

# Dimethyl(*N,N,N',N'*-tetramethylethanediamine)palladium(II) and Dimethyl[1,2-bis(dimethylphosphino)ethane]palladium(II): Syntheses, X-ray Crystal Structures, and Thermolysis, Oxidative-Addition, and Ligand-Exchange Reactions

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PdMe<sub>2</sub>(tmeda) (**2a**) (tmeda = *N,N,N',N'*-tetramethylethanediamine) has been prepared and characterized by means of NMR spectroscopy and X-ray crystallography. Crystals of PdMe<sub>2</sub>(tmeda) are monoclinic, space group *P2<sub>1</sub>/n*, with unit-cell dimensions *a* = 8.518 (4) Å, *b* = 10.798 (4) Å, *c* = 12.132 (5) Å,  $\beta$  = 99.02 (4)°, and *Z* = 4. Thermolysis of **2a** in benzene affords a 3/1 mixture of methane and ethane in a total amount of 1.0–1.2 equiv/palladium. Deuterium crossover experiments show that the formation of methane is likely to be the result of an  $\alpha$ -elimination process. The reactions of PdMe<sub>2</sub>(tmeda) with MeX [X = I, Br, and SO<sub>2</sub>CF<sub>3</sub> (OTf)], studied by means of low-temperature NMR spectroscopy, showed the formation of *fac*-PdXMe<sub>3</sub>(tmeda) (**4a,b**) ( $\leq -40$  °C for X = I;  $-20$  °C for X = Br). When these solutions are warmed up ( $\geq -20$  °C for **4a**;  $\geq 0$  °C for **4b**), ethane is eliminated with the formation of PdXMe(tmeda) (**3a,b**). PdMe<sub>2</sub>(tmeda) reacts with MeOTf in acetonitrile-*d*<sub>3</sub> or acetone-*d*<sub>6</sub> at  $\leq -40$  °C to give the cationic complex [PdMe<sub>3</sub>(solvent)(tmeda)][OTf] (**4d**). In the palladium(IV) complexes (**4a,b,d**), there is exchange between the equatorial and the axial methyl groups, whose rate depends on the coordination ability of the solvent and/or halide present; the exchange rate decreases in the order acetone > acetonitrile > I<sup>-</sup> > Br<sup>-</sup>. The ease of reductive elimination from these palladium(IV) complexes follows the same order. The tmeda ligand in PdMe<sub>2</sub>(tmeda) is very easily displaced by mono- and diphosphines, 2,2'-bipyridyl, and even other chelating aliphatic di- and triamines. PdMe<sub>2</sub>(dmpe) (**5**) [dmpe = 1,2-bis(dimethylphosphino)ethane] was prepared, using this method, and studied by X-ray crystallography. Crystals of PdMe<sub>2</sub>(dmpe) are monoclinic, space group *C2/c*, with unit-cell dimensions *a* = 9.442 (1) Å, *b* = 14.968 (1) Å, *c* = 10.354 (1) Å,  $\beta$  = 115.62 (1)°, and *Z* = 4. The palladium-carbon bond length in PdMe<sub>2</sub>(dmpe) (2.088 (4) Å) is longer than in PdMe<sub>2</sub>(tmeda) (2.026 (3) and 2.029 (3) Å) due to the larger trans influence of phosphorus. Thermal decomposition of PdMe<sub>2</sub>(dmpe) in solution gave, like PdMe<sub>2</sub>(tmeda), methane and ethane in a 3/1 ratio, and its reaction with MeI proceeds only slowly at room temperature to give ethane and PdIME(dmpe). The much higher reactivity of PdMe<sub>2</sub>(tmeda) than PdMe<sub>2</sub>(dmpe) toward MeI can be explained by the enhanced nucleophilic character of the palladium center in the former compound due to the presence of two amine sites which are exclusively  $\sigma$ -donors.

## Introduction

Palladium tertiary phosphine complexes have found wide application as homogeneous catalysts in organic synthesis,<sup>1</sup> and, accordingly, organopalladium tertiary phosphine complexes have been the subject of many mechanistic studies.<sup>2-4</sup> However, although PdMe<sub>2</sub>(bpy)<sup>5</sup> (bpy = 2,2'-bipyridyl) and ortho-metalated palladium arylamine complexes are known,<sup>6</sup> information about simple alkylpalladium(II) complexes with aliphatic (di)amines is very scarce. Only one cycloalkyl(*N,N,N',N'*-tetramethylethanediamine)palladium complex, i.e. Pd(CH<sub>2</sub>)<sub>4</sub>(tmeda) (tmeda = *N,N,N',N'*-tetramethylethanediamine), has been described,<sup>7a</sup> and PdMe<sub>2</sub>(tmeda) has been suggested as a reaction intermediate<sup>7b</sup> on the basis of NMR evidence. The paucity of compounds of this class is in keeping with the common view<sup>8a</sup> that divalent palladium is a "soft" metal center and that the presence of good "soft"  $\sigma$ -donor ligands, such as tertiary phosphines, is necessary for the stabilization of its organometallic complexes. Recently, we found that organometallic complexes of palladium with bidentate ligands having both a phosphorus and a nitrogen donor site<sup>9</sup> are readily accessible and that the six-membered Pd-N-C-C-C-P chelate ring in these species is very stable. This result encouraged us to attempt the preparation of new organopalladium complexes with

the diamine ligand tmeda. A preliminary account of some of our results has been published.<sup>10</sup>

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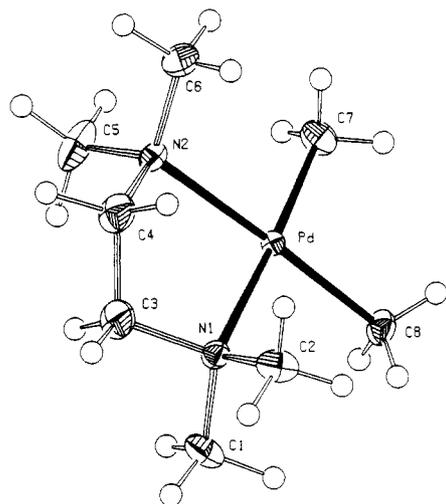
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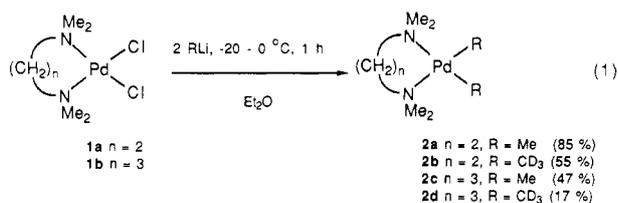
**Figure 1.** Thermal motion ellipsoid plot of  $\text{PdMe}_2(\text{tmeda})$  (**2a**) at the 50% probability level, with the adopted atom numbering.

We here report the preparation and characterization of dimethyl(*N,N,N',N'*-tetramethylethanediamine)palladium(II) and describe details of its thermolysis both in the solid state and in solution. Furthermore,  $\text{PdMe}_2(\text{tmeda})$  undergoes (a) oxidative addition reactions leading to the first organopalladium(IV) complexes with aliphatic amine ligands and (b) ligand exchange reactions with monophosphines, bis(phosphines), bpy, and chelating aliphatic amine ligands that provide a very easy synthetic route to many kinds of dimethylpalladium complexes. The complex  $\text{PdMe}_2(\text{dmpe})$  [dmpe = 1,2-bis(dimethylphosphino)ethane], the phosphorus analogue of  $\text{PdMe}_2(\text{tmeda})$ , has been prepared in the latter way. For comparison with  $\text{PdMe}_2(\text{tmeda})$ ,  $\text{PdMe}_2(\text{dmpe})$  has also been thermolyzed, reacted with MeI, and analyzed by X-ray crystallography.

## Results

### Synthesis and Properties of $\text{PdMe}_2(\text{tmeda})$ .

$\text{PdMe}_2(\text{tmeda})$  (**2a**) was prepared by reacting 2 equiv of MeLi with  $\text{PdCl}_2(\text{tmeda})$  (**1a**) in diethyl ether at 0 °C (eq 1).



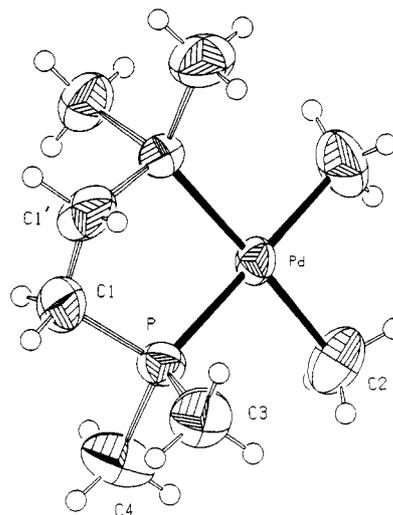
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**Figure 2.** Thermal motion ellipsoid plot of  $\text{PdMe}_2(\text{dmpe})$  (**5**) at the 50% probability level, with the adopted atom numbering.

Washing the reaction mixture with cold water and subsequent evaporation of the separated organic layer gave colorless crystals of pure **2a** in good yield. Similarly, reaction of **1a** with  $\text{CD}_3\text{Li}$  afforded  $\text{Pd}(\text{CD}_3)_2(\text{tmeda})$  (**2b**). Complexes **2a** and **2b** are thermally stable and can be stored for weeks in an inert atmosphere at room temperature without decomposition. They can even be handled in air, although they slowly turn yellow when exposed to the atmosphere for a few days.

An X-ray crystal structure determination<sup>10</sup> of  $\text{PdMe}_2(\text{tmeda})$  (**2a**) (Figure 1) established that it is mononuclear and square-planar coordinated with chelating tmeda and cis-positioned methyl groups. The Pd–Me distances of 2.026 (3) and 2.029 (3) Å are relatively short compared to those in the phosphine complexes  $\text{PdMe}_2(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)$  (2.088 (4) Å; vide infra) and *cis*- $\text{PdMe}_2(\text{PMePh}_2)_2$  (2.090 (3) Å).<sup>11</sup> The Pd–N distances of 2.197 (2) and 2.200 (2) Å are very long (normal range 1.94–2.13 Å).<sup>12</sup> The relatively short Pd–C and long Pd–N bond lengths are consistent with the trans influence of the ligands,<sup>13</sup> which is small for amines and large for  $\sigma$ -bonded carbon ligands. The five-membered Pd–N–C–C–N ring is puckered in the solid state due to the preference of the  $\text{NCH}_2\text{CH}_2\text{N}$  moiety for a staggered conformation.<sup>14</sup> The N–C–C–N torsion angle is 57.1 (3)°, and the N(1)–Pd–N(2) angle is 82.73 (8)°. However, the deviations from 60 and 90° are small and the ring strain is probably minimal.

Variable-temperature <sup>1</sup>H NMR studies in acetone-*d*<sub>6</sub> indicate that  $\text{PdMe}_2(\text{tmeda})$  (**2a**) undergoes conformational changes in solution. At room temperature three sharp singlets are observed at  $\delta$  2.58 (NMe<sub>2</sub>), 2.40 (CH<sub>2</sub>), and –0.34 ppm (PdMe). Lowering the temperature first causes broadening of the CH<sub>2</sub> signal (coalescence temperature  $T_c = 223$  K) and subsequent splitting into a broad AB-type pattern at 193 K ( $\Delta\delta = 0.76$  ppm). The NMe<sub>2</sub> signal also broadens slightly on cooling and appears as two singlets at 183 K ( $T_c = 193$  K;  $\Delta\delta = 0.02$  ppm). The activation energy for both the CH<sub>2</sub> and NMe<sub>2</sub> coalescence phenomena are in mutual agreement ( $\Delta G^\ddagger = 43.0$  kJ/mol). This fluxional behavior corresponds to ring puckering move-

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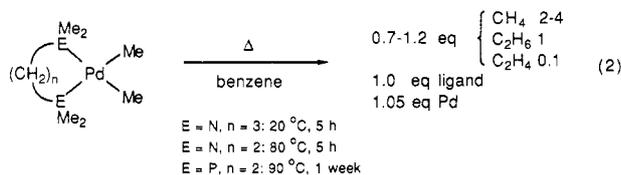
ments that are fast on the NMR time scale at room temperature.

<sup>1</sup>H NMR spectra of **2a** in benzene-*d*<sub>6</sub> containing additional tmeda showed independent signals of **2a** and tmeda at room temperature, and even at 80 °C there was no significant line broadening; i.e., in solution there is no rapid exchange between free and coordinated ligand in **2a**.

In a similar way to the preparation of PdMe<sub>2</sub>(tmeda) we have also prepared PdMe<sub>2</sub>(tmpda) (**2c**) and Pd(CD<sub>3</sub>)<sub>2</sub>(tmpda) (**2d**) [tmpda = *N,N,N',N'*-tetramethyl-1,3-propanediamine] (eq 1), both of which are thermally very unstable. These compounds decompose explosively in the solid state at 40 °C and turn slowly black at room temperature; in solution they decompose rapidly at room temperature. The <sup>1</sup>H NMR spectra of **2c** and **2d** measured at -20 °C in acetone-*d*<sub>6</sub> show only a small amount of free ligand impurity. Remarkably, the exchange of this free tmpda with PdMe<sub>2</sub>(tmpda) (**2c**) is fast on NMR time scale above 0 °C. This contrast in the behavior of **2a** and **2c** with free diamine ligand is discussed later.

**Thermal Decomposition of the Dimethylpalladium Complexes.** The thermal stability of PdMe<sub>2</sub>(tmeda) (**2a**) is remarkable [it can even be sublimed at 60 °C (0.01 mmHg)]. The compound starts slowly turning black at about 70 °C but decomposes explosively only when heated to 125–130 °C. The gases formed during the solid-state thermal decomposition reactions were found to be a mixture of methane and ethane in a 3/1 ratio with varying small amounts of other C<sub>2</sub>-hydrocarbons. [Detection of C<sub>2</sub>H<sub>4</sub> is difficult because it has the same retention time as acetylene. Moreover, its molecular ion *m/z* = 28 also corresponds to that of N<sub>2</sub> and/or ethane fragments. However, in the case of Pd(CD<sub>3</sub>)<sub>2</sub>(tmeda) C<sub>2</sub>D<sub>4</sub> was clearly identified by its molecular ion at *m/z* = 32.]

The formation of methane is unexpected since dimethylpalladium phosphine complexes give rise to the formation of ethane by a 1,1-reductive elimination process,<sup>2a-e</sup> and this prompted us to study the thermal decomposition of **2a** and **2b** in greater detail (eq 2). The results are compiled in Table I.



In all reactions, both in the solid state and in solution, a 3/1 mixture of methane and ethane was formed. Thermolysis in benzene solution gives about 1 mol of gases/mol of starting compound, the palladium precipitates as a metal mirror, and the amine ligand is released quantitatively. This product distribution and stoichiometry points toward an  $\alpha$ -elimination process. Solid-state thermolyses are less well-defined and give about 1.5 mol of gases/mol of starting compound and less than 1 equiv of tmeda.

This formation of methane implies that one PdMe group has abstracted an hydrogen atom from either the solvent, the amine ligand, or the other methyl group ( $\alpha$ -elimination). Experiments using deuterated materials were carried out in order to gain evidence concerning the operative mechanism(s).

Solid-state thermolysis of Pd(CD<sub>3</sub>)<sub>2</sub>(tmeda) (**2b**) gave methane, which was mainly CD<sub>4</sub>, and when PdMe<sub>2</sub>(tmeda) (**2a**) was thermolyzed in C<sub>6</sub>D<sub>6</sub> solution, the methane was mainly CH<sub>4</sub>. However, when **2b** was thermolyzed in C<sub>6</sub>H<sub>6</sub>, a 2/1 mixture of CD<sub>3</sub>H and CD<sub>4</sub> was formed, together with

Table I. Products of the Thermolysis of PdMe<sub>2</sub>(tmeda) (**2a**), Pd(CD<sub>3</sub>)<sub>2</sub>(tmeda) (**2b**), PdMe<sub>2</sub>(tmpda) (**2c**), Pd(CD<sub>3</sub>)<sub>2</sub>(tmpda) (**2d**), and PdMe<sub>2</sub>(dmpe) (**5**)

entry	1	2	3	4	5	6	7	8	9	10
compd	<b>2a</b>	<b>2b</b>	<b>2a</b>	<b>2a</b>	<b>2a</b>	<b>2b</b>	<b>2b</b>	<b>2c</b>	<b>2d</b>	<b>5</b>
solv			C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> D <sub>6</sub>	C <sub>6</sub> D <sub>6</sub>	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> D <sub>6</sub>	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>6</sub>
concn, mol/L			0.08	0.8	0.35	0.2	0.23	0.24	0.12	0.33
conditns	expl	expl	80 °C	80 °C	80 °C	80 °C	90 °C	20 °C	20 °C	90 °C
convn, <sup>a</sup> %	100	100	67	87	87	90	100	100	100	1.05
residue, <sup>b</sup> equiv	1.05	0.50	1.05	1.05	1.05	1.0	0.80	0.96	0.65	
ligand, <sup>c</sup> equiv	0.71	(1.68)	1.0	1.0	1.0	1.0	(1.17)	(1.5)	(0.77)	(0.83)
gases <sup>c</sup> (equiv)	CH <sub>4</sub> (1.20)	CD <sub>4</sub> (0.77) CD <sub>3</sub> H (0.22)	CH <sub>4</sub> (0.59)	CH <sub>4</sub> (0.65) CH <sub>3</sub> D (0.13)	CH <sub>4</sub> (0.81) CH <sub>3</sub> D (0.08)	CD <sub>4</sub> (0.26) CD <sub>3</sub> H (0.53)	CD <sub>4</sub> (0.56) CD <sub>3</sub> H (0.18)	CH <sub>4</sub> (0.9)	CD <sub>4</sub> (0.29) CD <sub>3</sub> H (0.14)	CH <sub>4</sub> (0.67) C <sub>2</sub> H <sub>6</sub> (0.15)
	C <sub>2</sub> H <sub>6</sub> (0.40) [C <sub>2</sub> ] <sup>d</sup> (0.08)	C <sub>2</sub> D <sub>6</sub> (0.32) C <sub>2</sub> D <sub>4</sub> (0.18)	C <sub>2</sub> H <sub>6</sub> (0.18)	C <sub>2</sub> H <sub>6</sub> (0.26) [C <sub>2</sub> ] (0.05)	C <sub>2</sub> H <sub>6</sub> (0.35) [C <sub>2</sub> ] (0.03)	C <sub>2</sub> D <sub>6</sub> (0.34) [C <sub>2</sub> ] (0.03)	C <sub>2</sub> H <sub>6</sub> (0.5) [C <sub>2</sub> ] (0.1)	C <sub>2</sub> H <sub>6</sub> (0.5) [C <sub>2</sub> ] (0.1)	C <sub>2</sub> D <sub>6</sub> (0.30) [C <sub>2</sub> ] (0.04)	C <sub>2</sub> H <sub>6</sub> (0.15) [C <sub>2</sub> ] (0.02)

<sup>a</sup> Estimated by <sup>1</sup>H NMR integration against Me<sub>3</sub>SiOSiMe<sub>3</sub> which was added after reaction. <sup>b</sup> Based on atomic weight of palladium. <sup>c</sup> Mol of gases/mol of decomposed starting material. <sup>d</sup> [C<sub>2</sub>] = C<sub>2</sub>H<sub>4</sub> or C<sub>2</sub>H<sub>2</sub>.

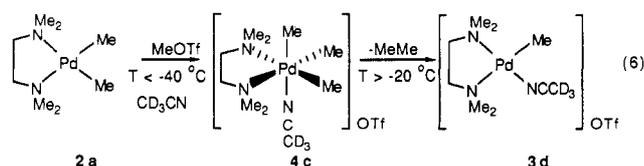


and the axial methyl group resonance occurs at  $\delta$  32.76 ppm. The  $NMe_2$  groups give rise to two signals because the methyl groups above and below the equatorial plane are not equivalent. There is only one signal observed for the  $CH_2CH_2$  unit, and this indicates that **4a** is the *fac* rather than the *mer* isomer. The  $^1H$  NMR spectrum at  $-40^\circ C$  in acetone- $d_6$  is also in accord with this proposed structure. After about 10–15 min **4a** usually crystallized from the solution. The colorless crystals can be isolated but are very unstable. They explode when brought to room temperature and decompose slowly even when stored at  $-30^\circ C$  within a few days into yellow  $PdIME(tmeda)$  (**3a**). Decomposition in solution starts already at  $-20^\circ C$ , and at  $0^\circ C$  decomposition into ethane and **3a** takes place in a few minutes. The isolated complex **4a**, redissolved in  $CDCl_3$  at  $-40^\circ C$ , has essentially the same  $^1H$  and  $^{13}C$  NMR spectra as the in situ prepared **4a** in acetone- $d_6$ .

The reaction of **2a** with methyl bromide to give *fac*- $PdBrMe_3(tmeda)$  (**4b**) (eq 5) is completed after 15 min at  $0^\circ C$  and is thus much slower than the corresponding reaction with methyl iodide. Compound **4b** did not crystallize from the solution like **4a**, but evaporation of the solvent below  $0^\circ C$  yielded **4b** as a white solid. It is stable at room temperature for a short time (ca. 15 min) and explodes when brought to  $40^\circ C$ . In solution as well in the solid state **4b** decomposes cleanly at room temperature into  $PdBrMe(tmeda)$  (**3b**) and ethane.

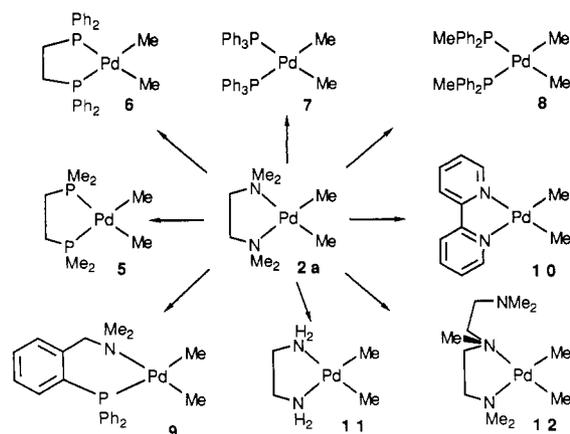
The regioselectivity of the oxidative addition and the configurational stability of **4a** were also studied by reacting **2a** with  $CD_3I$  and **2b** with  $CH_3I$ . These reactions were carried out at  $-40^\circ C$  in acetone- $d_6$  and monitored by  $^1H$  NMR spectroscopy. In both cases the ratio of the signals of the *equatorial* to *axial*  $PdMe$  groups in the palladium(IV) adduct was 2/1, proving that methyl groups scrambling has occurred. When the reaction of **2a** with  $CD_3I$  was carried out at room temperature, the intensity of the  $PdMe$  signal of the product  $PdI(CH_3/CD_3)(tmeda)$  was diminished by a factor 2/3 and the ethane that was liberated had a mass spectrum consistent with a  $CH_3-CH_3/CH_3CD_3$  ratio of 1/2. No  $CD_3CD_3$  was detected. This latter result is clear evidence that the formation of ethane occurs in an intramolecular process.

Reaction of **2a** with  $MeI$  in acetonitrile- $d_6$  at  $-40^\circ C$  gives a complex in solution whose  $^1H$  and  $^{13}C$  NMR spectra are significantly different from those of **4a** obtained in  $CDCl_3$  or acetone- $d_6$  (Table II). The differences in chemical shifts suggest that in acetonitrile cationic complexes of the type *fac*- $[PdMe_3(tmeda)(CD_3CN)]^+[I]^-$  are formed. Further evidence for such cationic complexes was obtained from the reaction of **2a** with methyl triflate ( $MeOTf = MeOSO_2CF_3$ ) in  $CD_3CN$  at  $-40^\circ C$ . The  $^1H$  and  $^{13}C$  NMR spectra of this solution are almost the same as those obtained from the product of the reaction of **2a** with  $MeI$  in  $CD_3CN$  and are thus consistent with formation of *fac*- $[PdMe_3(tmeda)(CD_3CN)]^+[OTf]^-$  (**4c**) (eq 6).



The  $PdMe$  signals in the  $^1H$  NMR spectrum of  $[PdMe_3(tmeda)(CD_3CN)]^+$ , obtained from the reaction of either  $MeI$  or  $MeOTf$  with **2a**, coalesce at  $-20^\circ C$ , (corresponding to an activation energy ( $\Delta G^\ddagger$ ) of  $53 \text{ kJ mol}^{-1}$ ). Above  $-20^\circ C$ , **4c** eliminates ethane with the formation of  $[PdMe(CD_3CN)(tmeda)]^+[OTf]^-$  (**3d**), which can be isolated as a white solid. It is unstable in the solid state at room

### Scheme I. Dimethylpalladium Complexes Derived from **2a** by Ligand Exchange Reactions



temperature but can be stored without change at  $-30^\circ C$  for several weeks. Isolated  $[PdMe(MeCN)(tmeda)]^+[OTf]^-$  in  $CD_3CN$  showed the presence of 1 equiv of acetonitrile by  $^1H$  NMR integration.

When the reaction of **2a** with  $MeOTf$  was carried out in acetone- $d_6$ , which is a weakly coordinating solvent, a cationic palladium(IV) species, most probably  $[PdMe_3(tmeda)(acetone-d_6)]^+[OTf]^-$ , was obtained. In the  $^1H$  NMR spectra of this species between  $-40$  and  $-60^\circ C$  the  $PdMe$  groups were in fast exchange. Elimination of ethane occurred between  $-40$  and  $-20^\circ C$ . The resulting palladium(II) species, assumed to be  $[PdMe(tmeda)(acetone-d_6)]^+[OTf]^-$ , decomposed at  $20^\circ C$  with formation of metallic palladium.

**Synthetic Utility of Organopalladium  $N,N,N',N'$ -tetramethylethanediamine Complexes.** Dimethyl( $N,N,N',N'$ -tetramethylethanediamine)palladium (**2a**) proved to be an excellent starting material for the synthesis of a large variety of known dimethylpalladium complexes (see Scheme I). Mono(phosphines) and bis(phosphines) and also bpy smoothly replace the *tmeda* ligand, when added in a stoichiometric ratio to a solution of **2a** in benzene. Complexes **5–10** were identified by comparing the  $^1H$  NMR spectra with the literature data.

Replacement of *tmeda* by ethanediamine was performed by dissolving **2a** in ethanediamine followed by evaporation of the solution to dryness. The new complex, however, was insoluble in common organic solvents, like its platinum analogue,<sup>17</sup> and was identified by elemental analysis (C, H, N). Similarly, dissolution of **2a** in  $N,N,N',N'',N''$ -pentamethyldiethylenetriamine (*pmdeta*) gave after removal of the excess of *pmdeta*, the complex  $PdMe_2(pmdeta)$  (**12**) as a liquid that crystallized from cold pentane. Satisfactory elemental analysis (C, H, N) were obtained for this complex. At  $20^\circ C$  and lower the  $^1H$  and  $^{13}C$  NMR spectra of **12** in benzene- $d_6$  and acetone- $d_6$  show clearly that one amine site is not coordinated. In the  $^1H$  NMR spectra, the signals of the  $NMe_2$  groups coalesce at  $47^\circ C$  and those of the  $PdMe$  groups at  $57^\circ C$ . The energies of activation were calculated, and these differed by only  $0.5 \text{ kJ/mol}$  ( $\Delta G^\ddagger(NMe_2) = 77.5 \text{ kJ/mol}$  and  $\Delta G^\ddagger(PdMe) = 80.0 \text{ kJ/mol}$ ).

(16) (a) Byers, P. K.; Cauty, A. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* 1986, 1722. (b) Byers, P. K.; Cauty, A. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* 1987, 1093. (c) Byers, P. K.; Cauty, A. J. *J. Chem. Soc., Chem. Commun.* 1988, 939. (d) Byers, P. K.; Cauty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D. *Organometallics* 1988, 7, 1363–1367.

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

**Structure and Properties of PdMe<sub>2</sub>(dmpe).** PdMe<sub>2</sub>(dmpe) (**5**) was obtained from PdMe<sub>2</sub>(tmeda) (vide supra) as colorless crystals. The monoclinic unit cell contains four discrete molecules with 2-fold axial symmetry. The molecular structure resembles, as expected, that of PdMe<sub>2</sub>(tmeda).

The palladium-carbon bond length of 2.087 (4) Å is in close agreement with that in the only other reported dimethylpalladium bis(phosphine) complex,<sup>11</sup> *cis*-PdMe<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub> (2.089 (3) and 2.090 (3) Å) but is significantly longer than that in PdMe<sub>2</sub>(tmeda) (2.026 (3) and 2.029 (3) Å); this is indicative of the larger trans influence of the diphosphine ligand. The palladium-phosphorus bond length is 2.274 (1) Å, which is slightly shorter than those in *cis*-PdMe<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub> (2.321 (1) and 2.326 (1) Å). The dmpe ligand has the same type of puckering as the tmeda ligand in PdMe<sub>2</sub>(tmeda). The P-C-C-P torsion angle is 48.91 (4)°, and the P-Pd-P angle is 85.33 (3)°.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5** show coupling with the two phosphorus nuclei. These coupling patterns are very clear in the <sup>13</sup>C NMR spectrum. The PMe<sub>2</sub> carbon atoms in **5** show a six-line pattern of the A part of an AXX' spin system, but the CH<sub>2</sub>CH<sub>2</sub> group appears as a deceptively simple triplet and the PdMe carbon atoms as a double doublet.

PdMe<sub>2</sub>(dmpe) (**5**) reacts, in contrast to PdMe<sub>2</sub>(tmeda), only slowly with MeI to give PdIMe(dmpe) (**13**) in quantitative yield. The reaction takes about 2 h, and 0.8 equiv of only ethane was detected.

### Discussion

**Palladium-Amine versus Palladium-Phosphine Coordination.** Oxidative addition to palladium(0)<sup>2a</sup> and reductive elimination from palladium(II)<sup>3,4</sup> have been the subject of many studies, primarily because of their relevance to carbon-carbon bond formation processes. Such studies deal mainly with palladium complexes containing tertiary phosphine ligands. The two main differences between phosphines and amines are, first, that the lone pair on phosphorus is located in a larger and more diffuse sp<sup>3</sup> orbital, which can overlap better with transition metals, and, second, that phosphorus has empty 3d orbitals of relatively low energy that can participate in back-donation from the transition metal. This metal to ligand back-donation is thought to be essential for the formation of palladium(0) complexes,<sup>8b,c</sup> though in palladium(II) complexes it is not an essential component in metal-ligand bond formation.<sup>8b,c</sup> Indeed we found that the aliphatic amine site in P,N-bidentate ligands (cf. the ligand present in compound **9**; Scheme I) does not coordinate to palladium(0) but coordinates quite well in organometallic complexes of palladium(II),<sup>9</sup> and it was this finding that encouraged us to prepare organopalladium complexes with aliphatic diamines.<sup>10</sup>

Because all monophosphines and bis(phosphines) displace the tmeda moiety in these organopalladium(II) *N,N,N',N'*-tetramethylethanediamine complexes, we conclude that the palladium-nitrogen coordination is, as expected, thermodynamically weaker than palladium-phosphorus coordination. This relative weak coordination is most probably due to the bad overlap between the comparatively small sp<sup>3</sup> hybrid orbital of the amine and the more diffuse sp<sup>2</sup>d orbital of palladium(II).

The Pd-N distances of 2.197 (2) and 2.200 (2) Å in PdMe<sub>2</sub>(tmeda) and 2.220 (6) Å in PdBrMe[o-(diphenylphosphino)-*N,N*-dimethylbenzylamine]<sup>9</sup> are the longest Pd-N bond lengths reported so far. In both structures the methyl groups are trans to an amine function, and it is this that undoubtedly causes the long Pd-N bonds due to the

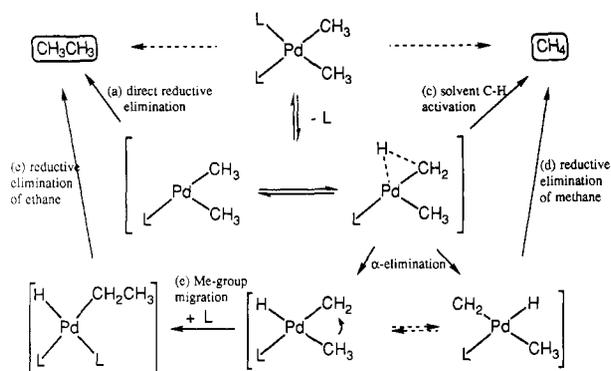
large trans influence of carbon.<sup>13</sup> Reversely, because the "hard" amine ligands have a relatively inefficient overlap with the sp<sup>2</sup>d hybrid orbital of palladium and hence a small trans influence, the palladium-carbon bonds in PdMe<sub>2</sub>(tmeda) are shorter than those in PdMe<sub>2</sub>(dmpe) and PdMe<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>. In spite of the presence of a trans organic ligand the Pd-N bond in PdBrMe[o-(diphenylphosphino)-*N,N*-dimethylbenzylamine] does not show dissociation or displacement on the NMR time scale.<sup>9</sup> The same is true for PdMe<sub>2</sub>(tmeda) (**2a**) for which there is no evidence for rapid exchange between free and ligated tmeda. However, PdMe<sub>2</sub>(tmpda) (**2c**) does show rapid intermolecular exchange above 0 °C between free and bonded ligands (vide infra). In the tridentate amine complex PdMe<sub>2</sub>(pmdeta) (**12**) there is above 20 °C an intramolecular exchange of the NMe<sub>2</sub> groups and also of the PdMe groups. Remarkably, the activation energies of these two exchange phenomena are almost the same and thus are likely to have a common basis. We have, however, insufficient evidence to ascertain whether this is a dissociative or an associative process.

**Thermal Decomposition of the Dimethylpalladium Complexes.** The high thermal stability of the complex **2a** and its behavior on thermolysis are noteworthy. In particular the formation of mainly methane on thermolysis of **2a** indicates that reductive elimination is not the main decomposition route. Formation of methane and ethane was also found for the phosphorus analogue of **2a**, PdMe<sub>2</sub>(dmpe) (**5**). [Very recently the synthesis of NiMe<sub>2</sub>(tmeda) was reported.<sup>28</sup> This compound is, like PdMe<sub>2</sub>(tmeda), thermally very stable (decomp 79 °C) and gives after thermolysis methane (1.04/Ni) and a minor amount of ethane (0.13/Ni).] This behavior contrasts with that of dimethylbis(phosphine)palladium complexes that have been shown to reductively eliminate ethane with prior dissociation of a ligand.<sup>3a-e</sup> Theoretical calculations have shown that reductive elimination may take place directly from a four-coordinate complex and the presence of weak σ-donors trans to the leaving groups was thought to decrease the barrier for this process. However, after dissociation of a ligand, reductive elimination can take place more favorably from a three-coordinate "T"-shaped intermediate.<sup>4</sup>

Traces of methane have been found in the experimental studies on reductive elimination from dimethylpalladium complexes, but only the thermolysis of PdMe<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub> in the presence of a large excess of PMePh<sub>2</sub> yielded mainly methane. Since the dissociative reductive elimination pathway was blocked this formation of methane was ascribed to hydrogen activation from the ligand.<sup>3a</sup> However, PdMe<sub>2</sub>(dppe) [dppe = 1,2-bis(diphenylphosphino)ethane] was reported to eliminate ethane only, despite the presence of the chelating dppe ligand.<sup>3c</sup>

Although there are large differences in the decomposition temperature between the dimethylpalladium complexes with dmpe (**5**), tmeda (**2a,b**), and tmpda (**2c,d**), the product distribution remains essentially the same. These differences in stability are in agreement with (a) the easier dissociation of the six-membered chelate ring of tmpda relative to that of the five-membered chelate ring of tmeda and (b) a higher stability of the dmpe chelate ring compared with that of tmeda, due to the stronger palladium-phosphorus bond. Hence, we believe that the thermal decomposition of **2a-d** and **5** is preceded by dissociation of a ligand arm. This feature is in accord with the general observation that ligand dissociation, leaving an empty coordination site on the metal, precedes an α, β, or reductive elimination process.<sup>18</sup> There are then five possible

## Scheme II. Pathways for Thermal Decomposition of Dimethylpalladium Species



(b) formation of methane and ethane is also possible from methyl-radicals caused by homolytic bond cleavage

pathways (Scheme II): (a) direct reductive elimination of ethane, (b) Pd–Me homolytic bond cleavage, (c) solvent C–H activation and formation of methane, (d)  $\alpha$ -elimination, followed by reductive elimination of methane, and (e)  $\alpha$ -elimination, followed by migration of the methyl group to give a hydrido ethyl species, which eliminates ethane. The latter route has been suggested for the reductive elimination from palladium(IV) (*vide infra*).<sup>16d</sup>

The formation of methane on thermolysis of PdMe<sub>2</sub>(tmeda) implies that a methyl group on palladium removes a hydrogen from somewhere. Furthermore, the thermolysis reactions in solution leave the diamine ligand unchanged and the amount of gases formed is consistent with only one of the methyl groups ending up as methane. The various deuterium cross-over experiments (Table I, entries 2, 4, 5, 7, and 8) show that the fourth hydrogen of the methane formed, generally originates for the major part from the other methyl group on palladium and for a minor part from the solvent. The most striking feature in the deuterium crossover reactions is the large difference in the ratio CH<sub>3</sub>D/CH<sub>4</sub> and CD<sub>3</sub>H/CD<sub>4</sub> in the formation of methane from PdMe<sub>2</sub>(tmeda) in C<sub>6</sub>D<sub>6</sub> and from Pd(CD<sub>3</sub>)<sub>2</sub>(tmeda) in C<sub>6</sub>H<sub>6</sub> (Table I; entries 4–6).

Let us examine the five possibilities for the dimethylpalladium diamine complexes: the direct reductive elimination (a) can be the explanation for the formation of ethane but is not necessarily the only explanation. The occurrence of a homolytic Pd–Me bond cleavage (b) can explain the formation of both methane and ethane and cannot be excluded for any of the decomposition reactions. However, it is an unlikely process because it cannot explain the difference between the decomposition temperature of the tmpda and the tmeda complexes.

We believe that the best description for thermolysis of these dimethylpalladium diamine complexes is a competition between a solvent C–H activation (c) or a PdCH<sub>3</sub> activation ( $\alpha$ -elimination) (d) on the empty coordination site after dissociation of an amine arm. The difference between the amount of CH<sub>3</sub>D from PdMe<sub>2</sub>(tmeda) in C<sub>6</sub>D<sub>6</sub> and CD<sub>3</sub>H from Pd(CD<sub>3</sub>)<sub>2</sub>(tmeda) in C<sub>6</sub>H<sub>6</sub> can then be explained by an isotope effect in the C–D bond cleavage during an  $\alpha$ -elimination. In the case of a deuterated dimethylpalladium compound a benzene C–H bond will be activated more readily and give rise to the formation of more CD<sub>3</sub>H.

The alternative pathway to a direct reductive elimination (a) that can explain the formation of ethane is an  $\alpha$ -elimination step followed by a methyl group shift to the "carbene" moiety (e).<sup>18a</sup> Elimination from the resulting ethyl hydrido species will give ethane, and  $\beta$ -elimination may be responsible for the formation of traces of ethene.

**Reaction of PdMe<sub>2</sub>(tmeda) with Electrophiles.** Reductive elimination from palladium(II) has been found to be accelerated by the addition of electrophiles.<sup>3c-e</sup> This feature is ascribed to an oxidative addition to palladium(II), forming a palladium(IV) intermediate, followed by a reductive elimination. However, only recently have examples of relatively stable palladium(IV) compounds been found in which aromatic di- and triamine ligands are present.<sup>16</sup>

During the preparation of this manuscript a paper appeared<sup>16d</sup> on the reactivity and mechanism in oxidative addition of MeI to palladium(II) and reductive elimination from palladium(IV) based on PdMe<sub>2</sub>(bpy). The chemical reactivity of PdMe<sub>2</sub>(tmeda) (2a) resembles PdMe<sub>2</sub>(bpy) in many aspects. For instance, PdMe<sub>2</sub>(tmeda) is also very reaction toward MeI and forms already at temperatures lower than –40 °C a palladium(IV) compound, PdIME<sub>3</sub>(tmeda). In this complex the broadening of the <sup>1</sup>H NMR signals of the PdMe groups and the scrambling with CD<sub>3</sub>I is similar to that observed in PdIME<sub>3</sub>(bpy).

As has been shown for the platinum complex PtMe<sub>2</sub>(bpy)<sup>19</sup> oxidative addition of MeI at low temperature in CD<sub>3</sub>CN as solvent follows a S<sub>N</sub>2 mechanism involving [PtMe<sub>3</sub>(CD<sub>3</sub>CN)(bpy)]<sup>+</sup> as intermediate, which then reorganizes to PtIME<sub>3</sub>(bpy). Reaction of PdMe<sub>2</sub>(bpy) with MeI affords an equilibrium mixture of [PdMe<sub>3</sub>(CD<sub>3</sub>CN)(bpy)]<sup>+</sup> and PdIME<sub>3</sub>(bpy). However, reaction of PdMe<sub>2</sub>(tmeda) with either MeI or MeOTf in acetonitrile at low temperature only produces cationic complexes [PdMe<sub>3</sub>(tmeda)(CH<sub>3</sub>CN)]<sup>+</sup>. The formation of such cationic complexes is indicative of steric interference exerted by the axial NMe groups that prevents recoordination of the iodide ion to form the neutral complexes PdIME<sub>3</sub>(tmeda) (4a). Indeed a space-filling model of 4a shows that there is a large steric interference between the halogen and two of the four NMe groups.

Reaction of PdMe<sub>2</sub>(tmeda) with MeOTf in acetone-*d*<sub>6</sub> gave immediately a very labile cationic complex, probably [PdMe<sub>3</sub>(acetone-*d*<sub>6</sub>)(tmeda)]<sup>+</sup>, in which the equatorial and axial methyl groups are exchanging even at –60 °C. This ready scrambling at low temperature is in accord with the occurrence of a five-coordinate transition state,<sup>16d</sup> acetone as well as OTf<sup>–</sup> are very weak ligands for palladium.

In CD<sub>3</sub>CN, which is a much better ligand, this scrambling was less rapid and coalescence of the PdMe signals was found at –20 °C. Hence, the energy of activation ( $\Delta G^\ddagger = 53$  kJ/mol) that was calculated for this process must be associated with the dissociation of an acetonitrile ligand.

The <sup>1</sup>H NMR spectrum of PdIME<sub>3</sub>(tmeda) (4a), compared with that of PdBrMe<sub>3</sub>(tmeda) (4b), shows a significant line broadening of all signals that increases with increasing temperature. The only significant differences in the <sup>13</sup>C spectra of 4b and 4a are the shifts of the axial PdMe and one of the NMe signals; the  $\Delta\delta$  is 6.9 ppm for the axial PdMe groups, 2.4 ppm for one of the NMe peaks, and less than 0.5 ppm for the other signals. The large trans influence of the halogen on the <sup>13</sup>C chemical shift of the axial PdMe group is noteworthy. These differences in the spectra of 4a and 4b must have their origin in the size of the axial halide. Furthermore, the fact that PdIME<sub>3</sub>(bpy)

(18) (a) Thorn, D. L. *Organometallics* 1986, 5, 1897–1903. (b) Bennett, M. A.; Crisp, G. T. *Organometallics* 1986, 5, 1792–1800. (c) Bennett, M. A.; Crisp, G. T. *Organometallics* 1986, 5, 1800–1806. (d) Carr, N.; Dunne, B. J.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* 1988, 926–928.

(19) Crespo, M.; Puddephatt, R. J. *Organometallics* 1987, 6, 2548–2550.

is more stable than  $\text{PdBrMe}_3(\text{tmeda})$  (**4b**), which is more stable than  $\text{PdIME}_3(\text{tmeda})$  (**4a**) also suggests that the steric interference of the halide ion when coordinated to palladium is the limiting factor in the stability of the trimethylpalladium(IV) diamine complexes.

From the current study we conclude that the reductive elimination from the palladium(IV) complexes  $\text{PdXMe}_3(\text{tmeda})$  (**4a-c**) ( $\text{X} = \text{halide or solvent}$ ) is preceded by a ligand dissociation which occurs more easily in the order:  $\text{X} = \text{acetone} > \text{acetonitrile} > \text{iodide} > \text{bromide}$ . Accordingly, reductive elimination occurs most probably from a cationic, five-coordinate palladium(IV) species. This has also been proposed for the  $\text{PdXMe}_3(\text{bpy})$  system.<sup>16d</sup> It was suggested that an  $\alpha$ -elimination, followed by methylene insertion (cf. Scheme II, route e), could be an alternative route for the direct reductive elimination from palladium(IV). But this is very unlikely, since we found no traces of methane in the thermal decomposition of the trimethylpalladium(IV) $N,N,N',N'$ -tetramethylethanediamine complexes.

The much greater rate of reaction of MeI with  $\text{PdMe}_2(\text{tmeda})$  (**2a**) than with  $\text{PdMe}_2(\text{dmpe})$  (**5**) (see also ref 2a-c) leads us to the conclusion that the presence of two purely  $\sigma$ -donating amines and two covalent PdMe bonds render the palladium center more nucleophilic. This reasoning also explains the high reactivity of  $\text{PdMe}_2(\text{bpy})$  toward MeI. It remains an open question as to whether the diamine really stabilizes the Pd(IV) oxidation state or whether it makes palladium(II) more reactive.

**Ligand-Exchange Reactions.** The ligand exchange reactions using  $\text{PdMe}_2(\text{tmeda})$  (**2a**) provide a new and very convenient synthetic route to a large variety of new and known dimethylpalladium complexes. Such exchange reactions were already shown by Diversi et al. for  $\text{Pd}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{tmeda})$ .<sup>4a</sup> Recently a more general method for preparing organopalladium complexes by ligand exchange of  $[\text{PdMe}_2(\text{pyridazine})_n]$  and  $[\text{PdMe}(\text{SMe}_2)(\mu\text{-I})_2]$  was reported by Canty et al.<sup>20</sup> However,  $\text{PdMe}_2(\text{tmeda})$  has the advantage that it is stable at room temperature and is in our opinion much more versatile because it can be easily transformed to air-stable compounds of the type  $\text{PdXR}(\text{tmeda})$  (see also ref 10, 15) which can obviously be converted by similar ligand exchange reactions to a large variety of complexes of the general formula  $\text{PdXRL}_2$ .

## Experimental Section

**General Data.** All operations were conducted in 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. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AC 200 spectrometer, and the data are compiled in Tables II and III. IR spectra were recorded on a Perkin-Elmer 457 spectrometer. Elemental analyses were performed by the Institute of Applied Chemistry (TNO), Zeist, The Netherlands.

**Warning.** Complexes **2a-d** and **4a,b** are potentially explosive. Due care should be taken with the use and handling of these materials, especially when amounts greater than 1 g are prepared.

**$\text{PdCl}_2(\text{tmeda})$  (**1a**).**  $\text{PdCl}_2$  (1.76 g, 10 mmol) was dissolved in acetonitrile (50 mL) at reflux. After the solution was cooled, to 20 °C,  $N,N,N',N'$ -tetramethylethanediamine (2 mL, 15 mmol) was added and the yellow precipitate of **1a** that formed was filtered off, washed with diethyl ether, and dried in vacuo: yield 2.5 g (90%); mp 225–230 °C dec. Anal. Calcd for  $\text{C}_8\text{H}_{16}\text{Cl}_2\text{N}_2\text{Pd}$ : C, 24.55; H, 5.49; N, 9.54. Found: C, 24.60; H, 5.42; N, 9.59.

**$\text{PdCl}_2(\text{tmpda})$  (**1b**).** This compound was prepared by using a procedure similar to that used for **1a**; yield 90%. Anal. Calcd for  $\text{C}_7\text{H}_{18}\text{Cl}_2\text{N}_2\text{Pd}$ : C, 27.34; H, 5.90; N, 9.11. Found: C, 27.29; H, 5.96; N, 9.24.

**$\text{PdMe}_2(\text{tmeda})$  (**2a**).**  $\text{PdCl}_2(\text{tmeda})$  (2.37 g, 8 mmol) was suspended in diethyl ether (30 mL). The stirred suspension was cooled to -30 °C and treated with an diethyl ether solution of salt-free MeLi (12 mL of a 1.44 M solution, 17 mmol). With continued stirring the mixture was allowed to warm slowly to 0 °C and was kept for 1 h at that temperature. A grayish white suspension formed. Then, ice-cold water (10 mL) was slowly added with stirring until a clear diethyl ether layer and a black water layer had formed. The organic layer was separated, dried over  $\text{Na}_2\text{SO}_4$ , and evaporated in vacuo to give colorless crystals of **2a**: yields varied between 1.20 and 1.70 g (60–85%); mp 125–130 °C dec expl. IR (KBr): 448, 477  $\text{cm}^{-1}$  [ $\nu(\text{PdMe})$ ]. Anal. Calcd for  $\text{C}_8\text{H}_{22}\text{N}_2\text{Pd}$ : C, 38.03; H, 8.78; N, 11.09. Found: C, 38.02; H, 8.59; N, 11.02. <sup>1</sup>H NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ) 303 K,  $\delta$  -0.34 (s, 3 H, PdMe), 2.40 (s, 6 H, NMe<sub>2</sub>), 2.57 (s, 2 H, CH<sub>2</sub>); 183 K,  $\delta$  -0.36 (s, PdMe), 2.20 (dd,  $J(\text{H,H}) = 10$  Hz, CHH-CHH), 2.33 (s, NMeMe), 2.34 (s, NMeMe), 2.96 (dd,  $J(\text{H,H}) = 10$  Hz, CHH-CHH).

**$\text{Pd}(\text{CD}_3)_2(\text{tmeda})$  (**2b**).** This compound was prepared by using a procedure similar to that used for **2a**: yield 53%; mp 125–130 °C dec expl. <sup>1</sup>H NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  2.41 (s, 6 H, NMe<sub>2</sub>), 2.57 (s, 2 H, CH<sub>2</sub>).

**$\text{PdMe}_2(\text{tmpda})$  (**2c**).** This compound was prepared by using a procedure similar to that used for **2a** with the reaction temperature kept at -20 °C. Washing with water was carried out very rapidly at 0 °C, and the mixture was then recooled to -20 °C. The clear diethyl ether solution was separated by decantation and evaporated in vacuo at -20 °C (in order to avoid decomposition) to afford **2c** as a gray-white powder, yield 47%. **2c** is very unstable and should be handled at temperatures lower than 0 °C; mp 40 °C dec. expl. <sup>1</sup>H NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  -0.29 (s, 3 H, PdMe), 1.73 (m, 1 H, CH<sub>2</sub>), 2.30 (s, 6 H, NMe<sub>2</sub>), 2.51 (t, 2 H, CH<sub>2</sub>N).

**$\text{Pd}(\text{CD}_3)_2(\text{tmpda})$  (**2d**).** The preparation of this compound was carried out by using a procedure similar to that used for **2c**: yield 17%; mp 40 °C dec. expl. <sup>1</sup>H NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta$  1.73 (m, 1 H, CH<sub>2</sub>), 2.29 (s, 6 H, NMe<sub>2</sub>), 2.50 (t, 2 H, CH<sub>2</sub>N).

**Thermal Decomposition of Dimethylpalladium Complexes **2a-d** and **5**.** The thermolysis reactions were carried out in a homemade system. This comprised a single-necked thick-walled glass vessel of 50 or 100 mL capacity that could be accessed through a single high-vacuum Teflon stopcock with a right-angle side arm. Onto this side arm was blown a small (ca. 5 mL) glass gas sampling cell having two ports, one being a gas-tight septum and the second being a groundglass two-way tap that could be connected to either a N<sub>2</sub>-filled gas burette or a combined vacuum/nitrogen line as required. For solid samples and solutions of **2a,b** and **5** two slightly different procedures were followed.

In order to study the thermal decomposition of solids the vessel was charged with preweighted sample (150–250 mg) and the volume of the reaction vessel (held in a water bath of fixed temperature ( $\pm 0.2$  °C)) was determined by evacuation and refilling with nitrogen from the gas burette. After reevacuating the vessel ( $10^{-2}$  Torr) the Teflon stopcock was closed and the vessel heated with an open flame until the thermal decomposition reaction occurs; i.e., the solid explodes and turns black. The vessel was then replaced in the water bath and nitrogen from the gas burette readmitted to atmospheric pressure.

For solutions the vessel was first charged with a preweighted solid sample (150–250 mg), the benzene solvent added (2–5 mL), and the vessel then evacuated until the benzene had boiled for a few seconds. The effective vessel volume was then found by placing the vessel in the water bath and admitting nitrogen from the gas burette; the vessel was occasionally swirled to ensure equilibrium between the solution and its vapor. For the thermolysis reaction the vessel was reevacuated until the solution boiled for a few seconds and the Teflon stopcock then closed. After thermolysis (under the conditions specified in Table I) the vessel was replaced in the water bath and nitrogen was readmitted from the gas burette with occasional swirling of the vessel.

In both cases the difference between the vessel volume and the N<sub>2</sub> gas refill volume was regarded as the total amount of gases

(20) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* 1987, 336, C55–C60.

formed. After the volume measurement, the groundglass tap was closed, and, after at least 30 min, gas samples were taken through the septum and analyzed by means of GLC (Poropack column) and/or mass spectroscopy (MS).

In the case of the solid-state reactions, after sampling of the gases, benzene (3 mL) was added. The amounts of  $PdMe_2(tmeda)$  and  $tmeda$  in the solution were determined by  $^1H$  NMR integration against  $Me_3SiOSiMe_3$ , which was added as internal standard. The vessel was then emptied of solvent, washed with acetone, dried in vacuo, and reweighed; the weight increase was taken to be the amount of palladium formed. The reaction conditions and results are compiled in Table I.

Because the compounds  $PdMe_2(tmpda)$  (2c) and  $Pd(CD_3)_2(tmpda)$  (2d) are very unstable, their solution thermolysis reactions were carried out in a similar way in a nitrogen atmosphere in the Schlenk tube in which they were isolated.

**Reaction of 2a with Hydrochloric Acid.** A Schlenk tube was charged with  $PdMe_2(tmeda)$  (0.13 g, 0.51 mmol), and toluene (5 mL) was added. The vessel was placed in a water bath of 20 °C and connected to a gas burette. Concentrated hydrochloric acid (0.3 mL, 6 mmol) was then added to the magnetically stirred solution. During the next 5 min 24.3 mL of gas evolved (1.0 mmol), which was analyzed as methane by GLC. After the reaction the toluene was decanted from the yellow precipitate of  $PdCl_2(tmeda)$  which was washed with acetone (10 mL) and dried in vacuo; yield 0.14 g (90%).

**Reaction of 2a with Hydrogen.** The reaction vessel for gas analyses was charged with  $PdMe_2(tmeda)$  (180 mg, 0.68 mmol) and benzene (5 mL) and then evacuated until the benzene had boiled for a few seconds. The vessel was then filled with hydrogen gas to atmospheric pressure. The solution slowly turned black. After 6 h, 9.0 mL of gas had evolved, and after 24 h a further 5.6 mL of gas had been formed to give a total amount of 14.6 mL (0.61 mmol). Only methane and no ethane were detected by GLC. The remaining solution contained 0.70 mmol of  $tmeda$  ( $^1H$  NMR) and a solid residue (70 mg) that corresponds to 0.66 mmol of palladium. The experiment was repeated with deuterium instead of hydrogen, and the methane formed was found by mass spectrometry to be pure  $CH_3D$ .

**$PdIme(tmeda)$  (3a).** To  $PdMe_2(tmeda)$  (0.25 g; 0.99 mmol) dissolved in benzene (5 mL) was added MeI (0.2 mL, slight excess). The mixture turned yellow immediately with gas evolution [in separate experiments this was found to be ethane (25 mL, 1.0 mmol)], and yellow crystals soon precipitated. After 15 min the solution was decanted from these crystals of 3a which were dried in vacuo: yield 0.31 g (85%); mp 145–290 °C dec. Anal. Calcd for  $C_7H_{10}IN_2Pd$ : C, 23.06; H, 5.25; N, 7.68. Found: C, 23.09; H, 5.14; N, 7.45.

**$PdBrMe(tmeda)$  (3b).**  $PdMe_2(tmeda)$  (0.13 g, 0.51 mmol) was dissolved in benzene (5 mL), a slow stream of MeBr gas was introduced for ca. 1 min, and the solution quickly turned yellow. The yellow product 3b, which crystallized from solution during the next 0.5 h, was collected by decantation and dried in vacuo: yield 0.17 g (85%); mp 145–200 °C dec. IR (KBr): 460  $cm^{-1}$  [ $\nu(PdMe)$ ]. Anal. Calcd for  $C_7H_{10}BrN_2Pd$ : C, 26.48; H, 6.03; N, 8.82. Found: C, 26.40; H, 6.10; N, 8.68.

**$PdClMe(tmeda)$  (3c).**  $PdMe_2(tmeda)$  (0.13 g, 0.51 mmol) was dissolved in benzene (5 mL), and a slow stream of MeCl gas was introduced for ca. 1 min. After being left standing overnight, the solution afforded light yellow crystals, which were collected by decantation and dried in vacuo; yield 0.08 g (50%). The  $^1H$  and  $^{13}C$  NMR spectra of 3c showed it to be contaminated with ca. 10% of 3b (see text); mp 145–200 °C dec. Anal. Calcd for  $C_7H_{10}ClN_2Pd$ : C, 30.79; H, 7.01; N, 10.26. Found: C, 30.54; H, 6.99; N, 10.26.

**$[PdMe(CH_3CN)(tmeda)]OTf$  (3e).**  $PdMe_2(tmeda)$  (0.13 g, 0.50 mmol) was dissolved in acetonitrile (5 mL) and the solution stirred well while MeOTf (0.075 g, 0.48 mmol) was added. During the next 10 min 9.5 mL (0.40 mmol) of a gas evolved that was identified as ethane by GLC. The remaining colorless solution was evaporated to afford a gray oil. Pentane (5 mL) was added, and scratching for some minutes induced crystallization. The pentane was decanted and the gray-white solid dried in vacuo; yield 0.18 g (80%). The compound turns slowly black when kept at room temperature: mp 60–62 °C.  $^1H$  NMR ( $CD_3CN$ , 200 MHz):  $\delta$  0.45 (s, 3 H, PdMe), 1.97 (s, 3 H,  $CH_3CN$ ), 2.55 (s, 6 H,

$NMe_2$ ), 2.60 (s, 6 H,  $N'Me_2$ ), 2.68 (m, AA'BB', 4 H,  $CH_2$ ).  $^{13}C$  NMR ( $CD_3CN$ , 50 MHz):  $\delta$  -1.34 (PdMe), 48.26, 51.15 ( $NMe_2$ ), 57.91, 64.52 ( $CH_2$ ).

**Low-Temperature NMR Study of the Reaction of  $PdMe_2(tmeda)$  (2a) with MeI, MeBr, and MeOTf.** A 5-mm o.d. NMR tube was charged with ca. 50 mg of 2a, and 0.3 mL of solvent was added to give a clear solution. The solution was cooled to -60 °C, one drop of MeI or MeOTf was added (2–5-fold excess), and the contents of the tube were well mixed. MeBr was introduced as a gas above the solution. The tube was then placed in the precooled (-40 °C) probe of the NMR spectrometer.

Warning! Compounds 4a and 4b are thermally very unstable and explode when brought to room temperature or higher. Only limited amounts (<0.25 g) of the dry compounds should be prepared and handled.

**$PdIme_3(tmeda)$  (4a).** Methyl iodide (0.2 mL, excess) was added to a cooled solution (-60 °C) of  $PdMe_2(tmeda)$  (0.18 g, 0.72 mmol) in acetone (3 mL). After ca. 15 min white crystalline 4a slowly deposited. After 1 h the supernatant liquid was removed and the solid dried in vacuo at 0 °C: yield 0.23 g (80%); mp 15–20 °C dec expl.

**$PdBrMe_3(tmeda)$  (4b).**  $PdMe_2(tmeda)$  (0.18 g, 0.70 mmol) was dissolved in acetone (5 mL) and cooled to 0 °C. A slow stream of MeBr gas was bubbled through the solution for about 10 s (temperature increased to 3 °C). The mixture was kept at 0 °C for 15 min and evaporated to dryness in vacuo at  $\leq 0$  °C to afford a white solid: yield 0.24 g (100%); mp 36–40 °C dec expl.

**Ligand-Exchange Reactions.  $PdMe_2(PMe_2CH_2CH_2PMe_2)$  (5).** To a solution of  $PdMe_2(tmeda)$  (0.80 g, 3.17 mmol) in benzene (5 mL) was added  $Me_2PCH_2CH_2PMe_2$  (0.50 g, 3.30 mmol). Evaporation of the solvent yielded white crystals of 5 (0.93 g, 100%).

$^1H$  NMR (200 MHz,  $C_6D_6$ ):  $\delta$  0.83 (m, 6 H, PdMe), 0.92 (d,  $^2J(H,P) = 78$  Hz, 12 H,  $PMe_2$ ).  $^{13}C$  NMR (50 MHz,  $C_6D_6$ ):  $\delta$  -2.00 (dd,  $^2J(C,P) = 464$  Hz,  $^3J(C,P) = 44$  Hz, PdMe), 12.41 (m,  $^1J(C,P) + ^2J(C,P) = 68$  Hz,  $PMe_2$ ), 28.37 (t,  $^1J(C,P) + ^2J(C,P) = 176$  Hz,  $CH_2$ ).

**$PdMe_2(Ph_2PCH_2CH_2PPh_2)$  (6).** To a solution of  $PdMe_2(tmeda)$  (0.13 g, 0.51 mmol) in benzene (3 mL) was added  $Ph_2PCH_2CH_2PPh_2$  (0.20 g; 0.51 mmol). Trituration with pentane (10 mL) gave a white precipitate, which was isolated by decantation and washed with pentane. The precipitate was dried in vacuo: yield 0.22 g of white powder (82%);  $^1H$  NMR (80 MHz,  $C_6D_6$ )  $\delta$  0.90 (dd,  $^3J(P,H) = 3$  Hz,  $^3J(P',H) = 7$  Hz), 1.36 (d,  $^2J(P,H) = 5.3$  Hz), 6.8–7.6 (m,  $PhP$ ).

***cis*- $PdMe_2(PMePh_2)_2$  (7).** To a solution of  $PdMe_2(tmeda)$  (0.13 g, 0.51 mmol) in benzene (3 mL) was added  $PMePh_2$  (0.4 g, 2 mmol) and pentane (15 mL). Cooling the mixture to -30 °C afforded pale pink crystals of 7. The supernatant solution was decanted off, and the crystals were washed with pentane and dried in vacuo; yield 0.27 g (90%).

***cis*- $PdMe_2(PPh_3)_2$  (8).** A solution of  $PPh_3$  (0.55 g, 2.02 mmol) in benzene (5 mL) was added to a solution of  $PdMe_2(tmeda)$  (0.25 g, 0.98 mmol) in benzene (5 mL), and white crystals of 8 slowly precipitated. After 5 min pentane (10 mL) was added in order to optimize the yield. The supernatant solution was decanted off and the crystalline product washed with pentane and dried in vacuo; yield 0.62 g (90%).  $^1H$  NMR (200 MHz,  $CDCl_3$ ):  $\delta$  0.20 (dd,  $^3J(P,H) = 4$  Hz,  $^3J(P',H) = 7$  Hz), 7.2 (m, 30 H, arom).

**$PdMe_2[o-(diphenylphosphino)-N,N-dimethylbenzylamine]$  (9).** The preparation of this compound was carried out by using a procedure similar to that used for 7; yield 0.22 g of white crystals (82%).  $^1H$  NMR (80 MHz,  $C_6D_6$ ):  $\delta$  0.82 (d), 0.86 (d) (6 H,  $^3J(H,P) = 6.7$  Hz and 8.7 Hz, respectively, PdMe), 2.23 (s, 6 H,  $NMe_2$ ), 3.05 (br s, 2 H,  $CH_2$ ), 6.6–7.7 (m, 14 H, arom).

**$PdMe_2(bpy)$  (10).**  $PdMe_2(tmeda)$  (0.25 g, 0.99 mmol) and bipyridine (0.16 g, 1.02 mmol) were dissolved in benzene (5 mL) to afford an orange solution from which orange crystals precipitated within 15 min. The crystals of 10 were collected by filtration and dried in vacuo; yield 0.25 g (85%).  $^1H$  NMR (200 MHz,  $CD_3CO$ ):  $\delta$  0.24 (s, PdMe), 7.69 (ddd,  $^3J(4,5) = 8$  Hz,  $^3J(5,6) = 5$  Hz,  $^4J(3,5) = 1$  Hz), 8.17 (td,  $^3J(3,4)$  and  $^3J(4,5) = 8$  Hz,  $^4J(4,6) = 2$  Hz), 8.46 (dd,  $^3J(3,4) = 8$  Hz,  $^4J(3,5) = 1$  Hz), 8.78 (dd,  $^3J(5,6) = 5$  Hz), 8.78 (dd,  $^4J(4,6) = 1$  Hz).

**$PdMe_2(en)$  (11).**  $PdMe_2(tmeda)$  (0.26 g, 1.03 mmol) was dissolved in ethanediamine (5 mL, excess) to give a colorless

Table IV. Crystal Data and Details of the Structure Determinations

	2a	5
(a) Crystal Data		
formula	C <sub>8</sub> H <sub>22</sub> N <sub>2</sub> Pd	C <sub>8</sub> H <sub>22</sub> P <sub>2</sub> Pd
mol wt	252.70	286.63
cryst system	monoclinic	monoclinic
space group	P2 <sub>1</sub> /n (No. 14)	C2/c (No. 15)
a, Å	8.518 (4)	9.442 (1)
b, Å	10.798 (4)	14.968 (1)
c, Å	12.132 (5)	10.354 (1)
β, deg	99.02 (4)	115.62 (1)
V, Å <sup>3</sup>	1102.1 (8)	1319.5 (2)
Z	4	4
D <sub>calcd</sub> , g·cm <sup>-3</sup>	1.523	1.443
F(000)	520	584
μ(Mo Kα), cm <sup>-1</sup>	16.2	15.8
cryst size (mm)	0.18 × 0.18 × 0.18	0.68 × 0.33 × 0.30
(b) Data Collection		
temp, K	100	295
θ <sub>min</sub> , θ <sub>max</sub> , deg	1.7, 27.5	2.2, 35.0
radiatn	Mo Kα (Zr-filtered), 0.710 73 Å	Mo Kα (Zr-filtered), 0.710 73 Å
scan type	ω/2θ	ω/2θ
Δω, deg	0.80 + 0.35 tan θ	0.70 + 0.35 tan θ
hor and vert aperture, mm	3.0, 3.0	4.0, 6.0
dist cryst to detector, mm	173	173
ref reflectns	11 $\bar{3}$ , 1 $\bar{2}$ 1	200, 222, 210
data set	h, -11, 11; k, -14, 14; l, -15, 15	h, 0, 15; k, 0, 24; l, -16, 15
total data	8330	3127
total unique data	2518	2894
obsd data	2310	1698
(I > 2.5σ(I))		
(c) Refinement		
no. of refined parameters	167	61
weighting scheme	w = 1.0/σ <sup>2</sup> (F)	w = 1.0/σ <sup>2</sup> (F)
final R, wR, S	0.022, 0.022, 0.92	0.036, 0.034, 1.14
(Δ/σ) <sub>max</sub> in final cycle	0.1	0.1
min and max resid dens, e/Å <sup>3</sup>	-0.69, 0.94	-0.33, 0.61

solution. This solution on evaporation to dryness in vacuo afforded pale beige solid 11, yield 0.22 g (100%). The product is insoluble in most common organic solvents; mp 128 °C dec expl. Anal. Calcd for C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>Pd: C, 24.72; H, 7.23; N, 14.63. Found: C, 24.44; H, 7.18; N, 14.25.

**PdMe<sub>2</sub>(pmdeta) (12).** PdMe<sub>2</sub>(tmeda) (0.26 g; 1.03 mmol) was dissolved in N,N,N',N''-pentamethyldiethylenetriamine (1 mL, excess) to give a colorless solution. Volatiles were evaporated by bulb to bulb distillation at 40 °C and 0.02 mmHg leaving a light-gray oil from which large colorless crystals slowly separated. The crystals were washed with cold pentane and dried in vacuo; yield 0.27 g (80%). Anal. Calcd for C<sub>11</sub>H<sub>29</sub>N<sub>3</sub>Pd: C, 42.65; H, 9.44; N, 13.56. Found: C, 42.47; H, 9.50; N, 13.34. <sup>1</sup>H NMR (200 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ -0.39 (3 H, s, PdMe), -0.32 (3 H, s, PdMe), 2.19 (6 H, s, NMe<sub>2</sub>(noncoordinated)), 2.39 (3 H, s, NMe), 2.40 (3 H, s, NMe), 2.49 (3 H, s, NMe), 2.1-2.55 (ca. 3 H, m, CH<sub>2</sub>), 2.67 (2 H, dt, CH<sub>2</sub>); 2.75/3.24/3.43 (1 H, m, CH<sub>2</sub>). <sup>13</sup>C NMR (50 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ -9.29/-8.15 (PdMe), 46.08 (br s, NMe<sub>2</sub>), 46.58/47.18/49.87/56.18/57.43/58.49/60.11 (CH<sub>2</sub>).

**PdIme(dmpe) (13).** PdMe<sub>2</sub>(dmpe) (0.38 g, 1.3 mmol) was dissolved in benzene (10 mL). MeI (0.3 mL, 2.5 mmol) was added, and with gas evolution the solution slowly turned yellow. After 2 h 23 mL (0.81 equiv) of pure ethane (GLC) was collected. The yellow solid that also formed was collected by decantation and dried in vacuo; yield 0.53 g (100%); mp 150-152 °C dec. Anal. Calcd: C, 21.10; H, 4.81; I, 31.84. Found: C, 20.83, H, 4.72; I, 31.63. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.61 (dd, <sup>3</sup>J(H,P) = 8.0 Hz, <sup>3</sup>J(H,P') = 4.3 Hz, PdMe), 1.56 (dd, <sup>2</sup>J(H,P) = 10.7 Hz, <sup>4</sup>J(H,P') = 0.8 Hz, PMe<sub>2</sub>), 1.58 (d, <sup>2</sup>J(H,P) = 8.8 Hz, 6 H, P'Me<sub>2</sub>), 1.58-2.04 (m, 4 H, CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ -2.36

Table V. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters with Esd's in Parentheses for PdMe<sub>2</sub>(tmeda) (2a)

	x	y	z	U <sub>eq</sub> , Å <sup>2</sup>
Pd	0.06412 (2)	0.19410 (1)	0.13629 (1)	0.0112 (1)
N(1)	0.2706 (2)	0.0726 (2)	0.1329 (2)	0.0163 (5)
N(2)	0.0491 (2)	0.0929 (2)	0.2914 (2)	0.0162 (6)
C(1)	0.2724 (3)	0.0135 (3)	0.0240 (2)	0.0260 (8)
C(2)	0.4206 (3)	0.1409 (3)	0.1628 (2)	0.0253 (8)
C(3)	0.2535 (3)	-0.0266 (3)	0.2146 (2)	0.0292 (8)
C(4)	0.2015 (3)	0.0233 (3)	0.3168 (2)	0.0284 (8)
C(5)	-0.0872 (4)	0.0079 (3)	0.2749 (2)	0.036 (1)
C(6)	0.0370 (4)	0.1718 (3)	0.3881 (2)	0.0333 (9)
C(7)	-0.1314 (3)	0.2987 (3)	0.1437 (2)	0.0233 (7)
C(8)	0.0827 (3)	0.2820 (2)	-0.0089 (2)	0.0214 (7)

$$^{\circ}U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Table VI. Bond Distances (Å) and Angles (deg) for the Non-Hydrogen Atoms of PdMe<sub>2</sub>(tmeda) (2a)

Bond Distances			
Pd-N(1)	2.200 (2)	N(1)-C(3)	1.482 (3)
Pd-N(2)	2.197 (2)	N(2)-C(4)	1.490 (3)
Pd-C(7)	2.026 (3)	N(2)-C(5)	1.469 (4)
Pd-C(8)	2.029 (3)	N(2)-C(6)	1.466 (3)
N(1)-C(1)	1.470 (3)	C(3)-C(4)	1.482 (4)
N(1)-C(2)	1.471 (3)		
Bond Angles			
N(1)-Pd-N(2)	82.73 (8)	C(1)-N(1)-C(3)	107.7 (2)
N(1)-Pd-C(7)	176.9 (1)	C(2)-N(1)-C(3)	111.7 (2)
N(1)-Pd-C(8)	95.24 (9)	Pd-N(2)-C(4)	105.2 (1)
N(2)-Pd-C(7)	94.6 (1)	Pd-N(2)-C(5)	110.2 (1)
N(2)-Pd-C(8)	177.80 (9)	Pd-N(2)-C(6)	114.7 (2)
C(7)-Pd-C(8)	87.4 (1)	C(4)-N(2)-C(5)	110.9 (2)
Pd-N(1)-C(1)	113.4 (2)	C(4)-N(2)-C(6)	107.2 (2)
Pd-N(1)-C(2)	111.3 (2)	C(5)-N(2)-C(6)	108.6 (2)
Pd-N(1)-C(3)	104.8 (1)	N(1)-C(3)-C(4)	111.7 (3)
C(1)-N(1)-C(2)	108.0 (2)	N(2)-C(4)-C(3)	112.1 (2)

(d, <sup>2</sup>J(C,P) = 116 Hz, PdMe); 13.26 (d, <sup>1</sup>J(C,P) = 30 Hz, P'Me<sub>2</sub>), 13.55 (d, <sup>1</sup>J(C,P) = 20 Hz, P'Me<sub>2</sub>), 25.96 (dd, <sup>1</sup>J(C,P) = 26 Hz, <sup>2</sup>J(C,P') = 12 Hz, -CH<sub>2</sub>P'), 30.91 (dd, <sup>1</sup>J(C,P') = 32 Hz, <sup>2</sup>J(C,P) = 23 Hz, -CH<sub>2</sub>P'). <sup>31</sup>P (80 MHz, CDCl<sub>3</sub>): δ +25.65 (d, <sup>2</sup>J(P,P') = 28 Hz), +42.34 (d, <sup>2</sup>J(P,P') = 28 Hz).

**Structure Determination and Refinement of PdMe<sub>2</sub>(tmeda) (2a).** X-ray data were collected on an Enraf-Nonius CAD-4F diffractometer at 100 K for a block-shaped crystal that was mounted on top of a glass fiber. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 20 reflections in the range 12.0 < θ < 14.0° and checked for the presence of higher lattice symmetry.<sup>21</sup> Data were corrected for Lp but not for absorption and averaged (R<sub>av</sub> = 0.027). There was no decay during the 23 h of X-ray exposure time. Standard deviations as obtained by counting statistics were increased according to an analysis of the excess variance of the three reference reflections: σ<sup>2</sup>(I) = σ<sup>2</sup><sub>cs</sub>(I) + (0.017I)<sup>2</sup>.<sup>22</sup> The space group was determined from the observed systematic extinctions: h0l, h + l = 2n + 1, and 0k0, k = 2n + 1. The structure was solved by standard Patterson and Fourier techniques and refined on F by weighted full-matrix least squares. Hydrogen atoms were located from a difference Fourier map and their positions refined along with one common isotropic thermal parameter [U = 0.043 (2) Å<sup>2</sup>]. Weights were introduced in the final refinement cycles; convergence was reached at R = 0.022. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table V; data on the geometry are given in Table VI.

**Structure Determination and Refinement of PdMe<sub>2</sub>(dmpe) (5).** A suitable colorless block shaped crystal was mounted under nitrogen in a Lindemann-glass capillary and transferred to an Enraf-Nonius CAD-4F diffractometer for data collection. Unit-cell parameters were determined from a least-squares

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**Table VII. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters with Esd's in Parentheses for  $PdMe_2(dmpe)$  (5)**

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}^a$ Å <sup>2</sup>
Pd	1/2	0.23072 (2)	1/4	0.0466 (1)
P	0.34010 (9)	0.34242 (5)	0.25668 (9)	0.0520 (2)
C(1)	0.4114 (5)	0.4466 (2)	0.2158 (5)	0.080 (2)
C(2)	0.3443 (5)	0.1311 (2)	0.2478 (5)	0.088 (2)
C(3)	0.3426 (5)	0.3642 (3)	0.4296 (4)	0.079 (2)
C(4)	0.1320 (4)	0.3440 (3)	0.1398 (4)	0.094 (2)

$$^a U_{eq} = \frac{1}{3} \sum_i \sum_j J_{ij} a_i^* a_j^* a_i a_j$$

**Table VIII. Bond Distances (Å) and Angles (deg) for the Non-Hydrogen Atoms<sup>a</sup> of  $PdMe_2(dmpe)$  (5)**

Bond Distances			
Pd-P	2.2737 (9)	P-C(3)	1.810 (4)
Pd-C(2)	2.087 (4)	P-C(4)	1.808 (4)
P-C(1)	1.819 (4)	C(1)-C(1)'	1.509 (7)
Bond Angles			
P-Pd-P'	85.33 (3)	Pd-P-C(4)	122.2 (1)
P-Pd-C(2)	93.0 (1)	C(1)-P-C(3)	103.2 (2)
P-Pd-C(2)'	177.2 (1)	C(1)-P-C(4)	103.7 (2)
C(2)-Pd-C(2)'	88.8 (2)	C(3)-P-C(4)	101.9 (2)
Pd-P-C(1)	107.8 (2)	P-C(1)-C(1)'	109.7 (3)
Pd-P-C(3)	116.0 (2)		

<sup>a</sup> The prime indicates the symmetry operation:  $1 - x, y, 0.5 - z$ .

treatment of the SET4 setting angles of 23 reflections in the range  $14.0 < \theta < 17.7^\circ$ . The unit-cell parameters were checked for the presence of higher lattice symmetry.<sup>21</sup> Data were corrected for  $L_p$  and for a linear decay of 5.6% during the 26 h of X-ray exposure time but not for absorption. Standard deviations as obtained by counting statistics were increased according to an analysis of the excess variance of the three reference reflections:  $\sigma^2(I) = \sigma_{cs}^2(I) + (0.029I)^2$ .<sup>22</sup> Space group  $C2/c$  was determined from the systematic extinctions:  $hkl, h + k = 2n + 1$ , and  $h0l, l = 2n + 1$ . The heavy atoms (Pd and P) were located with direct methods (SHELXS86);<sup>23</sup> the remaining non-H atoms were located from subsequent difference Fourier maps. Refinement of  $F$  was carried out by full-matrix least-squares techniques. All non-hy-

drogen atoms were refined with anisotropic thermal parameters. H atoms were introduced on calculated positions [ $C-H = 0.98$  Å] and included in the refinement riding on their carrier atoms. All H atoms were refined with one common isotropic thermal parameter [ $U = 0.128$  (5) Å<sup>2</sup>]. Weights were introduced in the final refinement cycles; convergence was reached at  $R = 0.0364$ . Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table VII; data on the geometry are given in Table VIII.

Crystal data and numerical details of both structure determinations are given in Table IV. Neutral atom scattering factors were taken from ref 24 and corrected for anomalous dispersion.<sup>25</sup> All calculations were performed with SHELX76<sup>26</sup> and the EUCLID package<sup>27</sup> (geometrical calculations and illustrations) on a MicroVAX-II computer.

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**Supplementary Material Available:** Tables of anisotropic thermal parameters (Table S1), hydrogen atom positions and isotropic thermal parameters (Table S2) and bond distances and angles for 2a (Table S3) and tables of anisotropic thermal parameters (Table S4), hydrogen atom positions and isotropic thermal parameters (Table S5), bond distances (Table S6) and angles (Table S7), and torsion angles (Table S8) for 5 (5 pages); listings of structure factor amplitudes for 2a and 5 (34 pages). Ordering information is given on any current masthead page.

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