REACTIONS OF TRIMETHYL GROUP IVA HALIDES (Si, Ge, Sn) WITH PHOSPHINE-BRIDGED PALLADIUM, PLATINUM, AND SILVER DIMERS

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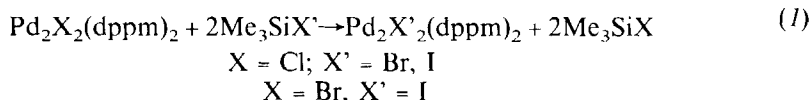
Reactions of a series of binuclear, phosphine bridged late transition metal complexes, $Pd_2Cl_2(dppm)_2$, $Pd_2Cl_2(dmpm)_2$, $Pd_2Cl_2(Ph_2Ppy)_2$, $Pt_2Cl_2(dppm)_2$, and $Ag_2Br_2(dmpm)_2$, with Me_3SiX (X = Br, I), Me_3GeBr and Me_3SnBr were examined by ^{31}P NMR spectroscopy. Rapid exchange of Pd-Cl, Pt-Cl and Ag-Br bonds for Pd-X, Pt-X (X = Br, I) and Ag-I bonds was observed to be independent of the nature of the phosphine ligand, the nature of the metal center or the group IV element. Differences in Lewis acidity of the transition metal center as a function of the ligands and the identity of the transition metal and differences in the basicity of the Me_3EBr ligands are proposed to account for the failure to detect intermediates in these reactions similar to those reported for reactions between $Pd_2Cl_2(dppm)_2$ and Me_3SiX.

INTRODUCTION

The ability of halocarbons to both oxidatively add and coordinate to sixteen electron transition metal centers is well known.[1] By comparison, examples of oxidative addition of organosilicon, germanium and tin halides are rare.[2] Recently, we reported on the apparent coordination of trimethylsilylhalides to bis(diphenylphosphine) bridged palladium(I) dimers and the resulting halide exchange reactions (reaction 1).[3] In the present paper we address the effects of changing the bridging ligand, the trimethyl group IVB halides and the transition metal on the halide exchange reaction between dinuclear platinum group metal phosphine complexes and trimethyl group IVB halides.

$$Pd_2X_2(dppm)_2 + 2Me_3SiX' \rightarrow Pd_2X'_2(dppm)_2 + 2Me_3SiX \qquad (1)$$
$$X = Cl; X' = Br, I$$
$$X = Br, X' = I$$

EXPERIMENTAL

All compounds described in this work were handled using Schlenk techniques, a M.I. Braun glovebox under a purified argon atmosphere or on a vacuum line

equipped with oil diffusion and mechanical pumps (10^{-3} Torr).[4] 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 transferred 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 under vacuum. Great care was taken to dry the reagents and to rigorously exclude oxygen from the system. Me_3SiI was transferred from a sealed vial in the glove box, stored over copper and degassed as described. $PdCl_2$, $PdBr_2$, bis(diphenylphosphino)methane (dppm), bis(dimethylphosphino)methane (dmpm), Me_3GeBr, and Me_3SnBr were purchased from Strem Chemical and used as received. $Pd_2Cl_2(dppm)_2$,[5] $Pd_2Cl_2(dmpm)_2$,[6] $Pd_2Br_2(dmpm)_2$,[7] $Pd_2Cl_2(Ph_2Ppy)_2$,[8] $Pt_2Cl_2(dppm)_2$,[9] and $Ag_2Br_2(dmpm)_2$,[10] were prepared by literature methods where dppm is bis(diphenylphosphino)methane and dmpm is bis(dimethylphosphino)methane.

^1H and $^{31}P\{^1H\}$ spectra were recorded on a Varian 300XL spectrometer in either flame sealed 5 mm NMR tubes or 5 mm tubes equipped with a Teflon valve (Wilmad Glass, Inc.). Proton chemical shifts are relative to residual protons in the solvent ($CDHCl_2$ at δ 5.24 ppm). Phosphorus chemical shifts are relative to external 85% H_3PO_4. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Synthesis of $Pd_2I_2(dmpm)_2$

0.0976 g (1.8×10^{-5} mols) of $Pd_2Cl_2(dmpm)_2$ was dissolved in 50 mL CH_2Cl_2 under nitrogen. An excess of KI was added and the mixture stirred at room temperature for 72 hours. A color change from yellow-orange to a red-orange was observed. The mixture was filtered through Celite and solvent evaporated from the filtrate. After recrystallization from CH_2Cl_2/diethyl ether, a yellow-orange solid, 0.020 g (15% yield) was isolated. No attempts were made to optimize the yield. ^1H NMR (CD_2Cl_2): δ 1.73 ppm (d, J = 1.2 Hz, 12H, CH_3), 2.76 (m, 2H, CH_2); $^{31}P(CD_2Cl_2)$: δ −38.7 ppm (s). *Anal.* Calcd for $C_{10}H_{28}I_2P_4Pd_2$: C, 16.26; H, 3.82; I, 34.35. Found: C, 16.49; H, 3.81; I, 34.30.

$Pd_2I_2(dmpm)_2$ was also prepared by addition of 0.16 mL (0.22 g, 1.1×10^{-3} mols) Me_3SiI to a solution of 0.123 g (2.2×10^{-4} mols) $Pd_2Cl_2(dmpm)_2$ in 10 mL of CH_2Cl_2 under nitrogen at room temperature. The solution turned significantly more orange. After stirring for 12 h, the solution was evaporated to dryness under vacuum and the crude product recrystallized from CH_2Cl_2/diethyl ether.

Titration of and $Pd_2Cl_2(dmpm)_2$with Me_3SiBr

Titration of a CH_2Cl_2 solution of $Pd_2Cl_2(dmpm)_2$ (0.0420 g , 7.6×10^{-5} mols in 10 mL of CH_2Cl_2) with a 22 mM solution of Me_3SiBr (0.0341 g, 2.23×10^{-4} mols in 10 mL CH_2Cl_2) produced an immediate darkening in the color of the solution from orange to red. The composition of the solution was monitored by ^{31}P NMR. After addition of 1 equivalent, ^{31}P NMR indicated a single broad resonance between −31 and −34 ppm, consistent with rapid halide exchange. After addition of three

equivalents of Me_3SiBr, the ^{31}P NMR spectrum consisted of a sharp singlet at -34 ppm, assigned to $Pd_2Br_2(dmpm)_2$, as the sole resonance.

NMR Studies of the Reactions of Metal Complexes with Me_3E-halide bonds

General Procedure

Solid samples of the transition metal complexes 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 CD_2Cl_2 was vacuum transferred into the tubes. After thawing to allow the metal complexes to dissolve, the 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. Products were identified by comparison of the chemical shifts with authentic samples while product ratios were determined by integration of the peak areas for the products and are judged to be accurate to $\pm 5\%$.

Samples containing Me_3GeBr and Me_3SnBr used the following modified procedure. 5 mm tubes equipped with a Teflon valve were charged with small amounts (≈ 10-20 mg) of the transition metal compound in the glove box under argon. The tubes were laid on their sides and the liquid group IV halides added to the top of the tube so that the two reagents did not mix. The tubes were sealed by closing the Teflon valve. After removing the tubes from the glove box they were quickly attached to a vacuum line and the bottom of the tube immediately cooled to $-196°C$ to prevent reaction. In this fashion, as the Me_3GeBr and Me_3SnBr flowed down the tube, they were frozen prior to reacting with the transition metal compound. The frozen tubes were evacuated and dichloromethane-d_2 was vacuum transferred into the tubes. The tubes could be stored for days at $-196°C$ with no apparent changes. The tubes were thawed immediately prior to insertion into the NMR probe to look for color changes. Products were identified by comparison of the chemical shifts with authentic samples while product ratios were again determined by integration of the peak areas for the products.

Reaction of $Pd_2Cl_2(dppm)_2$ with Me_3GeBr

Upon thawing a CD_2Cl_2 solution of 0.0183 g (1.7×10^{-5} mols) $Pd_2Cl_2(dppm)_2$ and 0.0915 g (4.6×10^{-4} mols) Me_3GeBr at $-78°C$, the yellow orange color of $Pd_2Cl_2(dppm)_2$ darkened to a slightly more red hue. ^{31}P NMR indicated formation of $Pd_2Br_2(dppm)_2$ (δ -4.89 ppm, 90%)[3] The variable temperature behavior of the sample was identical to that of authentic $Pd_2Br_2(dppm)_2$.[3] $\approx$ 10% $PdBr_2(dppm)$ (δ -55.3 ppm) was also observed in the reaction mixture.

Reaction of $Pd_2I_2(dppm)_2$ with Me_3GeBr

Upon thawing a CD_2Cl_2 solution of 0.0120 g (9.7×10^{-6} mols) $Pd_2I_2(dppm)_2$ containing 8×10^{-4} mols Me_3GeBr at $-78°C$, no color changes were observed in

the dark red solution. The ^{31}P NMR spectrum remained identical to that of authentic Pd$_2$I$_2$(dppm)$_2$ over the temperature range $-78°$C to room temperature indicating the absence of any halide exchange.[3]

Reaction of Pd$_2$Cl$_2$(dppm)$_2$ with Me$_3$SnBr

Upon thawing a CD$_2$Cl$_2$ solution of 0.0215 g (2.0 × 10^{-5} mols)Pd$_2$Cl$_2$(dppm)$_2$ and 0.0535 g (2.2 × 10^{-4} mols) Me$_3$SnBr at $-78°$C, the yellow orange color of Pd$_2$Cl$_2$(dppm)$_2$ became significantly more red. ^{31}P NMR indicated formation of PdBr$_2$(dppm)$_2$ (δ -4.89 ppm, 90%)[3] The variable temperature behavior of the sample was identical to that of authentic Pd$_2$Br$_2$(dppm)$_2$.[3] $\approx$ 10% PdBr$_2$(dppm) (δ -55.3 ppm) was also observed in the reaction mixture.

Reaction of Pd$_2$I$_2$(dppm)$_2$ with Me$_3$SnBr

Upon thawing a CD$_2$Cl$_2$ solution of 0.0100 g (8.1 × 10^{-6} mols) Pd$_2$I$_2$(dppm)$_2$ containing 8 × 10^{-4} Me$_3$SnBr at $-78°$C, no color changes were observed in the dark red solution. The ^{31}P NMR spectrum remained identical to that of authentic Pd$_2$I$_2$(dppm)$_2$ over the temperature range $-78°$C to room temperature indicating the absence of any halide exchange.[3]

Reaction of Pd$_2$Cl$_2$(dmpm)$_2$ with Me$_3$SiBr

Upon thawing a CD$_2$Cl$_2$ solution of 0.0093 g (1.7 × 10^{-5}mols) Pd$_2$Cl$_2$(dmpm)$_2$ and 2.6 × 10^{-5} mols Me$_3$SiBr at $-78°$C, a red solution was observed. The only ^{31}P NMR signal observed at $-78°$C was a singlet at -34 ppm assigned to PdBr$_2$(dmpm)$_2$. No changes were observed in the ^{31}P NMR spectrum after three weeks at room temperature.

Reaction of Pd$_2$Cl$_2$(dmpm)$_2$ with Me$_3$GeBr

Upon thawing a CD$_2$Cl$_2$ solution of 0.0154 g (2.8 × 10^{-5} mols) Pd$_2$Cl$_2$(dmpm)$_2$ and 0.070 g (3.6 × 10^{-5} mols) Me$_3$GeBr at $-78°$C, the solution turned orange, accompanied by formation of a slight amount of a very pale yellow precipitate. The only ^{31}P NMR signal observed at $-78°$C was a singlet at -34 ppm assigned to PdBr$_2$(dmpm)$_2$. No changes were observed in the ^{31}P NMR spectrum after three weeks at room temperature.

Reaction of Pd$_2$Cl$_2$(dmpm)$_2$ with Me$_3$SnBr

Upon thawing, a CD$_2$Cl$_2$ solution of 0.0099 g (1.810^{-5} mols) Pd$_2$Cl$_2$(dmpm)$_2$ and 0.0573 g (2.4 × 10^{-4} mols)Me$_3$SnBr at $-78°$C, turned slightly more orange. The only ^{31}P NMR signal observed at $-78°$C was a singlet at -34 ppm assigned to PdBr$_2$(dmpm)$_2$. No changes were observed in the ^{31}P NMR spectrum after three weeks at room temperature.

Reaction of Pd$_2$Cl$_2$(Ph$_2$Ppy)$_2$ with Me$_3$SiBr

Upon thawing a CD$_2$Cl$_2$ solution of 0.0270 g (3.5 × 10^{-5} mols) Pd$_2$Cl$_2$(Ph$_2$Ppy)$_2$

and 3.6×10^{-5} mols Me_3SiBr at $-78°C$, the color of the red solution appeared to deepen slightly. The only signal observed at $-78°C$ was a singlet at 2.03 ppm; by analogy to the trends observed for other palladium (I) dimers, was assigned to $Pd_2Br_2(Ph_2Ppy)_2$. The chemical shifts of the resonances in the ^{31}P NMR spectrum were found to be temperature dependant; at ambient temperature (18–19°C) the resonance assigned to $Pd_2Br_2(Ph_2Ppy)_2$ was observed at 2.18 ppm.

Reactiion of $Pd_2Cl_2(Ph_2Ppy)_2$ with Me_3SiI

Upon thawing a CD_2Cl_2 solution of 0.0183 g (2.3×10^{-5} mols) $Pd_2Cl_2(Ph_2Ppy)_2$ and 4.0×10^{-5} mols Me_3SiI at $-78°C$, the color of the solution changed from red to purple. The only signal observed at $-78°C$ was a singlet at -1.05 ppm and by analogy to the trends observed for other palladium (I) dimers, it was assigned to $Pd_2I_2(Ph_2Ppy)_2$.

Reaction of $Pt_2Cl_2(dppm)_2$ with Me_3SiBr

Upon thawing a CD_2Cl_2 solution of 0.0230 g (1.9×10^{-5} mols) $Pt_2Cl_2(dppm)_2$ and 1.8×10^{-5} mols Me_3SiBr at $-78°C$, the yellow solution turned orange. A singlet at 8.65 ppm (66% of products at $-78°C$, $J^{195}_{PtP} = 2334$ Hz) was assigned to unreacted $Pt_2Cl_2(dppm)_2$. By analogy to the trends observed for palladium (I) dppm dimers and literature data in tetrachloroethane,[9] a broad singlet at ≈ 5 ppm (22% of products at $-78°C$, $J^{195}_{PtP} = 2344$ Hz) was assigned to $PtBr_2(dppm)_2$. The only other resonance at -65.4 ppm (12% of products at $-78°C$, $J^{195}_{PtP} = 3083$ Hz) was assigned to $PtBr_2(dppm)$. After warming to room temperature (probe temperature 18–19°C), the resonances assigned to $Pt_2Cl_2(dppm)_2$ had disappeared leaving only those for $Pt_2Br_2(dppm)_2$ at 5.28 ppm (s, 55% of products) and $PtBr_2(dppm)$ at -64.9 ppm (s, 45% of products).

Reaction of $Pt_2Cl_2(dppm)_2$ with Me_3SiI

Upon thawing a CD_2Cl_2 sloution of 0.0337 g (2.7×10^{-5} mols) $Pt_2Cl_2(dppm)_2$ and 4.0×10^{-5} mols Me_3SiI at $-78°C$, the yellow solution turned red. By analogy to the trends observed for palladium (I) dppm dimers and literature data in tetrachloroethane,[9] the singlet at 1.05 ppm (77% of products at $-78°C$, $J^{195}_{PtP} = 2300$ Hz) was assigned to $Pt_2I_2(dppm)_2$. The only other resonance at -70.3 ppm (23% of products at $-78°C$, $J^{195}_{PtP} = 2867$ Hz) was assigned to $PtI_2(dppm)$.

Reaction of $Ag_2Br_2(dmpm)_2$ with Me_3SiI

Addition of a large excess of Me_3SiI to a CD_2Cl_2 solution of 0.040 g ($6.2-10^{-5}$ mols) $Ag_2Br_2(dmpm)_2$ at room temperature in the glove box led to formation of a white precipitate. ^{31}P NMR spectra indicated disappearance of the resonance at -27.5 ppm (s) for $Ag_2Br_2(dmpm)_2$ and appearance of a new singlet resonance at -32.4 ppm. The product was assigned as $Ag_2Br_2(dmpm)_2$ and appearance of a new singlet resonance at -32.4 ppm. The product was assigned as $Ag_2I_2(dmpm)_2$ by analogy to the observed trends in chemical shift of dmpm lignads bonded to palladium as a function of halide. The white solid product is light sensitive, slowly

turning brown in room light while the starting $Ag_2Br_2(dmpm)_2$ compound is stable to light for months.

RESULTS

Synthesis of Pd$_2$I$_2$(dmpm)$_2$

At the outset of this work, the synthesis and characterization of $Pd_2I_2(dmpm)_2$ had not been reported. Analogous to the literature procedure for the preparation of $Pd_2Br_2(dmpm)_2$,[7] reaction of $Pd_2Cl_2(dmpm)_2$ with an excess of potassium iodide in dichloromethane results in conversion of the chloride to the iodide, albeit in low yield. The ^{31}P resonance of $Pd_2I_2(dmpm)_2$ (-38 ppm) is shifted upfield from the corresponding $Pd_2Br_2(dmpm)_2$ (-34 ppm) and $Pd_2Cl_2(dmpm)_2$ (-31 ppm) compounds,[6,7] reflecting the observed upfield shift in the ^{31}P resonances for $Pd_2X_2(dppm)_2$ complexes when the halide was changed from Cl to Br to I.

Effect Of The Bridging Ligand, Group IVA Element, and Transition Metal On The Halide Exchange Reactions

Changing the bridging ligand from bis(diphenylphosphino) methane to bis (dimethylphosphino) methane or 2-pyridyldiphenylphosphine ligands in $Pd_2Cl_2(L\wedge L)_2$ complexes (L∧L = $Ph_2PCH_2PPh_2,Me_2PCH_2PMe_2,Ph_2Ppy$), had no effect on the halide exchange between Pd-Cl and Si-Br or Si-I bonds. The products of the reactions between $Pd_2Cl_2(dmpm)_2$ and Me_3SiBr or Me_3SiI in CD_2Cl_2 were assigned by comparison with the ^{31}P spectra of independently prepared $Pd_2X_2(dmpm)_2$ (Table 1, X = Br, I). Low temperature spectra of reactions between Me_3SiX and $Pd_2Cl_2(dmpm)_2$ indicated that halide exchange was complete immediately after thawing even at $-78°C$ without formation of any detectable intermediates analogous to the σ-complexes isolated from reactions of $Pd_2Br_2(dppm)_2$ or $Pd_2I_2(dppm)_2$ with Me_3SiBr and Me_3SiI, respectively. The halide exchange of Pd-Cl for Pd-Br bonds was also unaffected by changing from Me_3SiBr to Me_3GeBr or Me_3SnBr for both $Pd_2Cl_2(dppm)_2$ and $Pd_2Cl_2(dmpm)_2$.

Reaction of $Pd_2Cl_2(Ph_2Ppy)_2$ and Me_3SiX (X = Br, I) resulted in the disappearance of the ^{31}P resonance for $Pd_2Cl_2(Ph_2Ppy)_2$ at 3.73 ppm (at $-78°C$) and appearance of new singlets at 2.03 ppm (X = Br at $-78°C$) and -1.05 ppm (X = I at $-78°C$), upfield of the resonance for $Pd_2Cl_2(Ph_2Ppy)_2$. The chemical shift of these resonances was temperature dependant and mimicked the observed trend for ^{31}P resonances for $Pd_2X_2(dppm)_2$ and $Pd_2X_2(dmpm)_2$ as a function of X. The resonances at 2.03 and -1.05 ppm were assigned to $Pd_2Br_2(Ph_2Ppy)_2$ and

Table 1 [31]P Chemical Shifts For Dppm and Dmpm Bridged Dinuclear Complexes[a].

Compound	X = Cl	X = Br	X = I
$Pd_2X_2(dppm)_2$	-2.89	-4.89	-10.6
$Pd_2X_2(dmpm)_2$	-31	-34	-38.7
$Pd_2X_2(PPh_2py)_2$	3.73	2.18	-1.05
$Pt_2X_2(dppm)_2$	7.65	5.28	0.48
$Ag_2X_2(dmpm)_2$		-27.4	-32.4

[a] in CH_2Cl_2 relative to external 85% H_3PO_4.

$Pd_2I_2(Ph_2Ppy)_2$, respectively. Low temperature spectra of the reaction between Me_3SiX and $Pd_2Cl_2(Ph_2Ppy)_2$ again indicated rapid halide exchange but failed to result in detectable intermediates.

Reactions of Me_3SiX (X = Br, I) with the isoelectronic phosphine bridged dimers $Pt_2Cl_2(dppm)_2$ and $Ag_2Br_2(dmpm)_2$ led to the observation of halide exchange without observation of any intermediates. In reactions of $Pt_2Cl_2(dppm)_2$ with Me_3SiX, yellow dichloromethane solutions of $Pt_2Cl_2(dppm)_2$(δ 7.65 ppm) turned orange upon mixing with the trimethylsilyl halides. By analogy to $Pd_2X_2(dppm)_2$ compounds, the observed ^{31}P chemical shifts were consistent with formation of $Pt_2Br_2(dppm)_2$(δ 5.28 ppm) and $Pd_2I_2(dppm)_2$(δ 0.48 ppm). Reaction of $Ag_2Br_2(dmpm)_2$(^{31}P NMR δ –27.4 ppm) with excess Me_3SiI led to the observation of a new resonance in the ^{31}P NMR spectrum at δ –32.4 ppm which was assigned to $Ag_2I_2(dmpm)_2$ based on the documented upfield shift of ^{31}P resonances of phosphine-bridged palladium dimers as a function of halide.

DISCUSSION

While the halide exchange between Me_3EX and late transition metal dimers appears to be unaffected by the nature of the bridging ligand, the group IV element (E = Si, Ge, Sn) and the transition metal, formation of spectroscopically detectable intermediates analogous to those in reactions between $Pd_2X_2(dppm)_2$ and Me_3SiX was not observed (Figure 1).

Both $Pd_2Cl_2(dmpm)_2$ and $Pd_2Cl_2(dppm)_2$ react with strong Lewis bases such as carbon monoxide and sulfur dioxide to form isolable 1:1 complexes,[7,11b] Bubbling nitrogen through a solution containing $Pd_2Cl_2(\mu-CO)(dmpm)_2$ at room temperature is sufficient to remove the asymmetrically bridging CO ligand[7] while refluxing $Pd_2Cl_2(\mu-CO)(dppm)_2$ in CH_2Cl_2 or heating the solid at 56°C under vacuum appears to be necessary for complete removal of the CO ligand from $Pd_2Cl_2(\mu-CO)(dppm)_2$.[11] One possible explanation for the different reactivity of $Pd_2Cl_2(dppm)_2$ and $Pd_2Cl_2(dmpm)_2$ toward Me_3SiX is that the more electron rich, bis(methylphosphino)methane ligand reduces the Lewis acidity of the sixteen-electron palladium center so as to prevent the formation of a σ-complex. While it seems reasonable that the 2-pyridyl diphenylphosphine does not dramatically alter the Lewis acidity of the palladium center in $Pd_2Cl_2(Ph_2Ppy)_2$ compared to $Pd_2Cl_2(dppm)_2$, $Pd_2Cl_2(Ph_2Ppy)_2$ forms a weak, terminal, carbon monoxide adduct which can be completely decarbonylated by heating for 1 minute in CH_2Cl_2.[8] The 2-pyridyldiphenylphosphine ligand has been proposed to be less flexible, preventing complexes of this ligand from forming strong adducts with either carbon monoxide or sulfur dioxide.[8] Similar structural considerations may prevent $Pd_2Cl_2(Ph_2Ppy)_2$ from forming stable adducts with trimethylsilyl halides.

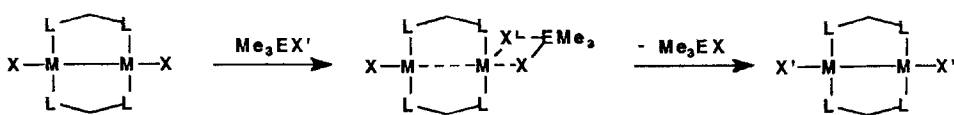**Figure 1** Reactions of $Pd_2Cl_2(LL)_2$ with Me_3EX'

While the halide exchange of Pd-Cl for Pd-Br bonds was unaffected by changing from Me_3SiBr to Me_3GeBr or Me_3SnBr in reactions with either $Pd_2Cl_2(dppm)_2$ or $Pd_2Cl_2(dmpm)_2$, only in the reactions of $Pd_2Cl_2(dppm)_2$ with Me_3SiBr were intermediates observed.[3] These observations are consistent with the expected polarization of Me_3E-Br bonds, i.e. Si-Br > Ge-Br > Sn-Br,[3,12] and the resultant prediction of donor strength, Si-Br>Ge-Br>Sn-Br.

Failure to detect intermediates analogous to $Pd_2X_2(dppm)_2 \cdot Me_3SiX$ in reactions of isoelectronic and isostructural platinum complexes may reflect Lewis acidity differences between second and third row elements. The absence of a metal bond in $Ag_2Br_2(dmpm)_2$ precludes the observation of color changes resulting from weakening of the M-M interaction as proposed in the case of $Pd_2X_2(dppm)_2 \cdot Me_3SiX$ adducts.[3]

CONCLUSIONS

In summary, halide exchange reactions between trimethyl group IVA halides and phosphine-bridged, late transition metal dimers appear to be independent of the nature of the chelating ligand, (dppm, dmpm, or Ph_2Ppy), the nature of the group IVA element, (Si, Ge or Sn), or the transition metal (Pd(I), Pt(I) or Ag(I)). The formation of detectable σ-complexes as intermediates in the reactions between $Pd_2X_2(dppm)_2$ and Me_3SiX may reflect differences in the relative Lewis acid/base properties of the transition metal compounds and the trimethyl group IVA halides.

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