Cross-Coupling versus Homocoupling in the Reactions of Dimethyl(*N*,*N*,*N*′,*N*′-tetramethylethanediamine)palladium with Organic Halides[†]

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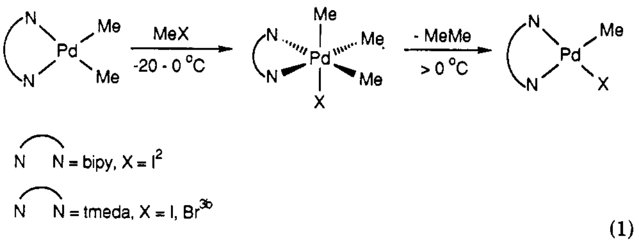
Received September 15, 1989

Reaction of $PdMe_2$(tmeda) (tmeda = *N,N,N′,N′*-tetramethylethanediamine) with benzyl and allyl bromide at 20 °C affords the homocoupled product ethane and the organometallic complexes PdBr(η^1-benzyl)(tmeda) and [Pd(η^3-allyl)(tmeda)]Br, respectively. The reaction of $PdMe_2$(tmeda) with acetyl chloride did not give the acetyl complex PdCl(COMe)(tmeda). Instead, the cross-coupled product acetone and the organometallic product PdClMe(tmeda) were obtained. Acetyl complexes PdX(COMe)(tmeda) were easily obtained by reaction of PdXMe(tmeda) with carbon monoxide at ambient temperature and pressure. The reaction of $PdMe_2$(tmeda) with ethyl iodide is not selective and gives a 3:2 mixture of PdIMe(tmeda) and PdIEt(tmeda) together with a 3:2 mixture of propane and ethane. At 0 °C, the reaction of $PdMe_2$(tmeda) with benzyl bromide and the reaction of PdMe(benzyl)(tmeda) with methyl bromide both afford the palladium(IV) species *a*-benzyl-*b*-bromo-*cd*-dimethyl-*ef*-(tmeda)palladium(IV) (**4a**), in which the benzyl group and the bromine atom are in a cis position. ^1H NMR spectroscopy in acetone-d_6 at 0 °C shows that in the reaction of the platinum(IV) complex $PtMe_2$(tmeda) with benzyl bromide a trans oxidative-addition product, *a*-benzyl-*f*-bromo-*bc*-dimethyl-*de*-(tmeda)platinum(IV) (**8a**), is formed initially and that this complex rapidly isomerizes to *a*-benzyl-*b*-bromo-*cd*-dimethyl-*ef*-(tmeda)platinum(IV) (**8b**). We believe that similar addition/isomerization sequences occur in the reactions leading to **4a**. The configuration of the thermodynamically stable palladium(IV) and platinum(IV) cis oxidative-addition products (**4a** and **8b**) seems to be controlled by steric interaction between the benzyl group and the tmeda ligand.

Introduction

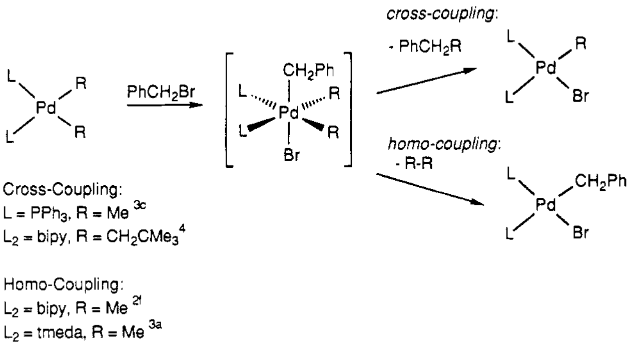
Reductive elimination from dialkylpalladium phosphine complexes with the formation of carbon–carbon single bonds can take place directly from the palladium(II) state as well as from the palladium(IV) state after oxidative addition of an organic halide.[1] Although organopalladium(IV) phosphine complexes have not yet been observed, there is indirect evidence for their likely intermediacy from the reaction of dimethylpalladium diamine complexes with methyl halides.[2,3b] These latter reactions afford the thermolabile palladium(IV) complexes *fac*-$PdXMe_3$(diamine) (X = I, Br; diamine = 2,2′-bipyridine (bpy),[2] tmeda[3b]), which eliminate ethane when heated (eq 1).



(1)

Both $PdMe_2$(bpy) and $PdMe_2$(tmeda) react with CD_3I at room temperature to give a 1:2 mixture of MeMe and $MeCD_3$; this ratio is in agreement with the rapid methyl group scrambling that occurs in the *fac*-$PdXMe_3$(diamine) intermediates.[2d,3b] Scrambling was also observed in the reaction of CD_3I with $PdMe_2(PR_3)_2$ (PR_3 = tertiary phosphine), though here the MeMe:$MeCD_3$ ratio was found to depend on the ligands and solvent.[1g]

After oxidative addition of electrophiles other than methyl halides, the intermediate species $Pd(X)(R)Me_2L_2$ can eliminate two products (RMe and/or MeMe) and the outcome of such reactions appears to depend on the nature of the ligands L. It has been reported that benzyl bromide reacts with $PdMe_2(PPh_3)_2$ to give only ethylbenzene (and $PdBrMe(PPh_3)_2$)[1b] and with $Pd(CH_2CMe_3)_2$(bpy) to give $PhCH_2CH_2CMe_3$ (and $PdBr(CH_2CMe_3)$(bpy)).[4] In both reactions an oxidative-addition/reductive-elimination sequence (eq 2) in which the benzyl group selectively



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[†] Dedicated to the memory of Prof. Dr. J. K. Stille.

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cross-couples with one R group was thought to take place. However, we observed that, in the reaction of $PdMe_2$(tmeda) with benzyl bromide, the benzyl group is retained in the final organometallic product $PdBr(CH_2Ph)$(tmeda) and that the two palladium-bonded methyl groups are involved in homocoupling, giving ethane.[3a] Also, Canty et al. recently showed that the oxidative addition of benzylic bromides, p-$XC_6H_4CH_2Br$, to $PdMe_2$(bpy) gives the isolable trans adducts $PdBr(p\text{-}XC_6H_4CH_2)Me_2$(bpy) but subsequent reductive elimination affords preferably the homocoupled product ethane (eq 2).[2f]

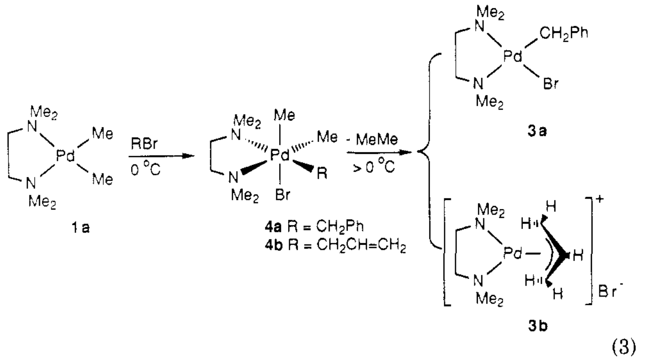
Finally, we found that the course of the reaction of $PdMe_2$(P-N) (P-N = *o*-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine) with benzyl bromide took a completely different course: PdBrMe(P-N) was obtained together with a mixture of ethane, ethylbenzene, and bibenzyl.[5]

In order to gain further insight into carbon–carbon coupling reactions proceeding via a palladium(IV)/palladium(II) oxidative-addition/reductive-elimination sequence, we have now studied in detail the reaction of $PdMe_2$(tmeda) with benzyl bromide and some other electrophiles.

Furthermore, we have reinvestigated the earlier reaction of benzyl bromide with $PdMe_2(PPh_3)_2$ (this complex is now easily available in pure form via the ligand-exchange reaction of $PdMe_2$(tmeda) with PPh_3).[3]

Results

Reaction of $PdMe_2$(tmeda) (1a) with Benzyl Bromide and Allyl Bromide. Benzyl and allyl bromide react with $PdMe_2$(tmeda) (**1a**) at room temperature to give the homocoupled product ethane and $PdBr(\eta^1\text{-benzyl})$(tmeda) (**3a**) and $[Pd(\eta^3\text{-allyl})(tmeda)]Br$ (**3b**), respectively (eq 3).



(3)

The reaction of **1a** with benzyl bromide is not completely selective and always yields some PdBrMe(tmeda) (**2b**) as a byproduct. The reaction is most selective (≥95%) in acetone with use of high reagent concentrations; significantly more PdBrMe(tmeda) (5–15%) is found when the reaction is carried out in benzene. The complexes **3a** and **3b** have been isolated in good yields (85%) and were characterized by NMR spectroscopy and elemental analysis.

Table I. ^{13}C NMR Data[a] for $PdBr(benzyl)Me_2$(tmeda) (4a), $PdBr(allyl)Me_2$(tmeda) (4b), $PdBrMe_3$(tmeda) (4c), and $PtBr(benzyl)Me_2$(tmeda) (8b)

	4a	4b	4c	8b
PdMe	25.59, 27.88	23.65, 29.36	15.50, 25.60	−0.31, 7.00
$PdCH_2$–	36.46	36.36		14.00
NMe	46.73, 46.98, 51.01, 51.28	46.85, 46.97, 51.16, 51.26	47.03, 51.41	46.85, 46.94, 51.49 51.95
$-CH_2-$	59.23, 59.70	59.22, 59.65	59.44	61.40, 61.94
Ph	125.70, 128.00, 130.52, 145.81			124.60, 128.28, 130.25, 147.12
$-CH{=}CH_2$		113.01, 143.88		

[a] Solvent acetone-d_6; all values in δ relative to TMS internal standard.

The ^1H and ^{13}C NMR spectra of **3a** are consistent with an η^1-bonded benzyl group. However, in the ^1H NMR spectrum (200 MHz, $CDCl_3$, 23 °C) the two signals for the NMe_2 groups at δ 2.43 and 2.53 ppm are noticeably broadened. At 33 °C these signals coalesce, and further increase of the temperature gives a single peak at δ 2.48 ppm. This fluxional behavior of **3a** is not influenced by the addition of extra tmeda and does not, therefore, involve dissociation of the tmeda ligand. The most likely explanation for this fluxionality is the formation of a cationic intermediate with an η^3-bonded benzyl group (similar to the η^3-bonded allyl group in compound **3b**) through which the benzyl and the bromide group can interchange positions.[6]

The ^1H NMR spectrum (200 MHz, $CDCl_3$) of $[Pd(\eta^3\text{-allyl})(tmeda)]Br$ (**3b**) at room temperature shows broadened resonances. When the temperature is lowered below 0 °C, the lines sharpen and a spectrum is obtained that is consistent with **3b** being an η^3-allyl complex; the allyl group appears as a multiplet at δ 5.68 ppm (CH_2CHCH_2) and two doublets at δ 3.22 ($^3J_{H,H}$(anti) = 12.6 Hz) and 3.68 ppm ($^3J_{H,H}$(syn) = 7.0 Hz).[7]

Reaction of $PdMe_2$(tmeda) (1a) with Benzyl Bromide at Low Temperature: Formation of *a*-Benzyl-*b*-bromo-*cd*-dimethyl-*ef*-(*N*,*N*,*N*′,*N*′-tetramethylethanediamine)palladium(IV). Since the reaction of $PdMe_2$(tmeda) (**1a**) with benzyl bromide at room temperature unexpectedly gives $PdBr(CH_2Ph)$(tmeda) (**3a**; vide supra), it was decided to investigate the course of the reaction further at low temperature by ^1H NMR spectroscopy. When a solution of **1a** in acetone-d_6 is reacted with a 5-fold excess of benzyl bromide at 0 °C, the oxidative-addition product $PdBrMe_2(CH_2Ph)$(tmeda) (**4a**) is formed quantitatively within about 15 min (eq 3). If the reaction is carried out in toluene, this novel palladium(IV) complex can be precipitated as a yellow-white fibrous precipitate in almost quantitative yield by addition of cold pentane and storage of the mixture at −30 °C overnight. The isolated compound is very soluble in organic solvents, and its NMR spectra when redissolved in acetone (at −20 °C) are the same as those of the in situ prepared **4a**. In the solid state **4a** has limited thermal stability and, although it can be handled for short periods at room temperature, when it stands for some days it is completely converted into $PdBr(CH_2Ph)$(tmeda) (**3a**).

Complex **4a** has been characterized on the basis of its ^1H and ^{13}C NMR spectra (Figure 1 and Table I, respectively). From the four singlets for the four methyl groups of the tmeda ligand (^1H and ^{13}C NMR) it was concluded that the hexacoordinate molecule has no equatorial or axial symmetry planes. In its ^1H NMR spectrum this lack of symmetry is also reflected in the AB pattern for the two inequivalent α-hydrogen atoms of the benzyl group and in the presence of two PdMe signals. These data indicate that one methyl group is in an axial and the other one is

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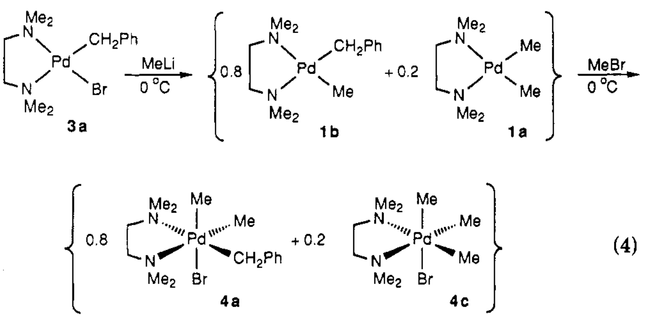
in an equatorial position relative to the palladium diamine plane. There are in fact only two possible structures, with interchanged positions of the benzyl and the bromine group, to be discriminated; the one has a facial and the other a meridional orientation of the C-bonded organic groups.

A careful comparison of the ^{13}C NMR data (in particular of the NCH_2 δ values) of **4a** with those of $PdBrMe_3$(tmeda) (**4c**)[3b] and PdBrMe(tmeda) (Table I) allows us to conclude that **4a** has a facial orientation of the organic groups.

Reaction of $PdMe_2$(tmeda) (1a) with Allyl Bromide at Low Temperature: Formation of *a*-Allyl-*b*-bromo-*cd*-dimethyl-*ef*-(*N,N,N′,N′*-tetramethylethanediamine)palladium(IV). Addition of allyl bromide to a solution of $PdMe_2$(tmeda) in acetone at −20 °C affords, as with benzyl bromide, an oxidative-addition product that has been identified in situ by NMR spectroscopy as *a*-allyl-*b*-bromo-*cd*-dimethyl-*ef*-(*N,N,N′,N′*-tetramethylethanediamine)palladium(IV) (**4b**). In its ^{13}C NMR spectrum, which bears many similarities to that of **4a**, the characteristic signals for an η^1-bonded allyl group occur at δ 36.36, 113.01, and 143.88 ppm. This allyl product **4b** is far less stable with respect to the elimination of ethane than **4a**, and this instability has to date prevented its isolation. Ethane elimination, which results on warming a solution of 4b to 0 °C, is accompanied by the formation of the η^3-allylic complex [Pd(η^3-allyl)(tmeda)]Br (**3b**) as the only organometallic product.

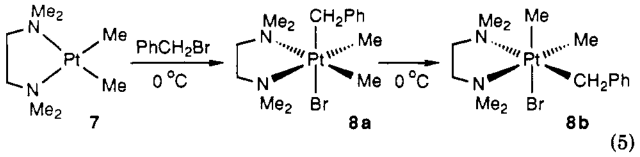
Preparation of $PdMe(CH_2Ph)$(tmeda) and Reaction with Methyl Bromide. Treatment of $PdBr(CH_2Ph)$(tmeda) (**3a**) with 1 equiv of MeLi in diethyl ether as solvent at 0 °C gave, after hydrolysis, a mixture of $PdMe(CH_2Ph)$(tmeda) (**1b**, 80–90%) and $PdMe_2$(tmeda) (**1a**, 10–20%) (eq 4). The new complex **1b** proved difficult to separate from **1a**, and it has only been identified spectroscopically contaminated with this byproduct. The total yield of **1a** and **1b** is almost quantitative.



(4)

Reaction of $PdMe(CH_2Ph)$(tmeda) (**1b**, contaminated with **1a**) with MeBr at 0 °C for 15 min affords *a*-benzyl-*b*-bromo-*cd*-dimethyl-*ef*-(*N,N,N′,N′*-tetramethylethanediamine)palladium(IV) (**4a**) plus $PdBrMe_3$(tmeda) (**4c**) (eq 4). The significance of this result is discussed later.

Reaction of $PtMe_2$(tmeda) (7) with Benzyl Bromide. For comparative purposes the reaction of the platinum complex $PtMe_2$(tmeda) (**7**)[8] with benzyl bromide in acetone-d_6 at 0 °C has been followed by ^1H NMR spectroscopy; the results are summarized in eq 5.



(5)

After 10 min the sample showed peaks of the starting material **7** (10%) together with those of the symmetrical trans oxidative-addition product *a*-benzyl-*f*-bromo-*bc*-dimethyl-*de*-(*N,N,N′,N′*-tetramethylethanediamine)platinum(IV) (**8a**, 35%) and the cis oxidative-addition product *a*-benzyl-*b*-bromo-*cd*-dimethyl-*ef*-(*N,N,N′,N′*-tetramethylethanediamine)platinum(IV) (**8b**, 55%). Typical for the trans oxidative-addition product **8a** are the signals at δ 0.95 ppm for the two $PtMe_2$ groups, the two signals at δ 2.66 and 2.98 ppm for the NMe_2 groups, and the signal at δ 3.18 ppm for the benzylic CH_2 group, all with the corresponding ^{195}Pt satellites. After 60 min neither starting material nor **8a** was present any more and all the peaks in the spectrum could be assigned to **8b**. Evaporation of the solvent gave **8b** in high yield; it is thermally very stable and melts without decomposition at 135–138 °C. The geometry of **8b** has been established through its ^1H and ^{13}C NMR data, and the latter, in particular, closely resemble those of the palladium(IV) compound **4a** (Table I).

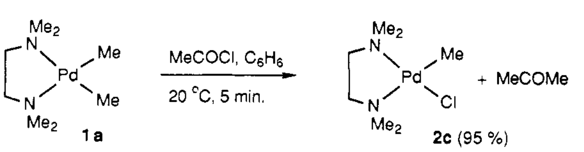
The appearance and subsequent disappearance of NMR signals attributable to the trans addition product **8a** are strong evidence for a reaction sequence in which benzyl bromide adds initially in a trans oxidative addition to **7**, followed by an isomerization to the final cis product **8b**. We believe that a similar reaction sequence is involved in the formation of the palladium analogue **4a**.

Reaction of $PdMe_2$(tmeda) (1a) with Ethyl Iodide. The reaction of $PdMe_2$(tmeda) (**1a**) with ethyl iodide at room temperature in benzene proceeds rapidly with evolution of 1.06 equiv of gas that was found to be a 2:3 mixture of ethane and propane with a trace of ethene. On the basis of ^1H NMR data, the remaining yellow-gray precipitate consists of a 3:2 mixture of PdIMe(tmeda) (**2a**) and PdIEt(tmeda) (**2d**). This reaction is summarized in eq 6.

$$\mathrm{PdMe_2(tmeda)} \xrightarrow[\mathrm{C_6H_6,\ 20\ ^\circ C}]{\mathrm{EtI}} \tfrac{3}{5}\underset{\mathbf{2a}}{\mathrm{PdIMe(tmeda)}} + \tfrac{2}{5}\underset{\mathbf{2d}}{\mathrm{PdIEt(tmeda)}} + \tfrac{3}{5}\mathrm{EtMe} + \tfrac{2}{5}\mathrm{MeMe} \quad (6)$$

Unfortunately, we have not succeeded in separating the novel ethylpalladium compound **2d** from **2a**, but the in situ NMR data are fully consistent with square-planar PdIEt(tmeda); in its ^1H NMR spectrum the ethyl group appears as a quartet at 1.48 ppm and a triplet at 0.76 ppm. Ethyl complex **2d** is unstable in $CDCl_3$ solution at room temperature and under these conditions decomposes completely upon standing for 1 day to give metallic palladium. Under these conditions PdIMe(tmeda) is stable and remains in solution.

Reaction of $PdMe_2$(tmeda) (1a) with Acetyl Chloride. When $PdMe_2$(tmeda) (**1a**) is reacted with acetyl chloride, PdClMe(tmeda) (**2c**) is obtained in high yield, with acetone (0.93 equiv) as the only organic product (eq 7). This preparative route for **2c** is a good alternative for the rather inefficient reaction of **1a** with methyl chloride.[3a]



(7)

CO Insertion Reactions of $PdMe_2$(tmeda) (1a) and PdXMe(tmeda) (X = Cl, Br, I; 2a–c). $PdMe_2$(tmeda) in benzene-d_6 reacts with CO, though very slowly. Initially, the solution turns blue and after about 15 min black, finely divided palladium starts to precipitate. The consumption

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(8) Appleton, T. G.; Hall, J. R.; Williams, M. A. *J. Organomet. Chem.* **1986**, *303*, 139–149.

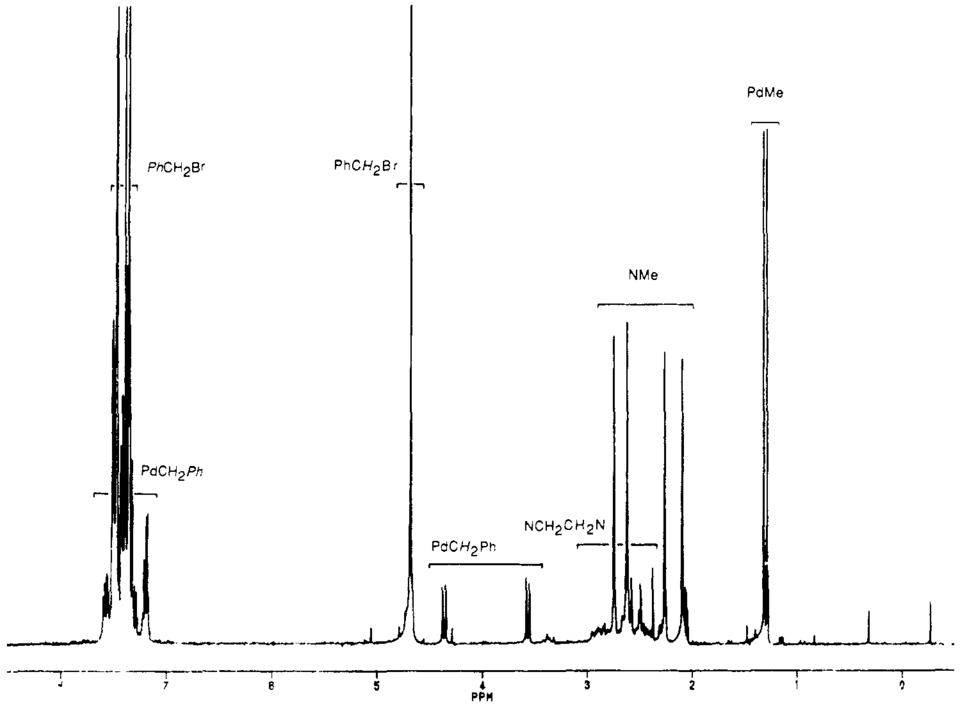
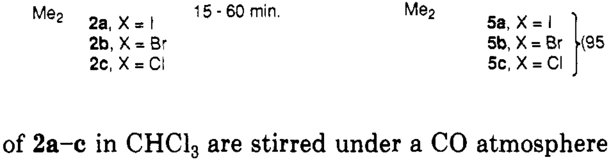


Figure 1. ^{1}H NMR spectrum of $PdBrMe_2(CH_2Ph)(tmeda)$ (**4a**) in acetone-d_6 at −20 °C.

of carbon monoxide (1 equiv) is complete only after 24 h, and after this time 1 equiv of palladium has been formed; the mother liquor contains 0.65 equiv of acetone and 1.0 equiv of tmeda.

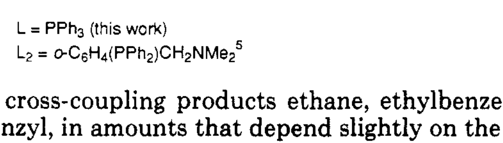
In contrast, complexes of the type $PdX(COMe)(tmeda)$ (**5a–c**) are easily obtained by CO insertion into the Pd–Me bond of $PdXMe(tmeda)$ (**2a–c**) (eq 8). When solutions



(8)

of **2a–c** in $CHCl_3$ are stirred under a CO atmosphere at ambient temperature and pressure, these reactions are complete within 15–60 min and the products **5a–c** can be isolated in almost quantitative yields. In the ^{1}H NMR spectra of **5a–c** the acetyl groups afford a singlet at ca. 2.50 ppm and the tmeda methyl groups give rise to two signals.

Reaction of $PdMe_2(PPh_3)_2$ (6) with Benzyl Bromide. $PdMe_2(PPh_3)_2$ (**6**), prepared by subsitution of the tmeda ligand in **1a** by two triphenylphosphine ligands, reacts with benzyl bromide at room temperature, in chloroform and in benzene as solvent, to give $PdBrMe(PPh_3)_2$ in 95% yield (eq 9). The solution contains the organic homocoupling



(9)

and cross-coupling products ethane, ethylbenzene, and bibenzyl, in amounts that depend slightly on the solvent used. In benzene, the ethylbenzene:bibenzyl:ethane ratio was 3:2:1, and this result is similar to that obtained for the reaction of $PdMe_2$(*o*-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine) with benzyl bromide.[5] The product distribution did not change when a 6% excess of triphenylphosphine was added as a stabilizer of $PdMe_2(PPh_3)_2$.

Discussion

Very recently, the first examples of triorganopalladium(IV) complexes have been isolated and characterized.[2,3] In this new branch of organopalladium(IV) chemistry it appears that the presence of a chelating diamine ligand, e.g. bpy or tmeda, is essential for complex formation and stability. As organopalladium(IV) species are believed to play an important role in synthetically important cross-coupling reactions, the study of the nature and reactivity of these new diamine complexes is relevant.

Homocoupling versus Cross-Coupling. The reaction of $PdMe_2$(diamine) (diamine = tmeda, bpy) with both CD_3I[2d,3b] and EtI gives product mixtures that result from nonselective coupling in the reductive-elimination step. We believe that scrambling of the organic groups in the initial Pd(IV) adducts, which has indeed been observed in $Pd(I)(CD_3)Me_2$(diamine), is also responsible for the nonselective reaction of $PdMe_2(tmeda)$ with EtI. The 2:3 mixture of ethane and propane and the 2:3 mixture of PdIEt(tmeda) and PdIMe(tmeda) found in the latter reaction is very close to the random 1:2 distribution of products found in the corresponding reaction with CD_3I. The reaction of $PdMe_2(bpy)$ with EtI has been reported to give a similar result, but the ratio was not exactly determined.[2c]

It is noteworthy that in the reactions of $PdMe_2$(diamine) with EtI propane is formed without extensive β-elimination as found in the reaction of the diethylplatinum compound *cis*-$PtEt_2(PMe_2Ph)_2$ with MeI.[9a]

The reactions of **1a** with allyl and benzyl bromide are quite different from those of the alkyl iodides and result in selective methyl–methyl homocoupling with the for-

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[9] (a) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E.; Lavington, S. W. *J. Chem. Soc., Dalton Trans.* **1974**, 1613. (b) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1974**, *65*, 275. (c) Crespo, M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 2548–2550.

mation of (η^1-benzyl)- and (η^3-allyl)palladium species, respectively. The selectivity of the reaction of **1a** with acetyl chloride is of the opposite type, and acetone and PdClMe(tmeda) were formed as a result of methyl–acetyl cross-coupling. A preference of coupling of a methyl and an acetyl group over that of two methyl groups has been observed earlier in the platinum(IV) complex $Pt(Cl)Me_2(COMe)(PMe_2Ph)_2$.[9a,b] Furthermore, reductive elimination from Pd(II) of a methyl group and an sp^2-hybridized organic ligand, such as a styryl group[1f] or a phenyl group,[10] is known to be easier than that of two methyl groups.

The reaction of the phosphine complex $PdMe_2(PPh_3)_2$ with benzyl bromide at room temperature gave $PdBrMe(PPh_3)$ and a mixture of ethylbenzene, bibenzyl, and a small amount of ethane. The presence of bibenzyl in the product mixture indicates that at least part of this reaction takes a radical pathway, which is a basic difference from the corresponding reaction of the amine complex $PdMe_2$(tmeda) (**1a**).[11]

Mechanistic Path of Oxidative Addition and Reductive Elimination. Platinum complexes are generally kinetically much more stable than the corresponding palladium complexes.[1g,2d] For reasons of comparison, we therefore carried out the reaction of the platinum complex $PtMe_2$(tmeda) (**7**)[8] with benzyl bromide. It appeared that trans oxidative addition to give **8a** occurs first and that this is followed by an isomerization to the thermodynamically more stable formally cis oxidative-addition product **8b** (eq 5). (The overall cis oxidative addition that has been reported for the reaction of benzyl and allyl bromide with *cis*-$PtMe_2(PMe_2Ph)_2$ may as well be the result of a trans oxidative addition followed by an isomerization.[9])

We believe that a similar addition/isomerization sequence also occurs in the oxidative addition of benzyl and allyl bromide to the palladium–amine analogue **1a**. The factor that most likely initiates isomerization in a trans oxidative-addition species is steric interference between the incoming organic group and the axially positioned methyl groups of the tmeda ligand. This particular steric interference is absent with the planar bpy ligand, and the reactions of $PdMe_2$(bpy) with benzylic bromides produce the trans oxidative-addition products only.[2f] An experiment carried out to confirm that the configuration of the organic groups in *cis*-$PdBrMe_2(CH_2Ph)$(tmeda) (**4a**) is thermodynamically controlled was the reaction of $PdMe(CH_2Ph)$(tmeda) with MeBr. A formal trans oxidative addition took place with formation of **4a**, in contrast to the formal cis oxidative addition of benzyl bromide to $PdMe_2$(tmeda). Since there is no reason to believe that oxidative addition of benzyl bromide should be specifically cis and that of methyl bromide trans, we conclude that the configuration of **4a** is thermodynamically controlled.

The selective reductive elimination of ethane from the benzyl- and allyldimethylpalladium(IV) complexes **4a** and **4b** can have several origins. First, an η^1-benzyl– or an η^1-allyl–metal bond has more s character than a metal–alkyl bond, and this may be the reason that the two more weakly bonded methyl groups couple preferentially. Furthermore, reductive elimination from the complexes $PdXMe_3$(diamine) has been found to be preceded by ligand dissociation,[2d,3b] and the empty coordination site that results would allow the benzyl and particularly the allyl group to bind in an η^3 mode to palladium prior to the reductive-elimination process. This strong η^3 bonding will then favor even more the elimination of ethane rather than ethylbenzene or butene.

Experimental Section

General Considerations. All operations were conducted under an atmosphere of dry nitrogen with the use of established Schlenk-type techniques. Benzene, diethyl ether, and pentane were freshly distilled from sodium benzophenone ketyl. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 200 spectrometer. Elemental analyses were performed by the Institute of Applied Chemistry (TNO), Zeist, The Netherlands. The amount of evolved gases was measured by a gas buret. Gases were analyzed on a Hewlett-Packard research chromatograph equipped with a Porapak column. $PdMe_2$(tmeda) (**1a**), PdIMe(tmeda) (**2a**), and PdBrMe(tmeda) (**2b**) were prepared as reported.[3] $PdMe_2(PPh_3)_2$[1] was prepared from **1a**, and $PtCl_2$(tmeda) was prepared from K_2PtCl_4 in water by addition of tmeda and hydrochloric acid.

Reaction of $PdMe_2$(tmeda) with Ethyl Iodide. $PdMe_2$(tmeda) (0.13 g, 0.49 mmol) was dissolved in benzene (5 mL) in a closed vessel. Ethyl iodide (0.2 mL, slight excess) was added with a syringe. The mixture slowly turned yellow, and after ca. 15 min a yellow crystalline solid precipitated. After 3 h the gases (0.52 mmol) were removed by means of a Töpler pump and analyzed by GLC to be a 3:2 mixture of propane and ethane. After removal of the gases the benzene was diluted with 25 mL of pentane in order to precipitate the organometallic compounds. The precipitate was isolated by decantation and dried in vacuo; yield 0.17 g of a yellow-gray solid (ca. 85%). ^1H NMR (200 MHz, $CDCl_3$, δ): 0.44 (s, 3, PdMe), 0.76 (t, 1.8, $PdCH_2CH_3$), 1.48 (q, 1.2, $PdCH_2CH_3$), 2.4–2.7 (m, $-CH_2-$), 2.62, 2.63 (s, NMe_2 assigned to PdIMe(tmeda) (**2a**)[3b]), 2.56, 2.67 (s, NMe_2 assigned to PdIEt(tmeda) (**2d**)). ^{13}C NMR (50 MHz, $CDCl_3$, δ): −9.74 (PdMe), 8.31 ($PdCH_2CH_3$), 18.68 ($PdCH_2CH_3$); 49.56, 49.78 (NMe_2), 57.78, 62.53 ($-CH_2-$), assigned to **2a**[3b]; 49.49, 49.32 (NMe_2) 62.49, 57.42 ($-CH_2-$), assigned to **2d**.

Pd(Cl)Me(tmeda) (2c). Acetyl chloride (0.2 mL, excess) was added to a solution of $PdMe_2$(tmeda) (0.25 g, 0.96 mmol) in benzene (5 mL) at room temperature, and a pale yellow microcrystalline precipitate formed immediately. The precipitate was isolated by decantation and was dried in vacuo; yield 0.23 g (90%). Spectra data have been reported earlier.[3] Acetone was detected in the remaining reaction mixture by ^1H NMR spectroscopy and GC–MS. The amount (0.93 mmol) was estimated by ^1H NMR integration against added $Me_3SiOSiMe_3$.

$PdBr(CH_2Ph)$(tmeda) (3a). To a solution of $PdMe_2$(tmeda) (0.13 g, 0.49 mmol) in acetone (2 mL) was added benzyl bromide (0.2 mL). The mixture slowly turned yellow, and within 15 min bright yellow **3a** crystallized from the solution, while a gas evolved. The yellow crystals were isolated by decantation and dried in vacuo; yield 0.17 g (85%). The gas evolved (9.5 mL, 0.4 mmol) was analyzed to be ethane by GLC and MS. Mp: 170–175 °C dec. Anal. Calcd: C, 39.67; H, 5.89; N; 7.12. Found: C, 38.96; H, 5.77; N, 6.76. ^1H NMR (200 MHz, $CDCl_3$, δ): 2.43, 2.53 (br s, 3, NMe_2), 2.4–2.8 (m, $-CH_2-$), 2.97 (s, 2, CHPh), 7.06, 7.56 (m, 5, AB_2C_2, arom). ^{13}C NMR (50 MHz, $CDCl_3$, δ): 15.36 (CH_2Ph), 48.76, 49.84 (br s, NMe_2), 57.50, 63.41 (br s, $-CH_2-$), 123.50, 128.05, 129.39, 147.51 (Ph).

[Pd(η^3-allyl)(tmeda)]Br (3b). To a solution of $PdMe_2$(tmeda) (0.13 g, 0.49 mmol) in toluene (5 mL) cooled to 0 °C was added allyl bromide (0.2 mL). The mixture was gently shaken and turned pale yellow. After 15 min at 0 °C the mixture was cooled to −60 °C and a yellow-white compound precipitated. The supernatant liquid was removed and the precipitate washed at 0 °C with pentane. The precipitate was isolated by decantation and dried in vacuo; yield 0.15 g (85%). Mp: 95–100 °C dec. Anal. Calcd: C, 31.46; H, 6.16; Br, 23.26; N, 8.15. Found: C, 31.55; H, 6.45; Br, 24.59; N, 7.82. ^1H NMR (200 MHz, $CDCl_3$, 0 °C δ): 2.91 (s, 4, $-CH_2-$), 2.95 (s, 12, NMe_2), 3.22 (d, 2, $^3J_{H,H}$ = 12.6 Hz, *anti*-CHHCHCHH), 3.68 (d, 2, $^3J_{H,H}$ = 7.0 Hz, *syn*-CHHCHCHH), 5.68

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[10] (a) Ozawa, F.; Kurihara, K.; Fujimori, M.; Hidaka, T.; Toyoshima, T.; Yamamoto, A. *Organometallics* **1989**, *8*, 180. (b) Brown, J. M.; Cooley, N. A. *Chem. Rev.* **1988**, *88*, 1031.

[11] Stille and co-workers have claimed that the reaction of $PdMe_2(PPh_3)_2$ with benzyl bromide gives a similar product mixture, containing $PdBr(benzyl)(PPh_3)_2$ instead of bibenzyl.[1b] The presence of $PdBr(benzyl)(PPh_3)_2$ was inferred from a peak at 2.90 ppm in the ^1H NMR spectrum. This assignment, however, is incorrect, since we have verified that the benzylic hydrogens of $PdBr(benzyl)(PPh_3)_2$ absorb at 2.76 ppm, instead of 2.98 ppm, and that the latter absorption is due to bibenzyl.

(m, 1, CCHC). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, δ): 52.69 (NMe_2), 60.87, 60.90 ($-CH_2-$ and $\mathit{C}H_2CH{=}\mathit{C}H_2$), 118.17 ($CH_2\mathit{C}HCH_2$).

***a*-*Benzyl*-*b*-bromo-*cd*-dimethyl-*ef*-(*N*,*N*,*N′*,*N′*-tetramethylethanediamine)palladium (4a).** *Warning*: This compound has limited thermal stability and decomposes explosively when heated to ca. 50 °C. It should be stored at temperatures below 0 °C.

Benzyl bromide (0.5 mL) was added to a cooled solution of $PdMe_2$(tmeda) (0.13 g, 0.51 mmol) in toluene (3 mL) at 0 °C. After 15 min pentane (25 mL), precooled to 0 °C, was added and the mixture was stored at −30 °C for 18 h. The light yellow fibrous precipitate of **4a** that had formed was separated from the supernatant solution by decantation. The product was washed with cold pentane (0 °C, 2 × 5 mL) and dried in vacuo at 0 °C; yield 0.22 g (100%). Mp: ~50 °C (explosive decomposition). ^1H NMR (200 MHz, acetone-d_6, −20 °C, δ): 1.21 (s, 3, PdMe), 1.31 (s, 3, PdMe), 2.14 (s, 3, NMe), 2.31 (s, 3, NMe), 2.55 (s, 3, NMe), 2.74 (s, 3, NMe), 2.4–3.0 (m, 4, $-CH_2-$), 3.52 (d, 1, $^2J_{H,H}$ = 6.1 Hz, PhCH*H*), 4.33 (d, 1, $^2J_{H,H}$ = 6.1 Hz, PhCH*H*), 7.17, 7.52 (AB_2C_2, 5, Ph). ^{13}C NMR (50 MHz, acetone-d_6, −20 °C, δ): 25.59 (PdMe), 27.88 (PdMe), 36.46 ($Pd\mathit{C}H_2Ph$), 46.73, 46.98, 51.01, 51.28 (NMe), 59.23, 59.70 ($-CH_2-$), 125.70, 128.00, 130.52, 145.81 (Ph).

$PdBrMe_2(CH_2CH{=}CH_2)$(tmeda) (4b). A solution of $PdMe_2$(tmeda) (30 mg) in acetone–d_6 (0.35 mL) was prepared in a 5-mm NMR tube that was then cooled to −20 °C. Allyl bromide (0.15 mL, 15-fold excess) was added and the NMR tube shaken in order to obtain a homogeneous solution. The tube was placed in the NMR spectrometer probe at 0 °C. The reaction was followed by ^1H NMR spectroscopy and after **1a** had almost been consumed, the sample was cooled to −20 °C and ^1H NMR and ^{13}C NMR spectra were recorded. The ^1H NMR assignment is incomplete because the excess of allyl bromide obscures the Pd–allyl signals. **4b**: ^1H NMR (200 MHz, acetone-d_6, −20 °C, δ) 0.81 (s, 3, ethane), 1.21 (s, 3, PdMe), 1.46 (s, 3, PdMe), 2.34 (s, 6, NMe_2), 2.73 (s, 3, NMe), 2.74 (s, 3, NMe); ^{13}C NMR (50 MHz, acetone-d_6, −20 °C, δ) 23.65, 29.36 (PdMe), 36.36 ($Pd\mathit{C}H_2CH{=}CH_2$), 46.85, 46.97, 51.16, 51.26 (NMe), 59.22, 59.65 ($-CH_2-$), 113.01, 143.88 ($-CH{=}CH_2$) (^{13}C NMR signals attributed to **3b**: δ 52.13 (NMe_2), 60.93 ($-CH_2-$), 61.00 ($\mathit{C}H_2CH{=}\mathit{C}H_2$), 118.51 ($CH_2\mathit{C}H{=}CH_2$)).

$PdMe(CH_2Ph)$(tmeda) (1b). To a well-stirred suspension of $PdBr(CH_2Ph)$(tmeda) (0.49 g, 1.25 mmol) in diethyl ether (75 mL) at −20 °C was added MeLi (0.8 mL of a 1.6 M solution in diethyl ether, 1.28 mmol), and the mixture was warmed up during $^1/_2$ h to 0 °C. After the mixture was stirred for a further 60 min, a clear colorless solution was obtained. The reaction mixture was then quenched with ice–cold water (10 mL). After 1 min the organic layer was separated and dried over $MgSO_4$. Evaporation of the solvent gave 0.14 g of a white solid (ca. 90%). It consisted of a 4:1 mixture of $PdMe(CH_2Ph)$(tmeda) (**1b**) and $PdMe_2$(tmeda) (**1a**). **1b**: ^1H NMR (200 MHz, benzene-d_6, δ) 0.47 (s, 3, PdMe), 1.54, 1.55 (brd, 4, $-CH_2-$), 1.88 (s, 6, NMe_2), 1.96 (s, 6, NMe_2), 2.74 (s, 2, CH_2Ph), 6.86 (t, 1, *p*-H, Ph), 7.23 (t, 2, *m*-H, Ph), 7.58 (d, 2, *o*-H, Ph) (^1H NMR signals attributed to **1a**: δ 0.49 (s, 1.5, PdMe), 1.63 (s, 1, $-CH_2-$), 2.01 (s, 3, NMe_2)).

$PtMe_2$(tmeda) (7). This compound was prepared by using the procedure for the synthesis of $PdMe_2$(tmeda);[3] yield 20% of white powder. ^1H NMR (200 MHz, acetone-d_6, δ): 0.22 (s, 3, $^2J_{H,^{195}Pt}$ = 88.2 Hz, PtMe), 2.60 (s, 6, $^3J_{H,^{195}Pt}$ = 23.8 Hz, NMe), 2.67 (s, 2, $^3J_{H,^{195}Pt}$ = 12.1 Hz, $-CH_2-$).

$PtBrMe_2(CH_2Ph)$(tmeda) (8b). A solution of $PtMe_2$(tmeda) (**7**; 47 mg, 0.13 mmol) in acetone-d_6 (0.35 mL) was prepared in a 5-mm NMR tube that was then cooled to −20 °C. Benzyl bromide was added (0.15 mL, excess), and after being shaken for a few seconds, the tube was placed in the NMR spectrometer probe at −20 °C. When the probe was warmed to 0 °C, the reaction was found to proceed slowly, and after 10 min a ^1H NMR spectrum was recorded. This spectrum showed the intermediacy of **8a**. During the next 60 min a ^{13}C NMR spectrum was recorded and after that a second ^1H NMR spectrum. This second ^1H NMR spectrum showed only peaks that could be attributed to **8b**. The contents of the NMR tube were evaporated to dryness, and the residual white solid was washed with pentane and dried in vacuo; yield 67 mg (96%). Mp: 135–138 °C. **8b**: ^1H NMR (200 MHz, acetone-d_6, 0 °C, δ) 0.76 (s, 3, $^2J_{H,^{195}Pt}$ = 71.8 Hz, PtMe), 0.96 (s, 3, $^2J_{H,^{195}Pt}$ = 72.8 Hz), 2.27 (s, 3, $^3J_{H,^{195}Pt}$ = 14.0 Hz, NMe), 2.39 (s, 3, $^3J_{H,^{195}Pt}$ = 16.6 Hz, NMe), 2.81 (s, 3, $^3J_{H,^{195}Pt}$ = 8.8 Hz, NMe), 2.92 (s, 3, $^3J_{H,^{195}Pt}$ = 12.0 Hz), 3.29 (d, 1, $^2J_{H,H}$ = 16.6 Hz, $^2J_{H,^{195}Pt}$ = 118.8 Hz, C*H*HPh), 3.93 (d, 1, $^2J_{H,H}$ = 8.3 Hz, $^2J_{H,^{195}Pt}$ = 110.8 Hz, C*H*HPh), 7.0–7.5 (m, arom); ^{13}C NMR (50 MHz, acetone-d_6, δ) −0.31, 7.00 (PtMe), 14.00 ($\mathit{C}H_2Ph$), 46.85, 46.94, 51.49, 51.95 (NMe), 61.40, 61.94, ($-CH_2-$), 124.60, 128.28, 130.25, 147.12 (Ph). **8a**: ^1H NMR (200 MHz, acetone-d_6, 0 °C, δ) 0.95 (s, 3, $^2J_{H,^{195}Pt}$ = 72.6 Hz, PtMe), 2.66 (s, 3, $^3J_{H,^{195}Pt}$ = 13.8 Hz, NMe), 2.98 (s, 3, $^3J_{H,^{195}Pt}$ = 11.0 Hz), 3.18 (s, 1, $^2J_{H,^{195}Pt}$ = 121.0 Hz, $C\mathit{H}_2Ph$).

Reaction of $PdMe_2$(tmeda) (1a) with Carbon Monoxide. A closed reaction vessel was charged with $PdMe_2$(tmeda) (220 mg, 0.87 mmol) and benzene (2 mL) and filled with carbon monoxide to atmospheric pressure. The benzene solution slowly turned from light blue to black. After 3 days a total gas consumption of 21 mL (0.87 mmol) was recorded by means of a gas buret. ^1H NMR spectroscopy showed the solution to contain 0.56 mmol of acetone and 0.86 mmol of tmeda.

PdI(COMe)(tmeda) (5a). A slow stream of carbon monoxide was bubbled through a solution of PdIMe(tmeda) (0.20 g, 0.55 mmol) in $CHCl_3$ (5 mL) for 1 min, and the color faded from bright yellow to pale yellow. After this solution had been stirred for 1 h under a CO atmosphere, its volume was reduced to 1 mL by evaporation of the solvent in vacuo. Pentane (10 mL) was then added, and a light yellow solid precipitated. The solution was decanted from the precipitate of **5a** and the product dried in vacuo; yield 0.20 g (95%). Mp: 164–165 °C dec. Anal. Calcd for $C_8H_{19}IN_2OPd$: C, 24.47; H, 4.88; N, 7.16. Found: C, 24.12; H, 4.83; N; 7.35. ^1H NMR (200 MHz, $CDCl_3$, δ): 2.50 (s, 3, MeCO), 2.43, 2.58 (br s, 6, NMe_2), 2.42–2.48, 2.66–2.73 (AA′BB′, 4, $-CH_2-$). ^{13}C NMR (50 MHz, $CDCl_3$, δ): 41.64 (*Me*CO), 48.46, 51.93 (NMe_2), 58.34, 61.43 ($-CH_2-$), 195.97 (−CO−). IR: $\nu_{C=O}$ 1660 cm^{-1}.

PdBr(COMe)(tmeda) (5b). This compound was prepared similarly to PdI(COMe) (**5a**); yield 90%. Mp: 108 °C dec. Anal. Calcd for $C_8H_{19}BrN_2OPd$: C, 27.80; H, 5.54; N, 8.11. Found: C, 26.93; H, 5.43; N, 7.69. ^1H NMR (200 MHz, $CDCl_3$, δ): 2.46 (s, 3 H, MeCO), 2.44, 2.68 (br s, 6 H, NMe_2), 2.42–2.48, 2.66–2.73 (AA′BB′, 4, $-CH_2-$). IR: $\nu_{C=O}$ 1662 cm^{-1}.

PdCl(COMe)(tmeda) (5c). This compound was prepared in a way similar to the preparation of PdI(COMe) (**5a**); yield 90%. Mp: 126 °C dec. Anal. Calcd for $C_8H_{19}ClN_2OPd$: C, 31.91; H, 6.36; N, 79.30. Found: C, 31.67; H, 6.27; N; 79.46. ^1H NMR (200 MHz, $CDCl_3$, δ): 2.51 (s, 3, MeCO), 2.45, 2.63 (br s, 6, NMe_2), 2.42–2.48, 2.66–2.73 (AA′BB′, 4, $-CH_2-$). ^{13}C NMR (50 MHz, $CDCl_3$, δ): 35.16 (*Me*CO), 47.18, 50.41 (NMe_2), 57.36, 62.02 ($-CH_2-$), 210.0 (−CO−). IR: $\nu_{C=O}$ 1662 cm^{-1}.

Reaction of $PdMe_2(PPh_3)_2$ with Benzyl Bromide. Solid $PdMe_2(PPh_3)_2$ (0.35 g, 0.53 mmol) was dissolved in benzene (5 mL) that contained 0.02 g of PPh_3 (to prevent decomposition of $PdMe_2(PPh_3)_2$)). $Me_3SiOSiMe_3$ (24.3 mg, 0.15 mmol) was added as internal standard to the colorless solution followed by benzyl bromide (0.15 g, 0.87 mmol). The solution slowly turned yellow, and after 1 h a yellow solid of $PdBrMe(PPh_3)_2$ deposited. The yellow solid was isolated by decantation, washed with pentane, and dried in vacuo; yield 0.35 g (95%). The decanted mother liquor was analyzed by means of ^1H NMR spectroscopy and found to contain 0.21 mmol of ethylbenzene, 0.14 mmol of $PhCH_2CH_2Ph$, 0.07 mmol of ethane, and 0.35 mmol of unreacted benzyl bromide.

Acknowledgment. We thank B. A. Markies for carrying out a number of verification experiments suggested by the comments of one of the reviewers. Dr. D. M. Grove is kindly thanked for valuable suggestions and careful reading of the manuscript. We thank Johnson Matthey PLC (U.K.) for the generous loan of precious-metal salts.