of oxapalladacycles was achieved under mild conditions by reaction of 2-iodo- or 2-bromophenyloxymethylstannanes with [Pd(PPh$_3$)$_4$]. The synthesis of an aza analogue was similarly carried out from the corresponding 2-iodoaniline derivative. One of the substituted oxapalladacycles rearranged to release steric strain between the palladium and a chloride substituent on the aryl ring, an isomerization promoted by traces of water. In one case, the arylpalladium(II) intermediate of oxidative addition was isolated by using a palladium(0) complex with a bidentate diphosphane. A variety of new palladacycles, including complexes with weakly coordinating ligands, were prepared by ligand substitution. Reaction of the palladacycles with dimethyl acetylenedicarboxylate led to the formation of chromenes or dihydroquinolines by insertion followed by reductive elimination.

**Keywords**
organostannanes · palladium complexes · palladacycles · Stille reaction · transmetalation

## Introduction

Palladium-catalyzed cross-coupling reactions of organic halides with organometallic nucleophiles have emerged as one of the most powerful synthetic methods developed in the last few years for the formation of carbon–carbon bonds.[1, 2] Methods employing mild organometallic reagents such as tetraorganostannanes (Stille reaction)[3] and organoboranes (Suzuki reaction)[4] as the nucleophilic reagents are particularly useful, because of their ready availability and compatibility with most functional groups.

The Stille coupling reaction of organostannanes takes place under relatively mild conditions with a variety of organic electrophiles including halides and triflates as the most common substrates (Scheme 1).[2] The reaction is broadly accepted to proceed according to the mechanism outlined in Scheme 1.[2, 3, 5] The oxidative addition of organic electrophiles $R^1X$ to a coordinatively unsaturated palladium(0) complex **I** affords square-planar palladium(II) complex **II**,[6, 7, 8] whose transmetalation with the stannane leads to the formation of a second square-planar palladium(II) complex **III**. A *trans*-to-*cis* isomerization, probably by a dissociative pathway,[9] leads to the formation of intermediate **IV**, which undergoes a fast reductive elimination to form a carbon–carbon bond and the catalytically active palladium(0) species **I**.[10] However, the transmetalation step has not been studied in detail and is still not well understood.[11, 12, 13] Thus, for example, although inversion of configuration was reported in the transmetalation reaction with benzylstannanes,[13] clean retention of the configuration has been recently observed in the palladium-catalyzed coupling of




Scheme 1.

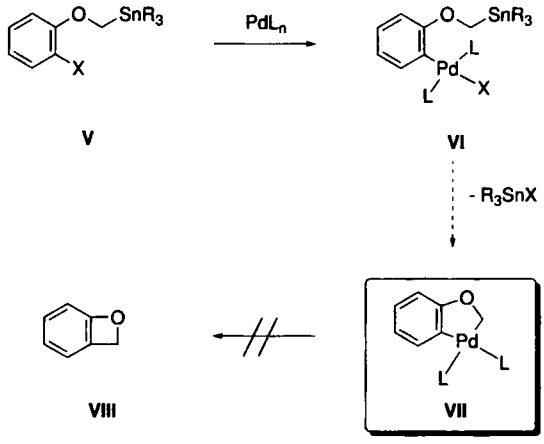
[*] Prof. A. M. Echavarren, Dr. D. J. Cárdenas, C. Mateo, C. Fernández-Rivas
Departamento de Química Orgánica, Universidad Autónoma de Madrid
Cantoblanco, 28049 Madrid (Spain)
Fax: Int. code +(1)397-3966
e-mail: aechav@ccuam3.sdi.uam.es



0947-6539/96/0212-1596 $ 15.00+.25/0

chiral α-alkoxystannanes in the presence of copper(I) cyanide.[13, 14] Although many complexes of structure **II** have been isolated by oxidative addition reactions,[15] it has not been possible to isolate complexes **III** or **IV** by transmetalation reactions of complexes **II** under the conditions of the Stille reaction,[16] since transmetalation is followed by faster isomerization and reductive elimination.[11b, 17] The fact that the last two steps are not rate-determining has indeed been applied successfully in the synthesis of strained cyclobutanes[18] and large rings.[19]

We conceived a solution for the synthesis of intermediates **IV** of the type *cis*-[PdArR(L)$_2$] by using a Stille reaction interrupted at the reductive elimination reaction (Scheme 2).[20] Thus, it was anticipated that the oxidative addition of haloarylstannane **V** (X = Br, I) to a palladium(0) complex would furnish intermediate **VI**, whose intramolecular transmetalation[21] through the $OCH_2$–Sn bond would give the desired palladacyclic complexes **VII**, cyclic relatives of complexes **IV** in Scheme 1. The endocyclic restriction[22] imposed by the tether connecting Pd and Sn should disfavor the alternative cleavage of the Sn–R bonds. We also expected that the reductive elimination would be slow owing to the high energy of the derived organic product benzoxetene (2*H*-benzoxete) (**VIII**).[23] A point of concern was the possible decomposition of the palladacycles **VII** by reaction with the electrophilic by-products $R_3SnX$ (X = Br, I) to afford acyclic palladium(II) complexes. Another motivation for attempting the synthesis of palladacycles **VII** was the recent proposal by Dyker that compounds of this type were involved as intermediates in novel palladium-catalyzed cascade reactions leading to the formation of terphenyl derivatives.[24, 25] Here, the proposed intermediates of type **VII**, in which palladium(II) is probably coordinated to two molecules of *N*,*N*-dimethylformamide (DMF), arise by a novel C–H activation of the methoxy group of *o*-iodoanisole.[24] Other palladacycles related to **VII** have been proposed[26] as intermediates in a number of interesting transformations allowing several carbon–carbon bonds to be formed sequentially in a single step.[27]

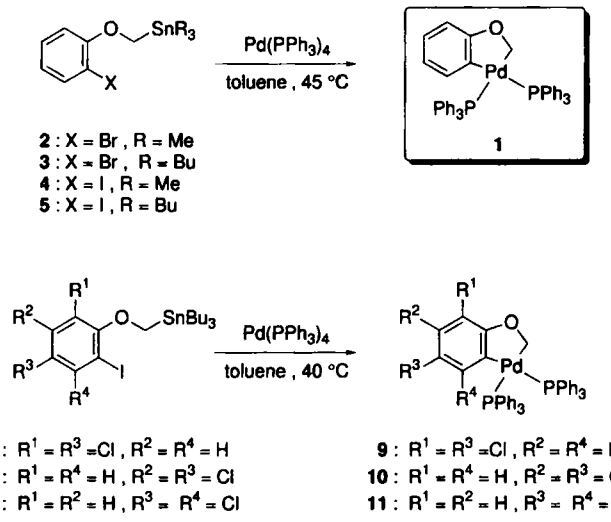



Scheme 2.

In this paper we report the synthesis of oxapalladacycles **VII** and an aza derivative by using the strategy outlined in Scheme 2.[28, 29, 30, 31] In the course of this study we have uncovered a rearrangement of one of the palladacycles that proceeds by an intramolecular C–H activation. We also report the synthesis of new palladacycles by ligand substitution reactions as well as some insertion reactions of alkynes. In particular, and as a prelude to a more detailed study of the reactivity of the palladacycles towards electrophilic reagents, we describe a new method for the replacement of phosphane ligands of complexes **VII** (L = phosphane) by less strongly coordinating ligands such as alkenes and arsanes.

## Results and Discussion

**Synthesis of oxapalladacycles**: The synthesis of parent oxapalladacycle **1** with two triphenylphosphane ligands was carried out uneventfully as originally planned (Scheme 3). Thus, alkyla-




Scheme 3.

tion of *o*-bromophenol or *o*-iodophenol with (iodomethyl)trimethyl- or (iodomethyl)tributylstannane[32] in DMF in the presence of $K_2CO_3$[33] gave stannanes **2**–**5** in good yields. Reaction of either of these tetraalkylstannanes with [Pd(PPh$_3$)$_4$] proceeded smoothly in toluene at 45 °C for 24 h to give the desired palladacycle **1** as an air-stable, white powder. Fortunately, under the reaction conditions, palladacycle **1** does not react with the by-products $Me_3SnX$ or $Bu_3SnX$ (X = Br, I). Despite repeated attempts at lower temperature and shorter reaction times, the primary palladium(II) complex of type **II** (Scheme 1), resulting from oxidative addition of the iodoarene to the palladium(0) reagent, could not be isolated in this case. The structure of **1** was secured on the basis of $^1$H, $^{13}$C, and $^{31}$P NMR, including $^1$H–$^{13}$C HMQC and HMBC correlations.[34] Characteristic signals in the $^1$H NMR spectrum were four multiplets at $\delta$ = 6.78, 6.71, 6.61, and 6.06 for the aromatic hydrogens and a doublet of doublets at $\delta$ = 5.18 corresponding to the methylene hydrogens coupled with two inequivalent phosphorus atoms ($J$ = 5.6, 3.3 Hz). In the $^{13}$C NMR the methylene carbon resonates at $\delta$ = 93.49 and is coupled with the *trans*- ($J$ = 90.8 Hz) and *cis*-phosphanes ($J$ = 6.4 Hz). The resonance of the oxygen-bonded aromatic carbon appeared at rather low field ($\delta$ = 174.70) owing to the withdrawing effect of the *ortho* palladium(II). The phosphane ligands give rise to the expected AX system in the $^{31}$P NMR spectrum with a $^2J$ of 25.6 Hz. As we had originally expected, palladacycle **1** did not undergo reductive elimination to give the product **VIII** (Scheme 2), even after being heated in benzene at 80 °C for several hours. This palladacycle was quite inert towards aqueous hydrolysis. Thus, cleavage of both palladium–carbon bonds could only be achieved in

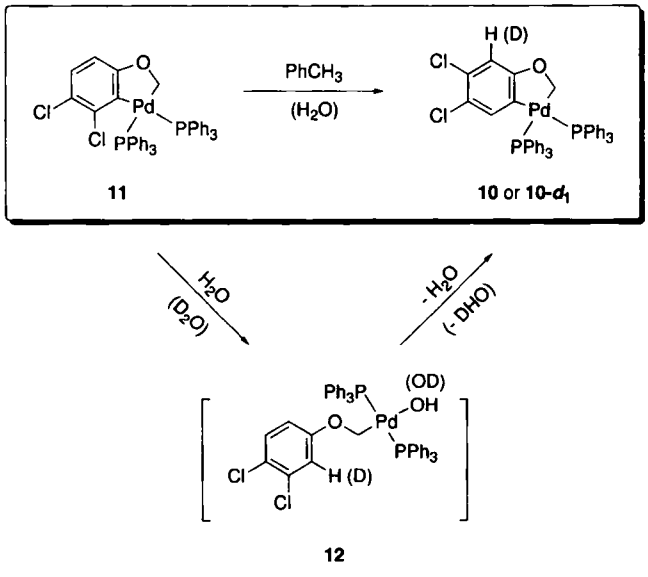
  0947-6539/96/0212-1597 $ 15.00+.25/0 

wet $CDCl_3$ after 5 d at 23 °C, yielding anisole in quantitative yield.

The method developed for the synthesis of **1** could also be applied for the preparation of other substituted oxapalladacycles. Thus, dichloroiodophenylstannanes **6** and **7** led to the corresponding oxapalladacycles **9** and **10** in good yields (82 and 93%, respectively). These palladacycles showed similar NMR spectral data to those of **1**. Particularly diagnostic were the pair of doublets observed in the $^{31}P$ NMR spectrum at $\delta = 28-29$ and 24–25 with a coupling constant of 25–27 Hz and a doublet of doublets in the $^1H$ NMR spectrum corresponding to the methylene hydrogens at $\delta = 5.0-5.2$ ($J = 5.5-5.6$ and 3.1–3.3 Hz).

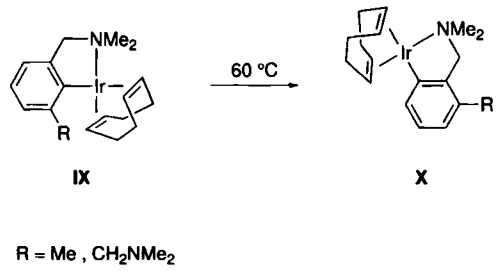
3,4-Dichloro derivative **8** led quantitatively to a palladacycle **11**, which showed a methylene at $\delta = 5.11$, coupled only to one phosphorus with $J = 6.6$ Hz. The $^{31}P$ NMR spectrum at 25 °C showed two broad signals at $\delta = 24.26$ and 17.11. On lowering the temperature to 0 °C a pair of doublets were observed at $\delta = 24.41$ and 16.98 ($J = 26.8$ Hz). No further changes occurred between 0 and −60 °C. These results are consistent with a highly distorted square-planar coordination of the palladium in complex **11** with the phosphane *cis* to the aryl slightly out of the coordination plane of palladium(II) to avoid steric interference with the chloride substituent.

Because of the steric crowding around the metal, palladacycle **11** was less stable than **1**, **9**, or **10** and rearranged on standing in toluene to give complex **10** (Scheme 4). This quantitative transformation most probably takes place by electrophilic cleavage of the more reactive aryl–palladium bond by traces of water in the toluene solvent to form a reactive hydroxopalladium(II) intermediate **12**, or the corresponding hydroxo-bridged dimer,[35, 36] which reacts intramolecularly by aromatic activation of the less hindered C–H bond. The last step has precedence in related intramolecular arylation reactions promoted by hydroxide or alkoxide as the bases.[26a, 26b, 37] Accordingly, when **11** was warmed at 80 °C in toluene saturated with $D_2O$, complex [$D_1$]**10** deuterated at C-3 was cleanly obtained as the only product of the rearrangement.



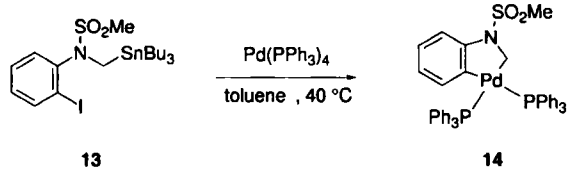

Scheme 4.

The isomerization of **11** to **10** is somewhat reminiscent of the rearrangement of aryliridium(I) complexes **IX** to give **X** observed by van Koten et al. (Scheme 5).[38] Although the mechanisms of the rearrangement of the palladium(II) and iridium(I) complexes are clearly different,[38] the driving force for the rearrangements in both transformations is the release of steric hindrance between the metal and the substituents on the aryl rings.




Scheme 5.

**Synthesis of azapalladacycle 14**: The methanesulfonylaminostannane **13** was readily prepared in two steps from *o*-iodoaniline by sulfonylation followed by N-alkylation with $Bu_3SnCH_2I$. This functionalized stannane reacted cleanly with $[Pd(PPh_3)_4]$ in toluene at 40 °C to afford the novel azapalladacycle **14** as a white solid (78% yield) (Scheme 6). Its $^1H$ NMR spectrum showed the diagnostic methylene hydrogens at $\delta = 3.98$ coupled with two phosphorus atoms ($J = 6.6$, 4.2 Hz). Palladacycle **14** decomposed slowly in solution to give uncharacterized products which might derive from the heterocycle benzazetine (2*H*-benzazete),[39] the product of reductive elimination. Since benzazetine probably undergoes electrocyclic reversion to form a highly reactive heterodiene, we have tried to proove that this unstable heterocycle is formed by performing the decomposition of **14** in the presence of the dienophile *N*-methylmaleimide. However, under all the conditions examined, we failed to trap any product resulting from the presumed benzazetine.



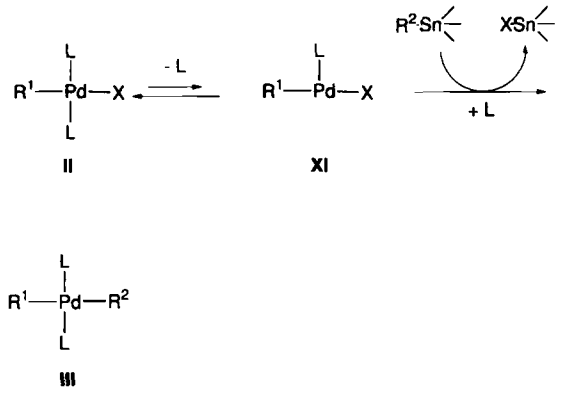

Scheme 6.

**Isolation of an oxidative addition intermediate**: As already mentioned, we could not isolate the oxidative addition intermediates formed in the reaction of arylhalides **2**–**5** with $[Pd(PPh_3)_4]$ at 23–50 °C. Therefore, under these conditions, the intramolecular transmetalation is faster than the oxidative addition. When the process was carried out in the presence of excess triphenylphosphane (2 equiv), the reaction slowed down considerably, leading only to traces of **1** with recovery of the starting stannane. This is not unexpected, since the oxidative addition requires the formation of coordinatively unsaturated $[Pd(PPh_3)_2]$, formed in situ from $[Pd(PPh_3)_4]$.[7, 8] In addition, it has been recently proposed that the transmetalation reaction (**II** → **III**, Scheme 1) follows a dissociative pathway which proceeds through a three-coordinate, T-shaped, 14-electron complex **XI** (Scheme 7).[11a]

Accordingly, we anticipated that, by using a more strongly coordinating bidentate diphosphane which would disfavor the

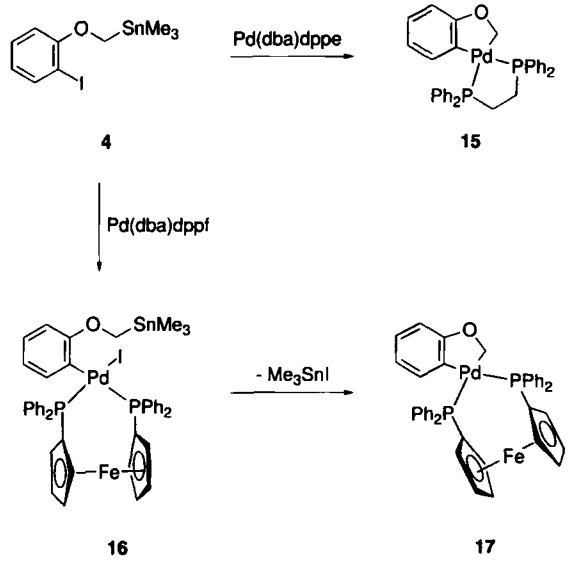


0947-6539/96/0212-1598 $ 15.00+.25/0 Chem. Eur. J. 1996, 2, No. 12



Scheme 7.

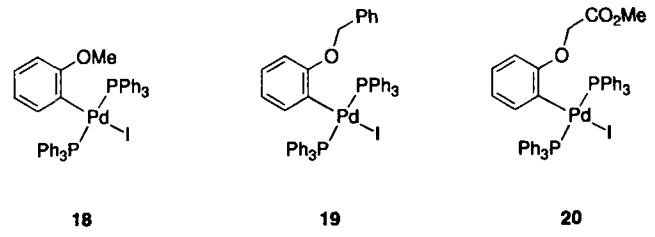
ligand dissociation required for the transmetalation, intermediates of type **VI** (Scheme 2) could be isolated under the conditions developed for the synthesis of palladacycles. Our implementation of this strategy is shown in Scheme 8. Unfortunately, the reaction of aryliodostannane **4** with [Pd(dba)dppe] (dba = dibenzylideneacetone, dppe = 1,2-bis(diphenylphosphane)-ethane),[40,41] prepared from $[Pd_2(dba)_3 \cdot dba]$[42] and dppe, gave oxapalladacycle **15** directly. However, reaction of **4** with [Pd(dba)dppf] (dppf = 1,1′-bis(diphenylphosphane)ferrocene)[41,43] at 23 °C for 20 min led to the isolation of the oxidative addition product **16** in 54% yield. This palladium complex is chiral[44] displaying the diastereotopic methylene hydrogens as an AB system at $\delta = 3.76$ and 3.69 with a $^2J$(H,H) of 10.8 Hz. Complex **16** was not stable in solution and slowly cyclized to give the corresponding palladacycle **17**. This transformation could also be triggered by the addition of $Ag_2CO_3$ in acetonitrile. Under these conditions the conversion of **16** into **17** proceeded within a few minutes quantitatively, as judged by NMR.



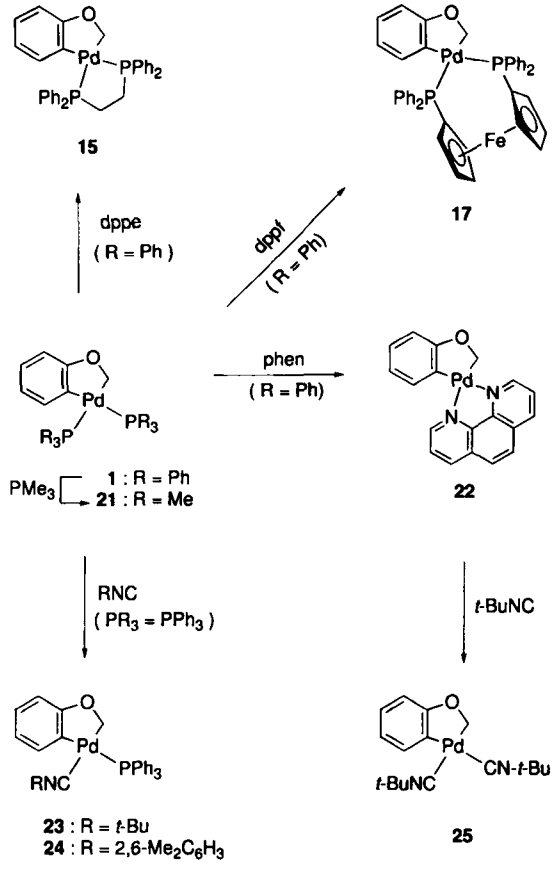
Scheme 8.

**Attempted formation of oxapalladacycles by C–H activation:** The synthesis of palladacycle **1** was also attempted by aliphatic C–H activation, a reaction that has been proposed by Dyker as one of the key steps in a cascade process leading to the formation of a terphenyl derivative.[24]

The synthesis of the required starting palladium complex **18** was readily achieved in almost quantitative yield by oxidative addition of *o*-iodoanisole to $[Pd(PPh_3)_4]$. However, complex **18** was recovered unchanged after treatment with a variety of bases (NaOAc, NaOH, NaOMe, KO*t*Bu) at 23–50 °C or after being heated in organic solvents. Similarly fruitless was the treatment with $Ag^I$ salts in acetonitrile in an attempt to increase the electrophilicity of the $Pd^{II}$ center. Unfortunately, complexes **19** and **20**, prepared similarly from the corresponding aryl iodides, also failed to give the corresponding C–H activated palladacycles.[45]



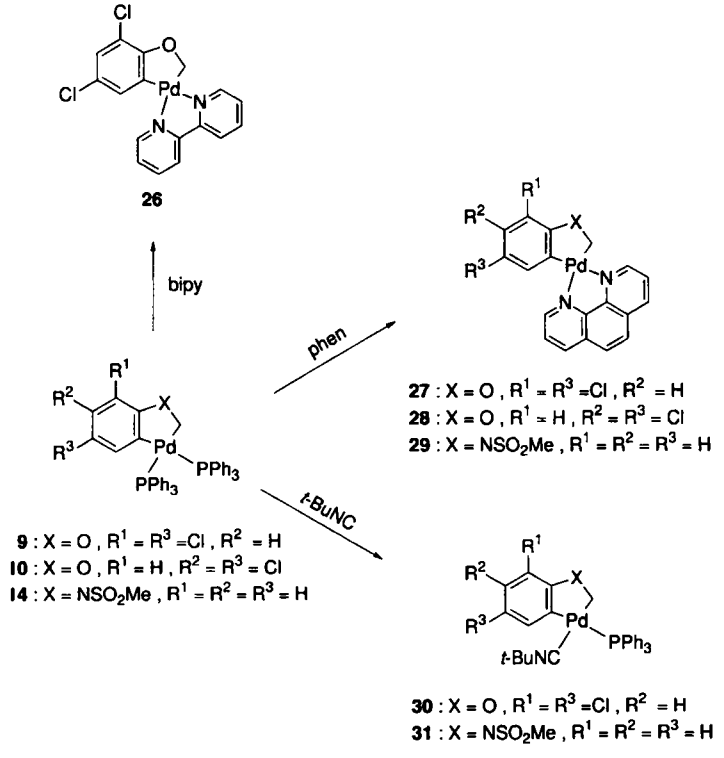
**Ligand exchange reactions:** Ligand substitution reactions at the palladium(II) center[46] of parent palladacycle **1** provided a method for the preparation of new complexes (Scheme 9). Thus, treatment of **1** with excess $PMe_3$ in toluene gave **21**, which could not be obtained pure owing to its high solubility. Similarly, reaction of **1** with chelating phosphanes dppe and dppf yielded **15** and **17**, respectively. Reaction of **1** with 10 equiv of 9,10-phenanthroline (phen) in dichloromethane under reflux led to **22** in very good yields. This complex is substantially less soluble than those with phosphane ligands.



Scheme 9.

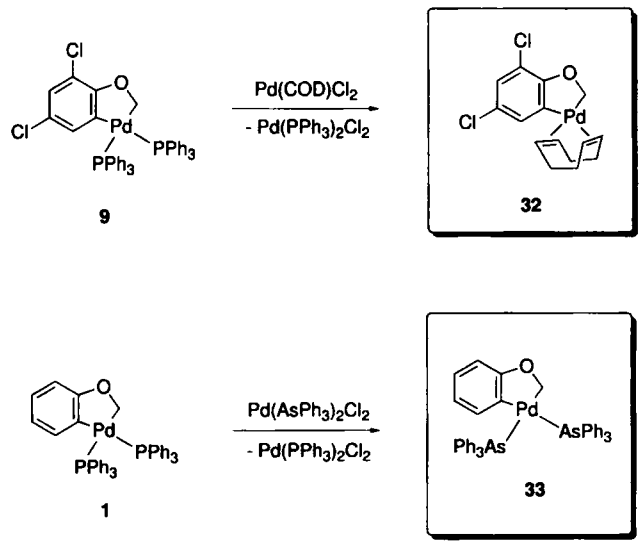
Reaction of **1** with *tert*-butyl- or 2,6-dimethylphenylisocyanide led to complexes **23** and **24**, respectively, by selective substitution of the phosphane *trans* to the alkyl, a result that reflects the higher *trans* effect of the $OCH_2$ ligand. A similar reaction was observed with a nickelacycle related to **1**.[29] Neither substitution of the second phosphane ligand nor isocyanide insertion reaction[47] were observed under more severe conditions. Interestingly, a similar reaction of **22** with *tert*-butylisocyanide at 23 °C led to clean substitution of the phen ligand to furnish palladacycle **25** with two *cis* isocyanide ligands. This organometallic palladium(II) complex is a rare example of an organopalladium derivative with four Pd–C carbon bonds.[48] Treatment of **1** with carbon monoxide (3.5 atm, 60 °C, 15 h) failed to give any stable coordination complex or insertion derivative.

Palladacycles **9**, **10**, and **14** reacted similarly with 2,2′-bipyridine (bpy) or phen to give highly insoluble complexes **26**–**29** in excellent yields (Scheme 10). Reaction of **9** and **14** with *tert*-butylisocyanide also proceeded selectively leading to oxapalladacycles **30** and **31**, respectively, by exclusive substitution of the phosphane *cis* to the aryl ligand.




Scheme 10.

In order to mimic more closely the reactivity of the oxapalladacycle generated under catalytic conditions by Dyker[24] (oxapalladacycle **VII**, probably coordinated with two molecules of DMF) we wanted to prepare analogous palladium complexes with two easily displaceable substituents. However, the synthesis of palladacycles **VII** with less strongly coordinating ligands such as alkenes or triphenylarsane could not be carried out starting from the corresponding palladium(0) complexes since the oxidative addition to aryl halides **2**–**5** has to be carried out with a palladium(0) coordinated with $\sigma$-donor ligands.[49] Not surprisingly, direct substitution of the triphenyphosphane ligands by triphenylarsane or dienes like 1,5-cyclooctadiene (COD) or norbornadiene failed to provide the desired complexes. After much experimentation, we found that the desired ligand exchange reaction could be carried out by taking advantage of the high affinity of $PdCl_2$ for donor ligands such as triphenylphosphane.[50] Thus, reaction of oxapalladacycle **9** with 1 equiv of $[Pd(COD)Cl_2]$[51] in $CH_2Cl_2$ at 23 °C for 3 h yielded a mixture of $[Pd(PPh_3)_2Cl_2]$ (82% yield) and the desired complex **32** (quantitative yield) (Scheme 11). Surprisingly, a similar reaction with the parent oxapalladacycle **1** with $[Pd(COD)Cl_2]$ led to complex mixtures of several complexes. However, reaction of **1** with $[Pd(AsPh_3)_2Cl_2]$ was successful, leading to **33** in 51% yield ($CH_2Cl_2$ at 23 °C). Similarly, complex **26**, previously synthesized by direct ligand substitution from **9**, could also be prepared by the exchange reaction between **9** and $[Pd(bpy)Cl_2]$.




Scheme 11.

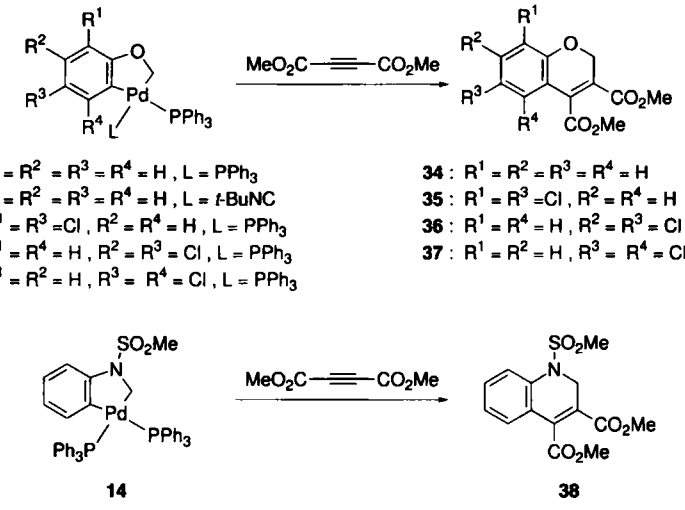
**Insertion reactions**: Dimethyl acetylenedicarboxylate smoothly reacted with **1** ($CHCl_3$, 40 °C, 1 h) by insertion into a C–Pd bond followed by reductive elimination leading to chromene **34** (Scheme 12). The known complex $[Pd(MeO_2CC{\equiv}CCO_2Me)(PPh_3)_2]$ was also isolated in this reaction (91% yield).[52] Chromene **34** could also be obtained from the isocyanide complex **23** (23 °C, 13 h) in almost quantitative yield (Scheme 12). Since a palladium(0) complex is formed at the end of these reactions, we tried to perform the transformation of the starting iodoarylstannanes into chromenes catalytically. Indeed, this transformation could be carried out from stannane **5** and dimethyl acetylenedicarboxylate in the presence of $[Pd(PPh_3)_4]$ (7 mol%) in toluene at 50–60 °C. However, the yield of isolated **34** was rather low (21%) under these conditions. The reaction of dimethyl acetylenedicarboxylate with dichlorooxapalladacycles **9**–**11** proceeded similarly, yielding the corresponding chromenes **35**–**37**. Azapalladacycle **14** also reacted with the alkyne to furnish dihydroquinoline **38**.

## Conclusions

In this paper we have described for the first time the isolation of stable transmetalation intermediates *cis*-$[PdArR(L)_2]$ formed under the conditions of the Stille cross-coupling reaction of organostannanes. The new procedure developed for the synthesis of these oxa- and azapalladacycles extends considerably the



0947-6539/96/0212-1600 $ 15.00+.25/0 Chem. Eur. J. 1996, 2, No. 12




**1** : $R^1 = R^2 = R^3 = R^4 = H$, L = $PPh_3$
**23** : $R^1 = R^2 = R^3 = R^4 = H$, L = *t*-BuNC
**9** : $R^1 = R^3 = Cl$, $R^2 = R^4 = H$, L = $PPh_3$
**10** : $R^1 = R^4 = H$, $R^2 = R^3 = Cl$, L = $PPh_3$
**11** : $R^1 = R^2 = H$, $R^3 = R^4 = Cl$, L = $PPh_3$

**34** : $R^1 = R^2 = R^3 = R^4 = H$
**35** : $R^1 = R^3 = Cl$, $R^2 = R^4 = H$
**36** : $R^1 = R^4 = H$, $R^2 = R^3 = Cl$
**37** : $R^1 = R^2 = H$, $R^3 = R^4 = Cl$

**14** **38**

Scheme 12.

existing methods for the preparation of metallacycles. We have also uncovered a second example of intramolecular isomerization of a metallacycle that is driven by the release of steric hindrance between the metal and a substituent in the aryl ring. This rearrangement has been shown to be promoted by traces of water. The isolation of complex **16** has allowed us to observe, for the first time, the Sn/Pd transmetalation product inferred from other reactions such as oxidative addition and reductive elimination. An application of the same approach to the study of the Si/Pd transmetalation, a key step in the Hiyama coupling reactions,[53] is in progress and will be reported in due course. An in-depth study of the ligand substitution chemistry of the palladacycles has led to a new procedure for the replacement of strong donor ligands by more weakly coordinating ones. A thorough study of the reactions of these palladacycles with alkyl, alkenyl, and aryl halides is currently under way.

## Experimental Section

NMR spectra were recorded at 23 °C on Bruker AC 200, AMX-300, or Varian-Unity 400 spectrometers. Some second-order couplings are treated as pseudo first order systems. IR spectra were recorded on a Pye-Unicam SP-3-300 S spectrometer using KBr disks. UV/Vis spectra were determined on a Perkin Elmer Lambda 6 spectrophotometer. Mass spectra were recorded with a VG-AutoSpec (EI and FAB) apparatus. Elemental analysis were performed at the UAM (SIdI) with a Perkin Elmer 2400 analyzer. The presence of water in some of the microanalyzed samples was confirmed by $^1H$ NMR in dry $CDCl_3$. Solvents were purified and dried by standard procedures. Chromatography was carried out on flash-grade silica gel with distilled solvents. Extractive workup refers to partitioning of the crude reaction between an organic solvent and water, phase separation, drying ($Na_2SO_4$), and evaporation under reduced pressure. All reactions were carried out under an Ar atmosphere. Commercially available 1,10-phenanthroline hydrate was dried by heating at 80 °C for 24 h at 0.1 mm Hg. The following compounds were prepared from the stated starting materials according to known procedures: (iodomethyl)-trimethylstannane and (iodomethyl)tributylstannane (from diiodomethane) [32], 2,4-dichloro-6-iodophenol (from 2,4-dichlorophenol) [54], and *N*-(2-iodophenyl)-methanesulfonamide (from 2-iodoaniline) [55]. The following palladium complexes were prepared according to the described procedures: $[Pd(PPh_3)_4]$ [56], $[Pd(COD)Cl_2]$ [51], $[Pd(AsPh_3)_2Cl_2]$ [57], and $[Pd(bpy)Cl_2]$ [58].

**(2-Bromophenoxymethyl)trimethylstannane (2)**: To a solution of 2-bromophenol (568 mg, 3.3 mmol) and (iodomethyl)trimethylstannane (1.0 g, 3.3 mmol) in DMSO (20 mL) was added $K_2CO_3$ (553 mg, 4.0 mmol), and the mixture was heated at 75 °C for 20 h. After being cooled to room temperature, the mixture was diluted with 1:1 hexane–$Et_2O$. After the usual extractive workup and chromatography (hexane) **2** was obtained as a colorless oil (681 mg, 59%): $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 7.50$ (dd, $J = 7.8$, 1.6 Hz, 1H), 7.27 (m, 1H), 6.99 (dd, $J = 8.2$, 1.5 Hz, 1H), 6.79 (m, 1H), 4.20 [s, $^2J(^1H-Sn) = 16$ Hz, 2H], 0.27 [s, $^2J(^1H-^{119}Sn) = 55.5$ Hz, $^2J(^1H-^{117}Sn) = 53.1$ Hz, 9H]; $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta = 157.50$, 133.05, 128.28, 121.26, 112.29, 112.10, 60.52 [s, $^1J(^{13}C-^{119}Sn) = 391$ Hz, $^1J(^{13}C-^{117}Sn) = 375$ Hz], −10.01 [s, $^1J(^{13}C-^{119}Sn) = 341$ Hz, $^1J(^{13}C-^{117}Sn) = 325.0$ Hz, 3C]; $C_{10}H_{15}BrOSn$ (349.8): calcd C 34.33, H 4.32; found C 34.01, H 4.60.

**(2-Bromophenoxymethyl)tributylstannane (3)**: This stannane was prepared in 85% yield as a colorless oil by using the same procedure as above with (iodomethyl)tributylstannane. **3**: $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 7.50$ (dd, $J = 7.8$, 1.6 Hz, 1H), 7.26 (m, 1H), 7.02 (dd, $J = 8.2$, 1.5 Hz, 1H), 6.78 (m, 1H), 4.19 [s, $^2J(^1H-Sn) = 14$ Hz, 2H], 1.70–1.45 (m, 6H), 1.40–1.20 (m, 6H), 1.15–0.80 (m, 15H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta = 157.96$ [s, $^3J(^{13}C-Sn) = 33$ Hz], 133.05, 128.23, 121.12, 112.14, 112.08, 59.41 [s, $^1J(^{13}C-^{119}Sn) = 325.7$ Hz, $^1J(^{13}C-^{117}Sn) = 310.8$ Hz], 29.11 [s, $^3J(^{13}C-Sn) = 21$ Hz], 27.39 [s, $^2J(^{13}C-Sn) = 41$ Hz], 13.73, 9.39 [s, $^1J(^{13}C-^{119}Sn) = 330.3$ Hz, $^1J(^{13}C-^{117}Sn) = 315.5$ Hz]; MS (70 eV, EI): *m/z* (%): 477 (0.6) [$M^+$], 475 (1.2) [$M^+ - 1$], 473 (0.7), 421 (68), 420 (33), 419 (100), 418 (41), 417 (70), 365 (14), 363 (22), 361 (15), 291 (53), 289 (40), 287 (24), 235 (67), 233 (53), 231 (31), 179 (74), 177 (72), 175 (48), 121 (28), 119 (22); $C_{19}H_{33}BrOSn$ (476.1): calcd C 47.94, H 6.99; found C 47.96, H 6.89.

**(2-Iodophenoxymethyl)trimethylstannane (4)**: This stannane was prepared in 98% yield as a colorless oil by using the same procedure as above from 2-iodophenol with (iodomethyl)trimethylstannane and replacing DMSO for DMF as the solvent. **4**: $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 7.74$ (m, 1H), 7.30 (m, 1H), 6.93 (m, 1H), 6.67 (m, 1H), 4.17 [s, $^2J(^1H-Sn) = 16$ Hz, 2H], 0.24 [s, $^2J(^1H-^{119}Sn) = 61.1$ Hz, $^2J(^1H-^{117}Sn) = 54.4$ Hz, 9H]; $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta = 159.72$, 139.19, 129.31, 122.04, 111.22, 86.49, 60.63 [s, $^1J(^{13}C-^{119}Sn) = 390$ Hz, $^1J(^{13}C-^{117}Sn) = 376$ Hz], −9.89 [s, $^1J(^{13}C-^{119}Sn) = 341.0$ Hz, $^1J(^{13}C-^{117}Sn) = 325$ Hz, 3C]; $C_{10}H_{15}IOSn$ (396.8): calcd C 30.27, H 3.81; found C 30.61, H 3.70.

**(2-Iodophenoxymethyl)tributylstannane (5)**: This stannane was prepared in 94% yield as a colorless oil by using the same procedure as above with (iodomethyl)tributylstannane. **5**: $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 7.74$ (dd, $J = 7.6$, 1.6 Hz, 1H), 7.31 (m, 1H), 6.97 (dd, $J = 8.2$, 1.3 Hz, 1H), 6.67 (m, 1H), 4.17 [s, $^2J(^1H-Sn) = 15.0$ Hz, 2H], 1.65–1.45 (m, 6H), 1.40–1.20 (m, 6H), 1.10–0.80 (m, 15H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta = 160.09$, 139.19, 129.24, 121.89, 111.02, 86.45, 59.51 [s, $^1J(^{13}C-^{119}Sn) = 325.6$ Hz, $^1J(^{13}C-^{117}Sn) = 311.4$ Hz], 29.10 [s, $^3J(^{13}C-Sn) = 21$ Hz], 27.36 [s, $^2J(^{13}C-Sn) = 55$ Hz], 13.72, 9.40 [s, $^1J(^{13}C-^{119}Sn) = 331.0$ Hz, $^1J(^{13}C-^{117}Sn) = 316.1$ Hz]; MS (70 eV, EI): *m/z* (%): 467 (100), 466 (40), 465 (76), 464 (31), 463 (35), 291 (37), 289 (28), 235 (52), 233 (42), 231 (24), 179 (60), 177 (56), 175 (36), 121 (20), 119 (16) (the molecular ion was not observed); $C_{19}H_{33}IOSn$ (523.1): calcd C 43.63, H 6.36; found C 43.35, H 6.07.

**3,4-Dichloro-2-iodophenol and 3,4-Dichloro-6-iodophenol**: A mixture of 3,4-dichlorophenol (2.08 g, 12.78 mmol) and NaI (2.299 g, 15.34 mmol) was dissolved at 25 °C in DMF (55 mL), and chloramine-T hydrate (4.321 g, 15.34 mmol) was added to give a reddish solution. After being stirred at 25 °C for 1 h the mixture was diluted with water (10 mL) and acidified with 5% aqueous HCl (5%). After extractive workup (EtOAc and 5% aqueous $Na_2S_2O_3$) the residue was chromatographed (10:1 hexane–EtOAc) to give 3,4-dichloro-2-iodophenol as a white solid (489 mg, 13%) and a mixture of 3,4-dichloro-6-iodophenol and 3,4-dichloro-2,6-diiodophenol. Chromatography of this mixture (5:1 hexane–$CH_2Cl_2$) yielded 3,4-dichloro-6-iodophenol (849 mg, 23%) as a white solid. **3,4-Dichloro-2-iodophenol**: M.p. 63–64 °C; $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 7.35$ (d, $J = 8.7$ Hz, 1H), 6.88 (d, $J = 8.7$ Hz, 1H), 5.71 (brs, OH); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 155.18$, 136.20, 130.71, 123.69, 113.71, 91.92; MS (70 eV, EI) *m/z* (%): 292 [$M^+ + 4$] (13), 290 [$M^+ + 2$] (70), 289 [$M^+ + 1$] (8), 288 [$M^+$] (100), 161 (6), 133 (34), 97 (34); $C_6H_3Cl_2IO$ (288.9): calcd C 24.95, H 1.05; found C 25.35, H 1.15. **3,4-Dichloro-6-iodophenol**: M.p. 55–56 °C; $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 7.71$ (s, 1H), 7.09 (s, 1H), 5.30 (brs, OH); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 154.29$, 138.15, 133.68, 124.75, 116.31, 82.91; MS (70 eV, EI): *m/z* (%): 292 (10) [$M^+ + 4$], 290 (65) [$M^+ + 2$], 289 (6) [$M^+ + 1$], 288 (100) [$M^+$], 161 (13), 133, (34), 97 (21); $C_6H_3Cl_2IO$ (288.9): calcd C 24.95, H 1.05; found C 24.93, H 0.92.

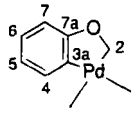
**(2,4-Dichloro-6-iodophenoxymethyl)tributylstannane (6)**: A mixture of 2,4-dichloro-6-iodophenol (2.374 g, 8.22 mmol) and $K_2CO_3$ (1.548 g, 11.20 mmol) in DMF (15 mL) was stirred at 25 °C for 20 min. A solution of (iodomethyl)tributylstannane (3.220 g, 7.47 mmol) in DMF (5 mL) was added, and the mixture stirred at 60 °C for 14 h. After extractive workup (1:1 hexane–$Et_2O$, water) and chromatography (hexane) **6** was obtained as a colorless oil (3.654 g, 83%): $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 7.63$ (d, $J = 2.5$ Hz, 1H), 7.35 (d, $J = 2.5$ Hz, 1H), 4.21 [s, $^2J(^1H-Sn) = 17$ Hz, 2H], 1.88–1.42 (m, 6H), 1.37–1.07 (m, 6H), 1.04–0.93 (m, 6H), 0.91–0.78 (m, 9H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 157.37$, 137.08, 130.45, 129.68, 127.76, 92.33, 77.40 [s, $^1J(^{13}C-^{119}Sn) = 312.9$ Hz, $^1J(^{13}C-^{117}Sn) = 299.6$ Hz], 29.11 [s, $^3J(^{13}C,Sn) = 22$ Hz), 27.35 [$^2J(^{13}C-Sn) = 55$ Hz], 13.72, 9.31 [s, $^1J(^{13}C-^{119}Sn) = 333.5$ Hz, $^1J(^{13}C-^{117}Sn) = 318.2$ Hz]; MS (70 eV, EI): *m/z* (%): 592 (<1) [$M^+$], 537 (67), 536 (40), 535 (100), 534 (49), 533 (76), 479 (17), 351 (26), 291 (63), 235 (61), 179 (68), 177 (67), 121 (32), 57 (20); $C_{19}H_{31}Cl_2IOSn$ (592.0): calcd C 38.55, H 5.28; found C 39.06, H 5.58.

**(3,4-Dichloro-6-iodophenoxymethyl)tributylstannane (7)**: A mixture of 3,4-dichloro-6-iodophenol (700 mg, 2.43 mmol) and $K_2CO_3$ (456 mg, 3.30 mmol) in DMF (6 mL) was stirred at 25 °C for 20 min. A solution of (iodomethyl)tributylstannane (949 mg, 2.20 mmol) in DMF (3 mL) was added, and the mixture was stirred at 60 °C for 14 h. After extractive workup (1:1 hexane–$Et_2O$, water) and chromatography (hexane) **7** was obtained as a colorless oil (705 mg, 55%): $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.78 (s, 1H), 7.01 (s, 1H), 4.13 [s, $^2J(^1H-Sn)$ = 15 Hz, 2H], 1.65–1.50 (m, 6H), 1.49–1.29 (m, 6H), 1.09–1.01 (m, 6H), 0.96–0.88 (m, 9H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ = 159.55, 139.03, 132.90, 124.03, 112.44, 83.86, 60.57 [s, $^1J(^{13}C-Sn)$ = 306 Hz], 29.01 [s, $^3J(^{13}C-Sn)$ = 22 Hz], 27.30 [s, $^2J(Sn,C)$ = 55 Hz], 13.67, 9.43 [s, $^1J(^{13}C-^{119}Sn)$ = 333.4 Hz, $^1J(^{13}C-^{117}Sn)$ = 318.3 Hz]; MS (70 eV, EI): *m/z* (%): 592 (< 1) [$M^+$], 537 (46), 536 (25), 535 (75), 534 (31), 533 (54), 351 (29), 295 (40), 293 (31), 292 (20), 291 (100), 235 (87), 233 (70), 121 (40), 57 (21); $C_{19}H_{31}Cl_2IOSn$ (592.0): calcd C 38.55, H 5.28; found C 38.76, H 5.17.

**(3,4-Dichloro-2-iodophenoxymethyl)tributylstannane (8)**: A mixture of 3,4-dichloro-2-iodophenol (1.293 g, 4.48 mmol) and $K_2CO_3$ (956 mg, 6.92 mmol) in DMF (25 mL) was stirred at 25 °C for 20 min. A solution of (iodomethyl)tributylstannane (1.929 g, 4.48 mmol) in DMF (5 mL) was added and the mixture was stirred at 60 °C for 14 h. After extractive workup (1:1 hexane–$Et_2O$, water) and chromatography (hexane) **8** was obtained as a colorless oil (2.231 mg, 84%): $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.41 (d, $J$ = 8.9 Hz, 1H), 6.82 (d, $J$ = 8.9 Hz, 1H), 4.13 [s, $^2J(^1H-Sn)$ = 15 Hz, 2H], 1.59–1.48 (m, 6H), 1.41–1.23 (m, 6H), 1.07–0.99 (m, 6H), 0.93–0.83 (m, 9H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ = 160.72, 137.18, 129.80, 123.25, 109.44, 92.56, 60.60 [s, $^1J(^{119}Sn-^{13}C)$ = 310.1 Hz, $^1J(^{13}C-^{117}Sn)$ = 297.5 Hz], 29.02 [s, $^3J(^{13}C-Sn)$ = 21 Hz], 27.29 [s, $^2J(^{13}C-Sn)$ = 55 Hz], 13.66, 9.42 [s, $^1J(^{13}C-^{119}Sn)$ = 332.7 Hz, $^1J(^{13}C-^{117}Sn)$ = 318.2 Hz]; MS (70 eV, EI): *m/z* (%): 592 (< 1) [$M^+$], 559 (45), 557 (63), 537 (51), 535 (88), 534 (34), 533 (61), 353 (33), 351, (58), 349 (39), 295 (28), 291 (87), 290 (62), 289 (66), 288 (75), 235 (90), 233 (70), 179 (97), 177 (100), 175 (68), 149 (58), 121 (43), 57 (68); $C_{19}H_{31}Cl_2IOSn$ (592.0): calcd C 38.55, H 5.28; found C 38.55, H 5.16.

***N*-(2-Iodophenyl)-*N*-[(tributylstannyl)methyl]methanesulfonamide (13)**: A mixture of *N*-(2-iodophenyl)methanesulfonamide (2.417 g, 8.14 mmol) and $K_2CO_3$ (1.688 g, 12.21 mmol) in DMF (25 mL) was stirred at 25 °C for 20 min. A solution of (iodomethyl)tributylstannane (3.508 g, 8.14 mmol) in DMF (10 mL) was added, and the mixture was stirred at 60 °C for 14 h. After extractive workup (1:1 hexane–$Et_2O$, water) and chromatography (7:1 hexane–EtOAc) **13** was obtained as a colorless oil (3.968 g, 81%): $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.91 (brd, $J$ = 8.3 Hz, 1H), 7.40–7.38 (m, 2H), 7.10–7.00 (m, 1H), 3.49 (d, $J$ = 12.3 Hz, 1H), 3.35 (d, $J$ = 12.3 Hz, 1H), 3.06 (s, 3H), 1.42–1.14 (m, 12H), 0.88–0.66 (m, 15H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta$ = 144.59, 140.40, 129.82, 129.27, 101.25, 37.78, 35.67, 28.76 [s, $^3J(^{13}C-Sn)$ = 24 Hz], 27.19 [s, $^2J(Sn-C)$ = 58 Hz], 13.55, 9.96 [s, $^1J(^{119}Sn-^{13}C)$ = 333.7 Hz, $^1J(^{117}Sn-^{13}C)$ = 319.2 Hz]; $C_{20}H_{36}INO_2SSn$ (600.2): calcd C 40.03, H 6.05, N 2.33; found C 40.39, H 6.11, N 2.20.

**(Methyleneoxy-1,2-phenylene)bis(triphenylphosphane)palladium (1)**: A mixture of **2**, **3**, **4**, or **5** (4.6 mmol) and freshly prepared $[Pd(PPh_3)_4]$ (5.10 g, 4.4 mmol) in toluene (60 mL) was heated at 40 °C for 24 h. The resulting reddish suspension contained a white solid, which was filtered off and washed with $Et_2O$ to give **1** (2.94 g, 78%) (usual yields ranged between 75 and 87%): $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.50–7.35 (m, 12H), 7.32–7.11 (m, 12H), 7.09–7.05 (m, 6H), 6.78 (m, H-6), 6.71 (ddd, $J$ = 7.9, 2.8, 1.6 Hz, H-7), 6.61 (tdd, $J$ = 7.5, 2.5, 1.5 Hz, H-4), 6.06 (ddt, $J$ = 7.6, 6.9, 1.6 Hz, H-5), 5.18 [dd, $^3J(^1H-^{31}P)$ = 5.6, 3.3 Hz, 2H]; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$; DEPT): $\delta$ = 174.60 [dd, $^3J(^{13}C-^{31}P)$ = 7.3, 5.5 Hz; C, C-7a], 149.27 [dd, $^2J(^{13}C-^{31}P)$ = 100.0, 11.7 Hz; C, C-3a], 141.71 [dd, $^3J(^{13}C-^{31}P)$ = 8.9, 3.0 Hz; CH, C-4], 135.20 [d, $^2J(^{13}C-^{31}P)$ = 13.3 Hz; CH, $PPh_3$], 134.19 [d, $^2J(^{13}C-^{31}P)$ = 13.2 Hz; CH, $PPh_3$], 134.03 [dd, $^1J(^{13}C-^{31}P)$ = 30.9 Hz, $^3J(^{13}C-^{31}P)$ = 1.9 Hz; C, $PPh_3$], 132.10 [dd, $^1J(^{13}C-^{31}P)$ = 35.5 Hz, $^3J(^{13}C-^{31}P)$ = 1.8 Hz; C, $PPh_3$], 129.84 [d, $^4J(^{13}C-^{31}P)$ = 2.0 Hz; CH, $PPh_3$], 129.47 [d, $^4J(^{13}C-^{31}P)$ = 1.9 Hz; CH, $PPh_3$], 127.99 [d, $^3J(^{13}C-^{31}P)$ = 9.8 Hz; CH, $PPh_3$], 127.76 [d, $^3J(^{13}C-^{31}P)$ = 9.3 Hz; CH, $PPh_3$], 125.30 (CH C-6), 116.65 [dd, $^4J(^{13}C-^{31}P)$ = 7.9, 3.0 Hz; CH, C-5], 107.82 (CH, C-7), 93.49 [dd, $^2J(^{13}C-^{31}P)$ = 90.8, 6.4 Hz; $CH_2$] ($^1$H and $^{13}$C assignments were based on HMQC and HMBC experiments); $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta$ = 28.39 (d, $^2J$ = 25.6 Hz, 1P), 25.52 (d, $^2J$ = 25.6 Hz, 1P); IR (KBr): $\tilde{\nu}$ = 3040 (w), 1585 (w), 1570 (w), 1480 (s), 1465 (m), 1435 (s), 1420 (m), 1285 (m), 1280 (sh), 1100 (s), 985 (s), 970 (s), 750 (vs), 700 (s), 520 (vs), 500 (vs), 495 (sh), 450 (m), 430 (m) cm$^{-1}$; MS (FAB): *m/z* (%): 739 (9.1), 738 (5.1), 737 (12) [$M^+$], 736 (8.5), 735 (3.9), 632 (7.7), 631 (8.1), 630 (10), 629 (12), 628 (6.7), 477 (19), 475 (24), 474 (17), 339 (100), 263 (28), 183 (33); $C_{43}H_{36}OP_2Pd$ (737.1): calcd C 70.07, H 4.92; found C 69.78, H 5.08.




**[(3,5-Dichloro-1,2-phenylene)oxymethylene]bis(triphenylphosphane)palladium (9)**: A mixture of $[Pd(PPh_3)_4]$ (1.065 g, 0.92 mmol) and **6** (600 mg, 1.01 mmol) in toluene (8 mL) was stirred at 40 °C for 24 h. The resulting solid was filtered off and washed with $Et_2O$ to give **9** as a white solid (605 mg, 82%): $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.43–7.06 (m, 30H), 6.80 (d, $J$ = 2.3 Hz, 1H), 6.31 [ddd, $J$ = 2.3 Hz, $^4J(^1H-^{31}P)$ = 7.7, 2.3 Hz, 1H], 5.20 [dd, $^3J(^1H-^{31}P)$ = 5.6, 3.1 Hz, 2H]; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ = 167.71 [dd, $^3J(^{13}C-^{31}P)$ = 7.2, 5.8 Hz], 151.55 [dd, $^2J(^{13}C-^{31}P)$ = 101.8, 11.9 Hz], 138.58 [dd, $^3J(^{13}C-^{31}P)$ = 9.1, 3.0 Hz], 135.00 [(d, $^2J(^{13}C-^{31}P)$ = 13.0 Hz, $PPh_3$], 134.12 [d, $^2J(^{13}C-^{31}P)$ = 13.2 Hz, $PPh_3$], 133.05 [brd, $^1J(^{13}C-^{31}P)$ = 31 Hz, $PPh_3$], 131.50 [brd, $^1J(^{13}C-^{31}P)$ = 39 Hz, $PPh_3$], 130.12 (br s), 129.80 [d, $^4J(^{13}C-^{31}P)$ = 1.6 Hz, $PPh_3$], 128.16 [d, $^3J(^{13}C-^{31}P)$ = 9.9 Hz, $PPh_3$], 127.93 (d, $^3J(^{13}C-^{31}P)$ = 9.6 Hz], 125.28, 121.29 [dd, $^4J(^{13}C-^{31}P)$ = 13.6, 3.0 Hz], 113.36 [d, $^4J(^{13}C-^{31}P)$ = 4.3 Hz], 93.21 [dd, $^2J(^{13}C-^{31}P)$ = 91.7, 5.6 Hz]; $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta$ = 28.85 (d, $^2J$ = 27.5 Hz, 1P), 24.73 (d, $^2J$ = 27.5 Hz, 1P); $C_{43}H_{34}Cl_2OP_2Pd$ (806.0): calcd C 64.08, H 4.25; found C 64.66, H 4.25.

**[(4,5-Dichloro-1,2-phenylene)oxymethylene]bis(triphenylphosphane)palladium (10)**: A mixture of $[Pd(PPh_3)_4]$ (1.817 g, 1.57 mmol) and **7** (1.024 g, 1.73 mmol) in toluene (6 mL) was stirred at 40 °C for 24 h. The resulting solid was filtered off and washed with $Et_2O$ to give **10** as a white solid (1.179 mg, 93%): $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.43–7.09 (m, 30H), 6.72 [d, $^5J(^1H-^{31}P)$ = 2.9 Hz, 1H], 6.46 [dd, $^4J(^1H-^{31}P)$ = 7.9, 2.3 Hz, 1H], 5.08 [dd, $^3J(^1H-^{31}P)$ = 5.5, 3.2 Hz, 2H]; $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta$ = 28.80 (d, $^2J$ = 27.6 Hz, 1P), 24.96 (d, $^2J$ = 27.6 Hz, 1P); $C_{43}H_{34}Cl_2OP_2Pd$ (806.0): calcd C 64.08, H 4.25; found C 63.83, H 4.48.

**[(5,6-Dichloro-1,2-phenylene)oxymethylene]bis(triphenylphosphane)palladium (11)**: A mixture of $[Pd(PPh_3)_4]$ (908 mg, 0.79 mmol) and **8** (512 mg, 0.86 mmol) in toluene (6 mL) was stirred at 40 °C for 24 h. The resulting solid was filtered off and washed with $Et_2O$ to give **11** as a pale yellow solid (637 mg, quantitative): $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.42–7.05 (m, 30H), 6.84 (d, $J$ = 8.3 Hz, 1H), 6.47 [dd, $J$ = 8.3 Hz, $^5J(^1H-^{31}P)$ = 2.6 Hz, 1H], 5.11 [d, $^3J(^1H-^{31}P)$ = 6.6 Hz, 2H]; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ = 167.92 [d, $J(^{13}C-^{31}P)$ = 6.2 Hz], 138.84, 134.27 [d, $^2J(^{13}C-^{31}P)$ = 12.5 Hz, $PPh_3$], 134.02 [d, $^2J(^{13}C-^{31}P)$ = 12.5 Hz, $PPh_3$] 132.04 [d, $^1J(^{13}C-^{31}P)$ = 36.0 Hz, $PPh_3$], 129.84 [d, $^4J(^{13}C-^{31}P)$ = 1.8 Hz, $PPh_3$], 129.18 (brs, $PPh_3$), 128.13 [d, $^3J(^{13}C-^{31}P)$ = 9.6 Hz, $PPh_3$], 127.52 [d, $^3J(^{13}C-^{31}P)$ = 8.5 Hz, $PPh_3$], 126.75, 122.31 [d, $J(^{13}C-^{31}P)$ = 8.2 Hz], 107.21 [d, $J(^{13}C-^{31}P)$ = 2.7 Hz] (three carbon signals were not observed); $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$; 25 °C): $\delta$ = 24.26 (br), 17.11 (br); $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$; −60 to 0 °C): $\delta$ = 24.41 (d, $^2J$ = 26.8 Hz, 1P), 16.98 (d, $^2J$ = 26.8 Hz, 1P); $C_{43}H_{34}Cl_2OP_2Pd$ (806.0): calcd C 64.08, H 4.25; found C 63.50, H 4.50.

**Isomerization of palladacycle 11 into 10**: **a)** A suspension of **11** (40 mg, 0.05 mmol) in toluene (3.5 mL) containing $H_2O$ (4 μL) was stirred at 100 °C for 1 h. After being cooled to room temperature, the solid was filtered off and washed with $Et_2O$ to give **10** (18 mg, 45%). **b)** A suspension of **11** (100 mg, 0.12 mmol) in toluene (10 mL) containing $D_2O$ (4 μL) was stirred at 80 °C for 2 h. After being cooled to room temperature, the solid was filtered off and washed with $Et_2O$ to give [$D_1$]**10** (37 mg, 37%). In the $^1$H NMR (200 MHz, $CDCl_3$) of [$D_1$]**10** the signal at $\delta$ = 6.72 was absent.

**[Methylene[(methylsulfonyl)imino]-1,2-phenylene]bis(triphenylphosphane)palladium (14)**: A mixture of $[Pd(PPh_3)_4]$ (3.265 g, 2.83 mmol) and **13** (3.866 g, 3.11 mmol) in toluene (6 mL) was stirred at 40 °C for 24 h. The resulting solid was filtered off and washed with $Et_2O$ to give **14** as a white solid (1.789 g, 78%): $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.60–7.05 (m, 31H), 6.82–6.71 (m, 2H), 6.25 (brt, $J$ = 7 Hz, 1H), 3.98 [dd, $^3J(^1H-^{31}P)$ = 6.6, 4.2 Hz, 2H], 2.76 (s, 3H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta$ = 154.39 [dd, $^2J(^{13}C-^{31}P)$ = 105.3, 8.3 Hz], 141.66 [brd, $^3J(^{13}C-^{31}P)$ = 11.4 Hz], 135.02 [d, $^2J(^{13}C-^{31}P)$ = 13.4 Hz, $PPh_3$], 134.03 [d, $^2J(^{13}C-^{31}P)$ = 13.8 Hz, $PPh_3$], 132.86 [brd, $^1J(^{13}C-^{31}P)$ = 44.6 Hz, $PPh_3$], 131.83 [brd, $^1J(^{13}C-^{31}P)$ = 30.7 Hz, $PPh_3$], 129.97 (brs, $PPh_3$), 129.64 (brs, $PPh_3$), 128.14 [d, $^3J(^{13}C-^{31}P)$ = 8.6 Hz, $PPh_3$], 127.81 [d, $^3J(^{13}C-^{31}P)$ = 9.2 Hz, $PPh_3$], 124.47, 122.54 (br s), 121.66 [brd, $^3J(^{13}C-^{31}P)$ = 9.0 Hz], 115.82, 61.62 [dd, $^2J(^{13}C-^{31}P)$ = 88.6, 5.4 Hz], 33.23; $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta$ = 27.45 (d, $^2J$ = 25.8 Hz, 1P), 25.84 (d, $^2J$ = 25.8 Hz, 1P); $C_{44}H_{39}NO_2SP_2Pd \cdot H_2O$ (832.1): calcd C 63.50, H 4.97, N 1.68; found C 63.56, H 4.81, N 3.97.

**[1,2-Bis(diphenylphosphane)ethane](methyleneoxy-1,2-phenylene)iodopalladium (15)**: A solution of **1** (81 mg, 0.11 mmol) in $CH_2Cl_2$ (3 mL) was treated with 1,2-bis(diphenylphosphane)ethane (dppe) (53 mg, 0.13 mmol) at 23 °C for 10 min. The solvent was evaporated, and the residue was triturated with $Et_2O$ (5 mL) to give a white solid which was filtered off and washed with $Et_2O$ to give **15** as a white solid (60 mg, 89%): $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.87–7.77 (m, 4H), 7.65–7.55 (m, 4H), 7.46–7.38 (m, 12H), 7.15–7.09 (m, 1H), 6.91 (td, $J$ = 7.9, 1.5 Hz, 1H), 6.85 (ddd, $J$ = 7.9, 3.0, 1.6 Hz, 1H), 6.34 (tt, $J$ = 7.1, 1.6 Hz, 1H), 5.91 [t, $^3J(^1H-^{31}P)$ = 4.0 Hz, 2H], 2.37–2.20 (m, 4H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ = 174.65 [dd, $^3J(^{13}C-^{31}P)$ = 7.4, 5.1 Hz], 150.77 [dd, $^2J(^{13}C-^{31}P)$ = 103.0, 9.2 Hz], 141.49 [dd, $^3J(^{13}C-^{31}P)$ = 10.0, 2.9 Hz], 133.77 [d, $^2J(^{13}C-^{31}P)$ = 14.0 Hz, $PPh_2$], 132.94 [d, $^2J(^{13}C-^{31}P)$ = 13.1 Hz, $PPh_2$], 132.23 [dd, $^1J(^{13}C-^{31}P)$ = 34.8 Hz, $^3J(^{13}C-^{31}P)$ = 1.6, $PPh_2$], 131.19 [dd, $^1J(^{13}C-^{31}P)$ = 30.2 Hz, $^3J(^{13}C-^{31}P)$ = 1.3 Hz, $PPh_2$], 130.63 [d, $^4J(^{13}C-^{31}P)$ = 2.1 Hz, $PPh_2$], 130.58 [d, $^4J(^{13}C-^{31}P)$ = 2.1 Hz, $PPh_2$], 128.89 [d, $^3J(^{13}C-^{31}P)$ = 9.6 Hz, $PPh_2$], 128.83 [d, $^3J(^{13}C-^{31}P)$ = 9.8 Hz, $PPh_2$], 125.95, 117.32 [dd, $^4J(^{13}C-^{31}P)$ = 8.1, 3.8 Hz], 108.54 [brd, $^4J(^{13}C-^{31}P)$ = 2.3 Hz], 90.14 [dd, $^2J(^{13}C-^{31}P)$ = 100.2, 6.4 Hz], 28.40 [dd, $^1J(^{13}C-^{31}P)$ = 24.8, $^2J(^{13}C-^{31}P)$ = 18.8 Hz], 27.54 [dd, $^1J(^{13}C-$



0947-6539/96/0212-1602 $ 15.00+.25/0 Chem. Eur. J. 1996, 2, No. 12

$^{31}P$) = 24.7, $^{2}J(^{13}C-^{31}P)$ = 18.0 Hz]; $^{31}P\{^{1}H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta$ = 40.01 [d, $^{2}J$ = 12.3 Hz, 1P), 38.32 (d, $^{2}J$ = 12.3 Hz, 1P); IR (KBr): $\tilde{\nu}$ 3030 (m), 2880 (w), 1430 (s), 1260 (m), 1090 (s), 940 (s), 865 (m), 805 (m), 740 (s), 690 (vs), 520 (s), 470 (m) $cm^{-1}$; MS (FAB): *m/z* (%): 614 (29), 613 (81), 612 (34), 611 (100) [$M^{+}$ + 1], 610 (74) [$M^{+}$], 609 (33), 506 (16), 505 (20), 504 (48), 503 (37), 429 (15), 427 (18), 426 (14); $C_{33}H_{30}OP_2Pd$ (610.9): calcd C 64.88, H 4.95; found C 64.24, H 5.02.

**[1,1′-Bis(diphenylphosphane)ferrocene][2-(trimethylstannylmethyloxy)phenyl]palladium (16)**: To a solution of [Pd(dba)(dppf)] (252 mg, 0.28 mmol) in toluene (20 mL) was added a solution of **4** (123 mg, 0.31 mmol) in toluene (5 mL). The resulting suspension was stirred at 23 °C for 20 min. The solvent was evaporated, and the residue was suspended in $Et_2O$, filtered off, and washed with $Et_2O$ to give **16** as a yellow solid (162 mg, 54%): $^{1}H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 8.14–7.86 (m, 6H), 7.60–7.45 (m, 6H), 7.28–7.04 (m, 5H), 6.88–6.67 (m, 4H), 6.50–6.42 (m, 2H), 5.92–5.88 (m, 1H), 5.11 (brs, 1H), 4.61 (brs, 1H), 4.37 (brs, 2H), 4.25 (brs, 2H), 3.76 (part A, AB system, $J$ = 10.8 Hz, 1H), 3.69 (part B, AB system, $J$ = 10.8 Hz, 1H), 3.57 (brs, 2H), 0.27 (s, $^{2}J(^{1}H-Sn)$ = 54 Hz, 9H). Complex **16** was not sufficiently stable in $CDCl_3$ at 23 °C and transmetalated to give derivative **17**.

**[1,1′-Bis(diphenylphosphane)ferrocene][(methyleneoxy-1,2-phenylene)palladium (17)**: **Method a:** A suspension of **16** (46 mg, 0.04 mmol) and $Ag_2CO_3$ (23 mg, 0.09 mmol) in acetonitrile (5 mL) was stirred at 23 °C for 2 h. The solvent was evaporated, and the residue suspended in $CH_2Cl_2$ and filtered through Celite. The resulting orange solution was evaporated and the residue was triturated with $Et_2O$ to give **17** as an orange solid (27 mg, 82%). **Method b:** A solution of **1** (80 mg, 0.11 mmol) in $CH_2Cl_2$ (3 mL) was treated with 1,1′-bis(diphenylphosphane)ferrocene (dppf) (72 mg, 0.13 mmol) at 23 °C for 30 min. The solvent was evaporated, and the residue suspended in $Et_2O$ (60 mL), filtered off and washed with $Et_2O$ to give **17** as an orange solid (70 mg, 83%): $^{1}H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.95–8.06 (m, 4H), 7.50–7.60 (m, 4H), 7.50–7.30 (m, 9H), 7.22 (m, 3H), 6.78 (m, 1H), 6.69 (ddd, $J$ = 7.9, 2.9, 1.4 Hz, 1H), 6.63 (tdd, $J$ = 7.7, 2.6, 1.5 Hz, 1H), 6.07 (tt, $J$ = 7.4, 1.6 Hz, 1H), 5.08 [dd, $^{3}J(^{1}H-^{31}P)$ = 5.4, 3.5 Hz, 2H], 4.69 (m, 2H), 4.45 (m, 2H), 4.08 (m, 2H), 3.38 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ = 174.86 [dd, $^{3}J(^{13}C-^{31}P)$ = 7.8, 5.6 Hz], 149.15 [dd, $^{2}J(^{13}C-^{31}P)$ = 103.0, 12.5 Hz], 141.45 [dd, $^{3}J(^{13}C-^{31}P)$ = 9.0, 3.3 Hz], 135.53 [d, $^{2}J(^{13}C-^{31}P)$ = 14.6 Hz, $PPh_2$], 134.12 [d, $^{2}J(^{13}C-^{31}P)$ = 13.2 Hz, $PPh_2$], 133.93 [d, $^{1}J(^{13}C-^{31}P)$ = 39.3 Hz, $PPh_2$], 133.65 [d, $^{1}J(^{13}C-^{31}P)$ = 30.0 Hz, $PPh_2$], 130.24 [d, $^{4}J(^{13}C-^{31}P)$ = 1.9 Hz, $PPh_2$], 130.15 [d, $^{4}J(^{13}C-^{31}P)$ = 1.8 Hz, $PPh_2$], 128.23 [d, $^{3}J(^{13}C-^{31}P)$ = 9.7 Hz, $PPh_2$], 127.93 [d, $^{3}J(^{13}C-^{31}P)$ = 9.8 Hz, $PPh_2$], 125.37, 116.61 [dd, $J(^{13}C-^{31}P)$ = 8.2, 3.2 Hz], 108.54 [brd, $J(^{13}C-^{31}P)$ = 2.3 Hz], 93.80 [dd, $^{2}J(^{13}C-^{31}P)$ = 96.3, 6.3 Hz], 80.66 [dd, $^{1}J(^{13}C-^{31}P)$ = 39.9 Hz, $^{3}J(^{13}C-^{31}P)$ = 5.3 Hz], 75.73 [d, $J(^{13}C-^{31}P)$ = 12.8 Hz, 2C], 75.49 [dd, $^{1}J(^{13}C-^{31}P)$ = 40.8 Hz, $^{3}J(^{13}C-^{31}P)$ = 3.2 Hz], 74.31 [d, $J(^{13}C-^{31}P)$ = 8.1 Hz, 2C], 73.12 [d, $J(^{13}C-^{31}P)$ = 6.9 Hz, 2C], 71.28 [d, $J(^{13}C-^{31}P)$ = 4.6 Hz, 2C]; $^{31}P\{^{1}H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta$ = 24.10 (d, $^{2}J$ = 30.6 Hz, 1P), 17.91 (d, $^{2}J$ = 30.6 Hz, 1P); IR (KBr): $\tilde{\nu}$ = 3040 (w), 2960 (w), 2860 (w), 1480 (m), 1460 (m), 1435 (s), 1170 (m), 1105 (s), 975 (s), 750 (vs), 700 (vs), 490 (s), 460 (m), 430 (m) $cm^{-1}$; MS (FAB): *m/z* (%): 771 (35), 770 (33), 769 (75), 768 (42), 767 (100), 766 (71) [$M^{+}$], 765 (35), 662 (68), 661 (46), 660 (90), 659 (76), 658 (41); $C_{41}H_{34}FeOP_2Pd \cdot H_2O$ (784.9): calcd C 62.73, H 4.62; found C 62.71, H 5.12.

***trans*-(2-Methoxyphenyl)iodobis(triphenylphosphane)palladium (18)**: A mixture of 2-iodoanisole (78 mg, 0.33 mmol) and [$Pd(PPh_3)_4$] (381 mg, 0.33 mmol) in toluene (10 mL) was heated at 40 °C for 22 h. After cooling to room temperature, the solid was filtered off and washed with $Et_2O$ to give **18** as a yellow solid (271 mg, 95%). $^{1}H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 7.60–7.50 (m, 12H), 7.35–7.20 (m, 18H), 6.87 (dq, $J$ = 7.4, 1.9 Hz, 1H), 6.38 (brt, $J$ = 7.8 Hz, 1H), 6.18 (brt, $J$ = 7.2 Hz, 1H), 5.41 (dq, $J$ = 8.1, 1.2 Hz, 1H), 3.07 (s, 3H); $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$): $\delta$ = 158.92 [t, $J(^{13}C-^{31}P)$ = 2.8 Hz], 145.95 [t, $J(^{13}C-^{31}P)$ = 3.3 Hz], 134.78 [t, $^{2}J(^{13}C-^{31}P)$ = 6.3 Hz; $PPh_3$], 134.08 [t, $J(^{13}C-^{31}P)$ = 4.1 Hz], 132.48 [t, $^{1}J(^{13}C-^{31}P)$ = 23.2; $PPh_3$], 129.48, 127.43 [t, $^{3}J(^{13}C-^{31}P)$ = 5.2 Hz; $PPh_3$], 123.96 [t, $J(^{13}C-^{31}P)$ = 1.4 Hz], 119.99, 109.13, 53.54; $^{31}P\{^{1}H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta$ = 23.53; IR (KBr): $\tilde{\nu}$ = 3040 (w), 1565 (w), 1490 (m), 1460 (m), 1440 (s), 1230 (s), 1185 (m), 1105 (s), 1060 (m), 1030 (m), 750 (vs), 700 (vs), 515 (vs), 435 (m) $cm^{-1}$; MS (FAB): *m/z* (%): 739 (7), 738 (4), 737 (9), 736 (6), 477 (4), 475 (5), 475 (4), 369 (100), 339 (19), 183 (10) ) (the molecular ion was not observed); $C_{43}H_{37}IOP_2Pd$ (865.0): calcd C 59.71, H 4.31; found C 60.00, H 4.25.

***trans*-[2-(Phenylmethyloxy)phenyl]iodobis(triphenylphosphane)palladium (19)**: A mixture of 2-iodo-1-(benzyloxy)benzene (350 mg, 1.23 mmol) and [$Pd(PPh_3)_4$] (1.30 g, 1.125 mmol) in toluene (3 mL) was heated at 40 °C for 17 h. After cooling to room temperature, the solid was filtered off and washed with $Et_2O$ to give **19** as a white solid (900 mg, 85%). $^{1}H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 7.55–7.11 (m, 35H), 7.04 (dq, $J$ = 9.5, 2.2 Hz, 1H), 6.44 (t, $J$ = 7.0 Hz, 1H), 6.28 [t, $J(^{1}H-^{1}H)$ = 7.0 Hz, 1H], 5.49 (dd, $J$ = 7.0, 1.6 Hz, 1H), 3.91 (s, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$; DEPT): $\delta$ = 158.70 [t, $J(^{13}C-^{31}P)$ = 2.9 Hz; C], 146.24 [t, $J(^{13}C-^{31}P)$ = 3.5 Hz; C], 137.60 (s; C), 134.86 [t, $^{2}J(^{13}C-^{31}P)$ = 6.3 Hz; $PPh_3$, CH], 134.00 [t, $J(^{13}C-^{31}P)$ = 3.9 Hz; CH], 132.36 [t, $^{1}J(^{13}C-^{31}P)$ = 23.1 Hz; $PPh_3$, C], 129.54 (br s; $PPh_3$, CH), 128.82 (s; 2CH), 128.54 (s; 2CH), 127.94 (s; CH), 127.46 [t, $^{3}J(^{13}C-^{31}P)$ = 5.1 Hz; $PPh_3$, CH], 124.00 (s; CH), 120.21 (s; CH), 110.38 (s; CH), 68.69 (s; $CH_2$); $^{31}P\{^{1}H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta$ = 23.40; $C_{49}H_{41}IOP_2Pd$ (941.1): calcd C 62.53, H 4.39; found C 62.12; H 4.21.

***trans*-[2-(Methoxycarbonylmethyloxy)phenyl]iodobis(triphenylphosphane)palladium (20)**: A mixture of methyl 2-iodophenyloxyethanoate (201 mg, 0.69 mmol) and [$Pd(PPh_3)_4$] (712 mg, 0.62 mmol) in toluene (3 mL) was heated at 40 °C for 15 h. After cooling to room temperature, the solid was filtered off and washed with $Et_2O$ to give **20** as a yellow solid (495 mg, 86%). $^{1}H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 7.65–7.50 (m, 12H), 7.30–7.15 (m, 18H), 6.98 (m, 1H), 6.37 (t, $J$ = 7.4 Hz, 1H), 6.28 (t, $J$ = 7.1 Hz, 1H), 5.26 (dd, $J$ = 8.1, 1.2 Hz, 1H), 3.89 (s, 3H), 3.53 (s, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$; DEPT): $\delta$ = 169.26 (s; C), 157.31 [t, $J(^{13}C-^{31}P)$ = 2.8 Hz; C], 146.65 [t, $J(^{13}C-^{31}P)$ = 3.7 Hz; C], 134.88 [t, $^{2}J(^{13}C-^{31}P)$ = 6.4 Hz; $PPh_3$, CH], 134.21 [t, $J(^{13}C-^{31}P)$ = 3.8 Hz; CH], 132.38 [t, $^{1}J(^{13}C-^{31}P)$ = 23.3 Hz; $PPh_3$, C], 129.56 (br s; $PPh_3$, CH) 127.46 [t, $^{3}J(^{13}C-^{31}P)$ = 5.2 Hz; $PPh_3$, CH], 123.91 (s; CH), 120.86 (s; CH), 109.94 (s; CH), 64.03 (s; $CH_2$), 51.94 (s; $CH_3$); $^{31}P\{^{1}H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta$ = 23.30; $C_{45}H_{39}IO_3P_2Pd$ (923.1): calcd C 58.56, H 4.26; found C 58.85, H 4.43.

**(Methyleneoxy-1,2-phenylene)bis(trimethylphosphane)palladium (21)**: This complex was obtained by reaction of **1** with $PMe_3$ in toluene at 23 °C for 2 h. The resulting complex could not be isolated pure because of its high solubility in $Et_2O$ and hexane. Evaporation of the solvent gave back the starting material **1** by displacement of $PMe_3$ by $PPh_3$. **21**: $^{1}H$ NMR (300 MHz, [$D_6$]benzene) (only significant signals) : $\delta$ = 5.53 [dd, $^{3}J(^{1}H-^{31}P)$ = 4.8, 3.7 Hz, 2H], 0.81 [d, $^{1}J(^{1}H-^{31}P)$ = 6.5 Hz, 3H], 0.39 [d, $^{1}J(^{1}H-^{31}P)$ = 7.3 Hz, 3H]; $^{31}P\{^{1}H\}$ NMR (121.4 MHz, [$D_6$]benzene): $\delta$ = −27.28 (d, $^{2}J$ = 28.6 Hz, 1P), −28.12 (d, $^{2}J$ = 28.6 Hz, 1P).

**(Methyleneoxy-1,2-phenylene)(1,10-phenanthroline-$N^1$,$N^{10}$)palladium (22)**: A mixture of complex **1** (530 mg, 0.72 mmol) and 1,10-phenanthroline (1.30 g, 7.20 mmol) in $CH_2Cl_2$ (18 mL) was heated under reflux conditions for 1 h. After being cooled to room temperature, the solvent was evaporated, and the residue was suspended in $Et_2O$ (50 mL), filtered off, and washed with $Et_2O$ to yield **22** contaminated with small amounts of 1,10-phenanthroline. Pure complex was obtained by trituration with boiling $Et_2O$ (60 mL) to give **22** as a bright yellow solid (226 mg, 80%): $^{1}H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 9.56 (dd, $J$ = 5.0, 1.5 Hz, 1H), 8.63 (dd, $J$ = 4.9, 1.4 Hz, 1H), 8.47 (m, 2H), 7.95 (AB system, part A, $J$ = 8.8 Hz, 1H), 7.93 (AB system, part B, $J$ = 8.8 Hz, 1H), 7.92 (dd, $J$ = 8.3, 5.0 Hz, 2H), 7.59 (dd, $J$ = 7.1, 1.4 Hz, 1H), 7.03 (td, $J$ = 7.5, 1.5 Hz, 1H), 6.79 (m, 2H), 6.25 (s, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ = 175.05, 150.36, 150.21, 148.54, 146.38, 146.27, 140.24, 137.36, 137.25, 134.55, 129.78, 127.28, 126.86, 125.83, 124.95, 124.88, 117.40, 108.05, 83.03; IR (KBr): $\tilde{\nu}$ = 3040 (w), 2890 (w), 2820 (w), 1505 (m), 1465 (m), 1415 (s), 1275 (s), 960 (m), 840 (s), 750 (m), 720 (m) $cm^{-1}$; MS (FAB): *m/z* (%): 395 (30), 394 (11), 393 (36), 392 (29) [$M^{+}$], 391 (19), 290 (50), 289 (58), 288 (78), 287 (38), 285 (90), 284 (70), 181 (100); $C_{19}H_{14}N_2OPd \cdot 0.5H_2O$ (401.9): calcd C 56.81, H 3.76, N 6.97; found C 56.96, H 3.51, N 6.96.

**(2-Isocyano-2-methylpropane)(methyleneoxy-1,2-phenylene)(triphenylphosphane)palladium (23)**: A solution of **1** (395 mg, 0.54 mmol) in $CH_2Cl_2$ (7 mL) was treated with *tert*-butylisocyanide (56 mg, 0.67 mmol) at 23 °C for 30 min. The solvent was evaporated and the residue was triturated with $Et_2O$ to yield a white solid, which was filtered off and washed with $Et_2O$ to give **23** (275 mg, 93%): $^{1}H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.62 (td, $J$ = 7.3, 1.5 Hz, 1H), 7.60–7.50 (m, 6H), 7.47–7.35 (m, 9H), 6.99 (m, 1H), 6.77 (ddd, $J$ = 8.0, 3.1, 1.2 Hz, 1H), 6.66 (tt, $J$ = 7.2, 1.7 Hz, 1H), 5.19 [d, $^{3}J(^{1}H-^{31}P)$ = 4.5 Hz, 2H], 1.27 (s, 9H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ = 174.15 [d, $^{3}J(^{13}C-^{31}P)$ = 5.1 Hz], 148.82 [d, $^{2}J(^{13}C-^{31}P)$ = 99.6 Hz], 144.04 (br), 138.72 [d, $J(^{13}C-^{31}P)$ = 2.3 Hz], 134.01 [d, $^{2}J(^{13}C-^{31}P)$ = 13.1 Hz, $PPh_3$], 132.68 [d, $^{1}J(^{13}C-^{31}P)$ = 35.4 Hz, $PPh_3$], 130.11 [d, $^{4}J(^{13}C-^{31}P)$ = 1.8 Hz, $PPh_3$], 128.37 [d, $^{3}J(^{13}C-^{31}P)$ = 13.7 Hz, $PPh_3$], 126.38, 117.40 [d, $J(^{13}C-^{31}P)$ = 7.7 Hz], 108.58 [d, $J(^{13}C-^{31}P)$ = 2.0 Hz], 89.75 [d, $^{2}J(^{13}C-^{31}P)$ = 7.3 Hz], 56.55 (br), 29.87; $^{31}P\{^{1}H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta$ = 22.15; IR (KBr): $\tilde{\nu}$ = 3040 (m), 2980 (m), 2880 (w), 2180 (vs), 1485 (m), 1465 (m), 1440 (s), 1280 (s), 1200 (m), 1110 (m), 1100 (m), 950 (vs), 750 (vs), 700 (vs), 525 (s), 500 (s), 485 (m) $cm^{-1}$; MS (FAB): *m/z* (%): 562 (38), 561 (27), 560 (80), 559 (31), 558 (100), 557 (74, $M^{+}$), 556 (33), 383 (13), 381 (19), 378 (14), 339 (96), 263 (53), 183 (52) [additionally, fragmentations corresponding to **1**, formed under the conditions required for ionization, were also observed at 739 (32), 737(42), 736 (31), 477 (59), 475 (71), 474 (54)]; $C_{30}H_{30}NOPPd \cdot 0.5H_2O$ (566.9): calcd C 63.55, H 5.69, N 2.47; found C 63.52, H 5.45, N 2.43.

**(2,6-Dimethylphenylisocyano)(methyleneoxy-1,2-phenylene)(triphenylphosphane)palladium (24)**: A solution of **1** (118 mg, 0.16 mmol) in $CH_2Cl_2$ (3 mL) was treated with 2,6-dimethylphenylisocyanide (25 mg, 0.19 mmol) at 23 °C for 10 min. The solvent was evaporated and the residue was triturated with 1:1 hexane–$Et_2O$ (5 mL) to yield a white solid which was filtered off and washed with 1:1 hexane–$Et_2O$ to give **24** (83 mg, 86%): $^{1}H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.75 (td, $J$ = 7.4, 1.6 Hz, 1H), 7.64–7.57 (m, 6H), 7.45–7.30 (m, 9H), 7.17 (dd, $J$ = 8.2, 7.0 Hz, 1H), 7.03 (dd, $J$ = 7.6, 0.6 Hz, 2H), 7.04–6.98 (m, 1H), 6.80 (ddd, $J$ = 8.0, 3.1, 1.2 Hz, 1H), 6.64 (tt, $J$ = 7.2, 1.7 Hz, 1H), 5.23 [d, $^{3}J(^{1}H-^{31}P)$ = 4.7 Hz, 2H], 2.13 (s, 6H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ = 174.25 [d, $^{3}J(^{13}C-^{31}P)$ = 5.0 Hz], 157.40 (br), 149.17 [d, $^{2}J(^{13}C-^{31}P)$ = 98.1 Hz], 139.28 [d, $J(^{13}C-^{31}P)$ = 2.3 Hz], 135.05, 134.08 [d, $^{2}J(^{13}C-^{31}P)$ = 13.1 Hz, $PPh_3$], 132.39 [d, $^{1}J(^{13}C-^{31}P)$ =

36.0 Hz, $PPh_3$], 130.26 [d, $^4J(^{13}C-^{31}P) = 2.0$ Hz, $PPh_3$], 129.10, 128.45 [d, $^3J(^{13}C-^{31}P) = 9.8$ Hz, $PPh_3$], 127.90, 126.53, 117.45 [d, $J(^{13}C-^{31}P) = 7.7$ Hz], 108.74 [d, $J(^{13}C-^{31}P) = 1.7$ Hz], 90.41 [d, $^2J(^{13}C-^{31}P) = 7.1$ Hz], 18.55 (one C signal was not observed); $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta = 22.40$; IR (KBr): $\tilde{\nu} = 3040$ (m), 2910 (w), 2150 (vs), 1570 (m), 1485 (s), 1475 (s), 1465 (s), 1440 (s), 1280 (s), 1105 (s), 950 (s), 750 (vs), 700 (vs), 520 (s), 500 (s), 440 (m) $cm^{-1}$; MS (FAB): *m/z* (%): 608 (38), 606 (46) [$M^+ + 1$], 605 (35) [$M^+$], 370 (43), 369 (30), 368 (51), 367 (46), 339 (100) [additionally, fragmentations corresponding to the starting complex **1**, formed under the conditions required for ionization, were also observed at 739 (33), 737 (44), 736 (31), 477 (44), 475 (54), 474 (41)]; $C_{34}H_{30}NOPPd \cdot 0.5H_2O$ (615.0): C 66.40, H 5.08, N 2.28; found C 66.40, H 4.92, N 2.32.

**Bis(2-isocyano-2-methylpropane)(methyleneoxy-1,2-phenylene)palladium (25)**: A suspension of **22** (5 mg, 0.013 μmol) in $CDCl_3$ (0.5 mL) at 23 °C was treated with *tert*-butylisocyanide (0.004 mL, 3 mg, 0.04 mmol). The reaction takes place immediately in quantitative yield as judged by $^1H$ NMR. However, **25** could not be isolated pure because its solubility is similar to that of 1,10-phenanthroline. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 7.39$ (dd, $J = 7.2$, 1.6 Hz, 1H), 6.90 (m, 1H), 6.70 (dd, $J = 8.0$, 1.2 Hz, 1H), 6.55 (td, $J = 7.2$, 1.2 Hz, 1H), 5.66 (s, 2H), 1.49 (brs, 9H), 1.40 (brs, 9H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 173.59$, 141.86 [t(1:1:1), $J(^{13}C-^{14}N) = 14.1$ Hz], 139.87 [t(1:1:1), $J(^{13}C-^{14}N) = 14.5$ Hz], 139.12, 128.51, 126.14, 117.13, 108.18, 84.14, 56.90 [t(1:1:1), $J(^{13}C-^{14}N) = 4.8$ Hz], 56.74 [t(1:1:1), $J(^{13}C-^{14}N) = 5.3$ Hz], 30.21 (3C), 30.20 (3C).

**(Methyleneoxy-1,2-(3,5-dichlorophenylene)(2,2′-bipyridine-$N^1$,$N^{1'}$)palladium (26)**: **Method a**: A mixture of complex **9** (109 mg, 0.14 mmol) and 2,2′-bipyridine (211 mg, 1.35 mmol) in $CH_2Cl_2$ (6 mL) was heated under reflux conditions for 7 h. After being cooled to room temperature, the solvent was evaporated, and the residue was suspended in $Et_2O$ (10 mL), filtered off, and washed with $Et_2O$ to give **26** (26 mg, 44%) as an orange solid. **Method b**: A mixture of complex **9** (75 mg, 0.09 mmol) and [Pd(bpy)$Cl_2$] (31 mg, 0.09 mmol) in $CH_2Cl_2$ (6 mL) was stirred at 23 °C for 15 min. The resulting solid was filtered off to give [Pd$(PPh_3)_2Cl_2$] (45 mg, 69%), and the solution evaporated. The residue was triturated with $CH_2Cl_2$ (2 mL) to give **26** (28 mg, 68%) as an orange solid. A $^{13}C\{^1H\}$ NMR spectrum could not be obtained because of the high insolubility of this complex in $CDCl_3$, [$D_6$]acetone, and $CD_3CN$. **26**: $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 9.05$ (brd, $J = 5.7$ Hz, 1H), 8.20 (brd, $J = 5.8$ Hz, 1H), 8.09–8.01 (m, 4H), 7.69–7.67 (m, 1H), 7.54–7.50 (m, 1H), 7.13 (d, $J = 2.3$ Hz, 1H), 7.01 (d, $J = 2.3$ Hz, 1H), 6.04 (s, 2H); UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 232 (23900), 299 (14900), 381 (3200); $C_{17}H_{12}Cl_2N_2OPd$ (437.6): calcd C 46.66, H 2.76, N 6.40; found C 46.41, H 2.66, N 6.03.

**[Methyleneoxy-1,2-(3,5-dichlorophenylene)](1,10-phenanthroline-$N^1$,$N^{10}$)palladium (27)**: A mixture of complex **9** (945 mg, 1.17 mmol) and 1,10-phenanthroline (2.113 g, 11.7 mmol) in $CH_2Cl_2$ (30 mL) was heated under reflux conditions for 3 h. After being cooled to room temperature, the solvent was evaporated and the residue was suspended in $Et_2O$ (50 mL), filtered off, and washed with $Et_2O$ to give **27** contaminated with small amounts of 1,10-phenanthroline. Pure complex was obtained by trituration with boiling $Et_2O$ (50 mL) to give **27** as a yellow solid (420 mg, 78%). A $^{13}C\{^1H\}$ NMR spectrum could not be obtained because of the high insolubility of this complex in $CDCl_3$, [$D_6$]acetone, and $CD_3CN$. **27**: $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 9.44$ (m, 1H), 9.22 (m, 1H), 8.65–8.50 (m, 2H), 8.30–8.25 (m, 1H), 8.05–7.99 (m, 2H), 7.90–7.85 (m, 1H), 7.32 (brs, 1H), 7.06 (brs, 1H), 6.28 (s, 2H); UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 240 (30700), 272 (28300), 387 (3700); $C_{19}H_{12}Cl_2N_2OPd$ (461.6): calcd C 49.44, H 2.62, N 6.97; found C 49.47, H 2.46, N 6.04.

**[Methyleneoxy-1,2-(4,5-dichlorophenylene)](1,10-phenanthroline-$N^1$,$N^{10}$)palladium (28)**: A mixture of complex **10** (158 mg, 0.19 mmol) and 1,10-phenanthroline (353 mg, 1.90 mmol) in $CH_2Cl_2$ (8 mL) was heated under reflux conditions for 3 h. After being cooled to room temperature, the solvent was evaporated, and the residue was suspended in $Et_2O$ (50 mL), filtered off, and washed with $Et_2O$ to give **28** (73 mg, 80%) as a yellow solid. A $^{13}C\{^1H\}$ NMR spectrum could not be obtained because of the high insolubility of this complex in $CDCl_3$, [$D_6$]acetone, and $CD_3CN$. **28**: $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 9.34$ (dd, $J = 5.2$, 1.6 Hz, 1H), 8.59–8.46 (m, 3H), 8.01–7.95 (m, 3H), 7.83 (dd, $J = 8.1$, 4.9 Hz, 1H), 7.38 (s, 1H), 6.72 (s, 1H), 6.11 (s, 2H); UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 234 (43900), 271 (35600), 390 (5000); $C_{19}H_{12}Cl_2N_2OPd$ (461.6): calcd C 49.44, H 2.62, N 6.07; found C 48.92, H 2.51, N 5.85.

**[Methylene[(methylsulfonyl)imino]1,2-phenylene] (1,10-phenanthroline-$N^1$,$N^{10}$)palladium (29)**: A mixture of complex **14** (416 mg, 0.51 mmol) and 1,10-phenanthroline (920 mg, 5.10 mmol) in $CH_2Cl_2$ (20 mL) was heated under reflux conditions for 1 h. After being cooled to room temperature, the solvent was evaporated, and the residue was suspended in $Et_2O$ (50 mL), filtered off, and washed with $Et_2O$. Pure complex was obtained by trituration with boiling $Et_2O$ (50 mL) to afford **29** as a yellow solid (70 mg, 29%). A $^{13}C\{^1H\}$ NMR spectrum could not be obtained because of the high insolubility of this complex in $CDCl_3$, [$D_6$]acetone, and $CD_3CN$. **29**: $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 9.56$ (brd, $J = 5.0$ Hz, 1H), 8.90 (brd, $J = 3.7$ Hz, 1H), 8.53 (brt, $J = 9.6$ Hz, 2H), 8.00–7.95 (m, 3H), 7.87–7.82 (m, 1H), 7.67 (brd, $J = 7.2$ Hz, 1H), 7.43 (brd, $J = 6.6$ Hz, 1H), 7.10 (brt, $J = 7.8$ Hz, 1H), 7.00 (brt, $J = 7.2$ Hz, 1H), 4.95 (s, 2H), 2.93 (s, 3H); UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 232 (34900), 272 (26900), 386 (2800); $C_{20}H_{17}N_3O_2PdS$ (469.8): calcd C 51.13, H 3.65, N 8.94; found C 50.64, H 3.51, N 8.77.

**[(3,5-Dichloro-1,2-phenylene)oxymethylene](2-isocyano-2-methylpropane)(triphenylphosphane)palladium (30)**: A suspension of **9** (70 mg, 0.09 mmol) in $CH_2Cl_2$ (6 mL) at 25 °C was treated with *tert*-butylisocyanide (15 mg, 0.17 mmol). The mixture was stirred at this temperature for 1 h. The resulting colorless solution was partially evaporated, and a 1:1 mixture of $Et_2O$–hexane was added to give a solid, which was filtered off and washed with 1:1 mixture of $Et_2O$–hexane to give **30** as a white solid (26 mg, 48%): $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 7.56-7.35$ (m, 16H), 7.02 (d, $J = 2.3$ Hz, 1H), 5.13 [d, $^3J(^1H,^{31}P) = 4.5$ Hz, 2H], 1.23 (s, 9H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 167.29$ [d, $J(^{13}C-^{31}P) = 5.3$ Hz], 150.82 [d, $J(^{13}C-^{31}P) = 100.5$ Hz], 136.05 (br s), 133.92 (d, $^2J(^{13}C-^{31}P) = 12.8$ Hz; $PPh_3$], 131.94 [d, $^1J(^{13}C-^{31}P) = 37.5$ Hz; $PPh_3$], 130.44 (brs, $PPh_3$), 128.56 [d, $^3J(^{13}C-^{31}P) = 9.8$ Hz; $PPh_3$], 125.46, 121.78 [d, $J(^{13}C-^{31}P) = 12.8$ Hz], 114.14 [d, $^2J(^{13}C-^{31}P) = 4.5$ Hz], 89.81 [d, $J(^{13}C-^{31}P) = 6.0$ Hz], 57.03 (br s), 29.82 (one carbon signal was not observed); $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta = 22.77$; $C_{30}H_{28}Cl_2NOPPd$ (626.8): calcd C 57.48, H 4.50, N 2.24; found C 57.35, H 4.45, N 2.12.

**[Methylene[(methylsulfonyl)imino]1,2-phenylene](2-isocyano-2-methylpropane)(triphenylphosphane)palladium (31)**: A suspension of **14** (300 mg, 0.37 mmol) in $CH_2Cl_2$ (5 mL) at 23 °C was treated with *tert*-butylisocyanide (38 mg, 0.48 mmol). The mixture was stirred at this temperature for 17 h. The resulting solution was partially evaporated and a 1:1 mixture of $Et_2O$–hexane was added to give a solid which was filtered off and washed with 1:1 $Et_2O$–hexane to give **31** as a white solid (124 mg, 53%): $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 7.60$ (td, $J = 7.4$, 1.6 Hz, 1H), 7.62–7.32 (m, 16H), 7.05 (td, $J = 7.4$, 1.6 Hz, 1H), 6.84 (tt, $J = 7.4$, 1.6 Hz, 1H), 3.95 [d, $^3J(^1H-^{31}P) = 5.3$ Hz, 2H], 2.67 (s, 3H), 1.23 (s, 9H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 155.98$ [d, $J(^{13}C-^{31}P) = 3.8$ Hz], 150.15 [d, $^2J(^{13}C-^{31}P) = 106$ Hz], 139.60 [d, $J(^{13}C-^{31}P) = 3.0$ Hz], 133.95 (d, $^2J(^{13}C-^{31}P) = 12.8$ Hz; $PPh_3$], 132.43 [d, $^1J(^{13}C-^{31}P) = 35.3$; $PPh_3$], 130.29 [d, $^4J(^{13}C-^{31}P) = 1.5$ Hz; $PPh_3$], 128.58 [d, $^3J(^{13}C-^{31}P) = 9.8$ Hz; $PPh_3$], 125.59, 121.54 [d, $J(^{13}C-^{31}P) = 8.3$ Hz], 115.18 [d, $J(^{13}C-^{31}P) = 1.5$ Hz], 56.79 [brd, $J(^{13}C-^{31}P) = 7.1$ Hz, 2C], 33.67, 29.76 (one carbon signal was not observed; $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta = 21.38$; $C_{31}H_{33}N_2O_2PPdS$ (635.0): calcd C 58.63, H 5.24, N 4.41, S 5.05; found C 58.17, H 5.07, N 4.40, S 4.98.

**($\mu^4$-1,5-Cyclooctadiene)[(3,5-dichloro-1,2-phenylene)oxymethylene]palladium (32)**: A mixture of complex **9** (209 mg, 0.26 mmol) and [Pd(COD)$Cl_2$] (74 mg, 0.26 mmol) in $CH_2Cl_2$ (10 mL) was stirred at 23 °C for 3 h. The solvent was evaporated, and the residue was triturated with $Et_2O$. The solid was filtered off to give [Pd$(PPh_3)_2Cl_2$] (150 mg, 82%), and the filtrate was evaporated to give **32** (130 mg, quantitative) as an orange solid: $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 7.04$ [d, $J(^1H-^1H) = 1.8$ Hz, 1H], 5.99 (br, 2H), 5.75 (s, 2H), 5.51 (s, 2H), 5.51 (br, 2H), 2.68–2.64 (m, 4H), 2.64–2.52 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 176.08$, 147.59, 132.45, 126.57, 122.26, 115.45, 114.74, 111.05, 88.24, 29.10, 28.54; $C_{15}H_{16}Cl_2OPd$ (389.6): calcd C 46.24, H 4.14; found C 46.49, H 3.95.

**(Methyleneoxy-1,2-phenylene)bis(triphenylarsane)palladium (33)**: A suspension of **1** (60 mg, 0.08 mmol) and [Pd$(AsPh_3)_2Cl_2$] (64 mg, 0.08 mmol) in $CH_2Cl_2$ (8 mL) was stirred at 23 °C for 1 h. The resulting solid was filtered off to give [Pd$(PPh_3)_2Cl_2$] (54 mg, 89%). The solution was evaporated, and the residue triturated with $Et_2O$ to give **33** as a white solid (34 mg, 51%): $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 7.38-7.10$ (m, 30H), 6.84–6.66 (m, 3H), 6.13 (brt, $J = 7.0$ Hz, 1H), 5.47 (s, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$; DEPT): $\delta = 174.09$ (C); 147.16 (C), 140.96 (CH), 135.98 (C), 134.27 ($AsPh_3$, CH), 134.19 ($AsPh_3$, C), 133.57 ($AsPh_3$, CH), 129.54 ($AsPh_3$, CH), 129.25 ($AsPh_3$, CH), 128.50 ($AsPh_3$, CH), 128.34 ($AsPh_3$, CH), 125.72 (CH), 116.96 (CH), 108.10 (CH), 91.27 (CH). Reaction of **33** with excess $PPh_3$ in $CH_2Cl_2$ or $CDCl_3$ at 23 °C gave rise quantitatively to palladacycle **1**.

**Dimethyl 2*H*-1-Benzopyrane-3,4-dicarboxylate (34)**: **Method a**: A mixture of **1** (80 mg, 0.11 mmol) and dimethyl acetylenedicarboxylate (31 mg, 0.22 mmol) in $CHCl_3$ (3 mL) was heated at 40 °C for 1 h. After being cooled to room temperature, the solvent was evaporated, and the residue triturated with $Et_2O$ (10 mL) to yield bis(triphenylphosphane)(dimethyl acetylenedicarboxylate)palladium [52] as an orange solid, which was filtered off and washed with $Et_2O$ (40 mg, 47%): $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 7.30-7.20$ (m, 18H), 7.20–7.10 (m, 12H), 3.23 (s, 3H); $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta = 30.78$. The filtrate was evaporated and the residue was chromatographed (5:1 hexane–EtOAc) to yield **34** as a colorless oil (28 mg, quantitative) and more bis(triphenylphosphane)(dimethyl acetylenedicarboxylate)palladium (37 mg, total yield: 91%). **Method b**: Complex **23** reacted similiarly with dimethyl acetylenedicarboxylate (2 equiv) in $CDCl_3$ solution at 23 °C for 24 h to give **34** in quantitative yield. **34**: $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 7.28$ (m, 1H), 7.09 (dd, $J = 7.7$, 1.6 Hz, 1H), 6.93 (m, 2H), 4.97 (s, 2H), 3.95 (s, 3H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 166.97$, 163.60, 154.88, 138.39, 132.58, 126.38, 122.10, 118.82, 118.73, 116.63, 63.73, 52.70, 52.36; MS (70 eV, EI): *m/z* (%): 248 (61) [$M^+$], 216 (60), 189 (100), 161 (29), 130 (71), 102 (24), 76 (10); HRMS (70 eV, EI): calcd for $C_{13}H_{12}O_5$ ($M^+$) 248.0685, found 248.0679.

**Dimethyl 6,8-Dichloro-2*H*-1-benzopyrane-3,4-dicarboxylate (35)**: A suspension of **9** (247 mg, 0.31 mmol) in $CH_2Cl_2$ (4 mL) at 25 °C was treated with dimethyl



0947-6539/96/0212-1604 $ 15.00+.25/0 Chem. Eur. J. 1996, 2, No. 12

acetylenedicarboxylate (81 mg, 0.57 mmol). The mixture was stirred at this temperature for 2 h to give a colorless solution. The solvent was evaporated, and $Et_2O$ was added to give a solid, which was filtered off to yield bis(triphenylphosphane)(dimethyl acetylenedicarboxylate)palladium(0) (63 mg, 27%). The filtrate was evaporated, and the residue chromatographed (6:1 hexane–EtOAc) to give **35** as a yellow solid (76 mg, 78%). Elution with 1:1 hexane–EtOAc furnished a viscous brown oil (54 mg) characterized as partially decomposed bis(triphenylphosphane)(dimethyl acetylenedicarboxylate)palladium(0). **33**: M.p. 106–107 °C; $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.34 (d, $J$ = 2.5 Hz, 1H), 7.00 (d, $J$ = 2.5 Hz, 1H), 5.07 (s, 2H), 3.96 (s, 3H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ = 165.95, 162.97, 149.25, 136.46, 132.91, 126.87, 124.43, 122.67, 121.13, 120.78, 64.51, 53.02, 52.67; MS (70 eV, EI): $m/z$ (%): 320 (7) [$M^+$ + 4], 318 (40), [$M^+$ + 2], 316 (58) [$M^+$], 286 (50), 285 (39), 284 (68), 259 (71), 257 (100), 229 (34), 199 (64), 198 (91); $C_{13}H_{10}Cl_2O_5$ (317.1): calcd C 49.24, H 3.18; found 49.32, H 2.89.

**Dimethyl 6,7-Dichloro-2*H*-1-benzopyrane-3,4-dicarboxylate (36)**: A suspension of **10** (229 mg, 0.28 mmol) in $CH_2Cl_2$ (8 mL) at 25 °C was treated with dimethyl acetylenedicarboxylate (81 mg, 0.57 mmol). The mixture was stirred at this temperature for 2 h to give a colorless solution. The solvent was evaporated, and $Et_2O$ added to give a solid, which was filtered off to yield bis(triphenylphosphane)(dimethyl acetylenedicarboxylate)palladium(0) (158 mg, 73%). The filtrate was evaporated and the residue was chromatographed (6:1, hexane–EtOAc) to give **36** as a white solid (88 mg, 98%). Additionally partially decomposed bis(triphenylphosphane)(dimethyl acetylenedicarboxylate)palladium(0) was obtained (18 mg). **36**: M.p. 146–147 °C; $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.16 (s, 1H), 7.02 (s, 1H), 4.98 (s, 2H), 3.96 (s, 3H), 3.82 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ = 166.04, 163.12, 153.49, 136.27, 135.81, 127.16, 125.66, 120.45, 118.62, 118.52, 64.15, 52.97, 52.56; MS (70 eV, EI): $m/z$ (%): 320 (6) [$M^+$ + 4], 318 (33) [$M^+$ + 2], 316 (49) [$M^+$], 286 (39), 284 (53), 259 (69), 257 (100), 229 (29), 200 (56), 198 (82); $C_{13}H_{10}Cl_2O_5$ (317.1): calcd C 49.24; H 3.18; found C 48.91, H 3.00.

**Dimethyl 5,6-Dichloro-2*H*-1-benzopyrane-3,4-dicarboxylate (37)**: A suspension of **11** (446 mg, 0.553 mmol) in $CH_2Cl_2$ (8 mL) at 25 °C was treated with dimethyl acetylenedicarboxylate (173 mg, 1.22 mmol). The mixture was stirred at this temperature for 24 h to give a colorless solution. The solvent was evaporated and $Et_2O$ was added to give a solid which was filtered off to yield bis(triphenylphosphane)(dimethyl acetylenedicarboxylate)palladium(0) (459 mg, quantitative). The filtrate was evaporated and the residue chromatographed (4:1 hexane–EtOAc) to give **37** as a yellow solid (56 mg, 32%): M.p. 124–125 °C; $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.39 (d, $J$ = 8.9 Hz, 1H), 6.88 (d, $J$ = 8.9 Hz, 1H), 4.79 (s, 2H), 3.92 (s, 3H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$; DEPT): $\delta$ = 166.39 (C), 163.32 (C), 155.72 (C), 135.43 (C), 132.69 (CH), 130.74 (C), 127.20 (C), 122.72 (C), 130.35 (C), 116.55 (CH), 63.82 ($CH_2$), 52.95 ($CH_3$), 52.58 ($CH_3$); $C_{13}H_{10}Cl_2O_5$ (317.1): calcd C 49.24, H 3.18; found C 49.72, H 2.89.

**Dimethyl 1,2-Dihydro-1-methanesulfonyl-3,4-quinolinedicarboxylate (38)**: A suspension of **14** (165 mg, 0.20 mmol) in $CH_2Cl_2$ (4 mL) at 25 °C was treated with dimethyl acetylenedicarboxylate (58 mg, 0.41 mmol). The mixture was stirred at this temperature for 6 h to give a suspension. The solvent was evaporated, and $Et_2O$ added to give a solid, which was filtered off to yield bis(triphenylphosphane)(dimethyl acetylenedicarboxylate)palladium(0) (24 mg, 16%). The filtrate was evaporated and the residue was chromatographed (3:1 hexane–EtOAc) to give **38** as a white solid (23 mg, 35%): M.p. 154–155 °C; $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.73–7.69 (m, 1H), 7.51–4.42 (m, 1H), 7.39–7.27 (m, 2H), 4.69 (s, 2H), 3.96 (s, 3H), 3.87 (s, 3H), 2.73 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ = 166.71, 163.67, 139.09, 136.00, 131.53, 127.23, 126.66, 126.59, 125.09, 122.87, 52.90, 52.77, 44.11, 38.16; MS (70 eV, EI): $m/z$ (%): 325 (30) [$M^+$], 246 (34), 214 (100), 156 (32), 128 (50); $C_{14}H_{15}NO_6S$ (325.3): calcd C 51.69, H 4.65, N 4.31; found C 51.53, H 4.86, N 3.95.

**Acknowledgements.** This work was supported by the DGICYT (project PB94-0163). D. J. C., C. M., and C. F.-R. acknowledge the receipt of predoctoral fellowships by the Ministerio de Educación y Ciencia. We thank Dr. A. M. Castaño for the NMR spectra of palladacycle **32**.

Received: May 13, 1996 [F368]

[1] J. Tsuji, *Palladium Reagents and Catalysts*; Wiley, Chichester, **1995**; Chapt. 4, Section 1.1.4.

[2] V. Farina, Chapt. 3.4 in *Comprehensive Organometallic Chemistry II, Vol 12* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**.

[3] a) J. K. Stille, *Angew. Chem.* **1986**, *98*, 504; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508; b) T. N. Mitchell, *Synthesis* **1992**, 803; c) K. Ritter, *ibid.* **1993**, 735.

[4] For a recent review, see: N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457.

[5] J. M. Brown, N. A. Cooley, *Chem. Rev.* **1988**, *88*, 1031.

[6] a) D. Milstein, J. K. Stille, *J. Am. Chem. Soc.* **1979**, *101*, 4992; b) K. S. Y. Lau, P. K. Wong, J. K. Stille, *J. Am. Chem. Soc.* **1976**, *98*, 5832; c) Y. Becker, J. K. Stille, *ibid.* **1978**, *100*, 838; d) P. J. Stang, M. H. Kowalski, M. D. Schiavelli, D. Longford, *ibid.* **1989**, *111*, 3347. e) J. M. Brown, N. A. Cooley, *Organometallics* **1990**, *9*, 353.

[7] J. K. Stille, Chapt. 9 in *The Chemistry of the Metal-Carbon Bond, Vol 2* (Eds. F. R. Hartley, S. Patai), Wiley, Chichester, **1985**.

[8] For recent key references on oxidative additions to $Pd^0$ complexes of relevance to the Stille and related reactions, see: a) C. Amatore, A. Jutand, A. Suarez, *J. Am. Chem. Soc.* **1993**, *115*, 9531; b) A. Jutand, A. Mosleh, *Organometallics* **1995**, *14*, 1810; c) C. Amatore, E. Carré, A. Jutand, M. A. M'Barki, *Organometallics* **1995**, *14*, 1818; d) C. Amatore, E. Carré, A. Jutand, M. A. M'Barki, G. Meyer, *ibid.* **1995**, *14*, 5605; e) J. M. Brown, K. K. Hii, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 657.

[9] a) K. Tatsumi; R. Hoffmann, A. Yamamoto, J. K. Stille, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857; b) A. Gillie, J. K. Stille, *J. Am. Chem. Soc.* **1980**, 102, 4933.

[10] D. Milstein, J. K. Stille, *ibid.* **1979**, *101*, 4981.

[11] a) J. Louie, J. F. Hartwig, *J. Am. Chem. Soc.* **1995**, *117*, 11598; b) D. K. Morita, J. K. Stille, J. R. Norton, *ibid.* **1995**, *117*, 8576.

[12] E. Vedejs, A. R. Haight, W. O. Moss, *J. Am. Chem. Soc.* **1992**, *114*, 6556.

[13] a) J. Ye, R. K. Bhatt, J. R. Falck, *J. Am. Chem. Soc.* **1994**, *116*, 1. b) J. Ye, R. K. Bhatt, J. R. Falck, *Tetrahedron Lett.* **1993**, *34*, 8007.

[14] For the coupling of organostannanes with organic iodides mediated by copper, see: G. D. Allred, L. S. Liebeskind, *J. Am. Chem. Soc.* **1996**, *118*, 2748.

[15] A. J. Canty, Chapt. 5 in *Comprehensive Organometallic Chemistry II, Vol 9* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**.

[16] For the synthesis of *trans*-[PdArR(L)$_2$] (R = Me, Ph) from *trans*-[PdAr(L)$_2$X] by transmetalation with Grignard reagents, see: G. W. Parshall, *J. Am. Chem. Soc.* **1974**, *96*, 2360.

[17] For the observation of intermediates in the Suzuki coupling by electrospray mass spectrometry, see: A. O. Aliprantis, J. W. Canary, *J. Am. Chem. Soc.* **1994**, *116*, 6985.

[18] a) E. Piers, Y.-F. Lu, *J. Org. Chem.* **1988**, *53*, 926; b) J. C. Bradley, T. Durst, *ibid.* **1991**, *56*, 5459.

[19] a) J. K. Stille, M. Tanaka, *J. Am. Chem. Soc.* **1987**, *109*, 3785; b) J. K. Stille, H. Su, D. H. Hill, P. Schneider, M. Tanaka, D. L. Morrison, L. S. Hegedus, *Organometallics* **1991**, *10*, 1993. c) A. Kalivretenos, J. K. Stille, L. S. Hegedus, *J. Org. Chem.* **1991**, *56*, 2883.; d) G. Pattenden, S. M. Thom, *Synlett* **1993**, 215.

[20] For the synthesis of stable *cis*-[PdR$_2$(L$_2$)] and *cis*-[PdArR(L$_2$)] complexes, see: a) B. A. Markies, A. J. Canty, W. de Graaf, J. Boersma, M. D. Janssen, M. P. Hogerheide, W. J. J. Smeets, A. L. Spek, G. van Koten, *J. Organomet. Chem.* **1994**, *482*, 191; b) B. A. Markies, A. J. Canty, M. D. Janssen, A. L. Spek, J. Boersma, G. van Koten, *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 477; c) W. de Graaf, J. Boersma, W. J. J. Smeets, A. L. Spek, G. van Koten, *Organometallics* **1989**, *8*, 2907; d) P. K. Byers, A. J. Canty, *ibid.* **1990**, *9*, 210; e) G. Calvin, G. E. Coates, *J. Chem. Soc.* **1960**, 2008.

[21] For a synthesis of a different type of palladacycles based on a transmetalation facilitated by chelation, see: H. Nishiyama, M. Matsumoto, T. Matsukura, R. Miura, K. Itoh, *Organometallics* **1985**, *4*, 1911.

[22] a) P. Beak, *Acc. Chem. Res.* **1992**, *25*, 215; b) M. L. Kurtzweil, D. Loo, P. Beak, *J. Am. Chem. Soc.* **1993**, *115*, 421.

[23] a) W. Adam, L. Hadjarapoglou, K. Peters, M. Sauter, *J. Am. Chem. Soc.* **1993**, *115*, 8603; b) W. Adam, M. Sauter, C. Zünkler, *Chem. Ber.* **1994**, *127*, 1115.

[24] a) G. Dyker, *Angew. Chem.* **1992**, *104*, 1079; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1023; b) G. Dyker, *J. Org. Chem.* **1993**, *58*, 6426; c) G. Dyker, *Chem. Ber.* **1994**, *127*, 739.

[25] For a related process leading to benzocyclobutene derivatives, see: G. Dyker, *Angew. Chem.* **1994**, *106*, 117; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 103.

[26] For lead references, see: a) M. Catellani, M. C. Fagnola, *Angew. Chem.* **1994**, *106*, 2559; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2421; b) M. Catellani, G. P. Chiusoli, *Gazz. Chim. Ital.* **1993**, *123*, 1, and references therein; c) K. Albrecht, A. de Meijere, *Chem. Ber.* **1994**, *127*, 2539; d) K. Albrecht, O. Reiser, M. Weber, B. Knieriem, A. de Meijere, *Tetrahedron* **1994**, *50*, 383. e) O. Reiser, M. Weber, A. de Meijere, *Angew. Chem.* **1989**, *101*, 1071; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1037.

[27] For recent reviews of sequential transformations in organic synthesis, see: a) L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115; b) L. F. Tietze, U. Beifuss, *Angew. Chem.* **1993**, *105*, 137; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131.

[28] Preliminary communication: D. J. Cárdenas, C. Mateo, A. M. Echavarren, *Angew. Chem.* **1994**, *106*, 2529; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2445.

[29] For a related nickelacycle, see: J. Cámpora, E. Gutiérrez, A. Monge, P. Palma, M. L. Poveda, C. Ruiz, E. Carmona, *Organometallics* **1994**, *13*, 1728.

[30] For related nickela- and platinacycles, see: a) B. C. Ankianiec, V. Christou, D. T. Hardy, S. K. Thomson, G. B. Young, *J. Am. Chem. Soc.* **1994**, *116*, 9963; b) B. C. Ankianiec, D. T. Hardy, S. K. Thomson, W. N. Watkins, G. B. Young, *Organometallics* **1992**, *11*, 2591; c) S. K. Thomson, G. B. Young, *ibid.* **1989**, *8*, 2068; d) D. C. Griffiths, G. B. Young, *ibid.* **1989**, *8*, 875; e) M. A. Bennett, T. W. Hambley, N. K. Roberts, G. B. Robertson, *ibid.* **1985**, *4*, 1992.

[31] For a related ruthenacycle, see: R. A. Jones, G. Wilkinson, *J. Chem. Soc. Dalton Trans.* **1979**, 472.

[32] a) D. Seyferth, S. B. Andrews, *J. Organomet. Chem.* **1971**, *30*, 151; b) D. Seyferth, S. B. Andrews, R. L. Lambert, *ibid.* **1972**, *37*, 69.

[33] J. J. Eisch, J. E. Galle, A. Piotrowski, M.-R. Tsai, *J. Org. Chem.* **1982**, *47*, 5051.

[34] (a) A. Bax, S. Subramanian, *J. Magn. Res.* **1986**, *67*, 565. (b) A. Bax, M. F. Summers, *J. Am. Chem. Soc.* **1986**, *108*, 2093.

[35] a) G. López, J. Ruiz, G. García, C. Vicente, J. M. Martí, M. D. Santana, *J. Organomet. Chem.* **1990**, *393*, C53. b) V. V. Grushin, H. Alper, *Organometallics* **1993**, *12*, 1890; c) V. V. Grushin, C. Bensimon, H. Alper, *ibid.* **1993**, *12*, 2737.

[36] For a lead reference on palladium(II) alkoxide complexes, see: G. M. Kapteijn, A. Dervisi, D. M. Grove, H. Kooijman, M. T. Lakin, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **1995**, *117*, 10939.

[37] a) C.-H. Liu, C.-S. Li, C.-H. Cheng, *Organometallics* **1994**, *13*, 18; b) C.-S. Li, D.-C. Jou, C.-H. Cheng, *ibid.* **1993**, *12*, 3945; c) C.-S. Li, C.-H. Cheng, F.-L. Liao, S.-L. Wang, *J. Chem. Soc. Chem. Commun.* **1991**, 710.

[38] A. A. H. Van der Zijden, G. van Koten, R. Luijk, R. A. Nordemann, A. L. Spek, *Organometallics* **1988**, *7*, 1549.

[39] a) E. M. Burgess, L. McCullagh, *J. Am. Chem. Soc.* **1966**, *88*, 1580; b) G. Pfister-Guillouzo, F. Gracian, A. Senio, M. Letulle, J.-L. Ripoll, *Tetrahedron Lett.* **1992**, *33*, 5753; c) W. Sander, J. Morawietz, *ibid.* **1993**, *34*, 1913; J. Morawietz, W. Sander, M. Träubel, *J. Org. Chem.* **1995**, *60*, 6368, and references therein.

[40] For the synthesis of related $[Pd(dba)L_2]$ complexes see: a) ($L_2$ = dppe, dppp): W. A. Herrmann, W. R. Thiel, C. Brossmer, K. Öfele, T. Priermeier, W. Scherer, *J. Organomet. Chem.* **1993**, *461*, 51; b) $L_2$ = chiral bidentate phosphane: B. M. Trost, B. Breit, M. G. Organ, *Tetrahedron Lett.* **1994**, *35*, 5817.

[41] Z. Xi, R. Yang, D. Jin, *Chin. Chem. Lett.* **1991**, *2*, 331; Chem. Abstr. **1992**, *116*, 21223.

[42] a) Y. Takahashi, T. Ito, S. Sakai, Y. Ishii, *J. Chem. Soc. Chem. Commun.* **1970**, 1065; b) T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, J. A. Ibers, *J. Organomet. Chem.* **1974**, *65*, 253.

[43] For a review on the coordination chemistry of dppf, see: K.-S. Gan, T. S. A. Hor in *Ferrocenes* (Eds.: A. Togni, T. Hayashi), VCH, Weinheim, **1995**.

[44] J. M. Brown, J. J. Pérez-Torrente, N. W. Alcock, H. J. Clase, *Organometallics* **1995**, *14*, 207.

[45] Reaction of complex **18** with $Ag^I$ salts leads to the formation of an unstable complex, which was not further characterized, presumably with the phenyl of the benzyl $\eta^2$-coordinated to palladium(II).

[46] A. C. Albéniz, P. Espinet p. 3010 in *Encyclopedia of Inorganic Chemistry Vol. 6* (Ed. R. B. King), Wiley, Chichester, **1994**.

[47] For recent lead references on the insertion of isocyanides into Pd–C bonds, see: a) Y. Yamamoto, T. Tanase, T. Yanai, T. Asano, K. Kobayashi, *J. Organomet. Chem.* **1993**, *456*, 287, and references therein; b) J. Cámpora, S. A. Hudson, E. Carmona, *Organometallics* **1995**, *14*, 2151.

[48] C. H. Davies, C. H. Game, M. Green, F. G. A. Stone *J. Chem. Soc. Dalton Trans.* **1974**, 357.

[49] However, the oxidative addition of analogous aryl iodides to $[Pd(dba)(AsPh_3)_2]$ has been successful: C. Fernández-Rivas, C. Mateo, unpublished results.

[50] W. Partenheimer, *Inorg. Chem.* **1972**, *11*, 743.

[51] J. Chatt, L. M. Vallarino, L. M. Venanzi, *J. Chem. Soc.* **1957**, 3413.

[52] H. Urata, H. Suzuki, Y. Moro-oka, T. Ikawa, *J. Organomet. Chem.* **1989**, *364*, 235.

[53] Reviews: a) Y. Hatanaka, T. Hiyama, *Synlett* **1991**, 845; b) T. Hiyama, Y. Hatanaka, *Pure Appl. Chem.* **1994**, *66*, 1471.

[54] T. Kometani, D. S. Watt, T. Ji, *Tetrahedron Lett.* **1985**, *26*, 2043.

[55] T. Sakamoto, Y. Kondo, S. Iwashita, T. Nagano, H. Yamanaka, *Chem. Pharm. Bull.* **1988**, *36*, 1305.

[56] F. A. Cotton, *Inorg. Synth.* **1972**, *13*, 121.

[57] H. Itatani, J. C. Bailar, *J. Am. Oil Chem. Soc.* **1967**, *44*, 147.

[58] B. J. McCormick, E. N. Jaynes, R. Y. Kaplan, *Inorg. Synth.* **1972**, *13*, 216.



0947-6539/96/0212-1606 $ 15.00+.25/0