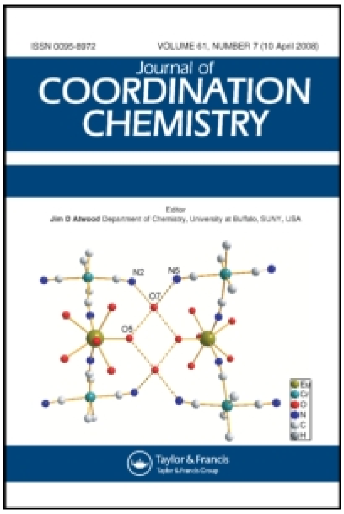

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REACTIONS OF SILANES AND SILYL HALIDES WITH TRANS-$MeIr(CO)[P(p\text{-tolyl})_3]_2$, CARBON–HYDROGEN AND CARBON–SILICON BOND FORMATION

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Reaction of silanes ($HSiR_3$, $R_3 = Me_2Ph$, $(OMe)_3$) with *trans*-$MeIr(CO)[P(p\text{-tolyl})_3]_2$ leads to methane and $HIr(SiR_3)_2(CO)[P(p\text{-tolyl})_3]_2$ through oxidative addition and reductive elimination sequences. These reactions contrast with those involving the addition of silanes to analogous alkoxo iridium complexes. Reaction of Me_3SiI with *trans*-$MeIr(CO)[P(p\text{-tolyl})_3]_2$ produces Me_4Si and $Ir(SiMe_3)(CO)[P(p\text{-tolyl})_3]_2I_2$, thus providing the first example of oxidative addition of silicon–iodide bonds at ambient conditions. These reactions demonstrate the formation of carbon–hydrogen and silicon–carbon bonds.

Keywords: Silanes, Iridium, phosphines, complexes, oxidative addition

INTRODUCTION

Formation of bonds through reductive elimination reactions is important in most applications of organometallic complexes.[1-6] A number of studies have focused on C–H[7-19] and C–C[20-27] bond formation and a few have examined C–O bond formation,[28-30] In this manuscript we report the formation of C–H and C–Si bonds through reactions of silanes and silyliodides, respectively, with *trans*-$MeIr(CO)[P(p\text{-tolyl})_3]_2$.

We have utilized complexes, *trans*-$RIr(CO)L_2$ (R = alkyl or alkoxy, L = phosphine ligand) to examine a number of reactions where bond formation through reductive elimination might be expected.[29-33] These studies have included C–H, O–H, C–C, O–C and O–Si bond formation. In the cases of C–C and O–C bond formation, possible bond formation depends on the nature of the two fragments.[29-32] As an example, C_2H_6 and CH_3OCH_3 are not observed when CH_3I is added to *trans*-$RIr(CO)L_2$ ($R = CH_3$ or OCH_3) while $CH_3C(O)CH_3$ and $CH_3C(O)OCH_3$ are readily formed when $CH_3C(O)Cl$ is reacted with *trans*-$RIr(CO)L_2$.

Addition of silanes to square planar complexes has often been studied as a result of the importance of hydrosilylation and *O*-silylation reactions.[1-3,34-38] Only recently has the addition of Si–X bonds to a metal centre been reported.[39,40] In one case, Me_3SiBr addition to $Pt(PEt_3)_3$ at 90°C gave *trans*-$Me_3SiPt(PEt_3)_2Br$.[39] In the

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second example $PhSiCl_3$ oxidatively added to $Pt(PCy_3)_2$ to give *trans*-$Pt(PCy_3)_2(Cl)(SiPhCl_2)$.[40] The lack of examples (and apparent difficulty in adding Si–X bonds) is unusual and apparently related to the Si–X bond energy.

We have recently reported the reactions of silanes and silyl chlorides with alkoxy iridium complexes, *trans*-$ROIr(CO)L_2$ (R = Me and Ph, L = P(*p*-tolyl)$_3$), leading to silyl ethers, $ROSiR_3'$ and $H_2Ir(CO)(SiR_3')L_2$ (for silanes) or *trans*-$Ir(CO)L_2Cl$ (for Me_3SiCl).[33] Here we report that, in contrast, addition of silanes ($HSiR_3'$) to *trans*-MeIr(CO)[P(*p*-tolyl)$_3$]$_2$ leads to CH_4 and $HIr(SiR_3')_2$(CO)[P(*p*-tolyl)$_3$]$_2$, Me_3SiCl does not react with *trans*-MeIr(CO)[P(*p*-tolyl)$_3$]$_2$ and that Me_3SiI gives $SiMe_4$ and $Ir(SiMe_3)(CO)I_2$[P(*p*-tolyl)$_3$]$_2$. The last reaction demonstrates C–Si bond formation and oxidative addition of silicon–iodide bonds to Ir(I).

EXPERIMENTAL

All solvents were purified according to standard techniques and were then distilled from appropriate drying agents under a dry nitrogen atmosphere. All syntheses were accomplished under an argon atmosphere. Dimethylphenylsilane (Petrarch), trimethoxysilane (Petrarch), and trimethylchlorosilane (Aldrich) were vacuum distilled from anhydrous sodium carbonate. Iridium trichloride, $IrCl_3 \cdot 3H_2O$, was loaned by Johnson Matthey Inc. Tri-*p*-tolylphosphine (Strem Chemical) was used as received. *Trans*-Ir(CO)[P(*p*-tolyl)$_3$]$_2$Cl was prepared as previously described.[33] NMR spectra were recorded on a Varian EM390 or a Joelco FX90Q spectrometer. Infrared spectra were recorded on a Beckman 4240 spectrophotometer. Gas chromatographic analysis was performed on a Varian 2440 instrument with a flame ionization detector and Poropak Q column.

Preparation of trans-$CH_3Ir(CO)[P($p-*tolyl*$)_3]_2$

In the drybox, a flask was charged with 0.846 g (0.979 mmol) of IrCl(CO)[P(*p*-tolyl)$_3$]$_2$ and 10 cm^3 of THF. To this suspension 1.50 cm^3 of 1.4 M MeLi were added. The yellow suspension immediately became red-orange. After 5 min., excess MeLi was destroyed by addition of Florisil. The solution was filtered, washing the Florisil with THF until the yellow colour had been discharged. Solvent was removed from the golden yellow solution. The yellow solid obtained was dissolved in toluene and the toluene removed under vacuum. The yellow solid was extracted with benzene and filtered through a fine frit. The volume of the solvent was reduced to 2–3 cm^3 and hexanes (15 cm^3) were added to induce precipitation of a yellow powder. Yield: 0.770 g (93%). IR (cyclohexane); 1943 cm^{-1}. ^{1}H NMR (d_8-toluene): 0.41(t) (J_{P-H} = 8.8 Hz), 2.00(s) and 6.8–7.8(m) ppm.

Reaction of trans-$CH_3Ir(CO)[P($p-*tolyl*$)_3]_2$ *with* Me_3SiCl

In the drybox, a saturated solution of $CH_3Ir(CO)$[P(*p*-tolyl)$_3$)]$_2$ was prepared by charging a flask with 0.296 g (0.349 mmol) of the complex and 4 cm^3 of toluene. The flask was transferred to a high-vacuum line where, using a calibrated manometer, 0.421 mmol of Me_3SiCl was condensed into the flask. The reaction mixture was thawed and after stirring rapidly at ambient temperature for 10 min., approx. 0.5 cm^3 of the solvent was collected by vacuum distillation. GC analysis of the solvent indicated that TMS was not present. An additional 0.439 mmol of Me_3SiCl was measured on a manometer and condensed into the flask. Over a period of 72 hours, no visual change in the solution had occurred. Volatile products were removed from the flask by distillation and analysed by GC. GC analysis indicated that TMS was not formed in the reaction. IR analysis of the residual solid indicated the presence of only the methyl iridium complex. IR (cyclohexane): 1943 cm^{-1}.

Reaction of trans-*$CH_3Ir(CO)[P($*p*-$tolyl)_3]_2$ with Me_3SiI*

A) In the drybox, a reaction tube was charged with 0.170 g (0.201 mmol) $CH_3Ir(CO)[P(p\text{-tolyl})_3]_2$, 0.102 g (0.681 mmol) of NaI and 5 cm^3 of acetonitrile. The suspension was degassed at high vacuum and then 1.0 mmol of Me_3SiCl was transferred to the reaction tube. The rapidly stirred reaction mixture was warmed to ambient temperature and over a period of approximately one hour a fine precipitate formed. GC analysis of the vapour phase revealed the presence of tetramethylsilane. The precipitate consisted of *trans*-$IrI(CO)[P(p\text{-tolyl})_3]_2$ (IR (cyclohexane): 1965 cm^{-1}) and $IrI_2(CO)(SiMe_3)[P(p\text{-tolyl})_3]_2$ (IR: (KBr) 2041 cm^{-1}, ^1H NMR ($CDCl_3$) −0.01(s), 2.03(s) and 6.8–7.6(m) ppm).

B) In the drybox, a reaction tube was filled with 0.102 g of *trans*-$MeIr(CO)[P(p\text{-tolyl})_3]_2$ which was dissolved in approximately 2 cm^3 of THF. To this light yellow solution 0.07 cm^3 of Me_3SiI (Aldrich) was added on a high vacuum line. The reaction was warmed to ambient temperature and stirred overnight. The solvent was removed and a light yellow/white solid remained. This solid was a combination of $IrI(CO)[P(p\text{-tolyl})_3]_2$ and $IrI_2(CO)(SiMe_3)[P(p\text{-tolyl})_3]_2$.

Reaction of trans-*$Ir(CO)[P($*p*-$tolyl)_3]Cl$ with Me_3SiI*

In the drybox, a reaction tube was filled with 0.102 g of *trans*-$Ir(CO)[P(p\text{-tolyl})_3]_2Cl$ dissolved in approximately 2.0 cm^3 of THF. To this clear yellow solution, using the high vacuum line, 0.07 cm^3 of $(CH_3)_3SiI$ (Aldrich) was added. The solution was warmed to ambient temperature and stirred rapidly. After 15 minutes, the solution turned cloudy and a white precipitate formed. The reaction stirred overnight. The white powder was collected and was shown to be $IrICl(CO)(SiMe_3)[P(p\text{-tolyl})_3]_2$; IR: (KBr) 2042 cm^{-1} and ^1H NMR: −0.10(s), 2.26(s).

Reaction of trans-*$CH_3Ir(CO)[P($*p*-$tolyl)_3]_2$ with $HSiMe_2Ph$*

A) In the drybox, a flask was charged with 0.224 g (0.264 mmol) of $CH_3Ir(CO)[P(p\text{-tolyl})_3]_2$. On a high-vacuum line, 1 cm^3 of d_8-toluene and 0.090 cm^3 (0.581 mmol) of $HSiMe_2Ph$ were condensed into the tube. The reaction was allowed to warm to room temperature and stirred for 18 hrs. Volatile products were collected and analyzed by ^1H NMR spectroscopy. NMR analysis indicated that $SiMe_3Ph$ had not been formed. The spectrum of the burnt orange solid was recorded. ^1H NMR (d_6 benzene): −10.28(dd) ($J_{P(trans)-H}$ = 126.96 Hz, $J_{P(cis)-H}$ = 16.61 Hz), 0.29(s), 2.01(s) and 6.7–7.9(m) ppm. Integration of the spectra (0.29(s) - 12H's and 2.01(s) - 18H's) is consistent with the presence of two silyl ligands. IR (cyclohexane): 2055(m), 1981(s).

B) In the drybox, a tube equipped with a gas adaptor was charged with 0.23 g of *trans*-$CH_3Ir(CO)[P(p\text{-tolyl})_3]_2$ and 1 cm^3 toluene. On the high vacuum line, 1.1 cm^3

$HSiMe_2Ph$ was added. The solution was warmed to room temperature and stirred overnight. The tube was backfilled to 1 atm with helium. The gas above the solution was then analyzed by gas chromatography. The GC analysis indicated methane was present.

Reaction of trans-$CH_3Ir(CO)[P($p-*tolyl*$)_3]_2$ *with* $HSi(OMe)_3$

A) In the drybox, a flask was charged with 0.20 g (0.237 mmol) of *trans*-$CH_3Ir(CO)[P(p\text{-tolyl})_3]_2$ and 3 cm^3 benzene. 0.10 cm^3 (0.82 mmol) of $HSi(OMe)_3$ was added to the flask and the solution stirred for 24 hrs. The benzene was removed and pentane added. Stirring for several hours resulted in a yellow solid that was collected by filtration. ^1H NMR (d_6-benzene): −8.65(t), (J_{P-H} = 16.95 Hz), 2.01(s), 3.45(s), 6.8–8.1(m) ppm. In addition, singlets of varying intensity were observed at 3.79, 3.67 and 3.35 ppm. IR (cyclohexane): 2075 and 1967 cm^{-1}.

B) In the drybox, an NMR tube equipped with a 14/20 joint was charged with 0.135 g (0.149 mmol) of $CH_3Ir(CO)[P(p\text{-tolyl})_3]_2$. On a high vacuum line, approx. 0.5 cm^3 of d_6-benzene and 0.050 cm^3 (0.35 mmol) of $HSi(OMe)_3$ were condensed into the tube. Upon warming to room temperature, the spectrum of the yellow solution was recorded. ^1H NMR (d_6-benzene): −8.69(t) (J_{P-H} = 16.85 Hz), 2.01(s), 3.45(s) and 6.6–8.2(m) ppm. A doublet of doublets was also observed in the hydride region, −10.75 ($J_{P(cis)-H}$ = 2.80 Hz and $J_{P(trans)-H}$ = 80.30 Hz) ppm, but this resonance disappeared over a period of several days.

C) In the drybox, a tube equipped with a gas adapter was charged with 0.185 g (0.218 mmol) of the methyl complex and 2 cm^3 of benzene. On a high vacuum line, 0.10 cm^3 (0.70 mmol) of $HSi(OMe)_3$ was condensed into the tube. A half hour after warming to room temperature, the tube was filled with one atmosphere of He and the vapour phase was analyzed by GC. GC analysis indicated the presence of methane.

RESULTS AND DISCUSSION

The methyliridium complex readily reacts with dimethylphenylsilane or trimethoxysilane to form hydridoiridium complexes.

$$CH_3Ir(CO)L_2 + 2\ HSiR_3' \longrightarrow HIr(CO)(SiR_3')_2L_2 + CH_4 \qquad (1)$$
$$L = P(p\text{-tolyl})_3;\ R_3' = (CH_3)_2Ph,\ (OCH_3)_3$$

The ready addition of $HSiMe_2Ph$ is in contrast to reactions with *trans*-$Ir(CO)(PPh_3)_2Cl$ where only silanes with electron-withdrawing substituents add oxidatively. Methane was characterized by gas chromatographic analysis on Poropak Q. The hydridoiridium complexes, $HIr(SiR_3)_2(CO)[P(p\text{-tolyl})_3]_2$ have not been previously reported. The ν_{Ir-H} values of 2055 ($R_3 = Me_2Ph$) and 2075 cm^{-1} (R = OMe) are very similar to those observed for the related $HIr(SiR_3)(CO)(PPh_3)_2Cl$ complexes.[40] Similarly, the ν_{CO} values of 1981 ($R_3 = Me_2Ph$) and 1967 cm^{-1} (R = OMe) are as expected.[41] Integration of the ^1H NMR spectra clearly indicates a 1:1 ratio of silyl and phosphine groups.

Although the reaction of the methyliridium complex with both dimethylphenyl- and trimethoxy-silane resulted in the formation of the hydridobis(silyl)iridium complex, the geometries of the two complexes are different, as shown by phosphorus–hydrogen coupling. When the trimethoxysilyl ligand is present, a triplet with J_{P-H} of

17 Hz is observed for the hydride. This is typical for a hydride ligand *cis* to two phosphine ligands. The presence of other signals in the $Si(OMe)_3$ region indicates that small amounts of other isomers also form. No geometric information could be obtained for these isomers. The presence of the dimethylphenylsilyl ligand resulted in a doublet of doublets for the hydrides with coupling expected for *cis* (16.6 ppm) and *trans* (127 ppm) phosphorus ligands. The observation of a doublet of doublets during the reaction of *trans*-$MeIr(CO)[P(p\text{-tolyl})_3]_2$ with $HSi(OMe)_3$, indicates an initial addition of silane to give the geometry shown in Figure 1. Such additions would be "perpendicular" in Crabtree's nomenclature.[42] Addition of H_2 to *trans*-$MeIr(CO)(PMe_3)_2$ also occurs in a "perpendicular" fashion.[42] The geometry of the isomerization product of $HIr[Si(OMe)_3]_2(CO)[P(p\text{-tolyl})_3]_2$ cannot be as confidently assigned, although the structure shown in the lower half of Figure 1 is consistent with the spectroscopic data.

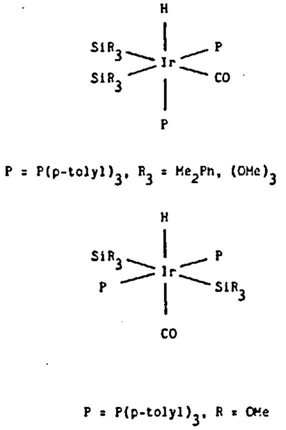

FIGURE 1 Suggested structures of $HIr(SiR_3)_2(CO)[P(p\text{-tolyl})_3]_2$.

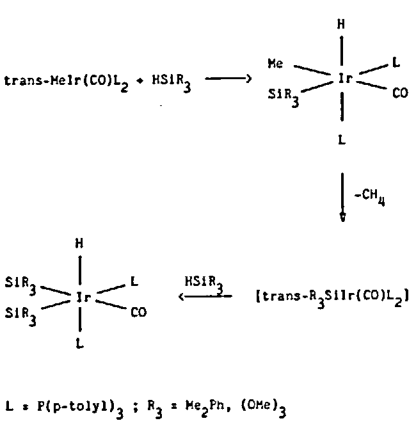

FIGURE 2. Suggested reaction path for reaction of silanes with *trans*-$MeIr(CO)[P(p\text{-tolyl})_3]_2$.

In contrast to results on alkyl platinum complexes in which reaction with electron withdrawing silanes resulted in Si–C bond formation,[43,44] we observe C–H bond formation for both donor and acceptor groups on the silane. A proposed reaction pathway for the reactions of silanes with the methyliridium complex is shown in Figure 2. The initial step is oxidative addition of the silane to produce an intermediate hydride complex which possesses a *cis* arrangement of the hydride and methyl ligands. Reductive elimination of methane yields an unsaturated silyliridium complex which undergoes oxidative addition of a second silane molecule to produce HIr(CO)-$(SiR_3')_2[P(p\text{-tolyl})_3]_2$.

The addition of silanes to square planar iridium(I) complexes leads to three distinct reductive elimination reactions; (1): reformation of the silicon–hydrogen bond occurs for *trans*-$Ir(CO)(PPh_3)_2Cl(SiR_3)(H)$,[45,46] (2): formation of a silicon–oxygen bond for alkoxy iridium complexes and (3): formation of carbon–hydrogen bonds for alkyl iridium complexes. If we assume that reductive elimination is the rate determining step for these reactions, the following order of ease of bond formation to silicon is observed, Si–O > Si–H > Si–Cl, as a kinetic order. Silicon–carbon bond formation cannot be included because of the rapid CH_4 elimination through C–H bond formation. Further (if isomerization is not rate-limiting) our data suggest that formation of Si–O bonds occurs in preference to O–H bonds and that C–H bonds form in preference to Si–C bonds.

The reaction of trimethylsilyliodide with *trans*-$MeIr(CO)[P(p\text{-tolyl})_3]_2$ results in the formation of an iodo analogue of Vaska's compound, a silyliridium complex and tetramethylsilane, as shown below.

$$trans\text{-}RIr(CO)L_2 + R_3SiI \rightarrow trans\text{-}IrI(CO)L_2 + SiR_4 \qquad (2)$$

$$trans\text{-}IrI(CO)L_2 + R_3SiI \rightarrow R_3SiIrI_2(CO)L_2 \qquad (3)$$
$$L = P(p\text{-tolyl})_3;\ R = CH_3$$

Tetramethylsilane was identified by gas chromatographic and NMR analysis. Under the experimental conditions a mixture of *trans*-$Ir(CO)[P(p\text{-tolyl})_3]_2I$ and $IrI_2(CO)$-$(SiMe_3)[P(p\text{-tolyl})_3]_2$ was formed. The ^1H NMR spectrum clearly shows the stoichiometry for $IrI_2(CO)(SiMe_3)[P(p\text{-tolyl})_3]_2$. The CO stretch at 2041 cm^{-1} is very similar to that observed for $IrI_2(CO)(CH_3)(PPh_3)_2$ at 2045 cm^{-1}.[47] To make certain that oxidative addition was occurring, we reacted *trans*-$Ir(CO)[P(p\text{-tolyl})_3]_2Cl$ with Me_3SiI and observed a product with similar characteristics (2042 cm^{-1}).

Reaction with trimethylsilyliodide readily occurs at ambient temperature; however, no reaction occurs with trimethylsilylchloride. That the iodide reacts in preference to the chloride is consistent with similar oxidative addition to $Pt(PEt_3)_3$.[39] The sequence leading to the observed products of reaction (*2*) involves an initial oxidative addition of Me_3SiI to *trans*-$MeIr(CO)[P(p\text{-tolyl})_3]_2$, reductive elimination of $SiMe_4$ to give *trans*-$Ir(CO)[P(p\text{-tolyl})_3]_2I$ and a second oxidative addition of Me_3SiI to give $Ir(SiMe_3)(CO)[P(p\text{-tolyl})_3]_2I_2$. This scheme is shown in Figure 3.

The ready formation of silicon–carbon bonds is in contrast to the stability of dialkyliridium(III) complexes.[32] The complexes $(CH_3)_2IrI(CO)(PPh_3)_2$, $[(CH_3)_2Ir$-$(CO)(PPh_3)_2]CF_3SO_3$ and $Ir(CH)_3(CH_2C(CH_3)_3)(N(Si(CH_3)_2CH_2PPh_2)_2)$ are thermally stable below 80°C. Efforts to thermally induce reductive elimination of ethane from the dimethyliridium complexes does not result in carbon–carbon bond formation but rather results in alpha-hydride abstraction.[32,48]

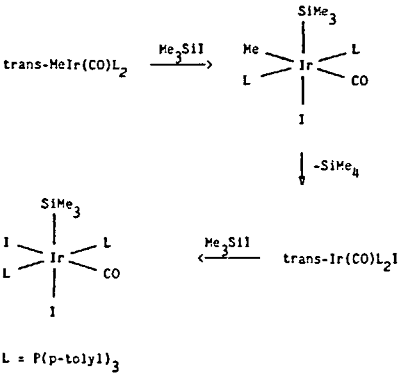

FIGURE 3. Scheme for the addition of Me_3SiI to *trans*-$MeIr(CO)[P(p\text{-tolyl})_3]_2$.

Facile oxidative addition of silicon–halide bonds to metal centres has not been previously observed.[39] The ready addition of $SiMe_3I$ to *trans*-$MeIr(CO)[P(p\text{-tolyl})_3]_2$ results in silicon–carbon bond formation while addition of a silane results in methane elimination with no formation of silicon–carbon bonds. While the addition of the silicon–iodide bond probably occurs with a *trans* distribution of silicon and iodide and addition of a silane almost certainly gives the hydride and silicon *cis*, either addition would give the methyl and silyl *cis* to one another in the most likely geometry. Thus the failure to form a silicon–carbon bond upon addition of silane probably indicates that carbon–hydrogen bond formation is considerably more facile. Certainly, carbon–hydrogen bond formation is facile in *trans*-$MeIr(CO)L_2$ complexes.[31,49]

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