(Phosphinoalkyl)silyl Complexes. 3.[1] "Chelate-Assisted" Hydrosilylation: Formation of Enantiomeric and Diastereoisomeric Iridium(III) Complexes with Chelating (Phosphinoethyl)silyl Ligands

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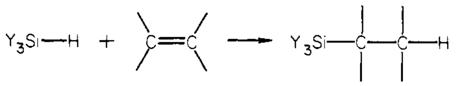
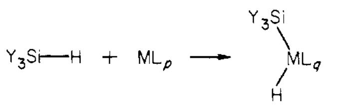
Abstract: Reaction of *trans*-[Ir(PPh$_3$)$_2$(CO)(Cl)] with the functionalized silanes PPh$_2$CH$_2$CH$_2$SiR^{1}R^{2}H (R^1 = R^2 = Me or Ph; R^1 = Me, R^2 = Ph; or R^1 = Me or Ph, R^2 = H) occurs immediately under ambient conditions to give white Ir(III) adducts **1–5** as single stereoisomers at the octahedral Ir center. On the basis of IR and NMR data, product **1** (R^1 = R^2 = Me) is assigned the structure [*rac*-(*OC*-6-45)-carbonylchlorohydrido[(2-(diphenylphosphino)ethyl)dimethylsilyl](triphenylphosphine)iridium], an arrangement that has been confirmed by X-ray crystallography and is shared by analogues **2–5**. Compounds **1–5** [Ir(PPh$_2$CH$_2$CH$_2$SiR^{1}R^2)(^{n}H)(Cl)(CO)(PPh$_3$)] (*n* = 1 or 2; R^1 = R^2 = Me or Ph; R^1 = Me, R^2 = Ph; or R^1 = Me or Ph, R^2 = H) are chiral at Ir, but while **1** and **2** are enantiomeric, **3–5** are diastereoisomeric as is established by ^{1}H and ^{31}P NMR data. Complex **1** reacts with LiAlH$_4$ to give the Ir(III) dihydride Ir(PPh$_2$CH$_2$CH$_2$SiMe$_2$)(PPh$_3$)(H)$_2$(CO) (**6**) which is also formed initially regiospecifically by oxidative addition of PPh$_2$CH$_2$CH$_2$SiMe$_2$H to HIr(PPh$_3$)$_3$CO, although deuteriation experiments demonstrate yet uncharacterized subsequent slow exchange between the two H positions. There was no evidence for reductive elimination from compounds **1** and **6** upon UV irradiation, and **1** resisted HCl loss on addition of NaOMe or NEt$_3$, although with the latter in the presence of excess Ph$_2$PCH$_2$CH$_2$SiMe$_2$H the bis(chelate) Ir(PPh$_2$CH$_2$CH$_2$SiMe$_2$)$_2$(H)(CO) (**7**) was obtained; this product was also isolated on reacting **6** with Ph$_2$PCH$_2$CH$_2$SiMe$_2$H.

Hydrosilylation (or hydrosilation, i.e., addition of a Si–H bond at a center of unsaturation), either of an olefinic or acetylenic organic substrate as in eq 1 or at a low-valent transition-metal atom, oxidatively, eq 2, represents a well-established and important synthetic reaction.[2] Formation of organosilicon derivatives according to eq 1, which is the key step in the industrial production of silicone precursors, can be effected under mild conditions by the use of H$_2$PtCl$_6$ (Speier's[3] catalyst) or a related platinum-group metal salt as a catalyst.[4] Specifics of the catalytic cycle have resisted characterization, but[2b,3,4] Si–H bond cleavage via silane addition at the activated metal center (i.e., eq 2) is regarded de fide as being crucial: while such a reaction is not general, it is observed to occur spontaneously[5] with a limited range of metal complexes (notably dicobalt octacarbonyl).[6,7]

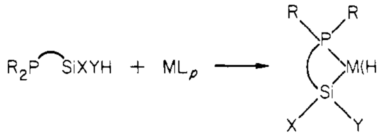


$$Y_3Si{-}H + {>}C{=}C{<} \longrightarrow Y_3Si{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H \qquad (1)$$



$$Y_3Si{-}H + ML_p \longrightarrow \overset{Y_3Si}{\underset{H}{\diagdown ML_q}} \qquad (2)$$

Equation 2 also offers a formal analogy with the transition-metal-mediated activation of an unperturbed C–H bond. The so-called "orthometalation" reaction provides a special case of C–H activation promoted by proximity to a metal center M: typically facile intramolecular transfer of H to M occurs from the ortho position in a coordinated (aryl)phosphine, with concomitant formation of a M–C bond.[8] In order to explore the influence of a related effect on the course of the hydrosilation reaction (2), we have synthesized a range[9] of modified organosilanes R$_2$P-(CH$_2$)$_n$SiR^{1}R^{2}H (*n* = 1, 2, or 3; R, R^1 = Me or Ph, R^2 = H, Me, or Ph) incorporating an organophosphorus fragment. The strong complexing properties of the latter result in "chelate-assisted" hydrosilation (eq 3) where *n* = 2: at Pt(0) or Pt(II), for example,



(3)

rapid quantitative formation of Pt(PPh$_2$CH$_2$CH$_2$SiR^{1}R^2)$_2$ (R^1 = R^2 = Me or Ph; or R^1 = Me, R^2 = Ph) has been observed under conditions where simple organosilanes are completely unreactive.[10]

To assess the scope of eq 3 we began by investigating the oxidative addition of phosphinoethylsilanes (i.e., *n* = 2) to coordinatively unsaturated iridium(I) compounds, in particular *trans*-[Ir(PPh$_3$)$_2$(CO)Cl] ("Vaska's complex"). Hydrosilation of the latter was accompanied in these reactions by displacement of one of the PPh$_3$ ligands, resulting in stereospecific chelate formation to afford Ir(III) products as single geometric isomers that are enantiomeric, i.e., chiral at the six-coordinate metal center. We also describe the influence of prochirality at Si on the addition step (eq 3, X ≠ Y): in these circumstances the formation of diastereoisomeric products has been demonstrated by using ^{1}H and ^{31}P NMR spectroscopy.

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Experimental Section

Standard inert atmosphere preparative techniques were employed throughout, using rotary oil-pump vacuum or operating under an atmosphere of dinitrogen gas. Solvents were dried, degassed, and redistilled immediately before use. IR spectra were measured with a Perkin-Elmer 283 spectrophotometer, and ^1H and ^{31}P NMR spectra were routinely recorded with Perkin-Elmer R32 or Nicolet TT-14 Fourier-transform spectrometers operating at 90.0 or 24.3 MHz, respectively. The ^1H NMR spectra of certain compounds were also measured at 250 MHz with a Bruker WM250 instrument. Microanalytical data were supplied by Canadian Microanalytical Services Ltd., Vancouver.

Synthesis of Starting Materials. Preparation of the phosphinoethylsilanes $Ph_2PCH_2CH_2SiR^1R^2H$ ($R^1 = R^2$ = Me or Ph; or R^1 = Me, R^2 = Ph) and $Ph_2PCH_2CH_2SiRH_2$ (R = Me or Ph) by $LiAlH_4$ reduction of the corresponding chloro(phosphinoethyl)silanes has recently[9] been described; in several cases the monodeuterio- analogues were obtained similarly, using $LiAl^2H_4$. The iridium(I) complexes *trans*-$Ir(Cl)(CO)(PPh_3)_2$ and $HIr(CO)(PPh_3)_3$ are readily accessible by using straightforward literature methods.[11]

Synthesis of [(Phosphinoethyl)silyl]iridium(III) Complexes. $Ir(PPh_2CH_2CH_2SiMe_2)(PPh_3)(H)(CO)(Cl)$ (1a). To a stirred solution of *trans*-$Ir(Cl)(CO)(PPh_3)_2$ (0.50 g, 0.64 mmol) in benzene (40 mL) was added liquid $Ph_2PCH_2CH_2SiMe_2H$ drop by drop with a syringe until the characteristic lemon-yellow color of the iridium(I) complex was completely discharged. After further stirring for 10 min the solvent was pumped away, leaving a colorless, oily residue, which was dissolved in boiling hexane (35 mL). After the solution was cooled, a white solid separated, from which the supernatant was carefully removed and discarded; recrystallization four times from dichloromethane/hexane mixtures afforded the product as a pure white powder, mp 160–161 °C (0.37 g, 0.47 mmol, 73%). Anal. Calcd for $C_{35}H_{36}ClIrOP_2Si$: C, 53.18; H, 4.56. Found: C, 52.98; H, 4.67. Repeated efforts to crystallize this compound deliberately were unsuccessful; however, on one occasion well-formed colorless cube-shaped crystals which proved to be suitable[12] for X-ray diffraction were obtained fortuitously by dissolution of the oily crude product (ca. 1.0 g) in a large excess (ca. 25 mL) of diethyl ether, followed by addition of an equal volume of hexane and exposure of the resulting clear solution to a rapid draught of cool air.

$Ir(PPh_2CH_2CH_2SiMe_2)(PPh_3)(^2H)(CO)(Cl)$ (1b). The deuterio analogue **1b** of complex **1a** was prepared by treatment of a benzene solution of *trans*-$Ir(Cl)(CO)(PPh_3)_2$ (0.10 g, 0.13 mmol) with just sufficient $Ph_2PCH_2CH_2SiMe_2{}^2H$ to cause decolorization of the former. The white product was recovered as described above.

$Ir(PPh_2CH_2CH_2SiPh_2)(PPh_3)(H)(CO)(Cl)$ (2a). Addition of a solution in benzene of $Ph_2PCH_2CH_2SiPh_2H$ to a stirred solution in benzene (15 ml) of *trans*-$Ir(Cl)(CO)(PPh_3)_2$ (0.20 g, 0.26 mmol) until the reaction mixture was completely colorless was followed by removal of solvent. The white residue was washed with hexane (4 × 10 mL), after which crystallization from dichloromethane/heptane afforded white microcrystals of the product, mp 174–176 °C (0.17 g, 0.19 mmol, 72%). Anal. Calcd for $C_{45}H_{40}ClIrOP_2Si$: C, 59.11; H, 4.38. Found: C, 58.26; H, 4.66.

$Ir(PPh_2CH_2CH_2SiPh_2)(PPh_3)(^2H)(CO)(Cl)$ (2b). After dropwise addition of a solution in benzene of $Ph_2PCH_2CH_2SiPh_2{}^2H$ to a stirring solution in the same solvent (15 mL) of *trans*-$Ir(Cl)(CO)(PPh_3)_2$ (0.10 g, 0.13 mmol) until the yellow color of the latter was discharged completely, the volume of the reaction mixture was reduced to 5 mL, and then heptane (15 mL) was added. The resulting white precipitate was thoroughly washed with heptane then dried in vacuo to give the product as a fine white powder (0.08 g, 0.09 mmol, 67%).

$Ir(PPh_2CH_2CH_2SiMePh)(PPh_3)(H)(CO)(Cl)$ (3a). To *trans*-$Ir(Cl)(CO)(PPh_3)_2$ (0.10 g, 0.13 mmol) dissolved in toluene (50 mL) and stirred at 60 °C was added liquid $Ph_2PCH_2CH_2SiMePhH$ until complete decolorization occurred, after which stirring of the reaction mixture was continued for 10 min and then solvent was removed to leave a colorless oil. Addition of pentane precipitated a white solid from which was recrystallized (dichloromethane/pentane) the product, mp 112–115 °C (0.072 g, 0.09 mmol, 65%). Anal. Calcd for $C_{40}H_{38}ClIrOP_2Si$: C, 56.38; H, 4.46. Found: C, 57.62; H, 4.81.

$Ir(PPh_2CH_2CH_2SiMePh)(PPh_3)(^2H)(CO)(Cl)$ (3b). An identical procedure with that described above was followed using the deuteriosilane $Ph_2PCH_2CH_2SiMePh^2H$ to yield the ^2H-analogue **3b** of complex **3a**.

$Ir(PPh_2CH_2CH_2SiMeH)(PPh_3)(H)(CO)(Cl)$ (4a); $Ir(PPh_2CH_2CH_2SiMe^2H)(PPh_3)(^2H)(CO)(Cl)$ (4b); and $Ir(PPh_2CH_2CH_2SiPhH)(PPh_3)(H)(CO)(Cl)$ (5). These compounds were synthesized in experiments similar to those described above by reacting Vaska's complex with the precursors $Ph_2PCH_2CH_2SiMe^nH_2$ (*n* = 1 or 2) or $Ph_2PCH_2CH_2SiPhH_2$, respectively. Yields were ca. 50% with mp 80–85 °C (**4a**, **4b**) or 100–105 °C (**5**); the colorless products were characterized by IR and NMR spectroscopy.

$Ir(PPh_2CH_2CH_2SiMe_2)(PPh_3)(H)_2(CO)$ (6). Method A. From Complex 1a. Complex **1a** (0.25 g, 0.32 mmol) was dissolved in THF (10 mL). After dropwise addition of a solution of $LiAlH_4$ (0.14 g, 3.7 mmol) in THF (15 mL) the reaction mixture was stirred overnight and then refluxed (8 h). Careful addition of MeOH to the resulting pale yellow solution afforded a colorless mixture from which all volatiles were removed. The solid residue was redissolved in the minimum of THF and filtered under a N_2 atmosphere through a plug of alumina. Slow addition of hexane precipitated the product as a cream-colored powder, ca. 60% yield. Anal. Calcd for $C_{35}H_{37}IrOP_2Si$: C, 55.64; H, 4.90. Found: C, 55.95; H, 5.10.

Method B. From $HIr(CO)(PPh_3)_3$. To a solution of $HIr(CO)(PPh_3)_3$ (0.10 g, 0.11 mmol) in THF (10 mL) was added $Ph_2PCH_2CH_2SiMe_2H$ (0.05 g, 0.18 mmol) dissolved in THF (8.5 mL). After stirring at ambient temperature for 60 min, during which time the reaction mixture became almost colorless, the THF was pumped away, and the residue was taken up in hexane (10 mL). Filtration to give a clear solution was followed by concentration to half volume and refrigeration (−20 °C). Colorless crystals of the product formed over 4 days (0.06 g, 0.08 mmol, 71%) and were shown to be identical with the material prepared by method A using IR and NMR spectroscopy.

$Ir(PPh_2CH_2CH_2SiMe_2)_2(H)(CO)$ (7). This compound was shown to be the major product of reactions in refluxing THF between (a) complex **1a** and excess $Ph_2PCH_2CH_2SiMe_2H$ (4 h) in the presence of NEt_3 and (b) complex **6** and excess $Ph_2PCH_2CH_2SiMe_2H$ (12 h). It was identified on the basis of the IR spectrum and ^1H and ^{31}P NMR data, all of which were found to be identical with those[13] of an authentic sample.

$Ir(PPh_2CH_2CH_2SiMe_2)(PPh_3)(H)(CO)(Br)$ (8). After complex **1a** was stirred with excess NaBr in acetone solution for 15 h, the solvent was removed; the remaining solid was then dissolved in the minimum of THF, and the resulting colorless solution was washed down a short column packed with alumina. Addition of hexane to the eluent precipitated the product as a cream-colored powder. Anal. Calcd for $C_{35}H_{36}BrIrOP_2Si$: C, 50.36; H, 4.35. Found: C, 50.69; H, 4.30.

$Ir(PPh_2CH_2CH_2SiMe_2)(PPh_3)(H)(CO)(I)$ (9). Complex **1a** (0.15 g, 0.19 mmol) in THF (10 mL) was treated with a slight excess of MeMgI in the same solvent (10 mL). After 15 min the reaction mixture was a very pale yellow color with a trace of solid present. After 10 h a white precipitate had separated leaving a yellow superantant. Filtration through alumina followed by addition of hexane (10 mL) afforded a yellow solid, which was washed with hexane and then recrystallized (THF/hexane) to give the pure product. Anal. Calcd for $C_{35}H_{36}IIrOP_2Si$: C, 47.67; H, 4.11; I, 14.39. Found: C, 47.48; H, 4.23; I, 14.10.

Results

[(Diphenylphosphino)ethyl]silanes[9] $Ph_2PCH_2CH_2SiR^1R^2H$ ($R^1 = R^2$ = Me or Ph; R^1 = Me, R^2 = Ph; or R^1 = Me or Ph, R^2 = H) react immediately with *trans*-$[Ir(PPh_3)_2(CO)(Cl)]$ ("Vaska's complex") in benzene solution under ambient conditions according to eq 4, affording in high yield (ca. 70%) Ir(III) adducts that were

$$Ir(PPh_3)_2(CO)(Cl) + Ph_2PCH_2CH_2SiR^1R^2H \rightarrow Ir(PPh_2CH_2CH_2SiR^1R^2)(PPh_3)(H)(CO)(Cl) + PPh_3 \quad (4)$$

recovered as white, air-stable powders. Formulation of these products as octahedral species incorporating a chelating (phosphinoethyl)silyl ligand was supported by microanalytical data as well as IR and NMR measurements and the detection of displaced triphenylphosphine.

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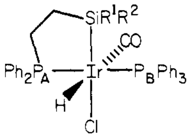
[13] Auburn, M. J.; Stobart, S. R., unpublished observations. Complex **7** has been prepared and characterized by an alternate route, in which reaction of $[Ir(PPh_2CH_2CH_2SiMe_2)_2Cl]$ with CO giving $[Ir(PPh_2CH_2CH_2SiMe_2)_2(CO)(Cl)]$ was followed by $NaBH_4$ reduction. Anal. Calcd for $C_{33}H_{41}IrOP_2Si_2$: C, 51.88, H, 5.41. Found: C, 51.92; H, 5.54.

Table I. Infrared Data (cm^{-1})[a] for Ir(III) Complexes

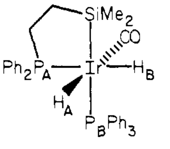
compd	ν_{CO}, cm^{-1}	ν_{IrH}[b], cm^{-1}	compd	ν_{CO}, cm^{-1}	ν_{IrH}[b], cm^{-1}
1a	1983	2081	5	1982	2095[c]
1b	2007		6	1949[e]	2012, 2060
2a	1988	2103	7	1952	2060
2b	2010		8	1978	2080
3a	1982	2090	9	1986	2089
3b	2007				
4a	1981	2088[c,d]			
4b	2012				

[a] KBr disk. [b] In the *deuterio*-iridium compounds ν_{IrD} could not be located with certainty. [c] ν_{SiH} assigned to same contour. [d] ν_{SiD} observed at 1533 cm^{-1} in compound 4b. [e] ν_{CO} = 1944 trans to D.

Isolation of the Ir(III) adducts in which $R^1 = R^2$ (= Me or Ph) as single geometric isomers was suggested by TLC experiments, by the sharp melting-point behavior of both compounds, and by the absence of multiple envelopes for characteristic features in IR or NMR spectra. The structures of compounds **1–5** were subsequently deduced unambiguously through further consideration of the spectroscopic properties. The strong IR absorptions near 1985 and 2090 cm^{-1} (Table I) are respectively attributable[14,15] to ν(CO) and ν(Ir–H).



1, $R^1 = R^2$ = Me
2, $R^1 = R^2$ = Ph
3, R^1 = Me; R^2 = Ph
4, R^1 = Me; R^2 = H
5, R^1 = Ph; R^2 = H



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In the ^{1}H NMR spectra (Table II), , Ir–H consistently appears near δ–7 split into an apparent triplet by coupling to P. The chemical shift values complement the IR data, confirming[14] the structural relationship between H and a strongly trans-influencing group like CO. The splitting (ca. 15 Hz, Table II) of the Ir–H resonance establishes that H is cis to both P atoms since trans PH coupling is characteristically much stronger (>120 Hz); the triplet structure results from near-equality of coupling constants to P_A and P_B. Finally, the ^{31}P NMR spectra for compounds **1–5** are composed of strongly coupled AB patterns that have been solved to yield the parameters included in Table II, the large $^2J_{AB}$ values of ~300 Hz requiring[16] P_A trans to P_B. All of the foregoing data are consistent with a configuration that for compound **1a** in terms of priority sequence[17] may be designated *rac*-(*OC*-6-45)-carbonylchlorohydrido[(2-(diphenylphosphino)ethyl)dimethylsilyl](triphenylphosphine)iridium, with identical coordination around the chiral *OC*-6-iridium center for each of the analogues **2–5**. This proposed geometry has been confirmed for complex **1** by a single-crystal X-ray structure determination.[12]

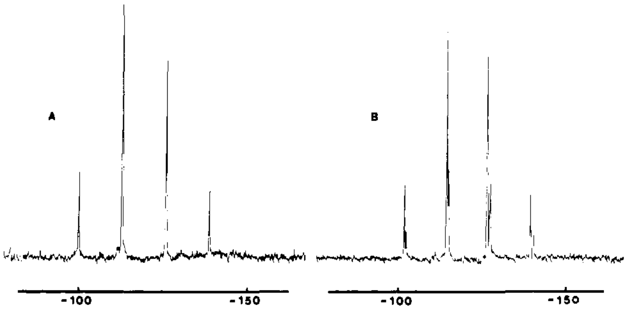

Figure 1. $^{31}P\{^1H\}$ NMR spectra of (A) [Ir(PPh$_2$CH$_2$CH$_2$SiMe$_2$)(PPh$_3$)(H)(CO)(Cl)] (**1**) and (B) [Ir(PPh$_2$CH$_2$CH$_2$SiMeH)(PPh$_3$)(H)(CO)(Cl)] (**4**).

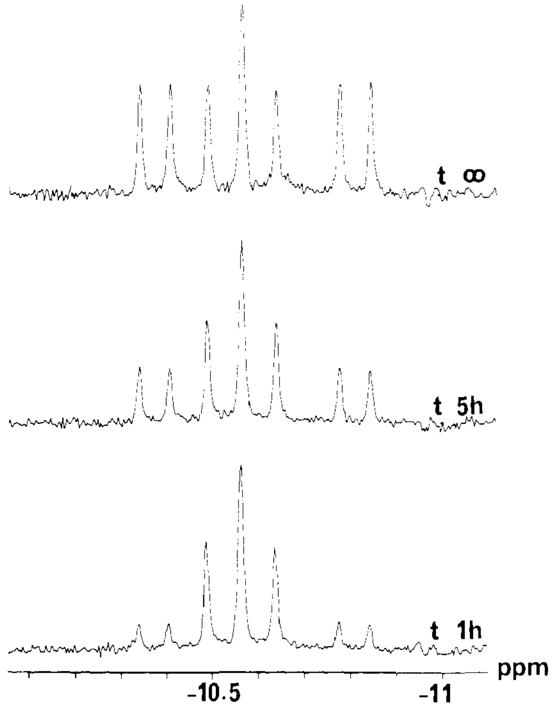

Figure 2. High-field ^{1}H NMR region of [Ir(PPh$_2$CH$_2$CH$_2$SiMe$_2$)(PPh$_3$)(CO)(H)(^{2}H)] (**6**) synthesized via eq 5, n = 2, showing changes in appearance with time.

Reaction as in eq 4 is expected to generate two independent chiral centers (at Ir and Si) for $R^1 \neq R^2$. Accordingly, the ^{31}P NMR spectra for compounds **3–5** each contained two overlapping AB patterns in unequal ratio, consistent with the existence of these materials as diastereoisomeric mixtures. This effect is illustrated in Figure 1, where the appropriate spectral ranges for complexes **1** and **4** are compared. Diastereoisomer ratios estimated from the ^{31}P NMR data were ca. 3:1 for compounds **3** and **4** and 2:1 for **5**, the minor component in each case being distinguished by a prime symbol (e.g., **3a′** vs. **3a**) in Table II. A corresponding effect was observed in the ^{1}H NMR spectra for compounds **3** and **4**, giving rise to doubling of the SiC*H*$_3$ resonance in each case (Table II) again in ca. 3:1 ratio. Attempts to crystallize complexes **3–5** were unsuccessful, so that separation of the individual diastereomers was not attempted.

On treatment with LiAlH$_4$, compound **1a** reacted smoothly to afford the iridium(III) dihydride **6**, formation of which was accompanied by stereochemical reorganization[18] at the metal center.

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(15) Higher wavenumber values would be expected for ν(CO) trans to SiR$_3$ or ν(Ir–H) trans to Cl. Isotopic substitution to give the deuterio analogues **1b–4b** of the protio complexes **1a–4a** accomplished by using the deuteriosilanes Ph$_2$PCH$_2$CH$_2$SiR^{1}R^{2}D (i.e., D = ^{2}H: eq 4) is accompanied by a significant shift (Table I) in ν(CO). This suggests a mutually trans disposition for CO and H at Ir, an arrangement that facilitates strong vibronic coupling between the two stretching modes modifying the energy of each and leading to intensity enhancement of the ν(Ir–H) absorption; the large difference in vibrational energy prohibits similar coupling between ν(CO) and ν(Ir–D) (expected near 1500 cm^{-1}), accounting both for the substantial isotope effect on the former and for the fact that the latter could not be detected (Table I) in the spectra of any of the deuterio complexes.

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(18) The trans P atoms of **1a** rearrange to a mutually cis orientation in the reaction product **6**, which shows a high-field Ir–*H* pattern (Table II) consisting of an apparent triplet (H_A; cis to both P_A and P_B) accompanied by a widely spaced pair of doublets (H_B; trans to P_A, cis to P_B).

Table II. Selected NMR Data[a] for Ir(III) Complexes

	^{31}P NMR, δ			^{1}H NMR, δ		
compd	P_A[b]	P_B	$^{2}J(P_AP_B)$, Hz	IrH	CH_3	^{2}J(HIrP), Hz
1a	−108.2	−131.3	313	−7.38	−0.38, −0.87	15.3[c]
2a	−110.6	−135.1	309	−6.96		15.0
3a	−107.0	−136.5	312	−6.84	−0.20	15.2
3a′	−105.6	−133.9	309	−7.60	−0.40	14.0
4a	−110.7	−131.8	311	−7.09	−0.02	15.5
4a′	−110.9	−133.1	310	n.o.[d]	−0.32	
5	−110.0	−135.0	311	−6.86		14.0, 17.0
5′	−109.7	−133.8	309	n.o.		
6	−112.8	−137.1	14.4	−10.59[e] −10.64[f]	0.59,[g] 0.47[h]	18,[e] 16.9,[f] 108.8[f]
7	−117.1			−10.47	0.98,[i] 0.89[j]	17.98
8	−109.6	−133.9	314	−7.17	0.41, −0.04	14.96
9	−111.56	−138.5	312	−8.67	0.22, −0.24	14.95

[a] ^{1}H spectra measured in $CDCl_3$. ^{31}P spectra in THF relative to external tmp with C_6D_6 lock. In all ^{1}H spectra multiplet resonances due to Ph protons were observed in the range δ 7.0–7.5, to CH_2 protons near δ 2.0 (PCH_2) and δ 0.5–1.0 ($SiCH_2$). For compounds 4a, 4a′, and 5 multiplet SiH resonances were observed as follows: δ 4.60 ($^{3}J = 3.3$ Hz); δ 4.15 ($^{3}J = 3.7$ Hz); δ 4.25. [b] Phosphinoethylsilyl P_A, P_BPh_3. [c] Difference between $^{2}J(HIrP_A)$, $^{2}J(HIrP_B)$ not resolved except for compounds **5** and **6**. [d] Not observed. [e] H cis to P_A and P_B. [f] H trans to P_A, cis to P_B. [g] $^{4}J(HP_B) = 2.2$ Hz. [h] $^{4}J(HP_B) = 2.9$ Hz. [i] $^{4}J(HP_A) = 1.1$ Hz. [j] $^{4}J(HP_A) = 1.9$ Hz.

The same complex was also isolated in good yield via treatment of $HIr(CO)(PPh_3)_3$ with $Ph_2PCH_2CH_2SiMe_2H$, eq 5. This

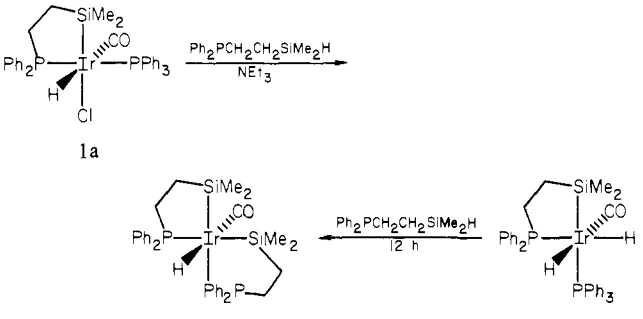
$$HIr(CO)(PPh_3)_3 + Ph_2PCH_2CH_2SiMe_2{}^{n}H \rightarrow \overline{Ir(PPh_2CH_2CH_2SiMe_2})(PPh_3)(CO)(H)({}^{n}H) + 2PPh_3 \quad (5)$$

$$n = 1 \text{ or } 2$$

reaction was repeated by using a molar excess of $Ph_2PCH_2CH_2SiMe_2D$ (eq 5, $n = 2$) and following the formation of the product with ^{1}H NMR spectroscopy. Initially, only the triplet resonance due to H_A was observed, consistent with silane addition, to give **6**, $H_B = {}^{2}H$, but thereafter, slow accumulation of the doublet structure attributable to H_B occurred (Figure 2), corresponding to incorporation of ^{1}H by some mechanism at this second site.

Halide ion exchange at Ir took place when compound **1a** was treated with NaBr or NaI in acetone, affording the bromo and iodo iridium(III) analogues **8** and **9**, the second of which was also formed as the major product in the reaction between **1a** and MeMgI. By contrast with the latter, use of MeMgCl provided tentative evidence for methylation at Ir: in situ measurements confirmed the presence of a species with ^{31}P NMR properties resembling those of **6** (cis inequivalent P atoms), but attempts to isolate this product were unsuccessful. Complex **1a** was found to be unaffected by prolonged treatment with NaOMe/MeOH or NEt_3; however on addition of the latter to a solution of **1a** containing an excess of $Ph_2PCH_2CH_2SiMe_2H$, a further reaction occurred giving a bis(chelate)iridium(III) complex. Configuration **7** is proposed for this product on the basis of the positions of ν(CO) and ν(IrH) (Table II), which suggest again a trans disposition for these two ligands and the resolution of long-range coupling $^{4}J(PIrSiCH)$. Compound **7** was also slowly produced on reacting the dihydrido complex **6** with an excess of $Ph_2PCH_2CH_2SiMe_2H$ (Scheme I).

Scheme I



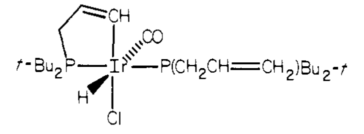
1a

7

6

Discussion

Addition of [(diphenylphosphino)ethyl]silanes (1-(diphenylphosphino)-2-silylethanes) to *trans*-$[Ir(PPh_3)_2(CO)(Cl)]$ occurs extremely rapidly according to eq 4, so that the two reactants can effectively be titrated against one another in benzene solution using the disappearance of the characteristic lemon-yellow color of the Ir(I) precursor as an end point. This well-defined behavior contrasts remarkably with the complications that are encountered when *trans*-$[Ir(PPh_3)_2(CO)(Cl)]$ enters into exchange reactions with triarylmonophosphines[19] or addition reactions with trialkylsilanes,[4b,14b] although the latter do react smoothly[20] with $HIr(PPh_3)_3CO$. Formation of the chelated [((diphenylphosphino)ethyl)silyl]iridium(III) products as single geometric isomers is consistent with complexation via phosphine exchange, which is followed by a rapid cis addition of Si–H at Ir. The resulting stereochemistry is identical with that of a cyclometalated complex **10**, emphasizing the relationship between the "chelate-assisted" hydrosilation described here and intramolecular C–H bond activation, with the powerfully electron-releasing silyl fragment attaching opposite the weakly trans-influencing Cl ligand. Coordination of six different ligands in an octahedral environment with two groups constrained to a mutually cis orientation permutes to allow 12 possible positional isomers, all of which are enantiomeric.[22] The selectivity observed in eq 4 represents one-step access to a specific chiral geometry at an octahedral metal site, a situation first realized in the classic work of Gel'man et al.[23] by a lengthy series of ligand exchange reactions that ultimately yielded separable isomers of the Pt(IV) complex $[Pt(Br)(Cl)(I)(NH_3)(NO_2)(py)]$. More recently cyclometalation reactions have provided a limited range of further examples, such as **10**, for which the stereochemistry has been argued[21] on the basis of spectroscopic data.



10

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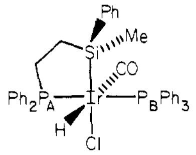
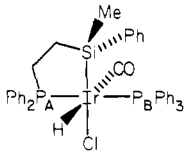
It is clear from the ^{31}P NMR data (cf. Figure 1) that compounds **3–5** exist as mixtures of diastereoisomers. Initial coordination at Ir through displacement of a PPh_3 molecule by P_A would allow subsequent formation of **3a** and **3a′** by Si–H addition



3a



3a′

to either face of a transient square arrangement, differential behavior in this second step amounting to induction at Ir by Si and accounting for the observed unequal diastereomer distribution. Steric considerations suggest that such a preference (which from the observed isomer ratio is obviously slight) may favor configuration **3a** over **3a′**, placing the spatially more demanding substituent at Si adjacent to axial H rather than CO; therefore in the absence of conclusive evidence (diastereomer separation, crystallographic structure determination) the NMR assignments proposed in Table II are based on this assumption. It should be noted that even the tentative argument outlined above does not apply in relation to possible pathways to diastereoisomeric **4a**, **4a′** and **5**, **5′**, because in eq 4 ($R^2 = H$) either Si–H bond can add to Ir, establishing distinguishable competing reactions each of which generates the opposite isomer.

Formation of the dihydrido complex **6** is accompanied by a metal-centered rearrangement that leaves Si opposite to P rather than to the more strongly trans-influencing H or CO ligands. More significantly, hydrosilylation at the Ir(I) center in $HIr(CO)(PPh_3)_3$ affords the same Ir(III) product regiospecifically, placing both the entering H and Si trans to P rather than H or CO, as shown by initial presence of H in one site only, following $Ph_2PCH_2CH_2SiMe_2D$ addition. The nature of the exchange process, which subsequently (Figure 2) introduces H into the second hydridic position, is not yet clear (although slow intramolecular rearrangement related to the fluxional character of certain other transition-metal di- and trihydrides represents an obvious possibility) and is being investigated further; similar behavior in octahedral Ir and Pt hydrido complexes has attracted very recent attention.[25] Preliminary experiments using either unfiltered or monochromatic (366 nm) UV irradiation with or without purging the solution with N_2 gave no evidence for H_2 elimination from compound **6** dissolved in CH_2Cl_2 or benzene; this provides an exception to the normal behavior[26] of mononuclear cis dihydrides. Similarly, though less surprisingly, it was found that HCl could not be eliminated from complex **1a** either by photolytic[27] methods or by treatment with base[28] (NEt_3 or NaOMe/MeOH). These observations may be correlated with the unusual stability toward H_2 loss of dihydridosilyliridium(III) complexes prepared previously[20] from $HIr(CO)(PPh_3)_3$ and more generally with the fact that there is yet no known example of a silyliridium(I) species. Indeed the stability of compound **1** and its analogues may constitute a further manifestation of this resistance to elimination from Ir(III): while rather forcing conditions are required to generate the cis bis(chelate) complex **7**, a rhodium analogue of the latter has been synthesized[13] under mild conditions with no evidence for formation of an isolable species corresponding to **1**.

Conclusion

The high reactivity of the modified silanes[1,9,10,13] toward iridium(I) complexes can be attributed to product formation by a "chelate-assisted" pathway that resembles intramolecular C–H bond activation promoted by proximity to a low-valent coordinatively unsaturated metal site. The resulting Ir(III) adducts illustrate in a rather straightforward way some of the effects of chirality at an octahedral center. More significantly, the reluctance of the dihydride **6** to lose H_2 photolytically[26,29] supports the supposition[20] that inductive electron release from silicon would impart highly nucleophilic (electron-rich) character to any silyl–iridium(I) intermediate stabilized with respect to Si–Ir cleavage; accordingly, possible routes to such species are being further investigated.

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Registry No. **1a**, 88453-23-0; **1b**, 88453-24-1; **2a**, 88453-25-2; **2b**, 88453-26-3; **3a**, 88453-27-4; **3a′**, 88495-19-6; **3b**, 88453-28-5; **3b′**, 88495-20-9; **4a**, 88453-29-6; **4a′**, 88495-21-0; **4b**, 88453-30-9; **4b′**, 88495-22-1; **5**, 88453-31-0; **5′**, 88495-23-2; **6**, 88453-32-1; **7**, 88453-33-2; **8**, 88453-34-3; **9**, 88453-35-4; *trans*-$Ir(Cl)(CO)(PPh_3)_2$, 15318-31-7; $HIr(CO)(PPh_3)_3$, 17250-25-8; $Ph_2PCH_2CH_2SiMe_2H$, 86934-58-9; $Ph_2PCH_2CH_2SiPh_2H$, 86934-62-5; $Ph_2PCH_2CH_2SiMePhH$, 86934-60-3; $Ph_2PCH_2CH_2SiMeH_2$, 86934-63-6.

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