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Cationic Iridium(I) Complexes as Catalysts for the Alcoholysis of Silanes

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The syntheses of five cationic iridium(I) complexes, containing the bidentate ligands bis(1-pyrazolyl)methane (BPM) and bis(3,5-dimethyl-1-pyrazolyl)methane (dmBPM), $\{[Ir(BPM)(COD)]^+(BPh_4)^-\}$ (**1**), $\{[Ir(dmBPM)(COD)]^+(BPh_4)^-\}$ (**2**), $\{[Ir(BPM)(COD)]^+[Ir(COD)Cl_2]^-\}$ (**4**), $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**), and $\{[Ir(dmBPM)(CO)_2]^+(BPh_4)^-\}$ (**5**), are reported. The complexes were characterized by NMR spectroscopy, and the solid-state structure of $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**) was determined by single-crystal X-ray crystallographic analysis. The complexes $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**) and $\{[Ir(dmBPM)(CO)_2]^+(BPh_4)^-\}$ (**5**) are effective catalysts for the alcoholysis of a range of alcohols and hydrosilanes, including secondary and tertiary hydrosilanes, under mild conditions.

Introduction

Silyl ethers are among the most widely used protecting groups for the hydroxyl functionality in organic synthesis.[1] They also play an important role in inorganic synthesis as precursors in the preparation of sol−gels and other condensed siloxane materials.[2] Silyl ethers are most commonly prepared from chlorosilanes ($R_{4-x}SiCl_x$) by reaction with alcohols or alkoxides, under acidic or basic reaction conditions.[3] The addition of hydrosilanes to alcohols is, however, also an attractive route to silyl ethers because the only side-product formed is hydrogen gas (Scheme 1).

Scheme 1

$$R_{4-x}SiH_x + xR'OH \xrightarrow{\text{catalyst}} R_{4-x}Si(OR')_x + xH_2$$

The alcoholysis of hydrosilanes requires a catalyst because alcohols are not generally sufficiently nucleophilic to attack hydrosilanes. Strongly nucleophilic or electrophilic catalysts can be used to promote the alcoholysis of silanes,[2] and a limited number of transition metal complexes have also been reported as catalysts.[2−18] Few metal catalysts are active at room temperature[2,12,13−17] and most are unreactive with the bulkier trialkylhydrosilanes (R_3SiH).[3] Wilkinson's catalyst, $[Rh(PPh_3)_3Cl]$, only catalyzes the alcoholysis of triethylsilane when refluxed in benzene.[6,9−11] [Cp_2TiCl_2/*n*-BuLi] is one of the more active catalysts, where the primary ($RSiH_3$) and secondary (R_2SiH_2) hydrosilanes are generally more reactive than tertiary hydrosilanes.[16] One of the most efficient transition metal catalysts for silane alcoholysis reported to date is the copper(I) hydride cluster, $[Ph_3PCuH]_6$, which is an active catalyst under mild conditions and has proved successful in alcoholysis of secondary and tertiary hydrosilanes.[2] Only a few iridium complexes have been reported to catalyze the alcoholysis of hydrosilanes.[8,12,14]

There have been a number of mechanistic studies on the transition-metal-mediated alcoholysis of silanes.[8−10,12,14,15,19] All involve the initial activation of the silane by the metal center either by oxidative addition of the silicon hydride or by binding of the silane to the metal center in an η^2 fashion, followed by reaction with the alcohol. All of the proposals involve no specific activation of the alcohol, and the driving force in the reaction is the formation of the strong silicon−oxygen bond.

In this paper we report a series of novel cationic iridium(I) complexes containing the bidentate ligands

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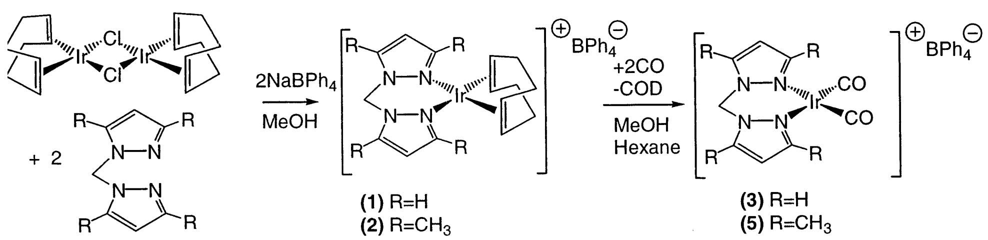
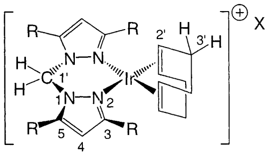
Scheme 2



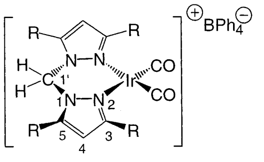
Scheme 3

$$\begin{tikzcd}
1\ \mathrm{R_2SiH_2} + 1\ \mathrm{R'OH} \arrow[r, "{[\mathrm{Ir}]}"] & 1\ \mathrm{R_2Si(H)(OR')} + 1\ \mathrm{H_2} \arrow[d, "{[\mathrm{Ir}]}", "1\ \mathrm{R'OH}"'] \\
 & 1\ \mathrm{R_2Si(OR')_2} + 1\ \mathrm{H_2} \arrow[l, phantom, ""]
\end{tikzcd}$$

bis(1-pyrazolyl)methane (BPM) and bis(3,5-dimethyl-1-pyrazolyl)methane (dmBPM): {[Ir(BPM)(COD)]$^+$(BPh$_4$)$^-$} (**1**), {[Ir(dmBPM)(COD)]$^+$(BPh$_4$)$^-$} (**2**), {[Ir(BPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (**3**), {[Ir(BPM)(COD)]$^+$[Ir(COD)Cl$_2$]$^-$} (**4**), and {[Ir(dmBP-M)(CO)$_2$]$^+$(BPh$_4$)$^-$} (**5**). The complexes **3** and **5** catalyze the alcoholysis of hydrosilanes under mild conditions, in both the absence and presence of air. The catalysts are effective for the alcoholysis of a range of alcohols and hydrosilanes, including secondary and tertiary hydrosilanes. The solid-state structure of **3** was determined by single-crystal X-ray crystallographic analysis.



(**1**) R=H, X=BPh$_4$
(**2**) R=Me, X= BPh$_4$
(**4**) R=H, X= [Ir(COD)Cl$_2$]



(**3**) R=H
(**5**) R=Me

Results and Discussion

Synthesis of Iridium Complexes. Where a large number of metal complexes containing polypyrazolylborate ligands have been previously described,[20–25] only a limited number of iridium and rhodium complexes containing the related poly(1-pyrazolyl)methane ligands have been reported.[26–28]

The complexes {[Ir(BPM)(COD)]$^+$(BPh$_4$)$^-$} (**1**) and {[Ir(dmBPM)(COD)]$^+$(BPh$_4$)$^-$} (**2**) were obtained by the reaction of the ligands BPM or dmBPM, respectively, in a 2:1 molar ratio with {[Ir(COD)Cl]$_2$} in the presence of 2 equiv of NaBPh$_4$ (Scheme 2). Complex **1** was isolated as an air-stable, bright yellow powder, and **2** was obtained as a mildly air-sensitive bright orange powder. Both complexes are cationic and four-coordinate and have essentially square-planar geometry about the metal center.

In the absence of NaBPh$_4$, reaction of equimolar amounts of BPM with {[Ir(COD)Cl]$_2$} afforded the air-sensitive bright orange microcrystalline solid {[Ir(BPM)(COD)]$^+$[Ir(COD)Cl$_2$]$^-$} (**4**).

Iridium(I) dicarbonyl complexes {[Ir(BPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (**3**) and {[Ir(dmBPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (**5**), containing the bidentate N-donor ligands BPM or dmBPM (Scheme 2), were synthesized via the displacement of COD from the iridium(I) COD complexes **1** and **2**, respectively, under an atmosphere of carbon monoxide. The dicarbonyl complexes **3** and **5** were also synthesized directly by reaction of 2 equiv of the bispyrazolyl ligand, BPM or dmBPM, with 1 equiv of {[Ir(COD)Cl]$_2$} and 2 equiv of NaBPh$_4$ under an atmosphere of carbon monoxide.

Both **3** and **5** were isotopically labeled with ^{13}C at the carbonyl positions by placing the reactants under an atmosphere of ^{13}C-carbon monoxide (99.4 atom %) to yield either {[Ir(BPM)(^{13}CO)$_2$]$^+$(BPh$_4$)$^-$} (**3-^{13}CO**) or {[Ir(dmBPM)(^{13}CO)$_2$]$^+$(BPh$_4$)$^-$} (**5-^{13}CO**).

The dicarbonyl complexes {[Ir(BPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (**3**) and {[Ir(dmBPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (**5**) and the COD complexes {[Ir(BPM)(COD)]$^+$(BPh$_4$)$^-$} (**1**) and {[Ir(dmBPM)(COD)]$^+$(BPh$_4$)$^-$} (**2**) were fully characterized by NMR spectroscopy. The complexes **1**, **2**, **3**, and **5** possess C_2 symmetry, with a plane of symmetry bisecting the bidentate pyrazolyl ligands such that the ^{1}H and ^{13}C resonances due to the two pyrazolyl rings of the bound ligands' NMR spectra are equivalent. The COD complexes **1** and **2** also have two perpendicular planes of symmetry within the bound COD ligand. The two carbonyl groups in each of **3** and **5** are equivalent by ^{13}C NMR spectroscopy.

Although the six-membered iridium metallacycle is undoubtedly not planar in solution, the resonances due to the bridging methylene protons of the BPM ligands of {[Ir(BPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (**3**) and {[Ir(BPM)(COD)]$^+$(BPh$_4$)$^-$} (**1**) appear as a singlet in the ^{1}H NMR spectra at room temperature,[29] probably as a result of averaging arising from rapid ring inversion. The corresponding resonances due to the methylene backbone protons of the dmBPM ligands in {[Ir(dmBPM)(COD)]$^+$(BPh$_4$)$^-$} (**2**) and {[Ir(dmBPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (**5**) are cleanly split into an AB system at room temperature. This indicates that the Ir(dmBPM) metallacycle in **5** and **2** adopts a more rigid conformation, where inversion is

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[29] In a freshly prepared solution of {[Ir(BPM)(COD)]$^+$(BPh$_4$)$^-$} (**1**) in deuterated acetone, the methylene protons slowly exchange for deuterons. The equivalent exchange process was not observed for {[Ir(dmBPM)(COD)]$^+$(BPh$_4$)$^-$} (**2**), {[Ir(BPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (**3**), or {[Ir(dmBPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (**5**).

Table 1. Crystallographic Data for {[Ir(BPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (3)

empirical formula	$IrC_{33}H_{28}N_4O_2B$
fw	715.64 g mol^{-1}
cryst dimens	0.32 × 0.125 × 0.10 mm
V	1469.6 Å^3
cryst syst	monoclinic
2θ range	$1 < \theta < 25$
space group	$P2_1$
Z value	2
D_{calc}	1.617 gcm^{-3}
F_{000}	704
cryst color	pale yellow
cryst habit	prism
lattice params	$a = 10.516(1)$ Å $b = 13.342(4)$ Å $c = 10.762(1)$ Å $\beta = 103.293(9)$°
radiation	Mo Kα ($\lambda = 0.71073$ Å) graphite monochromated
temperature	273.2K
hkl range	$-12 \rightarrow 12, 0 \rightarrow 15, 0 \rightarrow 12$
no. of reflns measd	total: 2833 unique: 2780; $N_0 = 2534$
corrections	Lorentz−polarization absorption (transmn factors: 0.679−0.588, analytical)
structure solution	direct methods with SHELXS-86
function minimized	$R = \sum(\|\|F_o\| - \|F_c\|\|)/\sum\|F_o\|^{1/2}$ $R_w = (\sum_w(\|F_o\| - \|F_c\|)^2/\sum_w\|F_o{}^2\|^{1/2}$
least squares weights	$w = 1/(\sigma^2(F_o))$
no. variables	370
residuals: R; R_w	0.021; 0.017
max. shift/error in final cycle	0.042
max. peak in final diff map	0.56 e$^-$/Å^3
min. peak in final diff map	−0.47 e$^-$/Å^3

inhibited by the added steric bulk of the methyl substituents on the bispyrazolyl ligand.[30]

The complexes **1**, **2**, **3**, and **5** all catalyze a degree of H/D exchange with deuterated solvents (d_6-acetone, d_8-THF, and d_4-methanol) on standing, and this can be rationalized by the propensity of these complexes for C−H activation.

X-ray Crystal Structure of {[Ir(BPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (3). The solid-state structure of {[Ir(BPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (**3**) was determined by single-crystal X-ray crystallographic analysis (Table 1). Pale yellow prismatic crystals suitable for X-ray crystal analysis were obtained by the addition of hexane to a concentrated solution of **3** in THF. ORTEP[31] plots, including the atom-numbering scheme, of the cation **3** are shown in Figure 1. The bond lengths and bond angles for the inner coordination sphere of **3** are listed in Table 2.

The iridium atom is essentially contained within the coordination plane defined by C(8), C(9), N(1), and N(3), as it is situated only 0.0091 Å from this plane. Distortion of the geometry from the idealized square-planar coordination is due to the bite angle (85.9(2)°) of the BPM ligand. Although the angle between the carbonyl ligands is nearly 90° (89.6(3)°), the N−Ir−C(O) angles (91.9(3)°, 92.6(2)°) compensate the reduced angle produced by BPM. The two *trans* bond angles through the iridium center of **3** approach linearity and measure 178.5° and 177.7°.

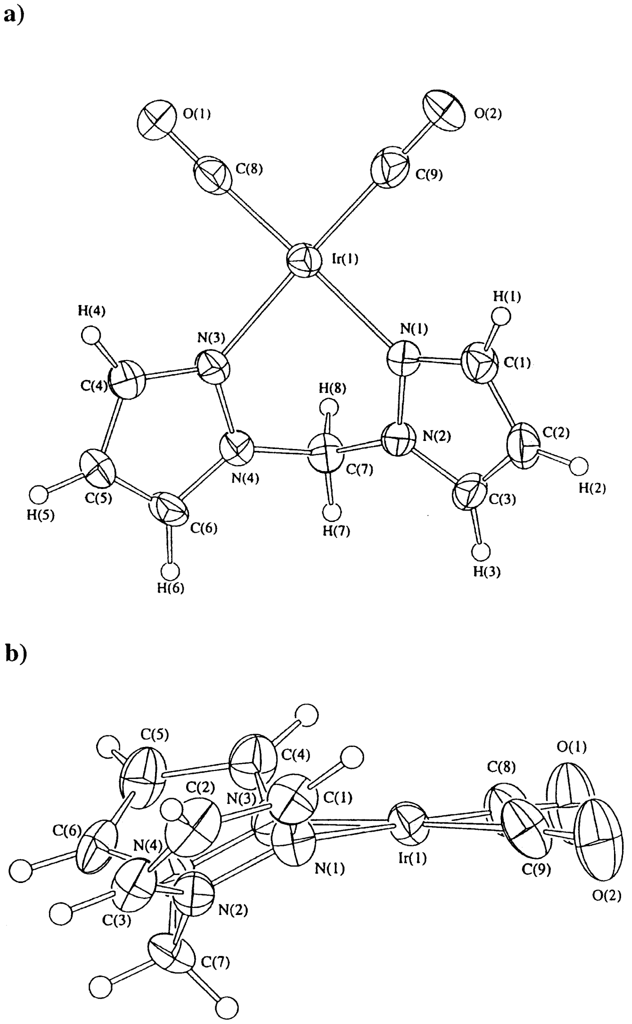

Figure 1. ORTEP (30% thermal ellipsoids) plots and crystal structure numbering of the cation fragment of {[Ir(BPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (**3**) (a) as viewed from above the coordination plane showing the puckering of the two pyrazolyl rings up into the plane and the puckering of the geminal atoms down into the plane; (b) as viewed from the side of the coordination plane showing the pseudo-boat conformation of the [Ir(NN)$_2$C] metallocycle and the planarity about the iridium atom.

Table 2. Bond Lengths and Angles[a] of the Inner Coordination Sphere of {[Ir(BPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (3)

atoms	bond lengths (Å)	atoms	bond angles (deg)
Ir−N(1)	2.057(5)	N(1)−Ir−N(3)	85.9(2)
Ir−N(3)	2.059(4)	C(8)−Ir−C(9)	89.6(3)
Ir−C(8)	1.827(7)	N(1)−Ir−C(9)	91.9(3)
Ir−C(9)	1.853(7)	N(3)−Ir−C(8)	92.6(2)
		N(1)−Ir−C(8)	178.5(2)
		N(3)−Ir−C(9)	177.7(2)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

A plane of symmetry bisects {[Ir(BPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (**3**) through the [Ir(NN)$_2$C] metallacycle and through the C(O)−Ir−C(O) bond angle. The six-membered iridium chelate ring, defined by Ir(1), N(1), N(2), C(7), N(4), and N(3), has a boat conformation but is distorted toward an envelope conformation because the Ir(1) flap is bent less (dihedral angle: 154.9°) than the C(7) flap (dihedral angle: 127.6°) with respect to the plane of the

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Table 3. Silyl Ethers Produced[a] from the Catalytic Alcoholysis of Hydrosilanes Using $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (3)

	MeOH	EtOH	^{i}PrOH
Et_3SiH	Et_3SiOMe 22 min, 306, 65%	Et_3SiOEt[b] 27 min, 249, 93%	Et_3SiO^iPr 50 min, 135, 72%
Me_2PhSiH[c]	$Me_2PhSiOMe$ 9 min, 747, 81%	$Me_2PhSiOEt$ 10 min, 673, 82%	Me_2PhSiO^iPr 7 min, 961, 87%
Ph_3SiH[d]	Ph_3SiOMe 26 min, 118, 80%	Ph_3SiOEt 47 min, 65, 87%	Ph_3SiO^iPr 31 min, 99, 88%
Et_2SiH_2	$Et_2Si(OMe)_2$ 14 min, 487, 80%	$Et_2Si(OEt)_2$ <5 min, >1362, 61%	$Et_2Si(O^iPr)_2$ 6 min, 1135, 76%
Ph_2SiH_2	$Ph_2Si(OMe)_2$ 8 min, 961, 82%	$Ph_2Si(OEt)_2$ 8 min, 841, 89%	$Ph_2Si(O^iPr)_2$ <15 min, >448, 93%

[a] Time for 50% conversion (min). Turn-over number (moles of product per mole of catalyst per hour) calculated at 50% conversion. Isolated yields with 0.45 mol % catalyst in air at 40 °C in THF solution. [b] At 25 °C and 1% catalyst loading, $T_{50\%} = 120$ min, 25 t.o./h. [c] Also reacted with ^{t}BuOH to form $PhMe_2SiO^tBu$, $T_{50\%} = 21$ min, 320 t.o./h, 82% yield (isolated). [d] Catalyst loading 0.98 mol % for all reactions involving Ph_3SiH.

metallacycle defined by the four nitrogen atoms. This is most likely a result of the different coordination geometry of iridium compared to that of carbon[32] and is not uncommon in metal complexes containing BPM.

The structure of the complex $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**) is the first reported crystal structure of an iridium complex containing the BPM ligand. There are very few crystal structures reported for iridium complexes that contain two N-donor ligands, and specifically few that contain a bidentate N-donor ligand. The structures of a number of related rhodium complexes containing bidentate N-donor ligands, including rhodium BPM complexes, have been reported, and these include $\{[Rh(BPM)(COD)]^+(ClO_4)^-\}$,[28] $\{[Rh(Ph\text{-}BPM)(NBD)]^+(PF_6)^-\}$,[27] $\{[Rh((mim)_2CH_2)(CO)_2]^+(BPh_4)^-\}$[33] $\{(mim)_2CH_2) =$ bis(*N*-methylimidazol-2-yl)methane}, and $\{[Rh((mBnzmim)_2CH_2)(CO)_2]^+(BPh_4)^-\}$[33] $\{(mBnzmim)_2CH_2) =$ bis(*N*-methylbenzimidazol-2-yl)methane}.

Alcoholysis of Hydrosilanes Catalyzed by $\{[Ir(BPM)(CO)_2]^+\text{-}(BPh_4)^-\}$ (3). A range of monofunctional alcohols (methanol, ethanol, and 2-propanol) was reacted with a series of tertiary hydrosilanes, R_3SiH (Et_3SiH, Me_2PhSiH, and Ph_3SiH), and secondary hydrosilanes, R_2SiH_2 (Et_2SiH_2 and Ph_2SiH_2), in the presence of $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**) in air. The trialkylsilyl ether (R_3SiOR') and dialkylsilyl ether ($R_2Si(OR')_2$) products (Scheme 1) were produced in good yields at high turnover rates (Table 3). The reactions were catalyzed at a loading of approximately 0.45 mol % of catalyst **3**, with the exception that the reactions with Ph_3SiH required a higher catalyst loading.

In these reactions, the hydrosilane substrate was added to a solution of the alcohol and catalyst in THF solution containing a small quantity of *n*-octane as an internal standard for GC analysis. The reaction mixture was heated to 40 °C in air. No significant induction period was observed for the reactions, and each of the reactions proceeded to completion with 100% conversion of the hydrosilane to silyl ether. The formation of the silyl ether products was monitored by GC and proceeded in an exponential manner. The time taken for the reaction to be 50% complete ($T_{50\%}$) was used to estimate the number of turnovers per hour for each reaction (Table 3). $^{29}Si\{^1H\}$ NMR spectroscopy was also used in the characterization of the silicon products. The ^{29}Si chemical shifts of the five hydrosilanes used in this work and their silyl ether derivatives from methanol, ethanol, and 2-propanol are tabulated in the Supporting Information.

For the alcoholysis of silanes catalyzed by $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**), the reactivities of the hydrosilanes, in order of decreasing activity are

MeOH: $Ph_2SiH_2 > Me_2PhSiH > Et_2SiH_2 > Et_3SiH > Ph_3SiH$

EtOH: $Et_2SiH_2 > Ph_2SiH_2 > Me_2PhSiH > Et_3SiH > Ph_3SiH$

^{i}PrOH: $Et_2SiH_2 > Me_2PhSiH > Ph_2SiH_2 > Et_3SiH > Ph_3SiH$

The least reactive hydrosilanes for all three of the alcohols tested are Et_3SiH and Ph_3SiH, with Ph_3SiH being consistently the least reactive of the hydrosilanes. The reactions with Me_2PhSiH were also notably exothermic. Reactions of alcohols with secondary silanes proceeded at a significantly higher rate than the analogous reactions with tertiary silanes; however, complete conversion to the dialkyl silyl ether occurred in all cases.

Most reported alcoholysis reactions promoted by transition metal catalysts have been carried out under inert atmospheres, such as argon or nitrogen[9−17] since the catalysts tend to be highly air-sensitive. However, a number of catalysts have now been reported, e.g., the copper(I) hydride cluster $[Ph_3PCuH]_6$ (**6**), that are more active under an atmosphere of air than an inert atmosphere.[2] To assess the effect of an atmosphere of argon on the catalytic efficiency of $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**), the ethanolysis of Et_3SiH was followed by GC under reaction conditions identical to those used for the analogous reaction conducted under an atmosphere of air. The presence of air (249 t.o./h, $T_{50\%} = 27$ min) or the absence of air (269 t.o./h, $T_{50\%} = 25$ min) had no significant effect on the catalytic activity of **3**.

Alcoholysis of Dihydrosilanes Catalyzed by $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (3). On the addition of diphenylsilane to ethanol in the presence of **3**, at 25 °C, rapid conversion to the final product $Ph_2Si(OEt)_2$ was observed by NMR, with 50% conversion to $Ph_2Si(OEt)_2$ after 10 min. In addition, some initial conversion to the monohydrosilane $Ph_2SiH(OEt)$ was observed (Figure 2). A maximum conversion to $Ph_2SiH(OEt)$ (approximately 20%) occurred after 10 min, after which time the quantity of $Ph_2SiH(OEt)$ decreased along with the increase in conversion to the final product $Ph_2Si(OEt)_2$

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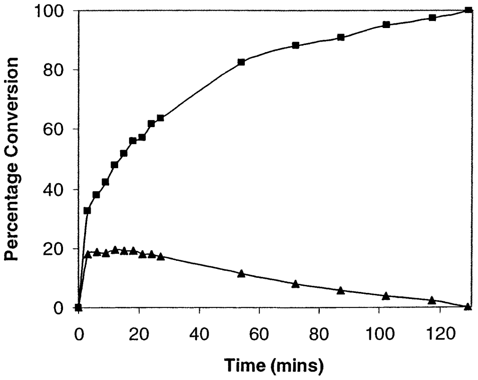


Figure 2. Stepwise conversion of Ph_2SiH_2 to $Ph_2SiH(OEt)$ and $Ph_2Si(OEt)_2$ as catalyzed by $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**). The reaction was monitored by NMR spectroscopy: ▲ = $Ph_2SiH(OEt)$ and ■ $Ph_2Si(OEt)_2$.

Table 4. Efficiency of $\{[Ir(dmBPM)(CO)_2]^+(BPh_4)^-\}$ (5) for the Ethanolysis of Hydrosilanes[a]

product	$T_{50\%}$,[b] t.o./h[c]
Et_3SiOEt	26 min, 348
$Me_2PhSiOEt$	11 min, 824
Ph_3SiOEt [d]	38 min, 120
$Et_2Si(OEt)_2$	301 min, 31
$Ph_2Si(OEt)_2$	28 min, 324

[a] Catalyst loading 0.33 mol %, in air at 40 °C. [b] Time for 50% conversion (min). [c] Turn-over number (moles of product per mole of catalyst per hour) calculated at 50% conversion. [d] Catalyst loading 0.66 mol %.

(Figure 2). The addition of ethanol to the dihydrosilane occurs in a stepwise fashion, with initial formation of the mono silyl ether $Ph_2SiH(OEt)$, followed by a second slower addition to form $Ph_2Si(OEt)_2$.

Alcoholysis of Hydrosilanes Catalyzed by $\{[Ir(dmBPM)(CO)_2]^+(BPh_4)^-\}$ (5). The dicarbonyl iridium complex $\{[Ir(dmBPM)(CO)_2]^+(BPh_4)^-\}$ (**5**) was also catalytically active for the alcoholysis of hydrosilanes and was reactive under both aerobic and anaerobic conditions. The catalytic efficiency of **5** in air was assessed in the reaction of ethanol with a range of hydrosilanes (Table 4) under conditions similar to those used for $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**). All of the reactions proceeded to completion with 100% conversion of the hydrosilane to silyl ether.

The rates of silane ethanolysis catalyzed by $\{[Ir(dmBPM)(CO)_2]^+(BPh_4)^-\}$ (**5**) were comparable to those catalyzed by $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**) for the range of tertiary silanes studied. However, for the two-stage double ethanolysis reaction of dihydrosilanes, catalysis by **5** proceeded at a significantly slower rate, and this must be attributed to the influence of the methyl substituents on the pyrazolyl backbone of **5**.

Comparison of O-Silylation Catalytic Activities of $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (3) and $\{[Ir(dmBPM)(CO)_2]^+(BPh_4)^-\}$ (5) with Other Catalysts. The majority of the transition metal catalysts that are known to catalyze the alcoholysis of silanes either are inactive with tertiary hydrosilanes or show diminished reactivity in the alcoholysis of trialkylhydrosilanes.[3] Table 5 compares the catalytic efficiency of $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**) and $\{[Ir(dmBPM)(CO)_2]^+(BPh_4)^-\}$ (**5**) with other known O-silylation catalysts. Of those catalysts that are reactive with tertiary hydrosilanes, few catalyze the alcoholysis of Et_3SiH. The complexes **3** and **5** are reactive with both dialkyl- and trialkylhydrosilanes in the alcoholysis of hydrosilanes, including reactions with the less reactive Et_3SiH. While the complexes $\{[IrH_2S_2(PPh_3)_2]^+(SbF_6)^-\}$ (S = solvent) (**7**) and $[Ru(PMe_3)_2(CO)_2Cl_2]$ (**8**) are significantly more effective catalysts than **3** and **5** in the alcoholysis of Et_3SiH, the complexes **3** and **5** are more effective for the synthesis of silyl ethers from aromatic silanes such as Me_2PhSiH, Ph_3SiH, and Ph_2SiH_2.

Table 5. Comparison of Rates of Alcoholysis of Hydrosilanes Catalyzed by a Range of Transition Metal Catalysts: $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (3), $\{[Ir(dmBPM)(CO)_2]^+(BPh_4)^-\}$ (5), $[Ph_3PCuH]_6$ (6),[2] $\{[IrH_2S_2(PPh_3)_2]^+(SbF_6)^-\}$ (S = THF) (7),[14] $[Ru(PMe_3)_2(CO)_2Cl_2]$ (8),[13] and $[Cp_2TiCl_2/n\text{-}BuLi]$ (9)[16]

catalyst		turnover number[a]		
Et_3SiH		Et_3SiOMe	Et_3SiOEt	Et_3SiO^iPr
	3[b]	306	249	135
	5[b]		348	
	6[c,d,e]	>8	>8	7
	7[f]	530,000	47,000	130,000
	8[g]	2500	1500	580
Me_2PhSiH		$Me_2PhSiOMe$	$Me_2PhSiOEt$	Me_2PhSiO^iPr
	3[b]	747	673	961
	5[b]		824	
	6[c,e]	>213	>160	>79
	9[h]		1.1[i]	no reaction[j]
Ph_3SiH		Ph_3SiOMe	Ph_3SiOEt	Ph_3SiO^iPr
	3[b]	118	65	99
	5[b]		120	
	6[c,e]	>36	>33	>29
Ph_2SiH_2		$Ph_2Si(OMe)_2$	$Ph_2Si(OEt)_2$	$Ph_2Si(O^iPr)_2$
	3[b]	961	841	448
	5[b]		324	
	6[c,e]	>126	>64	>74
	9[h]		45[h]	4[i]

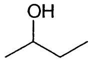
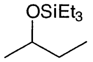
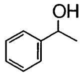
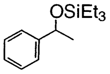
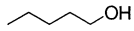
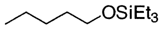
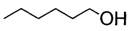
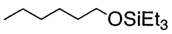
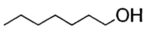
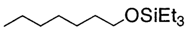
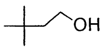
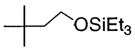
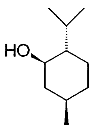
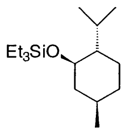
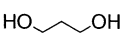
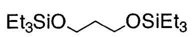
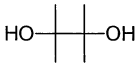
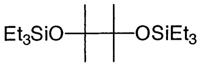
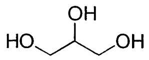
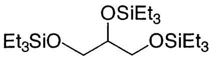
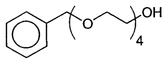
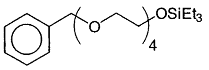
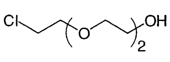
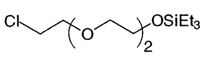
[a] Turn-over number (moles of product per pole of catalyst per hour) calculated at 50% conversion. [b] In THF solution under air at 40 °C; the rates of reaction were determined by GC. [c] In benzene under air at room temperature. [d] Reactions with Et_3SiH were incomplete at 48 h. [e] Estimated using the isolated yield, the reaction time, and ratio of catalyst to reactants. The real reaction rate could be significantly higher. [f] In DCM solution under N_2 at 25 °C; the rate of reaction was determined by monitoring hydrogen gas evolution. [g] In THF solution at 18 °C under argon; the rate of reaction was determined by GC. [h] The rate of reaction was estimated using GC. [i] In THF solution, under N_2 initially at 0 °C then raised to room temperature. [j] In THF solution, under N_2 initially at 0 °C then brought to reflux.

Scope of Alcoholysis with Et_3SiH Catalyzed by $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (3). The scope of the catalytic activity of $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**) with Et_3SiH was assessed with a series of alcohols that varied in terms of alkyl chain length, branching, and complexity (Table 6). The influence of multiple hydroxyl functionalities, ether functionalities, and chloro substituents was also examined, as well as the catalyzed reaction of water with Et_3SiH. In all cases, the time at which the reactions were stopped was noted, although this only serves to indicate an upper limit to the reaction time and not to provide quantitative catalytic rates.

Complex **3** catalyzes the alcoholysis of Et_3SiH with all of the alcohol substrates tested, including primary, secondary, tertiary, aromatic, and bulky alcohols as well as diols, a triol, and alcohols containing multiple-ether functionalities and a chloro substituent.

The reaction of Et_3SiH with primary alcohols catalyzed by $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**) proceeded in near quantitative yields for most of the alcohols. The catalytic

Table 6. Alcoholysis[a] of Et_3SiH Catalyzed by $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (3)

Substrate	Product[b]	Time[c] (hours)	% yield (isolated)
H_2O	Et_3SiOH	24	85
H_2O	$Et_3SiOSiEt_3$	48	60
		48	80
		48	50
^tBuOH	Et_3SiO^tBu	48	34
PhOH	Et_3SiOPh	48	33
		14	93
		14	95
		14	93
		14	94
		14	42
		24	94
		24	95[d]
		24	79
		48	80
		48	78

[a] Typically 3.1 mmol of Et_3SiH and an equimolar ratio of alcohol (in terms of OH groups available) in 3 mL of THF was stirred in the presence of 0.4 mol % of catalyst at room temperature under argon. [b] Characterization data including ^1H, ^{13}C, and ^{29}Si NMR chemical shifts of the triethylsilyl ethers are listed in the Supporting Information. [c] Time (hours) elapsed before the isolation of the silyl ether from the reaction mixture. The reaction may have been complete in significantly less time. [d] Products not isolated. The % conversion was determined by integration of the ^1H NMR spectrum.

activity of **3** does not diminish with elongation and branching of the alkyl group on the alcohols. As the bulk of the secondary alcohols was increased, the isolated yields decreased, suggesting that the increased steric bulk around the hydroxyl functionality influences the catalytic activity of **3**. The reaction of (−)-menthol with Et_3SiH catalyzed by **3** proceeded very slowly with a low product yield.

Other transition metal complexes that have been reported to catalyze the alcoholysis of triethylsilane, e.g., $\{[IrH_2S_2(PPh_3)_2]^+(SbF_6)^-\}$ (S = solvent) (**7**)[14] and $[Ru(PMe_3)_2(CO)_2Cl_2]$ (**8**),[13] show significantly lessened activity with the elongation and branching of the alkyl group of the alcohol and are more sensitive to the steric bulk near the hydroxyl group.

Complex **3** efficiently catalyzed the O-silylation of the OH groups of water. The reaction proceeds stepwise with the rapid initial reaction of H_2O and Et_3SiH to produce, exclusively, triethylsilanol, Et_3SiOH, which then reacts with another equivalent of Et_3SiH, over a period of several hours, to generate the silyl ether, hexaethyldisiloxane, $Et_3SiOSiEt_3$. The silanol, Et_3SiOH, and silyl ether, $Et_3SiOSiEt_3$, products were observed as side-products in several of the O-silylation reactions when the reactants or solvents were not scrupulously dry.

The reaction of 1,3-propanediol with 2 equiv of Et_3SiH in the presence of **3** led to the exclusive formation of the bis-silylated product. The reaction proceeded quickly, and the product was isolated in high yield (94%, 109 t.o.). The reaction of pinacol, a bis-tertiary diol, with 2 equiv of Et_3SiH catalyzed by **3**, led to the formation of a mixture of the mono- and the bis-silylated pinacol compounds. Of the few catalysts that have been reported to date that promote the alcoholysis of diols with trialkylsilanes, $[Ph_3PCuH]_6$ (**6**) is the only one to produce the fully bis-silylated species from pinacol.[2] The reaction of the triol glycerol with 3 equiv of Et_3SiH in the presence of **3** led to exclusive production (79%) of the tris-silylated product.

The presence of multiple ether groups on the reactants appeared to have little effect on the catalytic capability of $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**). The compound **3** was catalytically active in the reaction of Et_3SiH with benzyl tetraethyleneglycol to produce the expected silyl ether. The substitution of a chloro group for a proton on the methyl end of a polyether alcohol, 2-[2-(2-chloroethoxy)ethoxy]ethanol, also did not inhibit the alcoholysis of Et_3SiH catalyzed by **3**. In contrast, ether groups with the oxygen atom β to the hydroxyl group and the presence of a chloro group on the methyl group of ethanol both have been reported to inhibit the catalytic activity of both $\{[IrH_2S_2(PPh_3)_2]^+(SbF_6)^-\}$ (S = solvent) (**7**)[14] and $[Ru(PMe_3)_2(CO)_2Cl_2]$ (**8**)[13] in the alcoholysis of Et_3SiH.

Catalytic Activity of $\{[Ir(BPM)(COD)]^+(BPh_4)^-\}$ (1) in the Alcoholysis of Et_3SiH. The iridium 1,5-cyclooctadiene (COD) complex, $\{[Ir(BPM)(COD)]^+(BPh_4)^-\}$ (**1**), was significantly less effective as a catalyst for the alcoholysis of hydrosilanes. In the reaction between Et_3SiH and 1-phenylethanol in $CDCl_3$, only a yield of 10% was observed after 24 h.

Conclusions

Iridium(I) complexes containing the bidentate pyrazolylmethane ligands BPM and dmBPM were prepared readily and in high yield from the iridium precursor $\{[Ir(COD)Cl]_2\}$. The complexes $\{[Ir(BPM)(COD)]^+(BPh_4)^-\}$ (**1**), $\{[Ir(dmBPM)(COD)]^+(BPh_4)^-\}$ (**2**), $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**), and $\{[Ir(dmBPM)(CO)_2]^+(BPh_4)^-\}$ (**5**) are cationic, square-planar, and air-stable. If BPM is reacted with $\{[Ir(COD)Cl]_2\}$ in the absence of $NaBPh_4$, the complex $\{[Ir(BPM)(COD)]^+[Ir(COD)Cl_2]^-\}$ (**4**) is formed.

The compounds $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**) and $\{[Ir(dmBPM)(CO)_2]^+(BPh_4)^-\}$ (**5**) were effective catalysts for the alcoholysis of hydrosilanes with a range of hydrosilanes and alcohols. The turn-over frequency of **3** with secondary (dihydrosilane) substrates was significantly greater than with tertiary (hydrosilane) substrates. Complex **5** was more effective as a catalyst for the alcoholysis of tertiary silanes than the reactions with secondary hydrosilanes. Both **3** and **5** are effective catalysts for the alcoholysis of silanes and have different reactivity profiles, and this probably reflects the differences in the steric environment at the metal center as a result of the different ligand structures. The fact that the reaction displays some sensitivity to variations in the ligand structure may well provide an avenue for engineering greater substrate selectivity into catalytic silane alcoholysis. The presence, or absence, of air had little effect on the turn-over frequency of the alcoholysis of hydrosilane reactions.

The complex $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**) catalyzed the O-silylation of a range of complex alcohols with Et_3SiH. The catalytic activity of **3** did not diminish significantly with elongation and branching of the alkyl chain on the alcohol. With bulky secondary alcohols, tertiary alcohols, and aromatic alcohols, the rate of reaction with Et_3SiH was slowed. The O-silylation of the polyols, 1,3-propanediol and pinacol, and glycerol with Et_3SiH was cleanly catalyzed by **3**. The presence of chloro and/or ether functionalities in the alcohol substrate has little effect on the catalytic activity of **3**. Water was also catalytically O-silylated by **3** with Et_3SiH to give the products Et_3SiOH and/or $Et_3SiOSiEt_3$ in high yield.

For a range of alcoholysis reactions, **3** and **5** are significantly more effective catalysts than other catalysts previously reported. The turn-over frequencies reported for the same reactions that were catalyzed by previously reported transition metal catalysts showed that the iridium complexes **3** and **5** display a competitive level of reactivity, especially with the traditionally more unreactive tertiary hydrosilanes. Furthermore, hydrosilation reactions catalyzed by **3** and **5** may be readily carried out under relatively simple and mild reaction conditions, under an atmosphere of air and at room temperature.

Experimental Section

The synthesis and manipulation of all ligands and metal complexes were performed under an inert atmosphere of argon or nitrogen unless otherwise stated, either by performing reactions in an inert atmosphere drybox or by employing standard Schlenk and vacuum line techniques. Hexane, heptane, and tetrahydrofuran (THF) were predried over sodium wire and were distilled with benzophenone over sodium wire immediately prior to use. Absolute ethanol and methanol were distilled from diethoxymagnesium and dimethoxymagnesium, respectively. Acetone was dried over P_2O_5 before distillation. 2-Propanol (AR grade) was used without further purification. Light petroleum was stirred over H_2SO_4 for at least 24 h prior to distillation. Dichloromethane (DCM) was washed sequentially with H_2SO_4, H_2O, aqueous K_2CO_3 (5%) solution, and H_2O, prior to distillation from $CaCl_2$. Deuterated solvents were first dried, as for their proteo-analogues, then were degassed via three consecutive freeze/pump/thaw cycles, then vacuum distilled and stored under vacuum. All solvents used in air-sensitive reactions were deareated prior to use either by saturation with nitrogen or via four to five freeze/pump/thaw cycles.

All compressed gases were obtained from B.O.C. Gases. The following agents were used as received: tetraphenylborate (Aldrich), pyrazole (Aldrich), 3,5-dimethylpyrazole (Aldrich), sodium tetraphenylborate (Aldrich), 1,5-cyclooctadiene (Aldrich), Et_3SiH (Aldrich), Me_2PhSiH (Fluka), Ph_3SiH (Aldrich), Et_2SiH_2 (Fluka), and Ph_2SiH_2 (Aldrich). Ph_3SiH was distilled under vacuum to ensure it was completely dry. Alcohols were dried and distilled prior to use, with the exception of *tert*-butanol and (−)-menthol, which were dried under vacuum prior to use, and 1-pentanol, 1-hexanol, 1-heptanol, 3,3-dimethyl-2-butanol, and $ClCH_2CH_2(OCH_2CH_2)_2OH$, which were obtained from Aldrich and were used without further purification. Iridium trichloride trihydrate was obtained as a generous loan from Johnson Matthey & Co. $\{[Ir(COD)Cl]_2\}$ was synthesized using the method of Herde et al.[34] $C_6H_5CH_2(OCH_2CH_2)_4OH$ was synthesized using the method of Burns et al.[35]

NMR spectra were recorded on Bruker DRX NMR spectrometers at 300.1 (^1H) MHz, 400.1 (^1H) MHz, and 500.1 (^1H) MHz, or with a Bruker AMX600 NMR spectrometer at 600.1 (^1H) MHz. ^1H NMR and ^{13}C NMR chemical shifts were referenced internally to residual solvent resonances. Unless otherwise stated, spectra were acquired at 300 K and the temperatures quoted for acquisition of NMR spectra are approximate (±2 K).

GC analyses were performed using a Hewlett-Packard 5890 Series II gas chromatograph. Microanalyses were performed by the Chemical Microanalytical Services Pty. Ltd, Melbourne, Australia, and the Campbell Microanalytical Laboratory, The University of Otago, New Zealand.

Synthesis of Poly(1-pyrazolyl)methane Ligands. Synthesis of Bis(1-pyrazolyl)methane (BPM). Bis(1-pyrazolyl)methane (BPM) was synthesized using a modification of the procedure developed by Elguero et al. for the synthesis of related bis(1-pyrazolyl)methane ligands.[36] Dichloromethane (CH_2Cl_2) (50 mL) was added to a mixture of pyrazole (6.13 g, 90.0 mmol), tetrabutylammonium hydrogen sulfate $\{[N(C_4H_9)_4]^+(HSO_4)^-\}$ (2.5 g, 7.36 mmol), powdered potassium hydroxide (85%) (8.2 g, 6.8 mol), and potassium carbonate (K_2CO_3) (20.3 g, 147 mmol). The reaction mixture was stirred vigorously and heated under reflux for 36 h. After filtration, the residue was washed with hot CH_2Cl_2 (3 × 10 mL) and the organic portions were combined. The solvent was removed from the organic portions under reduced pressure to give the crude product as white crystals. The crude product was recrystallized from heptane to give bis(1-pyrazolyl)methane (BPM) as white needlelike crystals (6.53 g, 98%). Mp: 111−114 °C (lit.[37] 111−112 °C; lit.[38,39] 108 °C). Complete NMR data are reported in the Supporting Information.

Synthesis of Bis(3,5-dimethyl-1-pyrazolyl)methane (dmBPM). Bis(3,5-dimethyl-1-pyrazolyl)methane (dmBPM) was synthesized using a modification of the procedure developed by Julia, del Mazo, Avila, and Elguero.[36] Dichloromethane (CH_2Cl_2) (30 mL) was added to a mixture of 3,5-dimethylpyrazole (3.00 g, 31.2 mmol), tetrabutylammonium hydrogen sulfate $\{[N(C_4H_9)_4]^+(HSO_4)^-\}$ (816 mg, 2.40 mmol), powdered potassium hydroxide (85%) (2.70 g, 48.1 mmol), and potassium carbonate (K_2CO_3) (6.64 g, 48.0 mmol). The reaction mixture was stirred vigorously and heated under reflux for 36 h. After filtration, the residue was washed with hot CH_2Cl_2 (3 × 10 mL), and the organic portions were combined. The solvent was removed from the organic portions under reduced pressure to give the crude product as white crystals. The crude product was recrystallized from heptane to give bis(3,5-dimethyl-1-pyrazolyl)methane (dmBPM) as white needlelike crystals (3.12 g, 98%). Mp: 107−110 °C (lit.[37] 83−84 °C; lit.[39] 105 °C). Complete NMR data are reported in the Supporting Information.

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Synthesis of Iridium Complexes. {[Ir(BPM)(COD)]$^+$(BPh$_4$)$^-$} (1). Methanol (20 mL) was added to a mixture of BPM (124 mg, 0.835 mmol), {[Ir(COD)Cl]$_2$} (216 mg, 0.322 mmol), and NaBPh$_4$ (290 mg, 0.847 mmol), and the solution was stirred for 12 h at room temperature, during which time a bright orange precipitate developed. The precipitate was collected by filtration and washed with hexane (10 mL), methanol (3 mL), and hexane (10 mL) and dried under vacuum to give [bis(1-pyrazolyl)methane](1,5-cyclooctadiene)iridium(I) tetraphenylborate, {[Ir(BPM)(COD)]$^+$(BPh$_4$)$^-$} (**1**), as a bright orange powder (247 mg, 50%). Mp: 184−185 °C. Found: C, 60.85; H, 5.24; N, 7.25. $C_{39}H_{40}N_4IrB$ requires: C, 61.00; H, 5.24; N, 7.30. ^{1}H NMR (400 MHz, acetone-d_6, 300 K): δ 8.36 (d, 2H, $^3J_{H5-H4} = 2.6$ Hz, H5), 8.21 (d, 2H, $^3J_{H3-H4} = 2.2$ Hz, H3), 7.50 (br m, 8H, *ortho*-BPh_4), 7.07 (t, 8H, $^3J = 7.4$ Hz, *meta*-BPh_4), 7.01 (s, 2H, $H1'$), 6.94 (dd, 4H, $^3J = 6.6$, 6.5 Hz, *para*-BPh_4), 6.81 (dd, 2H, $^3J_{H4-H3,\ H4-H5} = 2.6$, 2.5 Hz, H4), 4.50 (br s, 4H, $H2'$), 2.53 (br m, 4H, $H3'a$), 2.04 (dd, 4H, $^3J = 15.7$ Hz, $H3'b$) ppm. ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6, 300 K): δ 165.4 (q, $^1J_{BC} = 49.6$ Hz, *ipso*-BPh_4), 144.4 (C3), 137.4 (*ortho*-BPh_4), 136.4 (C5), 126.4 (*meta*-BPh_4), 122.6 (*para*-BPh_4), 109.6 (C4), 70.3 ($C2'$), 64.8 ($C1'$), 32.1 ($C3'$) ppm. IR (KBr, cm^{-1}): 2361 (s), 1684 (m), 1653 (s), 1559 (s), 1540 (m), 1507 (m), 1425 (m), 1284 (s), 1066 (m), 761 (s), 734 (vs), 707 (vs), 612 (m). Mass spectrum (CI, NH$_3$, *m/z* (%)): 449 (100, M$^+$, $C_{15}H_{20}N_4Ir$), 447 (72).

{[Ir(dmBPM)(COD)]$^+$(BPh$_4$)$^-$} (2). NaBPh$_4$ (100 mg, 0.292 mmol) was added to a solution of {[Ir(COD)Cl]$_2$} (87.0 mg, 0.130 mmol) in EtOH (20 mL). A solution of dmBPM (80.0 mg, 0.392 mmol) in EtOH (5 mL) was added, and the reaction mixture was stirred 2.5 h at room temperature, during which time a bright orange precipitate formed. The solid was collected by filtration and washed with EtOH (3 × 3 mL) to give the product [bis(3,5-dimethyl-1-pyrazolyl)methane](1,5-cyclooctadiene)iridium(I) tetraphenylborate, {[Ir(dmBPM)(COD)]$^+$(BPh$_4$)$^-$} (**2**), as a bright orange powder (191 mg, 89%); mp 168−169 °C. ^{1}H NMR (600 MHz, THF-d_8, 303 K): δ 6.82 (br m, 8H, *ortho*-BPh_4), 6.35 (t, 8H, $^3J = 7.4$ Hz, *meta*-BPh_4), 6.21 (t, 4H, $^3J = 6.8$ Hz, *para*-BPh_4), 6.17 (d, 1H, $^3J_{H1'a-H1'b} = 15.3$ Hz, $H1'a$), 5.51 (s, 2H, H4), 5.32 (d, 1H, $^3J_{\ H1'a-H1'b} = 15.3$ Hz, $H1'b$), 3.94 (br s, 4H, $H2'$), 1.85 (s, 6H, C3−CH_3), 1.81 (m, 4H, $H3'a$), 1.69 (s, 6H, C5−CH_3), 1.22 (m, 4H, $H3'b$) ppm. ^{13}C NMR (150 MHz, THF-d_8, 303 K): δ 166.6 (q, $^1J_{BC} = 49.9$ Hz, *ipso*-BPh_4), 155.4 (C3 or C5), 145.7 (C3 or C5), 138.6 (*ortho*-BPh_4), 127.2 (*meta*-BPh_4), 123.3 (*para*-BPh_4), 111.5 (C4), 68.9 ($C2'$), 61.3 ($C1'$), 33.2 ($C3'$), 15.6 (C3-CH$_3$), 12.2 (C5-CH$_3$) ppm. IR (KBr, cm^{-1}): 3053 (w), 1561 (m), 1467 (m), 1425 (m), 1411 (m), 1276 (m), 1031 (w), 828 (m), 799 (w), 739 (s), 732 (2), 705 (vs), 673 (w), 613 (s). Mass spectrum (ESI, MeOH, *m/z* (%)): 505 (100, M$^+$, $C_{19}H_{28}N_4Ir$), 503 (55), 431 (88), 291 (24), 259 (53).

Synthesis of {[Ir(BPM)(COD)]$^+$[Ir(COD)(Cl)$_2$]$^-$} (4). A solution of BPM (59 mg, 0.400 mmol) in acetone (20 mL) was added to a solution of {[Ir(COD)Cl]$_2$} (125 mg, 0.186 mmol) in acetone (10 mL). As the ligand was added, the solution changed from a strong orange color to a strong yellow color. The reaction mixture was stirred at room temperature for 2 h. The volume was reduced to 5 mL to precipitate the product, which was collected by filtration and washed with acetone to yield [bis(1-pyrazolyl)methane](1,5-cyclooctadiene)iridium(I) dichloro(1,5-cyclooctadiene)iridium(I), {[Ir(BPM)(COD)]$^+$[Ir(COD)(Cl)$_2$]$^-$} **(4)**, as an air-sensitive yellow microcrystalline solid (70 mg, 46%). ^{1}H NMR (400 MHz, acetone-d_6, 300 K): δ 8.81 (s, 2H, H_{BPM}), 8.16 (s, 2H, H_{BPM}), 7.38 (s, 2H, H_{BPM}), 6.79 (s, 2H, H_{BPM}), 4.47 (s, 4H, $H_{COD-anion}$), 3.88 (s, 4H, $H_{COD-cation}$), 2.51 (s, 4H, $H_{COD-anion}$), 2.16 (s, 4H, $H_{COD-cation}$), 1.99 (s, 4H, $H_{COD-cation}$), 1.39 (s, 4H, $H_{COD-anion}$) ppm. IR (KBr, cm^{-1}): 2995 (w), 2881 (m), 2831 (w), 1468 (w), 1424 (s), 1282 (s), 1223 (w), 1109 (m), 1065 (m), 999 (m), 896 (w), 871 (w), 766 (vs), 601 (w). Mass spectrum (MALDI (+), *m/z* (%)): 449 (100, M$^+$, $C_{15}H_{20}N_4Ir$), 447 (85). Mass spectrum (MALDI (−), *m/z* (%)): 371 (85, M$^-$, $C_8H_{12}Cl_2Ir$), 370 (100). Mass spectrum (CI, NH$_3$, *m/z* (%)): 449 (100, M$^+$, $C_{15}H_{20}N_4Ir$), 447 (70).

Synthesis of {[Ir(BPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (3). From {[Ir(COD)Cl]$_2$}. Methanol (25 mL) and hexane (7 mL) were added to a mixture of BPM (228 mg, 1.54 mmol), {[Ir(COD)Cl]$_2$} (398 mg, 0.593 mmol), and NaBPh$_4$ (458.7 mg, 1.34 mmol). The solution was stirred for 45 min at room temperature, then degassed via three freeze/pump/thaw cycles. The reaction mixture was stirred under an atmosphere of carbon monoxide for 12 h at room temperature, during which time a pale yellow precipitate developed. The precipitate was collected by filtration and washed with hexane (10 mL), methanol (3 mL), and hexane (10 mL) and dried under vacuum to give [bis(1-pyrazolyl)methane]dicarbonyliridium(I) tetraphenylborate, {[Ir(BPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (**3**), as a pale yellow powder (765 mg, 90%). Found: C, 55.0; H, 3.7; N, 7.8. $C_{33}H_{28}N_4O_2IrB$ requires: C, 55.39; H, 3.94; N, 7.83. ^{1}H NMR (600 MHz, THF-d_8, 303 K): δ 8.21 (s, 2H, H3), 7.44 (s, 2H, H5), 7.43 (br m, 8H, *ortho*-BPh_4), 6.94 (t, 8H, *meta*-BPh_4), 6.81 (t, 4H, *para*-BPh_4), 6.56 (s, 2H, H4), 5.42 (s, 2H, $H1'$) ppm. ^{13}C{^{1}H} NMR (100 MHz, THF-d_8, 300 K): δ 172.5 (Ir-CO), 166.3 (q, $^1J_{BC} = 49.4$ Hz, *ipso*-BPh_4), 149.7 (C3), 138.3 (*ortho*-BPh_4), 138.0 (C5), 127.4 (*meta*-BPh_4), 123.6 (*para*-BPh_4), 111.0 (C4), 64.4 ($C1'$) ppm. IR (KBr, cm^{-1}): 3141 (m), 3124 (m), 3157 (m), 3000 (m), 2081 (vs, Ir−C≡O), 2065 (w, Ir-^{13}C≡O), 2015 (vs, Ir−C≡O), 1983 (w, Ir-^{13}C≡O), 1480 (w), 1408 (m), 1280 (s), 1109 (w), 1075 (m), 781 (m), 739 (m), 732 (m), 713 (s), 706 (s), 612 (m), 536 (w). Mass spectrum (ESI, MeOH, *m/z* (%)): 397 (100, M$^+$, $C_9H_8N_4O_2Ir$), 395 (59). (CI, NH$_3$, *m/z* (%)): 397 (100, M$^+$, $C_9H_8N_4O_2Ir$), 395 (55).

From {[Ir(BPM)(COD)]$^+$(BPh$_4$)$^-$} (1). {[Ir(BPM)(COD)]$^+$(BPh$_4$)$^-$} (**1**) (825 mg, 1.07 mmol) was mixed with methanol (15 mL) and hexane (4 mL), and the resulting cloudy bright yellow solution was degassed via three freeze/pump/thaw cycles. The solution was stirred under an atmosphere of carbon monoxide at room temperature for 1 h. The solution became clear immediately, and within 2−3 min a pale yellow precipitate formed. The solid was collected by filtration and washed with hexane (3 × 5 mL) to give [bis(1-pyrazolyl)methane]dicarbonyliridium(I) tetraphenylborate, {[Ir(BPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (**3**), as a yellow powder (638 mg, 83%); mp 185−186 °C. The spectroscopic data were identical to the sample produced from {[Ir(COD)Cl]$_2$}.

Synthesis of {[Ir(dmBPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (5). From {[Ir(COD)Cl]$_2$}. Methanol (25 mL) and hexane (7 mL) were added to a mixture of dmBPM (110 mg, 0.54 mmol), {[Ir(COD)Cl]$_2$} (180 mg, 0.27 mmol), and NaBPh$_4$ (240 mg, 0.70 mmol). The solution was stirred for 45 min at room temperature, during which time the intermediate, {[Ir(dmBPM)(COD)]$^+$(BPh$_4$)$^-$} (**2**), formed as a bright orange powder. The solution was degassed via three freeze/pump/thaw cycles and stirred under an atmosphere of carbon monoxide at room temperature for 2 h. After 30 min, a yellow precipitate was formed. The precipitate was collected by filtration and washed with hexane (10 mL), methanol (3 mL), and hexane (10 mL) and dried under vacuum to give [bis(3,5-dimethyl-1-pyrazolyl)methane]dicarbonyliridium(I) tetraphenylborate, {[Ir(dmBPM)(CO)$_2$]$^+$(BPh$_4$)$^-$} (**5**), as a pale yellow powder (385 mg, 93%). ^{1}H NMR (600 MHz, THF-d_8, 303 K): δ 7.37 (br s, 8H, *ortho*-BPh_4), 6.89 (t, 8H, $^3J = 7.5$ Hz, *meta*-BPh_4), 6.75 (t, 4H, $^3J = 7.2$ Hz, *para*-BPh_4), 6.22 (s, 2H, H4), 5.80 (br s, 1H, $H1'a$ or $H1'b$), 5.70 (br s, 1H, $H1'a$ or $H1'b$), 2.49 (s, 6H, C3−CH_3), 2.27 (s, 6H, C5−CH_3) ppm.^{13}C NMR (150 MHz, THF-d_8, 303 K): δ 172.7 (Ir−CO), 166.5 (q, $^1J_{BC} = 48.9$ Hz, *ipso*-BPh_4), 138.5 (*ortho*-BPh_4), 125.2 (*meta*-BPh_4), 123.4 (*para*-BPh_4), 110.9 (C4), 59.1 ($C1'$), 16.3 (C3−CH$_3$), 12.2 (C5−CH$_3$) ppm.

From {[Ir(dmBPM)(COD)]$^+$(BPh$_4$)$^-$} (2). {[Ir(dmBPM)(COD)]$^+$(BPh$_4$)$^-$} (**2**) (113 mg, 0.137 mmol) was dissolved in a mixture of methanol (15 mL) and hexane (4 mL), and the resulting intense yellow-orange solution was degassed via three freeze/pump/thaw cycles. The solution was stirred under an atmosphere of carbon monoxide at room temperature for 2 h. After 0.5 h the solution became yellow and a yellow precipitate formed. The solid was collected by filtration and washed with hexane (3 × 5 mL) to give [bis(3,5-dimethyl-1-pyrazolyl)methane]dicarbonyliridium(I) tetraphenylborate, $\{[Ir(dmBPM)(CO)_2]^+(BPh_4)^-\}$ (**5**) as a yellow powder (98 mg, 99%); mp decomposes at 190 °C, melts at 216−219 °C. The spectroscopic data were identical to the sample produced from $\{[Ir(COD)Cl]_2\}$.

$\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (3) Crystal Structure Data. A crystal was mounted on a glass fiber with cyanoacrylate resin, and cell constants were determined by least-squares fits to the setting angles of 25 independent reflections collected on an Enraf Nonius CAD-4F four-circle diffractometer employing graphite-monochromated Mo Kα radiation.

Data reduction and application of Lorentz, polarization, and analytical absorption corrections were carried out using teXsan.[40] The structure was solved by direct methods using SHELXS-86[41] and refined using full-matrix least-squares methods with teXsan.[40] Hydrogen atoms were included at calculated sites with isotropic thermal parameters based on that of the riding atom, and the non-hydrogen atoms were refined anisotropically. Neutral atom scattering factors were taken from International Tables.[42] Anomalous dispersion effects were included in F_c.[43] The values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[44] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[45] All other calculations were performed using the teXsan[40] crystallographic software package of Molecular Structure Corporation. An ORTEP[31] projection of the molecule is provided in Figure 1.

Synthesis of Silyl Ethers via the Alcoholysis of Hydrosilanes Catalyzed by $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (3), $\{[Ir(dmBPM)(CO)_2]^+(BPh_4)^-\}$ (5), or $\{[Ir(BPM)(COD)]^+(BPh_4)^-\}$ (1). In a typical reaction, the hydrosilane substrate was added to a stirred solution of the alcohol, *n*-octane (internal standard), THF (solvent), and iridium catalyst at room temperature, and the reaction mixture was heated at 40 °C. Aliquots of the reaction mixture were taken at regular intervals, and the concentrations of starting materials and products were monitored by calibrated gas chromatography. For reactions with tertiary hydrosilanes (R_3SiH), the ratio of reactants, solvent, and standard was ROH: 2, R_3SiH: 1, THF: 10, *n*-octane: 0.2, except for the reactions with Ph_3SiH, where 4 equiv of alcohol was used. For reactions with secondary hydrosilanes (R_2SiH_2), the ratio of reactants, solvent, and standard was ROH: 4, R_2SiH_2: 1, THF: 10, *n*-octane: 0.2. Reactions were catalyzed by approximately 0.45 mol % of the $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**) catalyst or by approximately 0.33 mol % of the $\{[Ir(dmBPM)(CO)_2]^+(BPh_4)^-\}$ (**5**) catalyst, except where otherwise noted.

Silyl ether products from the reaction mixtures were isolated by careful removal of the THF solvent under reduced pressure. Hexane was added to precipitate the iridium species, and the reaction mixture was filtered through a plug of flash silica using hexane as the eluent. The hexane solvent was removed under reduced pressure and with the more volatile products, the solvent was removed, and the product isolated by fractional distillation.

The silyl ether products were characterized using ^1H, ^{13}C, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectroscopy. The assignments of the spectra were based on the observed couplings as well as comparison with literature reports.[2,15,16] Complete ^1H, ^{13}C, and ^{29}Si assignments are reported in the Supporting Information.

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Supporting Information Available: A listing of ^1H, ^{13}C NMR data for silyl ethers; ^{29}Si NMR data for hydrosilanes and their respective methoxy, ethoxy, and isopropyloxy-silyl ethers; additional spectroscopic data for selected compounds; and X-ray crystallographic data for $\{[Ir(BPM)(CO)_2]^+(BPh_4)^-\}$ (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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