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Trimethylsilyl Halide Adducts of Dinuclear Phosphine-Bridged Palladium Halide Complexes: Synthesis, Spectroscopy, and Reactions of $Pd_2X_2(dppm)_2·Me_3SiX'$ (X, X' = Cl, Br, I)

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Reaction of $Pd_2X_2(dppm)_2$ (**1**, X = Cl; **2**, X = Br; **3**, X = I) with Me_3SiX' (X' = Cl, Br, I) in dichloromethane produced transient dark green solutions for all combinations of X and X' with the exception of X = X' = Cl. Net halide exchange was observed for reactions of **1** with Me_3SiBr or Me_3SiI and for **2** with Me_3SiI, apparently without oxidative addition of the silicon–halide bond. Mono- and dinuclear palladium complexes $Pd_2(\mu\text{-}CH_2)Cl_2(dppm)_2$ (**4**) and $PdCl_2(dppm)$ (**5**) also exchanged Pd–Cl bonds for Pd–Br bonds in reactions with Me_3SiBr. Low-temperature ^1H and ^{31}P NMR spectroscopy provided evidence for formation of adducts of formulas $Pd_2Cl_2(dppm)_2·Me_3SiCl$, $Pd_2Br_2(dppm)_2·Me_3SiCl$, $Pd_2Br_2(dppm)_2·Me_3SiBr$, $Pd_2I_2(dppm)_2·Me_3SiBr$, and $Pd_2I_2(dppm)_2·Me_3SiI$ in the reactions of **1**–**3** with Me_3SiX'. Dark green solids of formula $Pd_2X_2(dppm)_2·Me_3SiX'$ (**6**: (**a**) X = Cl, X' = I; (**b**) X = Br, X' = I; (**c**) X = Br, X' = Br; (**d**) X = Cl, X' = Br; (**e**) X = I, X' = Br; (**f**) X = I, X' = I) could be isolated from the reaction mixtures. The green color is proposed to result from a weakening of the metal–metal bond in **1**–**3** upon coordination of the trimethylsilyl halide. The presence of oxygen in reactions of **1**–**3** with Me_3SiX' (X = Cl, Br, I) did not interfere with the formation of the adduct but led to the formation of siloxanes and mononuclear palladium complexes $PdXX'(dppm)$. There was no evidence for Si–Si bond formation in these systems. Halide exchange was also observed in reactions of **1**, **2**, and **5** with methyl iodide.

Introduction

Crystallographic evidence for the coordination of halocarbons to transition metal complexes demonstrated a continuum of reactivity for carbon–halide bonds ranging from carbon–halide oxidative addition[1] to the notion of the halocarbons as polar, noncoordinating solvents in organometallic chemistry.[2] By comparison, relatively few examples of oxidative addition of silicon–halide bonds to transition metal centers have been reported.[3]

The activation of silicon–element bonds in organosilicon compounds by transition metal complexes has relevance in the catalytic preparation of polysilanes and has served as a broad theme for the present research.[4] The work discussed herein stems from the observation of green solutions when trimethylsilyl halides $Me_3Si\text{–}X'$ (X' = Cl, Br, I) were reacted with orange to red solutions of $Pd_2X_2(dppm)_2$ (**1**, X = Cl; **2**, X = Br; **3**, X = I) (reaction 1). Halide-exchange reactions between Si–Br/Pd–Cl, Si–I/Pd–Cl, and Si–I/Pd–Br bonds were observed yet appeared to proceed *without* oxidative addition of the silicon–halide to the metal center.

$$Pd_2X_2(dppm)_2 + 2Me_3SiX' \rightarrow Pd_2X'_2(dppm)_2 + 2Me_3SiX$$

$$X = Cl;\ X' = Br, I$$

$$X = Br;\ X' = I \qquad (1)$$

Experimental Section

All compounds described in this work were handled using Schlenk techniques, using a M. I. Braun glovebox under a purified argon or nitrogen atmosphere or on a vacuum line equipped with oil diffusion and mechanical pumps (10^{-3} Torr).[5] Solvents were purified by refluxing over Na/benzophenone (benzene, toluene, tetrahydrofuran), Na (hexane), or P_2O_5 (dichloromethane) and distilled prior to use. Deuterated dichloromethane (CD_2Cl_2) was purchased from Aldrich and dried as described above. The dried solvent was degassed with five freeze/pump/thaw cycles on a vacuum line and transfered into NMR tubes under vacuum. Me_3SiCl, Me_3SiBr, and Me_3SiI were purchased from Huls-America (Petrarch) or Aldrich. Me_3SiCl and Me_3SiBr were dried over P_2O_5 and degassed with five freeze/pump/thaw cycles on a high-vacuum line before storing over $Pd_2(dppm)_2Cl_2$ under vacuum. Great care was taken to dry the reagents and to rigorously exclude oxygen from the system. It was found that $Pd_2(dppm)_2Cl_2$ (**1**) was a particularly effective oxygen scavenger in halosilanes. Me_3SiI was transferred from a sealed vial in the glovebox, stored over copper, and degassed as described. Methyl iodide was purchased from Aldrich, dried over P_2O_5, and treated in the same fashion as the silicon reagents. $PdCl_2$, $PdBr_2$, triphenylphosphine, and bis(diphenylphosphino)methane (dppm) were purchased from Strem Chemicals and used as received. $Pd_2X_2(dppm)_2$ (**1**–**3**),[6] $Pd_2(\mu\text{-}CH_2)Cl_2dppm_2$ (**4**),[7] and $PdCl_2(dppm)$ (**5**)[8] were prepared by literature methods.

^1H and $^{31}P\{^1H\}$ spectra were recorded on a Varian 300XL spectrometer in either flame-sealed 5-mm NMR tubes or in 5-mm tubes equipped with a Teflon valve (J. Youngs). Proton chemical shifts are relative to residual

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Table I. UV/Vis Spectral Data for Reactions of $Pd_2X_2(dppm)_2$

	λ_{max}		
ligand	$Pd_2Cl_2(dppm)_2$	$Pd_2Br_2(dppm)_2$	$Pd_2I_2(dppm)_2$
CH_2Cl_2[a]	426	427	439, 488
CH_2Br_2[a]	426	429	442, 485
MeI[b]	426	428	439, 488
Me_3SiCl[b]	426	599	650
Me_3SiBr[b]	603	608	648
Me_3SiL[b]	652	662	662

[a] Neat. [b] Solutions in CH_2Cl_2.

protons in the solvent ($CD\mathit{H}Cl_2$ at δ 5.24 ppm). Phosphorus chemical shifts are relative to external 85% H_3PO_4. UV/vis spectra were recorded on a Perkin-Elmer Lambda 4B UV/vis spectrometer (Table I). Volatile products were analyzed by a combination of gas chromatography/mass spectrometry (GC/MS) using a 0.20-mm × 1.25-m capillary silica column cross-linked with 5% methylphenyl silicone and helium carrier gas in a Hewlett Packard HP 5890A gas chromatograph equipped with a HP 5970 mass selective detector. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

NMR Studies of the Reactions of Metal Complexes with Silicon–Halide Bonds. General Procedure. Solid samples of **1–5** were placed in 5-mm NMR tubes and attached to the vacuum system. The tubes were evacuated overnight at room temperature and 10^{-3} Torr to remove any adsorbed oxygen. The samples were cooled to −196 °C, and dichloromethane-d_2 was vacuum transferred into the tubes. After thawing to allow the metal complexes to dissolve, the yellow to red solutions were refrozen at −196 °C. Me_3SiX' was expanded into a section of the vacuum system with a previously determined volume and condensed into the NMR tubes. The amount of Me_3SiX' used was determined by measurement of the pressure using a mercury manometer and calculation from the *PV* data. The tubes were subsequently sealed, by closing the Teflon valve or by flame sealing under vacuum. The tubes could be stored for days at −196 °C with no apparent changes.

Reaction of $Pd_2Cl_2(dppm)_2$ with Me_3SiCl. Upon thawing of a CD_2Cl_2 solution of 0.022 g (2.1×10^{-5} mol) of $Pd_2Cl_2(dppm)_2$ and 2.8×10^{-5} mol of Me_3SiCl at −78 °C, no color changes were observed in the orange solution. Low-temperature NMR spectra (−88 to +25 °C) are discussed under Results. After 5 d at room temperature, Me_3SiCl (^1H, δ 0.36, s, 94%), $Me_3SiOSiMe_3$ (^1H, δ 0.03, s, 6%), $Pd_2Cl_2(dppm)_2$ (^1H, δ 4.08, m, PCH_2P; ^{31}P, δ −2.90, s, 92%), and $PdCl_2(dppm)$ (^1H, δ 4.18, t, PCH_2P; ^{31}P, δ −54.1, s, 8%) were identified by NMR. Product ratios were determined by integration of the peak areas for the products and are judged to be accurate to ±5%, accounting for discrepancies between the ^1H and ^{31}P data.

Reaction of $Pd_2Cl_2(dppm)_2$ with Me_3SiBr. Upon thawing of a CD_2Cl_2 solution of 0.018 g (1.7×10^{-5} mol) of $Pd_2Cl_2dppm_2$ and 1.7×10^{-5} mol of Me_3SiBr at −78 °C, a dark green solution was observed. Shaking the tube did not discharge the color. The color persisted for 1–2 h at room temperature. The color could be maintained for >8 h at −78 °C. After 5 days at room temperature, Me_3SiCl (δ 0.36, s, 75%), $Me_3SiOSiMe_3$ (^1H, δ 0.03, s, 25%), $Pd_2Br_2(dppm)_2$ (^1H, δ 4.11, m, PCH_2P; ^{31}P, δ −5.29, s, 79%), $PdBr_2(dppm)$ (^1H, δ 4.25, t, PCH_2P; ^{31}P, −55.7, s), $PdCl_2(dppm)$ (^1H, δ 4.18, t, PCH_2P; ^{31}P, δ −54.1, s), and $PdClBr(dppm)$ (^{31}P, δ −53.9 d, J_{PP} = 62 Hz, −56.2, d) were identified by ^1H and ^{31}P NMR. The mononuclear products comprised 21% of the products as determined by ^{31}P NMR.

The volatiles were vacuum transferred from the reaction (carried out in the Teflon-capped NMR tube). Hexamethyldisiloxane ($Me_3SiOSiMe_3$) and trimethylsilyl chloride were identified as the sole silicon-containing products by GC/MS (parent peaks at *m/e* = 162 and 108, respectively).

Reaction of $Pd_2Cl_2(dppm)_2$ with Me_3SiI. Upon thawing of a CD_2Cl_2 solution of 0.021 g (2.0×10^{-5} mol) of $Pd_2Cl_2(dppm)_2$ and 3.8×10^{-5} mol of Me_3SiI, at −78 °C, a dark green solution was observed. Shaking the tube did not discharge the color. Low-temperature NMR spectra (−88 to +25 °C) are discussed under Results. The color persisted for at least 36 h at room temperature and much longer at −78 °C. After 36 h at room temperature, Me_3SiCl (^1H, δ 0.36, s, 68%), $Me_3SiOSiMe_3$ (^1H, δ 0.03, s, 12%), Me_3SiI (^1H, δ 0.72, s, 20%), $Pd_2I_2(dppm)_2$ (^1H, δ 4.20, m, PCH_2P; ^{31}P, δ −10.6, s, 30%) and $PdI_2(dppm)$ (^1H, δ 4.48, t, PCH_2P; ^{31}P, −62.0, s, 10%) were identified by ^1H and ^{31}P NMR. Other resonances (^1H, δ 5.06, br s, PCH_2P; ^{31}P, −2.70, br s, 60%) were assigned to the green compound.

Reaction of $Pd_2Br_2(dppm)_2$ with Me_3SiCl. Upon thawing of a CD_2Cl_2 solution of 0.017 g (1.5×10^{-5} mol) of $Pd_2Br_2(dppm)_2$ and 6.0×10^{-5} mol of Me_3SiCl, at −78 °C, a green solution was observed. Shaking the tube did not discharge the color. The color persisted for 1–2 h at room temperature. Low-temperature NMR spectra (−88 to +25 °C) are discussed under Results. After 5 days at room temperature, Me_3SiCl (^1H, δ 0.36, s, 86%), $Me_3SiOSiMe_3$ (^1H, δ 0.03, s, 14%), $Pd_2Br_2(dppm)_2$ (^1H, δ 4.11, m, PCH_2P; ^{31}P, δ −5.29, s, 86%), and $PdBr_2(dppm)$ (^1H, δ 4.25, t, PCH_2P; ^{31}P, −55.7, s, 14%) were identified by NMR.

Reaction of $Pd_2Br_2(dppm)_2$ with Me_3SiBr. Upon thawing of a CD_2Cl_2 solution of 0.024 g (2.1×10^{-5} mol) of $Pd_2Br_2(dppm)_2$ and 2.2×10^{-5} mol of Me_3SiBr, at −78 °C, a dark green solution was observed. The color persisted for at least 12 h at room temperature. Low-temperature NMR spectra (−88 to +25 °C) are discussed under Results. After 5 days at room temperature, Me_3SiBr (^1H, δ 0.51, s, 80%), $Me_3SiOSiMe_3$ (^1H, δ 0.03, s, 20%), $Pd_2Br_2(dppm)_2$ (^1H, δ 4.11, m, PCH_2P; ^{31}P, δ −5.29, s, 83%), and $PdBr_2(dppm)$ (^1H, δ 4.25, t, PCH_2P; ^{31}P, −55.7, s, 17%) were identified by NMR.

Reaction of $Pd_2Br_2(dppm)_2$ with Me_3SiI. Upon thawing of a CD_2Cl_2 solution of 0.012 g (1.0×10^{-5} mol) of $Pd_2Br_2(dppm)_2$ and 1.8×10^{-5} mol of Me_3SiI, at −78 °C, a dark green solution was observed. Shaking the tube did not discharge the color. The color persisted for 10–12 h at room temperature. Low-temperature NMR spectra (−88 to +25 °C) are discussed under Results. After 5 days at room temperature, Me_3SiBr (^1H, δ 0.51, s, 67%), Me_3SiI (^1H, δ 0.72, s, 11%), $Me_3SiOSiMe_3$ (^1H, δ 0.03, s, 22%), $Pd_2I_2(dppm)_2$ (^1H, δ 4.20, m, PCH_2P; ^{31}P, δ −10.6, s, 72%), and $PdI_2(dppm)$ (^1H, δ 4.48, t, PCH_2P; ^{31}P, −62.0, s, 28%) were identified by NMR.

Reaction of $Pd_2I_2(dppm)_2$ with Me_3SiCl. Upon thawing of a CD_2Cl_2 solution of 0.0056 g (4.5×10^{-6} mol) of $Pd_2Cl_2(dppm)_2$ and 2.0×10^{-5} mol of Me_3SiCl, at −78 °C, a dark green solution was observed. Low-temperature NMR spectra (−88 to +25 °C) are discussed under Results. Shaking the tube did not discharge the color. The color persisted for 10–12 h at room temperature and considerably longer at −78 °C. After 5 days at room temperature, Me_3SiCl (^1H, δ 0.36, s, 70%), $Me_3SiOSiMe_3$ (^1H, δ 0.03 ppm, s, 30%), $Pd_2I_2(dppm)_2$ (^1H, δ 4.20, m, PCH_2P; ^{31}P, δ −10.6, s, 67%), $PdCl_2(dppm)$ (^1H, δ 4.18, t, PCH_2P; ^{31}P, δ −54.1), $PdClI(dppm)$ (^{31}P, δ −52.5, d, J_{PP} = 59 Hz, −63.8, d), and $PdI_2(dppm)$ (^1H, δ 4.48, t, PCH_2P; ^{31}P, −62.0, s) were identified by NMR. The mononuclear palladium products comprised 33% of the palladium products as determined by ^{31}P NMR.

Reaction of $Pd_2I_2(dppm)_2$ with Me_3SiBr. Upon thawing of a CD_2Cl_2 solution of 0.014 g (1.1×10^{-5} mol) of $Pd_2I_2(dppm)_2$ and 2.2×10^{-5} mol of Me_3SiBr, at −78 °C, a dark green solution was observed. Shaking the tube did not discharge the color. Low-temperature NMR spectra (−88 to +25 °C) are discussed under Results. The color persisted for about 24 h at room temperature. After 5 days at room temperature, Me_3SiBr (^1H, δ 0.51, s, 94%), $Me_3SiOSiMe_3$ (^1H, δ 0.03, s, 6%), $Pd_2I_2(dppm)_2$ (^1H, δ 4.20, m, PCH_2P; ^{31}P, δ −10.6, s, 90%), and $PdI_2(dppm)$ (^1H, δ 4.48, t, PCH_2P; ^{31}P, −62.0, s, 10%) were identified by ^1H and ^{31}P NMR.

Reaction of $Pd_2I_2(dppm)_2$ with Me_3SiI. Upon thawing of a CD_2Cl_2 solution of 0.023 g (1.9×10^{-5} mol) of $Pd_2I_2(dppm)_2$ and 3.4×10^{-5} mol of Me_3SiI, at −78 °C, a dark green color was observed. Low-temperature NMR spectra (−88 to +25 °C) are discussed under Results. The color persisted for 36 h or more at room temperature before fading to a brown and then a red color. After 36 h at room temperature, Me_3SiI (^1H, δ 0.72, s, 90%), $Me_3SiOSiMe_3$ (^1H, δ 0.03, s, 10%), $Pd_2I_2(dppm)_2$ (^1H, δ 4.20, m, PCH_2P; ^{31}P, δ −10.6, s, 41%), and $PdI_2(dppm)$ (^1H, δ 4.48, t, PCH_2P; ^{31}P, −62.0, s, 4%) were identified by NMR. Other resonances (^1H, δ 5.02, br s, PCH_2P; ^{31}P, −2.73, br s, 55%) were assigned to the green compound.

Reaction of $Pd_2Cl_2(\mu\text{-}CH_2)(dppm)_2$ with Me_3SiBr. Upon thawing of a CD_2Cl_2 solution of 0.012 g (1.1×10^{-5} mol) of $Pd_2Cl_2(\mu\text{-}CH_2)(dppm)_2$ and 1.5×10^{-5} mol of Me_3SiBr, no color changes were observed. After 36 h at room temperature, Me_3SiCl (^1H, δ 0.36, s) and $Pd_2Br_2(\mu\text{-}CH_2)(dppm)_2$ (^1H, δ 4.28, m, PCH_2P) were identified by NMR. Formation of $Me_3SiOSiMe_3$ was not detected by ^1H NMR after the tube was opened to air and reacted for 5 days.

Reaction of $PdCl_2(dppm)$ with Me_3SiBr. Upon thawing of a solution of 0.010 g (1.8×10^{-5} mol) of $PdCl_2(dppm)$ and 4.0×10^{-5} mol of Me_3SiBr, no color changes were observed. After 36 h, the solution was slightly more yellow in color. Me_3SiCl (^1H, δ 0.36, s) and $PdBr_2(dppm)$ (^{31}P, δ −55.7, s) were identified by NMR. The tube was opened to air and allowed to react at room temperature for several days. Formation of $Me_3SiOSiMe_3$ was not detected by ^1H NMR.

Reactions of $Pd_2Cl_2(dppm)_2$ with Me_3SiBr in the Presence of Ligands L = C_2H_4, CO, HBr, and O_2. L = Ethylene. A CD_2Cl_2 solution containing 0.017 g (1.6×10^{-5} mol) of $Pd_2Cl_2(dppm)_2$ and 4.4×10^{-5} mol of ethylene was prepared as described above yielding an orange-red solution (no color change). Addition of 4.0×10^{-5} mol of $\mathrm{Me_3SiBr}$ at -196 °C and thawing produced the same green solution observed above. After 12 h at room temperature, $\mathrm{Me_3SiCl}$ (δ 0.36, s, 32% of Si-containing products), $\mathrm{Me_3SiBr}$ (δ 0.51, s, 66% of Si-containing products), $\mathrm{Me_3SiOSiMe_3}$ (δ 0.03, s, 2% of Si-containing products), $\mathrm{Pd_2X_2(dppm)_2}$ (^{1}H, δ 4.13, m, X = Cl, Br), and $\mathrm{PdBr_2(dppm)}$ (δ 4.25, t) were identified by ^{1}H NMR. While the green color disappeared after ~24 h, the ratio of Si-containing products remained essentially unchanged for 1 month at room temperature.

L = Carbon Monoxide. Two experiments were carried out under carbon monoxide. $\mathrm{Me_3SiBr}$, 3.3×10^{-5} mol, was condensed onto a frozen $\mathrm{CD_2Cl_2}$ solution containing 0.028 g (2.6×10^{-5} mol) of $\mathrm{Pd_2Cl_2(dppm)_2}$. A 510-Torr pressure of CO was introduced, and the tube was sealed. Upon thawing, a green color was observed but accompanied by rapid precipitation of a red solid. The green color was qualitatively less intense in this reaction than in mixtures of $\mathrm{Pd_2Cl_2(dppm)_2/Me_3SiBr}$. After 12 h at room temperature, $\mathrm{Me_3SiCl}$ (δ 0.36, s, 66%), $\mathrm{Me_3SiBr}$ (δ 0.51, s, 19%), $\mathrm{Me_3SiOSiMe_3}$ (δ 0.03, s, 15%), $\mathrm{Pd_2Br_2(\mu\text{-}CO)(dppm)_2}$ (^{31}P, δ 19.1, s, 65% of soluble palladium products), and $\mathrm{PdBr_2(dppm)}$ (δ 4.25, t, $\mathrm{PC}\mathit{H}_2\mathrm{P}$; ^{31}P, -55.7, s, 35%) were identified by ^{1}H and ^{31}P NMR.

In a second experiment, CO was added to a solution of $\mathrm{Pd_2Cl_2(dppm)_2}$ in $\mathrm{CD_2Cl_2}$ precipitating $\mathrm{Pd_2Cl_2(\mu\text{-}CO)(dppm)_2}$. This solution was frozen at -196 °C and $\mathrm{Me_3SiBr}$ condensed into the tube. After thawing, a green color was observed, although the color was qualitatively less intense in this reaction than in mixtures of $\mathrm{Pd_2Cl_2(dppm)_2/Me_3SiBr}$.

L = Hydrogen Bromide. A $\mathrm{CD_2Cl_2}$ solution containing 0.015 g (1.4×10^{-5} mol) of $\mathrm{Pd_2Cl_2(dppm)_2}$ was prepared as described above yielding an orange-red solution. HBr, 3.3×10^{-5} mol, was condensed into the tube at -196 °C. After sealing, the tube was thawed at 0 °C. As the top of the solution began to melt, a green color was observed. Shaking the partially thawed tube caused a discharge of the green color (<15 s). $\mathrm{Pd_2X_2(dppm)_2}$ (^{1}H, δ 4.13 br s, $\mathrm{PC}\mathit{H}_2\mathrm{P}$; ^{31}P, δ -5.29, s, X = Br, and δ -2.94, s, X = Cl, 45%) and $\mathrm{PdX_2(dppm)}$ (δ 4.25, t, $\mathrm{PC}\mathit{H}_2\mathrm{P}$; ^{31}P, -55.7, s, $\mathrm{X_2}$ = Br, -54.1, s, $\mathrm{X_2}$ = Cl, -53.9, d, J_{PP} = 62 Hz, and -56.2, d, $\mathrm{X_2}$ = ClBr, 55%) were identified by ^{1}H and ^{31}P NMR. After 24 h, the color of the reaction mixtures was yellow characteristic of mononuclear palladium(II) phosphine complexes ($\mathrm{PdX_2(dppm)}$, $\mathrm{X_2 = Cl_2, ClBr, Br_2}$). The products were identified by ^{31}P NMR.

Introduction of HBr in the presence of potential ligands $\mathrm{C_2H_4}$ (5 equiv) and CO (500 Torr) produced the same result. The green color persisted somewhat longer upon introduction of inert gases Ar (1 atm) or $\mathrm{H_2}$ (1–3 atm) or air (1 atm), but the green color was still discharged after 60 s.

L = Oxygen. When NMR tubes containing dichloromethane-d_2 solutions of $\mathrm{Pd_2X_2dppm_2}$ and $\mathrm{Me_3SiX'}$ were opened to air, the orange-red color was replaced by a light yellow color after 12 h. By ^{31}P NMR, the solutions contained equilibrium mixtures of $\mathrm{PdX_2(dppm)}$, $\mathrm{PdXX'(dppm)}$, and $\mathrm{PdX'_2(dppm)}$. $\mathrm{PdCl_2(dppm)}$: ^{1}H, δ 4.18, t, $\mathrm{PC}\mathit{H}_2\mathrm{P}$; ^{31}P, δ -54.1, s. $\mathrm{PdBr_2(dppm)}$: ^{1}H, δ 4.25, t, $\mathrm{PC}\mathit{H}_2\mathrm{P}$; ^{31}P, -55.7, s. PdClBr(dppm): ^{31}P, -53.9 ppm, d, J_{PP} = 62 Hz, -56.2, d. $\mathrm{PdI_2(dppm)}$: ^{1}H, δ 4.48, t, $\mathrm{PC}\mathit{H}_2\mathrm{P}$; ^{31}P, -62.0, s. PdClI(dppm): ^{31}P, δ -52.5, d, J_{PP} = 59 Hz, -63.8, d. PdBr(dppm): ^{31}P, δ -54.1, d, J_{PP} = 57 Hz, -64.2, d.

Hexamethyldisiloxane ($\mathrm{Me_3SiOSiMe_3}$) was identified as the sole silicon-containing product by ^{1}H NMR (δ 0.03, s) and GC/MS (*m/e* = 162).

Reactions of Metal Complexes with Methyl Iodide. Reaction of $\mathrm{Pd_2Cl_2(dppm)_2}$ with MeI. A $\mathrm{CD_2Cl_2}$ solution of 0.017 g (1.6×10^{-5} mol) of $\mathrm{Pd_2Cl_2(dppm)_2}$ containing 3.2×10^{-5} mol of $\mathrm{CH_3I}$ was thawed and warmed to room temperature. A slight deepening of the red color was observed. After 12 h of reaction at room temperature, MeI (^{1}H, δ 2.08, s, 94%), MeCl (^{1}H, δ 2.92, s, 6%), $\mathrm{Pd_2Cl_2(dppm)_2}$ (^{31}P, δ -2.90, s, 68%), $\mathrm{Pd_2I_2(dppm)_2}$ (^{31}P, δ -10.6, s, 2%), and $\mathrm{Pd_2ClI(dppm)_2}$ (^{31}P, δ -4.11, t, *J* = 40 Hz, -6.02, t, 30%) were identified by NMR. After 60 h of reaction at room temperature, only $\mathrm{Pd_2I_2(dppm)_2}$ was detected by ^{31}P NMR. Reaction of $\mathrm{Pd_2Br_2(dppm)_2}$ with MeI yielded similar results.

Reaction of $\mathrm{PdCl_2(dppm)}$ with MeI. A $\mathrm{CD_2Cl_2}$ solution containing 0.0086 g (1.5×10^{-5} mol) of $\mathrm{PdCl_2dppm}$ and 4.1×10^{-5} mol of MeI was thawed and allowed to react at room temperature. A gradual color change from a colorless solution to a deep red color was observed over a several week period. After 8 weeks, MeI (^{1}H, δ 2.08, s, 33%), MeCl (^{1}H, δ 2.93, s, 67%), $\mathrm{PdCl_2(dppm)}$ (^{1}H, δ 4.18, t, $\mathrm{PC}\mathit{H}_2\mathrm{P}$; ^{31}P, δ -54.1, s), $\mathrm{Pd_2ClI(dppm)_2}$ (^{1}H, δ 4.25, t, $\mathrm{PC}\mathit{H}_2\mathrm{P}$; ^{31}P, δ -4.11, t, *J* = 40 Hz, -6.02, t), $\mathrm{PdI_2(dppm)}$ (^{1}H, δ 4.48, t, $\mathrm{PC}\mathit{H}_2\mathrm{P}$; ^{31}P, δ -62.0, s), and $\mathrm{Pd_2I_2(dppm)_2}$ (^{1}H, δ 4.20 m, $\mathrm{PC}\mathit{H}_2\mathrm{P}$; ^{31}P, δ -10.6) were identified by NMR spectroscopy.

UV/Vis Spectroscopy. Samples of 1–3, ~0.02 g, in 10-mL Wheaton vials sealed with rubber septa and a metal crimp cap were prepared in the glovebox. Distilled, degassed dichloromethane or dibromomethane was added by syringe. Just before the spectra were to be recorded, an excess, 100 μL, of $\mathrm{Me_3SiX'}$ or MeI was added by syringe. The samples were shaken to generate the green colors and transferred to a 1-cm quartz cuvette by syringe at room temperature. Procedures for excluding air and water were not as rigorous as in the NMR studies. UV/visible spectra were recorded at room temperature at a scan rate of 1500 nm/min from 700 to 400 nm. The results are summarized in Table I.

Isolation and Characterization of Halosilane Adducts of $\mathrm{Pd_2X_2(dppm)_2}$ (X = Cl, Br, I). The procedure for preparing and isolating $\mathrm{Me_3SiX'}$ adducts of 1–3 were identical to and will be described in detail for the reaction of $\mathrm{Pd_2Cl_2(dppm)_2}$ and $\mathrm{Me_3SiI}$. No attempt was made to isolate the adducts of 1–3 with $\mathrm{Me_3SiCl}$ as these were relatively short lived compared to the adducts with $\mathrm{Me_3SiBr}$ and $\mathrm{Me_3SiI}$.

Reaction of $\mathrm{Pd_2Cl_2(dppm)_2}$ with $\mathrm{Me_3SiI}$. A two-neck flask equipped with a filtering frit was charged with 0.0941 g (8.9×10^{-5} mol) of $\mathrm{Pd_2Cl_2(dppm)_2}$ and evacuated on a vacuum line. The reaction vessel was cooled to -196 °C in liquid nitrogen, and 5 mL of $\mathrm{CH_2Cl_2}$ was vacuum transferred from calcium hydride. The mixture was thawed and the orange palladium compound allowed to dissolve completely. The solution was frozen at -196 °C, and 3.0×10^{-4} mol of $\mathrm{Me_3SiI}$ was condensed into the flask. The liquid nitrogen bath was replaced with a dry ice/ethanol bath (-78 °C) and allowed to react for ~1 h. A dark green solution formed immediately upon thawing. The apparatus was removed from the vacuum line and filled with dry nitrogen. A 10-mL volume of hexane was added by syringe at -78 °C, precipitating a dark green powder. The solution was filtered, and the dark green solid was dried under vacuum. A 0.0725-g amount of **6a** (61% yield based on $\mathrm{Pd_2I_2(dppm)_2{\cdot}Me_3SiCl}$) was isolated as a dark green solid. The compound began to turn brown above 140 °C without melting. The observed halide exchange between Pd–X and Si–X' bonds makes it difficult to obtain pure products from reactions where X ≠ X', and elemental analyses were not expected to be within acceptable error.

Reaction of $\mathrm{Pd_2Br_2(dppm)_2}$ with $\mathrm{Me_3SiI}$. Reaction of 0.0867 g (7.6×10^{-5} mol) of $\mathrm{Pd_2Br_2(dppm)_2}$ with 3×10^{-4} mol of $\mathrm{Me_3SiI}$ as described above yielded 0.0863 g of **6b** (82% yield based on $\mathrm{Pd_2I_2(dppm)_2{\cdot}Me_3SiBr}$) as a dark green solid. The compound began to turn brown above 140 °C without melting. The observed halide exchange between Pd–X and Si–X' bonds makes it difficult to obtain pure products from reactions where X ≠ X', and elemental analyses were not expected to be within acceptable error.

Reaction of $\mathrm{Pd_2Br_2(dppm)_2}$ with $\mathrm{Me_3SiBr}$. Reaction of 0.1136 g (1.0×10^{-4} mol) of $\mathrm{Pd_2Br_2(dppm)_2}$ with 7×10^{-4} mol of $\mathrm{Me_3SiBr}$ as described above yielded 0.0388 g of **6c** (31% yield based on $\mathrm{Pd_2Br_2(dppm)_2{\cdot}Me_3SiBr}$) as a dark green solid. The compound began to turn brown above 90 °C without melting. Anal. Calcd for $\mathrm{Pd_2Br_2(dppm)_2{\cdot}Me_3SiBr}$, $\mathrm{C_{53}H_{53}Br_3P_4Pd_2Si}$: C, 49.18; H, 4.13; Br, 18.52; Si, 2.17. Found: C, 48.75; H, 4.08.

Reaction of $\mathrm{Pd_2Cl_2(dppm)_2}$ with $\mathrm{Me_3SiBr}$. Reaction of 0.0971 g (9.2×10^{-5} mol) of $\mathrm{Pd_2Cl_2(dppm)_2}$ with 2.5×10^{-4} mol of $\mathrm{Me_3SiBr}$ as described above yielded 0.0815 g of **6d** (71% yield based on $\mathrm{Pd_2Br_2(dppm)_2{\cdot}Me_3SiCl}$) as a dark green solid. The compound began to turn brown above 90 °C without melting. The observed halide exchange between Pd–X and Si–X' bonds makes it difficult to obtain pure products from reactions where X ≠ X', and elemental analyses were not expected to be within acceptable error.

Reaction of $\mathrm{Pd_2I_2(dppm)_2}$ with $\mathrm{Me_3SiBr}$. Reaction of 0.0832 g (6.7×10^{-5} mol) of $\mathrm{Pd_2I_2(dppm)_2}$ with 2.2×10^{-4} mol of $\mathrm{Me_3SiBr}$ as described above yielded 0.0517 g of **6e** (56% yield based on $\mathrm{Pd_2I_2(dppm)_2{\cdot}Me_3SiBr}$) as a dark green solid. The compound began to turn brown above 90 °C without melting. The observed halide exchange between Pd–X and Si–X' bonds makes it difficult to obtain pure products from reactions where X ≠ X', and elemental analyses were not expected to be within acceptable error.

Reaction of $\mathrm{Pd_2I_2(dppm)_2}$ with $\mathrm{Me_3SiI}$. Reaction of 0.0812 g (6.6×10^{-5} mol) of $\mathrm{Pd_2I_2(dppm)_2}$ with 2.1×10^{-4} mol of $\mathrm{Me_3SiI}$ as described above yielded 0.0586 g of **6f** (62% yield based on $\mathrm{Pd_2I_2(dppm)_2{\cdot}Me_3SiI}$) as a dark green solid. The compound began to turn brown above 140 °C without melting. Anal. Calcd for $\mathrm{Pd_2I_2(dppm)_2{\cdot}Me_3SiI}$, $\mathrm{C_{53}H_{53}I_3P_4Pd_2Si}$: C, 44.35; H, 3.72; I, 26.52; Si, 1.96. Found: C, 43.69; H, 3.70.

Results

Halide-Exchange Reactions of $\mathrm{Pd_2(dppm)_2X_2}$, $\mathrm{Pd_2(\mu\text{-}CH_2)Cl_2(dppm)_2}$, and $\mathrm{PdCl_2(dppm)}$ (X = Cl, Br, I). Upon thawing of

Table II. Temperature-Dependent ^{31}P Chemical Shifts (δ) for Me_3SiX' Adducts of $Pd_2X_2(dppm)_2$ Complexes (X = X′ = Cl, Br, I; in CD_2Cl_2)

	^{31}P chem shifts at varying temp (°C)					
reacn	−88	−76	−48	−23	3	22
$Pd_2Cl_2(dppm)_2$	−2.75	−2.68	−2.58	−2.61	−2.73	−2.89
$Pd_2Br_2(dppm)_2$	−4.85	−4.84	−4.87	−4.94	−5.09	−5.22
$Pd_2I_2(dppm)_2$	−9.84	−9.83	−10.04	−10.25	−10.48	−10.61
$Pd_2Cl_2(dppm)_2$	12	12	−1.6	−1.4 br	−2.3	−2.7
+ Me_3SiCl	−2.6	−2.6	−2.5			
$Pd_2Br_2(dppm)_2$	6	6	5.7	5.7	5.7	4
+ Me_3SiBr	−4.9	−4.9	−4.9	−5.0	−5.3	−5.6
$Pd_2I_2(dppm)$	2.5	2.6	2.4	−0.4 br	−2.78	−2.73
+ Me_3SiI	−8.7	−8.9	−8.7			
$Pd_2Cl_4(dppm)_2$				8.5[a]		
$Pd_2Br_4(dppm)_2$				4.90[a]		
$Pd_2I_4(dppm)_2$	−0.67	−0.68	−0.67	−0.66	b	b

[a] At −40 °C.[9] [b] Decomposes.

mixtures of $Pd_2(dppm)_2X_2$ with 2 equiv of Me_3SiX' (X = Cl, Br, I; X′ = Cl, Br, I) in CD_2Cl_2, a dramatic color change from red-orange to dark green was immediately observed (Table I) in all cases with the exception of X = X′ = Cl. The green color remained after vigorous shaking. The solutions were ESR silent at room temperature. The green color persisted for time periods ranging from 1 to 48 h at room temperature before reverting to an orange-red hue characteristic of $Pd_2X_2(dppm)_2$ derivatives. Lifetimes of the green solutions were qualitatively found to be in the order X = X′ = Cl (no color change) < X = Br, X′ = Cl < X = I, X′ = Cl < X = Cl, X′ = Br ~ X = I, X′ = Cl < X = X′ = Br ~ X = Br, X = I ~ X = Cl, X′ = I < X = X′ = I. In cases where X = Cl and X′ = Br, I or X = Br and X′ = I, a net exchange of halide ligands was observed, yielding $Pd_2X'_2(dppm)_2$ and Me_3SiX. The products were identified by comparison of absorption spectra and ^1H and ^{31}P NMR chemical shifts with authentic samples. The ^{31}P chemical shifts of the dppm ligands in the orange to red solutions were observed to be nearly identical to those of authentic $Pd_2X_2(dppm)_2$ but were broadened by up to 20 Hz relative to the peak width at half-height of pure **1**–**3**.

Even in the presence of a large excess of Me_3SiCl, $Pd_2(dppm)_2Br_2$ and $Pd_2I_2(dppm)_2$ could not be converted to $Pd_2(dppm)_2Cl_2$. Similarly, $Pd_2I_2(dppm)_2$ could not be converted to $Pd_2Br_2(dppm)_2$ when reacted with excess Me_3SiBr.

Both $Pd_2Cl_2(\mu\text{-}CH_2)(dppm)_2$ and $PdCl_2(dppm)$ were observed to undergo halide exchange with Me_3SiBr. The reaction of $PdCl_2(dppm)$ with Me_3SiBr yielded Me_3SiCl and $PdBr_2(dppm)$. Reaction of the dinuclear Pd(II) derivative, $Pd_2Cl_2(\mu\text{-}CH_2)(dppm)_2$, with Me_3SiBr resulted in the formation of $Pd_2Br_2(\mu\text{-}CH_2)(dppm)_2$ and Me_3SiCl in CD_2Cl_2.

Low-Temperature NMR Studies. The nature of the green solutions was investigated by ^1H and ^{31}P NMR spectroscopy over the temperature range −98 to +22 °C (Table II). In CD_2Cl_2, the ^{31}P chemical shifts of $Pd_2X_2(dppm)_2$ complexes were observed to be temperature dependent over the temperature range −88 to +22 °C but did not broaden to an appreciable degree under these conditions (peak width at half-height ~ 5–15 Hz; Table II). Similar observations were reported for ^{31}P spectra of **1**–**3** recorded in chloroform.[9] When the reactions between $Pd_2X_2(dppm)_2$ and Me_3SiX' were initiated at −88 °C and studied over a temperature range −88 to +22 °C, a different dynamic behavior was observed for the ^{31}P NMR spectra. In addition to a resonance assignable to $Pd_2X_2(dppm)_2$, one or two broader, downfield, ^{31}P signals were observed in self-exchange reactions (X = X′) (Table II and Figures 1–3). For the case where X = X′ = I, one of these signals was observed at nearly the same chemical shift as $Pd_2I_2(dppm)_2$, while the other was shifted downfield by 12–15 ppm. These signals were assigned to Me_3SiI adducts of $Pd_2I_2(dppm)_2$.[10] At −88 and −78 °C, these resonances were observed in an approximately 1:1 ratio and appeared to have developed some fine structure (pseudotriplets; Figure 1). As the temperature was raised, the two sets of resonances broadened and coalesced into a broad singlet (peak width at half-height ~ >1000 Hz) at −23 °C (X = I). Raising the temperature further led to a sharpening of the resonance and a steady upfield movement of the chemical shift. Immediate cooling of the sample regenerated the same intermediate spectra. ^1H NMR spectra recorded at room temperature showed two

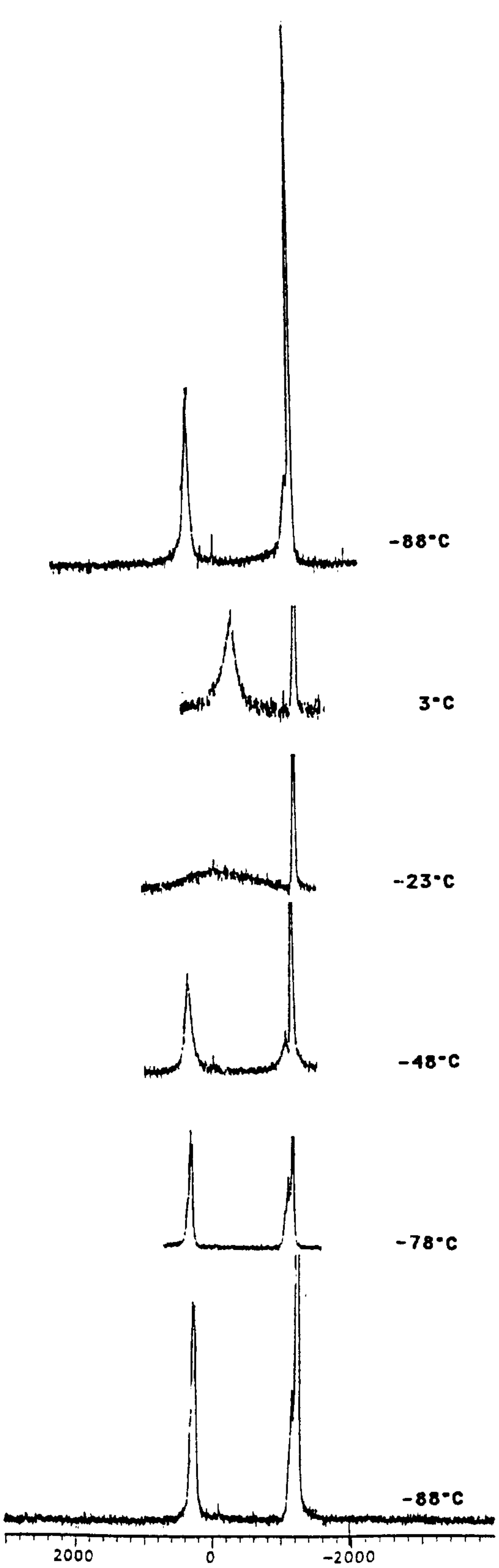

Figure 1. Variable-temperature ^{31}P NMR spectra of $Pd_2I_2(dppm)_2$ + Me_3SiI in CD_2Cl_2.

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(9) Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 1641.

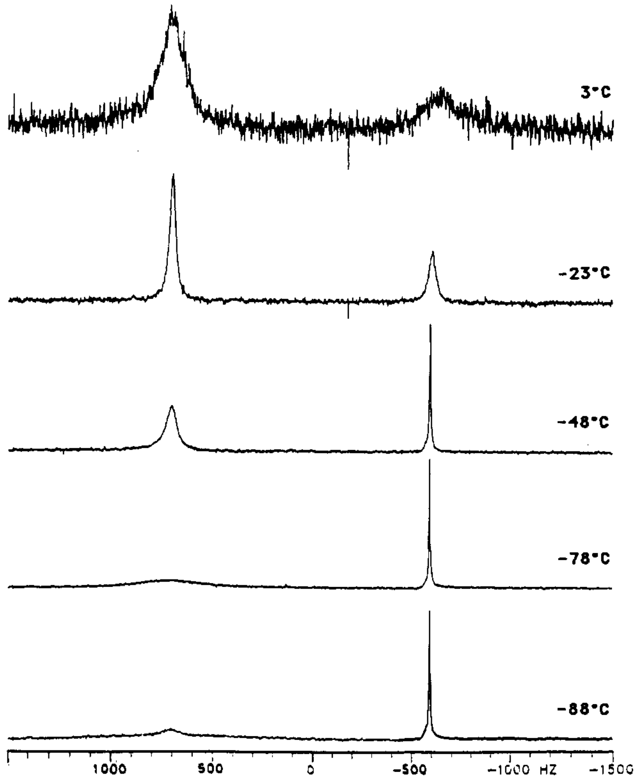

Figure 2. Variable-temperature ^{31}P NMR spectra of $Pd_2Br_2(dppm)_2$ + Me_3SiBr in CD_2Cl_2.

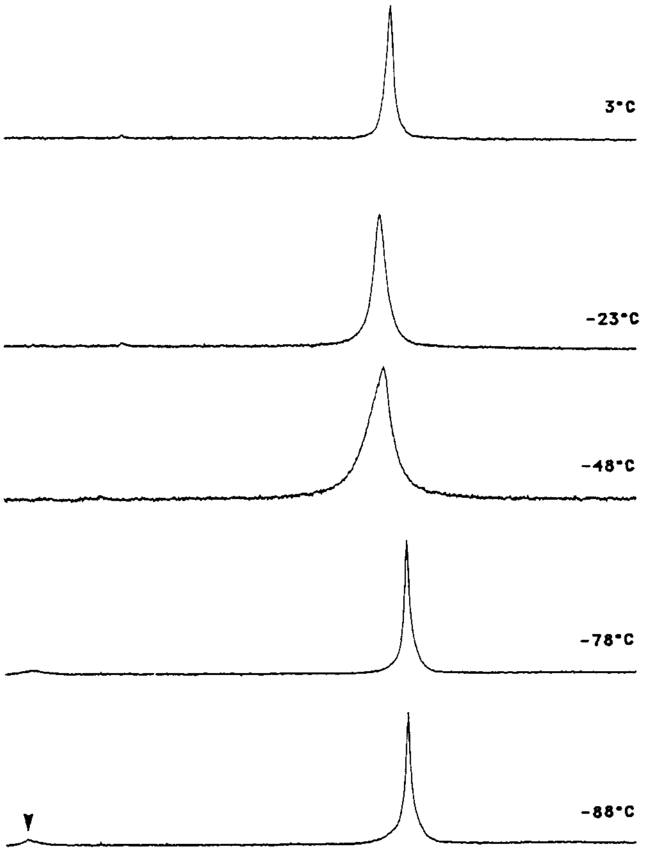

Figure 3. Variable-temperature ^{31}P NMR spectra of $Pd_2Cl_2(dppm)_2$ + Me_3SiCl in CD_2Cl_2.

closely spaced singlet resonances between 0 and 0.75 ppm. The chemical shift of one of these resonances was found to be identical with that of pure Me_3SiI in CD_2Cl_2 solution, allowing assignment of the other singlet to the coordinated Me_3SiI. Two broad resonances for the methylene protons of the dppm ligand were observed in a 1:1 ratio between 4 and 5 ppm. For reactions where X = X′ = Br and X = X′ = Cl, only a single new ^{31}P resonance was observed at -88 °C assigned to Me_3SiX' adducts of $Pd_2X_2(dppm)_2$. For X = X′ = Br, the single resonance for the Me_3SiBr adduct started to resolve into two broad resonances; however, further attempts at improving resolution were limited by the freezing point of the solutions. No changes were observed for the single resonance assigned to the Me_3SiCl adduct of $Pd_2Cl_2(dppm)_2$ upon cooling to -98 °C. Upon warming to -48 °C the resonances for starting material ($Pd_2X_2(dppm)_2$) and the trimethylsilyl halide adduct coalesced into a single broad resonance. ^1H NMR spectra were similar to those observed for the reaction of Me_3SiI with $Pd_2I_2(dppm)_2$. Complicated spectra containing mixtures of products were observed for the six permutations where $X \neq X'$.

As the ratio of Me_3SiX' to $Pd_2X_2(dppm)_2$ (X = X′) was increased from 1:1 to 5:1, the equilibrium in reaction 2 was driven

$$Pd_2X_2(dppm)_2 + Me_3SiX' \rightleftharpoons Pd_2X_2(dppm)_2{\cdot}Me_3SiX' \quad (2)$$

to the right, with no detectable $Pd_2X_2(dppm)_2$ by ^{31}P NMR. The equilibrium constants for X = X′ = Cl, Br and X = I were observed to be approximately 5, 130, and 200, respectively, independent of the ratio of reactants. Equilibrium constants for $X \neq X'$ were not determined because of the concurrent halide-exchange reactions which accompanied adduct formation. The ^{31}P NMR spectra at -98 °C of the $Pd_2I_2(dppm)_2{\cdot}Me_3SiI$ adduct at a Me_3SiX' to $Pd_2X_2(dppm)_2$ ratio of 5:1 is illustrated in Figure 4, showing two triplets with $J_{P-P} \sim 35$ Hz.

The ^{31}P chemical shifts of the trimethylsilyl halide complexes of $Pd_2X_2(dppm)_2$ were observed in the region of the spectrum where dinuclear dppm-bridged Pd(II) complexes $Pd_2X_4(dppm)_2$ were reported.[11] Reaction of $Pd_2X_2(dppm)_2$ (X = Cl, Br, I) with Br_2 and I_2, however, yielded red-brown solutions of dinuclear Pd(II) complexes $Pd_2X_4(dppm)_2$, verifying that the green solutions observed in the reactions of $Pd_2X_2(dppm)_2$ with Me_3SiX' did not result from the formation of $Pd_2X_4(dppm)_2$ intermediates. Temperature-dependent ^{31}P chemical shifts for the dppm ligands in $Pd_2I_4(dppm)_2$ were found in the same range but at different values from those observed in the reactions of $Pd_2I_2(dppm)_2$ with Me_3SiI (Table II).

Effect of Lewis Base Ligands on the Halide-Exchange Reactions. The halide-exchange reaction between $Pd_2Cl_2(dppm)_2$ and Me_3SiBr was carried out under ethylene and carbon monoxide atmospheres. The presence of 5 equiv of ethylene did not prevent the formation of the green color but decreased the rate of halide exchange. In the absence of ethylene, halide exchange was complete in 1-2 h compared to 12 h in the presence of ethylene at ambient temperature. Reaction of $Pd_2Cl_2(dppm)_2$ with Me_3SiBr and 500 Torr of CO in CD_2Cl_2 also led to the observation of a *pale* green color but was accompanied by rapid precipitation

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(10) The ^{31}P resonances furthest downfield in mixtures of Me_3SiX' and $Pd_2X_2(dppm)_2$ were assigned to the phosphorus atoms attached to the metal center bearing the halosilane ligand. Addition of halide ligands to dinuclear Pd(I) centers in $Pd_2X_2(dppm)_2$ complexes (forming $Pd_2X_2(dppm)_2$) has been shown to lead to a downfield shift in the dppm resonances relative to $Pd_2X_2(dppm)_2$ (Table II). The phosphorus atoms bonded to the uncomplexed palladium center were only slightly perturbed and retained a chemical shift similar to that of $Pd_2X_2(dppm)_2$. The latter observation was consistent with the observation of only one new resonance in the reactions where X = X′ = Br and X = X′ = Cl. The upfield resonance could not be resolved from the resonance assigned to $Pd_2X_2(dppm)_2$ in these cases.

(11) Eaborn, C.; Griffiths, R. W.; Pidcock, A. *J. Organomet. Chem.* **1982**, *225*, 331.

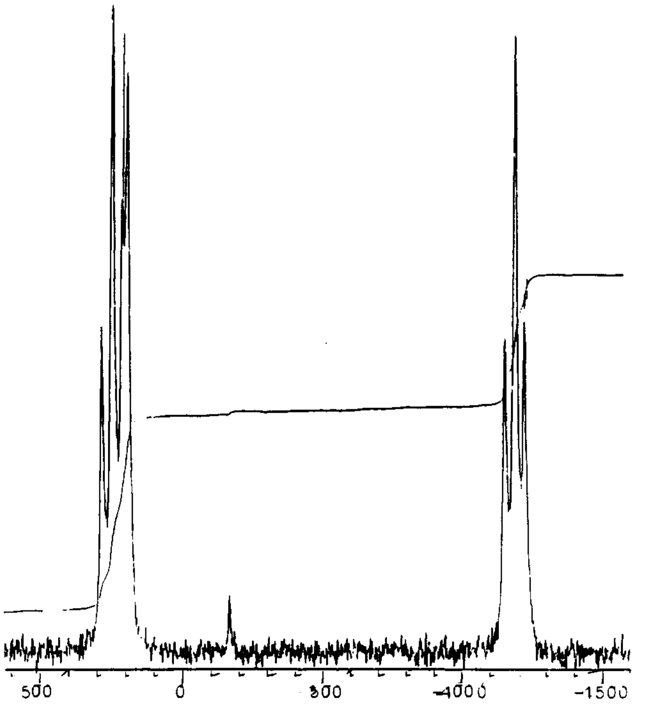

Figure 4. ^{31}P NMR spectrum of $Pd_2I_2(dppm)_2 \cdot Me_3SiI$ in CD_2Cl_2 at −98 °C.

of the known red complex, $Pd_2Cl_2(\mu\text{-}CO)(dppm)_2$. Addition of Me_3SiBr to a slurry of $Pd_2Cl_2(\mu\text{-}CO)(dppm)_2$ under a CO atmosphere also produced a weak green color which increased in intensity when the CO atmosphere was replaced by nitrogen.

A further series of reactions were conducted to test the role of HBr in the generation of the transient green color. Thawing mixtures of $Pd_2Cl_2(dppm)_2$ and 2–4 equiv of HBr produced a flash of dark green color just as the top of the frozen CD_2Cl_2 solution melted. By the time the solution had fully melted, the green color had disappeared. There was no effect of added ethylene (5 equiv) or CO (500 Torr, precipitation of $Pd_2Cl_2(\mu\text{-}CO)(dppm)_2$) on the lifetime of the green color. Addition of air (1 atm), argon (1 atm) or hydrogen (3 atm) had a minimal effect on the lifetime of the green color (minutes vs seconds). In all cases, mononuclear palladium(II) phosphine complexes ($PdCl_2(dppm)$, $PdBr_2(dppm)$, and $PdBrCl(dppm)$) were observed as the final reaction products with no evidence for $Pd_2Br_2(dppm)_2$ formation. The relative lifetime of the green color generated in mixtures of $Pd_2Cl_2(dppm)_2$ and Me_3SiBr (hours) vs $Pd_2Cl_2(dppm)_2$ and HBr (seconds) rules out hydrolysis of Me_3SiBr to HBr in the former reaction. The failure to observe mononuclear $PdX_2(dppm)$ in intensely green, oxygen-free reaction mixtures of $Pd_2Cl_2(dppm)_2$ and Me_3SiBr contrasted with the observation of $PdBr_2(dppm)$ as the only metal-containing product (100% by NMR) in reactions between $Pd_2Cl_2(dppm)_2$ and HBr.

Effect of Oxygen on the Halide Exchange. The generation of the green color in mixtures of $Pd_2X_2(dppm)_2$ and Me_3SiX' was unaffected by the presence of air. Under aerobic conditions, however, the orange-red color of $Pd_2X_2(dppm)_2$ (or $Pd_2X'_2(dppm)_2$) was slowly replaced by a lighter yellow color characteristic of $PdX_2(dppm)$ ($X_2 = Cl_2$, ClBr, Br_2) and was accompanied by formation of $Me_3SiOSiMe_3$. Addition of measured amounts of air to an NMR tube containing $Pd_2Cl_2(dppm)_2$ and Me_3SiBr (in CD_2Cl_2) produced an equilibrium mixture of $Pd(dppm)Cl_2$, $Pd(dppm)Br_2$, and $Pd(dppm)BrCl$ with an observed $K_{eq} = 3$, identical to results reported by Balch and co-workers.[9] The sensitivity of the reactions of $Pd_2X_2(dppm)_2$ with Me_3SiX' to trace amounts of oxygen was underscored by the need to pump on samples of $Pd_2X_2(dppm)_2$ overnight at room temperature (10^{-3} Torr) to avoid these side reactions leading to mononuclear palladium products and $Me_3SiOSiMe_3$. Hexamethyldisiloxane was not observed when air was admitted to the reaction tubes containing Me_3SiBr and $PdCl_2(dppm)$ or $Pd_2Cl_2(\mu\text{-}CH_2)(dppm)$.

Halide-Exchange Reactions Involving Alkyl Halides. Halide-exchange reactions were also observed between $Pd_2Cl_2(dppm)_2$ and MeI. A red-orange CD_2Cl_2 solution of $Pd_2Cl_2(dppm)_2$ (^{31}P, −2.97 ppm) containing excess MeI (^1H, 2.11 ppm, s) at room temperature slowly darkened to a deep red color yielding $Pd_2I_2(dppm)_2$ (^{31}P, −10.6 ppm, s) and MeCl (^1H, 2.94 ppm, s). There were no intermediate color changes. Halide exchange was also observed between MeI and $PdCl_2(dppm)$, where both mononuclear $PdI_2(dppm)$ and dinuclear $Pd_2I_2(dppm)_2$ were identified by ^{31}P NMR spectroscopy.

Isolation and Characterization of Me_3SiX' Adducts of $Pd_2X_2(dppm)_2$. The relatively long-lived green solutions of $Pd_2X_2(dppm)_2$ with Me_3SiBr and Me_3SiI encouraged us to isolate the green complexes. Addition of hexane to cold (−78 °C) dichloromethane solutions of $Pd_2X_2(dppm)_2$ containing an excess of Me_3SiX' precipitated green powders **6a–f** (**6a**, X = Cl, X′ = I; **6b**, X = Br, X′ = I; **6c**, X = Br, X′ = Br; **6d**, X = Cl, X′ = Br; **6e**, X = I, X′ = Br; **6f**, X = I, X′ = I) which were isolated in 30–85% yield after filtration and drying under vacuum. The green powders were somewhat soluble in toluene. The solubility of the powders improved for products containing I and Br over chloride-containing products; however, numerous attempts to grow X-ray-quality crystals of **6a–f** failed.

The green powders were unchanged after storage in an argon atmosphere glovebox overnight and could be stored for weeks at −20 °C. Toluene solutions under argon, however, turned brown and precipitated orange brown solids after several days at room temperature. Exposure of **6a–f** to air overnight also led to loss of the green color. The observed halide exchange between Pd–X and Si–X′ bonds makes it difficult to obtain pure products from reactions where X ≠ X′, and elemental analyses were not expected to be within acceptable error. *Compounds **6c** and **6f** are not susceptible to halide exchange but were subject to thermal loss of the weakly coordinated trimethylhalosilane ligand.* Nevertheless, carbon, hydrogen, silicon, and halide analyses were consistent with the formulations of **6c** and **6f** as $Pd_2Br_2(dppm)_2 \cdot Me_3SiBr$ and $Pd_2I_2(dppm)_2 \cdot Me_3SiI$, respectively.

Discussion

Possible Mechanisms for Halide Exchange. Three reaction pathways (Figure 5) were considered to account for the observed halide exchange between $Pd_2X_2(dppm)_2$ and Me_3SiX': (1) a radical pathway involving metal- or silicon-centered radicals, (2) oxidative addition of Me_3SiX' to the 16-electron Pd(I) centers, and (3) a σ-bond metathesis pathway.

We believe that evidence for silicon-centered or metal-centered radical intermediates is weak. Rapid reaction of radical species with oxygen was expected, yet the formation of the green solutions was unaffected by the presence of air. The ESR of the green solution generated from $Pd_2Cl_2(dppm)_2$ and Me_3SiBr was silent at room temperature, and the observation of well-resolved NMR signals at low temperature suggests the presence of diamagnetic intermediates.

The data also do not support a pathway involving oxidative addition of the silicon–halide bond to the palladium dimer. Examples of the oxidative addition of silicon–halide bonds to transition metal complexes are rare, occurring only in cases where the metal complex contains electron-rich phosphine ligands (e.g. $Pt(PCy_3)_3$, $Pt(PEt_3)_3$, and $(\eta^2\text{-}C_8H_{12})Ir(PMe_3)_3Cl$) or halosilanes bearing more than one halide substituent (e.g. $MeSiCl_3$) were used.[3] No reaction was observed between $Pd(PPh_3)_4$ or the dinuclear, zerovalent derivative $Pd_2(dppm)_3$ and Me_3SiX (X = Cl, Br, I) in the absence of air up to 80 °C in C_6D_6.[11,12] The

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(12) Kirss, R. U. Unpublished data.

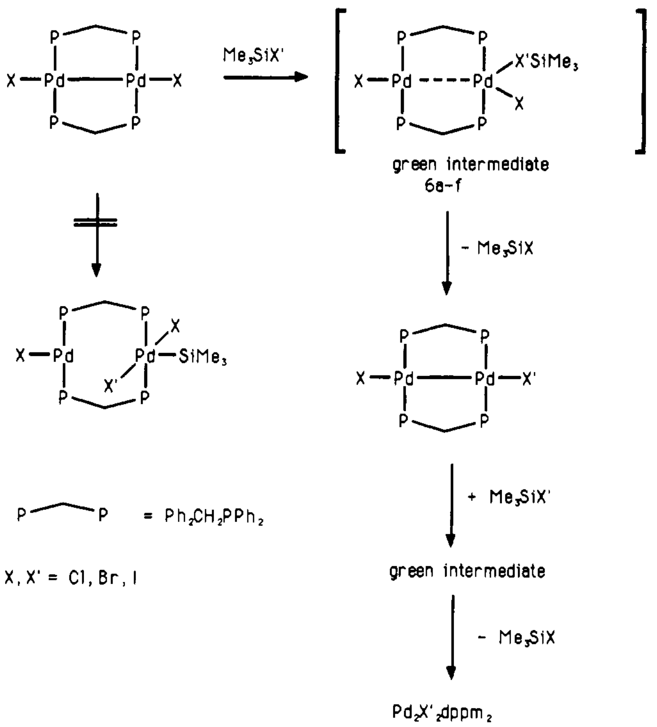
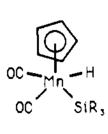


Figure 5. Proposed mechanism for halide exchange between $Pd_2X_2(dppm)_2$ (X = Cl, Br, I) and trimethylilyl halides Me_3SiX' (X' = Cl, Br, I).

absence of reactivity of coordinatively unsaturated $Pd_2(dppm)_3$ with silicon–halide bonds argues against oxidative addition to Pd(I) dimers. The Me_3Si resonances between 0.3 and 0.36 ppm in reactions of **1–3** with Me_3SiCl are observed at chemical shift values different from those typically associated with transition metal coordinated Me_3Si groups (doublets at –0.39 and –0.04 ppm, respectively, for the Me–Si resonances in $Pd(SiHMePh)_2(PMePh_2)_2$ and $Pd[SiMe_2CH_2CH_2PPh_2]_2$).[13]

The explanation most consistent with the spectroscopic data was the formation of an adduct between $Pd_2X_2(dppm)_2$ and Me_3SiX'. This adduct could involve either a σ-bonded Me_3SiX ligand (through the halide ligand as observed for alkyl or aryl halide complexes[2]) or a side-bound coordination observed for silane coordination to (η^5-cyclopentadienyl)manganese derivatives (Figure 5).[14] PES studies indicated that the choice between the two limiting structures, oxidative addition of Si–H (**7**) vs η^2-coordinated Si–H (**8**), was highly dependent on the nature of the substituents on silicon.



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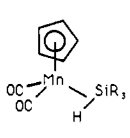

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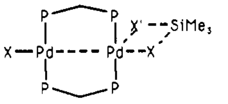

9

Coordination of Me_3SiX in a σ-fashion through the lone pairs on the X group followed by σ-bond metathesis (through a four-membered intermediate or transition state, **9**) can account for the observed halide-exchange reactions. A σ-bond metathesis mechanism was proposed for the dehydrogenative coupling of primary silanes in the presence of early transition metal complexes.[15] The role of η^2-R_3Si–H groups in dehydrogenative coupling reactions catalyzed by (arene)$Cr(CO)_3$ derivatives was also recently reported.[16]

Evidence Supporting σ-Coordination of Halosilanes. The strongest evidence for the existence and stoichiometry of halosilane adducts of formula $Pd_2X_2(dppm)_2{\cdot}Me_3SiX'$ (for X = X' and X ≠ X') comes from the isolation of green solids with the appropriate analytical data and from spectroscopic data. The volatility and the relatively weak interaction of the halosilane ligand with the Pd(I) dimers coupled with the air sensitivity of the adducts (generating PdXX'(dppm) and hexamethylsiloxane) requires great care in synthesizing analytically pure samples.

The dynamic ^{31}P NMR spectra for mixtures of $Pd_2X_2(dppm)_2$ and Me_3SiX' were consistent with rapid, reversible adduct formation (reaction 2). At the slow exchange limit (–88 °C), coordination to one of the formally 16-electron Pd(I) centers rendered the two ends of the dppm ligand magnetically inequivalent. Conversely, coordination to both metal centers could render the dppm ligands chemically inequivalent depending on the symmetry of the adduct. As the temperature was raised, rapid reversible coordination/loss of the Me_3SiX' ligand to either metal center led to coalescence of the spectrum into a single broad resonance. At room temperature (the fast-exchange limit), the rate of coordination/loss of Me_3SiX' is sufficiently rapid to yield only a broadened spectrum of $Pd_2X_2dppm_2$. The disappearance of the broad downfield resonance (12 ppm) between –78 and –48 °C in the reaction of $Pd_2Cl_2(dppm)_2$ with Me_3SiCl was consistent with Me_3SiCl exchange being faster than Me_3SiBr or Me_3SiI exchange and suggested that binding of Me_3SiCl was weaker than for the other halosilanes.

The increase in the concentration of the adduct as the ratio of Me_3SiX to $Pd_2X_2(dppm)_2$ increased is consistent with the measured equilibrium constants for reaction 2. The polarization of the Si–X bond is predicted to be in the in the order Me_3Si–I > Me_3Si–Br > Me_3Si–Cl, suggesting that donor strength toward $Pd_2X_2(dppm)_2$ should follow in the same sequence.[17]

A pathway involving coordination of Me_3SiX' (X' = Br, I), however, implies that in the presence of a strong σ-donor ligand the green color might not be observed and the rate of the halide exchange decreased. When the halide-exchange reaction was carried out under ethylene and carbon monoxide atmospheres, the results were consistent with a competition between potential ligands for a coordination site on the metal center. The presence of 5 equiv of ethylene did not prevent the formation of the green color but decreased the rate of halide exchange. In the presence of 500 Torr of CO, the intensity of the green color was significantly diminished in intensity and accompanied by the formation of the known complex $Pd_2X_2(\mu$-$CO)(dppm)_2$ (X = Cl, Br). These data are consistent with a competition between CO and Me_3SiX for the coordination site at the 16-electron palladium center.

Coordination of Lewis bases to $Pd_2Cl_2(dppm)_2$ is a common phenomenon. In addition to isolable CO adducts, complexes of $Pd_2Cl_2(dppm)_2$ with bridging isonitrile, sulfur, selenium, activated olefin, alkyne, and aryldiazenido, and alkylidene ligands have been prepared, mostly in halocarbon solvents.[18] These symmetrical complexes all range from yellow to red in color, and the metal–metal bond distances indicate the absence of Pd–Pd bonds. Since trimethylsilyl halides would not be predicted to be stronger Lewis bases than CO or olefins, the dramatic color change in the former suggests an intermediate bond order (between 0 and 1)

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for the Pd–Pd bond in the green intermediates. We propose that coordination of Me_3SiX' weakens the Pd–Pd bond, giving rise to a longer wavelength, lower energy transition. This is consistent with the observation of a green color. The weakening of the Pd–Pd bond is expected to be a function of the strength of the interaction between Me_3SiX' and **1–3**. The decrease in λ_{max} in the absorption spectrum (Table I) of the intermediate as a function of Me_3SiX generally supports the conclusion that strength of the interaction between Me_3SiX' and **1–3** is in the order $Me_3SiI > Me_3SiBr > Me_3SiCl$, consistent with the equilibrium constants for reaction 2. Care must be taken in interpreting the data in Table I, however, as halide-exchange reactions lead to mixtures of one or more intermediates.

The disappearance of the green color over time is consistent with competition between solvent (CD_2Cl_2) and Me_3SiX' for the coordination site on $Pd_2X_2(dppm)_2$ (reaction 3). While the Si–X bond is more polarized toward the halogen than C–X bonds (hence Me_3SiX should behave as a stronger donor than CD_2Cl_2), coordinated Me_3SiX' can be displaced by the *large excess* of solvent, pushing the equilibrium in reaction 3 to the right. Solutions of **1–3** and MeI showed no detectable shift in the absorption maximum relative to the starting material, yet halide exchange between $Pd_2Cl_2(dppm)_2$ or $Pd_2Br_2(dppm)_2$ and MeI was observed, consistent with halocarbons as weaker donors to **1–3**. The solvent (CD_2Cl_2) for the halide-exchange studies was itself a potential ligand; hence, the degree and *observed* rate of halide exchange depends on competition between solvent and MeI. The halide-exchange reactions involving alkyl halides may proceed through a similar σ-bond metathesis pathway proposed for the halide-exchange reactions involving trimethylsilyl halides. The halide exchange in reactions of $Pd_2X_2(dppm)_2$ with Me_3SiX' (X = Cl, X' = Br, I; X = Br, X' = I; X = I, X' = Br) may in fact be driven by formation of a stronger Si–X bond (relative to an Si–X' bond). $Me_3Si–X'$ bond energies have been measured as 113, 96, and 77 kcal/mol for X' = Cl, Br, and I, respectively.[19]

$$Pd_2X_2(dppm)_2\cdot Me_3SiX' + CD_2Cl_2 \rightleftharpoons Pd_2X_2(dppm)_2\cdot CD_2Cl_2 + Me_3SiX' \quad (3)$$

To our knowledge, the observation of a red color upon addition of Me_3SiCl to $W_2Cl_4(dppm)_2$ may be the only example of halosilanes behaving as Lewis bases toward coordinatively unsaturated transition metal complexes.[20] A shift in the absorption maximum from 486 to 498 nm was observed upon addition of Me_3SiCl to $W_2Cl_4(dppm)_2$, although the resulting red solution was not further characterized. Changes in the 380- and 737-nm absorptions of the tungsten(II) dimer upon reaction with Me_3SiCl were, unfortunately, not reported. The latter absorption was assigned to the $\delta \rightarrow \delta^*$ transition.

Semiempirical relativistic extended Huckel molecular orbital calculations were performed on $Pd_2Br_2(H_2PCH_2PH_2)_2$ as a model for $Pd_2X_2(dppm)_2$ (X = Cl, Br, I) to probe the nature of the electronic transitions observed in the course of the reactions with trimethylsilyl halides.[21] Crystallographically determined bond distances and angles (Pd–Br, Pd–P, P–C) for $Pd_2Br_2(dppm)_2$ were used to calculate coordinates for the heavy atoms.[22] Phosphorus–hydrogen distances and angles were estimated from data on PH_3.[23] The observed orange-red color of dichloromethane solutions of $Pd_2X_2(dppm)_2$ are unmistakably the result of transitions between a lower lying molecular orbital and the LUMO, predominantly metal in character with principal contributions from the metal d_{z^2} orbitals. The initial state for the transition is more difficult to discern as the calculation revealed numerous closely spaced occupied molecular orbitals, one of which was also predominantly metal d_{z^2} in character. Nevertheless, the results of the calculation qualitatively support the notion that the origin of a green color in the reactions of $Pd_2X_2(dppm)_2$ with Me_3SiX' results from reduction of metal–metal bond order.

Conclusions

Four conclusions are evident on the basis of the reactions of dppm-bridged, palladium(I) dimers with trimethylsilyl halides: (1) The reactions are rapid at low temperature and may involve a σ-bond metathesis pathway. Oxidative addition of silicon halide bonds to the transition metal center does not appear to be required. (2) Trimethylsilyl halides can behave as weak Lewis bases toward the coordinatively unsaturated palladium(I) dimers, forming kinetically favored green adducts between $Pd_2X_2(dppm)_2$ and Me_3SiX'. (3) The green intermediates are consistent with Me_3SiX' σ-coordination to one metal center, weakening the Pd–Pd bond and resulting in a red shift in the absorption spectrum. (4) While methyl iodide is also capable of effecting a halide ligand exchange, the absence of color changes during the course of the reaction may imply an ordering for the σ-donor ability as $Me_3SiI > Me_3SiBr > Me_3SiCl > MeI$. Contributions from d_π–p_π bonding could contribute in the case of Me_3SiBr and Me_3SiI. It is also possible that the halide-exchange reactions are driven by the strength of Si–X and/or Pd–X bond formation.[24]

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