Synthesis and Properties of Dimethyl- and Monomethylbis(phosphite)palladium(II) Complexes

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New dimethylpalladium complexes having alkyl and aryl phosphites as the supporting ligands, *cis*-[$PdMe_2\{P(OR)_3\}_2$] (R = Me, **1a**; Ph, **1b**), have been prepared by two routes, (1) by the reaction of [$Pd(acac)_2$] with [$AlMe_2(OEt)$] in the presence of the phosphite ligands, and (2) by the ligand exchange reaction of [$PdMe_2(cod)$] (COD = 1,5-cyclooctadiene) with two molar amounts of the phosphites. Monomethylpalladium chloride complexes, [$PdMe(Cl)\{P(OR)_3\}_2$] (R = Me, **2a**; Ph, **2b**; Pr^i, **2c**) have been prepared by ligand exchange reaction of [PdMe(Cl)(cod)] with two molar amounts of the phosphites, whereas [$PdMe(OAc)\{P(OR)_3\}_2$] (R = Me, **3a**; Ph, **3b**) has been synthesized by treatment of **1** with acetic acid. Strong influence of the coordinated phosphite ligand on the cis or trans configuration of the monomethylpalladium complexes was observed, the results being in contrast with those of complexes having the trimethylphosphine ligands that give preferentially trans complexes. Removal of the chloride ligand in **2** with an equimolar amount of $AgBF_4$ or treatment of the dimethylpalladium complex **1** with HBF_4 in the expectation of obtaining a bis(phosphite)-coordinated complex led to formation of a mixture of the tris(phosphite) complex, $[PdMe\{P(OR)_3\}_3]^+BF_4^-$ and the mono-phosphite complex $[PdMe\{P(OR)_3\}(s)_2]^+BF_4^-$ (s = solvent), presumably through the rapid disproportionation of an unstable intermediate $[PdMe\{P(OR)_3\}_2(s)]^+BF_4^-$.

Palladium complexes stabilized by tertiary phosphine ligands have been extensively used in organic synthesis[1] and chemistry of these phosphine-coordinated complexes[2] has been studied in considerable detail. However, reported examples of the use of corresponding complexes having phosphite ligands are very limited and the influences of the phosphite ligands on the properties of organopalladium complexes have remained virtually unexamined. In special cases, however, the influence of chiral bidentate ligands with phosphine and phosphite donors has been demonstrated to greatly enhance activities and enantioselectivities in hydroformylation of olefins by using rhodium catalysts[3] and in alternating copolymerization of propene and CO by palladium catalysts.[4] We report here syntheses of novel phosphite-coordinated alkylpalladium complexes with the hope of shedding light on the influence of the phosphite ligands on the properties of organopalladium complexes.

Results

Synthesis of Neutral Dimethyl- and Monomethylpalladium Complexes with Phosphite Ligands. Dimethylpalladium complex, *cis*-[$PdMe_2\{P(OMe)_3\}_2$] **1a**, having the trimethyl phosphite ligands has been prepared by treatment of [$Pd(acac)_2$] with [$AlMe_2(OEt)$] in the presence of $P(OMe)_3$ (Eq. 2) in a procedure similar to the preparation of the trimethylphosphine-coordinated complex, *trans*-[$PdMe_2(PMe_3)_2$] (Eq. 1).[5]

$$[Pd(acac)_2] + [AlMe_2(OEt)] + PMe_3 \xrightarrow[\text{ether, } -40 \sim 0\ ^\circ C]{} \underset{Me_3P}{\overset{Me}{Pd}}\!\!\underset{Me}{\overset{PMe_3}{}} \quad (1)$$

(2 mol. a. + 2 mol. a.)

$$[Pd(acac)_2] + [AlMe_2(OEt)] + P(OMe)_3 \xrightarrow[\text{ether, } -40 \sim 0\ ^\circ C]{} \underset{Me}{\overset{P(OMe)_3}{Pd}}\!\!\underset{Me}{\overset{P(OMe)_3}{}} \quad \textbf{1a} \quad (2)$$

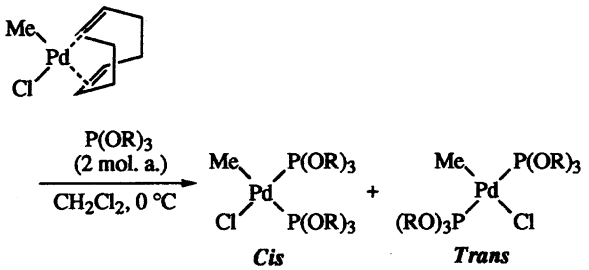
(2 mol. a. + 2 mol. a.)

In contrast to [$PdMe_2(PMe_3)_2$] that was obtained as a trans-rich mixture of cis and the trans isomers, [$PdMe_2\{P(OR)_3\}_2$] was obtained only in a cis form. The reaction of [$PdMe_2(cod)$] (cod = 1,5-cyclooctadiene) with two molar amounts of $P(OR)_3$ (R = Me, Ph) in CH_2Cl_2 at room temperature also proceeded smoothly to yield only *cis*-dimethylpalladium isomers **1a** and **1b** (Eq. 3). Isolation of the corresponding $P(OPr^i)_3$-coordinated complex has not been successful so far.

$$\underset{Me}{\overset{Me}{Pd}} \xrightarrow[CH_2Cl_2,\ 0\ ^\circ C]{P(OR)_3\ (2\ mol.\ a.)} \underset{Me}{\overset{P(OR)_3}{Pd}}\!\!\underset{P(OR)_3}{\overset{Me}{}} \quad \textit{Cis}\ \text{form} \quad R = Me, \textbf{1a}; Ph, \textbf{1b} \quad (3)$$

The characteristic five line-multiplet (an AXX′ pattern) at 3.3 ppm in the ^{13}C NMR spectrum of complex **1a** (Fig. 1) can be assigned to the two methyl carbons bound to palladium in the cis configuration.[6] Triphenyl phosphite-coordinated complex gave a similar spectrum.

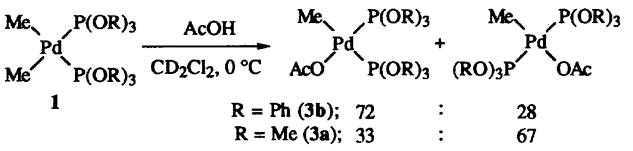
On the other hand, the ligand exchange reaction of cod in [PdMe(Cl)(cod)] with two molar amounts of the phosphite ligands produced monomethylpalladium chloride complexes having two $P(OR)_3$ ligands, [PdMe(Cl){$P(OR)_3$}$_2$] (**2**) (R= Me, **2a**; Ph, **2b**; Pr^i, **2c**), and the isomer ratio was found to vary depending on the phosphite ligands used (Eq. 4).



(4)

The configuration of the bis(phosphite) complexes **2a**—**2c** can be established readily by observing the ^{31}P NMR. The ^{31}P NMR of the trans complexes show the singlet pattern, while the cis complexes show two doublets. In the case of **2a** and **2b** having phenyl and methyl phosphite ligands, cis isomers were formed together with the trans complexes, whereas in the case of the basic and bulky triisopropyl phosphite ligand, *trans*-**2c** was isolated as a sole product. Generation of *cis*-[PdMe(Cl){$P(OR)_3$}$_2$] (**2**) is significant because the corresponding monodentate phosphine ligands always yield trans isomers of the formula: *trans*-[PdR′(Cl)(PR_3)] (R′=Ph, Me, and Et, PR_3=phosphine ligands).[7,8] Unfortunately, separation of the cis and trans isomers in **2a** and **2b** was unsuccessful. However, the distinct variation in the effect of the phosphite ligands from that of the phosphine ligands[8,9] on the configuration of the dimethyl and monomethylpalladium complexes is noteworthy.

Dimethylpalladium complexes **1** were also converted into monomethylpalladium complexes by treatment with an equimolar amount of protic acid; e.g., treatment of **1** with AcOH at 0 °C in CD_2Cl_2 gave the mixture of *cis*- and *trans*-acetato(methyl)palladium complexes **3a** and **3b** with evolution of methane (Eq. 5). The corresponding phosphine-coordinated complex gave only *trans*-[PdMe(OAc)(PR_3)$_2$] (R=Me[10] and Et[11]) (Eq. 6). The ratios of the cis and the trans isomers of **3a** and **3b** were similar to those of the corresponding monomethylpalladium chloride complexes in Eq. 4.



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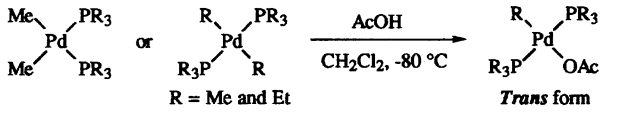

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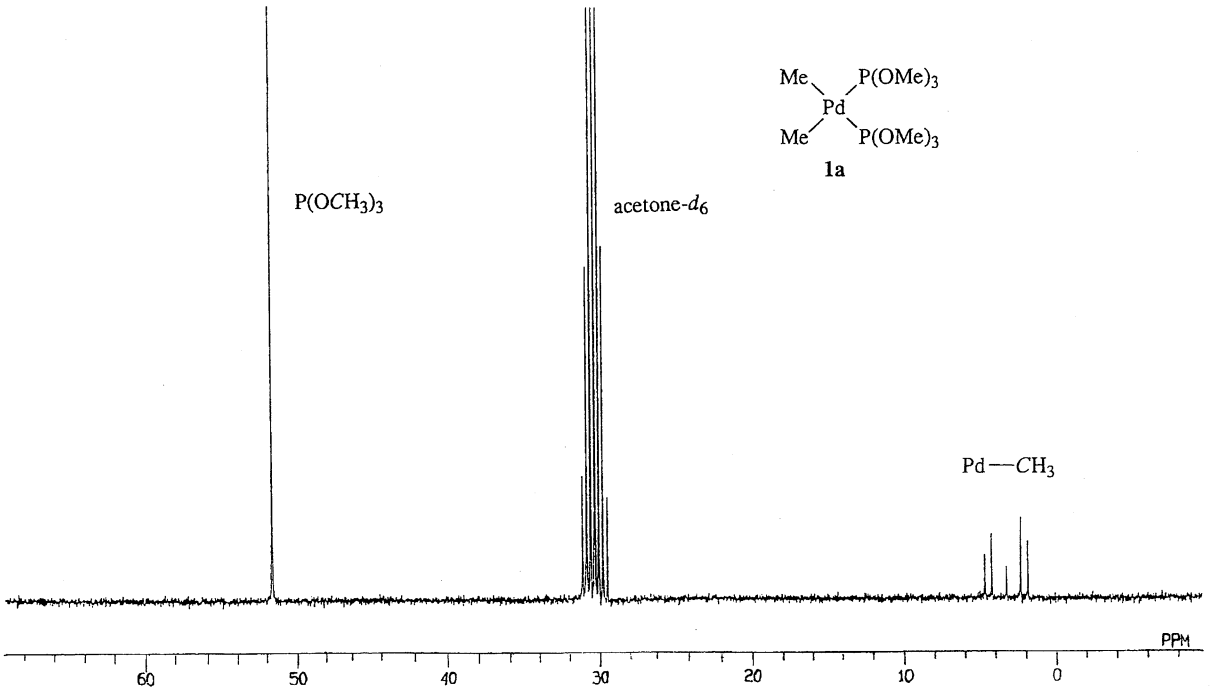
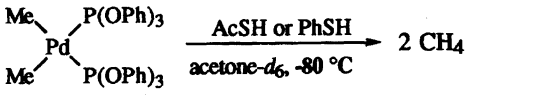


Fig. 1. ^{13}C NMR of **1a** at 67.9 MHz in acetone-d_6.

It is also noted that the rate of protonation of **1** with acetic acid was slower than that of the corresponding trimethylphosphine complexes; the reaction of **1b** with AcOH did not proceed at all at −40 °C in acetone-d_6, while *cis*- or *trans*-[$PdMe_2(PMe_3)_2$] reacts with AcOH instantly even at −80 °C to give *trans*-monomethylpalladium complex (Eq. 6).

On the other hand, thiophenol and thioacetic acid readily protonated **1b** at −80 °C with liberation of ca. two molar amounts of methane, despite of their weak acidities (Eq. 7).



1b (7)

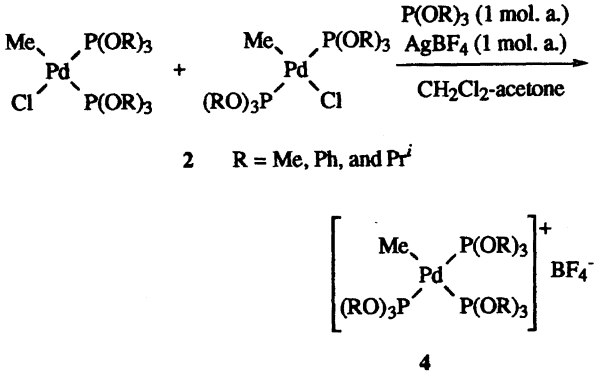
In the reactions of **1** with the sulfur-containing acids, the thiophilicity of the palladium center in **1** may dominate the reaction. The interaction of the sulfur-containing substrates with the palladium center may precede the protonolysis of the methyl ligand. The products of the reaction of **1** with AcSH and PhSH are probably [$Pd(SAc)_2\{P(OPh)_3\}_2$] and [$Pd(SPh)_2\{P(OPh)_3\}_2$], but identification of these complexes was not attempted.

Synthesis of Phosphite-Coordinated Cationic Methylpalladium Complexes. Previously we have confirmed that the cationic cis-complexes containing a chelating ligand showed higher reactivities than the corresponding cationic *trans*-alkylpalladium complexes having two PMe_3 ligands toward CO insertion.[8] The higher rate of the chelated cationic methylpalladium complexes toward CO insertion than that of the *trans*-methylpalladium complexes having mutually trans ligands was accounted for by the ease of migratory CO insertion in the complexes having a site available adjacent to the methyl ligand for the incoming CO. In the preceding paper, we have observed[12] also that a phosphine-coordinated methylpalladium complex, *cis*-[$PdMe(PMe_3)(s)_2$]BF_4 (s=solvent), having the coordination site available adjacent to the methyl ligand showed greater reactivity toward CO than the bis(phosphine)-coordinated complex *trans*-[$PdMe(PMe_3)_2(s)$]BF_4. For the sake of comparison, we attempted to prepare cationic *cis*-methylpalladium complexes having one and two phosphite ligands.

The attempted synthesis of cationic methylbis(phosphite)-palladium complexes, [$PdMe(s)\{P(OR)_3\}_2$]$^+BF_4^-$ (s = solvent), by removal of the halide ligand in [$PdMe(Cl)\{P(OR)_3\}_2$] (**2**) with a silver salt in a manner similar to the preparation of the corresponding bis(phosphine)-coordinated complex[8,10,13] resulted unexpectedly in formation of methylpalladium complex having three phosphite ligands, [$PdMe\{P(OR)_3\}_3$]$^+BF_4^-$ (**4**) and another methylpalladium species, **5** (Eq. 8).

$$\underset{\textbf{2}\ (cis+trans)}{PdMe(Cl)\{P(OR)_3\}_2} + AgBF_4 \rightarrow \underset{\textbf{4}}{[PdMe\{P(OR)_3\}_3]^+BF_4^-} + \textbf{5} \quad \text{(equimol.a.)} \qquad (8)$$

The cationic tris(phosphite)complexes [$PdMe\{P(OR)_3\}_3$]$^+BF_4^-$ **4** (R=Me, **4a**; Ph, **4b**; Pr^i, **4c**) were isolated and characterized by NMR and elemental analysis. The cationic complexes **4a**—**4c** can also be prepared by removal of the halide ligand in **2** in the presence of an equimolar amount of phosphite (Eq. 9).



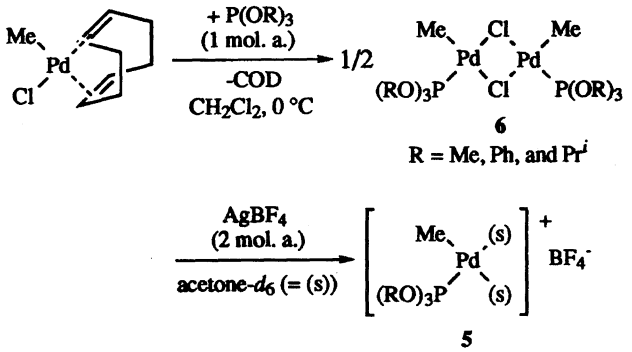
2 R = Me, Ph, and Pr^i

4 (9)

The formation of the tris(phosphite) complex **4** in the reaction of the neutral bis(phosphite) complex **2** with an equimolar amount of $AgBF_4$ (Eq. 8) suggests that the other product **5** is a cationic methyl(phosphite) complex. Characterization of the complex was carried out as follows by preparation of the assumed methyl(phosphite) complex by an independent route.

Neutral chloro-bridged dimeric complexes with the composition of [$PdMe(\mu\text{-}Cl)\{P(OR)_3\}]_2$ (R=Me, Ph, and Pr^i) (**6**) have been prepared from [PdMe(Cl)(cod)] by addition of an equimolar amount of phosphite. The complexes **6a**—**6c** reacted with $AgBF_4$ (one molar amount/Pd) to give the corresponding cationic (phosphite)palladium complexes **5** (Eq. 10), whose NMR spectra proved identical with those of the complex **5** produced together with **4** as in Eq. 8.

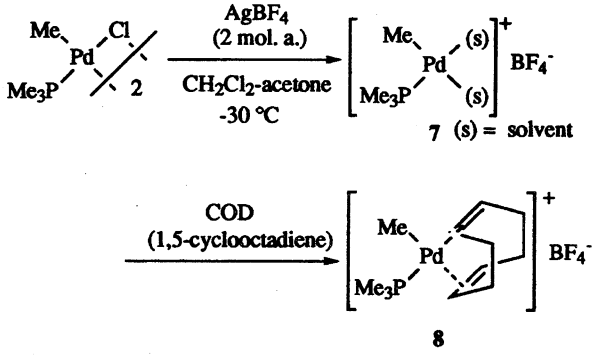
Since ^1H and ^{13}C methyl signals of the methylpalladium complex **5** having one phosphite ligand showed no coupling with the phosphite ligand at −10 °C, the $^2J_{PC}$ and $^3J_{PH}$ values may be too small to be observed. In the previous paper dealing with the PMe_3-coordinated complexes[12] we have observed the formation of a cationic methylpalladium complex having one PMe_3 ligand **7** and identified its configuration as cis by comparison of the NMR spectra with those of the COD-coordinated methyl(phosphine)palladium complex **8** (Eq. 11). Thus it is likely that the methyl complex **5** having the phosphite ligand also has a cis configuration like **7** with very small Me–$P(OR)_3$ coupling constants.



6

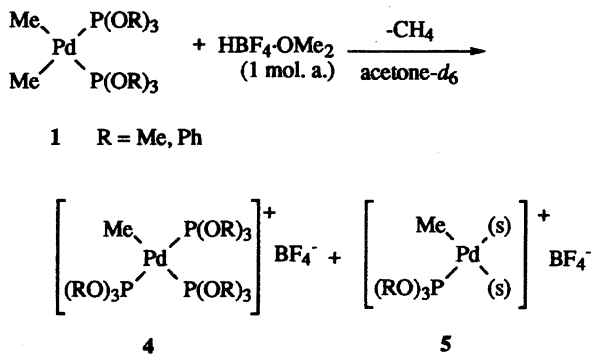
R = Me, Ph, and Pr^i

5 (10)



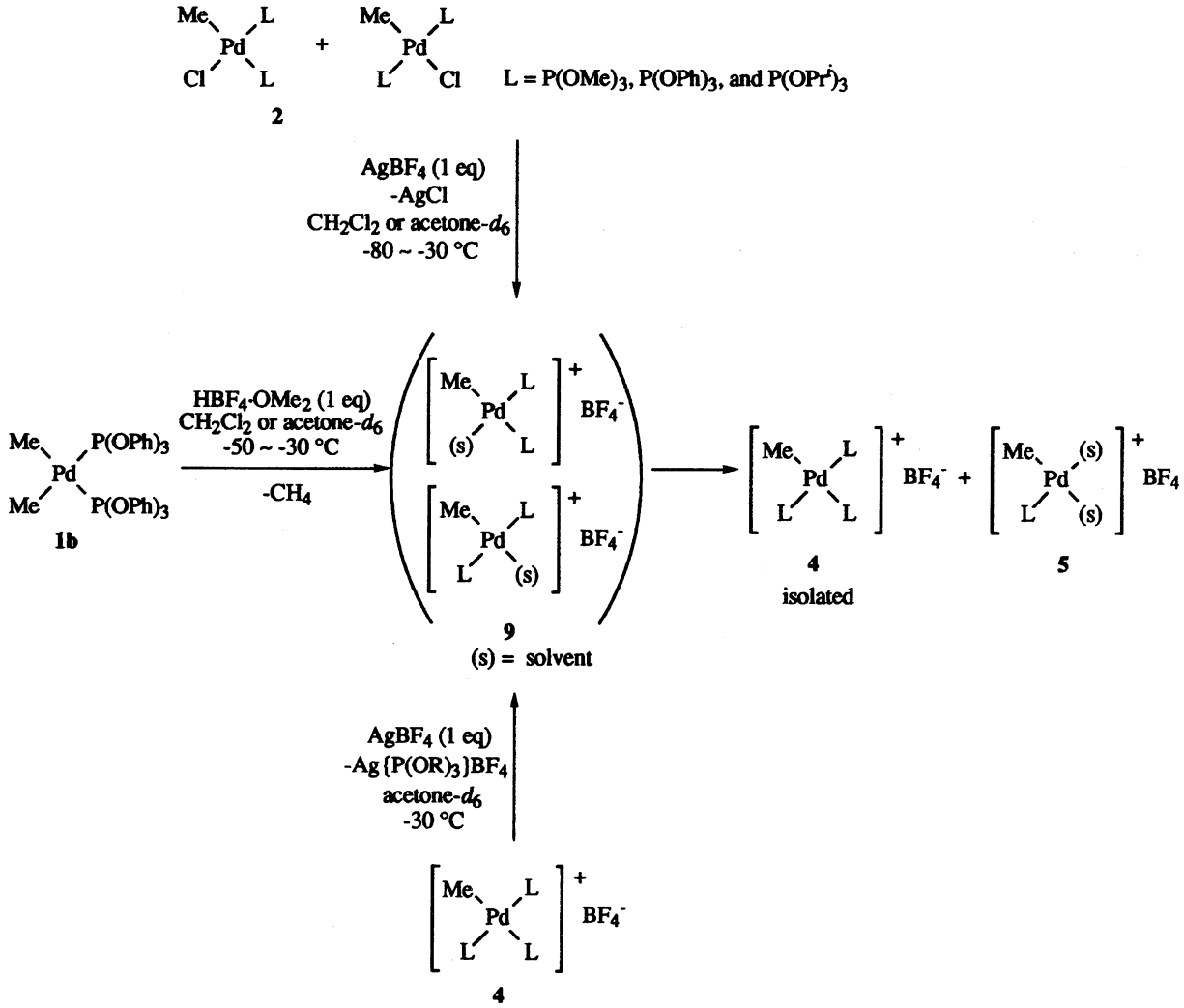
(11)

It was revealed that the tris(phosphite)complex **4** was also derived together with **5** by protonation of the dimethylpalladium complex **1** with an equimolar amount of HBF_4·OMe_2 (Eq. 12).



(12)

These results suggest that treatment of the bis(phosphite) complex **2** with an equimolar amount of $AgBF_4$ and protonation of the dimethylpalladium complex having two $P(OPh)_3$ ligands **1b** with one molar amount of HBF_4·OMe_2 first produces labile cationic methylpalladium complexes with two phosphite ligands and that a rapid disproportionation of the bis(phosphite) complexes **9** into the tris(phosphite) and mono(phosphite) complexes (**4** and **5**) may ensue. It was



Scheme 1.

also observed that the phosphite ligand at the site trans to the methyl group in the tris(phosphite) complex **4** can be readily removed by action of $AgBF_4$ to give the monophosphite complex **5** in addition to **4**. The result is in line with the labile nature of the intermediate bis(phosphite) complex **9** which has the tendency to disproportionate to **4** and **5** (Scheme 1). The results are in contrast to the configurational stability of the *trans*-$[PdMe(s)(PMe_3)_2]^+BF_4^-$ derived by removal of the chloride ligand in *trans*-$[PdMe(Cl)(PMe_3)_2]$ with one molar amount of $AgBF_4$ or by abstraction of the trans-situated PMe_3 ligand in the cationic tris(phosphine) complex $[PdMe(PMe_3)_3]^+BF_4^-$ with $AgBF_4$.[8]

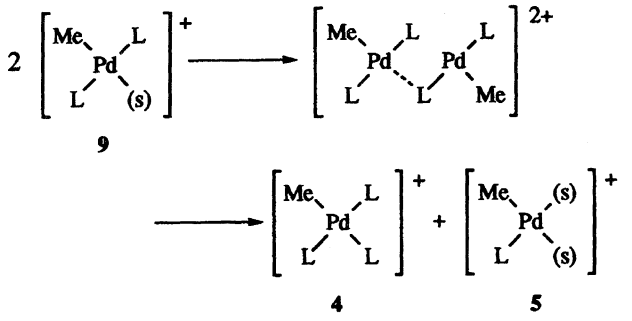
Discussion

The present study revealed the distinct difference in the effect of the phosphite ligands from that of the phosphine ligands in determining the configurations of the dimethyl and monomethylpalladium complexes. Whereas the bis(phosphine) complexes of the neutral dimethylpalladium complexes give stable complexes of trans[5,9,14] and cis[9,15] isomers depending on the preparative conditions, the corresponding neutral dimethylpalladium complexes having $P(OMe)_3$ and $P(OPh)_3$ ligands give exclusively cis isomers. On the other hand, the neutral methylpalladium chloride complexes with $P(OMe)_3$ and $P(OPh)_3$ ligands were obtained as the cis–trans mixture depending on the nature of the phosphite ligand, whereas the $P(OPr^i)_3$ ligand gave the bis(phosphite) complex only as the trans isomer **2c**. These results are in contrast with the PMe_3-coordinated neutral monomethylpalladium complexes for which only trans isomers have been obtained.

From the presently available data, no further argument to discuss the relative stabilities of the cis and trans configurations is warranted. The present data should be regarded as a basis for future discussion of the relative stability of the cis and trans isomers of the phosphine and phosphite-coordinated organopalladium complexes. However, the generally greater capability of the phosphite ligand to receive an electron by back bonding from palladium[16] may be related with the preference of the phosphite-coordinated complexes to take the cis forms, since disposition of the two alkyl and two phosphite ligands in mutually trans positions may work to destabilize the complex. Nolan et al. have reported concerning pentamethylcyclopentadienyl–ruthenium complexes that the coordinating ability of the phosphite ligands is higher than that of the phosphine ligands.[17]

The stability of the trans isomers coordinated with two PMe_3 ligands was also seen in the cationic methylpalladium complexes,[8,10,13] whereas the corresponding cationic methylpalladium complexes **9** having the two phosphite ligands seem to be very labile and tend to disproportionate instantly into the tris(phosphite) complex and monophosphite complex as soon as they are formed, unless one phosphite ligand is added to the system to trap the bis(phosphite) complex as the tris(phosphite) complex (Scheme 1).

The fact that the coordinating ability of the phosphite ligand is higher than that of the PMe_3 ligands makes the dissociation of the phosphite ligand from the palladium center less likely. The higher lability of the putative bis(phosphite)-coordinated cationic methylpalladium complex **9** to disproportionate into the tris- and monophosphite complexes may be due to the inclination of the cationic monomethylpalladium complexes having the two phosphite ligands **9** to interact with another bis(phosphite) species by a bimolecular mechanism, as shown below.



(13)

We plan to prepare the corresponding organoplatinum complexes with the phosphine and phosphite ligands and compare the NMR spectra with those of the palladium analogs to get further information concerning the difference in the behavior of the phosphine and phosphine-coordinated complexes.

Experimental

General Procedures. All the manipulations were performed under argon atmosphere by using Schlenk techniques. $[PdMe_2(cod)]$[15b] and [PdMe(Cl)(cod)][18] were synthesized by literature methods. All the phosphites and the other reagents were used as received from commercial suppliers. Solvents were dried, distilled, and stored under argon. ^1H (270 MHz, referenced to $SiMe_4$ via residual solvent protons), $^{13}C\{^1H\}$ (67.9 MHz, referenced to $SiMe_4$ via the solvent resonance), and $^{31}P\{^1H\}$ (109.4 MHz, referenced to 85% H_3PO_4 as an external standard) NMR were recorded on a JEOL EX-270 spectrometer. Coupling constants (J values) are given in hertz (Hz), and spin multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), sept (septet), m (multiplet), vt (virtual triplet), and br (broad). Gas chromatographic (GC) analyses were carried out on a Hitachi 263-50 equipped with a Gasukuropack 54 (80—100 mesh, 3 mm×2 m) column, using N_2 as carrier gas. Elemental analyses were carried out using a Yanako MT-3.

Preparation of Dimethylpalladium Complex *cis*-$[PdMe_2\{P(OMe)_3\}_2]$ (1a) by Treatment of $[Pd(acac)_2]$ with $[AlMe_2(OEt)]$ and $P(OMe)_3$. A suspension of $[Pd(acac)_2]$ (1.00 g, 3.3 mmol) in ether (40 mL) was cooled to −70 °C, and hexane solutions containing $AlMe_2(OEt)$ (7.0 mL, 7.0 mmol) and $P(OMe)_3$ (775 μL, 6.6 mmol) were added. After being stirred at −70—−30 °C for 3 h, the reactant changes to a colorless clear solution. The solution was reduced in volume to ca. 10 mL to give $Al(acac)_3$ and palladium black as precipitates, which were removed by filtration. After the mother liquid was allowed to stand for 1 week at −30 °C, colorless crystals were obtained. The crystals were washed with hexane (1 mL×2) and dried in vacuo. Yield: 334 mg (26%). ^1H NMR (acetone-d_6, −30 °C) δ=3.60—3.55 (18H, $P(OCH_3)_3$, m), 0.14 (6H, $PdCH_3$, s); $^{31}P\{^1H\}$ NMR (acetone-d_6, −30 °C) δ=143.1; $^{13}C\{^1H\}$ NMR (acetone-d_6, −30 °C) δ=51.6 ($P(OCH_3)_3$), 3.3 ($PdCH_3$, m, $^2J_{PC}$=29.6 and 161.3 Hz) (see: Fig. 1). Found: C, 24.98; H, 6.80%. Calcd for $C_8H_{24}O_6P_2Pd$: C, 24.98; H, 6.29%.

Preparation of Dimethylpalladium Complex *cis*-[$PdMe_2${P(OPh)$_3$}$_2$] (1b) by Treatment of [$PdMe_2$(cod)] with Two Molar Amounts of P(OPh)$_3$. P(OPh)$_3$ (1.6 mL, 6.14 mmol) was added dropwise to a CH_2Cl_2 (7.5 mL) solution of [$PdMe_2$(cod)] (724 mg, 2.96 mmol) at −30 °C. Stirring the solution for 1 h at −30 °C followed by evaporation of the solvent afforded white powder, which was washed with hexane (3×3 mL) and dried in vacuo. Yield: 2.120 g (95%). ^{1}H NMR (acetone-d_6, −20 °C) δ=7.35 (12H, *m*-Ph, dd, $^3J_{HH}$=7.3 and 8.1 Hz), 7.21 (6H, *p*-Ph, t, $^3J_{HH}$=7.3 Hz), 7.12 (12H, *o*-Ph, d, $^3J_{HH}$=8.1 Hz), −0.09 (6H, PdCH_3, s); ^{31}P{^{1}H} NMR (acetone-d_6, −20 °C) δ=124.2; ^{13}C{^{1}H} NMR (acetone-d_6, −20 °C) δ=152.4, 131.0, 126.0, 121.8 (*ipso*-Ph, t, $^3J_{PC}$=2.7 Hz), 4.6 (PdCH$_3$, m, $^2J_{PC}$=28.2 and 158.6 Hz). Found: C, 60.08; H, 5.07%. Calcd for $C_{38}H_{36}O_6P_2Pd$: C, 60.29; H, 4.79%.

The same procedure could be employed for the preparation of the P(OMe)$_3$-coordinated complex to give **1a** in 90% yield. The NMR spectrum showed identical resonances with the sample prepared by the procedure described above.

Preparation of Chloro(methyl)bis(phosphite)palladium Complexes [PdMe(Cl)(L)$_2$] (2) (L=P(OMe)$_3$, P(OPh)$_3$, and P(OPr^i)$_3$) by Treatment of [PdMe(Cl)(cod)] with Two Molar Amounts of Phosphite L. [PdMe(Cl){P(OPh)$_3$}$_2$] (2b): P(OPh)$_3$ (2.5 mL, 9.59 mmol) was added dropwise to [PdMe(Cl)(cod)] (1.06 g, 3.98 mmol) suspended in ether (25 mL) at −10 °C. After the suspension was stirred for 4 h at 0 °C, the upper organic layer was removed by filtration. The residue was washed with ether (2×3 mL) and hexane (3 mL) and dried in vacuo to give white powder, which was recrystallized from cold ether. Yield: 1.388 g (45%). ^{1}H NMR (acetone-d_6, 25 °C) δ=7.5—7.0 (30H, Ph, m), 0.58 (cis form, PdCH_3, dd, $^3J_{PH}$=2.6 and 11.7 Hz), 0.36 (trans form, PdCH_3, br); ^{31}P{^{1}H} NMR (acetone-d_6, 25 °C) δ=115.8 (cis form, d, $^2J_{PP}$=82 Hz), 109.8 (cis form, d, $^2J_{PP}$=82 Hz), 108.7 (trans form, s); ^{13}C{^{1}H} NMR (acetone-d_6, 25 °C) δ=152.5, 152.0, 151.9, 131.4, 131.2, 129.7, 126.9, 126.6, 126.4, 122.3, 122.0, 121.7 (P(O*Ph*)$_3$), 8.9 (cis form, PdCH$_3$, d, $^2J_{PC}$=143.9 Hz), −5.4 (trans form, PdCH$_3$, s). Found: C, 57.45; H, 4.36%. Calcd for $C_{37}H_{33}O_6P_2ClPd$: C, 57.16; H, 4.28%.

[PdMe(Cl){P(OMe)$_3$}$_2$] (2a): P(OMe)$_3$ (664 μl, 2.81 mmol) was added dropwise to [PdMe(Cl)(cod)] (745 mg, 2.81 mmol) dissolved in CH_2Cl_2 (10 mL) at −10 °C. After the solution was stirred for 2 h at 0 °C, the solvent was removed by evaporation. The residue was washed with hexane (5 mL×2) and dried in vacuo to give white powder, which was recrystallized from acetone and hexane. Yield: 482 mg (42%). ^{1}H NMR (acetone-d_6, −20 °C) δ=3.75 (18H, P(OCH_3)$_3$, vt, J_{PH}=6.2 Hz), 0.80 (cis form, PdCH_3, d, $^3J_{PH}$=11.4 Hz), 0.66 (trans form, PdCH_3, t, $^3J_{PH}$=5.0 Hz); ^{31}P{^{1}H} NMR (acetone-d_6, −20 °C) δ=131.7 (cis form, d, $^2J_{PP}$=76 Hz), 125.2 (trans form, s), 124.5 (cis form, d, $^2J_{PP}$=76 Hz); ^{13}C{^{1}H} NMR (acetone-d_6, −20 °C) δ=53.2 (P(OCH_3)$_3$, cis complex), 53.1 (P(OCH_3)$_3$, trans complex), 52.6 (cis complex, P(OCH_3)$_3$), −4.3 (PdCH$_3$), −7.2 (PdCH$_3$). Found: C, 20.79; H, 5.33%. Calcd for $C_7H_{21}O_6P_2ClPd$: C, 20.76; H, 5.23%.

[PdMe(Cl){P(OPr^i)$_3$}$_2$] (2c): P(OPr^i)$_3$ (1.88 mL, 8.22 mmol) was added dropwise to [PdMe(Cl)(cod)] (1.09 g, 4.11 mmol) dissolved in CH_2Cl_2 (10 mL) at −10 °C. After stirring the solution for 2 h at 0 °C, the solvent was removed by evaporation. The residue was washed with hexane (1 mL) and dried in vacuo to give white powder which was recrystallized from hexane. Yield: 526 mg (22%). ^{1}H NMR (acetone-d_6, −20 °C) δ=5.07 (6H, P{OCH(CH$_3$)$_2$}$_3$, sept, $^3J_{HH}$=5.9 Hz), 1.31 (36H, P{OCH(CH_3)$_2$}$_3$, d, $^3J_{HH}$=5.9 Hz), 0.76 (3H, PdCH_3, t, $^3J_{PH}$=4.6 Hz); ^{31}P{^{1}H} NMR (acetone-d_6, −20 °C) δ=116.2 (s); ^{13}C{^{1}H} NMR (acetone-d_6, −20 °C) δ=71.2 (P{O*C*H(CH$_3$)$_2$}$_3$), 24.7 (P{OCH(*C*H$_3$)$_2$}$_3$), −0.47 (PdCH$_3$). Found: C, 39.26; H, 7.66%. Calcd for $C_{19}H_{45}O_6P_2ClPd$: C, 39.80; H, 7.91%.

Reaction of Dimethylbis(phosphite)palladium Complexes with Protic Acid. [PdMe(OAc){P(OMe)$_3$}$_2$] (3a): AcOH (3.6 μL, 0.063 mmol) was added to an acetone-d_6 (0.45 mL) solution of [$PdMe_2${P(OMe)$_3$}$_2$] (24.3 mg, 0.063 mmol) at 0 °C in an NMR tube, which was shaken and kept for 1 d at 0 °C. ^{1}H NMR ($CDCl_3$, 22 °C) δ=3.80—3.60 (18H, P(OCH_3)$_3$, m), 2.01 (3H, OCOCH_3, br), 0.68 (cis form, PdCH_3, d, $^3J_{PH}$=10.6 Hz), 0.29 (trans form, PdCH_3, t, $^3J_{PH}$=5.7 Hz); ^{31}P{^{1}H} NMR (acetone-d_6, −20 °C) δ=133.1 (cis form, d, $^2J_{PP}$=73.4 Hz), 128.3 (cis form, d, $^2J_{PP}$=73.4 Hz), 124.7 (trans form, s).

The same procedure was employed for the reaction of the triphenyl phosphite-coordinated complex.

[PdMe(OAc){P(OPh)$_3$}$_2$] (3b): ^{1}H NMR (acetone-d_6, −20 °C) δ=7.6—6.8 (30H, Ph, m), 2.01 (3H, OCOCH_3, s), 0.28 (cis form, PdCH_3, d, $^3J_{PH}$=10.6 Hz), 0.26 (trans form, PdCH_3, s); ^{31}P{^{1}H} NMR (acetone-d_6, −20 °C) δ=123.7 (trans form, s), 116.6 (cis form, d, $^2J_{PP}$=79.2 Hz), 110.0 (cis form, d, $^2J_{PP}$=79.2 Hz).

Treatment of [$PdMe_2$(P(OPh)$_3$)$_2$] (2b) with AcSH and PhSH in NMR Tube. To a solution of [$PdMe_2$(P(OPh)$_3$)$_2$] (10.0 mg, 0.013 mmol) in acetone-d_6 (0.45 mL) was added 2.5 molar amounts of PhSH (3.4 μl, 0.033 mmol) at −80 °C in NMR tube. Formation of methane (about 2 mol/Pd) was confirmed by GC. The original ^{1}H NMR spectrum of **2b** was replaced by a spectrum suggesting the formation of [Pd(SPh)$_2${P(OPh)$_3$}$_2$]. Further isolation and characterization were not carried out. The same procedure was employed for the reaction with AcSH.

Preparation of [PdMe(L)$_3$]$^+$BF$_4^-$ (4) (L=P(OMe)$_3$, P(OPh)$_3$, and P(OPr^i)$_3$).[19] [PdMe{P(OPh)$_3$}$_3$]$^+$BF$_4^-$ (4b): A solution of $AgBF_4$ (95.4 mg, 0.490 mmol) in acetone (0.4 mL) was added dropwise to a CH_2Cl_2 (10 mL) solution of [PdMe(Cl){P(OPh)$_3$}$_2$] (**2b**) (381 mg, 0.490 mmol, cis and trans mixture) in the presence of P(OPh)$_3$ (128 μL, 0.491 mmol) at −78 °C. The immediately formed white precipitate was removed by filtration to give a colorless solution. The solution was evaporated to afford a white solid, which was washed with hexane (2×3 mL) and dried in vacuo to give a white powder. Yield: 431 mg (77%), white powder. ^{1}H NMR (acetone-d_6, −20 °C) δ=7.6—6.9 (45H, Ph, m), 0.18 (3H, PdCH_3, dt, $^3J_{PH}$=8.4 and 6.6 Hz); ^{31}P{^{1}H} NMR (acetone-d_6, −20 °C) δ=112.6 (1P, trans to the methyl ligand, t, $^2J_{PP}$=88.0 Hz), 105.4 (2P, cis to the methyl ligand, d, $^2J_{PP}$=88.0 Hz). Found: C, 57.07; H, 4.13%. Calcd for $C_{55}H_{48}BF_4O_9P_3Pd$: C, 57.99; H, 4.25%.

[PdMe{P(OMe)$_3$}$_3$]$^+$BF$_4^-$ (4a): ^{1}H NMR (acetone-d_6, −20 °C) δ=3.83 (27H, P(OCH_3)$_3$, br), 0.66 (3H, PdCH_3, dt, $^3J_{PH}$=9.2 and 6.2 Hz); ^{31}P{^{1}H} NMR (acetone-d_6, −20 °C) δ=126.5 (1P, trans to methyl ligand, t, $^2J_{PP}$=76.3 Hz,) 124.1 (2P, cis to methyl ligand, d, $^2J_{PP}$=76.3 Hz). Found: C, 21.42; H, 5.50%. Calcd for $C_{10}H_{30}BF_4O_9P_3Pd$: C, 20.69; H, 5.21%.

[PdMe{P(OPr^i)$_3$}$_3$]$^+$BF$_4^-$ (4c): Yield: 66%, white powder. ^{1}H NMR (acetone-d_6, −20 °C) δ=4.81 (9H, P{OCH(CH$_3$)$_2$}$_3$, m), 1.42 (54H, P{OCH(CH_3)$_2$}$_3$, m), 0.70 (3H, PdCH_3, dt, $^3J_{PH}$=9.2 and 6.2 Hz); ^{31}P{^{1}H} NMR (acetone-d_6, −20 °C) δ=112.7 (1P, trans to the methyl ligand, t, $^2J_{PP}$=76.3 Hz), 114.7 (2P, cis to the methyl ligand, d, $^2J_{PP}$=76.3 Hz). Found: C, 40.31; H, 8.15%. Calcd for $C_{28}H_{66}BF_4O_9P_3Pd$: C, 40.37; H, 7.99%.

Preparation of Chloro(methyl)(phosphite)palladium Complexes [PdMe(Cl)(L)]$_2$ (6) (L=P(OMe)$_3$, P(OPh)$_3$, and P(OPr^i)$_3$) by Treatment of [PdMe(Cl)(cod)] with One Molar Amount of Phosphite L. The synthesis of P(OMe)$_3$-coordinated dimeric methylpalladium complex **6a** has been already reported.[20] The

same procedure was employed for the preparation of the other phosphite complexes. The $P(OPr^i)_3$-coordinated complex **6c** was not isolated but generated in situ.

[PdMe(Cl){P(OMe)$_3$}]$_2$ (6a) : By treatment of [PdMe(Cl)-(cod)] (322 mg, 1.21 mmol) with $P(OMe)_3$ (144 μl, 1.22 mmol) 222mg (65%) of **6a** was obtained as white powder. ^{1}H NMR (acetone-d_6, 22 °C) δ=3.77 (18H, P(OCH_3)$_3$, d, J_{PH}=12.8 Hz), 0.78 (6H, PdCH_3, s); ^{31}P{^{1}H} NMR (acetone-d_6, 22 °C) δ=119.2 (s); ^{13}C{^{1}H} NMR (acetone-d_6, 22 °C) δ=53.5 (P(OCH_3)$_3$), 0.6 (d, PdCH_3, $^2J_{PC}$=4.1 Hz). Found: C, 17.53; H, 4.55%. Calcd for $C_8H_{24}O_6P_2Cl_2Pd_2$: C, 17.10; H, 4.30%.

[PdMe(Cl){P(OPh)$_3$}]$_2$ (6b) : By treatment of [PdMe(Cl)-(cod)] (334 mg, 1.26 mmol) with $P(OPh)_3$ (328 μl, 1.26 mmol) 419 mg (71%) of **6b** was obtained as white powder. ^{1}H NMR (acetone-d_6, 22 °C) δ=7.5—7.2 (30H, Ph, m), 0.74 (6H, PdCH_3, s); ^{31}P{^{1}H} NMR (acetone-d_6, 22 °C) δ=124.0 (s); ^{13}C{^{1}H} NMR (acetone-d_6, 22 °C) δ=151.9 (d, *ipso*-Ph, J_{PC}=6.7 Hz), 131.1, 126.5, 121.8 (d, *o*-Ph, J_{PC}=5.3 Hz), 2.1 (d, PdCH_3, $^2J_{PC}$=4.0 Hz). Found: C, 48.56; H, 4.05%. Calcd for $C_{38}H_{36}O_6P_2Cl_2Pd_2$: C, 48.85; H, 3.88%.

[PdMe(Cl){P(OPr^i)$_3$}]$_2$ (6c) : ^{1}H NMR (acetone-d_6, 22 °C) δ=5.1—4.9 (6H, P{OCH(CH_3)$_2$}$_3$, m), 1.42 (36H, P{OCH-(CH_3)$_2$}$_3$, d, $^3J_{HH}$=6.4 Hz), 0.84 (6H, PdCH_3, s); ^{31}P{^{1}H} NMR (acetone-d_6, 22 °C) δ=108.8 (s); ^{13}C{^{1}H} NMR (acetone-d_6, 22 °C) δ=72.1 (d, P{OCH(CH$_3$)$_2$}$_3$, J_{PC}=2.7 Hz), 24.7 (d, P{OCH-(CH_3)$_2$}$_3$, $^2J_{PC}$=4.1 Hz), 2.5 (d, PdCH_3, $^2J_{PC}$=5.4 Hz).

Treatment of [PdMe(Cl)(L)$_2$] (2) or [PdMe(Cl)(L)]$_2$ (6) with AgBF$_4$ in NMR Tube (L=P(OMe)$_3$, P(OPh)$_3$, and P(OPr^i)$_3$). To a solution of the respective complex in acetone-d_6 (0.35 mL) was added a solution of one molar amount of $AgBF_4$ in acetone-d_6 (0.10 mL) at −78 °C in NMR tube. The NMR tube was shaken 10 times (a white suspension of silver chloride was formed immediately) and the spectrum was taken after the upper layer became clear.

[PdMe(s)$_2${P(OMe)$_3$}]$^+$BF$_4^-$ (5a) : ^{1}H NMR (acetone-d_6, −20 °C) δ=3.81 (9H, P(OCH_3)$_3$, d, J_{PH}=13.2 Hz), 0.77 (3H, PdCH_3, s); ^{31}P{^{1}H} NMR (acetone-d_6, −20 °C) δ=116.3 (s).

[PdMe(s)$_2${P(OPh)$_3$}]$^+$BF$_4^-$ (5b) : ^{1}H NMR (acetone-d_6, −20 °C) δ=7.6—7.3 (15H, Ph, m), 0.86 (3H, PdCH_3, s); ^{31}P{^{1}H} NMR (acetone-d_6, −20 °C) δ=104.6 (s).

[PdMe(s)$_2${P(OPr^i)$_3$}]$^+$BF$_4^-$ (5c) : ^{1}H NMR (acetone-d_6, −20 °C) δ=5.0—4.8 (3H, P{OCH(CH$_3$)$_2$}$_3$, m), 1.35 (18H, P{OCH(CH_3)$_2$}$_3$, d, $^3J_{HH}$=6.2 Hz), 0.80 (3H, PdCH_3, s); ^{31}P{^{1}H} NMR (acetone-d_6, −20 °C) δ=103.6 (s).

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