was the transition metal, and a typical "piano-stool" arrangement was constructed around this atom. In the second, the initial atom was the phosphorus of the PPhH$_2$ ligand, the second atom was the transition metal, and the octahedral character of the complex was constructed by specifying the bond angles each ligand made with the phosphorus atom. That the two input approaches were identical was checked by comparison of the external coordinates of a complex whose structure was input in both modes. For calculations on **7**, **8**, **9**, **10**, **12**, **13**, and **14**, the symmetrical "piano-stool" arrangement was used with structural parameters either from related X-ray determinations or by assuming a pseudooctahedral complex of bond angles of 90°. For **11** and **15**, the second input mode was utilized and again the structural parameters were obtained from X-ray determinations. When experimental structural data was lacking, standard bond lengths (c.f.: Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley, New York, 1975; Tables 2-3 and 2-4) and bond angles (109.5° for tetrahedral, 120° for the phenyl ring bond angles) were used. All calculations were performed on the Oxford University Computer Service's ICL 2988 computer running under VME.
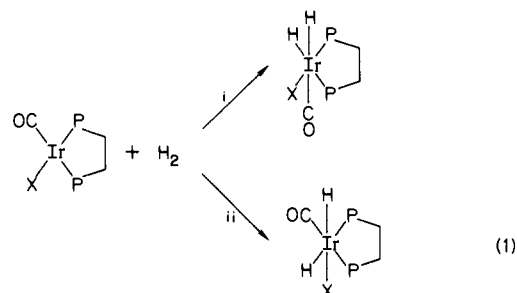
Stereoselective Oxidative Addition of Silanes and Hydrogen Halides to the Iridium(I) Cis Phosphine Complexes IrX(CO)(dppe) (X = Br, CN; dppe = 1,2-Bis(diphenylphosphino)ethane)

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Abstract: The oxidative addition of silanes, R$_n$Cl$_{3-n}$SiH (n = 3, R = Et, Ph, OEt; n = 2, R = Me; n = 1, R = Me), to the Ir(I) cis phosphine complexes IrX(CO)(dppe) (X = Br, CN; dppe = 1,2-bis(diphenylphosphino)ethane) has been found to proceed stereoselectively under kinetic control. Of the four possible diastereomers that can form by concerted cis addition of the Si–H bond to the iridium(I) center, the one having hydride trans to CO and Si trans to P(dppe) is formed initially with >98% stereoselectivity. For X = Br, this diastereomer is not the thermodynamically favored product. Isomerization of the initially formed silyl hydride product to the equilibrium mixture of diastereomers follows first-order kinetics for the triphenylsilyl derivative with k_1 = 0.015 min^{-1}. The rate of isomerization for the kinetic silyl hydride adducts decreases in the order Et$_3$SiH > Ph$_3$SiH > (OEt)$_3$SiH > Me$_2$ClSiH with the MeCl$_2$SiH derivative not isomerizing even after prolonged heating. The most stable diastereomer for X = Br has hydride trans to Br and silyl trans to P(dppe). For X = CN, the kinetic isomer with H trans to CO and Si trans to P(dppe) is also the most stable isomer, although other isomers are observed to form after initial reaction. Secondary chemistry of the triethylsilyl hydride products for X = Br and CN is observed over longer reaction times leading to the formation of IrHX$_2$(CO)(dppe) (X = Br), IrH$_2$(SiEt$_3$)(CO)(dppe), and Et$_3$SiSiEt$_3$. This secondary chemistry is consistent with reductive elimination/oxidative addition sequences. The oxidative addition of HX to IrX'(CO)(dppe) also proceeds stereoselectively, giving the isomer with H trans to X' and X trans to P(dppe). This diastereomer results from cis addition in which H–X approaches the square-planar Ir(I) complex with its axis parallel to X'–Ir–P. Thus, while R$_3$SiH and HX both add to IrX(CO)(dppe) by a cis concerted mechanism, the diastereoselection for HX is opposite to that for R$_3$SiH. It is proposed that this difference arises because the silane approach to the Ir(I) complex is nucleophilic while that of HX is electrophilic.

In previous reports we have described the kinetic stereoselectivity of H$_2$ oxidative addition to IrX(CO)(dppe) complexes, (dppe = 1,2-bis(diphenylphosphino)ethane), which are cis-phosphine analogues of Vaska's complex, *trans*-IrCl(CO)(PPh$_3$)$_2$.[1,2] This oxidative addition can proceed along two possible pathways, i and ii, as shown in eq 1, leading to different diastereomers for the concerted cis addition of H$_2$. Pathway i corresponds to H$_2$ approach to the square-planar complex with the molecular axis of H$_2$ parallel to P–Ir–CO as shown in A. The concerted oxidative

(1)

addition along i takes place with a bending of the trans P–Ir–CO axis so that one hydride of the product becomes trans to CO and
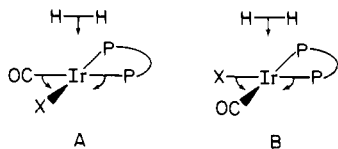
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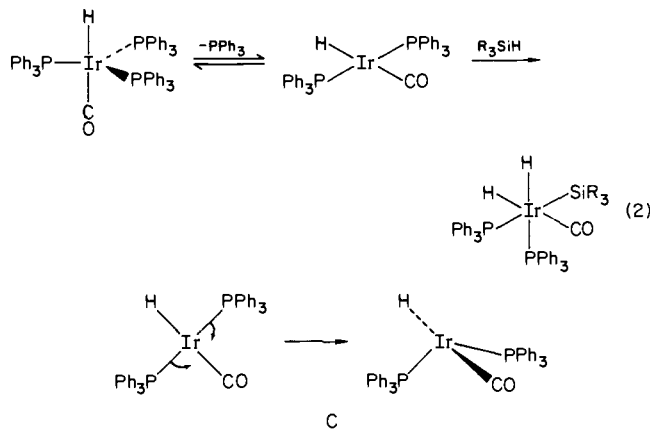
A   B

C

the other trans to P. Pathway ii corresponds to approach with the H_2 molecular axis parallel to P–Ir–X, as shown in B, and addition occurs with bending of the P–Ir–X axis.

While two diastereomers for concerted H_2 oxidative addition to IrX(CO)(dppe) are thus possible, we have found that for X = Cl, Br, I, H, and CN, the initial oxidative addition takes place diastereoselectively along pathway i. The reaction proceeds under kinetic control as illustrated by the fact that for X = Cl, Br, and I, the diastereomer formed initially slowly equilibrates with the more stable diastereomer corresponding to oxidative addition along pathway ii. Based on the variation of X, a steric basis for the diastereoselectivity of H_2 oxidative addition can be ruled out, leaving ligand electronic effects as the controlling factor in the diastereoselection process.

In order to probe more deeply the extent and basis of kinetically controlled diastereoselectivity in oxidative additions, we have examined the reaction chemistry between IrX(CO)(dppe) and the unsymmetrical substrates R_3SiH and HX. The oxidative addition of silanes to iridium(I) complexes has been studied extensively.[3-13] The reaction, which represents a required step in hydrosilation catalysis, is generally viewed as a concerted cis addition.[14] However, this has only been demonstrated or established convincingly in a limited number of cases. In an elegant series of investigations, Harrod and co-workers have studied silane oxidative addition to IrH(CO)(PPh₃)₃ kinetically and stereochemically.[3,4] Their analysis of the reaction in eq 2 through the determination of activation parameters led them to the conclusion that silane oxidative addition and phosphine addition are mechanistically similar processes with activation enthalpies due mainly to deformation of the square-planar complex prior to addition as shown in C.[3] Through the use of deuterated silane substrate, Fawcett and Harrod showed that the hydride ligand trans to PPh₃ in the product of eq 2 comes from the silane substrate in the cis addition process.[4a]

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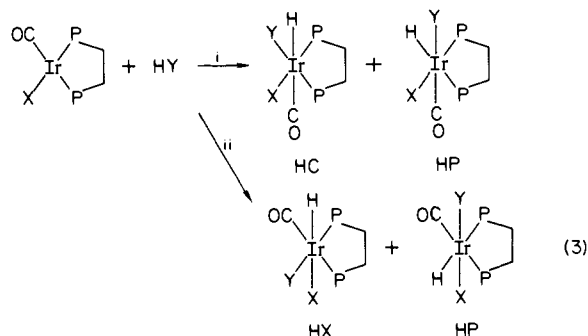
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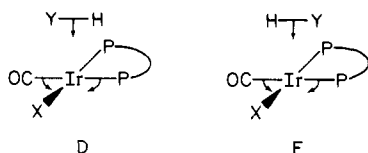
(2)

In a different study, Bennett et al.[7] examined silane addition to IrClL₃ (L = PPh₃, PMePh₂, AsPh₃) to give the Ir(III) silyl hydrides IrHCl(SiR₃)L_n, where n = 2 or 3. In all cases, the silyl and hydride groups in the product complexes are mutually cis, and this result is taken as supporting, but not proving, cis concerted addition of silane. A definitive study of the stereochemistry of R₃SiH addition to Vaska's complex as it relates to the mechanism of the reaction has not been performed to date because of insufficient solubility of initial IrHCl(SiR₃)(CO)(PPh₃)₂ products and facile secondary reactions leading to dihydride products. However, a study by Sommer et al. using optically active silanes R₃Si*H showed that Vaska's complex promotes Si*H/Si*D exchange with complete retention of configuration of Si, thereby giving support to the notion of cis concerted addition of silane to Vaska's complex.[11]

The mechanism of HX addition to IrCl(CO)(PPh₃)₂ and its analogues has also been investigated.[15-17] Vaska observed that gaseous HX oxidatively adds to *trans*-IrX(CO)(PPh₃)₂ (X = Cl, Br, I) in the solid state to form cis addition products.[15] Blake and Kubota[16] found that the cis stereochemistry of addition also holds for the reaction in benzene or chloroform solution. In the presence of more polar solvents such as methanol, acetonitrile, water, or dimethylformamide, however, mixtures of cis and trans HX isomers are formed. Longato et al. established a similar stereochemistry of HX addition to crystalline *trans*-Ir(carb)(CO)(PPh₃)₂ (carb = 2-R-1,2-C₂B₁₀H₁₀ or the 1,7-carborane).[17] The cis stereochemistry of addition to Ir(carb)(CO)(PPh₃)₂ is maintained in dry nonpolar solvents, but mixtures of cis and trans addition products are found in wet benzene and CH₃OH–CH₂Cl₂ solutions, and only trans addition is seen for the complex containing the bulky ligand 2-CH₃-1,2-B₁₀C₂H₁₀. It thus appears that the stereochemistry and mechanism of HX oxidative addition to Ir(I) complexes of the type IrX(CO)L₂ depend on the reaction conditions and Ir(I) ligands, with cis addition occurring in nonpolar media and the solid state.

For the cis-phosphine complexes IrX(CO)(dppe) used in the present study, cis oxidative addition of an unsymmetrical substrate HY corresponds to a double diastereoselection process in which the orientation of the HY substrate relative to the metal complex offers two possibilities for each of the pathways of addition shown in eq 1. The four diastereomers for cis addition of HY to IrX(CO)(dppe) are shown in eq 3. We will refer to the double-diastereoselection process as diastereoselection (i.e., pathway i or ii) with specific substrate orientation. The relative orientation of HY in a cis concerted addition is given by the position of the hydride ligand in the product. For oxidative addition along the P–Ir–CO axis, pathway i, two diastereomers are possible, the first with hydride trans to CO labeled as HC and the second with hydride trans to P labeled as HP. These two diastereomers correspond respectively to HY approach to IrX(CO)(dppe) shown

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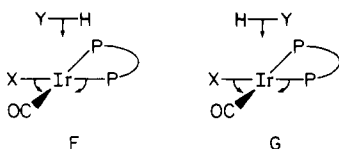(16) Blake, D. M.; Kubota, M. *Inorg. Chem.* 1970, *9*, 989–991.

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as D and E. Similarly for pathway ii (addition along the P–Ir–X axis), diastereomers with hydride trans to X (HX) and hydride trans to P (HP) are possible, corresponding to substrate approaches shown as F and G. This manner of labeling the diastereomers of HY addition by pathway of addition with ligand trans to hydride will be used throughout the rest of the paper.

Experimental Section

General. The following reagents were used as received: triethylsilane, triphenylsilane, triethoxysilane, chlorodimethylsilane, dichloromethylsilane, tetra-*n*-butylammonium (TBA) bromide (Aldrich), HBr (Matheson, 99.8%), and ^{13}CO (Monsanto Research Corp., 99%). Bis(triphenylphosphine)iminium (PPN) cyanide,[18] IrBr(CO)(dppe),[2] and IrI-(CO)(dppe)[19] were prepared by established procedures. Benzene-d_6 and acetone-d_6 (Aldrich Gold Label, 99.5% D) were distilled from Na/benzophenone and Linde 4A molecular sieves, respectively, for sealed-tube NMR experiments.

Reactions were generally carried out under a nitrogen atmosphere using a Schlenk-type vacuum line. Sealed-tube samples for ^1H NMR experiments were prepared on a high-vacuum line by condensing solvent and silane or HX reagent into a tube containing the Ir(I) complex.

^1H and ^{31}P NMR spectra were recorded on a Bruker WH-400 spectrometer at 400.13 and 162.00 MHz, respectively, and ^{13}C NMR spectra were recorded on a Nicolet QE-300 spectrometer at 75.48 MHz. Chemical shifts were generally calculated from residual solvent resonances (acetone-d_5 δ_H 2.04, benzene-d_5 δ_H 7.15, δ_C 128.0). ^{31}P chemical shifts were referenced to external H_3PO_4. IR spectra were recorded on a Perkin-Elmer 467 spectrophotometer. Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, TN. Mass spectra were recorded on a Dupont 21-490 B mass spectrometer.

Reaction of IrBr(CO)(dppe) with Et$_3$SiH. The reaction was carried out in a sealed NMR tube by first placing 7 mg of IrBr(CO)(dppe) in a 5-mm tube attached to a 14/20 glass joint. On a high-vacuum line 0.5 mL of solvent (benzene or acetone) and the desired amount of Et$_3$SiH were condensed into the tube at −196 °C, and the tube was flame sealed. After thawing, the progress of the reaction was monitored by ^1H NMR spectroscopy. The isomerized product, IrHBr(SiEt$_3$)(CO)(dppe), was isolated as a white powder from benzene–pentane solution. Anal. Calcd for IrBrC$_{33}$H$_{40}$OP$_2$Si: C, 48.64; H, 4.95; P, 7.60. Found: C, 48.71; H, 4.83; P, 7.80.

Reaction of IrBr(CO)(dppe) with Ph$_3$SiH, (EtO)$_3$SiH, Me$_2$ClSiH, and MeCl$_2$SiH. ^1H NMR studies of these reactions were carried out in nitrogen-purged septum-capped NMR tubes using typically 3 mg of IrBr(CO)(dppe) and 1–2 equiv of silane in C$_6$D$_6$ solvent.

Reaction of Ir(CN)(CO)(dppe) with Et$_3$SiH. The complex Ir(CN)-(CO)(dppe) was prepared in situ by condensing 0.5 mL of acetone into an NMR tube containing 7.3 mg (0.11 mmol) of IrBr(CO)(dppe) and 6.7 mg (0.12 mmol) of PPN(CN).[1] The mixture was shaken for 1 min at room temperature to give a homogeneous orange solution. After cooling to −196 °C, Et$_3$SiH was condensed in and the tube flame sealed.

Reaction of IrBr(CO)(dppe) with HI. A C$_6$D$_6$ solution of IrBr-(CO)(dppe) in a 5-mm NMR tube was purged with the gas evolved from the reaction of NaI with concentrated sulfuric acid using a nitrogen flow. This procedure, while not efficient for generating HI gas, proved adequate for this experiment.

Reaction of IrI(CO)(dppe) with HBr. HBr (0.2 mL, 5 equiv) (99.8%) was added via syringe to a C$_6$D$_6$ solution containing 1 mg of IrI(CO)-(dppe) in a septum-capped NMR tube and the sample was analyzed by ^1H NMR spectroscopy.

Preparation of IrHBr$_2$(CO)(dppe). HBr, 13 μL (0.011 mmol) of 47%, was added to 12 mL of an orange benzene solution containing 51 mg (0.073 mmol) of IrBr(CO)(dppe). The mixture was stirred for 2 h during which a light yellow precipitate formed and the solution turned nearly colorless. The precipitate was collected by filtration and washed with benzene to give 41 mg (72%) of IrHBr$_2$(CO)(dppe). Recrystallization from CH$_2$Cl$_2$–EtOH gave a cream-colored precipitate. Anal. Calcd for IrBr$_2$C$_{27}$H$_{25}$OP$_2$: C, 41.60; H, 3.23; P, 7.95. Found: C, 41.60; H, 3.53; P, 7.93.

Results and Discussion

All of the oxidative addition reactions and subsequent chemistry described here were followed by ^1H NMR spectroscopy. The chemical shifts and splitting patterns of the hydride resonances provide in almost all cases unambiguous assignment of the stereochemistry of the oxidative addition products.

As noted above, concerted cis addition of HY to the Ir(I) complexes IrX(CO)(dppe) yields in principle four different stereoisomers. These arise from oxidative addition of HY to the square plane by either pathway i or ii, each with either of two possible substrate orientations for the concerted process. For stereoisomers i-HC and ii-HX, the hydride resonance shows cis coupling to two nonequivalent phosphines and a chemical shift distinctive for the ligand trans to hydride. For stereoisomers i-HP and ii-HP, the hydride resonance occurs in the range −7.7 to −8.6 ppm with a distinctive doublet of doublets pattern and large trans J_{PH}. The magnitude of this trans coupling, together with previously established reaction chemistry, provides the basis for distinguishing between stereoisomers i-HP and ii-HP.

Reaction of Et$_3$SiH with IrBr(CO)(dppe). A benzene sample of IrBr(CO)(dppe) and 3 equiv of Et$_3$SiH yields a pale yellow solution after thawing and shaking for 1 min, indicating nearly complete reaction of the orange-colored Ir(I) compound IrBr-(CO)(dppe). The ^1H NMR spectrum taken 3 min after thawing shows resonances assignable to two complexes of the type IrHBr(SiEt$_3$)(CO)(dppe) along with peaks for unreacted Et$_3$SiH (NMR data are collected in Table I). The hydride resonances appear as an approximate triplet at δ −8.48 containing two nearly equivalent cis phosphorus couplings (~17.8 Hz) and a doublet of doublets at δ −16.64 containing two cis phosphorus couplings (5.8 and 15.1 Hz). The relative amounts of the two hydride products are 38% (δ −8.48) and 62% (δ −16.64). Over the course of 20 min the hydride resonance at δ −8.48 disappears as the δ −16.64 peak becomes larger and a new hydride resonance at δ −8.34 (dd, J_{PH} = 8.5, 153.5 Hz) appears. After 70 min an apparent equilibrium has been reached between the δ −16.64 complex (93%) and the δ −8.34 species (7%). Figure 1 shows ^1H NMR spectra of the reaction of IrBr(CO)(dppe) with 1.25 equiv of Et$_3$SiH. The first spectrum was taken after 3 min of reaction at 8 °C and consists mainly of resonances assigned to the kinetic product with the hydride multiplet at δ −8.48 (see Table I for peak assignments). The second spectrum was taken after several hours of reaction at 25 °C and contains predominantly the thermodynamic product with the hydride resonance at δ −16.64.

Similar results are obtained when the reaction is carried out in acetone solution. After 3 min two hydride resonances are observed at δ −8.73 (~t, J_{PH} ~ 17.9 Hz) and −16.96 (dd, J_{PH} = 5.9, 15.3 Hz) in the relative amounts 76% and 24%, respectively, while a third hydride species appears over the course of an hour at δ −8.86 (dd, J_{PH} = 8.5, 151 Hz) as the mixture reaches an

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Table I. ^{1}H NMR Data of Hydride Complexes[a]

compound		δ_{IrH} (J_{PH})	δ_{CH_2} (dppe)	$\delta_{ortho\,Ph}$(dppe)	$\delta(R_3Si)$
IrHBr(SiEt$_3$)(CO)(dppe)	1a	−8.48 (∼17.8)	2.02 (1 H),[b] 1.83 (2 H),[b] 1.49 (1 H)[b]	8.02 (2 H), 7.77 (2 H), 7.53 (4 H)	1.39 (3 H),[b] 1.34 (9 H),[b] 1.15 (3 H)[b]
	2a	−16.64 (5.8, 15.1)	3.02 (1 H), 2.20 (2 H), ∼1.22 (1 H)[c]	7.85 (2 H), 7.57 (4 H), 7.46 (2 H)	1.21 (15 H)
	3a	−8.34 (8.5, 153.5)			
IrHBr(SiPh$_3$)(CO)(dppe)	1b	−7.98 (16.7, 19.1)	2.12 (1 H), 1.83 (1 H), 1.65 (2 H)	8.04 (2 H), 7.73 (2 H), 7.32 (2 H)	7.94 (6 H, ortho Ph)
	2b	−15.97 (6.5, 17.0)	2.77 (1 H), 2.17 (1 H), 1.77 (1 H), 1.60 (1 H)	7.54 (2 H), 7.47 (2 H), 7.26 (2 H)	7.96 (6 H, ortho Ph)
	3b	−7.91 (8.0, 151.9)			
IrHBr(Si(OEt)$_3$)(CO)(dppe)	1c	−8.51 (∼18.2)	2.15 (1 H), 1.68−1.88 (3 H)	8.02 (2 H) 7.86 (2 H), 7.77 (2 H), 7.64 (2 H)	4.31 (3 H), 4.17 (3 H), 1.25 (9 H)
	2c	−16.49 (6.7, 15.4)	2.77 (1 H), 2.37 (1 H), 2.00 (1 H), 1.50 (1 H)	8.01 (2 H), 7.77 (2 H), 7.56 (2 H), 7.40 (2 H)	4.07 (3 H), 3.99 (3 H), 1.20 (9 H)
	4c	−8.32 (17.4, 127.6)			
IrHBr(SiMe$_2$Cl)(CO)(dppe)	1d	−8.60 (∼18.3)	2.23 (1 H), 1.76 (3 H)	7.96 (2 H), 7.70 (4 H), 7.62 (2 H)	1.53 (3 H), 1.43 (3 H)
	2d	−16.03 (7.3, 14.1)	2.99 (1 H), 2.30 (1 H), 2.20 (1 H), 1.12 (1 H)	7.80 (4 H), 7.51 (2 H) 7.31 (2 H)	1.25 (3 H), 0.54 (3 H)
	3d	−8.60 (9.5, 150.2)			
IrHBr(SiMeCl$_2$)(CO)(dppe)	1e	−8.77 (∼16.8)	2.14 (1 H), 1.86 (1 H), 1.67 (2 H)	7.91 (2 H), 7.60−7.70 (6 H)	1.84 (3 H)
IrH(CN)(SiEt$_3$)(CO)(dppe)	5[d]	−10.05 (∼17.3)	2.60 (2 H), 2.25 (1 H)	7.96 (4 H)	0.86 (9 H), 0.78 (3 H), 0.62 (3 H)
	6[d]	−10.13 (8.9, 124)			0.86 (9 H)
IrHBr$_2$(CO)(dppe)	7	−15.85 (11.2, 15.5)	3.24 (1 H),[e] 2.98 (1 H),[e] 2.53 (1 H),[e] 2.13 (1 H)[e]	7.83 (2 H),[e] 7.73 (2 H),[e] 7.60 (2 H),[e] 7.53 (2 H)[e]	
IrH$_2$(SiEt$_3$)(CO)(dppe)	8	−10.73 (11.1, 115.7), −11.09 (19.3)	2.18 (1 H), 1.99 (2 H), 1.78 (1 H)	7.90 (2 H), 7.63 (2 H), 7.52 (2 H), 7.46 (2 H)	1.31 (9 H), 1.11 (6 H)
IrHI$_2$(CO)(dppe)	9	−14.02 (8.7, 15.7)			
IrHBrI(CO)(dppe)	10	−13.39 (10.2, 15.9)	2.81 (1 H), 2.39 (1 H), 1.91 (1 H)	7.93 (2 H), 7.85 (2 H), 7.34 (2 H), 7.27 (2 H)	
	11	−15.99 (9.1, 15.5)			
IrH$_2$Br(CO)(dppe)	I	−7.87 (14.2, 152.2), −8.94 (∼19.3)	2.29 (1 H), 2.10 (1 H), 2.03 (1 H), 1.73 (1 H)	8.09 (2 H), 7.97 (2 H), 7.79 (2 H), 7.27 (2 H)	
	II	−8.34 (17.2, 132.9), −17.48 (8.6, 16.6)	2.60 (2 H), 1.92 (2 H)	7.82 (2 H), 7.66 (2 H), 7.56 (2 H), 7.47 (2 H)	
IrH$_2$(CN)(CO)(dppe)	III[d]	−10.13 (13.28, 129.9), −10.87 (∼17.9)	3.25 (1 H), 2.88 (2 H), 2.50 (1 H)	7.97 (4 H), 7.88 (2 H), 7.67 (2 H)	
	IV[d]	−10.43 (16.1, 121), −13.27 (12.5, 19.3)			

[a] Spectra are taken from benzene solutions at 400 MHz unless otherwise indicated. [b] Spectrum taken at 6 °C. [c] Resonance located by homonuclear decoupling experiments. [d] Acetone solution. [e] CDCl$_3$ solution.
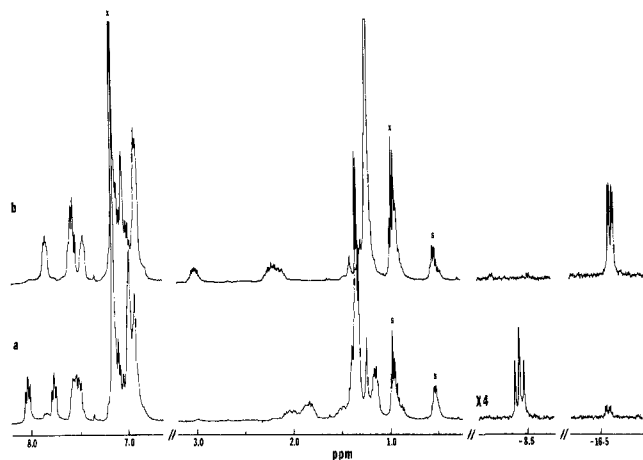
Oxidative Addition of Silanes and Hydrogen Halides

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Figure 1. ^{1}H NMR spectra of the reaction of IrBr(CO)(dppe) with Et$_3$SiH: (a) after 3 min of reaction at 8 °C; (b) after several hours of reaction at 25 °C. The peaks marked "s" are due to excess Et$_3$SiH, and the peak marked "x" corresponds to benzene solvent (C$_6$D$_5$H, δ 7.15).

equilibrium. After 54 h, the composition of hydride species in the acetone solution corresponds to 3.5% of the δ −8.73 compound, 88% of the δ −16.96 compound, and 8.5% of the δ −8.86 species. The three hydride resonances at δ −8.73, −16.96, and −8.86 in acetone and at δ −8.48, −16.64, and −8.34 in benzene are assigned to **1a**, **2a**, and **3a**, respectively, in eq 4. The stereoselectivity of
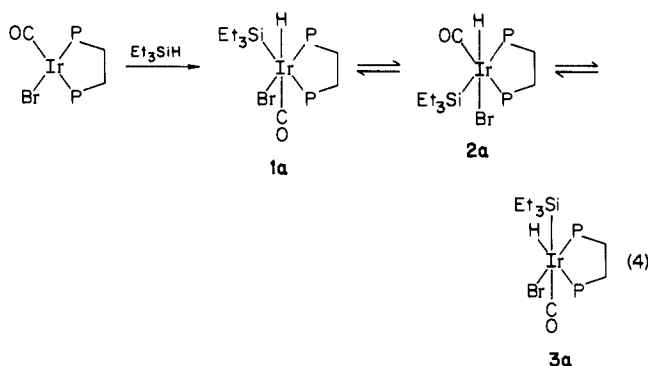
Et$_3$SiH addition to IrBr(CO)(dppe) has also been examined at −33 °C in acetone solution by ^{31}P NMR spectroscopy. Initially, only resonances assigned to **1a** are observed at δ 35.9 and 16.8, indicating that the amount of **2a** present must be ≤1%. Upon warming, new resonances appear at δ 27.3 and 24.3 for isomer **2a**. Selective ^{1}H decoupling experiments confirm that none of the observed resonances assigned to **1a** and **2a** are coupled to a trans hydride ligand.

The rapid formation of **1a** and slower formation of **2a** parallels exactly the chemistry seen in the oxidative addition of H$_2$ to IrX(CO)(dppe),[1] shown in eq 5 for X = Cl, Br, and I. For both Et$_3$SiH and H$_2$, oxidative addition proceeds under kinetic control along the P–Ir–CO axis of IrX(CO)(dppe) (pathway i in eq 1 and 3) and then isomerization occurs forming the thermodynamically preferred isomer (**2a** or **II**) which corresponds to oxidative addition along the P–Ir–X axis (pathway ii). An additional stereochemical feature of the Et$_3$SiH reaction is that although two substrate orientations are possible for each pathway of addition, the reaction kinetically favors the isomers that have mutually trans silyl and phosphine ligands, i.e., the HC product in pathway i (**1a**) and the HX product in pathway ii (**2a**). The hydride resonances in **1a** and **2a** agree closely in chemical shift and J_{PH} coupling constants with the corresponding hydride resonances in **I** and **II** of eq 5 (see Table I).

The assignment of structure **3a** for the third product, which exhibits a hydride resonance at δ −8.34 in benzene and −8.86 in acetone and remains a minor isomer, is based on the magnitude of $J_{PH(trans)}$. Examination of Table I shows that the observed J_{PH} of 151 (acetone) and 153.5 Hz (benzene) agrees more closely with
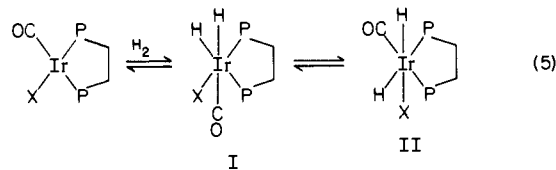

trans J_{PH} of 152.2 Hz seen in **I** than with the corresponding value of 132.9 Hz in **II**. Structure **3a** arises from the oxidative addition of Et$_3$SiH along the kinetically preferred direction of addition, pathway i, but with the HP substrate orientation. The alternative assignment for this product is structure **4a** which would result from
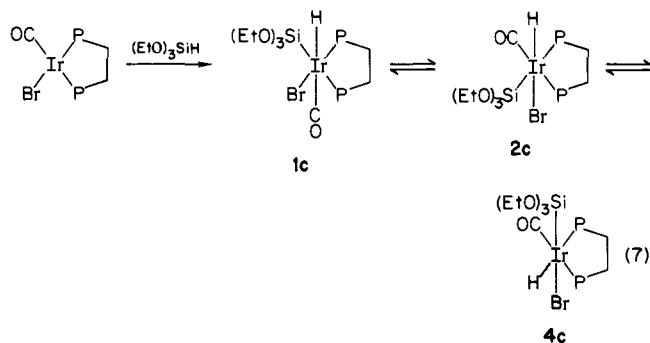

4a
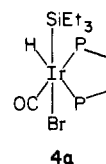
oxidative addition in the less favorable direction, pathway ii, with the HP substrate orientation. We think this is a less likely possibility. While the assignment of **3a** to the third product formed in the reaction between Et$_3$SiH and IrBr(CO)(dppe) is not unambiguous, the assignment does not affect analysis of the kinetic diastereoselectivity of the reaction leading to **1a** over the thermodynamically most stable isomer **2a**.

Reaction of Ph$_3$SiH, (EtO)$_3$SiH, Me$_2$ClSiH, and MeCl$_2$SiH with IrBr(CO)(dppe). The reaction of IrBr(CO)(dppe) with Ph$_3$SiH also leads to the formation of three isomers of IrHBr(SiPh$_3$)-(CO)(dppe), **1b**, **2b**, and **3b**, eq 6. Six minutes after adding
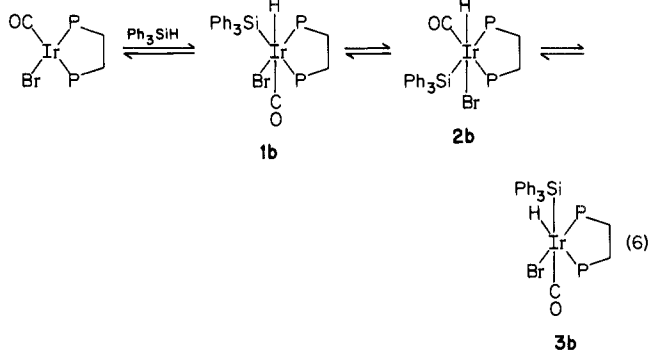
benzene to IrBr(CO)(dppe) and 3 equiv of Ph$_3$SiH the ^{1}H NMR spectrum shows two hydride resonances at δ −7.98 (dd, J_{PH} = 16.7, 19.1 Hz) and −15.97 (dd, J_{PH} = 6.5, 17.0 Hz) assigned to isomers **1b** and **2b**, respectively, by analogy to the corresponding triethylsilyl compounds **1a** and **2a** (see Table I). The relative amounts of **1b** and **2b** are 91% and 9% in the spectrum at t = 6 min. Isomerization to a mixture of three isomers occurs over several hours, eventually reaching an equilibrium of 2% **1b**, 93% **2b**, and 5% **3b**. Complex **3b** is characterized by a hydride resonance at δ −7.91 (dd, J_{PH} = 8.0, 151.9 Hz). The isomerization reaction follows first-order kinetics for the disappearance of **1b** until approaching equilibrium with k = 0.015 min^{-1} at 23 °C.

The reaction of IrBr(CO)(dppe) with (EtO)$_3$SiH follows a similar pattern where kinetic isomer **1c** forms initially and then isomerizes to an equilbrium mixture of three isomers, eq 7. In this case, unequivocal assignments for the three isomers can be made based on a combination of ^{1}H and ^{13}C NMR experiments. ^{13}CO-enriched IrBr(CO)(dppe) (88% ^{13}CO) was prepared by stirring a THF solution of IrBr(CO)(dppe) under ^{13}CO at 50 °C for 10 min and then precipitating the product. In the experiment using unlabeled IrBr(CO)(dppe), the ^{1}H NMR spectrum taken 6 min after the addition of 1 equiv of (EtO)$_3$SiH shows that a single silyl hydride product (≥99%) has formed characterized by a hydride product at δ −8.51 (~t, J_{PH} ~ 18.2 Hz). In the parallel experiment using ^{13}CO-enriched IrBr(CO)(dppe), the hydride resonance appears at δ −8.50 and contains an additional doublet splitting of 42.8 Hz due to coupling to the trans ^{13}CO ligand as expected for isomer **1c**. The ^{13}C NMR spectrum shows a reso-

nance at δ 176.8 (d of ~t, J_{HC} = 42.8, J_{PC} ~ 4.2 Hz) and ^{1}H decoupling confirms that the 42.8-Hz coupling is due to the hydride ligand.

Complex **1c** isomerizes much more slowly than the triethylsilyl and triphenylsilyl derivatives with a half-life of 45 h at room temperature. The thermodynamic product **2c** is characterized by a hydride resonance at δ −16.49 (dd, J_{PH} = 6.7, 15.4 Hz). In the ^{13}CO-enriched sample, this resonance contains an additional doublet splitting of 4.6 Hz due to the cis ^{13}CO ligand. The ^{13}CO resonance for **2c** appears at δ 175.01 (ddd, J_{HC} = 4.6, J_{PC} = 6.7, 118.7 Hz). The large phosphorus–carbon coupling confirms that the ligands are trans to each other. The third isomer formed must be **4c** based on the phosphorus coupling constants of the hydride resonance at δ −8.32 (dd, J_{PH} = 17.4, 127.6 Hz) and the ^{13}C NMR spectrum. The J_{PH} values compare favorably with those for the corresponding hydride in complex **II** (J_{PH} = 17.2, 132.9 Hz) and differ considerably from the couplings observed for diastereomers **3a** (J_{PH} = 8.5, 153.5 Hz) and **3b** (J_{PH} = 8.0, 151.9 Hz) from other silane additions. The ^{13}CO resonance for **4c** appears at δ 175.17 (ddd, J_{HC} = 4.6, J_{PC} = 6.3, 120 Hz), and the 120-Hz phosphorus–carbon coupling confirms that the CO ligand is trans to phosphorus. At equilibrium the three diastereomers for (EtO)$_3$SiH addition are present in the relative amounts 5% **1c**, 76% **2c**, and 19% **4c**.

The reactions of IrBr(CO)(dppe) with Me$_2$ClSiH forms initially the kinetic product **1d** which isomerizes upon heating ($t_{1/2}$ = 20 min at 72 °C) to two other isomers assigned as **2d** and **3d**, eq 8.
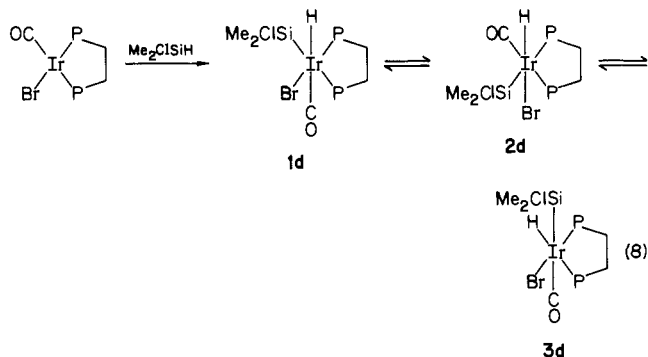
The assignments are based on the ^{1}H NMR data in Table I and comparison with those for the analogous Et$_3$Si, Ph$_3$Si, and (EtO)$_3$Si derivatives.

The oxidative addition of MeCl$_2$SiH to IrBr(CO)(dppe) yields the usual kinetic product **1e** (see NMR data in Table I), but, unlike the other silyl hydride products, no isomerization is observed, even upon heating the sample for 1 h at 74 °C. It appears that the isomerization rates for **1a–e** are influenced by the electronegativity of the substituents on silicon such that the more electronegative substituents Cl and OEt slow the rate of isomerization.

All four of the observed diastereomers of IrHBr(SiR$_3$)-(CO)(dppe), **1–4**, contain cis hydride and silyl ligands and can in principle form by cis oxidative addition of R$_3$SiH to IrBr-(CO)(dppe). If the isomerization of the initially formed diastereomer **1** proceeds via reductive elimination of R$_3$SiH, followed by oxidative addition with different stereochemistry, then the rate

of R$_3$SiH reductive elimination from **1** must be fast compared to the rate of isomerization in order to account for the observed diastereoselectivity of R$_3$SiH oxidative addition favoring isomer **1**. To test this hypothesis, we have attempted to measure the rate of reductive elimination of Ph$_3$SiH from **1b** by adding (EtO)$_3$SiH to a benzene solution of **1b**. A ^{1}H NMR spectrum taken 4 min after addition of 3.5 equiv of (EtO)$_3$SiH shows only resonances for **1c** and the amount of **1b** present must be <2% at this time.
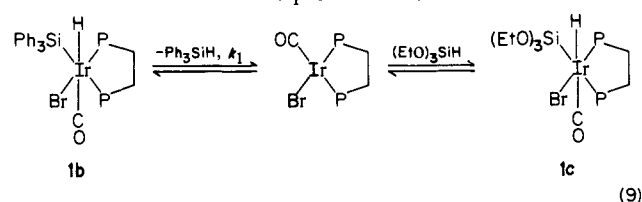
Assuming that the reaction proceeds via initial Ph$_3$SiH reductive elimination as in eq 9, this result indicates that the half-life of Ph$_3$SiH reductive elimination at 23 °C is less than 1 min and that k_1 > 0.7 min^{-1}. Since the isomerization reaction of **1b** proceeds with a first-order rate constant k_{obsd} = 0.015 min^{-1} at 23 °C, we see that k_1/k_{obsd} ≥ 50. This ratio can be used to place a lower limit on the diastereoselectivity of Ph$_3$SiH oxidative addition by analysis of the proposed isomerization mechanism, eq 10. Since
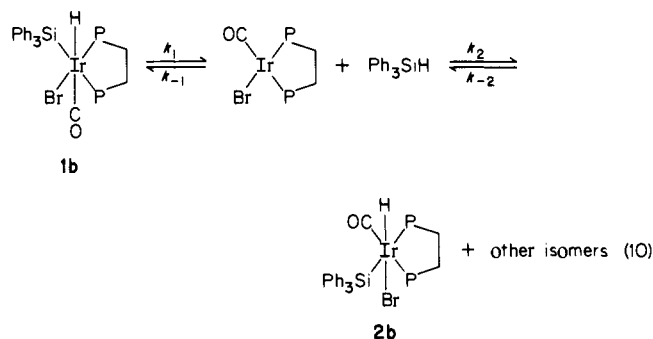
the reductive elimination step, k_1, is much faster than the rate of isomerization, k_{obsd}, the rate-determining step for eq 10 must involve k_2. By applying the steady-state approximation to the intermediate IrBr(CO)(dppe) and ignoring k_{-2}, we obtain the rate expression shown in eq 11. The diastereoselectivity of Ph$_3$SiH

$$\text{rate} = k_{obsd}[\mathbf{1b}] = \frac{k_1 k_2}{k_{-1} + k_2}[\mathbf{1b}] = \frac{k_1}{k_{-1}/k_2 + 1}[\mathbf{1b}] \quad (11)$$

oxidative addition is k_{-1}/k_2 and the observed result that k_1/k_{obsd} ≥ 50 leads to the requirement that k_{-1}/k_2 ≥ 50. This means that the minimum diastereoselectivity for the formation of **1b** over **2b** is 98%. Thus, while other first-order isomerization mechanisms cannot be ruled out, the two-step reductive elimination/oxidative addition mechanism in eq 7 does account for all of the experimental results and appears most likely since the rate of Ph$_3$SiH reductive elimination is much faster than the rate of isomerization.

Reaction of Et$_3$SiH with Ir(CN)(CO)(dppe). Secondary Reaction of Iridium Triethylsilyl Hydride Complexes. The complex Ir(CN)(CO)(dppe) was prepared in situ from IrBr(CO)(dppe) and PPN(CN) in acetone solution as reported previously[1] and reacted with 2 equiv of Et$_3$SiH in a sealed NMR tube. The ^{1}H NMR spectrum taken 5 min after thawing showed resonances for a single triethylsilyl hydride product.[20] Based on the hydride resonance at δ −10.05 (~t, J_{PH} ~ 17.3 Hz) and other spectroscopic data in Table I, the product is characterized as stereoisomer **5** in eq 12. Over the course of several hours at room temperature **5** partially isomerizes to one other diastereomer identified as **6** by its ^{1}H NMR hydride resonance at δ −10.13 (dd, J_{PH} = 8.9, 124 Hz). The two products, **5** and **6**, result from Et$_3$SiH oxidative

(20) A small amount (4%) of a second hydride product characterized as IrH(CN)$_2$(SiEt$_3$)(dppe)⁻ with H trans to CN (δ −13.74 (dd, J_{PH} = 12.3, 16.5 Hz)) was also observed. This complex was independently prepared from Ir(CN)$_2$(CO)(dppe)⁻ and Et$_3$SiH, indicating that its formation above was due to the use of a slight excess of PPN(CN) relative to IrBr(CO)(dppe).
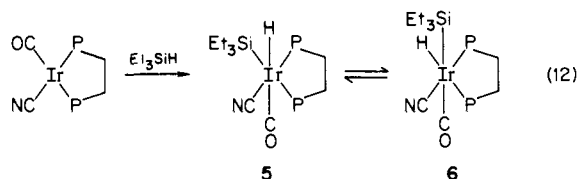
addition to Ir(CN)(CO)(dppe) via pathway i with relative substrate orientations HC and HP, respectively. The stability of **5** and **6** relative to the diastereomers that would form via pathway ii parallels closely the oxidative addition of H_2 to Ir(CN)-(CO)(dppe) where the kinetic isomer **III** is also the more stable
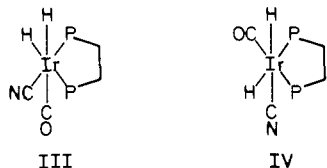
isomer.[1] In this reaction, isomer **IV**, which would result from H_2 oxidative addition along the P–Ir–CN axis, pathway ii, occurs as only a minor component at equilibrium. Thus, for the cyanide complex Ir(CN)(CO)(dppe) the same direction of oxidative addition (pathway i) is favored both kinetically and thermodynamically for the two substrates Et_3SiH and H_2.

In the later stages of the isomerization reaction of eq 12, a secondary reaction is observed whereby the IrH(CN)(SiEt$_3$)-(CO)(dppe) stereoisomers **5** and **6** are converted to IrH$_2$-(CN)(CO)(dppe) (three isomers are in equilibrium[14]) with concomitant consumption of Et_3SiH and formation of $Et_3SiSiEt_3$. The ^{1}H NMR spectrum after 3.5 h shows new hydride peaks at δ –10.11 and –10.86 identical with those of compound **III**, and the relative amounts of products are 37% **5**, 37% **6**, and 26% **III**. After 25 h there is 16% **5**, 8% **6**, and 76% isomers of IrH$_2$(CN)-(CO)(dppe). Figure 2 shows ^{1}H NMR spectra in the triethylsilyl region at different stages of the reaction. Eventually, ~95% of the triethylsilyl functional group is converted to $Et_3SiSiEt_3$ (δ 0.94 (t, CH$_3$, J = 7.9 Hz), δ 0.53 (q, CH$_2$), two equivalents of Et_3SiH were used initially), at which time >90% of the iridium containing species occurs as IrH$_2$(CN)(CO)(dppe).

Examination of the IrBr(CO)(dppe) + Et_3SiH samples, which were also prepared in sealed NMR tubes, reveals that secondary reaction chemistry is also occurring for the IrHBr(SiEt$_3$)-(CO)(dppe) isomers. The sample in acetone that originally contained IrBr(CO)(dppe) and 1 equiv of Et_3SiH becomes orange-yellow while sitting in the dark at room temperature for 1 year, and the ^{1}H NMR spectrum shows that the color is due to the regeneration of IrBr(CO)(dppe). The complex IrBr(CO)-(dppe) is identified by its four methylene resonances at δ 2.75, 2.68, 2.42, and 2.36 which integrate as 45% of the total dppe methylene peaks. Three major hydride products are also observed along with two organosilicon products. Integration of the hydride resonances against the phenyl region indicates that 25% of the dppe-containing species corresponds to the dihydride compound **II** (X = Br) which is partially deuterated (12% corresponds to the H_2 complex and 13% to the HD isotopomers as determined by direct integration of the resolved hydride resonances;[1] a small amount of the D_2 isotopomer may also be present). Slow deuteration of the hydrides has been observed in other acetone-d_6 solutions of **II**, with the deuterium presumably originating from acetone-d_6. This observation suggests the possibility of a high energy but accessible path for solvent C–H activation with these Ir complexes.

The other two hydride components of the dppe-containing species are the monohydride IrHBr$_2$(CO)(dppe) (**7**) (δ –15.85 (dd,
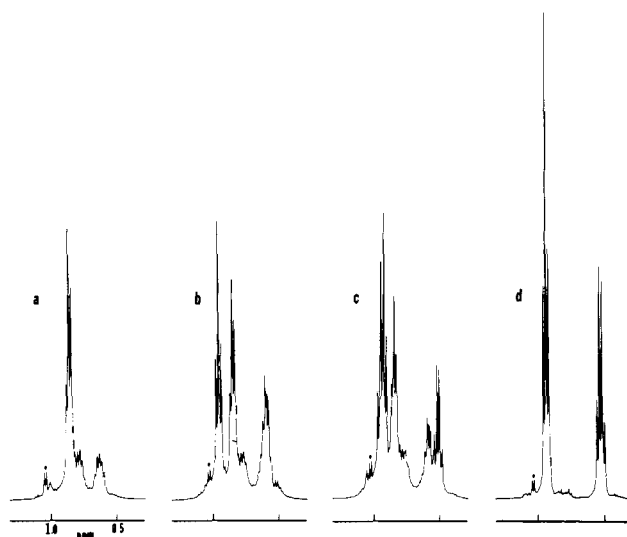

J_{PH} = 11.2, 15.5 Hz)), present as 8.5% of the dppe-containing species, and the dihydride IrH$_2$(SiEt$_3$)(CO)(dppe) (**8**) (δ –10.73 (dd, J_{PH} = 11.1, 115.7 Hz) and δ –11.09 (t, J_{PH} = 19.3 Hz)), present as 11% of the total. Complex **7** has been independently prepared from IrBr(CO)(dppe) + HBr as described in the next section. Complex **8** has been independently prepared from IrH$_3$(CO)(dppe) and Et_3SiH by heating a benzene solution at 73 °C for 20 min (quantitative yield by ^{1}H NMR spectroscopy). The triethylgermyl analogue of **8**, IrH$_2$(GeEt$_3$)(CO)(dppe), has been reported[21] and the ^{1}H NMR spectra of the two compounds in benzene solution are very similar: δ –10.04 (dd, J_{PH} = 11, 121 Hz), –10.82 (t, J_{PH} = 19 Hz) for the germyl compound, and δ –10.02 (dd, J_{PH} = 11.0, 117.0 Hz), –10.69 (t, J_{PH} = 19.1 Hz) for the silyl compound. The initial organosilicon product is $Et_3SiSiEt_3$ (δ 0.94 (t, CH$_3$, J = 8.0 Hz), 0.53 (q, CH$_2$)) while at longer times peaks apparently due to $Et_3SiOSiEt_3$ appear (δ 0.94 (t, CH$_3$, J = 8.0 Hz), 0.57 (q, CH$_2$)).

Similar results are obtained for the sample in benzene prepared from IrBr(CO)(dppe) and 3 equiv of Et_3SiH. After 25 days at room temperature the sample contains 75% IrHBr(SiEt$_3$)-(CO)(dppe) (70.5% **2a** and 4.5% **3a**), 1% IrH$_2$Br(CO)(dppe) (**II**), 11% IrHBr$_2$(CO)(dppe) (**7**), and 13% IrH$_2$(SiEt$_3$)(CO)(dppe) (**8**). Upon further standing a small amount of colorless crystals forms as the hydride resonance for **7** diminishes. The amount of complex **8** continues to increase at the expense of **2a** and **3a**, and a new organosilicon product is observed, Et_3SiBr (δ 0.89 (t, CH$_3$, J = 7.8 Hz), 0.67 (q, CH$_2$); mass spectrum, parent ions observed at m/e 194, 196). After 1 year at room temperature a small amount of precipitate remains and the relative solution composition of dppe-containing species based on integration of hydride resonances is 16% **2a**, 6% **II**, and 78% **8**. From analysis of the triethylsilyl spectral region (based on 3 equiv of Et_3Si) there exists 0.54 equiv of Et_3SiBr, 0.19 equiv of $Et_3SiSiEt_3$, and 1.23 equiv of unreacted Et_3SiH (along with 0.72 equiv of **8** and 0.15 equiv of **2a**).

The secondary chemistry of the reaction systems IrX(CO)-(dppe) + Et_3SiH (X = CN, Br) follows the stoichiometries of eq 13–15. While the secondary chemistry has not been studied

$$\text{IrHX(SiEt}_3\text{)(CO)(dppe)} \xrightarrow{Et_3SiH} \text{IrH}_2\text{X(CO)(dppe)} + Et_3SiSiEt_3 \quad (13)$$

$$2\text{IrHBr(SiEt}_3\text{)(CO)(dppe)} \xrightarrow{Et_3SiH}$$
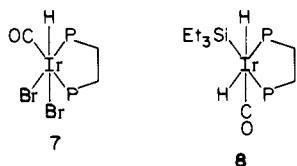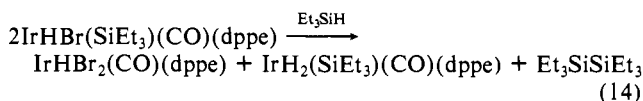$$\text{IrHBr}_2\text{(CO)(dppe)} + \text{IrH}_2\text{(SiEt}_3\text{)(CO)(dppe)} + Et_3SiSiEt_3 \quad (14)$$

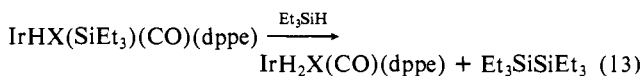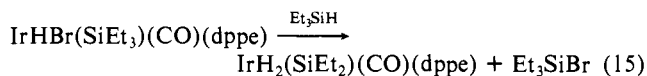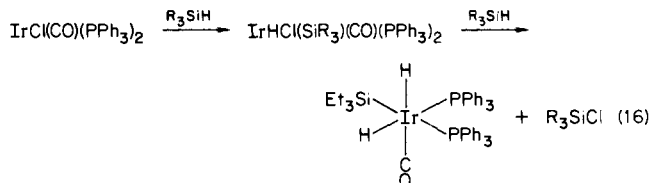**Figure 2.** ^{1}H NMR spectra in the triethylsilyl region for the reaction of Ir(CN)(CO)(dppe) and Et_3SiH in acetone solution: (a) Ir(CN)(CO)-(dppe) + 1.0 Et_3SiH after 5 min of reaction; (b) Ir(CN)(CO)(dppe) + 2.0 Et_3SiH after 12 min of reaction; (c) same sample at 207 min; (d) same sample after 4 months. The doublet marked "x" is due to a solvent impurity.

$$\text{IrHBr(SiEt}_3)(\text{CO})(\text{dppe}) \xrightarrow{\text{Et}_3\text{SiH}}$$
$$\text{IrH}_2(\text{SiEt}_2)(\text{CO})(\text{dppe}) + \text{Et}_3\text{SiBr} \quad (15)$$
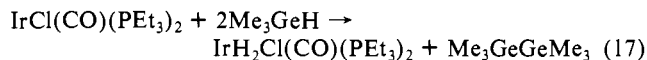
in detail mechanistically, the observed products can be accounted for within the framework of Ir(III)/Ir(I) reductive elimination/oxidative addition steps by the reactions in Scheme I. Reductive elimination of HX from IrHX(SiEt$_3$)(CO)(dppe) and subsequent reactions involving Et$_3$SiH and HX lead to either the formation of 1 equiv each of IrH$_2$X(CO)(dppe) and Et$_3$SiSiEt$_3$ as in eq 13 or the formation of equimolar amounts of **7**, **8**, and Et$_3$SiSiEt$_3$ as in eq 14. Equation 15 represents an alternative route to **8** that does not result in Et$_3$SiSiEt$_3$ formation. In eq 15 the reductive elimination of Et$_3$SiBr from IrHBr(SiEt$_3$)(CO)(dppe) is followed by Et$_3$SiH oxidative addition to IrH(CO)(dppe) yielding the silyl dihydride product. There is ample literature precedent for eq 15 as both Glockling et al.[10] and Chalk[6b] have reported analogous chemistry with Vaska's complex, eq 16. The

$$\text{IrCl(CO)(PPh}_3)_2 \xrightarrow{\text{R}_3\text{SiH}} \text{IrHCl(SiR}_3)(\text{CO})(\text{PPh}_3)_2 \xrightarrow{\text{R}_3\text{SiH}}$$

$$+ \text{ R}_3\text{SiCl} \quad (16)$$

initial oxidative addition product, IrHCl(SiR$_3$)(CO)(PPh$_3$)$_2$, has been isolated for R = OEt and Cl[6a,8] and is presumed to form for R = Me and Et as an unstable intermediate in eq 16. Parish and co-workers[8c] have also proposed that R$_3$SiCl reductive elimination occurs from IrHCl(SiR$_3$)(CO)(PPh$_3$)$_2$ in catalytic H/D exchange reactions of R$_3$SiH/D$_2$ and R$_3$SiH/R$_3$SiD. Vaska's complex reacts with trialkylgermanes in the same manner as eq 16, giving IrH$_2$(GeR$_3$)(CO)(PPh$_3$)$_2$ and R$_3$GeCl, and, at longer times, H$_2$ and R$_3$GeGeR$_3$.[21] When the triethylphosphine derivative of Vaska's complex is used, the reaction is selective for digermane formation, eq 17, paralleling our results in eq 13. As shown in

$$\text{IrCl(CO)(PEt}_3)_2 + 2\text{Me}_3\text{GeH} \rightarrow$$
$$\text{IrH}_2\text{Cl(CO)(PEt}_3)_2 + \text{Me}_3\text{GeGeMe}_3 \quad (17)$$

Scheme I, we believe that Et$_3$SiSiEt$_3$ is most likely formed via the intermediate Ir(SiEt$_3$)(CO)(dppe) which formally results from HX reductive elimination. It is not clear at this time whether unimolecular HX elimination occurs from IrHX(SiEt$_3$)(CO)-(dppe), but, in a possibly related reaction, we have observed that the corresponding dihydride complex II undergoes base-promoted dehydrohalogenation forming the intermediate IrH(CO)(dppe).[1] Also noteworthy with regard to the intermediacy of Ir(SiEt$_3$)-(CO)(dppe) and IrH(SiEt$_3$)$_2$(CO)(dppe) in Scheme I is the isolation of the germyl Ir(I) compounds Ir(GeR$_3$)(CO)(PPh$_3$)$_2$ (R = Me, Et)[21] and the chelated disilyl dihydride compound IrH-(SiMe$_2$OSiMe$_2$)(CO)(PPh$_3$)$_2$ (prepared from Vaska's complex and HMe$_2$SiOSiMe$_2$H).[12] Thus, reasonable precedents exist for all of the intermediates proposed in Scheme I. Other mechanisms for the formation of the secondary reaction products are, of course, possible and detailed studies will be needed to establish the correctness of Scheme I.

Reaction of IrX(CO)(dppe) with HY (X = Br, I; Y = Br, I). To an orange solution of IrI(CO)(dppe) in C$_6$D$_6$ was added 5 equiv of gaseous HBr giving a colorless solution which was analyzed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum shows complete conversion to one major monohydride product which slowly interconverts with three other monohydride species (see Figure 3). Two of the later products are identified as IrHBr$_2$(CO)(dppe) (**7**) (δ -15.38 (dd, J_{PH} = 10.6, 15.6 Hz)) and IrHI$_2$(CO)(dppe) (**9**) (δ -14.02 (dd, J_{PH} = 8.7, 15.7 Hz)), by independent syntheses from IrX(CO)(dppe) and HX. The other two products are characterized as isomers of IrHBrI(CO)(dppe), **10** and **11** in eq 18, by the chemical shift and splitting pattern of the hydride resonances. Complex **10** has a hydride resonance at δ -13.39 (dd,

(18)
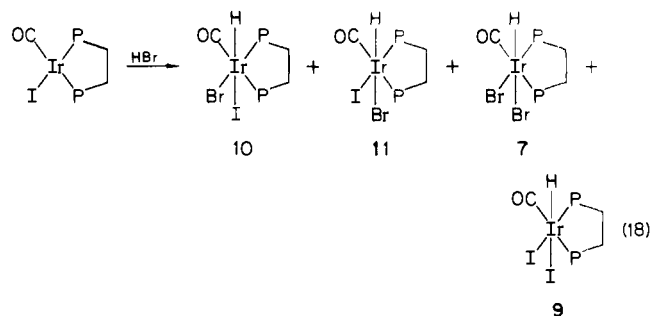
J_{PH} = 10.2, 15.9 Hz) indicative of a hydride trans to iodide, while **11** has a hydride resonance at δ -15.99 (dd, J_{PH} = 9.1, 15.5 Hz) indicative of a hydride trans to bromide. The similarity of the cis-phosphorus–hydride coupling constants in the four hydride products is in accord with the common IrHX$_2$(CO)(dppe) formulation where hydride is trans to X.

Complex **10** is the major initial product in reaction 18, comprising 86% of the mixture, and the other three products slowly increase in abundance over time as shown in Table II. After 550 h the halide ligands in the four products are nearly randomly distributed (i.e., 25% of each product).

It is clear that of the two isomers of IrHBrI(CO)(dppe) observed in reaction 18, isomer **10** with cis H and Br ligands is formed preferentially relative to **11**, which has trans H and Br ligands. Actually, there are six possible isomers for IrHBrI-(CO)(dppe), and on the basis of the above experiment, one cannot rule out the possibility that **10** is a secondary product from the reaction of IrI(CO)(dppe) and HBr and forms by isomerization of a different unobserved isomer.

To investigate this possibility we studied the reaction of IrBr(CO)(dppe) with HI. The same four products are observed, but now isomer **11** is the major product (70% of the product mixture according to the ^{1}H NMR spectrum taken after 15 min), and only a small amount (~7%) of **10** is observed. The relative amounts of **7** and **9** are 10% and 13%, respectively. Thus the stereochemistry of the halides is reversed for the reaction of IrBr(CO)(dppe) + HI compared to the reaction of IrI(CO)(dppe) + HBr, a strong indication that the major product in each reaction is indeed the kinetic product.

The major product in each case of HY addition is the isomer that would be formed by a concerted cis addition of HY along the P–Ir–X axis in IrX(CO)(dppe), corresponding to pathway ii in eq 3 with HX substrate orientation. This diastereoselection is opposite to that observed for both R$_3$SiH and H$_2$, which add along the P–Ir–CO axis, pathway i, and suggests that the initial interaction of IrX(CO)(dppe) with HY (Y = halide) differs significantly from that with R$_3$SiH or H$_2$.

Mechanism of R$_3$SiH and HY Oxidative Addition and Basis for Stereoselectivity. The oxidative addition of R$_3$SiH to IrX-(CO)(dppe) occurs by cis addition with kinetically controlled stereochemistry. The initially formed isomer in all cases corresponds to addition along pathway i with HC preferred substrate orientation. For IrBr(CO)(dppe), rapid formation of the i-HC kinetic isomer is followed by slower formation of the isomer corresponding to pathway ii addition with HX orientation. This latter isomer is the most stable of the four possible diastereomers of cis-silane addition to IrBr(CO)(dppe). In the case of Ir-(CN)(CO)(dppe), the same diastereoselectivity of silane addition is observed (>99.5% i-HC initially) but the relative stability of the diastereomers changes such that the kinetic isomer is also the most stable isomer.

With regard to both the kinetic diastereoselectivity and relative stability of product isomers, the oxidative addition of R$_3$SiH to IrX(CO)(dppe) shows remarkable parallels to that reported previously for H$_2$,[1] strongly suggesting the same mechanism of addition for R$_3$SiH and H$_2$. In the prior analysis of H$_2$ stereoselectivity, we discussed the preference for addition via pathway i over ii in terms of H$_2$ approach to the metal complex in a concerted process and suggested two factors which would work

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(21) Glockling, F.; Wilbey, M. D. *J. Chem. Soc. A* **1970**, 1675–1681.

Table II. Percent Composition of the Products from the Reaction of IrI(CO)(dppe) and HBr

time, h	IrHBrI(CO)(dppe) (10)	IrHIBr(CO)(dppe) (11)	IrHBr$_2$(CO)(dppe) (7)	IrHI$_2$(CO)(dppe) (9)
0.1	86	4	6	4
14	73	11	11	5
41	66	11	15	8
190	44	17	22	17
550	31	22	25	21
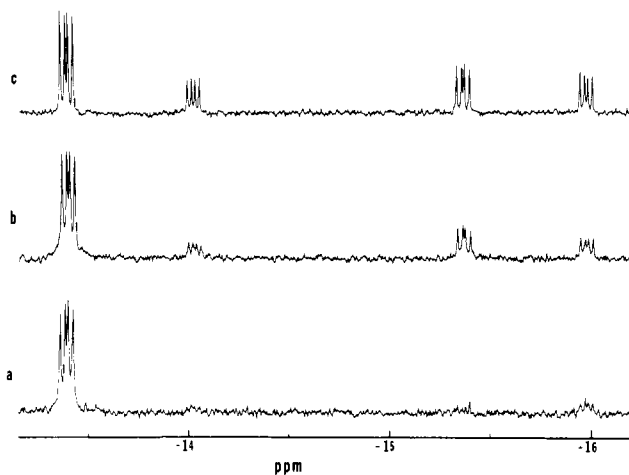
Figure 3. ^{1}H NMR spectra in the hydride region for the reaction of IrI(CO)(dppe) with HBr gas: (a) after 38 min of reaction at 25 °C; (b) 41 h; (c) 190 h.

Scheme I
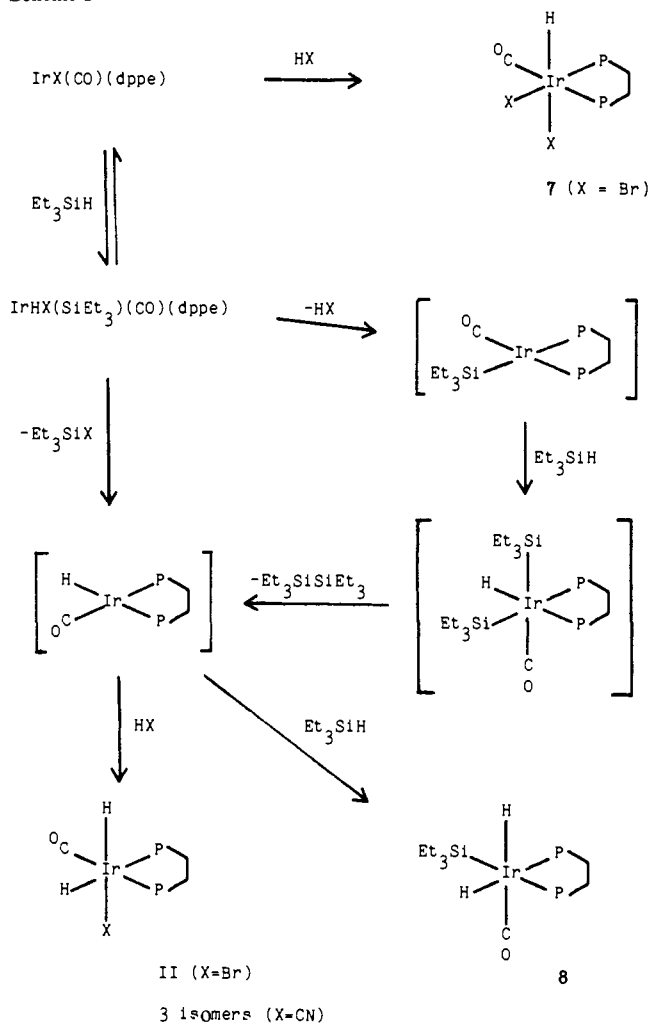
to favor A (H$_2$ parallel to P–Ir–CO) over B (H$_2$ parallel to P–Ir–X). These factors are (1) an orbital overlap effect wherein the π^* orbital of CO enhances the back-bonding interaction between a filled metal d$_\pi$ orbital and σ^*(H$_2$) through increased overlap and (2) a preferred bending of the set of trans ligands P and CO which become cis to each other and trans to the hydride ligands in the product. The latter factor is based on the notion that H$_2$ addition to the metal complex is similar to forming an adduct with an electron pair donor. As the H$_2$ substrate approaches the metal complex in this addition, one pair of trans ligands bends such that complex + substrate form a trigonal bipyramid as the transition state. The bending ligands and the H$_2$ substrate occupy the equatorial sites of this trigonal bipyramid. Preference for bending of the P–Ir–CO axis over the P–Ir–X axis occurs because this places the better π-acid ligand CO in the equatorial plane where it can better stabilize the developing trigonal bipyramid. This view is similar to that used to explain the trans effect in square-planar substitution reactions[22] and relates to the proposal put forth by Harrod[3] and shown as C that deformation of the square-planar complex is a major component of the activation barrier in H$_2$ oxidative addition. Both of the factors proposed to explain H$_2$ stereoselectivity can be extended to silane oxidative addition as well.

The question of relative substrate orientation does not arise in the oxidative addition chemistry of H$_2$ but must be addressed for silanes. For addition of Si–H along P–Ir–CO, pathway i, the formation of the HC isomer as the kinetic isomer corresponds to a clear preference of Si–H approach shown in D to that shown in E. The basis of this preference is probably steric and involves minimizing nonbonded interactions between the silyl group and the phosphine substituents. Approach D makes the silyl group cis to only one of the phosphines and trans to the other. Similarly for addition along pathway ii, approach F is favored over G, leading to formation of the HX isomer with R$_3$Si cis to one P donor and trans to the other. Steric interactions may also alter silane approach to the metal complex such that the Si–H bond is not parallel to the P–Ir–CO axis but rather is tilted toward an "end-on" approach, H, which emphasizes the hydridic character and donor
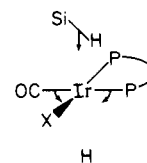

ability of the Si–H bond. Thus, the relative importance of bending the P–Ir–CO axis to stabilize the developing trigonal bipyramid increases in H relative to D, while that of the overlap effect involving π^*(CO) and the back-bonding interaction between filled metal d$_\pi$ and σ^*(Si–H) is significantly diminished. If the more end-on approach depicted in H does in fact occur for Si–H oxidative addition, then the observed stereochemical similarities of silane and H$_2$ addition suggest that the second factor given above (i.e., the relative ease of bending trans ligands) is the more important factor in determining the observed diastereoselectivity for both substrates.

The observation that hydrogen halides oxidatively add to IrX-(CO)(dppe) in the opposite direction, along the P–Ir–X axis,

(22) (a) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 1201. (b) Huheey, J. E. "Inorganic Chemistry", 2nd ed.; Harper and Row: New York, 1978; p 496.

6540

J. Am. Chem. Soc. **1985**, *107*, 6540–6546

pathway ii, clearly indicates that the ease of trans ligand deformation or bending in IrX(CO)(dppe) without regard to incoming substrate cannot by itself account for the stereoselectivity of these oxidative addition reactions. Thus, the complex–substrate interaction must be substantially different for HX vs. H_2 and R_3SiH. The first question that must be addressed is whether the HX addition is concerted or proceeds in two or more discrete steps. The stereoselective nature of the reaction where H and X ligands occupy cis positions in the kinetic product strongly suggests a concerted mechanism. In such a mechanism, the approach of the highly polar species HX along the P–Ir–I axis of IrI(CO)(dppe) will undoubtedly be unsymmetrical and can be either electrophilic or nucleophilic in character as shown in J and K, respectively.
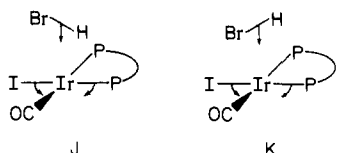
If HBr approach is nucleophilic as in K the situation resembles that of silane approach H and similar considerations would apply regarding the diastereoselectivity. Thus, the developing trigonal bipyramid of IrI(CO)(dppe) + HBr would be more stable with the better π-acid CO in the equatorial plane than with iodide there, and the concerted addition of HBr would be expected to proceed along P–Ir–CO, pathway i. This expectation is contrary to what is observed.

For electrophilic approach J, the bending of P–Ir–I leads to a complex + substrate trigonal bipyramid having the better donor iodide in the equatorial plane thus enhancing the ability of Ir(I)

to donate electrons to an incoming electrophile. It is well established that Ir(I) complexes can act as electron pair donors as in the reactions of $IrCl(CO)(PPh_3)_2$ with BF_3 and NO^+ and the oxidative addition reaction of MeI. In the present case, the donor ability of the Ir complex is better if P–Ir–X bends than if P–Ir–CO bends, and this leads to the observed diastereoselectivity. The primary interaction of hydrogen halides with IrX(CO)(dppe) in nonpolar media, while leading to concerted addition, clearly differs from that of H_2 and R_3SiH. We conclude that in concerted oxidative addition reactions to cis phosphine analogues of Vaska's complex, the stereochemistry of addition (i.e., pathway i or ii) can be controlled kinetically by the nucleophilic or electrophilic character of the substrate.

Ferric Ion Sequestering Agents. 14.[1] 1-Hydroxy-2(1H)-pyridinone Complexes: Properties and Structure of a Novel Fe–Fe Dimer

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Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. Received December 26, 1984

Abstract: The 1-hydroxy-2-pyridonate (1,2-opo) ligating group has structural and electronic similarities to hydroxamate and catecholate ligands. A ligand with two 1,2-opo groups, 1,5-bis[(1,2-dihydro-1-hydroxy-2-oxopyridin-6-yl)carbonyl]-1,5-diazapentane (LH₂, **5**), has been prepared and its properties have been compared with a dihydroxamate of microbial origin, rhodotorulic acid (H₂RA, **6**). Like RA, reaction of L^{2-} with Fe^{3+} in aqueous solution gives a dimeric complex, Fe₂L₃. The structural and solution thermodynamic properties of this novel analogue of the siderophore RA have been investigated. One form of Fe₂L₃ crystallizes from dichloromethane–methanol–water to give orange-red hexagonal needles, Fe₂L₃·2CH₃OH·H₂O, space group P6₁ (a = 13.731 (2) Å, c = 48.430 (5) Å, V = 7908 (2) Å³ at −99 ± 3 °C, d_{obsd} 1.53 at 25 °C, d_{calcd} 1.553 at −99 °C). The structure is composed of six discrete Fe₂L₃ molecules in which each Fe^{3+} is surrounded by three bidentate opo groups such that the inner coordination sphere of both iron atoms and the entire molecule have pseudo-D_3 symmetry and a left-handed screw conformation (Λ-cis coordination about each iron atom). Since the ligand is achiral, the chirality of the crystal results from resolution during crystallization. This is the same geometry as that proposed for Fe₂RA₃. Full-matrix least-squares refinement of the structure with 5077 reflections $[F_o{}^2 > 3\sigma(F_o{}^2)]$ and 756 variable parameters converged with R and R_w indices of 0.0438 and 0.0489, respectively. The formation constant (log β_{230}) for Fe₂L₃ is 52.3 (3) in aqueous solution, μ = 0.1 M. The pK_a's of H₂L were determined by potentiometric titration to be 5.35 (1) and 4.50 (1). Unlike hydroxamate siderophores, H₂L rapidly removes iron from the human serum iron protein transferrin: at 1.6 mM, H₂L removed iron from the protein (0.13 mM) in 0.1 M pH 7.4 tris buffer at 25 °C with a pseudo-first-order rate constant of $k_{obsd} = 1.08 \times 10^{-2}$ min⁻¹.

As reviewed recently,[2–4] we have been engaged in the preparation of synthetic analogues of the siderophores, highly specific ferric chelating agents of microbial origin.[5] Interest in these synthetic compounds includes their coordination chemistry as it relates to the siderophores[2,6] but extends to their potential ap-

plication as clinical iron removal agents in man. Particularly in the disease β-thalassemia, where iron overload occurs as a side

†Materials and Molecular Research Division, Lawrence Berkeley Laboratory.

(1) Previous paper in this series: Scarrow, R. C.; Riley, P. E.; Abu-Dari, K.; White, D. L.; Raymond, K. N. *Inorg. Chem.* **1985**, *24*, 954–67.
(2) Raymond, K. N.; Tufano, T. P. In "The Biological Chemistry of Iron"; Dunford, H. B.; Dolfin, D.; Raymond, K. N.; Seiker, L., Eds.; D. Reidel Publishing Co.: Dordrecht, Holland, 1982; pp 85–105.