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Xantphos-Type Complexes of Group 9: Rhodium versus Iridium

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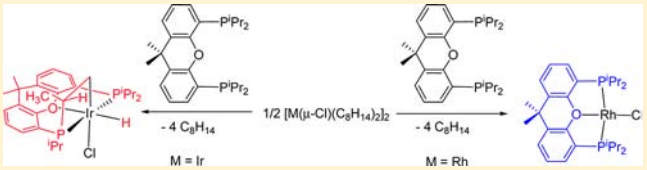
Supporting Information

ABSTRACT: Treatment of the dimer $[Rh(\mu\text{-Cl})(C_8H_{14})_2]_2$ (**1a**) with 9,9-dimethyl-4,5-bis(diisopropylphosphino)-xanthene [xant(P^iPr_2)$_2$] leads to the d^8 square-planar complex RhCl{xant(P^iPr_2)$_2$} (**2**), whereas reaction of the iridium counterpart $[Ir(\mu\text{-Cl})(C_8H_{14})_2]_2$ (**1b**) gives the d^6 octahedral compound IrHCl{xant(P^iPr_2)[^{i}PrPCH(Me)CH$_2$]} (**3**) as a result of the intramolecular C−H bond activation of one of the isopropyl substituents of the phosphine. Stirring **2** and **3** in 0.5 N KOH solutions of 2-propanol gives rise to the formation of hydrides RhH{xant(P^iPr_2)$_2$} (**4**) and IrH_3{xant(P^iPr_2)$_2$} (**5**), respectively. In *n*-octane at 60 °C, complex **2** is stable. However, compound **3** activates the alkane to give the *cis*-dihydride IrH_2Cl{xant(P^iPr_2)$_2$} (**6**) and a mixture of 3- and 4-octene. Complex **6** can be also obtained by the reaction of **3** with H_2. Under the same conditions, **2** affords the rhodium analogue RhH_2Cl{xant(P^iPr_2)$_2$} (**7**). Compounds **2**−**4** react with triflic acid (HOTf) to give RhHCl(OTf){xant(P^iPr_2)$_2$} (**8**), IrHCl(OTf){xant(P^iPr_2)$_2$} (**9**), and RhH_2(OTf){xant(P^iPr_2)$_2$} (**10**), respectively. The related iridium derivative IrH_2(OTf){xant(P^iPr_2)$_2$} (**11**) has also been prepared by the reaction of **6** with Tl(OTf). Complexes **2**, **6**, and **9** have been characterized by X-ray diffraction analysis. The {xant(P^iPr_2)$_2$}M skeleton is T-shaped with the metal center situated in the common vertex.

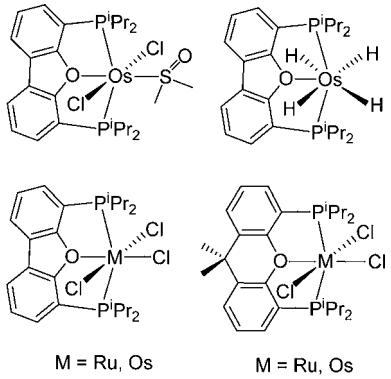


INTRODUCTION

We have been working on the chemistry of the fragments M(P^iPr_3)$_2$ (M = Ru, Os) for a long time, with the aim of designing metallic homogeneous systems that are effective in the synthesis of functionalized organic molecules from basic hydrocarbon units.[1] Because of its cone angle (160°) and basicity, triisopropylphosphine stabilizes saturated and unsaturated transition-metal complexes in low and high oxidation states. In bis(phosphine) compounds, the usual arrangement of this ligand is mutually trans. Thus, the M(P^iPr_3)$_2$ fragments leave available a wide region in the perpendicular plane to the P−M−P direction for the entry of organic substrates. In the search for more rigid and robust skeletons, but with similar properties, we have recently synthesized the POP[2] pincer ligands 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene [xant(P^iPr_2)$_2$] and 4,6-bis(diisopropylphosphino)dibenzofuran [dbf(P^iPr_2)$_2$],[3] which have been used to prepare osmium(II) and osmium(IV)[4] and osmium(III) and ruthenium(III)[3] compounds (Chart 1) from $OsCl_2(DMSO)_4$ and $MCl_3{\cdot}xH_2O$ (M = Os, Ru), respectively. Now, we have explored the entry to rhodium and iridium complexes with the xant(P^iPr_2)$_2$ ligand.

The chemistry of (POP)M complexes (M = Rh, Ir) is a little-known field in comparison with that based on the most common pincer groups consisting of either a metalated aryl ring in anionic PCP ligands[5] or uncharged PNP pyridines.[6] In 1976, Alcock and co-workers reported the first X-ray characterization of a rhodium complex. It contains the 1,5-bis(diphenylphosphino)-3-oxapentane ligand.[7] Subsequently, in 1999, the POP pincer coordination of 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (xantphos) was shown.[8]

Chart 1



Since 2008, several groups have investigated these types of compounds. Weller, Willis, and co-workers have developed catalysts for the hydroacylation of alkenes and alkynes that use bis(2-diphenylphosphinophenyl) ether (DPEphos), xantphos, and 1,5-bis(diphenylphosphino)-3-oxapentane to stabilize the key acyl hydride intermediates.[9] Haynes and co-workers have isolated an octahedral acetyl complex with the xantphos ligand coordinated in a pincer κ^3-POP fashion,[10] during the study of the mechanism of Rh-xantphos-catalyzed methanol carbonylation.[11] Julian and Hartwig have shown that a rhodium complex containing diaminophosphine, which binds in a κ^3-POP mode, is a highly active catalyst for the intramolecular

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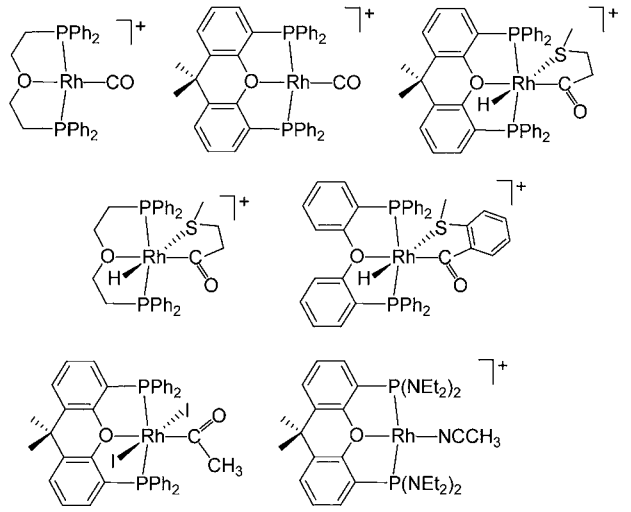
hydroamination of unprotected primary aminoalkenes.[12] In contrast to rhodium (Chart 2), a well-characterized iridium complex with POP ligands coordinated in a κ^3 fashion is extremely rare, with there being only a handful of xantphos examples.[13]

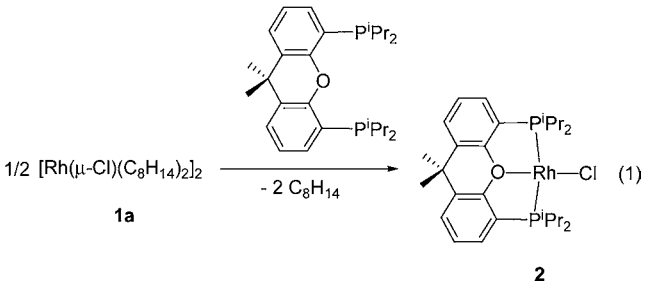
Chart 2



This paper reports entries to the rhodium and iridium chemistries, with the xant(P^iPr_2)$_2$ ligand acting as a pincer, and proves that there are notable differences in behavior between both elements.

RESULTS AND DISCUSSION

1. Starting Compounds. The M(P^iPr_3)$_2$ metal fragments (M = Rh, Ir) have shown to be useful templates for performing a lot of transformations involving C−C coupling reactions.[14] The starting point for rhodium chemistry was the highly reactive compound [RhCl(P^iPr_3)$_2$]$_n$, which is prepared from [Rh(μ-Cl)(C_8H_{14})$_2$]$_2$ (**1a**) and an excess of triisopropylphosphine.[15] The complex is monomeric in benzene[16] but dimeric in the solid state.[17] In light of this precedent, we started our work exploring a similar entry procedure (eq 1). Treatment of



n-octane suspensions of **1a** with 2.0 equiv of xant(P^iPr_2)$_2$, for 8 h, at 60 °C leads to RhCl{xant(P^iPr_2)$_2$} (**2**), which was isolated as a brown solid in almost quantitative yield and characterized by X-ray diffraction analysis.[18]

Figure 1 gives a view of the structure of **2**. The oxygen-donor atom of the POP ligand prevents the formation of a dimer. Thus, as expected, the {xant(P^iPr_2)$_2$}Rh skeleton is T-shaped, with the rhodium atom situated in the common vertex and P(1)−Rh−O, P(2)−Rh−O, and P(1)−Rh−P(2) angles of 83.44(9)°, 83.15(9)°, and 166.38(5)°, respectively. So, the

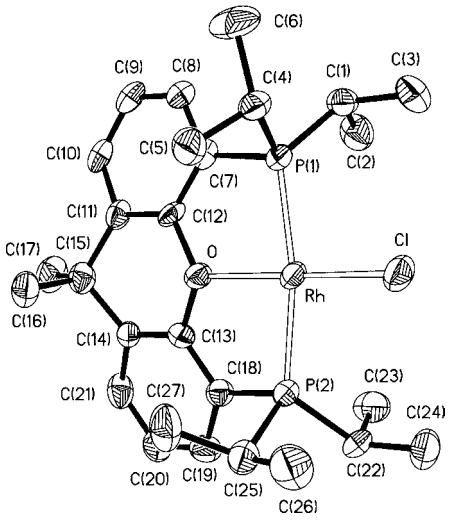


Figure 1. Molecular diagram of complex **2**. Selected bond lengths (Å) and angles (deg): Rh−Cl = 2.3017(14), Rh−O = 2.153(3), Rh−P(1) = 2.2396(14), Rh−P(2) = 2.2453(15); P(1)−Rh−O = 83.44(9), P(2)−Rh−O = 83.15(9), P(1)−Rh−P(2) = 166.38(5), O−Rh−Cl = 175.69(10).

coordination geometry around the metal center is almost square planar, with the chloride ligand trans-disposed to the oxygen atom [O−Rh−Cl = 175.69(10)°]. The greatest deviation from the best plane through the rhodium, chlorine, P(1), oxygen, and P(2) atoms is 0.0712(14) Å for oxygen. In agreement with the high symmetry of the molecule, the ^{1}H and ^{13}C{^{1}H} NMR spectra show two signals for the methyl groups of the phosphine isopropyl substituents ($\delta_{^1H}$, 1.26 and 1.66; $\delta_{^{13}C}$, 19.1 and 19.4) and a signal for the methyl substituents of the central heterocycle ($\delta_{^1H}$, 1.14; $\delta_{^{13}C}$, 32.7), whereas the ^{31}P{^{1}H} NMR spectrum contains at 36.1 ppm a doublet with a P−Rh coupling constant of 142 Hz.

Iridium is more reducing than rhodium and prefers to form saturated compounds. According to this, the iridium dimer [Ir(μ-Cl)(C_8H_{14})$_2$]$_2$ (**1b**) reacts with xant(P^iPr_2)$_2$ to afford a saturated d^6 species, in contrast to the rhodium dimer **1a**, which gives the unsaturated d^8 derivative complex **2**. Treatment of *n*-octane suspensions of **1b** with 2.0 equiv of the POP ligand, for 6 h, at 45 °C leads to IrHCl{xant(P^iPr_2)[^{i}PrPCH(Me)CH$_2$]} (**3**), which was isolated as a white solid in 60% yield, according to Scheme 1.

Complex **3** results from cyclometalation of an isopropyl substituent of the phosphine. A few cyclometalations at terminal alkyl groups have been recently reported.[19] Cyclometalation implies the concerted cis addition of a C−H bond of one of the methyl groups of an isopropyl substituent to the metal center of a square-planar IrCl{xant(P^iPr_2)$_2$} intermediate counterpart of **2**. The addition is a diasteroselective process with specific C−H bond orientation.[20] At first glance, complex **3** could be a mixture of the four stereoisomers shown in Scheme 1, and as a consequence of the chirality of the metal center, each one of them should have its corresponding enantiomer. In fact, the C−H bond activation could take place along the O−Ir−Cl axis with the hydrogen directed toward the oxygen of the phosphine or toward the chloride ligand. In the first case, hydride *trans*-chloride species should be formed, while in the second one, hydride *trans*-oxygen isomers could be obtained. Furthermore, because of the prochirality of the

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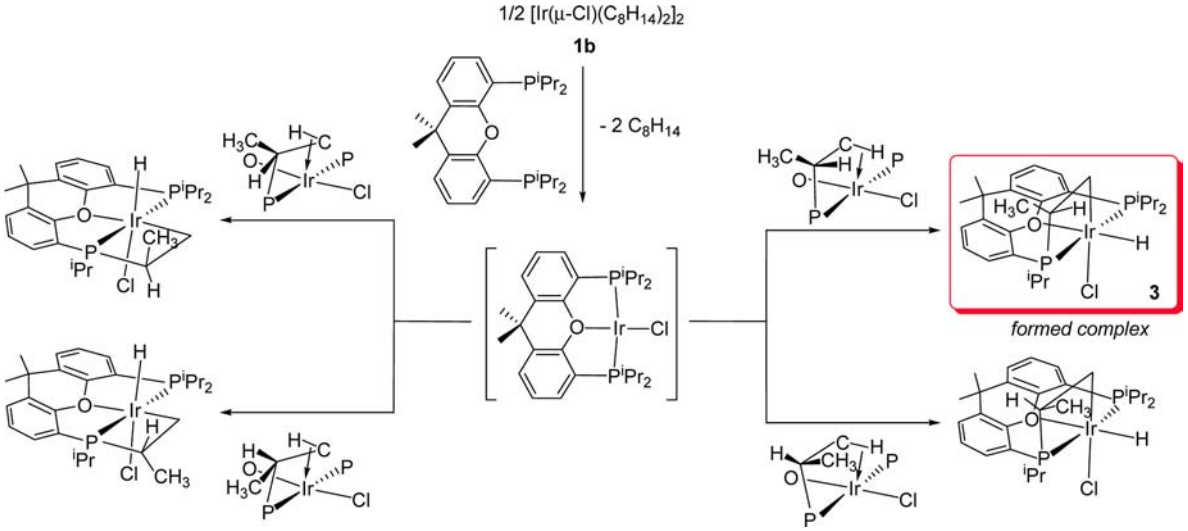
Scheme 1

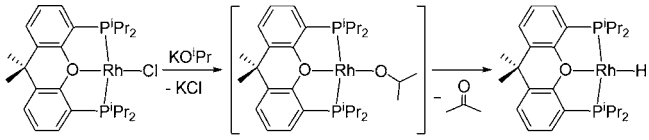


tertiary carbon atom of the isopropyl groups, two four-membered metalacycles are possible for each hydride position. The hydride ligand and the methyl substituent of the activated isopropyl group can lie on the same face or opposite faces of the metallacycle. However, in spite of the four possibilities, the ^{1}H NMR spectrum of the obtained solid, in benzene-d_6, at room temperature shows the exclusive formation of a single stereoisomer. The most noticeable resonances of the spectrum are as follows: that due to the hydride ligand, which appears at −25.70 ppm as a double doublet with both H−P coupling constants of 12 Hz and those corresponding to the PCH, $IrCH_2$, and CH_3 hydrogen atoms that are observed at 3.22, 2.56 and 0.22, and 0.54 ppm, respectively. The chemical shift of the hydride resonance, at noticeable high field, is consistent with the expected very weak trans influence of the ether unit of the phosphine, which is significantly lower than that of the chloride ligand. In this context, it should be mentioned that the chemical shifts of the hydride ligands trans-disposed to the oxygen atom of the phosphine, in the complexes of this study, range from −23.15 to −28.45 ppm, while the resonance corresponding to a hydride trans-disposed to chloride is observed at lower field than −22 ppm (vide infra). In agreement with the formation of a four-membered metalacycle containing the hydride ligand, the PCH hydrogen atom, and one of the diastereotopic hydrogen atoms of the metalated CH_2 group cis-disposed, irradiation of the hydride resonance increases the intensities of the signals at 3.22 (1.3%) and 2.56 (1.6%), whereas the nuclear Overhauser effect with the methyl substituent is not observed.

The ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra are also consistent with metalation of the phosphine.[21] The ^{13}C{^{1}H} NMR spectrum shows at −22.7 ppm a double doublet with C−P coupling constants of 26.0 and 4.2 Hz, due to the metalated carbon atom, whereas the ^{31}P{^{1}H} NMR spectrum contains an AB spin system centered at 11.1 ppm and defined by $\Delta\nu$ = 6000 Hz and J_{A-B} = 363 Hz, corresponding to the inequivalent phosphorus atoms.

2. Subtitution of the Chloride Ligand by Hydride. Stirring **2** in 0.5 N KOH−2-propanol solutions, at room temperature, produces the replacement of the chloride ligand by hydride. The resulting complex, RhH{xant(P^{i}Pr$_2$)$_2$} (**4**), is a notable example of a late-transition-metal unsaturated monohydride stable in alcohol.[22] Its formation implies an initial substitution of the chloride ligand of **2** by an isopropoxide group, generated in the basic medium, which undergoes β-elimination (Scheme 2).[23] Although the reaction is quantitative,

Scheme 2



complex **4** was isolated as a green solid in 69% yield. The presence of the hydride ligand is strongly supported by the ^{1}H NMR spectrum in benzene-d_6, at room temperature, which shows at −19.28 ppm a doublet triplet with H−Rh and H−P coupling constants of 34.4 and 21.5 Hz, respectively. Furthermore, both the ^{1}H and ^{13}C{^{1}H} NMR spectra reveal a high symmetry for the molecule, which is consistent with a square-planar geometry. Thus, in agreement with **2**, they contain two signals for the methyl groups of the phosphine isopropyl substituents ($\delta_{^1H}$, 1.12 and 1.44; $\delta_{^{13}C}$, 21.3 and 20.0) and a signal for the methyl substituents of the central heterocycle ($\delta_{^1H}$, 1.29; $\delta_{^{13}C}$, 31.6). The ^{31}P{^{1}H} NMR spectrum confirms the rhodium(I) monohydride nature of the species. Accordingly, it contains at 59.6 ppm a doublet with a P−Rh coupling constant of 168 Hz, which is split into a double doublet under off-resonance conditions.

The preparation of **4** in 2-propanol reveals a low capacity of the Rh{xant(P^{i}Pr$_2$)$_2$} metal fragment to stabilize saturated d^6 species, which could be formed from **4** by dehydrogenation of the alcohol.[24] This contrasts with the behavior of the iridium counterpart. Stirring **3** in 0.5 N KOH−2-propanol solutions, at room temperature, leads to the saturated d^6 trihydride IrH_3{xant(P^{i}Pr$_2$)$_2$} (**5**). Its formation, which agrees well with the higher reducing character of iridium and its preference for saturated species, probably involves demetalation of the phosphine to give the d^8 intermediate IrCl{xant(P^{i}Pr$_2$)$_2$}, which evolves into IrH{xant(P^{i}Pr$_2$)$_2$} in a manner similar to that of the rhodium counterpart **2**. In contrast to **4**, the iridium d^8 monohydride dehydrogenates 2-propanol to afford **5**. Although the transformation of **3** into **5** (eq 2) is quantitative,

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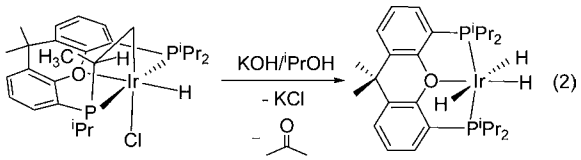


3 5

the white trihydride was isolated in low yield (about 30%) as a consequence of its high solubility in the usual organic solvents. The presence of three hydride ligands, two of them equivalent, in the complex is strongly supported by the ^{1}H NMR spectrum in benzene-d_6, at room temperature, which shows a double triplet at −8.67 ppm and a triple triplet at −28.45 ppm, in a 2:1 intensity ratio, with H−P coupling constants of 17.9 and 13.5 Hz, respectively, and a H−H coupling constant of 5.7 Hz. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 67.9 ppm.

3. C−H Bond Activation of *n*-Octane. The cyclometalated iridium complex **3** activates *n*-octane at 90 °C, to give the *cis*-dihydride derivative $IrH_2Cl\{xant(P^iPr_2)_2\}$ (**6**) and a mixture of 4-octene (major) and 3-octene (minor), in contrast to the rhodium(I) compound **2**, which is inert under the same conditions. The formation of **6** should involve a hydride alkyl intermediate, which undergoes a *β*-elimination reaction (Scheme 3). Its formation could take place by *σ*-bond metathesis on the metalated unit (pathway a) and/or initial demetalation by reductive elimination, to afford the iridium(I) species $IrCl\{xant(P^iPr_2)_2\}$, and subsequent C(sp^3)−H bond activation of the alkane (pathway b).

Complex **6** was isolated as a white solid in almost quantitative yield (about 95%) and characterized by X-ray diffraction analysis. Figure 2 shows a view of the molecule. Like in **2**, the $\{xant(P^iPr_2)_2\}M$ skeleton is T-shaped, with the metal situated in the common vertex. The P(1)−Ir−P(2), P(1)−Ir−O, and P(2)−Ir−O angles of 162.19(8)°, 83.04(14)°, and 82.86(14)° are consistent with the related parameters of **2**. The coordination geometry around the metal center can be rationalized as a distorted octahedron, with the chloride ligand trans-disposed to H(02) [Cl−Ir−H(02) = 163(4)°], while H(01) lies trans to the oxygen atom [H(01)−Ir−O = 171(4)°]. In agreement with the presence of two inequivalent hydride ligands in the molecule, the ^{1}H NMR spectrum in benzene-d_6, at room temperature, contains at −21.69 (trans to Cl) and −27.64 (trans to O) ppm double triplets with a H−H coupling constant of 8.9 Hz and H−P coupling constants of 16.3 and 12.5 Hz, respectively. According to equivalent phosphorus atoms, the ^{31}P{^{1}H} NMR spectrum shows a singlet at 51.3 ppm.

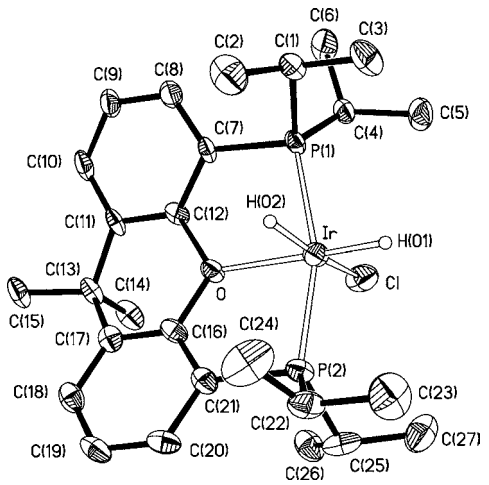
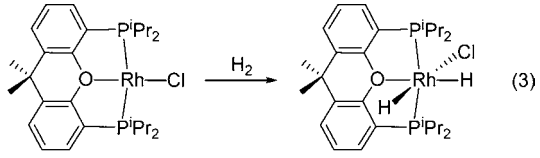


Figure 2. Molecular diagram of complex **6**. Selected bond lengths (Å) and angles (deg): Ir−Cl = 2.483(2), Ir−P(1) = 2.260(2), Ir−P(2) = 2.267(2), Ir−O = 2.251(5); P(1)−Ir−P(2) = 162.19(8), P(1)−Ir−O = 83.04(14), P(2)−Ir−O = 82.86(14), O−Ir−H(01) = 171(4), Cl−Ir−H(02) = 163(4).

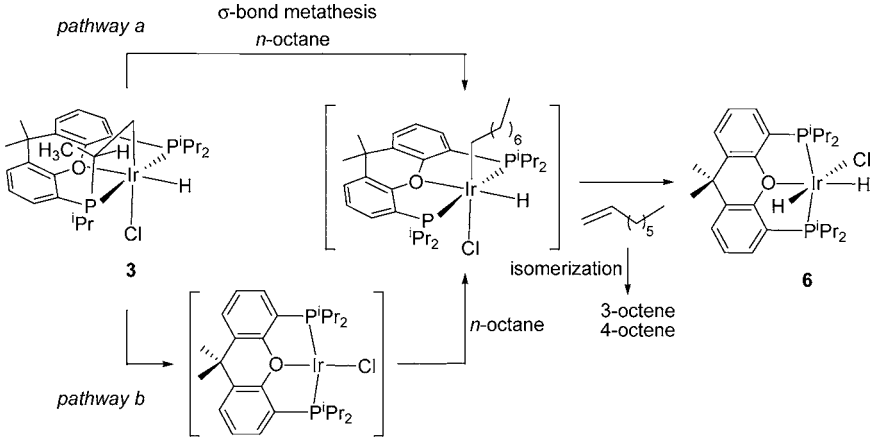
Complex **6** can also be obtained in almost quantitative yield by reaction of **3** with molecular hydrogen. The beige rhodium(III) counterpart complex $RhH_2Cl\{xant(P^iPr_2)_2\}$ (**7**) is similarly formed in 95% yield by stirring toluene solutions of **2** under atmosphere of hydrogen, at room temperature (eq 3).[18] In contrast to **2**, the related monohydride **4** is inert under



2 7

the same conditions. This suggests that the *π*-donor capacity of the chloride ligand is a determinant for the metal-to-hydrogen back-bonding in the dihydrogen intermediate of the oxidative addition process. In agreement with **6**, the ^{1}H NMR spectrum of **7** in benzene-d_6, at room temperature contains two hydride

Scheme 3



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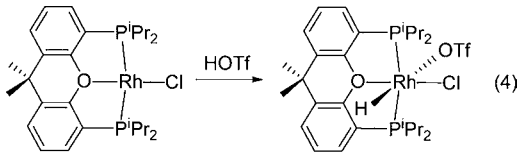
resonances at −17.43 (trans to Cl) and −20.02 (trans to O) ppm, which appear as double doublet of triplets with a H−H coupling constant of 9.6 Hz and H−P and H−Rh coupling constants of 15.0 and 14.0 Hz and of 24.5 and 23.8 Hz, respectively. The $^{31}P\{^{1}H\}$ NMR spectrum shows at 67.2 ppm a doublet with a P−Rh coupling constant of 113 Hz, which is about 30 and 50 Hz smaller than those of **2** and **4**, in agreement with oxidation of the metal center.

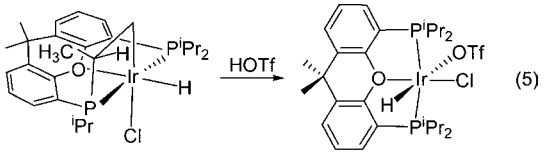
4. Brønsted Base Character of 2−4. Complex **2** shows the typical behavior of a Brønsted base in spite of its unsaturated character.[25] Thus, it undergoes protonation with triflic acid to give the hydride rhodium(III) complex RhHCl(OTf){xant(P^iPr_2)$_2$} (**8**), which is isolated as a white solid in 89% yield, according to eq 4. The presence of a hydride ligand



2 **8**

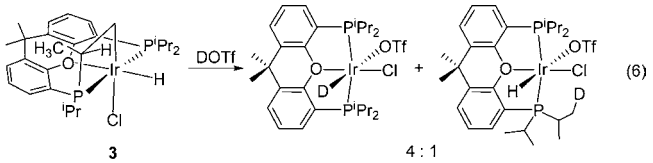
in the complex is strongly supported by the ^{1}H NMR spectrum in dichloromethane-d_2, at room temperature, which contains at −21.90 ppm a double triplet with H−P and H−Rh coupling constants of 11.4 and 26.1 Hz, respectively. The $^{31}P\{^{1}H\}$ NMR spectrum shows at 42.4 ppm a doublet with a P−Rh coupling constant of 99 Hz, which agrees well with that of **7** in accordance with the rhodium(III) nature of both compounds.

The metalated iridium(III) complex **3** also undergoes protonation with triflic acid, revealing a Brønsted base behavior. The addition of 1.0 equiv of the acid to dichloromethane solutions of the complex leads to IrHCl(OTf){xant(P^iPr_2)$_2$} (**9**), the iridium counterpart of **8**, which is isolated as a pale-yellow solid in 74% yield, according to eq 5.



3 **9**

Complex **3** has, at first glance, three nucleophilic sites: the metalated carbon atom, the metal center, and the hydride ligand. The attack of the proton of the acid to the metalated carbon atom should directly lead to **9**. The addition of the proton to the metal center should generate iridium(V) dihydride, which could undergo reductive elimination to afford **9**. Protonation of the hydride ligand should give a dihydrogen species, which could evolve into **9** by means of deprotonation of the coordinated hydrogen molecule with the metalated carbon atom. On the other hand, in view of Scheme 3, one could also think that the formation of **9** involves an initial demetalation of the phosphine to afford the square-planar species IrCl{xant(P^iPr_2)$_2$}, the iridium counterpart of **2**, which could add the acid as the latter. In this context, it should be noted that the π basicity of iridium is bigger than that of rhodium. In order to gain insight into the mechanism of protonation, we carried out the reaction of **3** with deuterated triflic acid. The formation of **9** by the direct protonation of **3** should put at least 50% of deuterium at the phosphine, while protonation of the square-planar species IrCl{xant(P^iPr_2)$_2$} should situate all deuterium at the hydride position. The reaction of **3** with deuterated triflic acid (eq 6) gives a 4:1



3 4 : 1 **9-d_1**

mixture of the deuteride complex IrDCl(OTf){xant(P^iPr_2)$_2$} and a related compound containing a deuterium atom at the isopropyl groups (**9**-d_1). This indicates that, although one cannot rule out the direct protonation of **3**, the formation of **9** mainly takes place through an initial demetalation of the phosphine followed by addition of the acid to the square-planar iridium(I) species. Equation 6 further proves that the metalated iridium(III) derivative **3** is a synthon of the square-planar iridium(I) species IrCl{xant(P^iPr_2)$_2$} (Scheme 1).

Complex **9** was characterized by X-ray diffraction analysis. The structure has two chemically equivalent but crystallografically independent molecules in the asymmetric unit. Figure 3

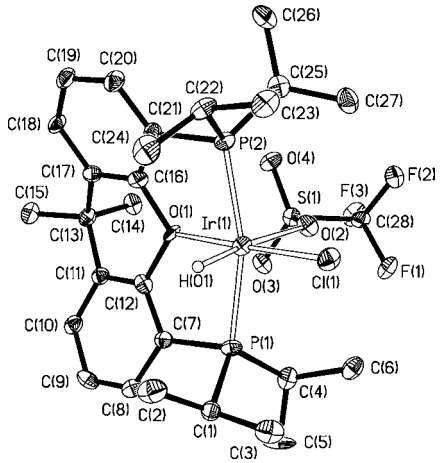


Figure 3. Molecular diagram of complex **9**. Selected bond lengths (Å) and angles (deg): Ir(1)−P(1) = 2.2931(16) and 2.2933(16), Ir(1)−P(2) = 2.2897(16) and 2.2966(15), Ir(1)−Cl(1) = 2.3159(15) and 2.3109(15), Ir(1)−O(1) = 2.142(4) and 2.137(4), Ir(1)−O(2) = 2.286(4) and 2.288(4); P(1)−Ir(1)−P(2) = 164.99(6) and 164.80(6), P(1)−Ir(1)−O(1) = 84.11(11) and 84.15(10), P(2)−Ir(1)−O(1) = 84.24(11) and 84.02(11), Cl(1)−Ir(1)−O(1) = 177.20(11) and 177.28(11), H(01)−Ir(1)−O(2) = 174(2) and 170(3)°.

shows a drawing of one of them. Like **2** and **6**, the {xant(P^iPr_2)$_2$}M skeleton is T-shaped, with the metal situated in the common vertex. In this case, the bite angles P(1)−Ir(1)−P(2), P(1)−Ir(1)−O(1), and P(2)−Ir(1)−O(1) are 164.99(6)° and 164.80(6)°, 84.11(11)° and 84.15(10)°, and 84.24(11)° and 84.02(11)°, respectively. The coordination geometry around the iridium atom can be described as a distorted octahedron, with the chloride ligand trans-disposed to the oxygen atom of the phosphine [Cl(1)−Ir(1)−O(1) = 177.20(11)° and 177.28(11)°] and the hydride trans-disposed to the trifluoromethanesulfonate group [H(01)−Ir(1)−O(2) = 174(2)° and 170(3)°].

The trans disposition of the added fragments suggests that the oxidative addition of the acid to the MCl{xant(P^iPr_2)$_2$} (M = Rh, Ir) species is certainly a two-step process, involving the

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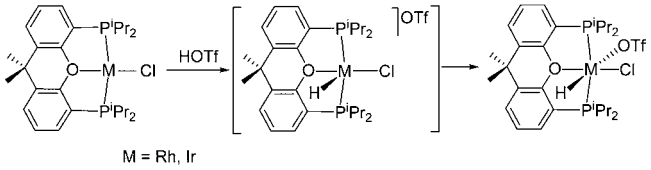
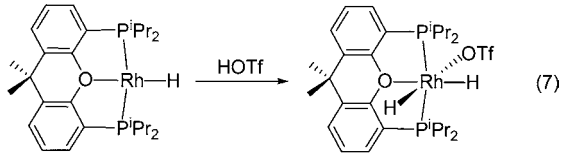
addition of the proton to the metal center to give a cationic five-coordinate monohydride intermediate that subsequently coordinates the trifluoromethanesulfonate anion (Scheme 4).

Scheme 4



The ^{1}H and ^{31}P{^{1}H} NMR spectra of **9** are consistent with Figure 3. Thus, the ^{1}H NMR spectrum in dichloromethane-d_2, at room temperature, contains a hydride resonance at −31.74 ppm, which appears as a triplet with a H−P coupling constant of 13.2 Hz. As expected for equivalent P^{i}Pr$_2$ groups, the ^{31}P{^{1}H} NMR spectrum shows a singlet at 23.9 ppm.

The monohydride **4** also has basic character, even though it does not add molecular hydrogen and does not dehydrogenate 2-propanol. Thus, in agreement with **2**, it reacts with triflic acid, in toluene, at room temperature to give the rhodium(III) derivative RhH$_2$(OTf){xant(P^{i}Pr$_2$)$_2$} (**10**) according to eq 7.



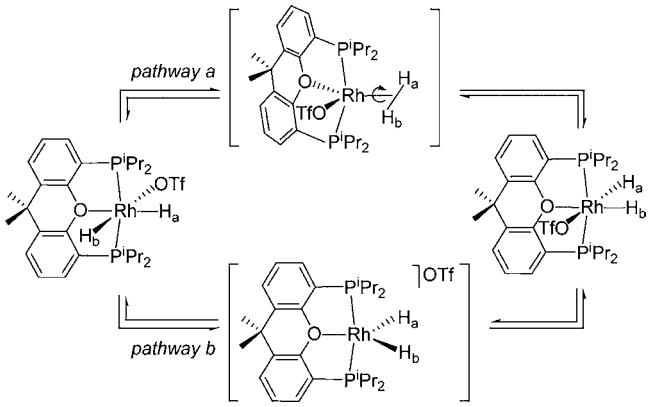
Although the reaction is quantitative, complex **10** was isolated as a yellow solid in moderate yield (about 55%) as a consequence of its high solubility in the usual organic solvents.

Complex **10** is the trifluoromethanesulfate counterpart of the chloride **7**. However, in solution, they show marked differences in behavior. In contrast to **7**, which displays a temperature-invariant ^{1}H NMR spectrum, the hydride resonances of **10** are temperature-dependent between 298 and 198 K. At 298 K, in dichloromethane-d_2, the spectrum shows a broad signal centered at −21.20 ppm. Between 277 and 253 K, decoalescense occurs, and at temperatures lower that 248 K, two resonances centered at −20.07 and −22.28 ppm are observed in agreement with the presence of two inequivalent hydride ligands in the molecule. In contrast to ^{1}H NMR, the ^{31}P{^{1}H} NMR spectrum is temperature-invariant between 298 and 198 K, showing at 64.8 ppm a doublet. In agreement with **7**, the H−H, H−P, H−Rh, and P−Rh coupling constants are 10.4, 12.5 and 14.7, 30.6 and 31.4, and 114 Hz, respectively.

The behavior of the ^{1}H NMR spectra with the temperature indicates a change in the disposition of the trifluoromethanesulfonate anion with regard to the hydride ligands, which is thermally activated. The phenomenon could occur by means of a site exchange of the hydride ligands through a dihydrogen intermediate or transition state (pathway a in Scheme 5) or alternatively by means of a rapid dissociation−coordination process involving the trifluoromethanesulfonate ligand (pathway b in Scheme 5).

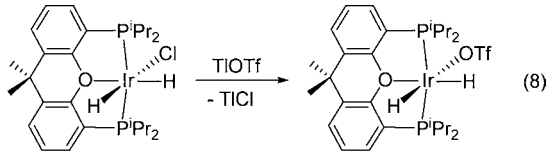
Line-shape analysis of the hydride region of the ^{1}H{^{31}P} NMR spectra (Figure 4) allows calculation of the rate constants for the phenomenon at each temperature. The activation parameters obtained from the corresponding Eyring analysis are

Scheme 5



$\Delta H^{\ddagger}$ = 15.5 ± 0.8 kcal·mol^{-1} and $\Delta S^{\ddagger}$ = 15.7 ± 1.9 cal·mol^{-1}·K^{-1}. The significantly positive value of the entropy of activation is consistent with the dissociation−coordination mechanism shown in pathway b of Scheme 5.

Complex **10** can also be obtained by the reaction of **7** with thallium(I) trifluoromethanesulfonate. Similarly, treatment of tetrahydrofuran solutions of **6** with 1.5 equiv of the thallium salt leads to the iridium counterpart IrH$_2$(OTf){xant(P^{i}Pr$_2$)$_2$} (**11**), which was isolated as a yellow solid in 82% yield (eq 8). As



expected for the higher tendency of iridium to stabilize saturated species, the structure of **11** is rigid in solution. Thus, in contrast to **10**, the ^{1}H NMR spectrum of **11** in dichloromethane-d_2, at room temperature, contains at −23.15 and −28.17 ppm two hydride resonances, which are temperature-invariant and appear as double triplets with a H−H coupling constant of 8.7 Hz and H−P coupling constants of 16.5 and 12.4 Hz, respectively. The ^{31}P{^{1}H} NMR spectrum shows at 50.4 ppm a singlet.

CONCLUDING REMARKS

This study shows an entry to the rhodium and iridium chemistry with the pincer POP ligand 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene and reveals marked differences in behavior between both metals, which are the result of the higher reducing character and preference for saturated compounds of iridium. The POP ligand reacts with the dimers [M(μ-Cl)(C$_8$H$_{14}$)$_2$]$_2$ (M = Rh, Ir) to afford d^8 square-planar species MCl{xant(P^{i}Pr$_2$)$_2$}, which can be transformed into the corresponding monohydrides. In contrast to the rhodium complexes, which are stable in the solid state, in alkanes and alcohols, the iridium counterparts have a marked tendency to activate C(sp^3)−H bonds, which prevents their isolation in the solid state and their existence in alkanes and alcohols. Thus, instead of the d^8 square-planar IrX{xant(P^{i}Pr$_2$)$_2$} (X = Cl, H) species, the d^6 octahedral complexes **3**, **6**, and **5** are isolated. In spite of this notable difference, both rhodium and iridium d^8 square-planar species are Brønsted bases, reacting with triflic acid to afford the corresponding d^6 complexes resulting from

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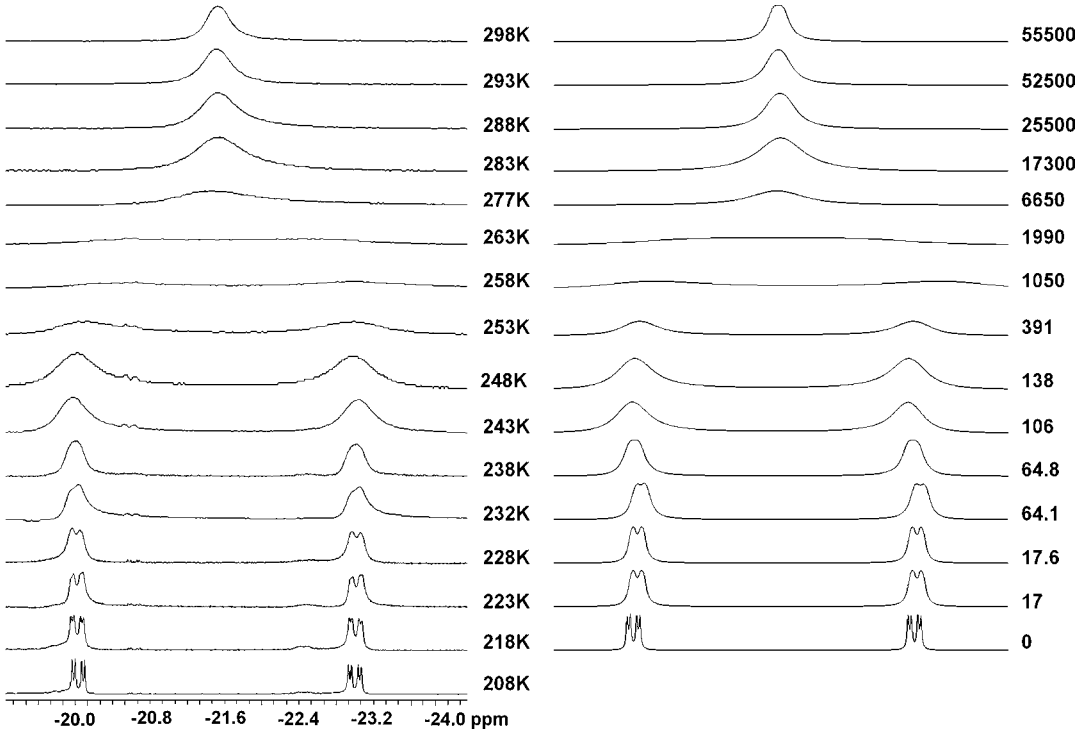

Figure 4. Left: Variable-temperature $^{1}H\{^{31}P\}$ NMR spectra (400 MHz, CD_2Cl_2) in the high-field region of complex **10**. Right: Simulated spectra. Rate constants (s^{-1}) for the hydride-exchange process are provided.

the trans addition of the acid to the metal center. In this context, it should also be mentioned that the π basicity of the chloride ligand enhances the nucleophilicity of MX{xant-(P^iPr_2)$_2$} with regard to the hydride ligand. Thus, in contrast to **4**, complex **2** adds molecular hydrogen to give the d^8 dihydride derivative.

In conclusion, while the chemistry of rhodium with 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene is governed by d^8 square-planar complexes, that of iridium is centered on d^6 octahedral derivatives.

EXPERIMENTAL SECTION

General Information. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents (except *n*-octane, 2-propanol, and methanol, which were dried and distilled under argon) were obtained oxygen- and water-free from an MBraun solvent purification apparatus. ^{1}H, $^{31}P\{^{1}H\}$, ^{19}F, and $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker 300 ARX, Bruker Avance 300 MHz, Bruker Avance 400 MHz, and Bruker Avance 500 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H and $^{13}C\{^{1}H\}$), external 85% H_3PO_4 ($^{31}P\{^{1}H\}$), or external $CFCl_3$ (^{19}F). Coupling constants J and N are given in hertz. Attenuated total reflection infrared spectra of solid samples were run on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectrometry (HRMS) spectra were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany). [M(μ-Cl)(C_8H_{14})$_2$]$_2$ [M = Rh (**1a**), Ir (**1b**)][26] and xant(P^iPr_2)$_2$[3] were prepared by published methods.

Kinetic Analyses. The activation parameters for hydride exchange in complex **10** were obtained by $^{1}H\{^{31}P\}$ NMR spectral simulation. Experimental exchange-broadened line shapes were iteratively fit using the *gNMR*[27] program, with the line width in the absence of exchange fixed at the lowest measured values. The activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were obtained from a linear least-squares fit of $\ln(k/T)$ vs $1/T$ (the Eyring equation). Errors were computed by published methods.[28]

*Preparation of RhCl{xant(P^iPr_2)$_2$} (**2**).* xant(P^iPr_2)$_2$ (630 mg, 1.42 mmol) was added to a yellow suspension of [Rh(μ-Cl)(C_8H_{14})$_2$]$_2$ (**1a**) (550 mg, 0.70 mmol) in *n*-octane (6 mL), and the resulting mixture was heated at 60 °C for 8 h, obtaining a dark-reddish suspension. The mixture was cooled to room temperature, and the liquid phase was removed. The brown solid was washed with pentane (6 × 4 mL) and finally dried in vacuo. Yield: 823 mg (93%). Anal. Calcd for $C_{27}H_{40}ClOP_2Rh$: C, 55.82; H, 6.94. Found: C, 55.66; H, 6.92. HRMS (electrospray). Calcd for $C_{27}H_{40}OP_2Rh$ ([M − Cl]$^+$): m/z 547.1775. Found: m/z 547.1760. IR (cm^{-1}): ν(C−O−C) 1099 (m). ^{1}H NMR (500.13 MHz, C_6D_6, 293 K): δ 7.24 (ddvt, J_{H-H} = 7.5 Hz, J_{H-H} = 1.5 Hz, N = 5.9, 2H, C*H* arom), 6.95 (dd, J_{H-H} = 7.5 Hz, J_{H-H} = 1.5 Hz, 2H, C*H* arom), 6.80 (t, J_{H-H} = 7.5 Hz, 2H, C*H* arom), 2.48 (m, 4H, PC*H*(CH_3)$_2$), 1.66 (dvt, J_{H-H} = 7.2 Hz, N = 16.1, 12H, PCH(CH_3)$_2$), 1.26 (dvt, J_{H-H} = 7.0 Hz, N = 14.3, 12H, PCH(CH_3)$_2$), 1.14 (s, 6H, CH_3). $^{13}C\{^{1}H\}$ NMR (125.77 MHz, C_6D_6, 293 K): δ 158.4 (vt, N = 16.7, *C* arom), 131.2 (s, *C* arom), 130.8 (s, CH arom), 127.5 (s, CH arom), 125.4 (dvt, N = 15.6, J_{C-Rh} = 1.5 Hz, *C* arom), 124.7 (vt, N = 4.2, CH arom), 33.8 (s, C(CH_3)$_2$), 32.7 (s, C(CH_3)$_2$), 26.4 (dvt, J_{C-Rh} = 1.0 Hz, N = 19.2, PCH(CH_3)$_2$), 19.4 (vt, N = 7.9, PCH(CH_3)$_2$), 19.1 (vt, N = 3.6, PCH(CH_3)$_2$). $^{31}P\{^{1}H\}$ NMR (161.98 MHz, C_6D_6, 293 K): δ 36.1 (d, J_{P-Rh} = 142.4 Hz).

*Preparation of IrHCl{xant(P^iPr_2)[^{i}PrPCH(Me)CH_2]}(**3**).* xant(P^iPr_2)$_2$ (296 mg, 0.67 mmol) was added to an orange suspension of [Ir(μ-Cl)(C_8H_{14})$_2$]$_2$ (**1b**) (300 mg, 0.33 mmol) in *n*-octane (5 mL), and the resulting mixture was heated at 45 °C for 6 h, affording a dark solution with a white precipitate. The mixture was cooled to room temperature, and the liquid phase was removed. The white solid was washed with pentane (6 × 3 mL) and finally dried in vacuo. Yield: 269 mg (60%). Anal. Calcd for $C_{27}H_{40}ClIrOP_2$: C, 48.39; H, 6.02. Found: C, 48.07; H, 6.24. HRMS (electrospray). Calcd for $C_{27}H_{41}ClIrOP_2$ ([M + H]$^+$): m/z 671.1938. Found: m/z 671.1933. IR (cm^{-1}): ν(Ir−H) 2221 (w); ν(C−O−C) 1091 (m). ^{1}H NMR (500.13 MHz, C_6D_6, 293 K): δ 7.21 (ddd, J_{H-P} = 7.0 Hz, J_{H-H} = 7.0 Hz, J_{H-H} = 1.6 Hz, 1H, C*H* arom), 7.13 (ddd, J_{H-P} = 7.7 Hz, J_{H-H} = 7.7 Hz, J_{H-H} = 1.7 Hz, 1H, C*H* arom), 7.10 (dd, J_{H-H} = 7.2 Hz, J_{H-H} = 1.7 Hz, 1H, C*H* arom), 7.06

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(dd, J_{H-H} = 7.7 Hz, J_{H-H} = 1.1 Hz, 1H, C*H* arom), 6.96 (dd, 1H, J_{H-H} = 7.3 Hz, J_{H-H} = 7.3 Hz, PC*H* arom), 6.91 (dd, 1H, J_{H-H} = 7.4 Hz, J_{H-H} = 7.4 Hz, C*H* arom), 3.22 (m, 1H, PC*H*(CH_3)CH_2Ir), 3.09 (m, 1H, PC*H*(CH_3)$_2$), 2.56 (ddd, J_{H-P} = 27.0 Hz, J_{H-H} = 9.0 Hz, J_{H-H} = 3.2 HZ, 1H, PCH(CH_3)CH_2Ir), 2.39 (m, 1H, PC*H*(CH_3)$_2$), 2.31 (m, 1H, PC*H*(CH_3)$_2$), 1.59 (dd, J_{H-P} = 16.2 Hz, J_{H-H} = 7.8 Hz, 3H, PCH(CH_3)$_2$), 1.48 (dd, J_{H-P} = 15.5 Hz, J_{H-H} = 7.0 Hz, 3H, PCH(CH_3)$_2$), 1.44 (dd, J_{H-P} = 17.8 Hz, J_{H-H} = 7.6 Hz, 3H, PCH(CH_3)$_2$), 1.40 (s, 3H, C(CH_3)$_2$), 1.36 (dd, J_{H-P} = 16.2 Hz, J_{H-H} = 6.9 Hz, 3H, PCH(CH_3)$_2$), 1.33 (dd, J_{H-P} = 15.8 Hz, J_{H-H} = 6.7 Hz, 3H, PCH(CH_3)$_2$), 1.11 (s, 3H, C(CH_3)$_2$), 0.89 (dd, J_{H-P} = 15.8 Hz, J_{H-H} = 7.3 Hz, 3H, PCH(CH_3)$_2$), 0.54 (dd, J_{H-P} = 15.7 Hz, J_{H-H} = 7.1 Hz, 3H, PCH(CH_3)CH_2Ir), 0.22 (m, 1H, PCH(CH_3)CH_2Ir), −25.70 (dd, J_{H-P} = 12.0 Hz, J_{H-P} = 12.0 Hz, 1H, Ir−H). $^{13}C\{^1H\}$ NMR (125.76 MHz, C_6D_6, 293 K): δ 157.1 (dd, J_{C-P} = 9.2 Hz, J_{C-P} = 2.6 Hz, *C* arom), 156.7 (dd, J_{C-P} = 9.7 Hz, J_{C-P} = 2.4 Hz, *C* arom), 133.4 (d, J_{C-P} = 5.7 Hz, *C* arom), 132.9 (d, J_{C-P} = 5.3 Hz, *C* arom), 132.7 (d, J_{C-P} = 1.7 Hz, *C*H arom), 132.6 (d, J_{C-P} = 1.7 Hz, *C*H arom), 128.3 (s, *C*H arom), 127.7 (s, *C*H arom), 125.3 (d, J_{C-P} = 5.0 Hz, *C*H arom), 124.9 (d, J_{C-P} = 4.6 Hz, *C*H arom), 122.9 (s, *C* arom), 122.7 (s, *C* arom), 47.3 (dd, J_{C-P} = 30.5 Hz, J_{C-P} = 2.5 Hz, PCH(CH_3)CH_2Ir), 35.6 (s, C(CH_3)$_2$), 35.1 (s, C(CH_3)$_2$), 27.2 (dd, J_{C-P} = 22.2 Hz, J_{C-P} = 3.7 Hz, PCH(CH_3)$_2$), 26.1 (s, C(CH_3)$_2$), 25.8 (dd, J_{C-P} = 27.6 Hz, J_{C-P} = 2.7 Hz, PCH(CH_3)$_2$), 22.7 (dd, J_{C-P} = 22.2 Hz, J_{C-P} = 3.7 Hz, PCH(CH_3)$_2$), 22.6 (vt, *N* = 20, PCH(CH_3)CH_2Ir), 22.3 (d, J_{C-P} = 2.7 Hz, PCH(*C*H$_3$)$_2$), 20.9 (s, PCH(*C*H$_3$)$_2$), 20.4 (d, J_{C-P} = 5.5 Hz, PCH(*C*H$_3$)$_2$), 19.5 (s, PCH(*C*H$_3$)$_2$), 19.1 (d, J_{C-P} = 4.7 Hz, PCH(*C*H$_3$)$_2$), 19.0 (d, J_{C-P} = 2.6 Hz, PCH(*C*H$_3$)$_2$), −22.7 (dd, J_{C-P} = 26.0 Hz, J_{C-P} = 4.2 Hz, IrCH_2). $^{31}P\{^1H\}$ NMR (202.46 MHz, C_6D_6, 293 K): δ 11.1 (AB spin system, $\Delta\nu$ = 6000 Hz, J_{A-B} = 363 Hz).

*Reaction of **2** with KOH in 2-Propanol: Preparation of RhH{xant(P^{i}Pr$_2$)$_2$} (**4**).* **2** (127.2 mg, 0.22 mmol) was treated with a solution of KOH in 2-propanol (2 mL, 0.5 N). After stirring for 2 h at room temperature, the resulting suspension was evaporated to dryness to afford a dark-brown residue. The addition of toluene afforded a suspension, which was filtered through Celite to remove the potassium salts. The solution thus obtained was evaporated to dryness to afford a brown residue. The addition of 2-propanol afforded a very air-sensitive greenish solid, which was washed with 2-propanol (2 × 0.5 mL) and dried in vacuo. Yield: 82 mg (69%). HRMS (electrospray). Calcd for $C_{27}H_{42}OP_2Rh$ ($[M + H]^+$): *m*/*z* 547.1760. Found: *m*/*z* 547.1759. ^1H NMR (300.13 MHz, C_6D_6, 293 K): δ 7.32 (ddvt, J_{H-H} = 7.1 Hz, J_{H-H} = 2.6 Hz, *N* = 10.1, 2H, CH arom), 7.10 (dd, J_{H-H} = 7.7 Hz, J_{H-H} = 1.5 Hz, 2H, CH arom), 6.92 (t, J_{H-H} = 7.5 Hz, 2H, CH arom), 2.22 (m, 4H, PC*H*(CH_3)$_2$), 1.44 (dvt, J_{H-H} = 7.1 Hz, *N* = 16.5, 12H, PCH(*C*H$_3$)$_2$), 1.29 (s, 6H, CH_3), 1.12 (dvt, J_{H-H} = 7.0 Hz, *N* = 14.2, 12H, PCH(*C*H$_3$)$_2$), −19.28 (dt, J_{H-Rh} = 34.4 Hz, J_{H-P} = 21.5 Hz, 1H, Rh−H). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 293 K): δ 157.3 (vt, *N* = 17.0, C arom), 131.6 (vt, *N* = 5.2, C arom), 130.8 (s, CH arom), 128.5 (s, C arom), 126.8 (s, CH arom), 124.9 (s, CH arom), 34.5 (s, C(CH_3)$_2$), 31.6 (s, C(CH_3)$_2$), 27.0 (dvt, J_{C-Rh} = 3.1 Hz, *N* = 18.8, PCH(CH_3)$_2$), 21.3 (vt, *N* = 12.2, PCH(CH_3)$_2$), 20.0 (s, PCH(CH_3)$_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 293 K): δ 59.6 (d, J_{P-Rh} = 168.7).

*Reaction of **3** with KOH in 2-Propanol: Preparation of IrH$_3${xant(P^{i}Pr$_2$)$_2$} (**5**).* **3** (200 mg, 0.29 mmol) was treated with a solution of KOH in 2-propanol (2 mL, 0.5 N). After stirring for 4 h at room temperature, the resulting yellowish suspension was evaporated to dryness to afford a yellow residue. The addition of toluene afforded a suspension, which was filtered through Celite to remove the potassium salts. The solution thus obtained was evaporated to dryness to afford a yellow residue. The addition of cold methanol afforded a white solid, which was washed with further portions of cold methanol (2 × 0.5 mL) and dried in vacuo. ^1H and $^{31}P\{^1H\}$ NMR spectra show that the reaction is quantitative, but the obtained yield is very low because of the high solubility of the complex in cold methanol. Yield: 60 mg (31%). Anal. Calcd for $C_{27}H_{43}OP_2Ir$: C, 50.85; H, 6.80. Found: C, 50.90; H, 6.85. HRMS (electrospray). Calcd for $C_{27}H_{42}OP_2Ir$ ($[M - H]^+$): *m*/*z* 637.2336. Found: *m*/*z* 637.2399. IR (cm^{-1}): ν(Ir−H) 2059 (w), 1713 (w), ν(C−O−C) 1091 (s). ^1H NMR (500.13 MHz, C_6D_6, 293 K): δ 7.22 (ddvt, J_{H-H} = 7.7 Hz, J_{H-H} = 1.7 Hz, *N* = 8.7, 2H, C*H* arom), 6.90 (dd, J_{H-H} = 7.7 Hz, J_{H-H} = 1.7 Hz, 2H, C*H* arom), 6.88 (t, J_{H-H} = 7.7 Hz, 2H, C*H* arom), 2.08 (m, 4H, PC*H*(CH_3)$_2$), 1.41 (dvt, J_{H-H} = 7.0 Hz, *N* = 16.9, 12H, PCH(*C*H$_3$)$_2$), 1.15 (dvt, J_{H-H} = 7.1 Hz, *N* = 13.7, 12H, PCH(*C*H$_3$)$_2$), 1.14 (s, 6H, CH_3), −8.67 (dt, J_{H-H} = 5.7 Hz, J_{H-P} = 17.9 Hz, 2H, Ir−H), −28.45 (dt, J_{H-H} = 5.7 Hz, J_{H-P} = 13.5 Hz, 1H, Ir−H). $^{13}C\{^1H\}$ NMR (125.76 MHz, C_6D_6, 293 K): δ 156.7 (vt, *N* = 12.6, C_{arom}), 131.0 (vt, *N* = 5.2, C_{arom}), 130.4 (s, *C*H arom), 129.3 (vt, *N* = 29.4, C_{arom}), 127.3 (s, *C*H arom), 124.8 (vt, *N* = 5.0, *C*H arom), 34.1 (s, *C*(CH$_3$)$_2$), 32.4 (s, C(CH_3)$_2$), 28.7 (vt, *N* = 31.7, PCH(CH_3)$_2$), 21.5 (vt, *N* = 9.9, PCH(CH_3)$_2$), 19.8 (s, PCH(CH_3)$_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 293 K): δ 67.9 (s).

*Preparation of IrH$_2$Cl{xant(P^{i}Pr$_2$)$_2$} (**6**).* This complex can be prepared by two different methods. *Method a:* A yellowish suspension of **3** (50 mg, 0.07 mmol) in *n*-octane (0.5 mL) was heated at 90 °C for 8 h, affording a yellowish solution with a white precipitate. The mixture was cooled to room temperature, the liquid phase was removed via a cannula, and the $^{13}C\{^1H\}$ NMR spectrum of this solution was recorded. In addition to the peaks corresponding to *n*-octane, peaks assigned to 4-octene (130.1, =*C*H) and 3-octene (132.5 and 130.9, =*C*H) were observed. The white solid was washed with pentane (2 × 0.5 mL) and dried in vacuo. Yield: 45 mg (95%). *Method b:* A Schlenk flask provided with a Teflon closure was charged with **3** (100 mg, 0.15 mmol) dissolved in toluene (3 mL), and the argon atmosphere was replaced by a hydrogen atmosphere. After stirring for 1 h at room temperature, the resulting solution was filtered through Celite and evaporated to dryness. Pentane was added to afford a white solid, which was washed with pentane (1 × 2 mL) and dried in vacuo. Yield: 95 mg (94%). Anal. Calcd for $C_{27}H_{42}ClIrOP_2$: C, 48.24; H: 6.30. Found: C, 48.34; H, 6.65. HRMS (electrospray). Calcd for $C_{27}H_{42}IrOP_2$ ($[M - Cl]^+$) *m*/*z* 637.2336. Found: *m*/*z* 637.2487. IR (cm^{-1}): ν(Ir−H) 2180 (w), ν(C−O−C) 1099 (m). ^1H NMR (300.13 MHz, C_6D_6, 293 K): δ 7.19 (ddvtd, J_{H-H} = 7.8 Hz, J_{H-H} = 1.5 Hz, *N* = 7.0, 2H, C*H* arom), 7.02 (dd, 2H, J_{H-H} = 7.8 Hz, J_{H-H} = 1.5 Hz, C*H* arom), 6.91 (t, J_{H-H} = 7.8 Hz, 2H, C*H* arom), 2.94 (m, 2H, PC*H*(CH_3)$_2$), 2.03 (m, 2H, PC*H*(CH_3)$_2$), 1.62 (dvt, J_{H-H} = 7.3 Hz, *N* = 15.8, 6H, PCH(*C*H$_3$)$_2$), 1.53 (dvt, J_{H-H} = 7.0 Hz, *N* = 15.2, 6H, PCH(*C*H$_3$)$_2$), 1.32 (s, 3H, CH_3), 1.24 (dvt, J_{H-H} = 7.4 Hz, *N* = 16.0, 12H, PCH(*C*H$_3$)$_2$), 1.13 (s, 3H, CH_3), 0.77 (dvt, J_{H-H} = 6.7 Hz, *N* = 15.1, 3H, PCH(*C*H$_3$)$_2$), −21.69 (dt, J_{H-H} = 8.9 Hz, J_{H-P} = 16.3 Hz, 1H, Ir−H), −27.64 (dt, J_{H-H} = 8.9 Hz, J_{H-P} = 12.5 Hz, 1H, Ir−H). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 293 K): δ 157.3 (vt, *N* = 12.2, C_{arom}), 132.5 (vt, *N* = 5.2, C_{arom}), 131.3 (s, *C*H arom), 127.7 (s, CH arom), 127.5 (vt, *N* = 31.6, C_{arom}), 125.2 (vt, *N* = 5.0, CH arom), 34.9 (s, C(CH_3)$_2$), 34.8 (s, C(CH_3)$_2$), 28.3 (vt, *N* = 26.6, PCH(CH_3)$_2$), 26.9 (s, C(CH_3)$_2$), 26.5 (vt, *N* = 34, PCH(CH_3)$_2$), 22.4 (s, PCH(CH_3)$_2$), 21.2 (vt, *N* = 9.4, PCH(*C*H$_3$)$_2$), 19.9 (s, PCH(*C*H$_3$)$_2$), 19.7 (vt, *N* = 4.2, PCH(CH_3)$_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 293 K): δ 51.3 (s).

*Reaction of **2** with Hydrogen: Preparation of RhH$_2$Cl{xant(P^{i}Pr$_2$)$_2$} (**7**).* A Schlenk flask provided with a Teflon closure was charged with **2** (100 mg, 0.17 mmol) and toluene (3 mL), and the argon atmosphere was replaced by a hydrogen atmosphere. After stirring for 1 h at room temperature, the resulting solution was filtered through Celite and evaporated to dryness. Pentane was added to afford a beige solid, which was washed with pentane (2 × 1 mL) and dried in vacuo. Yield: 95 mg (95%). Anal. Calcd for $C_{27}H_{42}ClOP_2Rh$: C, 55.63; H, 7.26. Found: C, 55.25; H, 7.18. HRMS (electrospray). Calcd for $C_{27}H_{42}OP_2Rh$ ($[M - Cl]^+$): *m*/*z* 547.1760. Found: *m*/*z* 547.1757. IR (cm^{-1}): ν(Rh−H) 2063 (w), ν(C−O−C) 1096 (m). ^1H NMR (400.16 MHz, C_6D_6, 293 K): δ 7.15 (ddvt, J_{H-H} = 7.4 Hz, J_{H-H} = 1.5 Hz, *N* = 7.1, C*H* arom), 7.07 (dd, J_{H-H} = 7.5 Hz, J_{H-H} = 1.5 Hz, 2H, C*H* arom), 6.92 (t, J_{H-H} = 7.6 Hz, 2H, C*H* arom), 2.78 (m, 2H, PC*H*(CH_3)$_2$), 2.07 (m, 2H, PC*H*(CH_3)$_2$), 1.63 (dvt, J_{H-H} = 7.4 Hz, *N* = 16.1, 6H, PCH(*C*H$_3$)$_2$), 1.55 (dvt, J_{H-H} = 7.1 Hz, *N* = 15.8, 6H, PCH(*C*H$_3$)$_2$), 1.33 (s, 3H, CH_3), 1.21 (dvt, J_{H-H} = 7.5 Hz, *N* = 16.4, 6H, PCH(*C*H$_3$)$_2$), 1.13 (s, 3H, CH_3), 0.79 (dvt, J_{H-H} = 7.1 Hz, *N* = 15.6, 6H, PCH(*C*H$_3$)$_2$), −17.43 (ddt, J_{H-Rh} = 24.5 Hz, J_{H-H} = 9.6 Hz, J_{H-P} = 15.0 Hz, 1H, Rh−H), −20.02 (ddt, J_{H-Rh} = 23.8 Hz, J_{H-H} = 9.6 Hz, J_{H-P} = 14.0 Hz, 1H, Rh−H). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6,

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293 K): δ 156.1 (vt, N = 13.6, C arom), 132.6 (vt, N = 5.3, C arom), 131.0 (s, CH arom), 127.6 (s, CH arom), 125.8 (vt, N = 24.1, C arom), 124.8 (s, CH arom), 35.0 (s, $C(CH_3)_2$), 34.6 (s, $C(CH_3)_2$), 28.8 (vt, N = 22.6, $PCH(CH_3)_2$), 26.7 (s, $C(CH_3)_2$), 26.3 (dvt, J_{Rh-C} = 3 Hz, N = 27.9, $PCH(CH_3)_2$), 22.2 (s, $PCH(CH_3)_2$), 20.8 (vt, N = 10.6, $PCH(CH_3)_2$), 20.0 (vt, N = 4, $PCH(CH_3)_2$), 19.9 (s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.99 MHz, C_6D_6, 293 K): δ 67.2 (d, J_{P-Rh} = 113.8 Hz).

*Protonation of **2** with HOTf: Preparation of RhHCl(OTf){xant-(P^{i}Pr$_2$)$_2$} (**8**).* Triflic acid (32.5 μL, 0.37 mmol) was added to an orange suspension of **2** (213.6 mg, 0.37 mmol) in diethyl ether (5 mL) cooled at −78 °C. Immediately a white solid was formed, which was washed with diethyl ether (2 × 2.5 mL) and dried in vacuo. Yield: 240 mg (89%). Anal. Calcd for $C_{28}H_{41}ClF_3O_4P_2RhS$: C, 46.01; H, 5.65; S, 4.39. Found: C, 46.23; H, 5.41; S, 4.63. HRMS (electrospray). Calcd for $C_{27}H_{41}ClOP_2Rh$ ($[M - SO_3CF_3]^+$): m/z 581.1371. Found: m/z 581.1336. IR (cm^{-1}): ν(Rh−H) 2172 (w), ν(C−O−C) 1086 (m). ^1H NMR (300.13 MHz, CD_2Cl_2, 293 K): δ 7.67 (ddvt, J_{H-H} = 7.2 Hz, J_{H-H} = 1.4 Hz, N = 10.9, 2H, CH arom), 7.63 (dd, J_{H-H} = 8.0 Hz, J_{H-H} = 1.4 Hz, 2H, CH arom), 7.39 (t, J_{H-H} = 7.2 Hz, 2H, CH arom), 3.16 (m, 2H, $PCH(CH_3)_2$), 2.94 (m, 2H, $PCH(CH_3)_2$), 1.83 (s, 3H, CH_3), 1.65 (dvt, J_{H-H} = 8.6 Hz, N = 17.1, 6H, $PCH(CH_3)_2$), 1.60 (dvt, J_{H-H} = 7.3 Hz, N = 14.1, 6H, $PCH(CH_3)_2$), 1.51 (dvt, J_{H-H} = 7.5 Hz, N = 15.9, 6H, $PCH(CH_3)_2$), 1.43 (s, 3H, CH_3), 1.10 (dvt, J_{H-H} = 7.9 Hz, N = 16.3, 6H, $PCH(CH_3)_2$), −21.91(dt, J_{H-Rh} = 26.1 Hz, J_{H-P} = 11.4 Hz, 1H, Rh−H). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 293 K): δ 158.0 (vt, N = 13.7, C arom), 133.3 (vt, N = 5.6, C arom), 130.9 (s, CH arom), 129.7 (s, CH arom), 126.8 (s, CH arom), 122.3 (vt, N = 29.3, C arom), 35.3 (s, $C(CH_3)_2$), 35.0 (s, $C(CH_3)_2$), 29.0 (vt, N = 21.1, $PCH(CH_3)_2$), 27.1 (s, $C(CH_3)_2$), 26.2 (vt, N = 27.6, $PCH(CH_3)_2$), 20.8, 20.1, 18.8, 18.2 (all s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 293 K): δ 42.4 (d, J_{P-Rh} = 99.0). ^{19}F NMR (282.34 MHz, CD_2Cl_2, 293 K): δ −78.7.

*Protonation of **3** with HOTf: Preparation of IrHCl(OTf){xant-(P^{i}Pr$_2$)$_2$} (**9**).* Triflic acid (16 μL, 0.18 mmol) was added to a yellow solution of **3** (120 mg, 0.18 mmol) in dichloromethane (2 mL) at room temperature. After 10 min, the solvent was removed to ca. 0.5 mL and pentane was added to afford a pale-yellow solid, which was washed with pentane (2 × 3 mL) and dried in vacuo. Yield: 109 mg (74%). Anal. Calcd for $C_{28}H_{41}ClF_3IrO_4P_2S$: C, 41.00; H, 5.04; S, 3.91. Found: C, 41.00; H, 4.89, S, 4.00. HRMS (electrospray). Calcd for $C_{27}H_{41}ClOP_2Ir$ ($[M - SO_3CF_3]^+$): m/z 671.1938. Found: m/z 671.2016. IR (cm^{-1}): ν(Ir−H) 2297 (w), ν(C−O−C) 1086 (m). ^1H NMR (300.13 MHz, CD_2Cl_2, 293 K): δ 7.68 (ddvt, J_{H-H} = 1.6 Hz, J_{H-H} = 3.9 Hz, N = 7.5, 2H, CH arom), 7.57 (dd, J_{H-H} = 7.1 Hz, J_{H-H} = 1.6 Hz, 2H, CH arom), 7.38 (dd, J_{H-H} = 7.1 Hz, J_{H-H} = 7.1 Hz, 2H, CH arom), 3.14 (m, 2H, $PCH(CH_3)_2$), 2.09 (m, 2H, $PCH(CH_3)_2$), 1.85 (s, 3H, CH_3), 1.62 (dvt, J_{H-H} = 7.1 Hz, N = 17.3, 6H, $PCH(CH_3)_2$), 1.58 (dvt, J_{H-H} = 7.0 Hz, N = 14.2, 6H, $PCH(CH_3)_2$), 1.49 (dvt, J_{H-H} = 7.2 Hz, N = 16.1, 6H, $PCH(CH_3)_2$), 1.43 (s, 3H, CH_3), 0.97 (dvt, J_{H-H} = 7.2 Hz, N = 16.4, 6H, $PCH(CH_3)_2$), −31.74 (t, J_{H-P} = 13.2 Hz, 1H, Ir−H). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 293 K): δ 160.6 (vt, N = 12.5, C_{arom}), 133.1 (vt, N = 5.6, C_{arom}), 131.0 (s, CH arom), 129.5 (s, CH arom), 127.3 (vt, N = 5.9, CH arom), 124.4 (vt, N = 36.6, C_{arom}), 35.4 (s, $C(CH_3)_2$), 35.1 (s, $C(CH_3)_2$), 29.2 (vt, N = 25.4, $PCH(CH_3)_2$), 26.7(s, $C(CH_3)_2$), 25.9 (vt, N = 33.1, $PCH(CH_3)_2$), 20.0, 19.7, 18.5, 18.2 (all s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 293 K): δ 23.9 (s). ^{19}F NMR (282.40 MHz, CD_2Cl_2, 293 K): δ −78.7 (s).

*Protonation of **3** with DOTf: Preparation of **9**-d_1.* Two NMR tubes were charged with **3** (30 mg, 0.045 mmol). To the first NMR tube was added 0.4 mL of dichloromethane and to the second 0.4 mL of dichloromethane-d_2. After that, DOTf (4 μL, 0.045 mmol) was added to each tube. ^2H NMR (61.42 MHz, CH_2Cl_2, 293 K): δ 1.49 (s, 0.2D, $PCH(CH_3)(CH_2D)$), −31.40 (br, 0.8D, Ir−D). ^1H NMR (400 MHz, CD_2Cl_2, 293 K, high-field region): δ −31.76 (br, 0.2H, Ir−H).

*Preparation of RhH$_2$(OTf){xant(P^{i}Pr$_2$)$_2$} (**10**).* This complex can be prepared by two different methods. *Method a:* Triflic acid (9.7 μL, 0.11 mmol) was added to a dark-brown solution of **4** (60 mg, 0.11 mmol) in toluene (2 mL) at room temperature. Immediately a pale-yellow solution was obtained. After 5 min, the solvent was removed and pentane was added to afford a pale-yellow solid, which was washed with pentane (2 × 2 mL) and dried in vacuo. Yield: 40 mg (53%). *Method b:* Thallium(I) trifluoromethanesulfonate (110 mg, 0.31 mmol) was added to a solution of **7** (140 mg, 0.24 mmol) in tetrahydrofuran (THF; 5 mL). After stirring for 18 h at room temperature, the resulting suspension was evaporated to dryness to afford a gray residue. The addition of toluene afforded a suspension, which was filtered through Celite to remove the thallium salts. The solution thus obtained was evaporated to dryness to afford a yellow residue. The addition of pentane afforded a yellow solid, which was washed with pentane (2 × 0.5 mL) and dried in vacuo. Yield: 92.0 mg (55%). Anal. Calcd for $C_{28}H_{42}F_3O_4P_2RhS$: C, 48.28; H, 6.08; S, 4.60. Found: C, 48.32; H, 6.20; S, 4.60. HRMS (electrospray). Calcd for $C_{27}H_{42}OP_2Rh$ ($[M - SO_3CF_3]^+$): m/z 547.1760. Found: m/z 547.1882. IR (cm^{-1}): ν(Rh−H) 2160(w), 2020 (w), ν(C−O−C) 1097 (m). ^1H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 7.62 (d, J_{H-H} = 7.6 Hz, 2H, CH arom), 7.53 (m, 2H, CH arom), 7.35 (t, J_{H-H} = 7.6 Hz, 2H, CH arom), 2.72 (m, 4H, $PCH(CH_3)_2$), 1.66 (s, 3H, CH_3), 1.32 (dvt, J_{H-H} = 7.2 Hz, N = 16.1, 12H, $PCH(CH_3)_2$), 1.07 (dvt, J_{H-H} = 7.3 Hz, N = 15.2, 12H, $PCH(CH_3)_2$), −21.20 (br, 2H, Rh−H). ^1H NMR (400.13 MHz, CD_2Cl_2, 198 K, high-field region): δ −20.07 (ddt, J_{H-Rh} = 30.6 Hz, J_{H-H} = 10.4 Hz, J_{H-P} = 12.5 Hz, 1H, Rh−H), −22.28 (ddt, J_{H-Rh} = 31.4 Hz, J_{H-H} = 10.4 Hz, J_{H-P} = 14.7 Hz, 1H, Rh−H). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 293 K): δ 157.4 (vt, N = 13.9, C_{arom}), 133.8 (vt, N = 4.8, C_{arom}), 130.4 (s, CH arom), 128.6 (s, CH arom), 125.4 (vt, N = 4.1, CH arom), 123.8 (vt, N = 26.6, C_{arom}), 35.4 (s, $C(CH_3)_2$), 34.4 (s, $C(CH_3)_2$), 27.3, 24.3 (both br, $PCH(CH_3)_2$), 22.7 (s, $C(CH_3)_2$), 22.0, 20.4, 19.6, 18.0 (all br s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.99 MHz, CD_2Cl_2, 298 K): δ 64.8 (d, J_{P-Rh} = 114 Hz). ^{19}F NMR (282.40 MHz, CD_2Cl_2, 293 K): δ −77.8 (s).

*Reaction of **6** with Thallium(I) Trifluoromethanesulfonate: Preparation of IrH$_2$(OTf){xant(P^{i}Pr$_2$)$_2$} (**11**).* Tl(OTf) (39 mg, 0.11 mmol) was added to a solution of **6** (47.2 mg, 0.07 mmol) in THF (5 mL). After stirring for 4 h at room temperature, the resulting suspension was evaporated to dryness to afford a gray residue. The addition of dichloromethane afforded a suspension, which was filtered through Celite to remove the thallium salts. The solution thus obtained was evaporated to dryness to afford a yellow residue. The addition of pentane afforded a yellow solid, which was washed with pentane (2 × 0.5 mL) and dried in vacuo. Yield: 45 mg (82%). Anal. Calcd for $C_{28}H_{42}F_3IrO_4P_2S$: C, 42.79; H, 5.39; S, 4.08. Found: C, 42.80; H, 5.30; S, 3.98. HRMS (electrospray). Calcd for $C_{27}H_{42}IrOP_2$ ($[M - SO_3CF_3]^+$): m/z 637.2336. Found: m/z 637.2394. IR (cm^{-1}): ν(Ir−H) 2236 (w), ν(C−O−C) 1092 (m). ^1H NMR (300.13 MHz, CD_2Cl_2, 293 K): δ 7.52 (d, J_{H-H} = 7.7 Hz, 2H, CH arom), 7.51 (m, 2H, CH arom), 7.29 (dd, J_{H-H} = 7.6 Hz, J_{H-H} = 7.6 Hz, 2H, CH arom), 2.88 (m, 2H, $PCH(CH_3)_2$), 2.38 (m, 2H, $PCH(CH_3)_2$), 1.82 (s, 3H, CH_3), 1.48 (dvt, J_{H-H} = 7.1 Hz, N = 15.4, 6H, $PCH(CH_3)_2$), 1.43 (s, 3H, CH_3) 1.36 (dvt, J_{H-H} = 7.4 Hz, N = 15.8, 6H, $PCH(CH_3)_2$), 1.24 (dvt, J_{H-H} = 6.8 Hz, N = 17.4, 6H, $PCH(CH_3)_2$), 0.73 (dvt, J_{H-H} = 7.0 Hz, N = 15.4, 6H, $PCH(CH_3)_2$), −23.15 (dt, J_{H-H} = 8.7 Hz, J_{H-P} = 16.3 Hz, 1H, Ir−H), −28.17 (dt, J_{H-H} = 8.7 Hz, J_{H-P} = 12.4 Hz, 1H, Ir−H). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 293 K): δ 157.7 (vt, N = 12.2, C_{arom}), 133.0 (vt, N = 5.5, C_{arom}), 131.3 (s, CH arom), 127.9 (s, CH arom), 126.8 (vt, N = 32.6, C_{arom}), 125.7 (vt, N = 5.7, CH arom), 35.3 (s, $C(CH_3)_2$), 34.6 (s, $C(CH_3)_2$), 28.4 (vt, N = 26.4, $PCH(CH_3)_2$), 27.0 (s, $C(CH_3)_2$), 26.6 (vt, N = 34.7, $PCH(CH_3)_2$), 21.7 (s, $PCH(CH_3)_2$), 21.2 (vt, N = 9.3, $PCH(CH_3)_2$), 19.7, 19.6 (both s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 293 K): δ 50.4 (s). ^{19}F NMR (282.40 MHz, CD_2Cl_2, 293 K): δ −81.3 (s).

*Structural Analysis of Complexes **2**, **6**, and **9**.* Crystals suitable for X-ray diffraction were obtained by cooling solutions in acetone (**2**), pentane (**6**), and dichloromethane (**9**). X-ray data were collected on a Bruker Smart APEX diffractometer equipped with a normal focus, 2.4 kW sealed-tube source (Mo radiation, λ = 0.71073 Å) operating at 50 kV and 30 (**6**) or 40 (**2** and **9**) mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s (30 s for **6**) covering 0.3° in ω. Data were corrected for

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absorption by using a multiscan method applied with the *SADABS* program.[29] The structures were solved by the Patterson (rhodium atom of **2** and iridium atoms of **6** and **9**) or direct methods and conventional Fourier techniques and refined by full-matrix least squares on F^2 with *SHELXL97*.[30] Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were observed or calculated and refined freely or using a restricted riding model. Hydride ligands were observed in the difference Fourier maps but refined with a restrained Ir−H bond length [1.59(1) Å, CSD]. For all structures, the highest electronic residuals were observed in close proximity of the metal centers and make no chemical sense.

Crystal Data for **2**: $C_{27}H_{40}ClOP_2Rh$, M_w = 580.89, orange, irregular block (0.16 × 0.10 × 0.04), monoclinic, space group $P2(1)/c$, a = 10.5402(17) Å, b = 16.299(3) Å, c = 16.600(3) Å, β = 105.855(2)°, V = 2743.3(8) Å^3, Z = 4, D_{calc} = 1.406 g cm^{-3}, $F(000)$ = 1208, T = 100(2) K, μ = 0.854 mm^{-1}. 31753 measured reflections (2θ = 3−57°; ω scans = 0.3°), 6524 unique (R_{int} = 0.1430); minimum/maximum transmission factors 0.723/0.938. Final agreement factors were R1 = 0.0496 [2964 observed reflections; $I > 2\sigma(I)$] and wR2 = 0.1006; data/restraints/parameters 6524/0/299; GOF = 0.826. Largest peak and hole 0.709 and −1.112 e Å^{-3}.

Crystal Data for **6**: $C_{27}H_{42}ClIrOP_2$, M_w = 672.20, colorless, prism (0.18 × 0.16 × 0.02), monoclinic, space group $C2/c$, a = 34.917(3) Å, b = 12.1423(10) Å, c = 14.2955(11) Å, β = 113.1140(10)°, V = 5574.3(8) Å^3, Z = 8, D_{calc} = 1.602 g cm^{-3}, $F(000)$ = 2688, T = 100(2) K, μ = 5.018 mm^{-1}. 32823 measured reflections (2θ = 2−57°; ω scans = 0.3°), 6685 unique (R_{int} = 0.0517); minimum/maximum transmission factors 0.465/0.906. Final agreement factors were R1 = 0.0586 [5037 observed reflections; $I > 2\sigma(I)$] and wR2 = 0.1189; data/restraints/parameters 6685/2/307; GOF = 1.234. Largest peak and hole 3.981 and −2.201 e Å^{-3}.

Crystal Data for **9**: $C_{28}H_{41}ClF_3IrO_4P_2S{\cdot}CH_2Cl_2$, M_w = 905.18, pale yellow, irregular block (0.24 × 0.20 × 0.06), triclinic, space group $P\bar{1}$, a = 13.6250(15) Å, b = 15.8477(18) Å, c = 16.5679(19) Å, α = 101.4220(10)°, β = 101.6680(10)°, γ = 90.3770(10)°, V = 3430.1(7) Å^3, Z = 4, D_{calc} = 1.753 g cm^{-3}, $F(000)$ = 1800, T = 100(2) K, μ = 4.330 mm^{-1}. 40404 measured reflections (2θ = 3−57°; ω scans = 0.3°), 15686 unique (R_{int} = 0.0685); minimum/maximum transmission factors 0.475/0.746. Final agreement factors were R1 = 0.0440 [10725 observed reflections; $I > 2\sigma(I)$] and wR2 = 0.0862; data/restraints/parameters 15686/8/803; GOF = 0.948. Largest peak and hole 1.597 and −1.365 e Å^{-3}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra of complex **4** and CIF files giving positional and displacement parameters, crystallographic data, and bond lengths and angles of compounds **2**, **6**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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