Thermal Reaction of Ethyl(hydrido){(2-phosphinoethyl)silyl}iridium(III) Complex –Formation of a {(2-Phosphinoethyl)silyl}(ethene)iridium(I) Complex–

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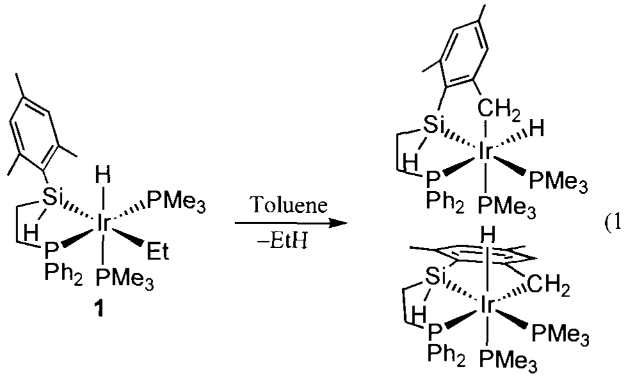
(Received September 12, 1997; CL-970714)

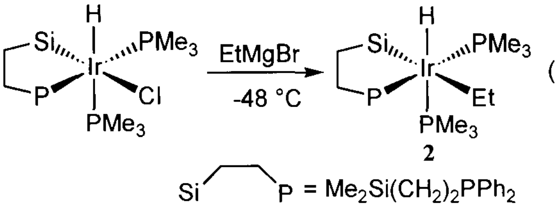
Thermolysis of $L_nIr(C_2H_5)(H)$ [L_n = {η^2-$Me_2Si(CH_2)_2PPh_2$}-$(PMe_3)_2$] led to the clean formation of a 1 : 1 mixture of ethene complex $L_nIr(C_2H_4)$ and dihydrido complex $L_nIr(H)_2$. The former product is proved to be an efficient precursor of an unsaturated silyliridium(I) species through dissociation of ethene.

Our previous paper described that thermolysis of ethyl(hydrido)iridium(III) complex **1** containing a bidentate ligand $MesHSi(CH_2)_2PPh_2$ underwent reductive elimination of ethane and intramolecular carbon-hydrogen bond activation to give silairidacycles as illustrated in eq 1. The reaction is rationalized by assuming the generation of an unsaturated {(2-phosphinoethyl)silyl}iridium(I) intermediate.[1] In this work, we employed $Me_2Si(CH_2)_2PPh_2$ as a bidentate ligand, which was not expected to undergo intramolecular C-H bond activation.



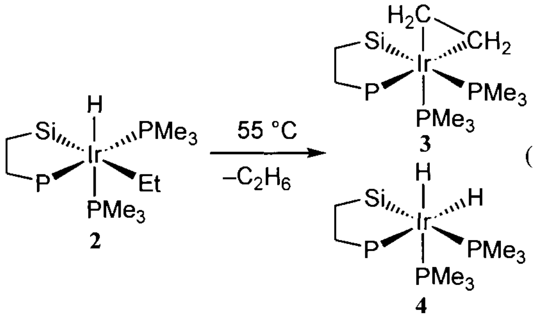
(1)

Treatment of *mer*-[Ir(Cl)(H){η^2-$Me_2Si(CH_2)_2PPh_2$}$(PMe_3)_2$][2] with EtMgBr at -48 °C resulted in the formation of *mer*-[$Ir(C_2H_5)(H)${η^2-$Me_2Si(CH_2)_2PPh_2$}$(PMe_3)_2$] (**2**) as colorless crystals in 62% isolated yield (eq 2).[3] The analytical and spectroscopic data are consistent with the geometry shown in eq 2. The ^{13}C NMR signal of $Ir\underline{C}H_2CH_3$ appears at –21.4 ppm as a ddd with three identical *cis* coupling constants (J(CP*cis*) = 7.9 Hz). This chemical shift is characteristic of the carbon directly bound to a transition-metal through a σ-bond. The $^{29}Si\{^1H\}$ NMR spectrum shows a ddd at 9.0 ppm coupled with three *cis* phosphorus nuclei (J(SiP*cis*) = 19.0, 11.8, 9.2 Hz). Ethyl(hydrido){(2-phosphinoethyl)silyl} complex **2** can be a good model for understanding the transition-metal catalyzed hydrosilation reactions.[4]



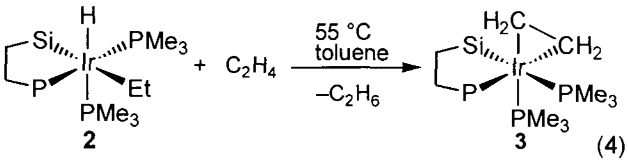
(2)

Thermolysis of **2** in C_6D_6 at 55 °C for 6 h mainly afforded a mixture of ethene complex **3**[5] and dihydrido complex **4**[6] as shown in eq 3. Based on the integration of the ^1H NMR signals, the molar ratio of **3** to **4** was approximately 1 : 1. The ^1H NMR spectrum showed formation of ethane(0.79 ppm in C_6D_6). The geometry of complex **3** was unequivocally determined by NMR spectroscopy. In the ^{13}C DEPT135 NMR spectrum of **3**, the two chemically nonequivalent methylene carbon atoms of the ethene ligand were observed as negative phase signals with nearly the same coupling patterns (ddd) at 14.8 ppm (J(CP*trans*) = 27.4 Hz, J(CP*cis*) = 4.6, 6.9 Hz) and at 9.1 ppm (J(CP*trans*) = 28.9 Hz, J(CP*cis*) = 2.4, 7.3 Hz), respectively. The negative phase of these signals indicates that an even number of hydrogen is attached to each carbon. In the ^{13}C-^1H HETCOR spectrum, the ^{13}C NMR signals of the ethene ligand at 14.8 and 9.1 ppm correlate with the ^1H NMR signals at 1.35 and 2.48 ppm and at 1.48 and 1.62 ppm, respectively, which are assignable to four protons on the ethene ligand. Moreover, in the ^1H-^1H COSY spectrum, these four protons of the ethene ligand at 1.35, 2.48, 1.48, and 1.62 ppm correlate with each other. These observations clearly demonstrate that the ethene ligand does not rotate at least on the NMR timescale. The $^{29}Si\{^1H\}$ NMR spectrum showed a ddd at 20.9 ppm with one large *trans* (J(SiP*trans*) = 147.2 Hz) and two nearly identical *cis* coupling constants (J(SiP*cis*) = 13.0, 10.8 Hz). The geometry of complex **4** was also determined by the NMR and IR spectroscopic data,[6] which clearly indicate that complex **4** possesses two kinds of hydrido ligands as shown in eq 3.



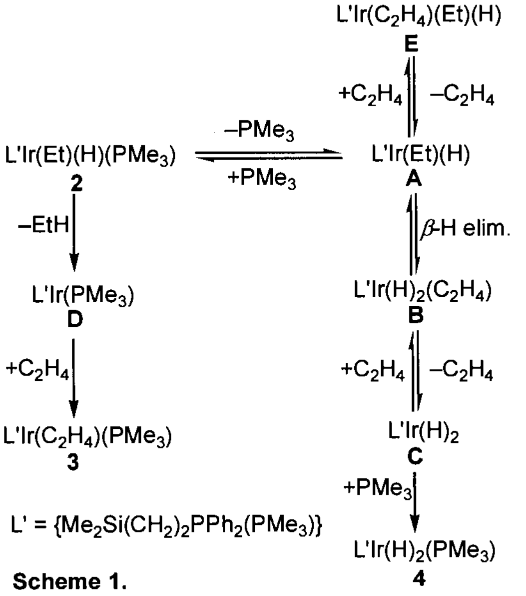
(3)

Complex **3** was also formed almost quantitatively by the reaction of **2** in the presence of ethene under a pressure of 1.5 atm (eq 4). Importantly, in the conditions, *β*-hydrogen elimination was completely inhibited.



(4)

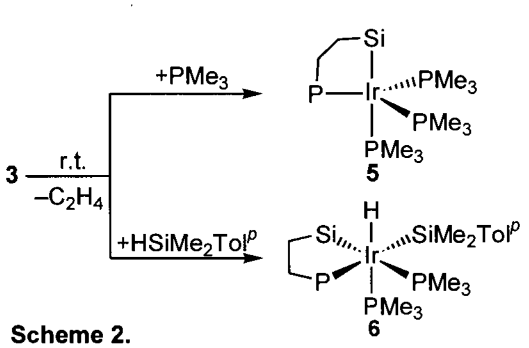
A possible mechanism for the thermal reaction of **2** is shown in Scheme 1. It involves initial dissociation of a PMe_3 ligand to give intermediate **A**, followed by the β-hydrogen elimination. The resulting dihydrido(ethene) complex **B** eliminates an ethene ligand reversibly to generate free ethene and intermediate **C**. Subsequently, intermediate **C** ligates PMe_3 to afford complex **4**. At the same time, ethyl(hydrido) complex **2** eliminates ethane reductively. The resulting 16e-intermediate **D** ligates ethene to give ethene complex **3**. In the presence of ethene, ethene traps a 16e-ethyl(hydrido)iridium(III) intermediate **A** and β-hydrogen elimination would be suppressed.



Scheme 1.

The complex possessing silyl and ethene ligands simultaneously is still rare, although it can be regarded as a key intermediate in the catalytic hydrosilation reaction.[4] Apart form **3**, other examples are $Fe(CO)_3(C_2H_4)(H)(SiPh_3)$[7], $Cp'Rh(C_2H_4)(SiR_3)(H)$ ($Cp' = C_5Me_5$[8], C_5H_5[9]), and (triso)$Ir(SiPh)_3(H)(C_2H_4)$ (triso = $C(Ph_2PO)_3^-$)[10]. Complex **3** is a new type of silyl(ethene) complex, which possesses no σ-bonded ligand except the silyl ligand.

To investigate the lability of the ethene ligand of **3**, the reactions of complex **3** with PMe_3 and $HSiMe_2Tol^p$ were carried out (Scheme 2). Complex **3** reacted with PMe_3 at room



Scheme 2.

temperature to give a {(2-phosphinoethyl)silyl}iridium(I) complex **5** quantitatively.[2,11] The starting complex also reacted with $HSiMe_2Tol^p$ at room temperature to give silyl(hydrido)-iridium(III) complex **6**.[6] In these two reactions, formation of ethene was confirmed by ^1H NMR spectroscopy. These results are consistent with generation of a 16e-{(2-phosphinoethyl)silyl}iridium(I) intermediate *via* dissociation of an ethene ligand. Recently, in some laboratories, attention has been paid to generation of unsaturated four-coordinate silyliridium(I) complex.[12-14] Only very recently, a 16e-silyliridium(I) complex $Ir\{Si(SiMe_3)_3\}(PMe_3)_3$ has been detected in solution at -80 °C spectroscopically, although its isolation was not successful.[14] Complex **3** can become a new efficient precursor of a 16e-silyliridium(I) species which works under very mild conditions.

References and Notes

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3 Data for **2**: ^1H NMR (C_6D_6, 300 MHz) δ -12.64 (dt, J(HP*trans*) = 119.4, J(HP*cis*) = 20.5 Hz, 1H, IrH), 0.54, 0.80 (s, 3H x 2, $SiMe_2$), 0.66, 0.88 (m, 1H x 2, $SiCH_2$), 0.83 (d, J(HP) = 7.4 Hz, 9H, PMe_3), 0.88, 1.52 (m, 2H, $IrCH_2$), 1.52 (d, J(HP) = 2.2, 8.7 Hz, 9H, PMe_3), 1.80 (t, J(HH) = 7.7 Hz, $IrCH_2C\underline{H}_3$), 2.07, 2.41 (m, 1H x 2, PCH_2), 6.97-7.11, 7.59-7.65, 7.89-7.96 (m, 10H, Ar). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz) δ -21.4 (q, J(CP*cis*) = 7.9 Hz, $Ir\underline{C}H_2CH_3$), 7.0 (d, J(CP) = 2.8 Hz, SiMe), 11.6 (d, J(CP) = 5.1 Hz, SiMe), 18.6 (ddd, J(CP) = 26.2, 5.2, 2.7 Hz, PMe_3), 19.1 (dd, J(CP) = 20.8, 3.9 Hz, $SiCH_2$), 22.2 (dt, J(CP) = 33.1, 4.3 Hz, PMe_3), 25.1 (d, J(CP) = 8.6 Hz, $IrCH_2\underline{C}H_3$), 36.5 (dd, J(CP) = 38.9, 2.3 Hz, PCH_2), 127.6, 128.2, 129.1, 129.2, 132.4, 133.6, 137.0, 138.0 (m, Ar). $^{29}Si\{^1H\}$ NMR (C_6D_6, 59.6 MHz) δ 9.0 (ddd, J(SiP*cis*) = 19.0, 11.8, 9.2 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz) δ -61.0 (dd, J(PP*cis*) = 21.9, 16.8 Hz, PMe_3 (*trans* to IrH)), -48.7 (dd, J(PP*trans*) = 348.3, J(PP*cis*) = 21.9 Hz, PMe_3 (*trans* to PPh_2)), 31.5 (dd, J(PP*trans*) = 348.3 Hz, J(PP*cis*) = 16.8 Hz, PPh_2). MS (70 eV, DEI) *m/z* 652 (2, M^+). Anal. Found: C, 45.54; H, 6.90%. Calcd for $C_{24}H_{44}IrP_3Si \cdot 1/8\ C_6H_5CH_3$: C, 45.45; H, 6.90%. The ratio of complex **3** to solvating toluene was confirmed to be 1 : 1/8 by a ^1H NMR spectrum.

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5 ^1H NMR (300 MHz, C_6D_6) δ 1.48, 1.62 (m, 1H x 2, $Ir(C\underline{H}_2{=}CH_2)$), 1.35, 2.48 (m, 1H x 2, $Ir(CH_2{=}C\underline{H}_2)$). $^{13}C\{^1H\}$ NMR δ 14.8 (ddd, J(CP*trans*) = 27.4, J(CP*cis*) = 4.6, 6.9 Hz, $Ir(\underline{C}H_2{=}CH_2)$), 9.1 (ddd, J(CP*trans*) = 28.9, J(CP*cis*) = 2.4, 7.3 Hz, $Ir(CH_2{=}\underline{C}H_2)$). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6) δ -61.7 (dd, J(PP*cis*) = 23, 47 Hz, PMe_3), -60.8 (dd, J(PP*cis*) = 22, 23 Hz, PMe_3), 30.6 (dd, J(PP*cis*) = 22, 47 Hz, PPh_2). $^{29}Si\{^1H\}$ NMR (59.6 MHz, C_6D_6) δ 20.9 (ddd, J(SiP*trans*) = 147.2 Hz, J(SiP*cis*) = 13.0, 10.8 Hz). Exact mass, (70 eV, DEI) *m/z* Calcd for $C_{24}H_{42}IrP_3Si$: 644.1936. Found: 644.1943.

6 Dihydridoiridium(III) complex **4** was also obtained by the reaction of *mer*-$Ir(Cl)(H)\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2$ with $LiAlH_4$. M. Okazaki, H. Tobita, and H. Ogino, *J. Chem. Soc., Dalton Trans.*, in press.

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