Perfluoroalkylation of Coordinated Ethene in Rh(I) and Ir(I) Complexes. Catalytic Addition of Iodoperfluoroalkanes to Ethene

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ABSTRACT: Complexes $[M(\eta^5\text{-Cp*})(\eta^2\text{-}C_2H_4)_2]$ (M = Rh, Ir) react with iodoperfluoroalkanes to give $[M(\eta^5\text{-Cp*})(CH_2CH_2R_F)(\mu\text{-}I)]_2$ (main product) and $[M(\eta^5\text{-Cp*})(CH_2CH_2R_F)(\mu\text{-}I)_2M(\eta^5\text{-Cp*})I]$ (R_F = *t*-C_4F_9, M = Ir; R_F = *c*-C_6F_{11}, M = Ir, Rh). Similarly, complexes $[M(\eta^5\text{-Cp*})(\eta^2\text{-}C_2H_4)(PPh_3)]$ react with iodoperfluoroalkanes to give $[M(\eta^5\text{-Cp*})(CH_2CH_2R_F)I(PPh_3)]$ (M = Ir, R_F = *t*-C_4F_9, *i*-C_3F_7; M = Rh, R_F = *t*-C_4F_9). Evidences of the generation of the heptafluoroisopropyl carbanion in the reaction of $[Ir(\eta^5\text{-Cp*})(\eta^2\text{-}C_2H_4)(PPh_3)]$ with I-*i*-C_3F_7 were obtained, which suggest that the reaction is initiated by the the transfer of two electrons from the Ir(I) complex to the iodoperfluoroalkane. The iodo-bridged complexes react with PPh_3 to give $[M(\eta^5\text{-Cp*})(CH_2CH_2R_F)I(PPh_3)]$ (M = Ir, R_F = *t*-C_4F_9, *c*-C_6F_{11}; M = Rh, R_F = *c*-C_6F_{11}). Complexes $[Ir(\eta^5\text{-Cp*})(CH_2CH_2R_F)I(PPh_3)]$ (R_F = *c*-C_6F_{11}, *i*-C_3F_7) react with AgOTf to give $[Ir(\eta^5\text{-Cp*})H(\eta^2\text{-}CH_2{=}CHR_F)(PPh_3)]OTf$. The analogous reaction of $[Ir(\eta^5\text{-Cp*})(CH_2CH_2\text{-}t\text{-}C_4F_9)I(PPh_3)]$ gives CH_3CH_2-*t*-C_4F_9 and $[Ir(\eta^5\text{-Cp*})(\eta^2\text{-}o\text{-}C_6H_4PPh_2)]OTf$, that reacts with PPh_3 to give $[Ir(\eta^5\text{-Cp*})(\eta^2\text{-}o\text{-}C_6H_4PPh_2)(PPh_3)]OTf$. This cyclometalated complex and its analogue $[Ir(\eta^5\text{-Cp*})(\eta^2\text{-}o\text{-}C_6H_4PPh_2)(P(p\text{-Tol})_3)]OTf$ are also prepared by reaction of $[Ir(\eta^5\text{-Cp*})(Me)Cl(PPh_3)]$ with AgOTf and PPh_3 or $P(p\text{-Tol})_3$. Derivatives $[Ir(\eta^5\text{-Cp*})(CH_2CH_2R_F)(PPh_3)L]OTf$ (L = CO, R_F = *c*-C_6F_{11}, *i*-C_3F_7; L = PPh_3, R_F = *i*-C_3F_7) are isolated in the reactions of the Ir hydrido alkene complexes with CO or PPh_3. The reactions of $[Rh(\eta^5\text{-Cp*})(CH_2CH_2R_F)I(PR_3)]$ (R = Me, R_F = *i*-C_3F_7, *n*-C_4F_9, *t*-C_4F_9; R = Ph, R_F = *i*-C_3F_7 *t*-C_4F_9, *c*-C_6F_{11}) with AgOTf afford unstable triflato complexes that decompose to give $CH_2{=}CHR_F$, but in the presence of PR_3 complexes $[Rh(\eta^5\text{-Cp*})(CH_2CH_2R_F)(PR_3)_2]OTf$ (R = Ph, R_F = *i*-C_3F_7, *t*-C_4F_9, *c*-C_6F_{11}; R = Me, R_F = *i*-C_3F_7, *t*-C_4F_9) were formed. When R = Ph, these complexes are unstable and decompose quantitatively to give $[Rh(\eta^5\text{-Cp*})H(PPh_3)_2]OTf$ and $CH_2{=}CHR_F$. Complexes of the type $[M(\eta^5\text{-Cp*})(\eta^2\text{-}C_2H_4)_2]$ (M = Rh or Ir) or $[Rh(\eta^5\text{-Cp*})(CH_2CH_2R_F)I(L)]$ are initiators for the radical addition of IR_F to ethene.

INTRODUCTION

The important applications of organofluorine compounds in medicinal[1] and agricultural chemistry[2] have strongly stimulated the search for efficient synthetic methods leading to fluorinated fine chemicals.[3,4] As a consequence of this impulse, many metal-mediated or -catalyzed perfluoroalkylation reactions have been developed during the last decade.[3,5] Among these reactions, the perfluoroalkylation of alkenes has received special attention, because the presence of a C=C bond in the substrate offers the opportunity to introduce further functionalization in combination with the perfluoroalkylation process.[6,7,8] Most metal-mediated or -catalyzed alkene perfluoroalkylation reactions are based on the generation of perfluoroalkyl radicals that add to the alkene C=C bond to give carbon-based radicals, which can evolve in different ways to originate different types of reaction products.[6,9-11] In general, the specific role of the metal species in these reactions is not clear. In most cases, it is assumed that the metal participates in the electron-transfer steps, facilitating the formation of the perfluoroalkyl radicals and the oxidation or reduction of radical or carbocationic intermediates.[7,9,12,13] Remarkably, organometallic intermediates have been proposed only in a few of these reactions. In some copper-catalyzed reactions, Cu(III) intermediates containing metal-bound vinyl and perfluoroalkyl groups have been suggested. These intermediates are supposed to afford the final perfluoroalkylated alkenes by a reductive elimination.[14,15] Also, intermediates of the type [M]-CHR-CH_2R_F (R_F = C_nF_{2n+1}) have been proposed in some Pd-[15-17] or Cu-catalyzed[18] reactions. These Heck-like intermediates would afford the perfluoroalkylated alkenes $RHC{=}CHR_F$ by β-hydride elimination.

The knowledge of the reactivity of alkene metal complexes and perfluoroalkylating agents, such as iodoperfluoroalkanes (IR_F), is expected to shed some light on the role of the metal catalysts in these reactions, and therefore to be helpful for the design of more efficient catalytic processes. However, very few studies of this reactivity have been reported. In this respect, Hughes and coworkers reported that complexes $[M(\eta^5\text{-Cp})_2(\eta^2\text{-}C_2H_4)]$ (M = Mo, W) react with IR_F (R_F = *i*-C_3F_7, *n*-C_4F_9, $CF_2C_6F_5$, C_6F_5) to afford different types of complexes resulting either from the oxidative addition to the metal, from perfluoro-alkylation or -arylation of a Cp ring, or from the perfluoroalkylation of the coordinated ethene.[19] We have reported the perfluoroalkylation of coordinated ethene in the reactions of $[Rh(\eta^5\text{-Cp*})(\eta^2\text{-}C_2H_4)_2]$ with IR_F (R_F = *i*-C_3F_7, *s*-C_4F_9, *t*-C_4F_9) to give complexes $[Rh(\eta^5\text{-Cp*})(CH_2CH_2R_F)(\mu\text{-}I)]_2$, or in the reactions of $[Rh(\eta^5\text{-Cp*})(\eta^2\text{-}C_2H_4)(PR_3)]$ with IR_F to give complexes $[Rh(\eta^5\text{-Cp*})(CH_2CH_2R_F)I(PR_3)]$ (R = Me, R_F = *i*-C_3F_7, *t*-C_4F_9, C_6F_5; R = Ph, R_F = *i*-C_3F_7, $CF_2C_6F_5$).[20] These reactions seem to

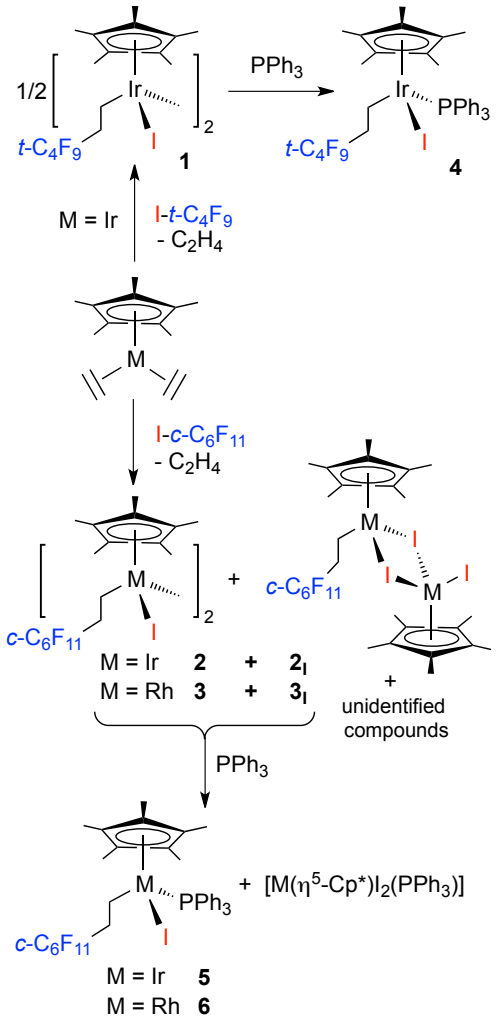
proceed by an unusual ionic mechanism in which a perfluoroalkyl carbanion –which is generated by reaction of the iodoperfluoroalkane with the electron-rich metal centers– attacks the coordinated alkene.[19,20] With these precedents, we became interested in investigating if Ir(I) ethene complexes would show a similar reactivity to their Rh(I) analogues, and if perfluoroalkylated alkenes can be formed in a stoichiometric or catalytic way from the resulting $[M]CH_2CH_2R_F$ complexes through β-hydride elimination reactions.[21,22] Thus, in this paper we report the results of the study of the reactivity of $[Ir(\eta^5\text{-Cp*})(\eta^2\text{-}C_2H_4)_2]$ and $[Ir(\eta^5\text{-Cp*})(\eta^2\text{-}C_2H_4)(PPh_3)]$ with primary, secondary or tertiary iodoperfluoroalkanes, and new reactions of their Rh(I) analogues with I-*c*-C_6F_{11} and I-*t*-C_4F_9. We also have studied β-hydride elimination reactions of the resulting $[M]CH_2CH_2R_F$ complexes that lead to alkenes of the type $CH_2{=}CHR_F$, and C–H activation reactions giving polyfluoroalkanes of the type $CH_3CH_2R_F$. Finally, we have studied the Rh- andr Ir-catalyzed reactions of ethene with iodoperfluoroalkanes which lead to products of the type $ICH_2CH_2R_F$. Evidences for a metal-initiated radical addition have been obtained.

RESULTS AND DISCUSSION

Reactions of Rh and Ir Ethylene Complexes with Perfluoroalkyl Iodides. The reaction of complex $[Ir(\eta^5\text{-Cp*})(\eta^2\text{-}C_2H_4)_2]$ with I-*t*-C_4F_9 in *n*-pentane gave ethene and $[Ir(\eta^5\text{-Cp*})(CH_2CH_2\text{-}t\text{-}C_4F_9)(\mu\text{-I})]_2$ (**1**) as a red precipitate (Scheme 1). Analogously, the reactions of $[Ir(\eta^5\text{-Cp*})(\eta^2\text{-}C_2H_4)_2]$ or $[Rh(\eta^5\text{-Cp*})(\eta^2\text{-}C_2H_4)_2]$ with I-*c*-C_6F_{11} gave the homologue complexes $[M(\eta^5\text{-Cp*})(CH_2CH_2\text{-}c\text{-}C_6F_{11})(\mu\text{-I})]_2$ (M = Ir (**2**), Rh (**3**)) as the main products, but in these cases the unsymmetrical iodo-bridged complex $[(\eta^5\text{-Cp*})IM(\mu\text{-I})_2M(\eta^5\text{-Cp*})(CH_2CH_2\text{-}c\text{-}C_6F_{11})]$ (M = Ir (**2_I**), Rh (**3_I**)) and minor amounts of unidentified byproducts were also formed. Compounds **2** and **3** could not be obtained free of **2_I** or **3_I** by crystallization, but the mixtures **2** + **2_I** and **3** + **3_I** were successfully used in the synthesis of pure derivatives containing phosphine ligands. Other investigated iodoperfluoroalkanes did not react with $[Ir(\eta^5\text{-Cp*})(\eta^2\text{-}C_2H_4)_2]$ (ICF_3 at 80 ºC, I-*n*-C_3F_7 at room temperature), or gave mixtures containing mainly $[Ir(\eta^5\text{-Cp*})I(\mu\text{-I})]_2$ (I-*i*-C_3F_7 or I-*s*-C_4F_9, both at room temperature).

The reaction of **1** with PPh_3 gave $[Ir(\eta^5\text{-Cp*})(CH_2CH_2t\text{-}C_4F_9)I(PPh_3)]$ (**4**) (Scheme 1). Analogously, the bridge-splitting reactions of the mixtures **2**+**2_I** or **3**+**3_I** gave compounds $[M(\eta^5\text{-Cp*})(CH_2CH_2c\text{-}C_6F_{11})I(PPh_3)]$ (M = Ir (**5**) or Rh (**6**)) together with the byproducts $[M(\eta^5\text{-Cp*})I_2(PPh_3)]$ (M = Ir or Rh). Compounds **4**–**6** were isolated in 43–78% yields by column chromatography.

Scheme 1



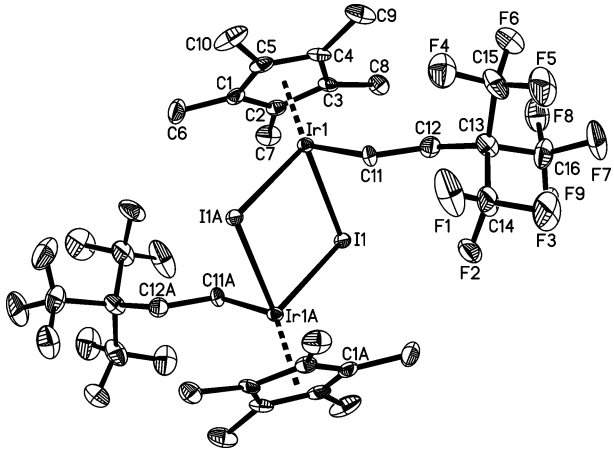
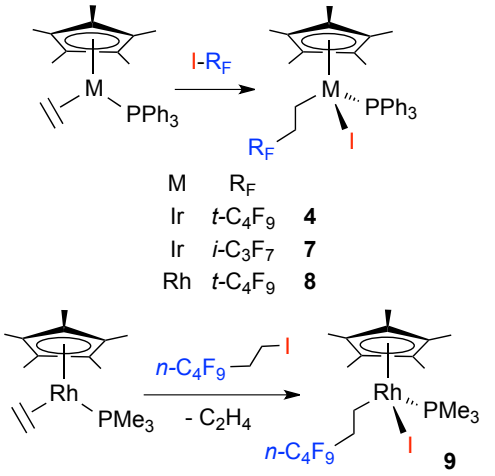


Figure 1. Crystal structure of **1** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Ir(1)–CNT1 (CNT1 = centroid of C1–5) 1.824 (4), Ir(1)–C(11) 2.176(9), Ir(1)–I(1) 2.7171(6), Ir(1)–I(1A) 2.7107(6), I(1)–Ir(1)–I(1A) 83.624(18), C(11)–Ir(1)–I(1) 88.8(2), C(11)–Ir(1)–I(1A) 86.6(2), Ir(1A)-I(1)-Ir(1) 96.378(17).

We have also explored the reactivity of complex [Ir(η^5-Cp*)(η^2-C_2H_4)(PPh_3)] toward different perfluoroalkyl iodides (Scheme 2). Thus, the reactions with I-*t*-C_4F_9 or I-*i*-C_3F_7 gave mainly compound **4**, which was identified by NMR, or [Ir(η^5-Cp*)(CH_2CH_2-*i*-C_3F_7)I(PPh_3)] (**7**), which was isolated in a 23% yield by column chromatography. The analogous reactions with ICF_3, I-*n*-C_3F_7, I-*s*-C_4F_9, or I-*c*-C_6F_{11} gave mixtures containing mainly [Ir(η^5-Cp*)I_2(PPh_3)]. In contrast, the reaction of the rhodium homologue [Rh(η^5-Cp*)(η^2-C_2H_4)(PPh_3)] with I-*t*-C_4F_9 gave [Rh(η^5-Cp*)(CH_2CH_2-*t*-C_4F_9)I(PPh_3)] (**8**), which was isolated in a 61% yield. A parallel behaviour has been previously observed in the analogous reactions between [Rh(η^5-Cp*)(η^2-C_2H_4)(PMe_3)] and IR_F (R_F = *i*-C_3F_7, *t*-C_4F_9 or C_6F_5).[20]

As the previousy reported reaction of I-*n*-C_4F_9 with [Rh(η^5-Cp*)(η^2-C_2H_4)(PMe_3)] gives mainly the oxidative addition product [Rh(η^5-Cp*)(*n*-C_4F_9)I(PMe_3)],[20] we prepared complex [Rh(η^5-Cp*)(CH_2CH_2-*n*-C_4F_9)(PMe_3)] (**9**) by reaction of [Rh(η^5-Cp*)(η^2-C_2H_4)(PMe_3)] with ICH_2CH_2-*n*-C_4F_9 (Scheme 2).

Scheme 2



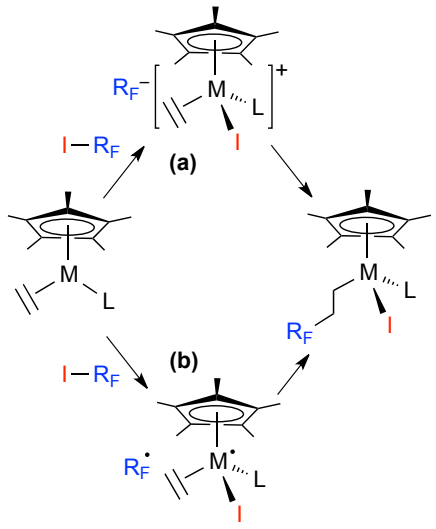
The identity of complexes **1**, **2**, and **3** was established on the basis of its ^1H, $^{13}C\{^1H\}$ and ^{19}F NMR data. Their signals appear in the same ranges than those previously reported for complexes [Rh(η^5-Cp*)($CH_2CH_2R_F$)(μ-I)]$_2$ (R_F = *i*-C_3F_7 or *s*-C_4F_9).[20] In particular, the ^1H NMR spectra shows characteristic signals for the methylenic protons, which appear as second-order multiplets in the range between 2.9 and 3.8 ppm. The presence of the perfluorocyclohexyl groups in complexes **2** and **3** was confirmed by their ^{19}F NMR spectra, which showed seven signals in both cases, in agreement with the C_{2h} symmetry of the complexes (see Supporting Information). In addition, the crystal structure of **1** was determined by single crystal X-ray diffraction, and shows a centrosymmetric iodo-bridged dimer with the pairs of η^5-Cp* and CH_2CH_2-*t*-C_4F_9 ligands mutually placed in *trans* (Figure 1). This disposition was also observed for complexes [Rh(η^5-Cp*)($CH_2CH_2R_F$)(μ-I)]$_2$ (R_F = *i*-C_3F_7, *s*-C_4F_9),[20] and is likely adopted to reduce the steric hindrance.

In the ^1H NMR spectra, complexes $\mathbf{2_I}$ and $\mathbf{3_I}$ gave two singlets corresponding to their inequivalent η^5-Cp* groups and a multiplet for the methylenic hydrogens. In the ^{19}F NMR spectra, the signals of $\mathbf{2_I}$ or $\mathbf{3_I}$ coincide with those of **2** or **3**. To confirm these assignments, NMR samples containing **2** and $\mathbf{2_I}$ or **3** and $\mathbf{3_I}$ in C_6D_6 were treated with [M(η^5-Cp*)I(μ-I)]$_2$ (M = Ir or Rh, respectively). As expected, an increase of the NMR signals assigned to the mixed complexes $\mathbf{2_I}$ and $\mathbf{3_I}$ was observed, which was produced by the cleavage of the iodo bridges of **2** or **3** and [M(η^5-Cp*)I(μ-I)]$_2$ and recombination of the resulting fragments.

Compounds **4**–**9** gave the expected signals in their ^1H or $^{31}P\{^1H\}$ NMR spectra, and their chemical shifts and coupling constants were similar to the corresponding values reported for complexes [Rh(η^5-Cp*)(CH_2CH_2-*i*-C_3F_7)I(PR_3)] (R = Me, Ph).[20] Acording to the lack of symmetry of these compounds, their ^1H spectra showed four second-order multiplets in the range from 1.56 to 3.74 ppm for the CH_2–CH_2 unit. For the same reason, all the fluorine nuclei of **5** and **6** (see Supporting Information) the CF_3 groups of **7** and the CH_2CF_2 group of **9** appeared inequivalent in their ^{19}F NMR spectra.

Our previous mechanistic studies of the reactions of [Rh(η^5-Cp*)(η^2-C_2H_4)(PMe_3)] with various secondary or tertiary iodoperfluoroalkanes showed that CH_3OD efficiently inhibits the perfluoroalkylation of coordinated ethene, giving DR_F as the main reaction product. This suggests an ionic mechanism (Scheme 3, pathway (a)), where the generated perfluoroalkyl anions can be trapped by a D^+ source. In contrast, the analogous reactions of [Rh(η^5-Cp*)(η^2-C_2H_4)$_2$] were not affected by methanol, but were inhibited by the radical scavenger 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), suggesting that in this case a radical mechanism could be the dominant one (Scheme 3, pathway (b)).[20]

Scheme 3

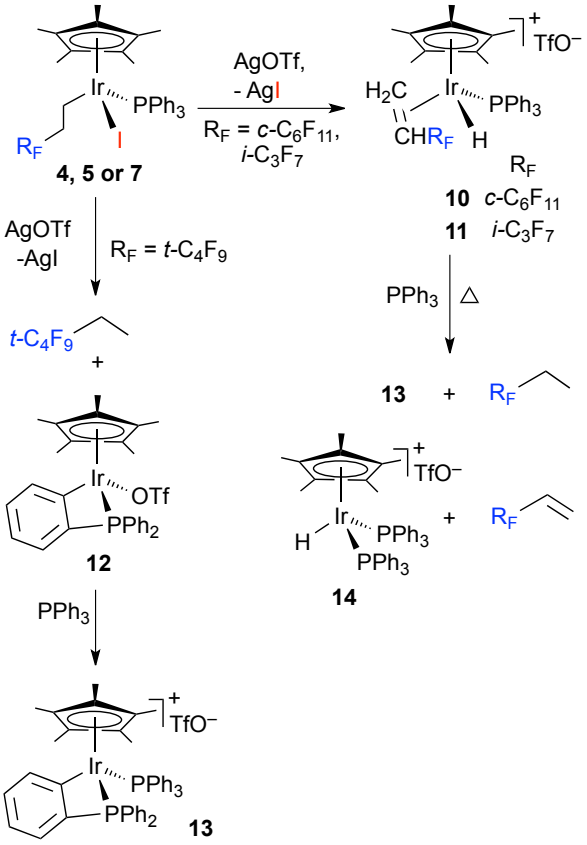


To get insight about the mechanism of the perfluoroalkylation reactions of [Ir(η^5-Cp*)(η^2-C_2H_4)(L)] by IR_F, we carried out representative reactions in the presence of CH_3OH or CH_3OD (2 equiv) using D_8-toluene as solvent. Thus, in analogy with the previous studies on Rh(I) complexes,[20] the reactions of [Ir(η^5-Cp*)(η^2-C_2H_4)(PPh_3)] with I-*i*-C_3F_7 and CH_3OX, gave X-*i*-C_3F_7 (X = H or D) almost quantitatively.[23] These results provide support to an ionic mechanism as the main reaction pathway (Scheme 3, pathway (a)). Moreover, the absence of DR_F among the products of the reactions performed in D_8-toluene with added CH_3OH suggests that free perfluoroalkyl radicals are not significantly involved in

these reactions, because perfluoroalkyl radicals are good hydrogen scavengers[10] and thus are expected to abstract a deuterium atom from D_8-toluene to give DR_F. These observations point to an ionic mechanism (Scheme 3, pathway (a)) in which a cationic Ir(III) ethene complex and a perfluoroalkyl anion are initially generated by reaction of the Ir(I) complexes with the IR_F. Addition of the perfluoroalkyl anion to the coordinated ethene molecule would afford the perfluoroalkylated complex. However, similar experiments carried out with other combinations of complex $[Ir(\eta^5\text{-Cp*})(\eta^2\text{-}C_2H_4)(L)]$ and IR_F (L = PPh_3, C_2H_4 and R_F = t-C_4F_9; L = C_2H_4 and R_F = c-C_6F_{11}) did not provide conclusive evidences of the anionic or radical nature of the mechanisms of these reactions.

Elimination of Perfluoroalkylated Organic Compounds in the Ir Complexes. The reaction of complexes **5** or **7** with AgOTf in CH_2Cl_2 gave AgI and complexes $[Ir(\eta^5\text{-Cp*})H(\eta^2\text{-}CH_2{=}CHR_F)(PPh_3)]OTf$ (R_F = c-C_6F_{11} (**10**), i-C_3F_7 (**11**)) (Scheme 4). These complexes were isolated as mixtures of two diastereomers, which arise from the coordination of the diastereotopic faces of the alkenes to the chiral metal fragment (see below). In contrast, the analogous reaction of complex **4** with AgOTf in CD_2Cl_2 gave CH_3CH_2-t-C_4F_9 and the previously reported cyclometalated complex $[Ir(\eta^5\text{-Cp*})(\eta^2\text{-}o\text{-}C_6H_4PPh_2)(OTf)]$ (**12**).[24] Addition of PPh_3 to this mixture gave complex $[Ir(\eta^5\text{-Cp*})(\eta^2\text{-}o\text{-}C_6H_4PPh_2)(PPh_3)]OTf$ (**13**), which was isolated and crystallographically characterized (see below).

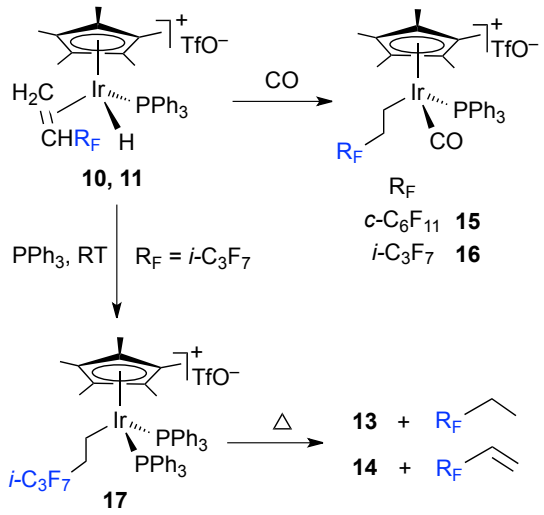
Scheme 4



After 10 hours in solution at room temperature, both **10** and **11** partially decomposed to give a mixture of products. Decomposition was complete on heating for 2 hours at 45 ºC. Among the decomposition products, complex **12**, and organic products $CH_3CH_2R_F$ and $CH_2{=}CHR_F$ (R_F = c-C_6F_{11}, i-C_3F_7) were detected. No hydride signals were observed in the ^1H NMR spectra of the reaction mixtures other than those of **10** or **11**, which suggests that the unstable hydrido complex formed after decoordination of the alkene evolve to give other products which could not be identified. In contrast, addition of PPh_3 to **11** and heating at 50 ºC for 15 h gave mainly complex **13** and CH_3CH_2-c-C_6F_{11}, along with minor amounts of $[Ir(\eta^5\text{-Cp*})H(PPh_3)_2]OTf$ (**14**) and $CH_2{=}CH_2$-c-C_6F_{11} (Scheme 4). The hydride **14** was identified by comparison of its NMR data with those reported for $[Ir(\eta^5\text{-Cp*})H(PPh_3)_2]BF_4$.[25]

The reactions of the diastereomeric pairs of **10** or **11** with CO quantitatively afforded complexes $[Ir(\eta^5\text{-Cp*})(CH_2CH_2R_F)(CO)(PPh_3)]OTf$ (R_F = c-C_6F_{11} (**15**), i-C_3F_7 (**16**), Scheme 5). The crystal structure of **16** supports the proposed structure (Figure 2).

Scheme 5



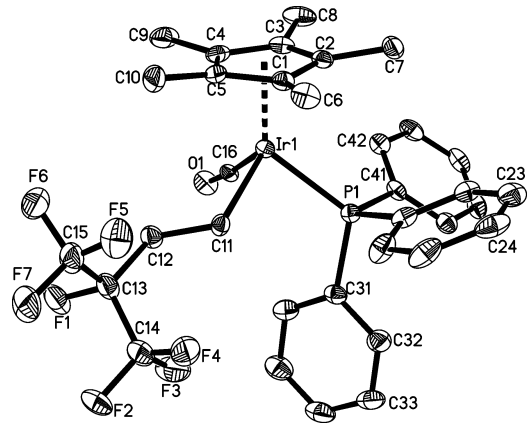


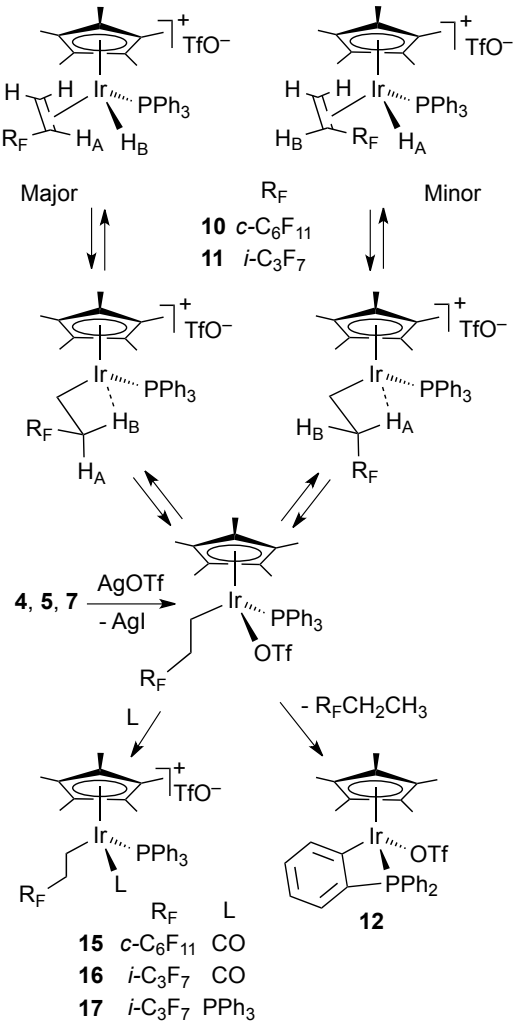
Figure 2. ORTEP representation (50% thermal ellipsoids) of the cation in the crystal structure of **16**. Selected bond lengths (Å) and angles (deg): Ir–CNT1 (CNT1 = centroid of C1–5) 1.9120(15), Ir(1)-C(16) 1.872(3), Ir(1)-C(11) 2.152(3), Ir(1)-P(1) 2.3240(8), C(16)-Ir(1)-C(11) 93.23(12), C(16)-Ir(1)-P(1) 94.54(10), C(11)-Ir(1)-P(1) 87.62(8).

Interestingly, when the reaction of both diastereomers of **11** with PPh_3 was carried out at room temperature for a shorter time (2 h), complex $[Ir(\eta^5\text{-}Cp^*)(CH_2CH_2\text{-}i\text{-}C_3F_7)(PPh_3)_2]OTf$ (**17**) was isolated in a 48% yield. The result of the thermal decomposition of **17** (CD_2Cl_2, 50 ºC) was analogous to that of the reaction of **11** with PPh_3, affording compounds **13**, $CH_3CH_2\text{-}i\text{-}C_3F_7$ (main products), **14** and $CH_2{=}CH\text{-}i\text{-}C_3F_7$.

The reactivity shown in Schemes 5 and 6 can be rationalized by considering that the reactions of **4**, **5** or **7** with AgOTf firstly afford the triflato complexes $[Ir(\eta^5\text{-}Cp^*)(CH_2CH_2R_F)(OTf)(PPh_3)]$ (R_F = *c*-C_6F_{11}, *i*-C_3F_7, *t*-C_4F_9) (Scheme 6). Owing to the poor donor ability of the triflate anion, these complexes are unstable and evolve in different ways depending on R_F. Thus, when R_F is *t*-C_4F_9, the triflato complex would undergo an intramolecular cyclometallation to give mainly $CH_3CH_2\text{-}t\text{-}C_4F_9$ and **12**, a reaction analogous to that observed for $[Ir(\eta^5\text{-}Cp^*)Me(OTf)(PPh_3)]$.[24] In contrast, when R_F is *c*-C_6F_{11} or *i*-C_3F_7, the intermediate triflato complex would evolve to the hydrido olefin complexes **10** or **11** through a β-agostic intermediate[22,26] (Scheme 6). This different behaviour is attributable to the greater bulkyness of the *t*-C_4F_9 substituent, which can effectively hinder the approach of the β-hydrogen atom to the metal center in the β-agostic complex. Nevertheless, compound **12** was also observed as one of the products resulting from the decomposition of **10** and **11**, and cyclometallation is the main decomposition pathway of these compounds in the presence of an extra equivalent of PPh_3. Formation of compounds **15–17** in the reactions of **10** and **11** with CO or PPh_3 can also be explained by considering that the formation of the hydrido olefin complexes is reversible. Thus, migratory insertion of the olefin into the Ir-H bond followed by coordination of the added ligand would give the observed products (Scheme 6).

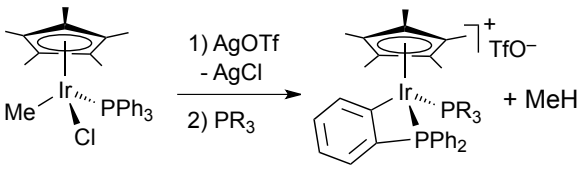
The diastereomeric ratios of **10** and **11** were 78:22 and 62:38, respectively, as determined by integration of their NMR spectra. The ^1H NMR spectra of **10** or **11** showed two signals in the hydride region: A broad singlet at –14.6 ppm and a doublet at –15.8 ppm, corresponding to the major and minor diastereomers, respectively. The broad singlet transformed into a doublet on cooling to 0 ºC. The J_{PH} values of the major diastereomers (26.5 and 25.6 Hz) were sligthly lower than those of the minor diastereomers (29.1 and 30.4 Hz), and both the δ and J_{PH} values are similar to those reported for related Ir complexes containing terminal hydrido ligands $[Ir(\eta^5\text{-}Cp)H(PPh_3)(C_2H_4)]^+$ (–15.60 ppm, 27 Hz),[27] $[Ir(\eta^5\text{-}Cp^*)H(PPh_3)_2]^+$ (–15.47 ppm, 27.8 Hz),[25] or $[Ir(\eta^5\text{-}Cp^*)H(PPh_3)(CO)]^+$ (–14.28 ppm, 26.1 Hz).[28] The instability of these hydrido olefin complexes in solution hampered their study by high temperature NMR spectroscopy, but mutual interconversion of the diastereomers at room temperature was observed in the NOESY spectra of both **10** and **11**, which showed EXSY peaks that correlate the major and minor diastereomers (see Supporting Information). This interconversion could take place through β-agostic complexes (Scheme 6) where the interaction of each of the two diastereotopic β-hydrogen atoms (H_A or H_B) with the metal would give a different diastereomer of the hydrido olefin complex. We could not obtain single crystals of these compounds for an X-ray crystal structure determination despite repeated attempts. However, (^{19}F, ^1H)-HOESY experiments revealed that, as expected on steric grounds, in both diastereomers of **10** and **11** the R_F group is oriented away from the PPh_3 ligand (Scheme 6), and that in the major diastereomers the R_F group is placed close to the methylic hydrogens of the Cp* ligand (see Supporting Information).

Scheme 6



Compound **13**, and its congener $[Ir(\eta^5\text{-}Cp^*)(\eta^2\text{-}o\text{-}C_6H_4PPh_2)\{P(p\text{-}Tol)_3\}]OTf$ (**18**) were synthesized more directly by the sequential reaction of $[Ir(\eta^5\text{-}Cp^*)(Me)Cl(PPh_3)]$ with AgOTf and PPh_3 or $P(p\text{-}Tol)_3$, respectively (Scheme 7). It is noteworthy that in **18** the $P(p\text{-}Tol)_3$ ligand is not cyclometalated. This suggests that the C-H activation step is previous to the coordination of the second phosphine and that the cyclometalated and the non-cyclometalated phosphine ligands do not undergo exchange.

Scheme 7



R = Ph (**13**), *p*-Tol (**18**)

In the crystal structure of **13** (Figure 4) the coordination environment of the Ir center is highly distored respect to a symmetrical piano-stool complex because of the formation of a four-membered metallacycle. The rigid disposition of the cyclometalated $P(C_6H_4)Ph_2$ ligand and the steric crowding can explain the slow rotation around the Ir–PPh_3 observed for both **13** and **18** by variable temperature ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (see Supporting Information). In addition, one of the phenyl rings of the PPh_3 ligand (labeled as C61–C66) is very close to the metallated ring and to one of the phenyl rings of the $Ph_2PC_6H_4$ ligand. In such disposition, the ortho hydrogens of this ring are placed very close to the nearby aromatic rings, as reflected by the short distances between these hydrogen atoms and the centroids of the phenyl rings. This would explain the slow rotation around one of the P–Ar bonds observed in the low-temperature ^1H NMR spectra of **13** and **18** and the unusually low chemical shift values of the *ortho* protons of this Ph ring, which appear in the range from 4.9 to 6.1 ppm (see Supporting Information).

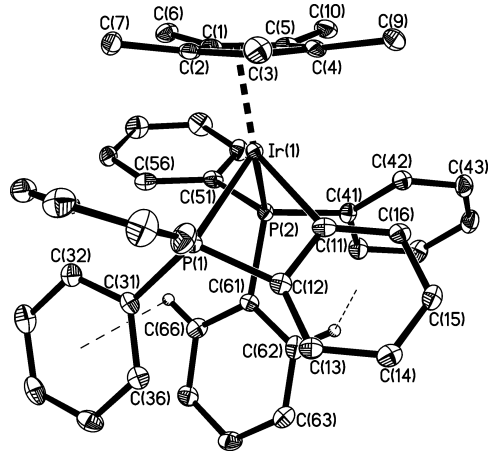


Figure 3. ORTEP representation of the cation in the crystal structure of **13**. Selected bond lengths (Å) and angles (deg): Ir–CNT1 (CNT1 = centroid of C1–5) 1.9133(15), Ir(1)-C(11) 2.103(4), Ir(1)-P(2) 2.3099(11), Ir(1)-P(1) 2.3209(9), C(11)-Ir(1)-P(2) 87.65(10), C(11)-Ir(1)-P(1) 66.79(11), P(2)-Ir(1)-P(1) 94.79(4). The pair of ortho hydrogens of one of the Ph groups of the PPh_3 ligand showing shortest distances to the phenylic rings of the $Ph_2PC_6H_4$ ligand is represented. H-[ring centroid] distances (Å): H(66)-cent[C(31)–C(36)] 3.468; H(62)-cent[C(11)–C(16)] 2.628.

β-Elimination of Perfluoroalkylated Alkenes in the Rh Complexes. To promote β-hydride elimination in complexes $[Rh(\eta^5\text{-}Cp^*)(CH_2CH_2R_F)I(PR_3)]$, we reacted complexes **6**, **8** and **9**, and their previously reported congeners $[Rh(\eta^5\text{-}Cp^*)(CH_2CH_2R_F)I(PR_3)]$ (R = Me, R_F = *i*-C_3F_7, *t*-C_4F_9; R = Ph, R_F = *i*-C_3F_7),[20] with AgOTf (OTf = OSO_2CF_3) in CH_2Cl_2 (Scheme 8). These reactions gave rise to precipitation of AgI and formation of the triflato complexes $[Rh(\eta^5\text{-}Cp^*)(CH_2CH_2R_F)(OTf)(PR_3)]$ (**19**–**24**). These unstable complexes were not isolated and their structure was tentatively proposed on the basis of their NMR spectra (see below). Thus, in situ generated samples in CD_2Cl_2 showed signals corresponding to the alkenes $H_2C{=}CHR_F$ (R_F = *i*-C_3F_7, *n*-C_4F_9, *t*-C_4F_9 or *c*-C_6F_{11}) and several unidentified Rh complexes after 2–3 hours at room temperature. Since these alkenes are likely produced by a β-hydride elimination reaction, we examined the high-field region of the ^1H NMR spectra of the mixtures to detect [Rh]-H species. However, no hydrido complexes were detected, except in the decomposition of **21**, which gave $[Rh(\eta^5\text{-}Cp^*)(H)(PPh_3)_2]OTf$ (**25**) as the main metal-containing product. These observations suggest that hydrido alkene complexes of the type $[Rh(\eta^5\text{-}Cp^*)(H)(H_2C{=}CHR_F)(PR_3)]OTf$, which should be formed from **19**–**24** by a β-hydride elimination, are unstable and decompose to afford the free alkenes and a mixture of unidentified Rh complexes. Compound **25** was unambiguously identified by comparison of its NMR signals with those reported for $[Rh(\eta^5\text{-}Cp^*)(H)(PPh_3)_2]PF_6$.[29]

Formation of **25** suggests that the decomposition of the triflato complexes could proceed in a more clean way in the presence of an equivalent of phosphine ligand. Thus, addition of PPh_3 to a solution of **19**, **20** or **21** in CD_2Cl_2 led to a mixture containing the initial triflato complex, the respective $H_2C{=}CHR_F$, the hydrido complex **25** and another complex which was tentatively assigned as $[Rh(\eta^5\text{-}Cp^*)(CH_2CH_2R_F)(PPh_3)_2]OTf$ (R_F = *t*-C_4F_9 (**26**), *c*-C_6F_{11} (**27**) or *i*-C_3F_7 (**28**)) (Scheme 8). Complexes **26**–**28** could not be isolated and their structure was proposed on the basis of their characteristic NMR signals (see below). On standing for 1–3 days at 30–40 ºC, the mixture evolved to give $H_2C{=}CHR_F$ and **25** almost quantitatively. In contrast, addition of PMe_3 to solutions of *in situ* generated **23** or **24** (Scheme 4), gave stable complexes $[Rh(\eta^5\text{-}Cp^*)(CH_2CH_2R_F)(PMe_3)_2]OTf$ (R_F = *t*-C_4F_9 (**29**) or *i*-C_3F_7 (**30**)), which were isolated. On heating these complexes in CD_2Cl_2 solution, they decomposed to give a mixture of products where no hydrido complexes were observed and only traces of the alkenes $H_2C{=}CHR_F$ (R_F = *i*-C_3F_7, *t*-C_4F_9) were detected by NMR spectroscopy. $[Rh(\eta^5\text{-}Cp^*)Cl(PMe_3)_2]OTf$ was the main component of these mixtures. It was identified in solution by comparing its ^1H and $^{31}P\{^1H\}$ NMR signals with those of an independently prepared sample (see Supporting Information). In addition, its X-ray structure (Figure 4) was determined.

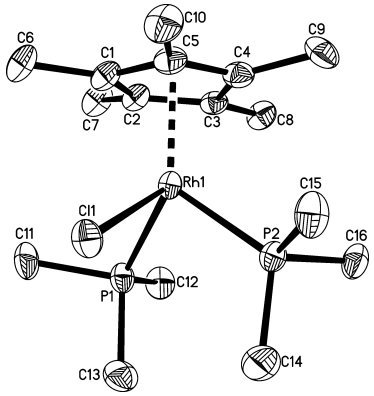
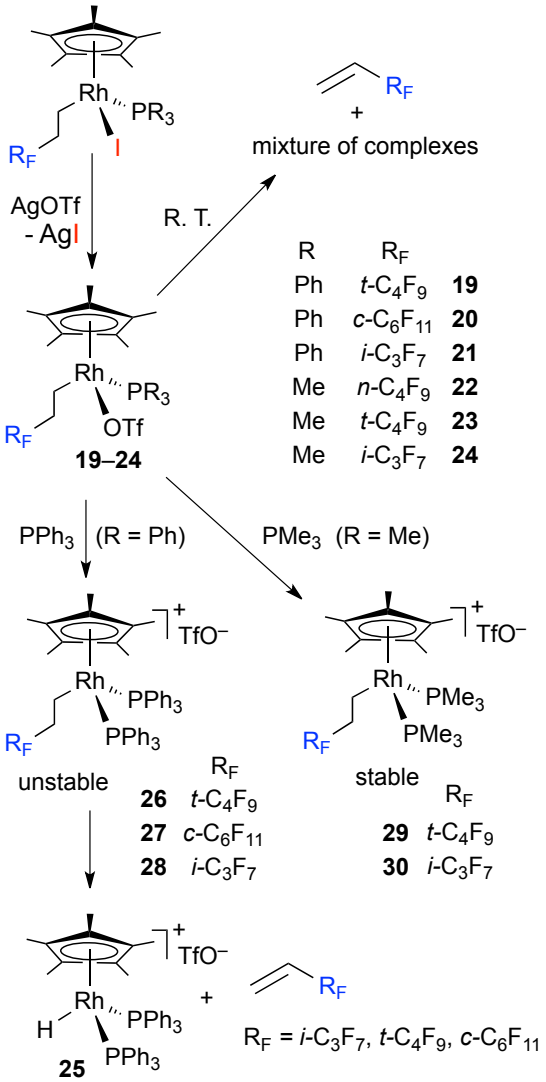


Figure 4. ORTEP representation (50% thermal ellipsoids) of the cation in the crystal structure of $[Rh(\eta^5\text{-}Cp^*)Cl(PMe_3)_2]OTf$. Selected bond lengths (Å) and angles (deg): Rh–CNT1 (CNT1 = centroid of C1–5) 1.8663(16), Rh-P(2) 2.2876(11), Rh-P(1) 2.3141(12), Rh-Cl 2.4064(10), P(2)-Rh-P(1) 97.11(3), P(2)-Rh-Cl 86.11(4), P(1)-Rh-Cl 87.03(4).

Scheme 8



The ^{1}H NMR spectra of the triflato complexes **19–24** displayed the expected signals for the η^5-Cp* and phosphine ligands, as well as for the methylenic protons. Their $^{31}P\{^{1}H\}$ NMR spectra showed a doublet with a $^{1}J_{RhP}$ value higher by 3.9–7.5 Hz than those of their iodo analogues, which is in agreement with the poor donor ability of the TfO^- anion. In the ^{19}F NMR spectra the CF_3SO_3 signal appeared as a broad singlet around –79 ppm. Similar $\delta(^{19}F)$ values have been found in ionic triflates, such as complexes **29** and **30**, and in Rh(III) or Ir(III) triflato complexes.[30] It is noteworthy that in complexes **21** and **24** the diastereotopic CF_3 groups of the perfluoroisopropyl moiety gave only one ^{19}F NMR signal instead of the expected two signals, which were observed for the analogous iodo complexes.[20] The broadening of the triflato signals and the equivalence of the CF_3 goups of complexes **21** and **24** could be produced by fast triflate dissociation followed by inversion of the configuration at the metal and triflate recoordination.[31]

Diagnostic features of the ^{1}H NMR spectra of complexes **26–30** were the triplet signal observed for the Cp* methyl protons, which is originated by the coupling with two equivalent ^{31}P nuclei, and the homotopic character of the CH_2 protons. The ^{19}F NMR spectra showed a sharp singlet for the $CF_3SO_3^-$ and, in **28** and **30**, a sharp doublet for the two equivalent CF_3 groups. The $^{1}J_{RhP}$ values of **26–28** were similar to those of **29** and **30**. These $^{1}J_{RhP}$ values are about 19 Hz lower than those of their parent triflato complexes, in agreement with the substitution of the triflate by a phosphine ligand.

Catalytic Addition of Iodoperfluoroalkanes to Ethene. After observing the formation of alkenes $H_2C{=}CHR_F$ from [M]-$CH_2CH_2R_F$ complexes (M = Rh or Ir), we investigated if these alkenes could be obtained from ethene and I-*i*-C_3F_7 by using complexes $[M(\eta^5\text{-Cp*})(\eta^2\text{-}C_2H_4)_2]$ or $[M(\eta^5\text{-Cp*})(CH_2CH_2\text{-}i\text{-}C_3F_7)I(PPh_3)]$ (M = Rh, Ir) as catalysts. The hypothetical catalytic cycle is outlined in Scheme 9-A. The perfluoroalkylation and β-elimination steps have been observed in the present and previous works.[20] Stoichiometric generation of a Rh(I) olefin complex by the deprotonation of a Rh(III) hydrido complex has been previously reported.[32]

The results of the performed catalytic tests are presented in Table 1. Only traces of the expected alkenes were detected in some cases. Instead, compound $ICH_2CH_2\text{-}i\text{-}C_3F_7$, resulting from the addition of the iodoperfluoroalkane to the alkene double bond, was formed. Complexes $[M(\eta^5\text{-Cp*})(\eta^2\text{-}C_2H_4)_2]$ (M = Rh or Ir) are able to initiate the addition of I-*i*-C_3F_7 to ethene (entries 1–4) in the absence of any additive, although addition of a base (NaOAc) increases modestly the conversion (entry 5). The Ir complexes are less active than the corresponding Rh ones, and Rh(III) or Ir(III) complexes are also able to initiate the addition, although with lower activity than the corresponding Rh(I) or Ir(I) complexes (entries 6–9). An exception to this trend was the reaction initiated by a mixture of $[Rh(\eta^5\text{-Cp*})(CH_2CH_2\text{-}i\text{-}C_3F_7)I(PPh_3)]$ and AgOTf (entry 10), which gave the fastest reaction among all tested. Although PPh_3 has been reported to initiate the addition of iodoperfluoroalkanes to alkenes,[33] initiation by dissociated PPh_3 from the Rh(III) complexes seems unlikely because no reaction was observed when PPh_3 or $[Rh(\eta^5\text{-Cp*})I_2(PPh_3)]$ were used as initiators (entries 11 and 12).

No reaction was observed in the absence of the complexes (entry 13). I-*n*-C_4F_9 gave a sluggish reaction at 80 ºC using $[Rh(\eta^5\text{-Cp*})(\eta^2\text{-}C_2H_4)_2]$ as initiator and, in addition to $ICH_2CH_2\text{-}n\text{-}C_4F_9$, other unidentified organofluorine products were detected. During the course of the reaction the initiators were progressively transformed into the corresponding Rh(III) or Ir(III) diiodo complexes $[M(\eta^5\text{-Cp*})I(\mu\text{-}I)]_2$ (M = Rh or Ir), or $[Rh(\eta^5\text{-Cp*})I_2(PPh_3)]$.

Radical addition of iodoperfluorolkanes to alkenes initiating by metal salts or complexes has been reported.[10,13,17,34] In this reaction, the main role of the metal species is to transfer one electron to IR_F, to give I^- and a perfluoroalkyl radical, which reacts with the alkene, initianting a radical chain reacion. To test if the investigated reactions follow a radical mechanism, we carried out the reaction of I-*i*-C_3F_7, ethene and $[Rh(\eta^5\text{-Cp*})(\eta^2\text{-}C_2H_4)_2]$ in the presence of TEMPO ([TEMPO]:[Rh] = 2). The radical scavenger TEMPO is expected to react with the generated perfluoroalkyl radical, disrupting the radical chain to form the stable adduct TEMPO-R_F.[35] In agreement with this expectation, no ethene perfluoroalkylation was observed, and signals corresponding to the TEMPO-*i*-C_3F_7 adduct were detected in the ^{1}H and ^{19}F NMR spectra of the reaction mixture (see Supporting Information), suggesting that a radical mechanism is operating.

To further test the radical nature of these reactions, $I^iC_3F_7$ was reacted with norbornene and [Rh(η^5-Cp*)(η^2-C_2H_4)$_2$], in a 20:5:1 molar proportion, respectively. A sluggish reaction was observed at room temperature, but on heating at 80 ºC for 2 h norbornene was quantitatively transformed into *endo*-2-iodo-*exo*-3-(heptafluoroprop-2-yl)norbornane. The selective formation of this product is typical for a radical-initiated addition.[36] The by-products ICH_2CH_2-*i*-C_3F_7 and C_2H_4 were also detected. Since norbornene does not replace the coordinated ethene in [Rh(η^5-Cp*)(η^2-C_2H_4)$_2$] under the experimental conditions (from room temperature to 80 ºC), the observed ethene should be liberated after the radical initiation step. Radical addition of $I^iC_3F_7$ to the generated ethene would form ICH_2CH_2-*i*-C_3F_7.

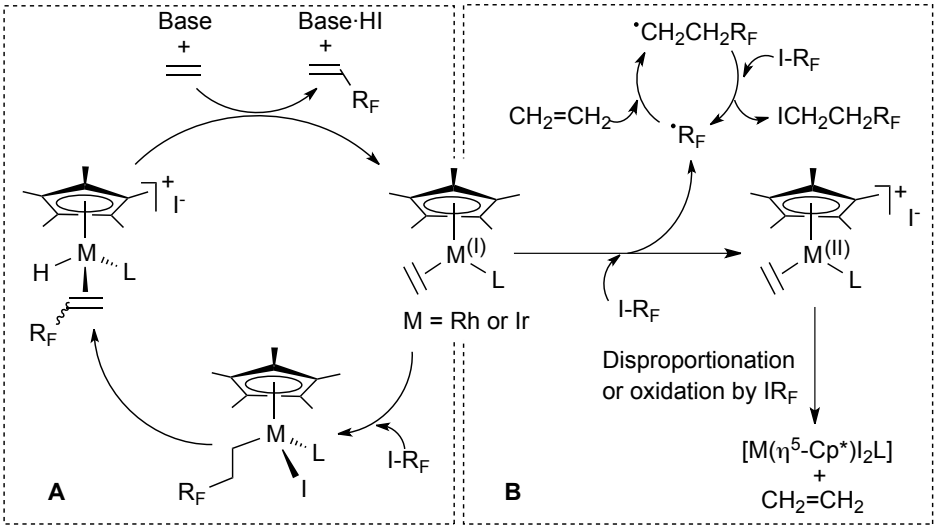
On the basis of these observations, a radical chain mechanism is proposed (Scheme 9-B). The reaction is initiated by single electron transfer from the Rh(I) or Ir(I) initiator to a molecule of IR_F, to give I^- and a $R_F\cdot$ radical, which would add to the alkene. The resulting radical would react with other molecule of IR_F to give $ICH_2CH_2R_F$ and another $R_F\cdot$ radical, which would continue the reaction. The M(II) species (M = Rh or Ir) generated in the initiation step could undergo a disproportionation reaction, which would generate a M(I) complex, a M(III) diiodo complex and free ethene, or be oxidized by IR_F to a M(III) diiodo complex and ethene (Scheme 9-B).

Table 1. Catalytic Addition of Perfluoroalkyl Iodides to Ethene.[a]

Entry	R_F	Initiator	Additive	Time (h)	T (ºC)	Conversion of $ICH_2CH_2R_F$(%)[b]
1	*i*-C_3F_7	[Rh(η^5-Cp*)(η^2-C_2H_4)$_2$]	None	2	25	3
2	*i*-C_3F_7	[Rh(η^5-Cp*)(η^2-C_2H_4)$_2$]	None	2	80	63
3	*i*-C_3F_7	[Ir(η^5-Cp*)(η^2-C_2H_4)$_2$]	None	9	25	5
4	*i*-C_3F_7	[Ir(η^5-Cp*)(η^2-C_2H_4)$_2$]	None	2	80	13
5	*i*-C_3F_7	[Rh(η^5-Cp*)(η^2-C_2H_4)$_2$]	NaOAc	2	80	71
6	*i*-C_3F_7	[Rh(η^5-Cp*)(CH_2CH_2-*i*-C_3F_7)(μ-I)]$_2$[c]	NaOAc	2	80	47
7	*i*-C_3F_7	[Rh(η^5-Cp*)(CH_2CH_2-*i*-C_3F_7)I(PPh_3)][c]	NaOAc	2	25	0
8	*i*-C_3F_7	[Rh(η^5-Cp*)(CH_2CH_2-*i*-C_3F_7)I(PPh_3)][c]	NaOAc	2	80	48
9	*i*-C_3F_7	**8**	NaOAc	2	80	<1
10	*i*-C_3F_7	[Rh(η^5-Cp*)(CH_2CH_2-*i*-C_3F_7)I(PPh_3)][c]	AgOTf	2.5	25	99
11	*i*-C_3F_7	PPh_3	None	2	80	0
12	*i*-C_3F_7	[Rh(η^5-Cp*)I_2(PPh_3)$_2$]	None	2	80	0
13	*i*-C_3F_7	None	None	18	80	0
14	*i*-C_3F_7	[Rh(η^5-Cp*)(η^2-C_2H_4)$_2$]	TEMPO	18	80	0

[a] Conditions: C_2H_4 (0.12 mmol), IR_F (0.12 mmol), initiator (0.0060 mmol), additive (0.15 mmol of NaOAc, 0.12 mmol of AgOTf or 0.012 mmol of TEMPO) in C_6D_6, except for entries 13 and 14, where an undetermined amount of ethene was introduced. [b] Determined by integration of the ^{19}F NMR spectrum of the reaction mixture using a internal standard. [c] Reference 20. [d] CD_2Cl_2 was used as solvent.

Scheme 9



According to the proposed mechanism, in those experiments where M(III) complexes are used as initiators (entries 6–10) there should be a previous reduction process to generate the true M(I) initiators. The detection of traces of the alkene H_2C=CH-*i*-C_3F_7 in the reaction mixtures of the experiments shown in entries 6 and 8 suggests that these M(I) species could be generated by a β-elimination reaction followed by deprotonation of the resulting hydrido complex. In entry 10, where no base was used, the active species could be formed by decomposition of the hydrido olefin intermediate. The generated [M(η^5-Cp*)(η^2-C_2H_4)L] complexes would react with IR_F to give [M(η^5-Cp*)($CH_2CH_2R_F$)I(L)], but they would also initiate a faster radical chain reaction that, in the presence of an excess of IR_F and ethene, would become the dominant reaction pathway.

CONCLUSIONS

Complexes [Ir(η^5-Cp*)(η^2-C_2H_4)$_2$] and [Ir(η^5-Cp*)(η^2-C_2H_4)(PPh_3)] react with secondary or tertiary iodoperfluoroalkanes to give complexes of the types [Ir(η^5-Cp*)($CH_2CH_2R_F$)(μ-I)]$_2$ and [Ir(η^5-Cp*)($CH_2CH_2R_F$)I(PPh_3)], respectively. Evidence for the generation of a perfluoroalkyl anion in the reaction of [Ir(η^5-Cp*)(η^2-C_2H_4)(PPh_3)] with I-*i*-C_3F_7 was obtained, which suggest that the reaction is initiated by the transfer of two electrons from the Ir(I) complex to the iodoperfluoroalkane. Hydrido alkene complexes of the type [Ir(η^5-Cp*)H(η^2-CH_2=CHR_F)(PPh_3)]OTf were isolated in the reactions of [Ir(η^5-Cp*)($CH_2CH_2R_F$)I(PR_3)] with AgOTf. The Ir-coordinated alkenes can be liberated by reaction with PPh_3, although a competitive C–H activation reaction, leading to [Ir(η^5-Cp*)(η^2-*o*-$C_6H_4PPh_2$)(PPh_3)]OTf and $CH_3CH_2R_F$, takes place. Stable derivatives of the type [M(η^5-Cp*)($CH_2CH_2R_F$)(PR_3)L]OTf (L = phosphine or CO) were isolated in these reactions. Alkenes of the type CH_2=CHR_F were detected in the reactions of complexes [Rh(η^5-Cp*)($CH_2CH_2R_F$)I(PR_3)] with AgOTf, probably resulting from β-hydride elimination reactions, although the intermediate hydrido alkene complexes were not observed. Finally, complexes of the type [M(η^5-Cp*)(η^2-C_2H_4)$_2$] or [M(η^5-Cp*)($CH_2CH_2R_F$)I(L)] are able to initiate the addition reaction of IR_F to ethene. However, although formation of alkenes CH_2=CHR_F was detected in some of these reactions, a metal-initiated radical addition to give $ICH_2CH_2R_F$ is the dominant pathway.

EXPERIMENTAL SECTION

General Considerations: Complexes [M(η^5-Cp*)(η^2-C_2H_4)$_2$] (M = Rh, Ir)[37] and [Ir(η^5–C_5Me_5)(Cl)(Me)(PPh_3)][38] were prepared as previously reported. Solutions of [Rh(η^5-Cp*)(η^2-C_2H_4)(PR_3)],(R = Me,[39] Ph[40]) were prepared by reaction of [Rh(η^5-Cp*)(η^2-C_2H_4)$_2$] with a stoichiometric amount of PMe_3 or PPh_3 in toluene. [Ir(η^5-C_5Me_5)(η^2-C_2H_4)(PPh_3)] was prepared as reported by Bergman and coworkers[25] and used immediately. Other reagents were obtained from commercial sources and used without further purification. The purity of all isolated new compounds was established by elemental analyses and NMR spectroscopy. Additional experimental details are included in the Supporting Information.

[Ir(η^5-Cp*)(CH_2CH_2-*t*-C_4F_9)(μ-I)]$_2$ (1). I-*t*-C_4F_9 (170 mg, 0.491 mmol) was added to a solution of [Ir(η^5-Cp*)(η^2-C_2H_4)$_2$] (109 mg, 0.284 mmol) in *n*-pentane (6 mL) and the mixture was stirred for 22 h at room temperature. The red precipitate was filtered, washed with *n*-pentane (5 mL) and dried under vacuum (128 mg, 0.0912 mmol, 64.2%). Mp: 163 ºC (d). Anal. Calcd for $C_{32}H_{38}F_{18}I_2Ir_2$: C, 27.40; H, 2.73. Found: C, 27.20; H, 2.53. ^{1}H NMR (400.9 MHz, C_6D_6): δ 3.81 (m, 4 H, CH_2), 2.90 (m, 4 H, CH_2), 1.37 (s, 30 H, C_5Me_5). ^{13}C{^{1}H} NMR (100.8 MHz, C_6D_6): δ 123.4 (q, $^1J_{CF}$ = 287.4 Hz, CF_3), (s, C_5Me_5), 61.7 (decaplet, $^2J_{CF}$ = 24.7 Hz, CCF_3), 37.7 (s, IrCH_2CH_2), 8.9 (s, C_5Me_5), –5.1 (s, IrCH_2CH_2). ^{19}F NMR (188.3 MHz, C_6D_6): δ –65.2 (s, CF_3). (+)ESI-MS *m/z* 454 ([Ir(C_5Me_5)I]$^+$), 783 ([Ir$_2$(C_5Me_5)$_2$$H_2$I]$^+$), 903 ([Ir$_2$($C_5Me_5$)$_2$($CH_2CH_2C_4F_9$)$H_2$]$^+$), 1155 ([Ir$_2$($C_5Me_5$)$_2$$I_2$($CH_2CH_2C_4F_9$)]$^+$).

[Ir(η^5-Cp*)(CH_2CH_2-*c*-C_6F_{11})(μ-I)]$_2$ (2) and [(η^5-Cp*)IIr(μ-I)$_2$Ir(η^5-Cp*)(CH_2CH_2-*c*-C_6F_{11})] ($\mathbf{2_I}$). I-*c*-C_6F_{11} (45 μL, 0.24 mmol) was added to a solution of [Ir(η^5-Cp*)(η^2-C_2H_4)$_2$] (91 mg, 0.24 mmol) in *n*-pentane (6 mL) and the mixture was stirred for 20 h at room temperature. The orange precipitate was filtered, washed with *n*-pentane (7 mL) and dried under vacuum. The isolated solid was a mixture of **2** and $\mathbf{2_I}$ in a ca. 2:1 molar ratio, as determined by integration of the ^{1}H NMR spectrum (112 mg, 64%). Mp: 168 ºC (d). Anal. Calcd for ($C_{36}H_{38}F_{22}I_2Ir_2$)$_2$($C_{28}H_{34}F_{11}I_3Ir_2$): C, 27.31; H, 2.52. Found: C, 27.11; H, 2.24. ^{1}H NMR (400.9 MHz, C_6D_6): δ 3.75 (m, 4 H, CH_2, **2**), 3.65 (m, 4 H, CH_2, $\mathbf{2_I}$), 3.04–2.91 (m, 4 H, CH_2, **2** and $\mathbf{2_I}$), 1.47 (s, 15 H, C_5Me_5, $\mathbf{2_I}$), 1.38 (s, 15 H, C_5Me_5, $\mathbf{2_I}$), 1.37 (s, 15 H, C_5Me_5, **2**). ^{13}C{^{1}H} NMR (100.8 MHz, C_6D_6): δ 88.3 (s, C_5Me_5, $\mathbf{2_I}$), 87.8 (s, C_5Me_5, $\mathbf{2_I}$), 87.7 (s, C_5Me_5, **2**), 35.2 (d, $^2J_{FC}$ = 21.8 Hz, IrCH_2CH_2, **2**), 10.2 (s, C_5Me_5, $\mathbf{2_I}$), 9.4 (s, C_5Me_5, $\mathbf{2_I}$), 9.0 (s, C_5Me_5, **2**), –7.6 (s, IrCH_2CH_2, **2**); the signals of the C_6F_{11} group and the CH_2 signals of $\mathbf{2_I}$ were not observed. ^{19}F NMR (282.4 MHz, C_6D_6): δ –118.2 (d, 2 F, $^2J_{FF}$ = 286.6 Hz, F_{eq}, **2**), –122.3 (d, 2 F, $^2J_{FF}$ = 286.9 Hz, F_{eq}, **2**), –124.0 (d, 1 F, $^2J_{FF}$ = 283.5 Hz, F_{eq}, **2**), –131.5 (d, 2 F, $^2J_{FF}$ = 295.7 Hz, F_{ax}, **2**), –139.2 (d, 2 F, $^2J_{FF}$ = 272.5 Hz, F_{ax}, **2**), –141.9 (d, 1 F, $^2J_{FF}$ = 289.5 Hz, F_{ax}, **2**), –184.1 (m, 1F, CH_2CF, **2**); the ^{19}F signals of $\mathbf{2_I}$ overlap with those of **2**. (+)ESI-MS *m/z* 455 ([Ir(C_5Me_5)I]$^+$), 701, 783 ([Ir$_2$(C_5Me_5)$_2$$H_2$I]$^+$), 909 ([Ir$_2$($C_5Me_5$)$_2$$I_2$H]$^+$), 965, 1217 ([Ir$_2$($C_5Me_5$)$_2$$I_2$($CH_2CH_2C_6F_{11}$)]$^+$), 1571.

[Rh(η^5-Cp*)(CH_2CH_2-*c*-C_6F_{11})(μ-I)]$_2$ (3) and [(η^5-Cp*)IRh(μ-I)$_2$Rh(η^5-Cp*)(CH_2CH_2-*c*-C_6F_{11})] ($\mathbf{3_I}$). I-*c*-C_6F_{11} (100 μL, 0.532 mmol) was added to a solution of [Rh(η^5-Cp*)(η^2-C_2H_4)$_2$] (128 mg, 0.435 mmol) in *n*-pentane (5 mL) and the mixture was stirred for 22 h at room temperature. The formed red precipitate was separated by centrifugation, washed with *n*-pentane (2 × 1 mL) and dried under vacuum (268 mg). The isolated solid was a mixture containing mainly **3** (ca. 80%, as determined by integration of the C_5Me_5 signals in the ^{1}H NMR spectrum of the mixture), together with small amounts of $\mathbf{3_I}$ (7%) and minor amounts of unidentified complexes containing the Rh(η^5-Cp*) unit. This material was used for further reactions. A dark red crystalline sample containing **3** and $\mathbf{3_I}$ in a ca. 93:7 molar ratio (determined by integration of the ^{1}H NMR spectrum) was obtained by recrystallization from Et_2O at –32ºC (45 mg, 15%). Mp: 175 ºC (d). Anal. Calcd for ($C_{36}H_{38}F_{22}I_2Rh_2$)$_{0.93}$($C_{28}H_{34}F_{11}I_3Rh_2$)$_{0.07}$: C, 31.87; H, 2.85. Found: C, 31.59; H, 2.84. ^{1}H NMR (400.9 MHz, C_6D_6): δ 3.21–3.04 (m, CH_2 of **3** and $\mathbf{3_I}$), 1.53 (s, 15 H, C_5Me_5, $\mathbf{3_I}$), 1.48 (s, 15 H, C_5Me_5, $\mathbf{3_I}$), 1.39 (s, 30 H, C_5Me_5, **3**). ^{13}C{^{1}H} (100.8 MHz, C_6D_6): δ 95.6 (d, $^1J_{RhC}$ = 6.6 Hz, C_5Me_5, $\mathbf{3_I}$), 94.9 (d, $^1J_{RhC}$ = 6.6 Hz, C_5Me_5, $\mathbf{3_I}$), 95.0 (d, $^1J_{RhC}$ = 7.5 Hz, C_5Me_5, **3**), 35.2 (d, $^2J_{FC}$ = 22.2 Hz, RhCH_2CH_2, **3**), 10.8 (s, C_5Me_5, $\mathbf{3_I}$), 9.5 (s, C_5Me_5, $\mathbf{3_I}$), 9.4 (s, C_5Me_5, **3**), 6.4 (d, $^1J_{RhC}$ = 24.2 Hz, RhCH_2CH_2, **3**); the signals of the C_6F_{11} groups and the CH_2 signals of $\mathbf{3_I}$ were not observed. ^{19}F (282.4 MHz, C_6D_6): δ –117.9 (d, 2 F, $^2J_{FF}$ = 299.6 Hz, F_{eq}, **3**), –122.0 (d, 2 F, $^2J_{FF}$ = 282.9 Hz, F_{eq}, **3**), –123.7 (d, 1 F, $^2J_{FF}$ = 289.2 Hz, F_{eq}, **3**), –131.1 (d, 2 F, $^2J_{FF}$ = 291.1 Hz, F_{ax}, **3**), –139.0 (d, 2 F, $^2J_{FF}$ = 285.5 Hz, F_{ax}, **3**), –141.7 (d, 1 F, $^2J_{FF}$ = 277.8 Hz, F_{ax}, **3**), –183.7 (m, 1 F, CH_2CF, **3**); all the ^{19}F NMR signals of $\mathbf{3_I}$ overlap with those of **3**. (+)ESI-MS *m/z* 365 ([Rh(C_5Me_5)I]$^+$), 635, 731 ([Rh$_2$(C_5Me_5)$_2$$H_2$H]$^+$), 857 ([Rh$_2$($C_5Me_5$)$_2$$I_3$]$^+$), 1039 ([Rh$_2$($C_5Me_5$)$_2$$I_2$($CH_2CH_2C_6F_{11}$)]$^+$), 1387 (M + K$^+$).

[Ir(η^5-Cp*)(CH_2CH_2-*t*-C_4F_9)I(PPh_3)] (4). I-*t*-C_4F_9 (202 mg, 0.584 mmol) was added to a solution of [Ir(η^5-C_5Me_5)(η^2-C_2H_4)$_2$] (155 mg, 0.404 mmol) in *n*-pentane (5 mL) and the mixture was stirred for 18 h at room temperature. The volatiles were removed under vacuum and the residue was dissolved in THF (6 mL). PPh_3 (115 mg, 0.44 mmol) was added to the resulting solution. After stirring for 3 h at room temperature, the mixture was evaporated to

dryness to give a pale orange residue, which was chromatographed on a silica gel column using Et_2O/*n*-hexane (1:2) as eluent. The collected orange fraction (R_f = 0.58) was concentrated until an orange crystalline solid precipitated. The solid was washed with cold *n*-hexane (3 × 2 mL) and dried under vacuum (302 mg, 0.313 mmol, 77.6%). Mp: 184–186 ºC. Anal. Calcd for $C_{34}H_{34}F_9IPIr$: C, 42.37; H, 3.56. Found: C, 42.44; H, 3.68. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.47 (br m, 6 H, Ph), 7.36 (br m, 9 H, Ph), 2.86 (m, 1 H, CH_2), 2.22–1.93 (m, 3 H, CH_2), 1.50 (d, $^4J_{PH}$ = 1.5 Hz, 15 H, C_5Me_5). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 135.4–132.6 (br m, Ph), 130.2 (s, C4, Ph), 127.8 (d, J_{PC} = 9.9 Hz, Ph), 122.3 (q, $^1J_{CF}$ = 288.3 Hz, CF_3), 93.7 (d, $^2J_{PC}$ = 2.8 Hz, C_5Me_5), 60.9 (decaplet, $^2J_{CF}$ = 24.1 Hz, CCF_3), 37.8 (d, $^3J_{PC}$ = 4.2 Hz, $IrCH_2CH_2$), 9.2 (s, C_5Me_5), –15.0 (d, $^2J_{PC}$ = 7.6 Hz, $IrCH_2CH_2$). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ –65.8 (s). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 0.3 (s). (+)ESI-MS: *m/z* 589 ($[Ir(C_5Me_4CH_2)(PPh_3)]^+$), 717 ($[Ir(C_5Me_5)I(PPh_3)]^+$), 982 ($M + NH_4^+$), 1003 ($M + K^+$).

[Ir(η^5-Cp*)(CH_2CH_2-*c*-C_6F_{11})I(PPh_3)] (5). PPh_3 (20 mg, 0.076 mmol) was added to a solution of **2** and **2I** (58 mg, molar ratio 4:1, ca. 0.08 mmol of Ir) in THF (5 mL). The mixture was stirred for 4.5 h at room temperature and evaporated to dryness under vacuum. The residue was purified by chromatography on a silica gel column using Et_2O/*n*-hexane (1:3) as eluent. The collected orange fraction (R_f = 0.55) was concentrated until a pale orange crystalline precipitate formed, which was filtered, washed with cold *n*-hexane (3 mL) and dried under vacuum (34 mg, 0.033 mmol, 43%). Mp: 204–206 ºC. Anal. Calcd for $C_{36}H_{34}F_{11}IPIr$: C, 42.15; H, 3.34. Found: C, 42.32; H, 3.20. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.37 (br m, 15 H, Ph), 2.77 (m, 1 H, CH_2), 2.17–1.98 (m, 3 H, CH_2), 1.52 (d, $^4J_{PH}$ = 1.5 Hz, 15 H, C_5Me_5). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 134.5 (br m, Ph), 130.2 (s, C4 of Ph), 127.8 (d, J_{PC} = 9.9 Hz, Ph), 93.9 (d, $^2J_{PC}$ = 2.9 Hz, C_5Me_5), 36.2 (dd, $^2J_{FC}$ = 21.2 Hz, $^4J_{PC}$ = 3.2 Hz, $IrCH_2CH_2$), 9.0 (s, C_5Me_5), –17.2 (d, $^2J_{PC}$ = 8.5 Hz, $IrCH_2CH_2$); the C_6F_{11} signals were not observed. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ –118.7 (d, $^2J_{FF}$ = 303.6 Hz, 2 F, F_{eq}), –122.6 (d, $^2J_{FF}$ = 290.3 Hz, 1 F, F_{eq}), –122.9 (d, $^2J_{FF}$ = 281.0 Hz, 1 F, F_{eq}), –124.3 (d, $^2J_{FF}$ = 282.4 Hz, 1 F, F_{eq}), –131.0 (d, $^2J_{FF}$ = 301.0 Hz, 1 F, F_{ax}), –133.0 (d, $^2J_{FF}$ = 296.5 Hz, 1 F, F_{ax}), –139.6 (d, $^2J_{FF}$ = 274.5 Hz, 2 F, F_{ax}), –142.3 (d, $^2J_{FF}$ = 277.6 Hz, 1F, F_{ax}), –184.7 (s, 1 F, CH_2CF). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 1.1 (s). (+)ESI-MS: *m/z* 589 ($[Ir(C_5Me_4CH_2)(PPh_3)]^+$), 717 ($[Ir(C_5Me_5)I(PPh_3)]^+$), 899 ($M - I^-$), 1044 ($M + NH_4^+$), 1065 ($M + K^+$).

[Rh(η^5-Cp*)(CH_2CH_2-*c*-C_6F_{11})I(PPh_3)] (6). A solution of $[Rh(\eta^5\text{–}C_5Me_5)(\eta^2\text{–}C_2H_4)_2]$ (75 mg, 0.25 mmol) in *n*-pentane (6 mL) was treated witch I-*c*-C_6F_{11} (50 µL, 0.27 mmol). After stirring for 19 h at room temperature, the volatiles were removed under vacuum. The residue was dissolved in THF (9 mL) and PPh_3 (68 mg, 0.26 mmol) was added. After stirring for 8 h at room temperature, the mixture was evaporated to dryness to give a dark orange residue. The residue was chromatographed on a silica gel column using Et_2O/*n*-hexane (1:2) as eluent. The collected orange fraction (R_f = 0.54) was concentrated to give an orange crystalline precipitate, which was washed with cold *n*-hexane (2 × 3 mL) and dried under vacuum (101 mg, 0.108 mmol, 43%). Mp: 173 ºC (d). Anal. Calcd for $C_{36}H_{34}F_{11}IPRh$: C, 46.17; H, 3.66. Found: C, 45.93; H, 3.59. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.60–7.25 (br m, 15 H, Ph), 3.01 (m, 1 H, $RhCH_2CH_2$), 2.12 (m, 1 H, $RhCH_2CH_2$), 1.74 (m, 2 H, $RhCH_2CH_2$), 1.51 (d, $^4J_{PH}$ = 2.4 Hz, 15 H, C_5Me_5). $^{13}C\{^1H\}$NMR (75.5 MHz, $CDCl_3$): δ 135.9–132.6 (br m, Ph), 130.3 (br s, C4, Ph), 128.0 (d, J_{PC} = 9.3 Hz, Ph), 99.8 (dd, $^1J_{RhC}$ = 4.6 Hz, $^2J_{PC}$ = 3.1 Hz, C_5Me_5), 35.9 (d, $^2J_{FC}$ = 21.3 Hz, $RhCH_2CH_2$), 9.5 (d, $^1J_{RhC}$ = 1.4 Hz, C_5Me_5), 2.3 (dd, $^1J_{RhC}$ = 24.8 Hz, $^2J_{PC}$ = 13.5 Hz, $RhCH_2CH_2$); the C_6F_{11} signals were not observed. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ –118.9 (d, 1 F, $^2J_{FF}$ = 295.4 Hz, F_{eq}), –119.1 (d, 1 F, $^2J_{FF}$ = 294.6 Hz, F_{eq}), –123.0 (d, 1 F, $^2J_{FF}$ = 274.7 Hz, F_{eq}), –123.3 (d, 1 F, $^2J_{FF}$ = 288.9 Hz, F_{eq}), –124.7 (d, 1 F, $^2J_{FF}$ = 288.6 Hz, F_{eq}), –130.8 (d, 1 F, $^2J_{FF}$ = 302.2 Hz, F_{ax}), –133.5 (d, 1 F, $^2J_{FF}$ = 294.2 Hz, F_{ax}), –140.0 (d, 2 F, $^2J_{FF}$ = 280.4 Hz, F_{ax}), –142.7 (d, 1 F, $^2J_{FF}$ = 287.5 Hz, F_{ax}), –184.8 (s, 1 F, CH_2CF). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 40.9 (d, $^1J_{RhP}$ = 162.2 Hz). (+)ESI-MS: *m/z* 499 ($[Rh(C_5Me_4CH_2)(PPh_3)]^+$), 627 ($[Rh(C_5Me_5)I(PPh_3)]^+$), 959 ($M + Na^+$), 975 ($M + K^+$).

[Ir(η^5-Cp*)(CH_2CH_2-*i*-C_3F_7)I(PPh_3)] (7). I-*i*-C_3F_7 (35 µL, 0.25 mmol) was added to a solution of $[Ir(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}C_2H_4)(PPh_3)]$ (153 mg, 0.248 mmol) in toluene (7 mL) and the mixture was stirred for 7 h at room temperature. The volatiles were removed under vacuum and the residue was purified by chromatography on a silica gel column using Et_2O/*n*-hexane (1:3) as eluent. The collected orange fraction (R_f = 0.45) was concentrated under vacuum until a pale orange microcrystalline precipitate formed, which was washed with cold *n*-hexane (3 × 1 mL) and dried under vacuum (53 mg, 0.058 mmol, 23%). Mp: 147–149 ºC (d). Anal. Calcd for $C_{33}H_{34}F_7IPIr$: C, 43.38; H, 3.75. Found: C, 43.41; H, 3.64. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.37 (br m, 15 H, Ph), 2.66 (m, 1 H, CH_2), 2.09–1.86 (m, 3 H, CH_2), 1.51 (d, $^4J_{PH}$ = 1.5 Hz, 15 H, C_5Me_5). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 134.8 (br m, Ph), 132.6 (br m, Ph), 130.2 (s, C4 of Ph), 127.8 (d, J_{PC} = 9.9 Hz, Ph), 121.3 (qd, $^1J_{FC}$ = 286.9 Hz, $^2J_{FC}$ = 28.2 Hz, CF_3), 93.9 (d, $^2J_{PC}$ = 2.7 Hz, C_5Me_5), 39.3 (dd, $^2J_{FC}$ = 20.6 Hz, $^3J_{PC}$ = 3.4 Hz, $IrCH_2CH_2$), 8.9 (s, C_5Me_5), –17.7 (d, $^2J_{PC}$ = 8.4 Hz, $IrCH_2CH_2$); the CF signal was observed in a separate measurement (100.8 MHz, $CDCl_3$): 93.4 (d(sept), $^1J_{FC}$ = 198.6 Hz, $^2J_{FC}$ = 30.0 Hz, CF). ^{19}F NMR (188.3 MHz, $CDCl_3$): δ –75.4 (dq, $^3J_{FF}$ = $^4J_{FF}$ = 8.4 Hz, 3 F, CF_3), –76.8 (dq, $^3J_{FF}$ = $^4J_{FF}$ = 8.6 Hz, 3 F, CF_3), –183.7 (m, 1 F, CF). $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$): δ 1.2 (s). (+)ESI-MS: *m/z* 589 ($[Ir(C_5Me_4CH_2)(PPh_3)]^+$), 717 ($[Ir(C_5Me_5)I(PPh_3)]^+$), 787 ($M - I^-$), 932 ($M + NH_4^+$), 953 ($M + K^+$).

[Rh(η^5-Cp*)(CH_2CH_2-*t*-C_4F_9)I(PPh_3)] (8). ***Method A***. $[Rh(\eta^5\text{-}Cp^*)(\eta^2\text{-}C_2H_4)(PPh_3)]$ was prepared *in situ* by heating a solution of $[Rh(\eta^5\text{-}Cp^*)(\eta^2\text{-}C_2H_4)_2]$ (104 mg, 0.353 mmol) and PPh_3 (102 mg, 0.389 mmol) in toluene (5 mL) at 120 ºC for 4 h in a Carius tube. The resulting solution was cooled to room temperature and I-*t*-C_4F_9 (130 mg, 0.376 mmol) was added. After stirring for 1.5 h at room temperature, the volatiles were removed under vacuum. The residue was chromatographed on a silica gel column using Et_2O/*n*-hexane (1:2) as eluent. The collected orange fraction (R_f = 0.53) was concentrated to ca. 2 mL and *n*-hexane (2 mL) was added. The orange crystalline precipitate was filtered, washed with cold *n*-hexane (3 × 2 mL) and dried under vacuum (186 mg, 0.213 mmol, 60.3%). ***Method B***. I-*t*-C_4F_9 (230 mg, 0.665 mmol) was added to a solution of $[Rh(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}C_2H_4)_2]$ (135 mg, 0.459 mmol) in *n*-pentane (4 mL), and the mixture was stirred for 20 h at room temperature. The volatiles were removed under vacuum, the residue was dissolved in THF (7 mL) and PPh_3 (138 mg, 0.526 mmol) was added. The resulting solution was stirred for 5 h more at room temperature and it was finally evaporated to dryness. The dark orange residue was chromatographed on a silica gel column using Et_2O/*n*-hexane (1:2) as eluent. The collected orange fraction (R_f = 0.53) was concentrated to give an orange crystalline solid which was filtered, washed with cold *n*-hexane (2 × 2 mL) and dried under vacuum (138 mg, 0.158 mmol, 34.4%). Mp: 171 ºC (d). Anal. Calcd for $C_{34}H_{34}F_9IPRh$: C, 46.70; H, 3.92. Found: C, 46.78; H, 3.93. ^{1}H NMR (300.1 MHz, C_6D_6): δ 7.70 (br m, 6 H, H2 of Ph), 7.00 (m, 9 H, H3 and H4 of Ph), 3.74 (m, 1 H, $RhCH_2CH_2$), 2.39 (m, 1 H, $RhCH_2CH_2$), 2.19–2.06 (m, 2 H, $RhCH_2CH_2$), 1.32 (d, $^4J_{PH}$ = 2.7 Hz, 15 H, Me). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 134.9 (br m, Ph), 132.7 (br m, Ph), 130.2 (s, C4 of Ph), 128.0 (d, J_{PC} = 9.6 Hz, Ph), 122.2 (q, $^1J_{CF}$ = 288.2 Hz, CF_3), 99.7 (dd, $^1J_{RhC}$ = 4.7 Hz, $^2J_{PC}$ = 3.2 Hz, C_5Me_5), 60.6 (decaplet, $^2J_{CF}$ = 24.4 Hz, CCF_3), 37.5 (s, $RhCH_2CH_2$), 9.6 (d, $^1J_{RhC}$ = 1.0 Hz, C_5Me_5), 4.3 (dd, $^1J_{RhC}$ = 24.4 Hz, $^2J_{PC}$ = 12.2 Hz, $RhCH_2CH_2$). ^{19}F NMR (282.4 MHz, C_6D_6): δ –64.8 (s). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 40.7 (d, $^1J_{RhP}$ = 161.5 Hz). (+)ESI-MS: *m/z* 499 ($[Rh(C_5Me_4CH_2)(PPh_3)]^+$), 627 ($[Rh(C_5Me_5)I(PPh_3)]^+$), 897 ($M + Na^+$), 913 ($M + K^+$).

[Rh(η^5-Cp*)(CH_2CH_2-*n*-C_4F_9)I(PMe_3)] (9). PMe_3 (0.52 mL of a 1 M toluene solution, 0.52 mmol) was added to a solution of $[Rh(\eta^5\text{-}Cp^*)(\eta^2\text{-}C_2H_4)_2]$ (153 mg, 0.520 mmol) in toluene (5 mL). The mixture was heated at 120 ºC for 17 h in a Carius tube. The resulting solution of $[Rh(\eta^5\text{-}Cp^*)(\eta^2\text{-}C_2H_4)(PMe_3)]$ was cooled at room temperature and ICH_2CH_2-*n*-C_4F_9 (195 mg, 0.521 mmol) was added. After stirring for 7 h at room temperature, the volatiles were

removed under vacuum. The residue was chromatographed on a silica gel column using Et_2O/*n*-hexane (1:1) as eluent. The collected fraction (R_f = 0.54) was evaporated to dryness and the residue was stirred with Et_2O (3 mL) to give an orange solid, which was washed with *n*-pentane (2 mL) and dried under vacuum (94 mg, 0.14 mmol, 26%). Mp: 101–103 ºC. Anal. Calcd. for $C_{19}H_{28}F_9IPRh$: C, 33.16; H, 4.10. Found: C, 32.94; H, 4.01. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.47 (m, 1 H, RhCH$_2$C*H*$_2$), 1.94 (m, 1 H, RhCH$_2$C*H*$_2$), 1.79 (d, $^4J_{PH}$ = 2.7 Hz, 15 H, C_5Me_5), 1.56 (m, 1 H, RhC*H*$_2$CH$_2$), 1.55 (d, $^2J_{PH}$ = 9.9 Hz, 9 H, PMe_3), 1.32 (m, 1 H, RhC*H*$_2$CH$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 98.6 (dd, $^1J_{RhC}$ = 4.6 Hz, $^2J_{PC}$ = 3.2 Hz, *C*$_5$Me$_5$), 38.6 (t, $^2J_{FC}$ = 22.5 Hz, RhCH$_2$*C*H$_2$), 17.5 (d, $^1J_{PC}$ = 32.4 Hz, PMe_3), 10.0 (d, $^2J_{RhC}$ = 1.0 Hz, C$_5$*Me*$_5$), –2.1 (dd, $^1J_{RhC}$ = 25.9 Hz, $^2J_{PC}$ = 15.1 Hz, Rh*C*H$_2$CH$_2$); the C_4F_9 signals were not observed. ^{19}F NMR (188.3 MHz, $CDCl_3$): δ –81.8 (t, $^3J_{FF}$ = 9.3, CF_3), –115.2 (dm, $^2J_{FAFB}$ = 272.8, CF_2CH_2), –116.9 (dm, $^2J_{FAFB}$ = 265.8, CF_2CH_2), –125.0 (m, CF_2), –126.7 (m, CF_2). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): δ 3.5 (d, $^1J_{RhP}$ = 157.3 Hz). (+)ESI-MS: *m/z* 441 ([Rh(C_5Me_5)I(PMe_3)]$^+$), 561 (M – I$^-$), 706 (M + NH_4^+).

[Ir(η^5-Cp*)(η^2-CH$_2$=CH-*c*-C$_6$F$_{11}$)H(PPh$_3$)]OTf (10). AgOTf (9 mg, 0.04 mmol) was added to a solution of **5** (30 mg, 0.029 mmol) in CH_2Cl_2 (4 mL). The suspension was stirred at room temperature for 2 h and filtered. The filtrate was evaporated to dryness under vacuum. The residue was cooled to 0 ºC and stirred with Et_2O (5 mL). An off-white solid precipitated, which was washed with cold Et_2O (3 × 0.5 mL) and dried under vacuum (22 mg, 0.021 mmol, 72%). Mp: 95 ºC (d). Anal. Calcd for $C_{37}H_{34}F_{14}PSO_3Ir$: C, 42.41; H, 3.27; S, 3.06. Found: C, 42.41; H, 3.33; S, 2.78. ^{1}H NMR (400.9 MHz, CD_2Cl_2, 21º C): δ 7.64–7.45 (m, Ph), 2.98 (m, CH=CH$_2$), 2.72 (dd, J_1 = 9.5 Hz, J_2 = 2.0 Hz, CH=CH$_2$), 2.49 (m, CH=CH$_2$), 2.40–2.22 (br m, CH=CH$_2$), 1.77 (dd, $^4J_{PH}$ = 2.3 Hz, $^4J_{HH}$ = 1.2 Hz, C_5Me_5, major diastereomer), 1.64 (d, $^4J_{PH}$ = 1.8 Hz, C_5Me_5, minor diastereomer), –14.64 (br s, Ir-H, major), –15.84 (br d, $^4J_{PH}$ = 29.3 Hz, Ir-H, minor); (–20 ºC, only hydride region) –14.67 (d, $^2J_{PH}$ = 26.5 Hz, Ir-H, major), –15.88 (dd, $^2J_{PH}$ = 29.1 Hz, *J* = 3.5 Hz, Ir-H, minor). A reliable ^{13}C{^{1}H} NMR spectrum could not be obtained because of decomposition. ^{19}F NMR (188.3 MHz, CD_2Cl_2, -40 ºC): δ –79.6 (s, CF_3SO_3), –116.7 (dm, $^2J_{FF}$ = 279.2 Hz, F$_{eq}$, minor diastereomer), –117.8 (dm, $^2J_{FF}$ = 295.1 Hz, F$_{eq}$, major diastereomer), –119.4 (dm, $^2J_{FF}$ = 244.4 Hz, F$_{eq}$, minor), –121.3 (dm, $^2J_{FF}$ = 297.3 Hz, F$_{eq}$, major), –123.5 (two overlapped dm, $^2J_{FF}$ = 291.5 Hz, 2 F$_{eq}$, major), –124.3 (dm, $^2J_{FF}$ = 283.7 Hz, F$_{eq}$, minor), –124.9 (dm, $^2J_{FF}$ = 292.7 Hz, F$_{eq}$, major), –130.5 (dm, $^2J_{FF}$ = 300.6 Hz, F$_{ax}$, major), –133.8 (d, $^2J_{FF}$ = 301.3 Hz, F$_{ax}$, minor), –134.4 (dm, $^2J_{FF}$ = 310.5 Hz, F$_{ax}$, major), –139.7 (d, $^2J_{FF}$ = 277.8 Hz, F$_{ax}$, major), –140.4 (d, $^2J_{FF}$ = 288.9 Hz, F$_{ax}$, major), –142.8 (d, $^2J_{FF}$ = 285.3 Hz, F$_{ax}$, major), –180.1 (m, CH_2CF minor), –182.9 (m, CH_2CF major); six signals of the minor diastereomer were overlapped with those of the major one. ^{31}P{^{1}H} NMR (162.2 MHz, CD_2Cl_2): δ 12.4 (s, major), 7.2 (s, minor). (+)ESI-MS: *m/z* 589 ([Ir($C_5Me_4CH_2$)(PPh_3)]$^+$), 899 (M – OTf$^-$); HRMS (+ESI) calcd. for M – OTf$^-$ ($C_{36}H_{34}F_{11}IrP$)$^+$: 899.1846; found: 899.1886; Δ = 4.4 ppm.

[Ir(η^5-Cp*)H(η^2-CH$_2$=CH-*i*-C$_3$F$_7$)(PPh$_3$)]OTf (11). AgOTf (38 mg, 0.15 mmol) was added to a solution of **7** (114 mg, 0.125 mmol) in CH_2Cl_2 (4 mL). The suspension was stirred at room temperature for 2 h and filtered. The filtrate was concentrated to ca. 1 mL under vacuum and cooled to 0 ºC. By addition of Et_2O (15 mL) an off-white solid precipitated, which was washed with cold Et_2O (0 ºC, 3 × 2 mL) and dried under vacuum (104 mg, 0.111 mmol, 88.9%). Mp: 145 ºC (d). Anal. Calcd for $C_{34}H_{34}F_{10}PSO_3Ir$: C, 43.64; H, 3.66; S, 3.43. Found: C, 43.57; H, 3.56; S, 3.40. ^{1}H NMR (400.9 MHz, CD_2Cl_2, 25 ºC): δ 7.65–7.44 (several m, Ph), 2.88 (m, CH=CH$_2$), 2.67 (dd, J_1 = 9.4 Hz, J_2 = 1.9 Hz, CH=CH$_2$), 2.47 (m, CH=CH$_2$), 2.19 (br m, CH=CH$_2$), 1.78 (dd, $^4J_{PH}$ = 2.1 Hz, $^4J_{HH}$ = 1.2 Hz, C_5Me_5, major diastereomer), 1.62 (d, $^4J_{PH}$ = 1.4 Hz, C_5Me_5, minor diastereomer), –14.65 (br s, Ir-H, major), –15.92 (d d, $^4J_{PH}$ = 28.0 Hz, Ir-H, minor); (–10 ºC, 200.1 MHz, only hydride region) –14.73 (d, $^4J_{PH}$ = 25.6 Hz, Ir-H, major), –15.87 (dd, $^4J_{PH}$ = 30.4 Hz, $^4J_{FH}$ = 4.1 Hz, Ir-H, minor). A reliable ^{13}C{^{1}H} NMR spectrum could not be obtained because of decomposition. ^{19}F NMR (188.3 MHz, CD_2Cl_2, 21 ºC): δ –75.0 (dq, $^3J_{FF}$ = $^4J_{FF}$ = 10.0 Hz, 3 F, CF_3, minor), –75.8 (br m, 3 F, CF_3, major), –76.8 (dq, $^3J_{FF}$ = $^4J_{FF}$ = 9.8 Hz, 3 F, CF_3, minor), –77.1 (br m, 3 F, CF_3, major), –79.4 (s, 3 F, CF_3SO_3), –181.5 (br m, 1 F, CF, minor and major); (188.3 MHz, CD_2Cl_2, -10 ºC): δ –75.0 (dq, $^3J_{FF}$ = $^4J_{FF}$ = 9.6 Hz, 3 F, CF_3, minor), –75.8 (dq, $^3J_{FF}$ = $^4J_{FF}$ = 9.3 Hz, 3 F, CF_3, major), –76.8 (dq, $^3J_{FF}$ = $^4J_{FF}$ = 9.2 Hz, 3 F, CF_3, minor), –76.6 (dq, $^3J_{FF}$ = $^4J_{FF}$ = 9.1 Hz, 3 F, CF_3, major), –79.2 (s, 3 F, CF_3SO_3), –182.4 (br m, 1 F, CF, minor and major). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 ºC): δ 12.6 (s, major), 7.5 (s, minor). (+)ESI-MS: *m/z* 268, 400, 589 ([Ir($C_5Me_4CH_2$)(PPh_3)]$^+$), 787 (M – OTf$^-$); HRMS (+ESI) calcd. for M – OTf$^-$ ($C_{33}H_{34}F_7IrP$)$^+$: 787.1910; found: 787.1917; Δ = 1.8 ppm.

[Ir(η^5-Cp*){κ^2-*C*,*P*-C$_6$H$_4$(PPh$_2$)}(PPh$_3$)]OTf (13). ***Method A***. AgOTf (34 mg, 0.13 mmol) was added to a solution of **4** (102 mg, 0.106 mmol) in CH_2Cl_2 (4 mL). The suspension was stirred for 2 h at room temperature and filtered. PPh_3 (32 mg, 0.12 mmol) was added to the filtrate. The mixture was stirred for 7 h at room temperature, concentrated to ca. 2 mL under vacuum and cooled at 0 ºC. By addition of Et_2O (8 mL) a greenish yellow solid precipitated, which was filtered and washed with cold Et_2O (2 × 2 mL). The obtained solid was further purified by slow diffusion of *n*-hexane into a CH_2Cl_2 solution to afford yellow crystals (43 mg, 0.043 mmol, 39%). ***Method B***. AgOTf (115 mg, 0.448 mmol) and PPh_3 (112 mg, 0.427 mmol) were added to a solution of ([Ir(η^5–C_5Me_5)Cl(Me)(PPh_3)]) (268 mg, 0.419 mmol) in CH_2Cl_2 (7 mL). The suspension was stirred for 2 h at room temperature, filtered, and heated at 60 ºC for 50 h in a Carius tube. The compound was isolated in the same way as in method A to give yellow crystals (104 mg, 0.104 mmol, 24.8%). Mp: 270–272 ºC. Anal. Calcd for $C_{47}H_{44}F_3P_2SO_3Ir$: C, 56.45; H, 4.43; S, 3.21. Found: C, 56.56; H, 4.28; S, 3.50. ^{1}H NMR (400.9 MHz, CD_2Cl_2, 25 ºC): δ 7.61–7.25 (several m, 21 H, Ph), 6.99 (br s, 1 H, Ph), 6.89 (m, 3 H, Ph), 6.54 (br m, 2 H), 5.69 (br m, 2 H), 1.41 (t, $^4J_{PH}$ = 2.3 Hz, 15 H, C_5Me_5); (–90 ºC) δ 7.80–7.06 (several m, 20 H, Ph), 6.92 (m, 2 H, Ph), 6.85 (m, 1 H, Ph), 6.67 (dd, $^2J_{HH}$ = 12.3 Hz, $^2J_{HH}$ = 7.8 Hz, 1 H, Ph), 6.54 (m, 2 H, Ph), 6.34 (m, 1 H, Ph), 6.06 (m, 1 H, Ph), 4.89 (m, 1 H, Ph), 1.29 (br s, 15 H, C_5Me_5). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 25 ºC): δ 152.1 (d, $^2J_{PC}$ = 64.0 Hz, IrC$_{Ar}$), 135.4–125.3 (several overlapped broad m, Ar), 98.6 (s, *C*$_5$Me$_5$), 9.3 (s, C$_5$*Me*$_5$); (100.8 MHz, $(CD_3)_2SO$, 85 ºC): δ 151.1 (d, J_{PC} = 64.2 Hz, IrC$_{Ar}$), 133.4 (br m, Ar), 131.8 (d, J_{PC} = 41.5 Hz, P-C), 131.8 (d, J_{PC} = 9.5 Hz, Ar), 131.6 (s, Ar), 131.0 (d, J_{PC} = 10.1 Hz, Ar), 130.4 (d, J_{PC} = 2.8 Hz, Ar), 130.2 (d, J_{PC} = 2.2 Hz, Ar), 130.1 (br m, Ar) 128.2 (d, J_{PC} = 10.7 Hz, Ar), 128.0 (d, J_{PC} = 10.9 Hz, Ar), 127.8 (d, J_{PC} = 52.4 Hz, C-P), 127.4 (d, J_{PC} = 10.2 Hz, Ar), 125.8 (d, J_{PC} = 41.5 Hz, C-P), 124.2 (d, J_{PC} = 10.2 Hz, Ar), 97.7 (t, $^2J_{PC}$ = 2.1 Hz, *C*$_5$Me$_5$), 7.9 (s, *C*$_5$Me$_5$); the CF_3 signal was not observed. ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ –78.7 (s, CF_3SO_3). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 25 ºC): δ 4.8 (d, $^2J_{PP}$ = 17.7 Hz, PPh_3), –77.9 (d, $^2J_{PP}$ = 17.7 Hz, $Ph_2PC_6H_4$). (+)ESI-MS: *m/z* 589 ([Ir($C_5Me_4CH_2$)(PPh_3)]$^+$), 851 (M – OTf$^-$); HRMS (+ESI) calcd. for M – OTf$^-$ ($C_{46}H_{44}IrP_2$)$^+$: 851.2542; found: 851.2551; Δ = 1.1 ppm.

[Ir(η^5-Cp*)(CH$_2$CH$_2$-*c*-C$_6$F$_{11}$)(CO)(PPh$_3$)]OTf (15). CO was bubbled through a solution of **10** (23 mg, 0.022 mmol, overall) in CH_2Cl_2 (6 mL) for 3 min. The solution was stirred for 2 h at room temperature under a CO atmosphere and finally evaporated to dryness under vacuum. Addition of Et_2O (5 mL) gave rise to a white solid, which was washed with Et_2O (3 × 5 mL) and dried under vacuum (18 mg, 0.017 mmol, 76%). Mp: 214–216 ºC. Anal. Calcd for $C_{38}H_{34}F_{14}PSO_4Ir$: C, 42.42; H, 3.19; S, 2.98. Found: C, 42.40; H, 3.30; S, 3.27. IR (Nujol, cm^{-1}): ν (CO) 2032. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.63–7.54 (m, 9 H, Ph), 7.29–7.24 (m, 6 H, Ph), 2.14 (m, 2 H, IrCH$_2$C*H*$_2$), 1.96 (m, 1 H, IrC*H*$_2$CH$_2$), 1.80 (d, $^4J_{PH}$ = 2.2 Hz, 15 H, C_5Me_5), 1.49 (m, 1 H, IrC*H*$_2$CH$_2$). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$): δ 169.1 (d, $^2J_{PC}$ = 12.3 Hz, CO), 133.3 (d, $^2J_{PC}$ = 10.3 Hz, C2 or C3, Ph), 132.8 (d, $^4J_{PC}$ = 2.6 Hz, C4, Ph), 129.8 (d, $^3J_{PC}$ = 11.4 Hz, C3 or C2, Ph), 127.7 (d, $^1J_{CP}$ = 57.8 Hz, C1, Ph), 121.1 (q, $^1J_{CF}$ = 320.1 Hz, CF_3S), 104.7 (d, $^2J_{PC}$ = 1.3 Hz, *C*$_5$Me$_5$), 33.0 (d, $^2J_{FC}$ = 20.5 Hz, IrCH$_2$*C*H$_2$), 9.0 (s, C$_5$*Me*$_5$), –13.5 (s, Ir*C*H$_2$CH$_2$); the C_6F_{11} signals were not observed. ^{19}F NMR (188.3 MHz, CD_2Cl_2): δ –79.1 (s, CF_3SO_3), –119.3 (d, 2 F, $^2J_{FF}$ = 286.9 Hz, F$_{eq}$), –123.4 (d, 2 F,

$^2J_{FF}$ = 293.9 Hz, F_{eq}), –124.9 (d, 1 F, $^2J_{FF}$ = 283.7 Hz, F_{eq}), –131.9 (d, 1 F, $^2J_{FF}$ = 264.5 Hz, F_{ax}), –133.3 (d, 1 F, $^2J_{FF}$ = 283.8 Hz, F_{ax}), –140.2 (d, 2 F, $^2J_{FF}$ = 288.6 Hz, F_{ax}), –142.8 (d, 1 F, $^2J_{FF}$ = 285.5 Hz, F_{ax}), –186.5 (s, 1 F, CH_2CF). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2): δ 3.6 (s). (+)ESI-MS: *m/z* 379, 927 (M – OTf^-); HRMS (+ESI) calcd. for M – OTf^- ($C_{37}H_{34}F_{11}IrOP)^+$: 927.1795; found: 927.1809; Δ = 1.5 ppm.

[Ir(η^5-Cp*)(CH$_2$CH$_2$-*i*-C$_3$F$_7$)(CO)(PPh$_3$)]OTf (16). It was prepared in the same way as for **15** from **11** (25 mg, 0.027 mmol overall) and CO. Off-white solid (21 mg, 0.022 mmol, 81%). Colorless analytically pure crystals were obtained by liquid diffusion of *n*-hexane into a CH_2Cl_2 solution. Mp: 195–197 ºC. Anal. Calcd for $C_{35}H_{34}F_{10}PSO_4Ir$: C, 43.61; H, 3.56; S, 3.33. Found: C, 43.40; H, 3.42; S, 3.28. IR (Nujol, cm^{-1}): ν(CO) 2015. ^1H NMR (400.9 MHz, CD_2Cl_2): δ 7.64–7.56 (m, 9 H, Ph), 7.30–7.25 (m, 6 H, Ph), 2.10–1.94 (m, 3 H, $IrCH_2CH_2$), 1.76 (d, $^4J_{PH}$ = 2.3 Hz, 15 H, C_5Me_5), 1.48 (m, 1 H, $IrCH_2$). $^{13}C\{^1H\}$ NMR (100.8 MHz, CD_2Cl_2): δ 168.5 (d, $^2J_{PC}$ = 12.8 Hz, CO), 133.5 (br d, $^2J_{PC}$ = 9.7 Hz, C2 or C3, Ph), 133.1 (d, $^4J_{PC}$ = 2.6 Hz, C4, Ph), 129.9 (d, $^3J_{PC}$ = 11.3 Hz, C3 or C2, Ph), 127.5 (d, $^1J_{CP}$ = 61.7 Hz, C1, Ph), 121.3 (q, $^1J_{FC}$ = 321.5 Hz, CF_3S), 120.9 (qdq, $^1J_{FC}$ = 286.8 Hz, $^2J_{FC}$ = 6.5 Hz, $^3J_{FC}$ = 29.1 Hz, CF_3C), 104.5 (d, $^2J_{PC}$ = 1.8 Hz, C_5Me_5), 36.3 (d, $^2J_{FC}$ = 21.1 Hz, $IrCH_2CH_2$), 8.9 (s, C_5Me_5), –12.5 (s, $IrCH_2CH_2$); the CF signal was not observed. ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ –75.1 (dq, $^3J_{FF}$ = $^4J_{FF}$ = 8.2 Hz, 3 F, CF_3), –76.4 (dq, $^3J_{FF}$ = $^4J_{FF}$ = 8.2 Hz, 3 F, CF_3), –78.7 (s, CF_3SO_3), –184.2 (m, 1 F, CF). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 3.6 (s). (+)ESI-MS: *m/z* 379, 815 (M – OTf^-); HRMS (+ESI) calcd. for M – OTf^- ($C_{34}H_{34}F_7IrOP)^+$: 815.1859; found: 815.1869; Δ = 1.2 ppm.

[Ir(η^5-Cp*)(CH$_2$CH$_2$-*i*-C$_3$F$_7$)(PPh$_3$)$_2$]OTf (17). PPh_3 (23 mg, 0.088 mmol) was added to a solution of **11** (79 mg, 0.084 mmol overall) in CH_2Cl_2 (5 mL). The mixture was stirred for 2 h at room temperature and evaporated to dryness. The residue was stirred with Et_2O (10 mL) at 0 ºC for 30 min to give a pale yellow solid, which was washed with Et_2O (2 × 2 mL) and dried under vacuum (49 mg, 0.041 mmol, 49%). Mp: 103–105 ºC. Anal. Calcd for $C_{52}H_{49}F_{10}P_2SO_3Ir$: C, 52.13; H, 4.12; S, 2.68. Found: C, 52.07; H, 4.18; S, 2.76. ^1H NMR (300.1 MHz, CD_2Cl_2): δ 7.58–6.95 (several m, 30 H, Ph), 2.66 (m, 2 H, CH_2), 2.21 (m, 2 H, CH_2), 1.27 (t, $^4J_{PH}$ = 2.3 Hz, 15 H, C_5Me_5). $^{13}C\{^1H\}$NMR (75.5 MHz, CD_2Cl_2): δ 134.7 (m, C2 or C3, Ph), 131.8 (s, C4, Ph), 128.7 (m, C3 or C2, Ph), 121.3 (qd, $^1J_{FC}$ = 287.2 Hz, $^2J_{FC}$ = 28.3 Hz, CF_3C), 102.1 (t, $^3J_{PC}$ = 2.2 Hz, C_5Me_5), 33.8 (dt, $^2J_{FC}$ = 20.5 Hz, $^3J_{PC}$ = 3.4 Hz, $IrCH_2CH_2$), 9.8 (s, C_5Me_5), –24.7 (t, $^2J_{PC}$ = 8.8 Hz, $IrCH_2CH_2$); owing to partial decomposition of the complex during the measurement the signals of C1-Ph, CF and CF_3S could not be located. ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ –75.3 (d, 6 F, $^3J_{FF}$ = 6.5 Hz, $CF(CF_3)_2$), –78.9 (s, 3 F, CF_3SO_3), –185.0 (m, 1 F, CF). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ –13.1 (s). (+)ESI-MS: *m/z* 118, 379, 589 ($[Ir(C_5Me_4CH_2)(PPh_3)]^+$), 787 (M – OTf^- – PPh_3), 980 (M – OTf^- – CF_3).

[Ir(η^5-Cp*){κ^2-*C*,*P*-C$_6$H$_4$(PPh$_2$)}(P(*p*-Tol)$_3$)]OTf (18). AgOTf (100 mg, 0.389 mmol) was added to a solution of [Ir(η^5-C_5Me_5)(Cl)(Me)(PPh_3)] (100 mg, 0.156 mmol) in CH_2Cl_2 (13 mL). The suspension was stirred for 40 min at room temperature and filtered. P(*p*-Tol)$_3$ (48 mg, 0.16 mmol) was added to the filtrate and the mixture was stirred for 2 h at room temperature. It was evaporated to dryness under vacuum and the residue was stirred with *n*-pentane (10 mL) to give a pale brown solid, which was washed with *n*-pentane (15 mL). Slow diffusion of *n*-hexane into a CH_2Cl_2 solution of the obtained solid afforded yellow crystals (52 mg, 0.047 mmol, 30%). Mp: 275–277 ºC. Anal. Calcd for $C_{50}H_{50}F_3P_2SO_3Ir\cdot(CH_2Cl_2)_{0.7}$: C, 55.28; H, 4.70; S, 2.91. Found: C, 55.13; H, 4.49; S, 2.90. ^1H MNR (400.9 MHz, CD_2Cl_2, 25 ºC): 7.53–7.27 (several m, 18 H, Ar), 7.16 (br s, 1 H, Ar), 6.88 (m, 3 H, Ar), 6.31 (br m, 2 H, C_6H_4), 5.51 (br m, 2 H, C_6H_4), 2.47 (br s, 3 H, CH_3), 2.42 (br s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 1.40 (t, $^4J_{PH}$ = 2.4 Hz, 15 H, C_5Me_5); (–90 ºC) δ 7.77–6.86 (several m, 20 H, Ar), 6.70 (m, 1 H, Ar), 6.51 (m, 1 H, Ar), 6.35 (m, 1 H, C_6H_4), 6.05 (m, 1 H, C_6H_4), 5.98 (m, 1 H, C_6H_4), 4.60 (m, 1 H, C_6H_4), 2.37 (s, 3 H, MeC_6H_4), 2.35 (s, 3 H, MeC_6H_4), 2.07 (s, 3 H, MeC_6H_4), 1.29 (s, 15 H, C_5Me_5). $^{13}C\{^1H\}$ NMR (100.8 MHz, CD_2Cl_2, 25 ºC): δ 152.4 (d, $^2J_{PC}$ = 64.2 Hz, IrC_{Ar}), 142.6 (br m, Ar), 140.0 (br m, Ar), 135.3 (br m, Ar), 133.1–132.3 (several overlapped m, Ar), 131.5 (s, Ar), 131.3 (s, Ar), 129.1–128.3 (several overlapped m, Ar), 126.8 (d, J_{PC} = 42.3 Hz, C-P), 126.4 (br s, Ar), 125.3 (d, J_{PC} = 10.1 Hz, Ar), 124.5 (m, Ar), 121.5 (q, $^1J_{FC}$ = 121.5 Hz, CF_3S), 98.4 (s, C_5Me_5), 21.4 (br s, CH_3), 9.3 (s, C_5Me_5). ^{19}F NMR (188.3 MHz, CD_2Cl_2): δ –79.1 (s). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 25 ºC): δ 2.8 (d, $^2J_{PP}$ = 17.5 Hz, P(*p*-Tol)$_3$, –77.5 (d, $^2J_{PP}$ = 17.5 Hz, $PPh_2(C_6H_4)$). (+)ESI-MS: *m/z* 146, 893 (M – OTf^-); HRMS (+ESI) calcd. for M – OTf^- ($C_{49}H_{50}IrP_2)^+$: 893.3011; found: 893.3015; Δ = 0.4 ppm.

NMR data of [Rh(η^5-Cp*)(CH$_2$CH$_2$-*t*-C$_4$F$_9$)(OTf)(PPh$_3$)] (19). A solution of **8** (8 mg, 0.009 mmol) in CD_2Cl_2 (0.7 mL) was prepared under a N_2 atmosphere into a 1.5 mL vial containing a magnetic stirring bar. AgOTf (1.5 eq) was added to this solution and the vial was sealed with a screw cap equipped with PTFE-covered septum. The suspension was stirred at room temperature for 2 h. It was taken with a syringe and filtered through a PTFE membrane filter. The filtrate was introduced into a NMR tube under N_2. ^1H NMR (300.1 MHz, CD_2Cl_2): δ 7.55–7.40 (m, 15 H, Ph), 2.48–2.20 (m, 4 H, CH_2), 1.33 (d, $^4J_{PH}$ = 3.0 Hz, 15 H, Me). ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ –65.7 (s, $C(CF_3)_3$), –78.6 (br s, CF_3SO_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 39.2 (d, $^1J_{RhP}$ = 165.8 Hz).

NMR data of [Rh(η^5-Cp*)(CH$_2$CH$_2$-*c*-C$_6$F$_{11}$)(OTf)(PPh$_3$)] (20). It was *in situ* generated from **6** in a similar way as for **19**. ^1H NMR (300.1 MHz, CD_2Cl_2): δ 7.60–7.42 (m, 15 H, Ph), 2.39–2.15 (m, 4 H, CH_2), 1.34 (d, $^4J_{PH}$ = 2.3 Hz, 15 H, Me). ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ –78.8 (br s, CF_3SO_3), –119.1 (d, 2 F, $^2J_{FF}$ = 287.6 Hz, F_{eq}), –123.3 (d, 2 F, $^2J_{FF}$ = 282.9 Hz, F_{eq}), –124.8 (d, 1 F, $^2J_{FF}$ = 282.9 Hz, F_{eq}), –132.3 (br d, 2 F, $^2J_{FF}$ = 197 Hz, F_{ax}), –140.1 (d, 2 F, $^2J_{FF}$ = 279.4 Hz, F_{ax}), –142.9 (d, 1 F, $^2J_{FF}$ = 277.0 Hz, F_{ax}), –185.5 (m, 1 F, CH_2CF). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 40.3 (d, $^1J_{RhP}$ = 166.1 Hz).

NMR data of [Rh(η^5-Cp*)(CH$_2$CH$_2$-*i*-C$_3$F$_7$)(OTf)(PPh$_3$)] (21). It was *in situ* generated from [Rh(η^5-Cp*)(CH_2CH_2-*i*-C_3F_7)I(PPh_3)][20] in a similar way as for **19**. ^1H NMR (300.1 MHz, CD_2Cl_2): δ 7.58–7.36 (m, 15 H, Ph), 2.36–2.02 (m, 4 H, CH_2), 1.33 (d, $^4J_{PH}$ = 2.9 Hz, 15 H, Me). ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ –76.1 (br m, $CF(CF_3)_2$), –79.2 (s, CF_3SO_3), –184.2 (m, CF). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 40.1 (d, $^1J_{RhP}$ = 166.0 Hz).

NMR data of [Rh(η^5-Cp*)(CH$_2$CH$_2$-*n*-C$_4$F$_9$)(OTf)(PMe$_3$)] (22). It was *in situ* generated from **9** in a similar way as for **19**. ^1H NMR (200.1 MHz, CD_2Cl_2): δ 1.62 (d, $^4J_{PH}$ = 2.8 Hz, 15 H, C_5Me_5), 1.50 (d, $^2J_{PH}$ = 10.2 Hz, PMe); the CH_2 multiplet overlapped with the Cp* signal and the signals of decomposition products. ^{19}F NMR (188.3 MHz, CD_2Cl_2): δ –78.9 (br s, CF_3SO_3), –81.6 (m, CF_2CF_3), –115.8 (br m, CF_2), –125.0 (m, CF_2), –126.4 (m, CF_2). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2): δ 7.5 (d, $^1J_{RhP}$ = 163.4 Hz).

NMR data of [Rh(η^5-Cp*)(CH$_2$CH$_2$-*t*-C$_4$F$_9$)(OTf)(PMe$_3$)] (23). It was *in situ* generated from [Rh(η^5-Cp*)(CH_2CH_2-*t*-C_4F_9)I(PMe_3)][20] in a similar way as for **19**. ^1H NMR (200.1 MHz, CD_2Cl_2): δ 2.25 (m, 2 H, CH_2), 1.65 (m, 2 H, CH_2), 1.63 (dd, $^4J_{PH}$ = 3.0 Hz, $^3J_{RhH}$ = 0.6 Hz, 15 H, C_5Me_5), 1.49 (dd, $^2J_{PH}$ = 10.4 Hz, $^3J_{RhH}$ = 0.8 Hz, PMe). ^{19}F NMR (188.3 MHz, CD_2Cl_2): δ –66.1 (s, $C(CF_3)_3$), –79.1 (br s, CF_3SO_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2): δ 7.3 (d, $^1J_{RhP}$ = 163.1 Hz).

NMR data of [Rh(η^5-Cp*)(CH$_2$CH$_2$-*i*-C$_3$F$_7$)(OTf)(PMe$_3$)] (24). It was *in situ* generated from [Rh(η^5-Cp*)(CH_2CH_2-*i*-C_3F_7)I(PMe_3)][20] in a similar way as for **19**. ^1H NMR (200.1 MHz, CD_2Cl_2): δ 1.62 (d, $^4J_{PH}$ = 2.8 Hz, 15 H, C_5Me_5), 1.49 (d, $^2J_{PH}$ = 10.4 Hz, PMe); the CH_2 multiplet overlapped with the Cp* signal and the signals of decomposition products. ^{19}F NMR (188.3 MHz, CD_2Cl_2): δ –75.9 (br m, $CF(CF_3)_2$), –79.1 (br s, CF_3SO_3) –183.4 (m, CF). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2): δ 7.4 (d, $^1J_{RhP}$ = 163.9 Hz).

NMR data of [Rh(η^5-Cp*)(CH$_2$CH$_2$-*t*-C$_4$F$_9$)(PPh$_3$)$_2$]OTf (26). The signals of this compound were observed in the reaction of *in situ* generated **19** with PPh_3 in an NMR tube. ^1H NMR (200.1 MHz, CD_2Cl_2): δ 1.26 (t, $^4J_{PH}$ = 3.4 Hz, 15 H, C_5Me_5); the Ph and CH_2 signals were overlapped with those of **19**. ^{19}F NMR (188.3 MHz, CD_2Cl_2): δ –65.7 (s, $C(CF_3)_3$). $^{31}P\{^1H\}$ NMR (81. MHz, CD_2Cl_2): δ 30.9 (d, $^1J_{RhP}$ = 147.4 Hz).

NMR data of [Rh(η^5-Cp*)(CH_2CH_2-*c*-C_6F_{11})(PPh_3)$_2$]OTf (27). The signals of this compound were observed in the reaction of *in situ* generated **20** with PPh_3 in an NMR tube. ^{1}H NMR (200.1 MHz, CD_2Cl_2): δ 1.26 (t, $^4J_{PH}$ = 3.2 Hz, 15 H, C_5Me_5); the Ph and CH_2 signals were overlapped with those of **20**. ^{19}F NMR (188.3 MHz, CD_2Cl_2): δ –186.2 (m, CF); the CF_2 signals overlapped with those of **20**. ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2): δ 29.9 (d, $^1J_{RhP}$ = 147.4 Hz).

NMR data of [Rh(η^5-Cp*)(CH_2CH_2-*i*-C_3F_7)(PPh_3)$_2$]OTf (28). The signals of this compound were observed in the reaction of *in situ* generated **21** with PPh_3 in an NMR tube. ^{1}H NMR (200.1 MHz, CD_2Cl_2): δ 1.24 (t, $^4J_{PH}$ = 3.2 Hz, 15 H, C_5Me_5); the Ph and CH_2 signals were overlapped with those of **21**. ^{19}F NMR (188.3 MHz, CD_2Cl_2): δ –75.5 (d, $^3J_{FF}$ = 7.3 Hz, $CF(CF_3)_2$), –184.9 (m, 2 F, CF). ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2): δ 29.9 (d, $^1J_{RhP}$ = 147.4 Hz).

[Rh(η^5-Cp*)(CH_2CH_2-*t*-C_4F_9)(PMe_3)$_2$]OTf (29). AgOTf (42 mg, 0.16 mmol) was added to a solution of [Rh(η^5-Cp*)(CH_2CH_2-*t*-C_4F_9)I(PMe_3)][20] (101 mg, 0.146 mmol) in CH_2Cl_2 (4 mL). The suspension was stirred at room temperature for 2 h and filtered. The filtrate was evaporated to dryness and the resulting orange residue was dissolved in Et_2O (3 mL). To this solution, PMe_3 (1 M in toluene, 0.47 mmol of PMe_3) was added and the mixture was stirred for 3h. The volatiles were removed under vacuum and the residue was stirred with Et_2O (3 × 5 mL) and dried under vacuum to give a pale yellow solid (100 mg, 0.127 mmol, 87.1%). Mp: 151–153 ºC. Anal. Calcd for $C_{23}H_{37}F_{12}P_2SO_3Rh$: C, 35.13; H, 4.74; S, 4.08. Found: C, 35.21; H, 4.70; S, 4.28. ^{1}H NMR (400.9 MHz, CD_2Cl_2): δ 2.12 (m, 2 H, $RhCH_2CH_2$), 1.79 (t, $^4J_{PH}$ = 2.8 Hz, 15 H, C_5Me_5), 1.51 (second order m, 18 H, PMe_3), 1.17 (m, 2 H, $RhCH_2CH_2$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ 122.4 (q, $^1J_{CF}$ = 288.3 Hz, CF_3C), 121.4 (q, $^1J_{CF}$ = 321.4 Hz, CF_3S), 103.4 (s, C_5Me_5), 60.0 (m, $^2J_{CF}$ = 26.5 Hz, CF_3C), 33.3 (s, $RhCH_2CH_2$), 17.3 (second order m, PMe), 10.3 (s, C_5Me_5), 3.0 (dt, $^1J_{RhC}$ = 24.7 Hz, $^2J_{PC}$ = 11.2 Hz, $RhCH_2CH_2$). ^{19}F NMR (188.3 MHz, CD_2Cl_2): δ –65.7 (s, $C(CF_3)_3$), –79.1 (s, CF_3SO_3). ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2): δ 0.3 (d, $^1J_{RhP}$ = 143.7 Hz). (+)ESI-MS: *m/z* 79, 195, 445, 637 (M – OTf$^-$); HRMS (+ESI) calcd. for M – OTf$^-$ ($C_{22}H_{37}F_9P_2Rh$)$^+$: 637.1276; found: 637.1291; *Δ* = 2.4 ppm.

[Rh(η^5-Cp*)(CH_2CH_2-*i*-C_3F_7)(PMe_3)$_2$]OTf (30). AgOTf (35 mg, 0.14 mmol) was added to a solution of [Rh(η^5-Cp*)(CH_2CH_2-*i*-C_3F_7)I(PMe_3)][20] (80 mg, 0.13 mmol) in CH_2Cl_2 (5 mL). The suspension was stirred at room temperature for 2 h and filtered. The filtrate was evaporated to dryness to give an orange residue, which was dissolved in Et_2O (6 mL). To this solution, PMe_3 (1 M in toluene, 0.13 mmol of PMe_3) was added and the mixture was stirred for 3 h at room temperature. The volatiles were removed under vacuum and the residue was stirred with Et_2O (2 × 2 mL) and dried under vacuum to give a pale yellow solid (76 mg, 0.10 mmol, 79%). Mp: 185–187 ºC. Anal. Calcd for $C_{22}H_{37}F_{10}P_2SO_3Rh$: C, 35.88; H, 5.06; S, 4.35. Found: C, 35.58; H, 5.16; S, 4.83. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.04 (m, 2 H, $RhCH_2CH_2$), 1.78 (t, $^4J_{PH}$ = 2.9 Hz, 15 H, C_5Me_5), 1.53 (second order m, 18 H, PMe_3), 0.99 (m, 2 H, $RhCH_2CH_2$). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 121.1 (qd, $^1J_{CF}$ = 287.5 Hz, $^2J_{CF}$ = 28.1 Hz, CF_3C), 121.0 (q, $^1J_{CF}$ = 320.8 Hz, CF_3S), 102.9 (dt, $^1J_{RhC}$ = 3.6 Hz, $^2J_{PC}$ = 2.4 Hz, C_5Me_5), 91.3 (d of m, $^1J_{CF}$ = 203.3 Hz, $^2J_{CF}$ = 31.1 Hz, CF), 34.0 (dt, $^2J_{FC}$ = 21.2 Hz, $^3J_{PC}$ = 4.6 Hz, $RhCH_2CH_2$), 17.0 (second order m, PMe_3), 10.2 (t, $^2J_{PC}$ = 1.1 Hz, C_5Me_5), 1.1 (dt, $^1J_{RhC}$ = 24.3 Hz, $^2J_{PC}$ = 10.6 Hz, $RhCH_2CH_2$).^{19}F NMR (188.3 MHz, CD_2Cl_2): δ –75.6 (d, $^3J_{FF}$ = 6.7 Hz, $CF(CF_3)_2$), –79.1 (s, CF_3SO_3), –184.4 (m, 1F, CF). ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2): δ –0.2 (d, $^1J_{RhP}$ = 144.1 Hz). (+)ESI-MS: *m/z* 118, 216, 587 (M – OTf$^-$); HRMS (+ESI) calcd. for M – OTf$^-$ ($C_{21}H_{37}F_7P_2Rh$)$^+$: 587.1308; found: 587.1308.

Anion or Radical Trapping Experiments in the Reaction of Complexes [Ir(η^5-Cp*)(η^2-C_2H_4)(PPh_3)] with I-*i*-C_3F_7. I-*i*-C_3F_7 (1 equiv) was added to a solution of [Ir(η^5-Cp*)(η^2-C_2H_4)(PPh_3)] (1 equiv) and the corresponding reagent (CH_3OH or CH_3OD, 2 equiv), in D_8-toluene (0.5 mL), in a NMR tube under N_2. After 1h, the NMR spectra of the solution were measured. The corresponding reaction products (H-*i*-C_3F_7, D-*i*-C_3F_7) were unambiguously identified by their ^{1}H and/or ^{19}F NMR signals.[20,41]

Reaction of 4 with AgOTf and PPh_3. AgOTf (4 mg, 0.02 mmol) was added to a solution of complex **4** (11 mg, 0.011 mmol) in CD_2Cl_2. The mixture was stirred for 2 h at room temperature, filtered and transfered to a NMR tube. The NMR spectra of the solution showed the presence of [Ir(η^5-Cp*)(η^2-o-$C_6H_4PPh_2$)(OTf)][24] and CH_3CH_2-*t*-C_4F_9 (see Supporting Information) as the main products, together with some unidentified broad signals. Then PPh_3 (4 mg, 0.015 mmol) was added and the solution was heated for 14 h at 70 ºC, leading to complete conversion into **13** and CH_3CH_2-*t*-C_4F_9.

Reaction of 10 with PPh_3. AgOTf (5 mg, 0.02 mmol) was added to a solution of complex **5** (9 mg, 0.0088 mmol) in CD_2Cl_2. The mixture was stirred for 2 h at room temperature, filtered and transfered to a NMR tube. The NMR spectra of the solution showed quantitative conversion to **10**. Then PPh_3 (3 mg, 0.01 mmol) was added and the solution was heated for 15 h at 50 ºC, leading to a mixture of **13** and CH_3CH_2-*c*-C_6F_{11}, resulting from PPh_3 cyclometallation, and **14** and H_2C=CH-*c*-C_6F_{11}, resulting from alkene substitution. The (cyclometallation products) / (substitution products) molar ratio was 13, as estimated by integration of the ^{1}H NMR and ^{31}P{^{1}H} spectra. The data of CH_3CH_2-*c*-C_6F_{11} and H_2C=CH-*c*-C_6F_{11} are given in the Supporting Information.

Decomposition of 17. A solution of **17** (5 mg, 0.004 mmol) in CD_2Cl_2 (0.5 mL) was heated at 50 ºC in a sealed NMR tube for 23 h. After this time, the NMR spectra of the solution showed quantitative conversion to **13**, CH_3CH_2-*i*-C_3F_7 (PPh_3 cyclometallation products), **14** and H_2C=CH-*i*-C_3F_7 (β-elimination products). The (cyclometallation products) / (β-elimination products) molar ratio was 3, as estimated by integration of the ^{19}F NMR and ^{31}P{^{1}H} NMR spectra of the mixture. The data of CH_3CH_2-*i*-C_3F_7 and H_2C=CH-*i*-C_3F_7 are given in the Supporting Information.

Calalytic Reactions. The initiator (0.006 mmol), the additive (see Table 1), C_6D_6 (0.5 mL), the standard ($PhCF_3$, 0.081 mmol) and the iodoperfluoroalkane (0.12 mmol) were introduced into a J. Young NMR tube under N_2. The tube was cooled with liquid N_2 and freeze-pump-thawed. Ethene (0.12 mmol) was condensed inside the cold tube and it was sealed, thawed, and warmed at the corresponding temperature. The progress of the reaction was monitored by NMR spectroscopy. The conversion was determined from the integrals of the CF_3 signals of the standard and the reaction product $ICH_2CH_2R_F$. The data of the halogenated organic products are given in the Supporting Information.

Crystal Structure Determinations. Single crystals were obtained by liquid diffusion of *n*-hexane in Et_2O (compound **1**), Et_2O in CH_2Cl_2 (compound **13**) or *n*-hexane in CH_2Cl_2 (compound **16**). Single crystals of [Rh(η^5-Cp*)Cl(PMe_3)$_2$]OTf spontaneously grew after the decomposition of **23** in CD_2Cl_2 solution. The compounds were measured on a Bruker D8 SMART diffractometer at 100K. Data were collected using a sealed tube with Mo-Kα radiation (0.71073Å) in w-scan. The structures were solved by direct methods. All were refined anisotropically on F^2. The methyl groups were refined using rigid groups and the other hydrogens were refined using a riding mode. *Special features of refinement:* For compound **1**, the CF_3 ligands are disordered over two positions, with a *ca*. 51:49% distribution. Crystal data and details about data acquisition and structure refinement are included in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Additional Experimental details, NMR spectra and crystallographic data (PDF).

Crystallographic Information (CIF).

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Notes

The authors declare no competing financial interest.

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