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Iridium(I), Iridium(III), and Iridium(V) Complexes Containing the (2-Methoxyethyl)cyclopentadienyl Ligand[†]

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Treatment of $[\mathrm{Ir}(\mu\text{-Cl})(\mathrm{COE})_2]_2$ (**1**) with $\mathrm{LiCp^O}$ gives $\mathrm{Ir}(\eta^5\text{-Cp}^\mathrm{O})(\mathrm{COE})_2$ (**2**; $\mathrm{Cp^O} = \mathrm{C_5H_4(CH_2)_2OCH_3}$, COE = *cis*-cyclooctene), which reacts with $\mathrm{X_2}$ to afford the iridium(III) derivatives $[\mathrm{Ir}(\eta^5\text{-Cp}^\mathrm{O})\mathrm{X}(\mu\text{-X})]_2$ (X = I (**3**), Cl (**4**)). Complexes **3** and **4** react with $\mathrm{P^iPr_3}$ to yield the corresponding species $\mathrm{Ir}(\eta^5\text{-Cp}^\mathrm{O})(\mathrm{P^iPr_3})\mathrm{X_2}$ (X = I (**5**), Cl (**6**)), which by addition of $\mathrm{LiHBEt_3}$ give $\mathrm{Ir}(\eta^5\text{-Cp}^\mathrm{O})(\mathrm{P^iPr_3})\mathrm{H_2}$ (**7**). The reactions of **5** and **6** with 2.0 equiv of $\mathrm{AgBF_4}$ in acetonitrile lead to $[\mathrm{Ir}(\eta^5\text{-Cp}^\mathrm{O})(\mathrm{P^iPr_3})(\mathrm{NCMe})_2][\mathrm{BF_4}]_2$ (**8**). Treatment of **3** with 2.0 equiv of $\mathrm{HSiEt_3}$ per iridium affords the monohydride dimer $[\mathrm{Ir}(\eta^5\text{-Cp}^\mathrm{O})\mathrm{I}]_2(\mu\text{-H})(\mu\text{-I})$ (**9**). Complex **4** reacts with 4.0 equiv of $\mathrm{HSiEt_3}$ per iridium to give the iridium(V) silyl trihydride derivative $\mathrm{IrH_3}(\eta^5\text{-Cp}^\mathrm{O})(\mathrm{SiEt_3})$ (**10**), which in the presence of excess of $\mathrm{HSiEt_3}$ is transformed into $\mathrm{IrH_2}(\eta^5\text{-Cp}^\mathrm{O})(\mathrm{SiEt_3})_2$ (**11**). Treatment at −40 °C of **4** with 2.0 equiv of $\mathrm{HSiEt_3}$ per iridium leads to a mixture of the hydride dichloro triethylsilyl complex $\mathrm{IrH}(\eta^5\text{-Cp}^\mathrm{O})\mathrm{Cl_2}(\mathrm{SiEt_3})$ (**12**), the dihydride chloro triethylsilyl compound $\mathrm{IrH_2}(\eta^5\text{-Cp}^\mathrm{O})\mathrm{Cl}(\mathrm{SiEt_3})$ (**14**), and the monohydride dimer $[\mathrm{Ir}(\eta^5\text{-Cp}^\mathrm{O})\mathrm{Cl}]_2(\mu\text{-H})(\mu\text{-Cl})$ (**16**). Complex **16** has been also prepared by reaction of **4** with 1.0 equiv of $\mathrm{HSiEt_3}$ per iridium. Complex **10** is easily deuterated in $\mathrm{C_6D_6}$ at 80 °C. The X-ray structures of **4**, **8**, and **9** are also reported.

Introduction

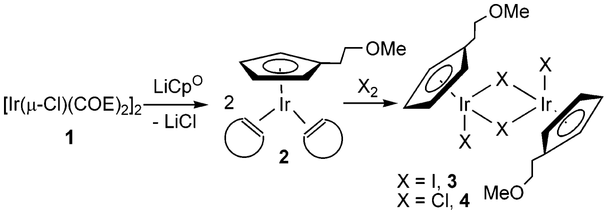
The σ-donor and π-acceptor abilities of the cyclopentadienyl ligands stabilize transition-metal complexes in low and high oxidation states.[1] Cyclopentadienyl ligands bearing pendant donor substituents have been attracting increased interest in the chemistry of the metals.[2] Cyclopentadienyl systems bearing pendant O-donors have been centered on the so-called early transition metals, mainly Ti, Zr, Hf, and the rare-earth elements.[3]

The typical procedure to introduce these groups into a transition metal involves the reaction between a cyclopentadienyl derivative of an s- or p-block element and a transition-metal halide. This method is also efficient in iridium chemistry.[4] Thus, as a part of our work on the chemistry of transition-metal complexes with $\mathrm{C_5H_4(CH_2)_2E}$ (E = $\mathrm{OCH_3}$, $\mathrm{NMe_2}$, $\mathrm{PPh_2}$) ligands,[5] here we report the synthesis and characterization of new iridium(I), -(III), and -(V) complexes containing the (2-methoxyethyl)cyclopentadienyl ligand.

Results and Discussion

1. Preparation of $[\mathrm{Ir}(\eta^5\text{-Cp}^\mathrm{O})\mathrm{X}(\mu\text{-X})]_2$ (X = I, Cl) Complexes. Treatment at 0 °C of the cyclooctene dimer $[\mathrm{Ir}(\mu\text{-Cl})(\mathrm{COE})_2]_2$ (**1**) with the lithium compound $\mathrm{LiCp^O}$ ($\mathrm{Cp^O} = \mathrm{C_5H_4(CH_2)_2OCH_3}$) in THF leads to the (2-methoxyethyl)cyclopentadienyl derivative $\mathrm{Ir}(\eta^5\text{-Cp}^\mathrm{O})(\mathrm{COE})_2$ (**2**), which is isolated as pale brown crystals in 90% yield (Scheme 1). The reaction of **2** with a dichloromethane solution of $\mathrm{I_2}$ produces the displacement of the coordinated olefins and the formation of the iridium(III) complex $[\mathrm{Ir}(\eta^5\text{-Cp}^\mathrm{O})\mathrm{I}(\mu\text{-I})]_2$ (**3**), which is isolated as a red solid in 84% yield, according to Scheme 1. Analogously, bubbling molecular chlorine through a dichloromethane solution of **2** leads to the complex $[\mathrm{Ir}(\eta^5\text{-Cp}^\mathrm{O})\mathrm{Cl}(\mu\text{-Cl})]_2$ (**4**), which is isolated as an orange solid in 80% yield.

Scheme 1



The dimeric nature of species **3** and **4**, which has been confirmed by an X-ray diffraction analysis of **4** (Figure 1), is noteworthy. In this context it should be noted that the derivative $\mathrm{Ir}\{\eta^5\text{-Cp}^\mathrm{N}\}(\mathrm{COE})_2$ ($\mathrm{Cp^N} = \mathrm{C_5H_4(CH_2)_2N(CH_3)_2}$), containing $\mathrm{NMe_2}$ instead of OMe as a pendant donor group, reacts with $\mathrm{I_2}$ to give the mononuclear species $\mathrm{IrI_2}\{\eta^5(C_5),\kappa N\text{-Cp}^\mathrm{N}\}$, which contains the pendant amino group coordinated to the iridium

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[†] Dedicated to Prof. Heinz Berke on the occasion of his 60th birthday.

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(4) See for example: Blais, M. S.; Rausch, M. D. *J. Organomet. Chem.* **1995**, *502*, 1.

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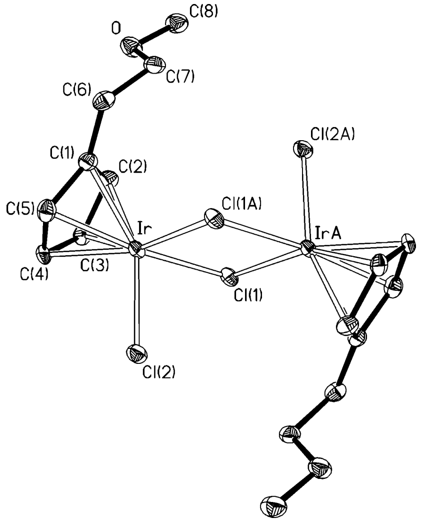


Figure 1. Molecular diagram of complex **4**. Selected bond lengths (Å) and angles (deg): Ir−Cl(1) = 2.4398(11), Ir−Cl(1A) = 2.4233(11), Ir−Cl(2) = 2.3780(12), Ir···Ir(A) = 3.7020(4), Ir−C(1) = 2.162(5), Ir−C(2) = 2.143(5), Ir−C(3) = 2.122(4), Ir−C(4) = 2.124(4), Ir−C(5) = 2.124(5); Cl(1)−Ir−Cl(1A) = 80.85(4), Cl(1)−Ir−Cl(2) = 87.54(4), Cl(1A)−Ir−Cl(2) = 87.03(4), Ir−Cl(1)−Ir(A) = 99.15(4).

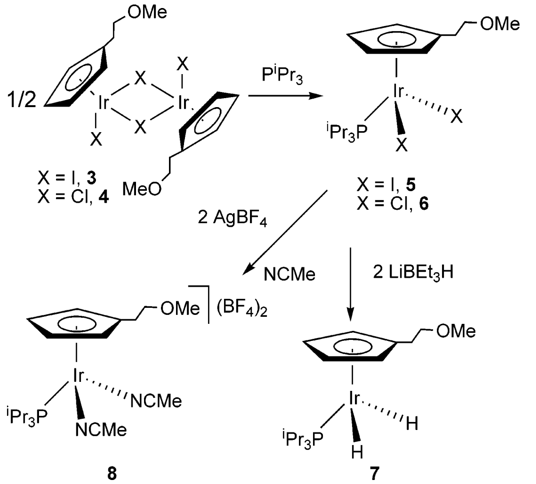
atom.[5a] A similar finding has been reported for the related half-sandwich rhodium complexes $[Rh(\eta^5\text{-}Cp^O)I(\mu\text{-}I)]_2$[6] and $RhCl_2\{\eta^5(C_5),\kappa N\text{-}Cp^N\}$.[7] This behavior agrees well with the greater coordination ability of the amine compared with that of the ether group, which has been also observed for the titanium complexes $TiCl_nR_{3-n}(Cp^E)$ ($Cp^E = Cp^N$, Cp^O; $n = 0-3$; R = Me).[5e,f]

The molecule of **4** has C_i symmetry in the solid state. It is composed of two $Ir(\eta^5\text{-}Cp^O)Cl$ units coupled via two bridging chloride ligands, Cl(1) and Cl(1A). Each Ir atom is η^5-bound to the cyclopentadienyl ring and σ-bound to the two bridging chloride ligands and to one terminal chloride (Cl(2)). The Ir−Cl(1) and Ir−Cl(1A) bond distances of 2.4398(11) and 2.4233(11) Å are significantly longer than the Ir−Cl(2) distance (2.3780(12) Å). The Ir−Cl bond distances in **4** are slightly shorter than the corresponding distances found for the complex $[Ir(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)]_2$ (2.456(3), 2.449(3), and 2.387(4) Å).[8]

The ^1H and $^{13}C\{^1H\}$ NMR spectra of CD_2Cl_2 solutions of species **3** and **4** are temperature independent. The ^1H NMR spectra exhibit an AA′BB′ pattern for the C_5H_4 ring between 5.7 and 5.6 ppm (**3**) and between 5.8 and 5.7 ppm (**4**). The ethylenic side chain protons give rise to two triplets (J_{H-H} = 5.7 Hz) at 3.65 (CH_2O) and 2.66 ppm (**3**) and at 3.67 (CH_2O) and 2.42 ppm (**4**). Singlets at 3.35 (**3**) and 3.34 ppm (**4**) are observed for the CH_3O protons. The most noticeable resonances in the $^{13}C\{^1H\}$ NMR spectrum are those due to the side chain, which are observed at 71.2 (CH_2O), 58.6 (CH_3), and 28.3 ppm (CH_2) (**3**) and at 70.0 (CH_2O), 58.5 (CH_3), and 27.3 ppm (CH_2) (**4**). These data are consistent with the noncoordination of the pendant ether to the iridium atom.[4,5c,f,6]

2. Triisopropylphosphine Complexes. Complexes **3** and **4** react with dichloromethane solutions of P^iPr_3 to yield quantitatively the corresponding species $Ir(\eta^5\text{-}Cp^O)(P^iPr_3)X_2$ (X = I (**5**), Cl (**6**)), which are isolated as red (**5**) and orange (**6**) solids. Toluene solutions of complexes **5** and **6** react with 2.3 equiv of $LiBEt_3H$ to give the dihydride species $IrH_2(\eta^5\text{-}Cp^O)(P^iPr_3)$ (**7**), which is isolated as an orange oil in 64% yield (Scheme 2). Complexes **5**−**7** have been characterized by elemental analysis and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. The resonance of the hydride ligands in the ^1H NMR spectrum of **7** appears as a doublet at −18.30 ppm (J_{H-P} = 29 Hz). Its IR spectrum supports the terminal nature of the hydride ligands, showing an intense band at 2148 cm^{-1}.

Scheme 2



The treatment of acetonitrile solutions of species **5** and **6** with 2 equiv of $AgBF_4$ leads to the BF_4^- salt of the dicationic solvate complex $[Ir(\eta^5\text{-}Cp^O)(NCMe)_2(P^iPr_3)]^{2+}$ (**8**), which is isolated according to Scheme 2 as a white solid in 90% yield.

The structure of **8** has been confirmed by an X-ray diffraction analysis, which proves that in the solid state the pendant ether substituent of the cyclopentadienyl ligand is also not coordinated to the cyclopentadienyl ligand (Figure 2). The geometry around the metal center can be described as an octahedron with the cyclopentadienyl group occupying a face. The Ir−N bond lengths (2.042(3) and 2.040(3) Å) are shorter than those recently reported for the related species $[Ir(\eta^5\text{-}C_5Me_5)(NCMe)_2(PPh_3)]^{2+}$ (2.086(8) and 2.066(8) Å).[9]

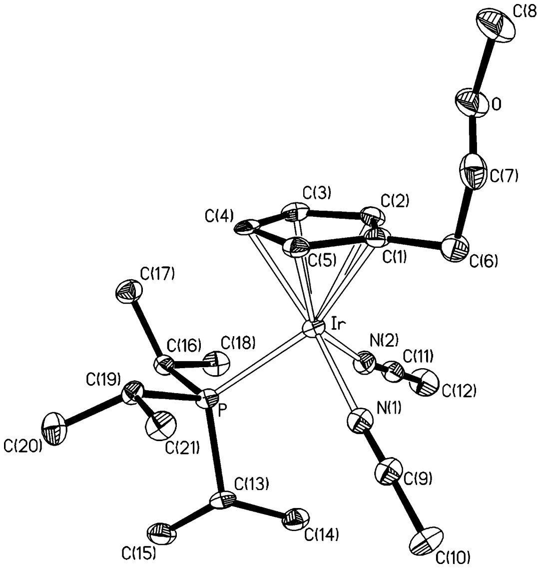


Figure 2. Molecular diagram of the dication **8**. Selected bond lengths (Å) and angles (deg): Ir−N(1) = 2.042(3), Ir−N(2) = 2.040(3), Ir−P = 2.3508(9), Ir−C(1) = 2.237(3), Ir−C(2) = 2.214(3), Ir−C(3) = 2.154(3), Ir−C(4) = 2.167(3), Ir−C(5) = 2.161(3); N(2)−Ir−N(1) = 89.22, N(1)−Ir−P = 89.86(8), N(2)−Ir−P = 91.53(9).

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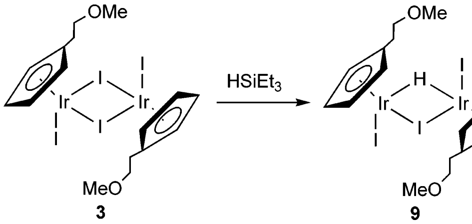
Scheme 3



The ^{1}H and ^{13}C{^{1}H} NMR spectra of **8** are in agreement with the noncoordination of the pendant ether to the iridium atom (see Experimental Section). The resonance due to the coordinated acetonitrile molecules in the ^{1}H NMR spectrum of **8** appears as a singlet at 2.75 ppm. The ^{13}C{^{1}H} NMR spectrum shows two resonances at 128.3 ppm (*C*N) and at 2.1 ppm (NC*C*H$_3$) and agrees well with those recently reported for related species.[9]

3. Reaction of [Ir(η^5-Cp^O)I(μ-I)]$_2$ with Et$_3$SiH. The treatment of dichloromethane solutions of **3** with 2.0 equiv of HSiEt$_3$ per iridium for 1 h affords a dark red solid, which has been characterized as the monohydride complex [Ir(η^5-Cp^O)I]$_2$(μ-H)(μ-I) (**9**) (Scheme 3). We have observed that increasing the reaction time or the HSiEt$_3$ concentration produces a complicated mixture of unidentifiable substances.

The structure of the dimer species **9** has been confirmed by X-ray methods (Figure 3). The molecule has C_2 symmetry, with its two crystallographically related IrCp^{O}I fragments being bridged by a iodide (I(2)) and a hydride ligand. As was the case for **4** and **8**, the structure proves the free character of the pendant ether group.

The geometry around each iridium atom can be described as a distorted octahedron with the cyclopentadienyl ring occupying a face. The terminal Ir−I(1) bond distance of 2.6890(6) Å is longer than the bridge Ir−I(2) separation of 2.6504(6) Å. These values are in contrast with the Ir−Cl bond distances found in the bis(μ-chloro) complex **4**, in which the Ir−Cl$_{\text{terminal}}$ distance is shorter than the Ir−Cl$_{\text{bridging}}$ distances. This is in agreement with the systematic decrease of the difference between the terminal and bridging Ir−X linkages with increasing size of the halide observed in the series [Ir(η^5-C$_5$Me$_5$)X(μ-X)]$_2$ (X = Cl,[8] Br, I).[10] This trend has been attributed to the easier polarizability and decreased electronegativity of the larger covalently linked halide ligands.[10] In this context, we note that no significant differences between the Rh−I$_{\text{terminal}}$ (2.6921(15) Å) and Rh−I$_{\text{bridging}}$ (2.6920(13) and 2.6959 (15) Å) bond distances have been found in the related rhodium complex [Rh(η^5-Cp^O)I(μ-I)]$_2$.[6]

The most remarkable feature of the structure of **9** is the Ir−Ir separation of 2.9440(6) Å, which is much shorter than that found in complex **4** (3.7020(4) Å) and compares well with the Ir−Ir distance in the related complex [Ir(η^5-C$_5$Me$_5$)Cl](μ-H)(μ-Cl) (2.903(1) Å),[8] where a two-electron−three-center Ir(μ-H)Ir linkage with substantial direct metal bonding has been proposed to exist. Although a simple electron count shows that the EAN rule predicts the existence of a single bond between the iridium atoms and the Ir−Ir distance in **9** is only 0.14 Å longer than the expected distance for an Ir(III)−Ir(III) single bond (2.804 ± 0.014 Å),[8] EHT calculations and topological analysis of the electron density in related complexes[11] indicate that the metal−H−metal unit should be viewed as a typical three-center−two-electron bond.

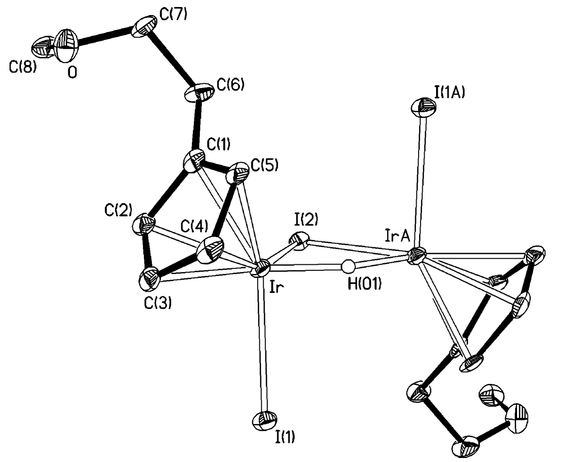


Figure 3. Molecular diagram of complex **9**. Selected bond lengths (Å) and angles (deg): Ir−I(1) = 2.6890(6), Ir−I(2) = 2.6504(6), Ir···Ir(A) = 2.9440(6), Ir−H(01) = 1.54(3), Ir−C(1) = 2.184(7), Ir−C(2) = 2.154(7), Ir−C(3) = 2.148(7), Ir−C(4) = 2.149(7), Ir−C(5) = 2.160(7); I(1)−Ir−I(2) = 94.830(14), I(1)−Ir−H(01) = 89.3(3), I(2)−Ir−H(01) = 74(3), Ir−I(2)−Ir(A) = 67.48(2), Ir−H(01)−Ir(A) = 145(7).

The ^{1}H NMR spectrum of **9** contains a singlet at −16.28 ppm due to the hydride ligand. In agreement with the chirality of the metal centers, the cyclopentadienyl ligands display an ABCD spin system between 5.41 and 5.05 ppm. In the ^{13}C{^{1}H} NMR spectrum, the C$_5$ rings give rise to five singlets, at 99.8 ppm (C$_{\text{ipso}}$) and between 81.5 and 76.8 ppm.

4. Reactions of [Ir(η^5-Cp^O)Cl(μ-Cl)]$_2$ with Et$_3$SiH. Complex **4** is related to the previously described complex [Ir(η^5-C$_5$Me$_5$)Cl(μ-Cl)]$_2$. However, in the presence of HSiEt$_3$, there are significant differences in behavior between them. Maitlis' groundbreaking work in the 1980s established that the iridium(III) pentamethylcyclopentadienyl dimer reacts with the silane in dichloromethane at 20 °C to give the iridium(V) dihydride chloro silyl derivative IrH$_2$(η^5-C$_5$Me$_5$)Cl(SiEt$_3$), which reacts with more triethylsilane in refluxing benzene to give the iridium(V) dihydride bis(triethylsilyl) complex IrH$_2$(η^5-C$_5$Me$_5$)(SiEt$_3$)$_2$.[12] In agreement with the formation of the latter, recently, Cheong, Kang, and co-workers have also proved that the reactions of [Ir(η^5-C$_5$Me$_5$)Cl(μ-Cl)]$_2$ with bis(silyl)-*o*-carboranes, (HSiR$_2$)$_2$(C$_2$B$_{10}$H$_{10}$), lead to the corresponding complexes IrH$_2$(η^5-C$_5$Me$_5$){(SiR$_2$)$_2$(C$_2$B$_{10}$H$_{10}$)}.[13] In contrast to the case for the iridium(III) pentamethylcyclopentadienyl dimer and also in contrast to the case for **3**, the treatment at room temperature of dichloromethane solutions of **4** with 4.0 equiv of HSiEt$_3$ per iridium affords the trihydride silyl derivative IrH$_3$(η^5-Cp^O)(SiEt$_3$) (**10**), which is isolated as an orange-red oil in 90% yield. The addition at room temperature of 12.5 equiv of HSiEt$_3$ per iridium to dichloromethane solutions of **10** gives rise to the formation of IrH$_2$(η^5-Cp^O)(SiEt$_3$)$_2$ (**11**) in almost quantitative yield after 1 day.

The formation of **10** can be rationalized according to Scheme 4. In solution, dimer **4** is in equilibrium with the monomer, which could be stabilized by coordination of the pendant oxygen

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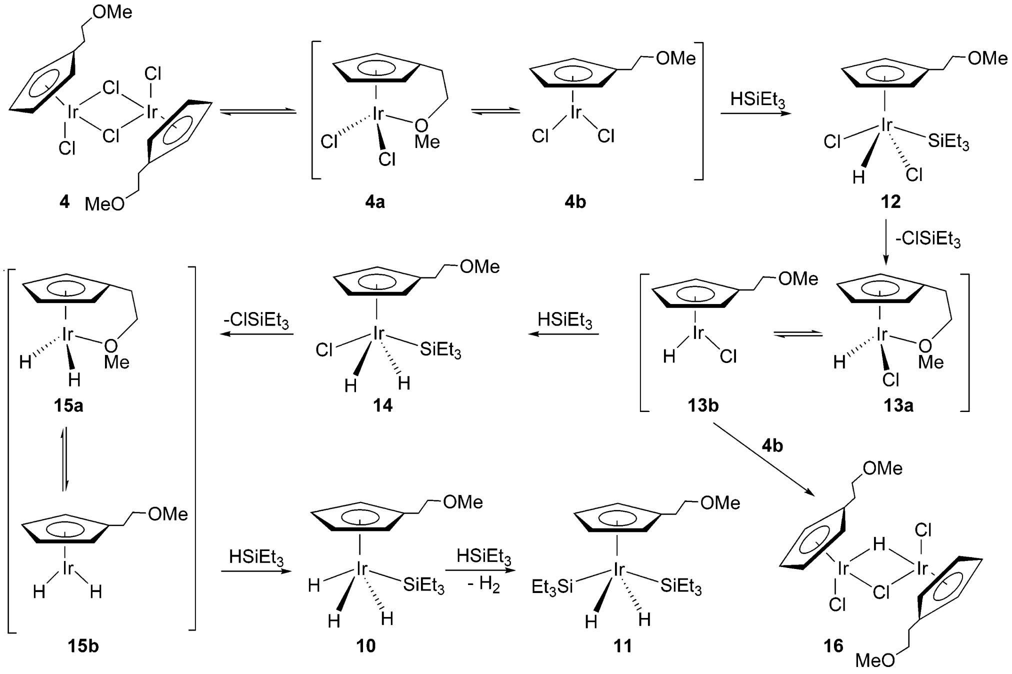
Scheme 4



donor atom to the metallic center. The oxidative addition of $HSiEt_3$ to the unsaturated form of **4** (**4b**) should give the intermediate **12**, which could afford **14** by reductive elimination of $ClSiEt_3$ and subsequent oxidative addition of a second molecule of $HSiEt_3$. A new reductive elimination of $ClSiEt_3$ from **14**, followed by the oxidative addition of $HSiEt_3$ to the resulting dihydride **15**, leads to **10**. In support of this proposal we have observed that the treatment at −40 °C in dichloromethane of **4** with 2.0 equiv of $HSiEt_3$ per iridium and the subsequent stirring for 30 min of the resulting solution lead to a mixture of the hydride dichloro triethylsilyl complex $IrH(\eta^5\text{-}Cp^O)Cl_2(SiEt_3)$ (**12**; δ_{Ir-H} −17.92 ppm), the dihydride chloro triethylsilyl compound $IrH_2(\eta^5\text{-}Cp^O)Cl(SiEt_3)$ (**14**; δ_{Ir-H} −12.70 ppm), and the monohydride dimer $[Ir(\eta^5\text{-}Cp^O)Cl]_2(\mu\text{-}H)(\mu\text{-}Cl)$ (**16**; δ_{Ir-H} −13.20 ppm) in a ratio of approximately 2:6:2.

Complex **12** was separated from the mixture by column chromatography on silica gel and isolated as a dark oil in 18% yield, whereas the monohydride **16** was prepared as a pure dark red solid in 70% yield, by treatment of a dichloromethane solution of **4** with 1.0 equiv of $HSiEt_3$ per iridium at 0 °C. The formation of **16** can be the result of the condensation of the unsaturated species **13b** and **4b**. Apart from the hydride resonance, the most noticeable spectroscopic features of **16** are the presence of four C_5H_4 resonances between 5.23 and 4.88 ppm in its ^1H NMR spectrum in C_6D_6 and between 77.9 and 72.6 ppm in its $^{13}C\{^1H\}$ NMR spectrum in CD_2Cl_2. This is a result of the chirality of the metal center.

At first glance, one could think that the reaction of **10** with $HSiEt_3$ to afford **11** involves the reductive elimination of molecular hydrogen and the subsequent oxidative addition of $HSiEt_3$ to the resulting hydrido silyl intermediate. However, this is not consistent with the fact that **10** does not react with PMe_2Ph or PMe_3, which are stronger Lewis bases than $HSiEt_3$. The formation of **11** may be the result of a σ-bond metathesis process.

The preparation of **10** from **4** in a one-pot synthesis is remarkable. We note that the trihydride pentamethylcyclopentadienyl complexes $IrH_3(\eta^5\text{-}C_5Me_5)(ER_3)$ ($ER_3 = SiMe_3, SnMe_3, SnPh_3$), related to **10**, have been previously reported.[14] However, their synthesis is a complex multistep procedure involving the reaction of $[Ir(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)]_2$ with molecular hydrogen and NH_4PF_6 to give $[\{Ir(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}H)_3][PF_6]$,[15] the treatment of this trihydride dimer with $LiEt_3BH$,[16] the subsequent deprotonation of the formed $IrH_4(\eta^5\text{-}C_5Me_5)$, and finally the reaction of the resulting salt with the corresponding XER_3 halide.[14]

The ^1H NMR spectrum of **10** is temperature dependent. At 283 K, in toluene-d_8 as solvent, the spectrum shows in the hydride region a singlet at −16.29 ppm. Between 243 and 233 K decoalescence occurs, and at 193 K an AB_2 spin system defined by δ_A −15.72, δ_B −16.25, and J_{A-B} = 6.6 Hz is observed. These changes indicate that complex **10** possesses a rigid structure in solution only at low temperature. The distribution of ligands around the iridium atom, consistent with the AB_2 spin system, can be described as a four-legged piano-stool geometry with the cyclopentadienyl group occupying the three-membered face. This structure agrees well with that found for the triphenylstannyl complex $IrH_3(\eta^5\text{-}C_5Me_5)(SnPh_3)$ by X-ray diffraction analysis.[14] However, it differs from those reported for the complexes $IrH_3\{PhB(CH_2P^iPr_3)_3\}(SiHEt_2)$[17] and $IrH_3(TpMe_2)(SiEt_3)$,[18] where the silyl group caps the hydride face of an otherwise distorted-octahedral structure.

In solution at temperatures higher than 193 K, the hydride ligand of **10** disposed transoid to the silyl group, H_A, exchanges its position with H_B. Line-shape analysis of the spectra allows the calculation of the rate constants for the thermally activated site exchange process at different temperatures (Figure 4). The activation parameters obtained from the corresponding Eyring analysis are $\Delta H^\ddagger = 11.8 \pm 1$ kcal mol^{-1} and $\Delta S^\ddagger = 1.8 \pm 2.5$ cal mol^{-1} K^{-1}. The value for the entropy of activation, close to zero, is in agreement with an intramolecular process, whereas the value for the enthalpy of activation is similar to those

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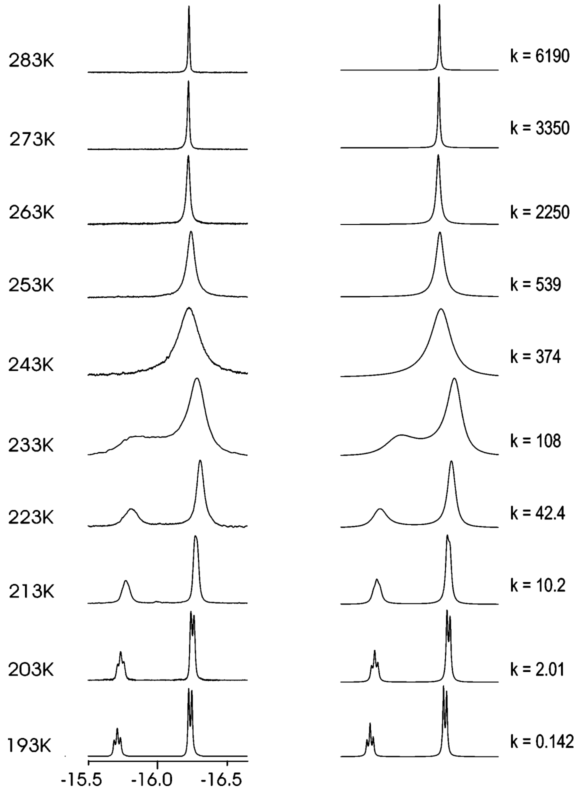


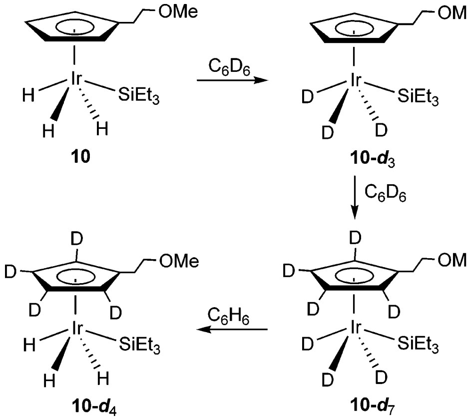
Figure 4. (left) Variable-temperature ^{1}H NMR spectra (300 MHz) in the high-field region of **10**. (right) Simulated spectra and rate constants (s^{-1}) for the intramolecular hydrogen site exchange process.

reported for complexes $IrH_3(\eta^5\text{-}C_5Me_5)(ER_3)$ (ER_3 = $SiMe_3$ (13.9(6) kcal mol^{-1}), $SnMe_3$ (10.7(2) kcal mol^{-1}), $SnPh_3$ (10.6(5) kcal mol^{-1})),[14] $[IrH_3(\eta^5\text{-}C_5Me_5)(PMe_3)]BF_4$ (12.0(4) kcal mol^{-1}),[19] and $IrH_3(acac)(SiEt_3)PCy_3$ (12.23 ± 0.76 kcal mol^{-1}).[20] In contrast to the case for **10**, the ^{1}H NMR spectrum of **11** is temperature invariant. The most noticeable resonance in this spectrum is a singlet at −17.20 ppm, corresponding to the hydride ligands.

5. Deuteration of the Trihydride Derivative $IrH_3(\eta^5\text{-}Cp^O)(SiEt_3)$. In addition to the hydride signal, the ^{1}H NMR spectrum of **10** shows resonances due to the (2-methoxyethyl)cyclopentadienyl and triethylsilyl ligands. Among them, worthy of note is an AA′BB′ spin system between 5.11 and 4.82 ppm, corresponding to the cyclopentadienyl protons. In benzene-d_6 at 80 °C, the hydride and cyclopentadienyl resonances disappear. Their extinction occurs by phases in a sequential manner. After 24 h, the spectrum does not show any hydride resonance. After 9 days, only the resonances due to the CH_2CH_2OMe pendant group and the triethylsilyl ligand are observed. In agreement with this, the selective deuteration of the hydride and cyclopentadienyl positions of **10** can be performed (Scheme 5).

The heating of **10** in benzene-d_6 at 80 °C for 24 h produces the selective deuteration of the hydride positions to afford $IrD_3(\eta^5\text{-}Cp^O)(SiEt_3)$ (**10-*d*$_3$**), which only shows a singlet at −16.15 ppm in the ^{2}H NMR spectrum. As for the formation of **11**, the complex **10-*d*$_3$** may be the result of a σ-bond metathesis process. The heating of **10** for 9 days, or that of **10-*d*$_3$** for 8 days, gives rise to $IrD_3\{\eta^5\text{-}C_5D_4(CH_2)_2OCH_3\}(SiEt_3)_2$ (**10-*d*$_7$**), containing deuterium at both the hydride and cyclopentadienyl positions.

Scheme 5



The formation of **10-*d*$_7$** involves $D(Ir)/H(C_5H_{4-x}D_x)$ exchange reactions (x = 0−4), followed by the fast deuteration of the resulting hydrides. The generation of substituted cyclopentadienyl ligands by exchange between cyclopentadienyl hydrogen atoms and σ-ligands coordinated to a cyclopentadienyl−transition-metal fragment is a well-known process.[21] The trihydride $IrH_3\{\eta^5\text{-}C_5D_4(CH_2)_2OCH_3\}(SiEt_3)$ (**10-*d*$_4$**) can be obtained by reaction of **10-*d*$_7$** with benzene. In contrast to the case for **10**, the heating of **11** in benzene-d_6 at 80 °C does not produce deuteration.

Conclusion

This study reveals that the (2-methoxyethyl)cyclopentadienyl ligand (Cp^O) stabilizes iridium(I), iridium(III), and iridium(V) derivatives. The complex $[Ir(\mu\text{-}Cl)(COE)_2]_2$ reacts with $LiCp^O$ to give the iridium(I) compound $Ir(\eta^5\text{-}Cp^O)(COE)_2$ in high yield. This species is the entry to the iridium(III) dimers $[Ir(\eta^5\text{-}Cp^O)X(\mu\text{-}X)]_2$ (X = I, Cl), which in turn are starting materials to obtain other iridium(III) dimers or iridium(V) derivatives by reaction with $HSiEt_3$.

The nature of the products from the reactions of the iridium(III) dimers with $HSiEt_3$ depends on the halide ligand. The complex $[Ir(\eta^5\text{-}Cp^O)I(\mu\text{-}I)]_2$ reacts with $HSiEt_3$ to afford the underrepresented μ-hydride μ-iodide species $[Ir(\eta^5\text{-}Cp^O)I]_2(\mu\text{-}H)(\mu\text{-}I)$, while, under similar conditions, the chloro dimer $[Ir(\eta^5\text{-}Cp^O)Cl(\mu\text{-}Cl)]_2$ affords the iridium(V) trihydride silyl derivative $IrH_3(\eta^5\text{-}Cp^O)(SiEt_3)$.

In benzene-d_6 at 80 °C, the selective deuteration of the hydride and cyclopentadienyl positions of the trihydride species $IrH_3(\eta^5\text{-}Cp^O)(SiEt_3)$ can be performed. As a result, the deuterated complexes $IrD_3(\eta^5\text{-}Cp^O)(SiEt_3)$, $IrD_3\{\eta^5\text{-}C_5D_4(CH_2)_2OCH_3\}(SiEt_3)$, and $IrH_3\{\eta^5\text{-}C_5D_4(CH_2)_2OCH_3\}(SiEt_3)$ are easily prepared.

Experimental Section

General Information. All manipulations were performed with rigorous exclusion of air at an argon/vacuo manifold using standard Schlenk-tube or glovebox techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Gemini

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2000, Bruker ARX, or Bruker Avance 300 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$) and 85% H_3PO_4 ($^{31}P\{^1H\}$). Coupling constants *J* are given in hertz. Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. C, H, and N analyses were carried out with a Perkin-Elmer 2400 CHNS/O analyzer. $[Ir(\mu\text{-}Cl)(COE)_2]_2$ [22] and $LiCp^O$ [23] were prepared according to previous reports. $HSiEt_3$ (Aldrich) was used without further purification.

Preparation of $Ir(\eta^5\text{-}Cp^O)(COE)_2$ (2). THF (20 mL) at 0 °C was added to a mixture of $[Ir(\mu\text{-}Cl)(COE)_2]_2$ (0.78 g, 0.87 mmol) and $LiCp^O$ (0.23 g, 1.77 mmol). The solution was stirred at 20 °C for 12 h. The solvent was removed in vacuo and the residue extracted with pentane (3 × 20 mL). The resulting solution was concentrated to 5 mL and cooled to −30 °C. Pale brown crystals were obtained. Yield: 0.84 g (90%). Anal. Calcd for $C_{24}H_{39}IrO$: C, 53.84; H, 7.33. Found: C, 53.80; H, 7.10. ^1H NMR (C_6D_6, 20 °C, 300 MHz): δ 4.83−4.43 (AA′BB′, C_5H_4), 3.42 (t, J = 6.6, 2H, CH_2O), 3.12 (s, 3H, CH_3), 2.59 (t, J = 6.6, 2H, CH_2), 2.20 (m, 4H, =CH, COE), 1.62 (m, 8H, CH_2, COE), 1.34 (m, 16H, CH_2, COE). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, 75.42 MHz): δ 100.6 (ipso-C_5H_4), 86.7 and 86.6 (C_5H_4), 74.4 (CH_2O), 58.2 (CH_3), 45.8 (=CH, COE), 33.5, 33.1, and 26.6 (CH_2, COE), 28.1 (CH_2).

Preparation of $[Ir(\eta^5\text{-}Cp^O)I_2]_2$ (3). I_2 (0.24 g, 0.94 mmol) was added to a CH_2Cl_2 solution (40 mL) of **2** (0.50 g, 0.94 mmol). The solvent was removed in vacuo, and the residue was washed with Et_2O (2 × 20 mL) and further extracted with CH_2Cl_2 (2 × 20 mL). The CH_2Cl_2 was removed in vacuo to yield a red solid. Yield: 0.45 g (84%). Anal. Calcd for $C_{16}H_{22}I_4Ir_2O_2$: C, 16.88; H, 1.95. Found: C, 16.54; H, 1.85. ^1H NMR (CD_2Cl_2, 20 °C, 300 MHz): δ 5.73−5.65 (AA′BB′, C_5H_4), 3.65 (t, J = 5.7, 4H, CH_2O), 3.35 (s, 6H, CH_3), 2.66 (t, J = 5.7, 4H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 75.42 MHz): δ 97.0 (ipso-C_5H_4), 78.8 and 76.4 (C_5H_4), 71.2 (CH_2O), 58.6 (CH_3), 28.3 (CH_2). MS (FAB+): *m/z* 1138 (M^+); 1011 ($M^+ - I$).

Preparation of $[Ir(\eta^5\text{-}Cp^O)Cl_2]_2$ (4). Cl_2 was bubbled for 15 min through a CH_2Cl_2 solution (40 mL) of **2** (0.50 g, 0.94 mmol). The solvent was removed in vacuo, and the residue was washed with Et_2O (2 × 20 mL) and further extracted with CH_2Cl_2 (2 × 20 mL). The CH_2Cl_2 was removed in vacuo to yield an orange solid. Yield: 0.29 g (80%). Anal. Calcd for $C_{16}H_{22}Cl_4Ir_2O_2$: C, 24.87; H, 2.87. Found: C, 24.92; H, 2.75. ^1H NMR (CD_2Cl_2, 20 °C, 300 MHz): δ 5.80−5.77 (AA′BB′, C_5H_4), 3.67 (t, J = 5.7, 4H, CH_2O), 3.34 (s, 6H, CH_3), 2.42 (t, J = 5.7, 4H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 75.42 MHz): δ 97.3 (ipso-C_5H_4), 75.6 and 72.8 (C_5H_4), 70.0 (CH_2O), 58.5 (CH_3), 27.3 (CH_2). MS (FAB+): *m/z* 737 ($M^+ - Cl$).

Preparation of $Ir(\eta^5\text{-}Cp^O)(P^iPr_3)I_2$ (5). P^iPr_3 (0.10 mL, 0.52 mmol) was added to a CH_2Cl_2 (20 mL) solution of **3** (0.30 g, 0.26 mmol). The mixture was stirred for 1 h, and the CH_2Cl_2 was removed in vacuo. The residue was washed with pentane (2 × 20 mL) to yield a red solid. Yield: 0.35 g (92%). Anal. Calcd for $C_{17}H_{32}I_2IrOP$: C, 27.99; H, 4.42. Found: C, 28.30; H, 4.40. ^1H NMR (CD_2Cl_2, 20 °C, 300 MHz): δ 5.27−4.79 (AA′BB′, C_5H_4), 3.42 (m, 2H, CH_2O), 3.05 (s, 3H, CH_3), 2.95 (m, 2H, CH_2), 2.75 (m, 3H, CH, P^iPr_3), 0.99 (m, 18H, P^iPr_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 121.48 MHz): 5.34. $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, 75.42 MHz): δ 106.2 (ipso-C_5H_4), 84.6 and 76.2 (C_5H_4), 72.0 (CH_2O), 58.6 (CH_3), 29.1 (CH_2), 29.0 (d, J = 29.3, CH, P^iPr_3), 20.9 (CH_3, P^iPr_3).

Preparation of $Ir(\eta^5\text{-}Cp^O)(P^iPr_3)Cl_2$ (6). P^iPr_3 (0.10 mL, 0.52 mmol) was added to a CH_2Cl_2 (20 mL) solution of **4** (0.20 g, 0.26 mmol). The mixture was stirred for 1 h, and the CH_2Cl_2 was removed in vacuo. The residue was washed with pentane (2 × 20 mL) to yield an orange solid. Yield: 0.25 g (90%). Anal. Calcd for $C_{17}H_{32}Cl_2IrOP$: C, 37.38; H, 5.86. Found: C, 37.16; H, 5.95. ^1H NMR (CD_2Cl_2, 20 °C, 300 MHz): δ 5.50−5.38 (AA′BB′, C_5H_4), 3.66 (m, 2H, CH_2O), 3.33 (s, 3H, CH_3), 2.80 (m, 3H, CH, P^iPr_3), 2.52 (m, 2H, CH_2), 1.29 (m, 18H, P^iPr_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 121.48 MHz): 17.64. $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, 75.42 MHz): δ 112.4 (ipso-C_5H_4), 78.9 and 75.5 (C_5H_4), 70.4 (CH_2O), 58.5 (CH_3), 26.8 (CH_2), 25.4 (d, J = 28.4, CH, P^iPr_3), 19.7 (CH_3, P^iPr_3).

Preparation of $Ir(\eta^5\text{-}Cp^O)(P^iPr_3)H_2$ (7). A 1.0 M solution of $LiBEt_3H$ in THF (0.9 mL) was added to a toluene solution (20 mL) of **3** (0.44 g, 0.39 mmol) or **4** (0.30 g, 0.39 mmol). The mixture was stirred at 20 °C for 12 h, and EtOH (5 mL) was added. The solvents were removed in vacuo, and the residue was extracted with toluene. The toluene was removed in vacuo, and the oily residue was extracted with pentane and purified by passing through a silica gel column using acetone as eluent. The solvent was removed in vacuo to give an orange oil. Yield: 0.12 g (64%). Anal. Calcd for $C_{17}H_{34}IrOP$: C, 42.74; H, 7.17. Found: C, 42.40; H, 7.39. ^1H NMR (C_6D_6, 20 °C, 300 MHz): δ 5.13−4.96 (AA′BB′, C_5H_4), 3.50 (m, 2H, CH_2O), 3.12 (s, 3H, CH_3), 2.66 (m, 2H, CH_2), 1.66 (m, 3H, CH, P^iPr_3), 0.95 (m, 18H, P^iPr_3), −18.30 (d, 2H, J = 29). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C, 121.48 MHz): 51.80. $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, 75.42 MHz): δ 101.7 (ipso-C_5H_4), 78.7 (C_5H_4), 77.5 (d, J = 3.7, C_5H_4), 76.8 (CH_2O), 58.0 (CH_3), 28.8 (CH_2), 28.2 (d, J = 31.5, CH, P^iPr_3), 20.3 (CH_3, P^iPr_3). MS (FAB+): *m/z* 476 (M^+). IR (Nujol, cm^{-1}): ν(Ir−H) 2148 cm^{-1} (m).

Preparation of $[Ir(\eta^5\text{-}Cp^O)(NCCH_3)_2(P^iPr_3)][BF_4]_2$ (8). A Schlenk flask protected from the light was charged with **3** (0.33 g, 0.46 mmol) or **4** (0.25 g, 0.46 mmol), $AgBF_4$ (0.20 g, 1.0 mmol), and acetonitrile (20 mL). The mixture was stirred at 20 °C for 12 h. The yellow solution was filtered, and the solvent was removed in vacuo to give a pale brown residue, which was washed with Et_2O and dried in vacuo to give a white solid. Yield: 0.30 g (90%). Anal. Calcd for $C_{21}H_{38}B_2F_8IrN_2OP$: C, 34.48; H, 5.23; N, 3.83. Found: C, 34.60; H, 5.42; N, 3.91. ^1H NMR (CD_3CN, 20 °C, 300 MHz): δ 6.07, (br, 4H, C_5H_4), 3.69 (m, 2H, CH_2O), 3.37 (s, 3H, CH_3), 2.75 (s, 6H, NCMe), 2.72 (m, 3H, CH, P^iPr_3), 2.61 (m, 2H, CH_2), 1.29 (m, 18H, P^iPr_3). $^{31}P\{^1H\}$ NMR (CD_3CN, 20 °C, 121.48 MHz): 29.24. $^{13}C\{^1H\}$ NMR plus APT (CD_3CN, 20 °C, 75.42 MHz): δ 128.3 (CN), 120.0 (ipso-C_5H_4), 82.9 (C_5H_4), 81.2 (C_5H_4), 70.5 (CH_2O), 59.3 (CH_3), 28.0 (d, J = 28.6, CH, P^iPr_3), 27.9 (CH_2), 20.0 (CH_3, P^iPr_3) 2.1 ($\mathit{C}H_3CN$).

Preparation of $[Ir(\eta^5\text{-}Cp^O)I]_2(\mu\text{-}H)(\mu\text{-}I)$ (9). $HSiEt_3$ (0.22 mL, 1.38 mmol) was added to a CH_2Cl_2 (20 mL) solution of **3** (0.40 g, 0.35 mmol) at 0 °C. The mixture was stirred for 1 h at 20 °C, and the CH_2Cl_2 was removed in vacuo. The residue was washed with pentane (2 × 20 mL) and Et_2O (20 mL) to yield a dark red solid. Yield: 0.23 g (65%). Anal. Calcd for $C_{16}H_{23}I_3Ir_2O_2$: C, 18.98; H, 2.29. Found: C, 19.10; H, 2.34. ^1H NMR (C_6D_6, 20 °C, 300 MHz): δ 5.41 (m, 2H, C_5H_4), 5.34 (m, 2H, C_5H_4), 5.09 (m, 2H, C_5H_4), 5.05 (m, 2H, C_5H_4), 3.28 (m, 4H, CH_2O), 3.00 (s, 6H, CH_3), 2.58 (m, 4H, CH_2), −16.28 (s, 1H, Ir−H−Ir). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, 75.42 MHz): δ 99.8 (ipso-C_5H_4), 81.5, 78.8, 77.7, and 76.8 (C_5H_4), 72.3 (CH_2O), 58.1 (CH_3), 28.6 (CH_2).

Preparation of $IrH_3(\eta^5\text{-}Cp^O)(SiEt_3)$ (10). $HSiEt_3$ (0.49 mL, 3.1 mmol) was added to a CH_2Cl_2 solution (40 mL) of **4** (0.30 g, 0.39 mmol). The mixture was stirred at 20 °C for 5 h. The solvent was removed in vacuo, and the residue was extracted with pentane (20 mL). The resulting solution was concentrated to 2 mL and passed through a silica gel column using toluene as eluent. The solvent was removed in vacuo to give an orange-red oil. Yield: 0.31 g (90%). Anal. Calcd for $C_{14}H_{29}IrOSi$: C, 38.77; H, 6.74. Found: C, 38.66; H, 6.68. ^1H NMR (C_7D_8, 20 °C, 300 MHz): δ 5.11−4.82 (AA′BB′, C_5H_4), 3.19 (t, 2H, J = 6.3, CH_2O), 3.07 (s, 3H, CH_3), 2.32 (t, 2H, J = 6.3, CH_2), 1.07 (t, 9H, J = 7.2, CH_3, Et_3Si),

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Table 1. Crystal Data and Data Collection and Refinement Details for 4, 8, and 9

	4	**8**	**9**
formula	$C_{16}H_{22}Cl_4Ir_2O_2$	$C_{21}H_{38}B_2F_8IrN_2OP$	$C_{16}H_{23}I_3Ir_2O_2$
mol wt	772.54	731.32	1012.44
color, habit	orange, irregular block	colorless, plate	dark red, needle
size, mm	0.20 × 0.10 × 0.06	0.20 × 0.20 × 0.12	0.14 × 0.04 × 0.02
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$C2/c$
a, Å	6.9056(6)	15.2590(9)	13.9744(13)
b, Å	6.8752(6)	8.6367(5)	14.0514(13)
c, Å	20.0834(17)	22.3225(13)	10.1937(10)
β, deg	91.1650(10)	108.0060(10)	96.276(2)
V, Å^3	953.31(14)	2797.7(3)	1989.6(3)
Z	2	4	4
D_c, g cm^{-3}	2.691	1.736	3.380
μ, mm^{-1}	14.513	4.900	18.024
2θ range, deg	3, 57	3, 57	3, 57
T, K	100.0(2)	100.0(2)	100.0(2)
no. of data collected	11 366	34 041	11 800
no. of unique data	2358 (R_{int} = 0.0409)	6950 (R_{int} = 0.0483)	2377 (R_{int} = 0.0513)
no. of params/restrains	110/0	334/0	108/0
R1^a ($F^2 > 2\sigma(F^2)$)	0.0234	0.0275	0.0295
wR2^b (all data)	0.0468	0.0545	0.0489
S^c (all data)	0.984	0.942	0.917

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $GOF = S = \{\sum[(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

0.87 (q, 6H, J = 7.2, CH_2, Et_3Si), −16.29 (s, 3H, Ir−H). ^{1}H NMR (C_7D_8, −80 °C, 300 MHz): δ −15.72 (t, 1H, J = 6.6, Ir−H), −16.25 (d, 2H, J = 6.6, Ir−H). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, 75.42 MHz plus HMQC): δ 106.9 (ipso-C_5H_4), 84.8 and 82.0 (C_5H_4), 76.0 (s, CH_2O), 58.1 (s, CH_3), 27.9 (s, CH_2), 14.3 (s, CH_2, Et_3Si), 9.7 (s, CH_3, Et_3Si). MS (FAB+): m/z 433 (M^+). IR (Nujol, cm^{-1}): ν(Ir−H) 2177 (m), 2198 (w).

Preparation of $IrH_2(\eta^5$-Cp$^O)(SiEt_3)_2$ (11). $HSiEt_3$ (1.5 mL, 10 mmol) was added to a CH_2Cl_2 suspension (4 mL) of **4** (0.30 g, 0.39 mmol). The mixture was stirred at 20 °C for 1 day. The solvent was removed in vacuo to give an oily residue, which was passed through a silica gel column using pentane as eluent. The solvent was removed in vacuo to give a red oil. Yield: 0.17 g (78%). Anal. Calcd for $C_{20}H_{43}IrOSi_2$: C, 43.84; H, 7.90. Found: C, 43.38; H, 7.58. ^{1}H NMR (C_6D_6, 20 °C, 300 MHz): δ 4.96−4.74 (AA′BB′, C_5H_4), 3.17 (t, 2H, J = 6.6, CH_2O), 3.04 (s, 3H, CH_3), 2.43 (t, 2H, J = 6.6, CH_2), 1.05 (t, 18H, J = 7.2, CH_3, Et_3Si), 0.88 (q, 12H, J = 7.2, CH_2, Et_3Si), −17.20 (s, 2H, Ir−H). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, 75.42 MHz): δ 106.10 (ipso-C_5H_4), 88.5 and 82.3 (C_5H_4), 74.6 (s, CH_2O), 58.1 (s, CH_3), 28.3 (s, CH_2), 13.1 (s, CH_2, Et_3Si), 9.1 (s, CH_3, Et_3Si). MS (FAB+): m/z 547 (M^+). IR (Nujol, cm^{-1}): ν(Ir−H) 2184 (m).

Reaction of 4 with $HSiEt_3$ at −40 °C. $HSiEt_3$ (0.25 mL, 1.56 mmol) was added to a CH_2Cl_2 solution (40 mL) of **4** (0.30 g, 0.39 mmol) at −40 °C. The mixture was stirred for 30 min. The solvent was removed in vacuo, and the oily residue was characterized by NMR as a mixture containing $IrH_2(\eta^5$-Cp$^O)Cl(SiEt_3)$ (**14**) as the major species (60%) together with **12** (20%) and **16** (20%). Data for **14**: ^{1}H NMR (CD_2Cl_2, 20 °C, 300 MHz) δ 5.72−5.00 (AA′BB′, C_5H_4), 3.56 (t, J = 5.7, 2H, CH_2O), 3.27 (s, 3H, CH_3), 2.51 (t, 2H, J = 5.7, CH_2), 0.93 (t, 9H, J = 7.2, CH_3, $SiEt_3$), 0.82 (q, 6H, J = 7.2, CH_2, $SiEt_3$), −12.70 (s, 2H, Ir−H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 75.43 MHz plus APT) δ 86.5 and 77.9 (C_5H_4), 71.4 (CH_2O), 58.7 (CH_3), 27.5 (CH_2), 13.2 (CH_2, Et_3Si), 9.0 (CH_3, Et_3Si).

The oily residue was washed with pentane (room temperature) and purified by passing through a silica gel column using toluene as eluent. The solvent was removed in vacuo to give a dark brown oil of $IrH(\eta^5$-Cp$^O)Cl_2(SiEt_3)$ (**12**). Yield: 0.07 g (18%). ^{1}H NMR (C_6D_6, 20 °C, 300 MHz): δ 5.62−5.38 (AA′BB′, C_5H_4), 3.18 (t, 2H, J = 6.3 Hz, CH_2O), 3.04 (s, 3H, CH_3), 2.43 (t, 2H, J = 6.3, CH_2), 1.38 (t, 9H, J = 7.2, CH_3, Et_3Si), 1.26 (q, 6H, J = 7.2, CH_2, Et_3Si), −17.92 (s, 1H, Ir−H). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, 75.42 MHz plus APT): δ 100.7 (ipso-C_5H_4), 81.3 and 79.9 (C_5H_4), 72.4 (CH_2O), 58.4 (CH_3), 27.6 (CH_2), 12.4 (CH_2, Et_3Si), 9.4 (CH_3, Et_3Si). MS (FAB+): m/z 502 (M^+). IR (Nujol, cm^{-1}): ν(Ir−H) 2208 (w).

Preparation of $[Ir(\eta^5$-Cp$^O)Cl]_2(\mu$-H$)(\mu$-Cl) (16). $HSiEt_3$ (0.12 mL, 0.76 mmol) was added to a CH_2Cl_2 (20 mL) solution of **4** (0.30 g, 0.39 mmol) at 0 °C. The mixture was stirred for 30 min, and the CH_2Cl_2 was removed in vacuo. The residue was washed with pentane (2 × 20 mL) and Et_2O (20 mL) to yield a dark red solid. Yield: 0.20 g (70%). Anal. Calcd for $C_{16}H_{23}Cl_3Ir_2O_2$: C, 26.02; H, 3.12. Found: C, 26.03; H, 3.06. ^{1}H NMR (CD_2Cl_2, 20 °C, 300 MHz): δ 5.66 (br, 6H, C_5H_4), 5.57 (m, 2H, C_5H_4), 3.65 (t, J = 5.7, 4H, CH_2O), 3.34 (s, 6H, CH_3), 2.58 (t, 4H, J = 5.7, CH_2), −13.20 (s, 1H, Ir−H−Ir). ^{1}H NMR (C_6D_6, 20 °C, 300 MHz): δ 5.23 (m, 2H, C_5H_4), 5.17 (m, 2H, C_5H_4), 5.13 (m, 2H, C_5H_4), 4.98 (m, 2H, C_5H_4), 3.31 (m, 4H, CH_2O), 2.97 (s, 6H, CH_3), 2.38 (m, 4H, CH_2), −13.10 (s, 1H, Ir−H−Ir). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 75.42 MHz): δ 101.7 (ipso-C_5H_4), 77.9, 76.5, 74.6, and 72.6 (C_5H_4), 71.2 (CH_2O), 58.5 (CH_3), 27.3 (CH_2).

Preparation of 10-d_x (x = 3, 7). An NMR tube containing a C_6D_6 solution (0.5 mL) of **10** (5 mg, 0.012 mmol) was heated at 80 °C for 1 day (x = 3) or 9 days (x = 7). The solvent was removed in vacuo to yield a dark red oil. Data for **10-d_3**: ^{2}H NMR (C_6H_6, 20 °C) δ −16.15 (3D, Ir-D). Data for **10-d_7**: ^{2}H NMR (C_6H_6, 20 °C) δ 5.09 and 4.79 (4D, C_5D_4), −16.15 (3D, Ir−D).

Preparation of 10-d_4. An NMR tube containing a C_6H_6 solution (0.5 mL) of **10-d_7** (5 mg, 0.012 mmol) was heated at 80 °C for 1 day. The solvent was removed in vacuo to yield a red oil. ^{2}H NMR (C_6H_6, 20 °C): δ 5.09 and 4.79 (4D, C_5D_4).

X-ray Analysis of 4, 8, and 9. Suitable crystals of complexes **4** and **8** were grown from diethyl ether/dichloromethane solutions, and crystals of complex **9** were obtained from diethyl ether solutions. The crystals of the complexes were mounted on the top of a glass fiber, and the data collections were carried out on a Bruker SMART CCD area diffractometer at 100 K (ω scans). Data were corrected for Lorentz and polarization effects, and absorption corrections were applied with the SADABS program.[24] Structures were solved by direct methods and subsequent difference Fourier syntheses using the program SHELXTL.[25] All non-hydrogen atoms were refined anisotropically, and H atoms were placed at calculated

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(24) Sheldrick, G. M. Program for Absorption Correction of Area Detector Frames; Bruker AXS Inc., Madison, WI, 1996.

(25) SHELXTL, version 6.02; Bruker AXS Inc., Madison, WI, 1999.

or observed positions and thereafter refined with $U_{iso}(H) = 1.2[U_{eq}(C)]$ or $U_{iso}(H) = 1.5[U_{eq}(C)]$ or freely (hydride ligand). Table 1 shows the crystal data and structural determination details for complexes **4**, **8**, and **9**.

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Supporting Information Available: Detailed X-ray crystallographic data (bond distances, bond angles, and anisotropic parameters) for **4**, **8,** and **9** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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