*Inorg. Chem.* **1995,** *34,* 2937−2941

# Seven-Coordinate Iridium(V) Polyhydrides with Chelating Bis(silyl) Ligands

**Maria Loza, J. W. Faller,* and Robert H. Crabtree***

Chemistry Department, Yale University, 225 Prospect Street, New Haven, Connecticut 06511

*Received December 28, 1994*[®]

The pentahydride $IrH_5(PPh_3)_2$ reacts with chelating silanes with loss of $H_2$ to form the classical seven-coordinate distorted pentagonal bipyramidal silyl polyhydride complexes $IrH_3$(disil)$(PPh_3)_2$ (disil: dmsb, **3a**; tids, **3b**) with monodentate silanes to give $IrH_4(SiR_3)(PPh_3)_2$ (R: Et, **4a**; Ph, **4b**) and with triphenyltin hydride to give $IrH_3(SnPh_3)_2(PPh_3)_2$ (**5**), all rare examples of Ir(V). A crystal structure was obtained for **3a**. Crystal data: orthorhombic; space group *Pbca* (No. 61); $a = 17.1534(6)$ Å; $b = 25.688(2)$ Å; $c = 19.0641(9)$ Å; $V = 8400(1)$ Å$^3$; $Z = 8$.

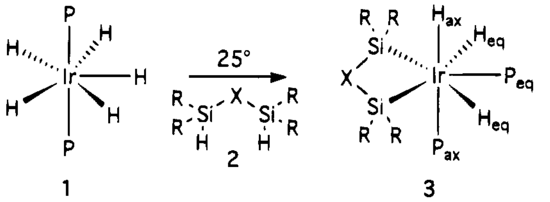
## Introduction

Seven-, eight-, and nine-coordination is rare for transition metal complexes, except for polyhydrides,[1] where the small size of the H ligand is thought to be the main factor permitting high coordination. The finding[2] that polyhydrides can readily be substituted by $SiR_3$ ligands on reaction with $HSiR_3$ led to the idea that the enhanced steric bulk of the sphere of atoms *directly* attached to the metal (the α coordination sphere) in the resulting silyl polyhydride might cause some of the remaining hydrides to associate to form dihydrogen ligands[3] so as to occupy less space in the α coordination sphere. Previous efforts to use steric effects to cause H ligands in polyhydrides to associate only involved attempts to use steric bulk in the γ and higher spheres by introducing bulky R groups in $PR_3$, and these all failed. By reaction of $ReH_7(PPh_3)_2$ with a *chelating* disilane we were able[2b] to introduce two silyl groups, and the resulting $ReH_3$(H··H)(disilyl)$(PPh_3)_2$ indeed contained an $H_2$ ligand, albeit stretched.[3b,4] In this paper we look at the related seven-coordinate polyhydride $IrH_5(PPh_3)_2$ to see what would happen in this case.

In this paper, we describe the synthesis and characterization of $IrH_3$(dmsb)$(PPh_3)_2$ (dmsb = 1,2-bis(dimethylsilyl)benzene) and related monodentate Ir−Si and Ir−Sn species. The spectroscopic data show no evidence for H··H or Si··H interactions, and the complexes are therefore formulated as a classical seven-coordinate complexes, all rare examples of iridium(V). Since silyl hydride complexes were recently implicated[5a] in C−H activation, we briefly look at the catalytic activity of **3**−**5**.

## Results and Discussion

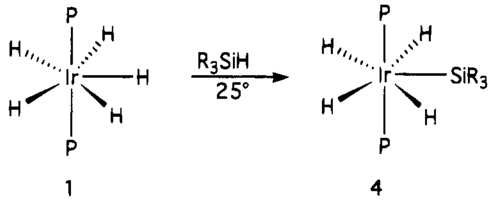
**Synthesis.** $[IrH_5(PPh_3)_2]$ (**1**) reacts with the chelating silanes 1,2-bis(dimethylsilyl)benzene ($dmsbH_2$, **2a**) and 1,1,3,3-tetraisopropyldisiloxane ($tidsH_2$, **2b**) in THF at room temperature to form the trihydrides $IrH_3$(disil)$(PPh_3)_2$ (disil: dmsb, **3a**; tids, **3b**) (eq 1). The stereochemistry of **3** follows from the spectroscopic and structural data, discussed below. In the case of the reaction of **2a** with $ReH_7(PPh_3)_2$,[4] an intermediate was isolated with one M−Si bond and one free Si−H, but such a species was never seen for Ir. Performing the reaction under reflux only led to decomposition. **3a**,**b** were isolated in analytically pure form as white, air-stable solids in good yields (**3a**, 78%; **3b**, 50%) by partial evaporation of the solvent and precipitation with hexanes. **3a** is stable in $CH_2Cl_2$, but a solution of **3b** darkens in minutes and even the solid is unstable. The difference in kinetic stability may result from the five-membered chelate ring for dmsb being more stable than the four-membered ring for tids. No products were isolated from the reaction of **1** with the potentially tridentate silane methyltris(dimethylsiloxy)silane.



(1)

a, X = $C_6H_4$, R = Me;
b, X = O, R = i-Pr.

The monosilanes $R_3SiH$ (R = Et, Ph) also react with **1** but only to form tetrahydride complexes $IrH_4(SiR_3)(PPh_3)_2$ (R: Et, **4a**; Ph, **4b**) (eq 2), and disilyl species are not observed even under forcing conditions. In contrast, reaction of **1** with $Ph_3SnH$ yields only the disubstituted trihydride $IrH_3(SnPh_3)_2(PPh_3)_2$ (**5**), no monosubstituted intermediate being seen (eq 3). Complexes **3**−**5** were characterized by microanalytical (see Experimental Section) and spectroscopic data (Table 1); **3a** was also characterized crystallographically.



(2)

a, R = $C_2H_5$
b, R = $C_6H_5$

**NMR Spectroscopic Studies.** $IrH_5(PPh_3)_2$ is in the high-temperature-limiting fluxionality regime at 20 °C, having a triplet at δ −9.03 ($^2J_{PH}$ = 14 Hz), but the $^1H$ NMR spectrum of **3a** (Table 1) in $CD_2Cl_2$ shows only broad resonances for

---

[®] Abstract published in *Advance ACS Abstracts,* May 1, 1995.

[1] Heinekey, D. M.; Oldham, W. J. *Chem. Rev.* **1993**, *93,* 913.

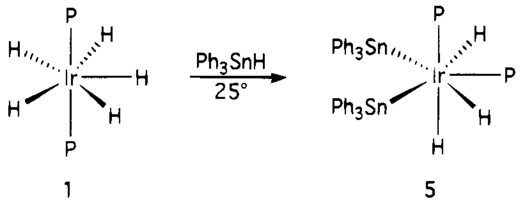
[2] (a) Luo, X. L.; Baudry, D.; Boydell, P.; Charpin, P.; Nierlich, M.; Ephritikhine, M.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29,* 1511. Howard, J. A. K.; Keller, P. A.; Vogt, T.; Taylor, A. L.; Dix, N. D.; Spencer, J. L. *Acta Crystallogr.* **1992**, *B48,* 438. (b) Loza, M. L.; de Gala, S.; Crabtree, R. H. *Inorg. Chem.*, in press.

[3] (a) Kubas, G. J. *Comments Inorg. Chem.* **1988**, *7,* 17; *Acc. Chem. Res.* **1988**, *21,* 120. (b) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121,* 155.

[4] Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32,* 789.

[5] (a) Djurovich, P. I.; Carroll, P. J.; Berry, D. H. *Organometallics* **1994**, *13,* 2551. (b) Takao, T.; Suzuki, H.; Tanaka, M. *Organometallics* **1994**, *13,* 2554.

0020-1669/95/1334-2937$09.00/0

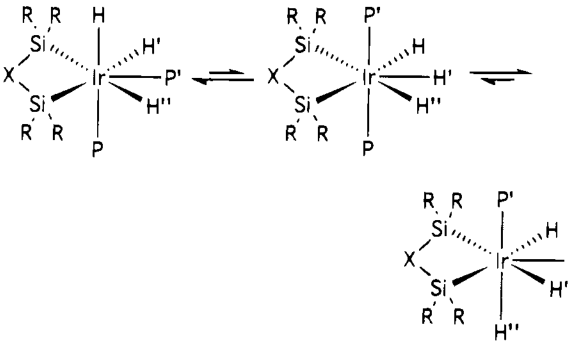


(3)

both Si−Me and M−H, indicating an intermediate fluxionality regime at 20 °C. At −80 °C, where the low-temperature-limiting spectrum is seen, the broad $IrH_{eq}$ resonance at $\delta$ −9.12 ($\nu_{1/2} \approx$ 60 Hz) transforms into a triplet at $\delta$ −9.18, $^2J_{PH}$ = 9 Hz, integrating for two protons, and the broad doublet for $IrH_{ax}$ at $\delta$ −13.4, integrating for 1 proton, transforms into a doublet of doublets at $\delta$ −13.5 ($^2J_{PHcis}$ = 18 Hz, $^2J_{PHtrans}$ = 117 Hz). The couplings indicate the pair of equivalent hydrides are cis to two P nuclei and the unique hydride is cis to one P ($P_{eq}$) and trans to another ($P_{ax}$), consistent with the stereochemistry shown in eq 1.

On warming, the hydrides coalesce at 70 °C, which implies a barrier to fluxional exchange of ca. 13 kcal/mol. The $^{31}P$ spectrum, broad at ambient temperatures, shows two signals at $\delta$ 8.71 and 7.66 at −60 °C, which coalesce on warming with the same barrier of 13 kcal/mol. This suggests that both the P and H ligands become equivalent in the same fluxional process, so that the hydrides are not simply exchanging, leaving the heavy atoms unaffected. The Me groups on silicon become inequivalent in the proton NMR at low temperature and by −80 °C consist of a pair of singlets at $\delta$ 0.621 and −0.081. This exchange has the same 13 kcal/mol barrier, and so the same process is probably responsible.

A plausible mechanism for fluxionality that accounts for the observations is the conversion of the starting complex into the trans-phosphine isomer by a turnstile rotation of $P_{eq}$, $H_{eq}$, and $H_{ax}$. This trans isomer has the same structure as $IrH_5(PPh_3)_2$ itself and is presumably thermodynamically disfavored because it maximizes repulsions between the bulky cis P and Si groups. In a second turnstile step, the other phosphine, originally axial, becomes equatorial.



(4)

The possibility that $H_2$ ligands were present was examined using $T_1$ data, obtained at 300 MHz as a function of temperature. A $T_1$ minimum was found for all the MH peaks at −60 °C, with values of 264 (equatorial) and 204 ms (axial), indicating a classical structure.

The $^1H$ NMR spectra of $IrH_4(SiPh_3)(PPh_3)_2$ (**4b**) are consistent with the structure shown in eq 2. Making a model of the structure suggests that the smaller steric repulsions resulting from the presence of only three heavy atoms in the a coordination sphere permit the trans-phosphine structure shown. A triplet hydride resonance at $\delta$ −10.18 ($^2J_{PH}$ = 12 Hz) at 25 °C becomes a broad feature at −40 °C ($\delta$ −10.22, $\nu_{1/2} \approx$ 31 Hz), but decoalescence was not reached down to −80 °C. The barrier to rearrangement is lower than that for **3a**, but an exact value could not be determined. No coupling to Si was observed in any case.

**Table 1.** Selected IR and NMR Data for New Iridium Complexes

| complex | IR $\nu$(Ir−H), $cm^{-1}$ [a] | NMR $^1H$ $\delta$(Ir−H)[b] | $^{31}P\{^1H\}$[c] $\delta$ |
|---|---|---|---|
| $IrH_3(dmsb)P_2$ | 2110, 1943 | −9.12 br s, −13.4 br d | 8.20 br d |
| $IrH_3(tids)P_2$ | 2112, 1879 | −11.20 br s | 11.8 |
| $IrH_4(SiEt_3)P_2$ | 2094, 1855 | −11.17 br s | 13.5 |
| $IrH_4(SiPh_3)P_2$ | 2122, 1829 | −10.20 t (12) | 10.6 |
| $IrH_3(SnPh_3)_2P_2$ | 2078, 1956 | −11.02 t (15) | 3.18 |

[a] Nujol mull. [b] In $CD_2Cl_2$ at 298 K and 300 MHz. Hydride resonances reported as follows: chemical shift (ppm) multiplicity (br = broad; s = singlet; d = doublet; t = triplet) (coupling constant $^2J_{PH}$, Hz). [c] Chemical shift is given in ppm downfield of external 85% $H_3PO_4$.

The $^1H$ NMR spectra of $IrH_3(SnPh_3)_2(PPh_3)_2$ (**5**) are consistent with the structure shown in eq 3, which is analogous to that of **3a**. The MH multiplet ($\delta$ −11.02; $^2J_{PH}$ = 15 Hz) present at 25 °C broadens and collapses into two separate resonances with an intensity ratio of 1:2, reminiscent of the spectrum for **3a**. At −80 °C we see a broad resonance at $\delta$ −9.22 ($\nu_{1/2} \approx$ 146 Hz) and a doublet at $\delta$ −12.04 ($^2J_{PH}$ = 85 Hz). The tin satellites due to $^{117}Sn$ (abundance = 7.61%, $I = {}^1/_2$) and $^{119}Sn$ (abundance = 8.58%, $I = {}^1/_2$) are not fully resolved at ambient temperature, but at −80 °C, two satellites ($J_{SnH}$ = 22 and 37 Hz) are clearly observed. The values appear to be normal geminal couplings and do not suggest the presence of any Sn••H interactions. Unfortunately, solubility and other problems prevented low-temperature spectra from being obtained for **3b** and **4a**.

**IR Studies.** The IR data for the complexes (Table 1) are consistent with the presence of terminal MH bonds. No $\nu\{M(\eta^2\text{-}H_2)\}$ band[6] was seen in the range 2400−3100 $cm^{-1}$. For **3a**, the band at 1943 $cm^{-1}$ could be interpreted as arising from an M−H or an agostic Si−H••M group.[6c] For this reason, a single-crystal X-ray study of **3a** was needed to establish the structure.

**X-ray Structure of 3a.** In order to obtain more information about the geometry of the complex, an X-ray crystallographic study was performed on **3a**. Crystals were obtained by slow diffusion of hexanes into a solution of **3a** in methylene chloride. Figure 1 shows the resulting ORTEP diagram, and the crystallographic data are presented in Tables 2−4. The hydrides were not detected, but we propose they are located in the three prominent gaps in the α coordination sphere, one trans to P2 and one each between P1 and Si1 and P1 and Si2. The structure is then consistent with the spectroscopic data. Both Si−H bonds of the chelating silane have oxidatively added to iridium and no agostic Si−H groups can be present. Like the parent pentahydride $IrH_5(PPh_3)_2$, **3a** is pentagonal bipyramidal.[7] The phosphines are unusual[8a] in being cis not trans, but other examples of cis complexes are known.[9]

---

(6) (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120 and references therein. (b) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913. (c) Driess, M.; Reisgys, M.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1510.

(7) Garlaschelli, L.; Khan, S. I.; Bau, R.; Longoni, G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1985**, *107*, 7212.

(8) (a) Drew, M. G. B. *Prog. Inorg. Chem.* **1977**, *23*, 67. (b) Luo, X.-L.; Schulte, G. K.; Demou, P.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 4268. (c) Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* **1977**, *16*, 511. (d) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th Ed.; Wiley: New York, 1980. (e) Dewan, J. C.; Wood, T. E.; Walton, R. A.; Lippard, S. J. *Inorg. Chem.* **1982**, *21*, 1854. (f) Kepert, D. L. *J. Chem. Soc., Dalton Trans.* **1974**, 617. (g) Kepert, D. L. *J. Chem. Soc., Dalton Trans.* **1975**, 963. (h) Kepert, D. L. *Inorg. Chem.* **1974**, *13*, 2754, 2758.

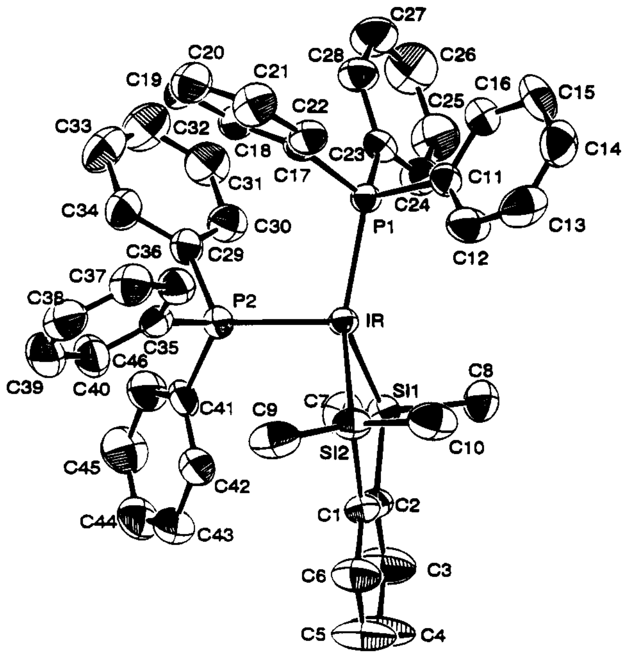


**Figure 1.** ORTEP diagram of the results of the X-ray crystal structure of complex **3a**. The hydride ligands were not located.

**Table 2.** Crystallographic Data for **3a**

| | |
|---|---|
| formula | $C_{46}H_{49}P_2Si_2Ir$ |
| fw | 912.23 |
| crystal color | colorless |
| crystal dimens, mm | 0.24 × 0.27 × 0.48 |
| crystal system | orthorhombic |
| space group | *Pbca* (No. 61) |
| $a$, Å | 17.1534(6) |
| $b$, Å | 25.688(2) |
| $c$, Å | 19.0641(9) |
| $V$, Å$^3$ | 8400(1) |
| $Z$ value | 8 |
| $\varrho_{calc}$, g cm$^{-3}$ | 1.444 |
| diffractometer | Enraf-Nonius CAD4 |
| radiation | Mo Kα ($\lambda$ = 0.710 69 Å) |
| $T$, K | 296 |
| no. of tot unique reflns > $3\sigma(I)$ | 4911 |
| $R^a$ | 0.022 |
| $R_w{}^b$ | 0.025 |
| max shift/error | 0.00 |

$^a R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2)]^{1/2}$.

**Table 3.** Selected Bond Distances (Å) and Angles (deg) for **3a**

| | | | |
|---|---|---|---|
| Ir−P1 | 2.371(1) | Ir−Si1 | 2.437(1) |
| Ir−P2 | 2.365(1) | Ir−Si2 | 2.430(1) |
| P1−Ir−P2 | 102.62(4) | P2−Ir−Si1 | 99.45(4) |
| P1−Ir−Si1 | 134.02(4) | P2−Ir−Si2 | 99.55(4) |
| P1−Ir−Si2 | 133.26(4) | Si1−Ir−Si2 | 80.68(4) |

The Si1−Ir−Si2 angle of 80.68(4)° and the P1−Ir−P2 angle of 102.62(4)° are both distorted from the ideal values of 72 and 90°, respectively. These distortions may not simply be steric in origin because it is known that the other ligands tend to bend toward M−H bonds for electronic reasons.[10a] The Ir−Si (average 2.434 Å) and the Ir−P distances (average 2.368 Å) are comparable to those seen in Ir(III) complexes.[10b]

**Table 4.** Positional and Isotropic Thermal Parameters for **3a**

| atom | $x$ | $y$ | $z$ | $B$(eq), Å$^2$ |
|---|---|---|---|---|
| Ir | 0.256558(7) | 0.146522(5) | 0.078354(8) | 2.480(6) |
| P1 | 0.35897(6) | 0.20641(4) | 0.05677(6) | 2.62(5) |
| P2 | 0.25771(6) | 0.09435(4) | −0.02387(6) | 3.01(5) |
| Si1 | 0.23456(6) | 0.07912(4) | 0.16607(6) | 2.87(5) |
| Si2 | 0.11668(6) | 0.15629(5) | 0.09368(7) | 3.25(6) |
| C1 | 0.0748(2) | 0.0995(2) | 0.1435(2) | 3.0(2) |
| C2 | 0.1268(2) | 0.0652(2) | 0.1748(2) | 3.3(2) |
| C3 | 0.0967(3) | 0.0234(2) | 0.2163(4) | 6.5(3) |
| C4 | 0.0162(3) | 0.0154(3) | 0.2174(5) | 8.5(4) |
| C5 | −0.0333(3) | 0.0490(2) | 0.1855(4) | 6.9(4) |
| C6 | −0.0049(3) | 0.0908(2) | 0.1492(3) | 5.1(3) |
| C7 | 0.2860(3) | 0.0143(2) | 0.1573(3) | 4.6(2) |
| C8 | 0.2654(3) | 0.1028(2) | 0.2552(3) | 4.6(2) |
| C9 | 0.0545(3) | 0.1619(2) | 0.0124(3) | 5.0(3) |
| C10 | 0.0906(3) | 0.2148(2) | 0.1478(3) | 5.5(3) |
| C11 | 0.3521(2) | 0.2665(2) | 0.1079(2) | 3.1(2) |
| C12 | 0.2798(3) | 0.2869(2) | 0.1257(3) | 5.0(3) |
| C13 | 0.2739(4) | 0.3356(2) | 0.1557(4) | 6.2(3) |
| C14 | 0.3395(4) | 0.3644(2) | 0.1707(3) | 5.7(3) |
| C15 | 0.4113(3) | 0.3443(2) | 0.1545(3) | 5.5(3) |
| C16 | 0.4175(3) | 0.2960(2) | 0.1237(3) | 4.1(2) |
| C17 | 0.3655(2) | 0.2332(2) | −0.0323(2) | 2.9(2) |
| C18 | 0.4003(2) | 0.2055(2) | −0.0860(2) | 3.5(2) |
| C19 | 0.3964(3) | 0.2233(2) | −0.1552(3) | 4.6(3) |
| C20 | 0.3589(3) | 0.2695(2) | −0.1698(3) | 5.0(3) |
| C21 | 0.3267(3) | 0.2981(2) | −0.1170(3) | 4.8(3) |
| C22 | 0.3295(2) | 0.2801(2) | −0.0486(3) | 3.7(2) |
| C23 | 0.4584(2) | 0.1848(2) | 0.0776(2) | 3.1(2) |
| C24 | 0.4693(3) | 0.1559(2) | 0.1382(3) | 4.4(2) |
| C25 | 0.5442(3) | 0.1408(2) | 0.1577(3) | 6.3(3) |
| C26 | 0.6062(3) | 0.1544(3) | 0.1171(4) | 7.0(4) |
| C27 | 0.5962(3) | 0.1836(2) | 0.0591(3) | 5.7(3) |
| C28 | 0.5230(2) | 0.1992(2) | 0.0387(3) | 4.0(2) |
| C29 | 0.3549(3) | 0.0823(2) | −0.0593(3) | 3.6(2) |
| C30 | 0.4156(3) | 0.0716(2) | −0.0140(3) | 4.3(2) |
| C31 | 0.4917(3) | 0.0651(2) | −0.0378(3) | 5.4(3) |
| C32 | 0.5064(3) | 0.0699(3) | −0.1091(4) | 6.9(4) |
| C33 | 0.4469(4) | 0.0806(2) | −0.1556(3) | 6.4(4) |
| C34 | 0.3712(3) | 0.0859(2) | −0.1316(3) | 4.9(3) |
| C35 | 0.2040(3) | 0.1183(2) | −0.1012(3) | 3.5(2) |
| C36 | 0.1987(3) | 0.1712(2) | −0.1119(5) | 4.1(2) |
| C37 | 0.1583(3) | 0.1910(2) | −0.1699(3) | 5.1(3) |
| C38 | 0.1219(3) | 0.1575(2) | −0.2162(3) | 5.5(3) |
| C39 | 0.1280(3) | 0.1046(2) | −0.2048(3) | 5.9(3) |
| C40 | 0.1683(3) | 0.0851(2) | −0.1478(3) | 4.8(3) |
| C41 | 0.2188(3) | 0.0278(2) | −0.0168(2) | 3.5(2) |
| C42 | 0.1436(3) | 0.0210(0) | 0.0082(3) | 4.0(2) |
| C43 | 0.1120(3) | −0.0283(2) | 0.0163(3) | 5.0(3) |
| C44 | 0.1552(4) | −0.0717(2) | 0.0006(3) | 5.5(3) |
| C45 | 0.2302(3) | −0.0653(2) | −0.0247(4) | 6.1(3) |
| C46 | 0.2618(3) | −0.0163(2) | −0.0330(3) | 4.9(3) |

**Reactivity Studies.** After initial loss of $H_2$,[11] polyhydrides, such as $IrH_5(PR_3)_2$ (R = $^i$Pr, Ph),[12] can react with alkanes to give alkenes or alkene or alkenyl complexes or with 2e donors, such as CO and $PR_3$. We therefore looked at similar reactions for the new complexes **3**−**5**.

**Reaction with CO and P(OMe)$_3$.** $IrH_5(PEt_2Ph)_2$ is known to react with CO to form a trihydride, $IrH_3(CO)(PEt_2Ph)_2$, which

---

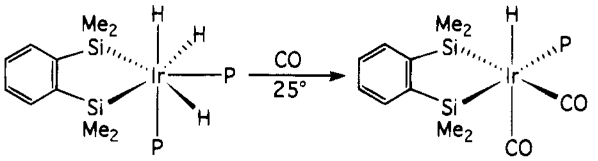
(9) (a) Harrod, J. F.; Gilson, D. F. R.; Charles, R. *Can. J. Chem.* **1969**, *47*, 2205. (b) Colomer, E.; Corriu, R. J. P.; Vioux, A. *Inorg. Chem.* **1979**, *18*, 695. (c) Colomer, E.; Corriu, R. J. P.; Marzin, C.; Vioux, A. *Inorg. Chem.* **1982**, *21*, 368. (d) Carré, F.; Colomer, E.; Corriu, R. J. P.; Vioux, A. *Organometallics*, **1984**, *3*, 1272.

(10) (a) Jackson, S. A.; Eisenstein, O.; Martin, J. D.; Albeniz, A. C.; Crabtree, R. H. *Organometallics* **1991**, *10*, 3062–9. (b) Hays, M. K.; Eisenberg, R. *Inorg. Chem.* **1991**, *30*, 2623.

(11) (a) Zanella, R.; Canziani, F.; Ros, R.; Graziani, M. *J. Organomet. Chem.* **1974**, *67*, 449. (b) Clerici, M. G.; Di Gloacchino, S.; Maspero, F.; Perrotti, E.; Zanobi, A. *J. Organomet. Chem.* **1975**, *84*, 379. (c) Crabtree, R. H. *Acc. Chem. Res.* **1979**, *12*, 331. (d) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1988.

(12) (a) Felkin, H.; Fillebeen-Khan, T.; Gault, Y.; Holmes-Smith, R.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, *25*, 1279. (b) Lin, Y.; Ma, D.; Lu, X. *J. Organomet. Chem.* **1987**, *323*, 407. (c) Lin, Y.; Ma, D.; Lu, X. *Tetrahedron Lett.* **1987**, *28*, 3115. (d) Lin, Y.; Ma, D.; Lu, X. *Tetrahedron Lett.* **1987**, *28*, 3249. (e) Perego, G.; Del Piero, G.; Cesari, M.; Clerici, M. G.; Perrotti, E. *J. Organomet. Chem.* **1973**, *54*, C51. (f) Clerici, M. G.; Di Gioacchino, S.; Maspero, F.; Perrotti, E.; Zanobi, A. *J. Organomet. Chem.* **1975**, *84*, 379. (g) Esteruelas, M. A.; Garcia, M. P.; Lahoz, F. J.; Martin, M.; Modrego, J.; Oñate, E.; Oro, L. A. *Inorg. Chem.* **1994**, *33*, 3473.

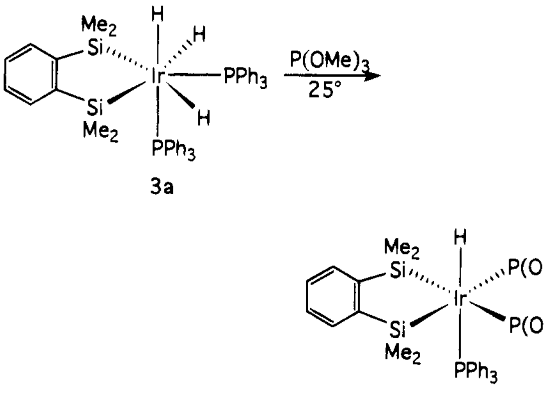
can react further to give $IrH(CO)_2(PEt_2Ph)_2$.[13] **3a** reacts readily with CO to give a mildly air-sensitive white solid which could never be isolated in a pure state but whose spectroscopic data suggest the formulation $IrH(dmsb)(CO)_2(PPh_3)$ (eq 5). The $^1H$ NMR of this complex exhibits a doublet for IrH at $\delta$ −10.0 ($^2J_{PH}$ = 13 Hz), and the SiMe groups are all inequivalent. The IR shows strong bands at 2091, 2043, and 1980 $cm^{-1}$, attributed to the hydride and CO ligands. The selectively hydride-coupled $^{31}P$ NMR shows a doublet at $\delta$ −3.22 ($J_{PH}$ = 15 Hz), confirming the presence of one hydride ligand.



3a

(5)

$IrH_5(PEt_2Ph)_2$ reacts with $P(OMe)_3$ to form *fac*-$IrH_3(PEt_2Ph)_2(POMe_3)$.[13a] **3a** also reacts with trimethyl phosphite at 20 °C in THF, to produce an air-stable white solid after isolation. The $^1H$ NMR shows two resonances for the SiMe groups and a doublet of triplets at $\delta$ −13.12 ($^2J_{PHcis}$ = 15 Hz, $^2J_{PHtrans}$ = 104 Hz) for the IrH group. The proton-decoupled $^{31}P$ NMR shows that the triplet for the phosphine at $\delta$ 98.7 results from coupling with the phosphite, a doublet at $\delta$ −2.56, indicating the presence of two equivalent phosphites cis to one phosphine The IR shows a $\nu$(IrH) band at 2104 $cm^{-1}$. The most likely structure for this complex is shown in eq 6.



(6)

The related polyhydride $IrH_5(PCy_3)_2$[14] failed to react with $dmsbH_2$, and no characterizable products were obtained from $[Ir(cod)Cl]_2$,[15a] $[Ir(coe)_2Cl]_2$,[15b] $[IrH_2(Me_2CO)_2(PPh_3)_2][SbF_6]$, or $[Ir_3H_7(PCy_3)_3py_3][SbF_6]_2$ (py = pyridine).

**Protonation Reactions.** Protonation of complex **3a** with $HBF_4{\cdot}OEt_2$ in acetonitrile gave the known complex $[IrH_2(CH_3CN)_2(PPh_3)_2][BF_4]$, in 57% yield, identified by its NMR spectrum and by comparison with an authentic sample prepared by an independent synthesis.[16]

**Alkane Dehydrogenation.** All the complexes were assayed for activity in the dehydrogenation of cyclooctane. The activity of the starting pentahydride was 0.99 turnovers (t.o.) in 24 h and moving to **3**−**5** gave little improvement (0.7−7.3 t.o./24 h; see Table 5).

Table 5. Cyclooctane Dehydrogenation Data for the Complexes

| complex | *T*, °C[a] | coe, t.o.[b] |
|---|---|---|
| $IrH_5(PPh_3)_2$ | 150 | 0.99 |
| $IrH_3(dmsb)(PPh_3)_2$ | 150 | 1.50 |
| $IrH_3(tids)(PPh_3)_2$ | 130 | 2.90 |
| $IrH_4(SiPh_3)(PPh_3)_2$ | 160 | 7.30 |
| $IrH_3(SnPh_3)_2(PPh_3)_2$ | 160 | 0.70 |

[a] All reactions in neat alkane with 0.01 mmol of catalyst and 74 equiv of tbe for 24 h. [b] In turnovers (t.o.) or moles of product per mole of catalyst. coe = cyclooctene.

## Conclusion

The pentahydride $IrH_5(PPh_3)_2$ reacts with chelating silanes to form the classical seven-coordinate silyl polyhydride complexes, $IrH_3(disil)(PPh_3)_2$ (disil: dmsb, **3a**; tids, **3b**), with monodentate silanes to form $IrH_4(SiR_3)(PPh_3)_2$ (R: Et, **4a**; Ph, **4b**), and with triphenyltin hydride to give $IrH_3(SnPh_3)_2(PPh_3)_2$. A crystal structure, obtained for **3a**, suggests a distorted pentagonal bipyramidal geometry. These are all rare examples of Ir(V).

## Experimental Section

**General Procedures.** All experiments were performed under a dry argon atmosphere using standard Schlenk techniques. Tetrahydrofuran and hexanes were distilled from $Na/Ph_2CO$, and methylene chloride was distilled from $CaH_2$. $^1H$ NMR spectra were recorded on a Bruker WM 250 or GE Omega 300 spectrometer; chemical shifts were measured with reference to the residual solvent resonance. $^{13}C$, $^{29}Si$, and $^{31}P$ (external 85% $H_3PO_4$ reference) spectra were recorded on a GE Omega 300 spectrometer. IR spectra were recorded on a Midac M1200 FT-IR spectrometer. Microanalyses were carried out by Atlantic Microlabs. The disilanes were purchased from Fluka and Hüls and were used as received. Triethylsilane, triphenylsilane, and triphenyltin hydride were obtained from Aldrich and used as received. $IrH_5(PPh_3)_2$ was prepared according to the literature method.[17]

**Trihydrido[bis(dimethylsilyl)benzene]bis(triphenylphosphine)-iridium (V) (3a).** A slurry of $IrH_5(PPh_3)_2$ (109 mg, 0.151 mmol) in THF (25 mL) was subjected to three freeze−pump−thaw cycles, and the silane (0.1 mL, 0.462 mmol) was added. This was stirred at room temperature for 72 h. Every 8 h the flask was evacuated and refilled with argon to remove any $H_2$ formed during the reaction. The solvent was removed in vacuo from the resulting clear yellow solution, and addition of hexanes led to the precipitation of a white, air-stable solid in analytically pure form. The product was filtered off, washed with hexanes (3 × 10 mL), and dried in vacuo. Yield: 107 mg, 78%. Anal. Calcd for $C_{46}H_{49}IrP_2Si_2$: C, 60.57; H, 5.41. Found: C, 60.69; H, 5.45. IR (Nujol): $\nu$(Ir−H) 2110, 2094, 1943 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 7.0−7.7 (c, 34 H, Ph), 0.341 (br s, $\nu_{1/2} \approx$ 150 Hz, 12 H, Me), −9.12 (br s, $\nu_{1/2} \approx$ 60 Hz, 2 H, Ir−$H_{eq}$), −13.5 (br d, 1 H, Ir−$H_{ax}$). $^1H$ NMR ($CD_2Cl_2$, 193 K): $\delta$ 6.5−7.4 (c, 34 H, Ph), 0.621 (s, 6 H, Me), −0.081 (s, 6 H, Me), −9.18 (br t, $^2J_{PH} \approx$ 9 Hz, 2 H, Ir−$H_{eq}$), −13.3, −13.7 (dd, $^2J_{PHcis}$ = 18 Hz, $^2J_{PHtrans}$ = 117 Hz, 1 H, Ir−$H_{ax}$). $^1H$ NMR (toluene-$d_8$, 293 K): $\delta$ 7.2−8.1 (c, 34 H, Ph), 1.38 (br s, $\nu_{1/2} \approx$ 56 Hz, 6 H, Me), 0.94 (br s, $\nu_{1/2} \approx$ 38 Hz, 6 H, Me), −8.39 (br s, $\nu_{1/2} \approx$ 41 Hz, 2 H, Ir−$H_{eq}$), −12.5 (br d, $^2J_{PH} \approx$ 118 Hz, 1 H, Ir−$H_{ax}$). $^1H$ NMR (toluene-$d_8$, 333 K): $\delta$ 7.2−8.0 (c, 34 H, Ph), 1.11 (s, $\nu_{1/2} \approx$ 21 Hz, 12 H, Me), −8.71 (br s, $\nu_{1/2} \approx$ 324 Hz, 2 H, Ir−$H_{eq}$), −11.99 (br s, 1 H, Ir−$H_{ax}$). $^1H$ NMR (toluene-$d_8$, 373 K): $\delta$ 7.2−8.0 (c, 34 H, Ph), 1.05 (s, 12 H, Me), −9.79 (br s, $\nu_{1/2} \approx$ 134 Hz, 3 H, Ir−H). $^{31}P$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 8.90, 7.41 (br, d). $^{31}P$ {$^1H$} NMR ($CD_2Cl_2$, 213 K): $\delta$ 8.71 (d, 15 Hz), 7.66 (d, 15 Hz).

**Trihydrido(tetraisopropyldisiloxane)bis(triphenylphosphine)-iridium (V) (3b).** A slurry of $IrH_5(PPh_3)_2$ (119 mg, 0.164 mmol) in THF (25 mL) was subjected to three freeze−pump−thaw cycles, and

---

(13) (a) Mann, B. E.; Masters, C.; Shaw, B. L. *Chem. Commun.* **1970**, 846. (b) Bennett, M. A.; Charles, R.; Fraser, P. J. *Aust. J. Chem.* **1977**, *30*, 1201.

(14) Quirk, J. M. Ph.D. Thesis, Yale University, 1981; p 101.

(15) (a) Crabtree, R. H.; Quirk, J. M.; Felkin, H.; Fillebeen-Khan, T. *Synth. React. Inorg. Met.-Org. Chem.* **1982**, *12*, 407. (b) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1982**, *21*, 99.

(16) (a) Crabtree, R. H.; Hlatky, G. G.; Parnell, C. P.; Segmüller, B. E.; Uriarte, R. J. *Inorg. Chem.* **1984**, *23*, 354. (b) Burk, M. J.; Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics* **1984**, *3*, 816.

(17) Crabtree, R. H.; Felkin, H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *141*, 205.

the silane (0.20 mL, 0.715 mmol) was added. This was stirred at room temperature for 72 h as described above. The solvent was removed in vacuo, and the residue was recrystallized from $CH_2Cl_2$/hexanes to give a pale yellow, air-sensitive solid. The product was filtered off, washed with hexanes (3 × 10 mL), and dried in vacuo. Yield: 80 mg, 50%. Anal. Calcd for $C_{48}H_{61}IrOP_2Si_2{\cdot}0.5CH_2Cl_2$: C, 57.85; H, 6.22. Found: C, 58.24; H, 6.44. IR (Nujol): $\nu$(Ir−H) 2112, 1879 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 7.1−7.3 (c, 30 H, Ph), 0.76 (c, 28 H, $^iPr$), −11.20 (br s, $\nu_{1/2} \approx 26$ Hz, 3 H, Ir−H). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 11.79 (s).

**Tetrahydrido(triethylsilyl)bis(triphenylphosphine)iridium (V) (4a).** $IrH_5(PPh_3)_2$ (73 mg, 0.101 mmol) was dissolved in THF (20 mL) and the slurry degassed. $Et_3SiH$ (0.15 mL, 0.939 mmol) was added and the slurry stirred at 20 °C until a clear pale yellow solution was obtained. The flask was periodically evacuated and refilled with argon. The solvent was removed in vacuo and the residue recrystallized from $CH_2Cl_2$/hexanes (2 mL/20 mL). The solid was washed with hexanes (2 × 10 mL) and dried in vacuo. Yield: 60 mg, 71%. Anal. Calcd for $C_{43}H_{51}IrCl_2P_2Si{\cdot}0.75CH_2Cl_2$: C, 57.05; H, 5.67. Found: C, 56.90; H, 5.45. IR (Nujol): $\nu$(Ir−H) 2094, 1855 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 7.1−7.7 (c, 30 H, Ph), 0.67 (t, 7.3 Hz, 6 H, Et), 0.51 (t, 7.3 Hz, 9 H, Et), −11.17 (br t, 20 Hz, 4 H, Ir−H). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 13.49 (s).

**Tetrahydrido(triphenylsilyl)bis(triphenylphosphine)iridium (V) (4b).** $IrH_5(PPh_3)_2$ (62 mg, 0.086 mmol) and $Ph_3SiH$ (232 mg, 0.864 mmol) dissolved in THF (20 mL) were subjected to three freeze−pump−thaw cycles. The flask was periodically evacuated and refilled with argon. This slurry was stirred at room temperature to give a clear pale yellow solution. The volume was then reduced in vacuo, and hexanes (20 mL) were added to precipitate an off-white solid, which was washed with hexanes (2 × 10 mL) and dried in vacuo. Yield: 75 mg, 89%. Anal. Calcd for $C_{54}H_{49}IrP_2Si$: C, 66.17; H, 5.04. Found: C, 65.93; H, 5.01. IR (Nujol): $\nu$(Ir−H) 2122, 1829 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 7.0−7.3 (c, 45 H, Ph), −10.18 (t, $^2J_{PH}$ = 12 Hz, 4 H, Ir−H). $^1H$ NMR ($CD_2Cl_2$, 193 K): $\delta$ 6.9−7.5 (c, 45 H, Ph), −10.58 (br s, $\nu_{1/2} \approx 252$ Hz). $^1H$ NMR (toluene-$d_8$, 293 K): $\delta$ 7.2−8.0 (c, 45 H, Ph), −9.22 (t, $^2J_{PH}$ = 12 Hz, 4 H, Ir−H). $^1H$ NMR (toluene-$d_8$, 373 K): $\delta$ 7.2−8.0 (c, 45 H, Ph), −9.32 (t, $^2J_{PH}$ = 11 Hz, 4 H, Ir−H). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 10.56 (s). Selectively hydride-coupled $^{31}P$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 10.55 (quintet, $^2J_{PH}$ = 11 Hz).

**Trihydridobis(triphenylstannyl)bis(triphenylphosphine)iridium (V) (5).** $IrH_5(PPh_3)_2$ (98 mg, 0.135 mmol) and $Ph_3SnH$ (596 mg, 1.70 mmol) dissolved in THF (20 mL) were subjected to three freeze−pump−thaw cycles. The flask was periodically evacuated and refilled with argon. This slurry was stirred at room temperature until a clear colorless solution was obtained. The volume was then reduced in vacuo, and hexanes (20 mL) were added to precipitate a white solid, which was washed with hexane (2 × 10 mL) and dried in vacuo. Yield: 173 mg, 90%. Anal. Calcd for $C_{72}H_{63}IrP_2Sn_2$: C, 60.91; H, 4.47. Found: C, 61.18; H, 4.54. IR (Nujol): $\nu$(Ir−H) 2078, 1956 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 6.9−7.6 (c, 60 H, Ph), −11.02 (t, $^2J_{PH}$ = 15 Hz, 3 H, Ir−H). $^1H$ NMR ($CD_2Cl_2$, 193 K): $\delta$ 7.1−8.0 (c, 60 H, Ph), −9.22 (br s, $\nu_{1/2} \approx 146$ Hz), −12.04 (br d, $^2J_{PH}$ = 85 Hz). $^1H$ NMR (toluene-$d_8$, 293 K): $\delta$ 7.1−8.0 (c, 60 H, Ph), −10.25 (br t, $\nu_{1/2} \approx 52$ Hz, 3 H, Ir−H). $^1H$ NMR (toluene-$d_8$, 373 K): $\delta$ 7.1−8.0 (c, 60 H, Ph), −10.34 (t, $^2J_{PH}$ = 15 Hz, $J_{SnH}$ = 22, 37 Hz, 3 H, Ir−H). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 3.18 (s). Selectively hydride-coupled $^{31}P$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 3.19 (quartet, $^2J_{PH}$ = 15 Hz).

**Reaction of 3a with CO and $P(OMe)_3$. (a) CO.** A solution of **3a** (51 mg, 0.056 mmol) in THF (20 mL) was carefully degassed using the freeze−pump−thaw method. This solution was then stirred under a CO atmosphere for 30 min. No color change was observed during the reaction. After this time, the volume was reduced in vacuo and hexanes were added. No solid was obtained, even after cooling, and attempts to isolate a solid using methanol also did not succeed. Therefore all solvent was removed in vacuo and the yellow oily residue was dried overnight. An analytically pure sample could not be isolated from the reaction mixture. A tentative assignment of the structure was made using the spectroscopic data. IR (Nujol): $\nu$(Ir−H) and $\nu$(CO) 2091, 2043, 1980 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 7.2−7.6 (c, 19 H, Ph), 0.81 (s, 3 H, Me), 0.72 (s, 3 H, Me), 0.33 (s, 3 H, Me), 0.13 (s, 3 H, Me), −9.97 (d, $^2J_{PH}$ = 11 Hz, 1 H, Ir−H). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 298 K): $\delta$ −3.29 (s), −4.62 (s). Selectively hydride-coupled $^{31}P$ NMR ($CD_2Cl_2$, 298 K): $\delta$ −3.28 (d, $^2J_{PH}$ = 15 Hz), −4.65 (s). Due to the instability of this compound, a suitable off-resonance $^1H$-decoupled $^{13}C$ NMR spectrum could not be obtained.

**(b) Trimethyl Phosphite.** To a solution of **3a** (32 mg, 0.035 mmol) dissolved in degassed THF (20 mL) was added 3 equiv of $P(OMe)_3$ (12.5 $\mu$L, 0.11 mmol), and the solution was stirred at room temperature for 12 h. After this time, the solvent was reduced in vacuo and hexanes were added to afford a white solid, which was filtered off, washed with hexanes (2 × 20 mL), and dried in vacuo. Yield: 24 mg, 77%. Anal. Calcd for $C_{34}H_{44}IrO_6P_3Si_2{\cdot}2H_2O$: C, 44.1; H, 5.23. Found: C, 44.5; H, 5.60. IR (Nujol): $\nu$(Ir−H) 2104 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 7.1−7.5 (c, 15 H, Ph), 3.48 (d, 8 Hz, 18 H, P(O*Me*)$_3$), 0.43 (s, 6 H, Me), −0.004 (s, 6 H, Me), −13.12 (dt, $^2J_{PHcis}$ = 15 Hz, $^2J_{PHtrans}$ = 104 Hz, 1 H, Ir−H). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 98.74 (t, 25 Hz), −2.56 (d, 25 Hz).

**Protonation of 3a with Fluoroboric Acid in Acetonitrile.** Complex **3a** (74 mg, 0.10 mmol) was dissolved in $CH_3CN$ (10 mL), and 10 equiv of $HBF_4{\cdot}OEt_2$ was added. No color change or gas evolution was observed, but after 30 min a clear pale yellow solution was present. The volume was reduced in vacuo, and a white solid was obtained by addition of $Et_2O$ (20 mL). Yield: 66 mg, 57%. $^1H$ NMR showed peaks at $\delta$ 1.58 (Re−$CH_3CN$) and $\delta$ −20.45 (t, $^2J_{PH}$ = 15 Hz, Ir−H), for the known complex $[IrH_2(CH_3CN)_2(PPh_3)_2]BF_4$. The identity of this complex was confirmed by independent synthesis.[16]

**Alkane Dehydrogenation Studies.** The methods used in this work were the same as described in ref 2b.

**X-ray Crystallographic Analysis of 3a.** Suitable crystals of **3a** were grown by slow diffusion of hexanes into a solution of **3a** in methylene chloride at low temperature. A colorless crystal of dimensions 0.24 × 0.27 × 0.48 mm was mounted on a capillary. All measurements were made on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K$\alpha$ radiation. Unit cell parameters were determined by least-squares refinement of the setting angles of 25 high-angle reflections. The data were collected at a temperature of 23 ± 2 °C using the $\omega-2\theta$ scan technique to a maximum $2\theta$ value of 51.9°. Three standard reflections monitored throughout the data collection showed no loss of intensity (average variation 0.5%). The linear absorption coefficient for Mo K$\alpha$ is 33.3 $cm^{-1}$. An empirical $\psi$ scan absorption correction was applied. A quadrant of data had been collected and equivalent reflections were averaged after the absorption correction. The data were corrected for Lorentz and polarization effects.

All calculations were carried out using the TEXSAN 5.1 software package[18] run on VAXstation 3100 and 4000 computers. The structure was solved using Patterson heavy atom methods to locate the iridium atom and subsequent difference Fourier techniques. Hydrogen atoms were included in calculated positions and non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement converged with agreement factors of $R$ = 0.022 and $R_w$ = 0.025.

**Acknowledgment.** We thank the Department of Education for a Fellowship (M.L.), Prof. J. Hartwig for discussions, and the Department of Energy for funding.

**Supplementary Material Available:** Tables giving experimental details of the crystallography, positional and thermal parameters, *U* values, and intramolecular distances and angles (10 pages). Ordering information is given on any current masthead page.

IC941470V

---

(18) *TEXSAN: Single Crystal Structure Analysis Software*, Version 5.1; Molecular Structure Corp.: The Woodlands, TX, 1989.