Ligand Rearrangement and Hemilability in Rhodium(I) and Iridium(I) Complexes Bearing Terphenyl Phosphines

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Abstract

We describe the synthesis of a series of cationic rhodium(I) and iridium(I) compounds stabilized by sterically demanding phosphines that contain a terphenyl substituent, PMe$_2$Ar’ (Ar’ = 2,6-diarylphenyl radical). Salt metathesis of metal precursors [MCl(COD)(PMe$_2$Ar)] (M = Rh, Ir; COD = cyclooctadiene) with NaBArF$_4$ (BArF$_4$ = B(3,5-C$_6$H$_3$(CF$_3$)$_2$)$_4$) results in a series of cationic complexes in which the loss of the chloride ligand is compensated by the appearance of weak π-interactions with one of the flanking aryl rings of the terphenyl substituent. The same experiments carried out with carbonyl compounds [MCl(CO)$_2$(PMe$_2$Ar)] led to the corresponding cationic carbonyl complexes, whose CO-induced rearrangement reactivity has been investigated, both experimentally and computationally. The differences in reactivity between rhodium and iridium complexes, and as a result of varying the sterics of terphenyl phosphines are discussed.

Introduction

Phosphines are among the most widely used ancillary ligands in coordination and organometallic chemistry, largely due to the possibility of finely modulating their steric and electronic properties in a predictive manner. The range of physicochemical properties of transition metal complexes that can be tuned by the judicious choice of a phosphine ligand is exceptional. In particular, phosphines that contain bulky substituents have been successfully applied to stabilize a variety of low-coordinate transition metal complexes with important implications in catalysis. A notorious example is found in the work of Buchwald and coworkers, who synthesized in 1998 the first example of a currently extensive family of biaryldialkyl phosphines.

The use of biaryl phosphines in homogeneous catalysis has found great success, particularly in palladium-catalysed cross coupling and amination reactions. Catalytic applications that rely on the combination of biaryl phosphines with iridium and rhodium precursors have also been described, although to a lesser extent. In an prominent example, Hartwig and co-workers demonstrated that the combination of [Rh(COD)$_2$]BF$_4$ (COD = 1,5-cyclooctadiene) and a biaryldialkyl phosphate functions as an excellent catalytic mixture for the intramolecular hydroamination of inactivated alkenes under mild conditions, with the active species containing the phosphate ligand bound to rhodium in a κ$^1$,η$^6$ coordination mode (A in Scheme 1). The group of Goldberg has investigated the chemistry of related rhodium complexes where the flanking aryl ring of several biaryl phosphines coordinates to the metal
centre with variable hapticity. These studies were later extended to the corresponding iridium systems. While rhodium designs were active catalyst for arene hydrogenation, their iridium counterparts revealed their potential for transfer hydrogenation reactions. More recently, the usefulness of Rh/biaryl phosphine combinations for the selective and catalytic functionalization of C-H bonds has been disclosed.

![Scheme 1](image)

Scheme 1. (a) Key intermediate A in the Hartwig’s Rh-mediated hydroamination of alkenes; (b) Terphenyl phosphine ligands employed in this work.

The ability of biaryl phosphines to function as hemilabile ligands by means of dynamic π-arene coordination seems to be crucial for its success in catalysis. Although this type of coordination enhances the stability of the active species, catalyst decomposition remains a major limitation, as observed with Goldberg and Hartwig’s systems. With this in mind, it is surprising that terphenyldialkyl phosphines, in which the biaryl substituent is replaced by a sterically more crowded terphenyl (2,6-diarylphenyl) group, have not been examined in deeper detail. We recently embarked to explore this type of ligands, demonstrating their potential to stabilize otherwise elusive organometallic frameworks. This work extends these studies to cationic rhodium and iridium systems bearing 1,5-cyclooctadiene and ethylene ligands. Thus, we analyse the coordination modes of two terphenyl phosphine ligands, namely PMe$_2$Ar$^{	ext{Xyl}}_2$ and PMe$_2$Ar$^{	ext{Dipp}}_2$ (Scheme 1). In addition, we have synthesized rhodium and iridium cationic derivatives where the olefins have been substituted by CO ligands, and have observed a CO-induced ligand rearrangement in which phosphine hemilability plays a key role.

Results and Discussion

Synthesis of Rh(I) and Ir(I) olefin compounds

Salt metathesis of chloride complexes 1 (1a: Ar′ = PMe$_2$Ar$^{	ext{Xyl}}_2$; 1b: Ar′ = PMe$_2$Ar$^{	ext{Dipp}}_2$), cleanly prepared by the 1:1 reaction of [RhCl(COD)] and the corresponding terphenyl phosphine, with NaBAR$_f$ (BAR$_f$ = B(3,5-C$_6$H$_3$(CF$_3$)$_2$)$_2$) in dichloromethane, afforded cationic complexes 2 quantitatively (Scheme 2). Chloride abstraction in compounds 1 triggers η$^6$-cooordination of the π-system of one of the flanking aryl substituents of the phosphine, forcing the COD ligand to change its bidentate η$^2$-binding mode to monodentate η$^2$-binding. Whereas there are examples of a phosphine aryl substituent coordinating to Rh(I) and Ir(I) in the η$^5$-mode while maintaining the M—P bond, only a few complexes of these metals that exhibit monodentate COD ligand coordination have been reported. To our knowledge, prior to this work, no complexes of this kind had been structurally characterized for rhodium.
The formulation proposed for complexes 2 in Scheme 2 was ascertained by NMR spectroscopy studies in solution and, in the case 2a, also by X-ray crystallography. In the $^{31}$P($^1$H) NMR spectrum, a doublet at ca. 48 ppm, with a relatively large $^1$J$_{Rh}$ coupling of 192 Hz was observed for both 2a and 2b. Complex 2a shows fluxional behaviour in solution, as inferred from the presence of some broad signals in the $^1$H NMR spectrum recorded at 25 ºC (500 MHz, CD$_2$Cl$_2$). Cooling at 0 ºC allowed freezing the structure pictured in Scheme 2 on the NMR time scale, thereby permitting assigning all the $^1$H and $^{13}$C NMR resonances in their respective spectra (see Supporting Information). Two of the aromatic proton resonances of compounds 2 appear somewhat shielded at around 6.7 (d, 2 H, $^3$J$_{Rh}$ ca. 7.5 Hz) and 5.9 ppm (t, 1 H, $^3$J$_{Rh}$ ca. 7.5 Hz), in accordance with the proposed $\eta^6$-coordination of one of the flanking aryl substituent of the terphenyl group. This is in contrast with corresponding resonances being found above 7.2 ppm for the analogous H atoms in the free flanking ring. In the $^{13}$C($^1$H) NMR spectrum of 2a, the associated $^{13}$C nuclei appear at 112.1 and 97.1 ppm for the Rh-bonded xylyl, and at 128.6 and 127.8 ppm for the non-coordinated xylyl substituent, and the same pattern is found for 2b. A similar dichotomy was found between these NMR parameters of the olefinic =CH groups of the COD ligand, with the proton and carbon nuclei of the Rh-bonded –CH=CH– moiety in 2 resonating at 3.38 and 74.0 ppm (d, $^3$J$_{Rh}$ = 13 Hz) respectively, while those corresponding to the uncoordinated C=C bond resonated at 5.55 and around 130 ppm.

At variance with 2a, compound 2b based on the bulkier PMe$_3$Ar$_{\text{Dipp}_2}$ phosphine led to sharp signals in its corresponding $^1$H NMR spectrum, with no sign of fluxionality on the NMR time scale. A plausible explanation for the dynamic behaviour of 2a could be the accomplishment of a fast dynamic equilibrium with unobserved amounts of an isomer featuring $\eta^5$-coordination of the xylyl ring and bidentate $\eta^2$-$\eta^2$-binding of the COD ligand at 25 ºC. In fact, this latter structure was the preferred isomer in a related complex based on [(2-Biphenyl)dicyclohexylphosphine] (CyJohnPhos). Taking in mind the importance of these π-arene interactions in catalysis, it is interesting to note that the prevalence of a particular π-coordination mode in these rhodium complexes containing biaryl or terphenyl phosphines may be modulated by the choice of the phosphorus ligand.

The proposed dynamic exchange between $\eta^2$- and $\eta^6$-coordination modes of the arene substituent is further supported by investigations on the analogous iridium system. Chloride abstraction by NaBAR$_f$ from two iridium(I) compounds of formula [IrCl(COD)(PR$_2$Ar')] (3a: Ar' = PMe$_3$Ar$_{\text{Dipp}_2}$, and 3b: Ar' = PMe$_3$Ar$_{\text{Dipp}_2}$) proceeded readily to yield cationic species 4 and 5. As depicted in Scheme 3 the equilibria between these complexes result from hapticity changes...
within both the flanking arene of the terphenyl substituent (κ vs. η⁶) and the COD ligand (η²:η² vs. η¹). The equilibrium for 4a seems to be more rapid than in the rhodium analogue 2a, as inferred from the sharp resonances detected in the corresponding NMR spectra, and was confirmed by the presence of several exchange peaks in 2D EXSY experiments. The isomeric distribution is phosphine dependent, with the smaller PMe₂ArP{sup 2} leading to isomer 4a as the major component (4a:5a; 59:41 ratio), whereas the more sterically congested PMe₂ArDipp₂ preferring COD η², monodentate coordination accompanied by η²-coordination of the flanking Dipp ring (4b:5b; 14:86 ratio).

The equilibrium was noticed (5.6 and 2.9 ppm) relative to free phosphine. For this system, however, κ⁻P monodentate coordination of the phosphine in 4a; 14:86 ratio) whereas the more sterically congested PMe₂ArDipp₂ preferring COD η², monodentate coordination accompanied by η²-coordination of the flanking Dipp ring (4b:5b; 14:86 ratio).

The nature of isomers 4 and 5 was postulated on the basis of NMR spectroscopy, although the formulation of 4a was further confirmed by X-ray studies. Compounds 4 present a 3¹P{sup 1}H resonance at around 15 ppm, slightly deshielded (ca. 2 ppm) relative to their η²-COD isomers 5. In the latter, η⁶-coordination of the flanking arene is ascertained by the somewhat upfield signals at 6.6 (d, 2 H, 3JHH = 6 Hz) and 5.7 (t, 1 H, 3JHH = 6 Hz) ppm. The two distinctive peaks recorded at around 5.6 and 2.9 ppm due to the COD fragment evince that only one of the two olefinic moieties is bound to iridium. In contrast, a set of two resonances in the interval 3.2 to 3.4 ppm in compounds 4 is consistent with the η²-coordination proposed for COD. In fact, this latter formulation is similar to that previously reported for related iridium complexes based on biarylalkyl phosphines. For this system, however, isomers alike 5 were not detected and no sign of solution equilibrium was noticed.

The addition of pyridine to the equilibrium mixture 4a/5a results in quantitative formation of compound 6a, a sterically encumbered version of the widely used Crabtree's catalyst (Scheme 4). The latter, as well as many other cyclooctadiene Ir(I) compounds bearing phosphine ligands, have found ample use in catalysis, highlighting the potential of compounds alike 6a for these purposes. This is a research avenue that we are currently pursuing in our laboratories. The κ⁻P monodentate coordination of the phosphine in 6a is confirmed by the symmetric pattern observed for its deshielded (7.1 - 7.6 ppm) aromatic ¹H NMR resonances, and by the presence of two signals, each corresponding to two protons, at 3.49 and 3.98 ppm, denoting η²:η²-coordination of cyclooctadiene. In turn, the corresponding ³¹P{sup 1}H NMR band of 6a appears at lower frequency (-12.1 ppm) than in isomers 4a (16.9 ppm) and 5a (2.0 ppm), i.e. shifted to higher frequency by only ca. 30 ppm relative to free phosphate.

As anticipated, the solid state structures of complexes 2a and 4a were confirmed by single crystal X-ray studies. Figure 1 depicts the molecular structures of the cations of 2a and 4a. As can be seen in the structure of 2a, its Rh(I) centre is formally five-coordinate to one of the C=C bonds of COD (C1—C2), one of the flanking η₆-aryl ring (C15—C20), and the phosphorus atom of the phosphine ligand. The Rh-η₂-COD linkage is characterized by Rh—C bonds with length ca. 2.15 Å, comparable to other known Rh(I)-alkene units. The Rh(I)-η₆-arene moiety presents, however, relatively long Rh—C bonds, with the exception of the Rh-Cᵦᵦ contact (Rh1—C15 in Figure 1), which at 2.142(4) Å is practically identical to the Rh—COD bond distances. The remaining Rh—C bonds to the η₆-aryl ring have lengths in the range 2.30-2.35 Å. These separations are similar to, albeit somewhat longer, than those reported for other Rh(I)-arene complexes. This coordination mode clearly differs from that of 4a, where the geometry around iridium is square planar, encompassing binding to phosphorus, η²:η²-coordination to COD and a κ¹, ηπ-coordination with a flanking aryl ring. The Ir-C bond distances within the Ir-η²-COD fragments have normal values, with those in trans to phosphorus being slightly elongated (ca. 2.24 Å) with respect to those trans to the ηπ-interaction (ca. 2.12 Å), as a result of the stronger trans influence of the phosphine. At variance with previous related systems based on biaryl phosphines, that exhibit η²-arene coordination defined by two close M-C₆ distances,11,12 the terphenyl phosphine of complex 4a is mainly coordinated through the phosphorous terminus and through the ipso carbon atom of a lateral aryl ring (Figure 1). The latter interaction is relatively strong, with an Ir1—C7 contact of 2.308(4) Å, which coupled with the ¹³C{¹H} NMR data discussed above support κ¹-P, κ¹-C₆-phosphine binding,23 in preference to κ¹-P, η²-arene coordination.11,12 Nonetheless, a slim tilt is noticeable in the interacting aryl substituent, and this distortion breaks the symmetry along the Ir-π-arene moiety facilitating the approach of one of the ortho carbon atoms. As a result, an Ir1—C8 contact of 2.609(7) Å can be measured, which is significantly shorter than the Ir1—C12 separation of 2.878(8) Å to the other ortho carbon atom. In principle, a non-symmetrical η²-coordination of the anchored arene cannot be disregarded.16
To complete this series of Rh(I)/Ir(I) olefin compounds we targeted ethylene structures analogous to Hartwig’s key intermediate in hydroamination reactions (A in Scheme 1). Accordingly, the ethylene rhodium (7) and iridium (8) adducts, closely related to complexes 2 and 5, respectively, were cleanly obtained from the reactions of the corresponding dimers \([\text{MCl}(\text{C}_2\text{H}_4)]_2\) (M = Rh, Ir) with NaBARf in the presence of the phosphine (CH\(_2\)Cl\(_2\), 25 °C, Scheme 5). Addition of NaBARf proved essential to favor quantitative formation of the desired ethylene adducts, as in its absence, cationic compounds 7 and 8 with chloride as counteranion formed along with various other species containing a metal-bound chloride ligand. Once more, the new compounds were characterized by microanalysis and NMR spectroscopy. The \(^1\text{H}\) and \(^{13}\text{C}\{^1\text{H}\}\) NMR spectra are in accord with the proposed \(\eta^6\)-coordination of one of the phosphine aryl substituents. In turn, in rhodium compounds 7, the ethylene ligand undergoes fast rotation on the NMR time scale at 25 °C, such that the four hydrogen atoms give rise to broad \(^1\text{H}\) NMR resonances at around 2.9 ppm, while the \(^{13}\text{C}\) nuclei resonate as a doublet in the proximity of 46 ppm (\(^1\text{J}_{\text{Crh}} = 13\) Hz). Ethylene rotation is hindered in their iridium analogues, reflecting the stronger Ir-\(\eta^2\)-C\(_2\)H\(_4\) bond when compared to Rh-\(\eta^2\)-C\(_2\)H\(_4\) bond due to the iridium higher basicity. This fact is evidenced by two distinctive signals at around 1.7 and 3.0 ppm due to the ethylene ligand in the \(^1\text{H}\) NMR spectra of compounds 8. The corresponding \(^{13}\text{C}\{^1\text{H}\}\) NMR
resonance appears at ca. 24 ppm. The $^{13}$C signals of the C$_2$H$_4$ ligand in complexes 8 are therefore shielded by more than 20 ppm with respect to those in the rhodium analogues, evincing a higher sp$^3$ character of the carbon atoms as a consequence of increased π-back donation from the Ir(I) centre. It is widely accepted that the low-frequency shift of the olefin carbon atoms relative to free ethylene (122.8 ppm) increases with π-back bonding.$^{25}$ The structure of compound 7b was authenticated by X-ray diffraction studies (Figure SX). The bound ethylene molecule presents a C-C bond distance of 1.386(6) Å, nearly identical to that of the related ethylene adduct reported by Hartwig (A in Scheme 1)$^{10}$ and close to the 1.37 distance in Zeise’ salt.$^{26}$ The remaining geometric parameters are essentially similar to those measured in structures A and 2a.

Scheme 5. Synthesis of complexes 7 and 8.

Synthesis of rhodium and iridium carbonyl compounds

Substitution of cyclooctadiene by two CO ligands in this type of complexes has been amply utilized to gauge the electronic properties of ancillary ligands,$^{27}$ particularly bulky phosphines, as well as to access catalysts with enhanced performance.$^{28}$ For instance, using this method we proved that the basicity of terphenyl phosphines PMe$_2$Ar$^\text{Xyl}$ and PMe$_2$Ar$^\text{Dipp}$ is comparable to that of the related widely employed PR$_2$Ar biarylphosphines.$^{17,29}$

We now decided to extend the chemistry of our neutral carbonyl compounds to more reactive cationic rhodium and iridium derivatives, once again by means of chloride abstraction. Treatment of CH$_2$Cl$_2$ solutions of 9 and 10 with NaBARF cleanly generated the desired cationic carbonyl complexes, although the outcome of the reaction was dependent on the selected metal. For instance, under the conditions of Scheme 6, rhodium precursors 9 led to monocarbonyl compounds 11-CO, whereas the iridium analogs provided dicarbonyl complexes 12-(CO)$_2$ (Scheme 6). Once again, abstraction of the chloride ligand by the Na$^+$ cation created a vacant coordination site that was occupied by a flanking aryl ring of the phosphine. In the rhodium system η$^6$-arene coordination was preferred, which along with phosphine bonding resulted in a (2+6)-electron binding mode that caused concomitant dissociation of one of the original carbonyl groups and formation of the formally five-coordinate 18-electron complexes 11-CO. On the contrary, the two carbonyl ligands remained bound to iridium in compounds 12-(CO)$_2$, and chloride elimination was simply compensated by a κ$^1$-C$_{aryl}$ coordination of a flanking aryl substituent, as occurs in compounds 4. The dissimilar behaviour of the two
systems may reflect once more the higher basicity of Ir(I) with respect to Rh(I), resulting in increased back donation to carbonyl ligands and stronger M-CO bonds.

As expected, a single ν(CO) intense band at around 2015 cm\(^{-1}\) appears in the IR spectra of compounds 11-CO, while dicarbonyl compounds 12-(CO)\(_2\) are characterized by two strong bands at ca. 2094 and 2027 cm\(^{-1}\) respectively, assigned to the antisymmetric and symmetric stretching vibrations of the CO groups. The molecular formulation of complexes 11-CO and 12-(CO)\(_2\) was also ascertained by means of NMR spectroscopy. The proposed η\(^6\)-coordination of the flanking aryl unit in the rhodium complexes is supported by the comparison of the \(^1\)H and \(^13\)C(\(^1\)H) NMR spectra with those of the related species 2 and 7. In addition, the carbonyl ligand of complexes 11-CO is responsible for a distinctive \(^13\)C resonance at 183 ppm (dd, \(J\)\(_{\text{Rh}}\) ≈ 95, \(J\)\(_{\text{CP}}\) ≈ 18 Hz) while the \(^13\)C(\(^1\)H) spectrum consists of a doublet at 49.3 ppm (\(J\)\(_{\text{Rh}}\) ≈ 169 Hz). The presence of two carbonyl groups in compounds 12-(CO)\(_2\) is evinced by two resonances at around 183 (d, \(J\)\(_{\text{CP}}\) = 102 Hz) and 163 (d, \(J\)\(_{\text{CP}}\) = 14 Hz) ppm due respectively to the ligands oriented trans and cis to the phosphine. Distinctive \(^13\)C NMR resonances at ca. 118 ppm (d, \(J\)\(_{\text{CP}}\) = 3 Hz) due to the ipso carbon atoms of one of the flanking aryl rings in compounds 12-(CO)\(_2\) are indicative of the existence of a weak κ\(^3\)-interaction with the metal to compensate for chloride abstraction.\(^{30}\)

Complexes 11a-CO and 12b-(CO)\(_2\) were also characterized by single crystal X-ray studies (Figure 2). The overall structures are similar to those previously discussed for complexes 2a and 4a, respectively. The molecules of 11a-CO have a Rh1—P1 bond essentially identical (2.2338(17) Å) to the Rh—P bond of 2a and to that present in related complexes containing η\(^6\), κ\(^3\)-arene-phosphine ligands.\(^{10,31}\) There are some small differences in the Rh-η\(^6\)-arene linkages of complexes 2a and 11a-CO, as in the latter the Rh—C\(_\text{arene}\) contacts are somewhat longer. Similar
to 2a, the Rh—C<sub>ipso</sub> bond exhibits the shortest separation (Rh1—C8 = 2.163(5) Å), but the remaining Rh—C<sub>arene</sub> bonds span over the range ca. 2.31-2.39 Å. The Rh—CO bonds feature regular metrics (Rh1—C1 = 1.846(6) Å; C1—O1 = 1.145(8) Å). The proposed η<sup>1</sup>-coordination of the flanking arene in 12b·(CO)<sub>2</sub> is confirmed by a short Ir1—C7 contact of 2.297(9) Å involving the ipso carbon of the π-aryl group. Similarly to the structure of 4a, this ring is slightly slanted in such a manner that one of the adjacent carbon atoms (Ir1—C8 = 2.571(4) Å) is closer to the iridium centre than the other one (Ir1—C12 = 2.742(4) Å). <sup>13</sup>C{<sup>1</sup>H} NMR data and the noticeable shorter Ir-C<sub>arene</sub> contact to the ipso carbon already alluded to favour κ<sup>1</sup>-C<sub>arene</sub> coordination, which is further supported by QTAIM calculations (see Supporting Information).

![ORTEP view of the cation of complex 11a·CO and 12b·(CO)<sub>2</sub>; hydrogen atoms are excluded and isopropyl groups are represented in wireframe format for clarity, while thermal ellipsoids are set at 50% level of probability.](image)

Figure 6. ORTEP view of the cations of complexes 11a·CO and 12b·(CO)<sub>2</sub>; hydrogen atoms are excluded and isopropyl groups are represented in wireframe format for clarity, while thermal ellipsoids are set at 50% level of probability.

Compounds 11·CO were isolated in good yields as air stable orange powders that remained unaltered for long periods of time. Their iridium counterparts, however, underwent in solution an interesting rearrangement of the carbon monoxide ligands. Thus, dichloromethane
solutions of compound 12a·(CO)₂ underwent spontaneous iridium-carbonyl disproportionation to 1:1 mixtures of the monocarbonyl species 12a·CO, that is, the iridium version of the aforementioned compound 11a·CO, and the tricarbonyl complex 12a·(CO)₃ (Scheme 7). The reaction was readily monitored by ³¹P{¹H} NMR spectroscopy. Resonances corresponding to complexes 12a·CO (6.7 ppm) and 12a·(CO)₃ (-20.2 ppm) gradually appeared shifted to higher fields when compared to 12a·(CO)₂ (16.2 ppm). Kinetic analysis of this rearrangement revealed a first-order dependence on dicarbonyl compound 12a·(CO)₂ at room temperature characterized by a first-order rate constant of 2.5·10⁻⁴ s⁻¹, which corresponds to ΔG°₂⁹⁸ ≈ 22.3 kcal·mol⁻¹ and t₁/₂ ≈ 45 min (see Supporting Information for details). This finding points out to a stepwise mechanism in which CO dissociation appears to be the rate limiting step. Coordination of the liberated CO to still unreacted 12a·(CO)₂ would rapidly yield the tricarbonyl species 12a·(CO)₃. In accordance with this proposal, exposure of dichloromethane solutions of 12a·(CO)₂ to carbon monoxide (1.2 bar, 25 ºC) results in immediate and quantitative formation of 12a·(CO)₃. DFT calculations support these findings and show an energy barrier of 18.3 kcal·mol⁻¹ for CO dissociation from 12a·(CO)₂ to yield 12a·CO and CO (+8.3 kcal·mol⁻¹), which can be captured by 12a·(CO)₂ through a low barrier of 7.8 kcal·mol⁻¹ to afford 12a·(CO)₃. The latter species is predicted to be the most stable thermodynamically (-9.5 kcal·mol⁻¹ from 12a·(CO)₂ + CO).

\[
\text{12a·(CO)₂} \xrightarrow{25 \degree C, 4 \text{ h}} \text{12a·(CO)₁} + \text{12a·(CO)₃}
\]

Scheme 7. Solution rearrangement of the carbonyl ligands of complex 12a·(CO)₂.

Compounds 12a·CO and 12a·(CO)₃ were synthesized independently (see Experimental Section) and their structures ascertained by spectroscopic methods and X-ray diffraction studies. As expected, compound 12a·CO exhibits an intense band in its IR spectrum at 2000 cm⁻¹ due to the carbonyl ligand, shifted by almost 20 cm⁻¹ at lower frequency in comparison with the rhodium analog 11a·CO. In turn, tricarbonyl compound 12a·(CO)₃ gives rise to two bands at 2126 and 2027 cm⁻¹, in agreement with previous compounds of formula [Ir(CO)₃PR₃]+. Overall, the average bond stretching frequencies for the three iridium compounds depicted in Scheme 7 follow the order 12a·(CO)₃>12a·(CO)₂>12a·CO, in accordance with the distribution of electron density donated by the Ir(I) centre to the π* antibonding orbital of the CO ligands.

The ¹H and ¹³C{¹H} NMR spectra of the new compounds are also in agreement with the proposed formulation. A ¹³C{¹H} NMR resonance due to the carbonyl ligand in 12a·CO had been recorded at 167.2 ppm (d, ²J_{CP} = 2 Hz), while for compound 12a·(CO)₂ two signals at 173.1 (d, ²J_{CP} = 15 Hz) and 168.2 (d, ²J_{CP} = 88 Hz) ppm can be assigned to the CO ligands cis and trans.
to the phosphorus atom. η⁶-Arene coordination in 12a-CO becomes notorious after analysing its ¹H and ¹³C{¹H} NMR data. Moreover, its nature was authenticated by X-ray diffraction studies (Figure 3), which revealed a structure closely similar to that of its rhodium counterpart 11a-CO. On the contrary, examination of the spectroscopic data recorded for complex 12a-(CO)₃ did not provide definitive evidence for the existence of weak interactions with the aryl substituents of the phosphine. The two flanking aryl rings of the terphenyl fragment appear equivalent at room temperature on the NMR time scale. Nevertheless, 12a-(CO)₃ exhibits dynamic behaviour in solution due to rapid exchange of the two phosphine aromatic rings, with a coalescence temperature of around -60 ºC measured in the variable temperature ¹H NMR spectrum. Besides, noticeable exchange peaks were observed in 2D-EXSY experiments. The ¹³C{¹H} NMR resonance due to the rapidly exchanging ipso carbon atoms of the xyllyl substituents appears slightly deshielded (132.3 ppm) when compared to non-coordinated xyllyl rings (ca. 136 ppm). In the solid state, complex 12a-(CO)₃ adopts a distorted square planar geometry, as determined by X-ray diffraction studies. One of the phosphine lateral xyllyl rings approaches the metal from an apical position and forces the CO groups cis to the phosphine to bend towards one another, enforcing a distorted trigonal bipyramid arrangement around iridium (OC₉₁—Ir—CO₉₁ = 147.17(6)º). The shortest contact between iridium and the proximal xyllyl ring occurs through the ipso carbon atom at a distance of 2.523(6) Å (Ir₁—C₇). This separation, albeit longer than in complexes 12a-CO and 12a-(CO)₃, is sufficiently short to be considered as involving a weak κ¹-Carene interaction. The DFT-optimized geometry of 12a-(CO)₃ is consistent with this arrangement, and topological analysis revealed the existence of a bond critical point and a unique bond path between the iridium and the ipso carbon atoms (see SI for details).
Despite many similarities, the carbon monoxide chemistry of the related iridium system bearing the bulkier PMe$_2$Ar$_2$Dipp phosphine revealed some subtle differences. For example, when dichloromethane solutions of 12b·(CO)$_2$ were allowed to stand at room temperature for several days, the only discernible product was the mono-carbonyl derivative 12b·CO, even if the reaction was monitored in a sealed NMR tube. It soon became clear that, at variance with the system based on PMe$_2$Ar$_2$Xyl, complex 12b·(CO)$_2$ is unable to trap at a reasonable rate the carbon monoxide it might eventually dissociate. In support of this, DFT calculations reveal that CO capture by the latter species has a barrier 6.2 kcal·mol$^{-1}$ higher than that found for its less hindered counterpart 12a·(CO)$_2$. Tricarbonyl complex 12b·(CO)$_3$ is again predicted by DFT to be the most stable of the three 12b·(CO)$_n$ species (2.6 kcal·mol$^{-1}$ from 12b·(CO)$_2$ + CO) and could, indeed, be quantitatively prepared by exposure of its mono or dicarbonyl precursors to an excess of CO (1.2 bar, CH$_2$Cl$_2$, 25 ºC, 10 min). According to the full spectroscopic characterization (IR and NMR) of these new compounds, their structures are equivalent to those depicted in Scheme 7. The chemical formulation of compound 12b·CO was further verified by single crystal X-ray studies. The geometric features determined are essentially identical to those in the related xyllyl phosphine system (see SI). Regarding complex 12b·(CO)$_3$, variable temperature NMR studies evidenced a fluxional behaviour similar to that discussed above for 12a·(CO)$_3$, with a nearly identical coalescence temperature. In this case, the DFT-optimized geometry of 12b·(CO)$_3$ is distorted from that of 12a·(CO)$_3$, probably due to steric hindrance between isopropyl and carbonyl groups, shifting the closest Ir-C$_{arene}$ interaction to the ortho carbon (see SI for details). Monitoring the evolution of 12b·(CO)$_2$ by $^{31}$P{$^1$H} NMR spectroscopy at 25 ºC provided kinetic information for the formation of monocarbonyl species 12b·CO ($k_1 = 1.2 \times 10^{-5}$ s$^{-1}$, $\Delta G^\ddagger_{298} = 24.1$ kcal·mol$^{-1}$, $t_{1/2} \approx 16$h; see SI for details), clearly reflecting the slower dissociation rate of carbon monoxide when compared to the system constructed around PMe$_2$Ar$_2$Xyl (22.1 v 18.3 kcal·mol$^{-1}$ according to the calculations).

To complete these studies we decided to explore whether the analogous cationic carbonyl rhodium compounds would exhibit similar rearrangement chemistry. Although exposure of
complexes 11-CO to 1 bar of carbon monoxide did not result in the formation of the expected tricarbonyl compounds, some interesting observations were disclosed when somewhat higher CO pressures (6 bar) were employed. The chemical changes were monitored by $^1$H, $^{31}$P($^1$H) and $^{13}$C($^1$H) NMR spectroscopy at variable temperature (from 25 to -60 ºC) and are summarized in Scheme 8. As can be seen, attainment of a fast equilibrium on the laboratory time scale between the starting monocarbonyl complex 11-CO and tricarbonyl species 11-(CO)$_3$ is proposed. Naturally, equilibria of this type are temperature dependent and low temperatures disfavour CO dissociation from 11-(CO)$_3$ and formation of the monocarbonyl compounds 11-CO, which exhibits in addition full phosphine chelation, i.e. $\kappa^1$-P:$\eta^6$-arene coordination of the terphenyl phosphine ligand. The variable temperature $^{13}$C($^1$H) NMR studies to be discussed next (between -60 and 25 ºC) back strongly this proposal. Likewise, variable temperature $^{31}$P($^1$H) NMR experiments using complex 11a-CO are also in accordance with the equilibrium represented in Scheme 8 and reveals besides that the tricarbonyl derivative exists in equilibrium with minor concentrations of a closely related complex. This equilibrium is fast on the NMR time scale and can only be frozen at temperatures below -50 ºC. It is important to mention that removal of CO under vacuum displaces the equilibrium of Scheme 8 toward the left, allowing quantitative recovery of the monocarbonyls 11-CO.

Scheme 8. Solution equilibria between complexes 11-CO and 11-(CO)$_3$ under a CO atmosphere (6 bar, CD$_2$Cl$_2$, 25 ºC to -60 ºC).

Figure 4 contains $^{13}$C($^1$H) NMR spectra of CD$_2$Cl$_2$ solutions of complex 11a-(CO)$_3$ recorded at 25, -40 and -60 ºC, under 6 bar of CO. For the sake of simplicity only the most informative carbonyl and aliphatic regions of the spectrum are shown (roughly 185-176 and 24-16 ppm, respectively). With reference to the room temperature spectrum, the monocarbonyl 11a-CO exhibits the expected doublet-of-doublet carbonyl resonance centred at 183.2 ppm, a PMe$_2$ doublet signal at 19.1 ppm (d, $^1$J$_{CP}$ = 37 Hz) and Me(Xyl) singlets with $\delta$ 22.0 and 20.3 ppm. In addition, there is a broad hump centred at ca. 182.1 ppm and a singlet at 22.4 ppm that are attributed to the CO ligands and Me(Xyl) groups, respectively, of the purported tricarbonyl 11a-(CO)$_3$. The signal due to the PMe$_2$ groups of the phosphine is very broad and can be conjectured to be located at 19.5 ppm, practically hidden into the base-line. Upon cooling, this signal becomes clearly discernible and appears at 18.5 ppm (d, $^1$J$_{CP}$ = 37 Hz) in the -60 ºC spectrum. At the latter temperature, the broad signal of the CO ligands of 11a-(CO)$_3$ centred at ca. 182.1 ppm, resolves into two doublet-of-doublet resonances in a ca. 2:1 ratio, observed at
180.6 ($^1J_{Crh} = 69$, $^2J_{Crh} = 16$ Hz) and 178.8 ppm ($^1J_{Crh} = 51$, $^2J_{Crh} = 92$ Hz), attributable respectively to two cis and one trans carbonyl groups, relative to the phosphine ligand. In accordance with these findings, the $^{31}$P($^1$H) NMR spectrum (see SI) at 25 ºC shows the expected doublet for 11a·CO with $\delta$ 49.3, together with a broad signal at -2.30 ppm. The latter converts into a sharp doublet at -1.21 ppm ($^1J_{Prh} = 91$ Hz) at -60 ºC and is due to 11a·(CO)$_2$. The low ratio of compound 11b·(CO)$_3$ (<5% at -60 ºC) precluded performing a similar analysis based on $^{13}$C NMR spectroscopy. Nonetheless, in the $^{31}$P($^1$H) NMR spectra a sharp doublet at -3.6 ppm ($^1J_{Prh} = 91$ Hz) that became discernible at temperatures below -40 ºC was recorded, at variance with the doublet of the parent monocarbonyl compound 11a·CO at 49.4 ppm ($^1J_{Prh} = 167$ Hz). The above data are in agreement with the already mentioned temperature-dependent equilibrium between cationic carbonyl rhodium complexes 11·(CO)$_n$ under 6 bar of CO (Scheme 8). At -60 ºC the mono and tricarbonyl complexes exist in variable ratios, probably depending on the steric requirements of the phosphine ligand. Beyond these considerations, the broadness of the $^{13}$C($^1$H) resonances recorded for 11a·CO at 25 ºC suggested the additional participation of this species in a second equilibrium, now on the NMR time scale. As stated, we propose that this equilibrium includes an unobserved dicarbonyl complex 11a·(CO)$_2$, analogous to its iridium counterpart, 12a·(CO)$_2$. DFT calculations support the participation of dicarbonylic species 11·(CO)$_2$ in the solution equilibrium observed by NMR in a process similar to that described for iridium. The calculations also reveal trends in the relative stability of species 11·(CO)$_n$ and the energy barriers for CO loss /capture that, when compared with the data for the iridium analogs, are consistent with the experimental observations. Thus, the calculated barriers for CO loss from 11·(CO)$_2$ are lower (14.9 and 16.8 kcal·mol$^{-1}$ for the xylyl and Dipp compounds respectively) than those from the iridium dicarbonyls (18.3 and 21.2 kcal·mol$^{-1}$), which is another manifestation of the higher basicity of iridium and is consistent with the divergent results for chlorine abstraction from species 9 and 10, with exclusive formation of monocarbonyl 11·CO from the rhodium precursors. In addition, formation of the monocarbonyl species by CO loss is less endergonic in the rhodium systems,$^{33}$ and the rhodium tricarbonyl species are predicted to be less stable when compared to 11·(CO)$_2$ + CO than in their iridium counterparts, in agreement with the data of Scheme 8.$^{34}$
Figure 4. Variable temperature $^{13}$C($^1$H) NMR spectra, in the carbonyl and aliphatic regions, of complex 11a-CO under 6 bar of CO (100 MHz, CD$_2$Cl$_2$, -60 ºC to 25 ºC).

Conclusion

The reactivity found out for the reported Rh(I) and Ir(I) complexes of dialkylterphenyl phosphines, PMe$_2$Ar’, such as PMe$_2$Ar’Xyl and PMe$_2$Ar’Dipp, demonstrates the coordination adaptability of this still understudied family of ligands which can be viewed as hemilabiles because of the active binding function exerted by one of their flanking aryl rings. Besides classical $\kappa^1$-P coordination, the molecules of PMe$_2$Ar’ can behave as bidentate, L$_2$, 4-electron donors in the $\kappa^1$-P:$\kappa^1$-C$_{\text{arene}}$ bonding mode demonstrated by X-ray crystallography for complexes 4a, 12b and 12a-(CO)$_3$. Likewise, formally tetradentate $\kappa^1$-P:$\eta^6$-arene coordination as L$_4$ ligands is also readily attainable, as for instance in 2a, 11a-CO and 12a-CO.

Our experimental and computational work also proves that changes from one coordination mode to a different one can occur triggered by simple variations in the binding mode of other ligands, as in the equilibria represented in Scheme 3, or by ligand association or dissociation, e.g. Scheme 8. It therefore becomes apparent that terphenyl phosphines possess the potential to stabilize through weak $\pi$-interactions low-coordinate intermediates which could play a crucial function in catalysis. We are currently exploring some catalytic applications of late transition metal complexes of terphenyl phosphate ligands and pursuing the synthesis of even bulkier and stronger electron-releasing PR$_2$Ar’ ligands, featuring bulkier alkyl substituents (R = Et, i-Pr, c-C$_3$H$_7$, c-C$_6$H$_{11}$ and others).
Experimental Section

\[ [\text{Rh(cod)PMe}_2\text{Ar}^{\text{Xyl}}]^{\text{Xyl}^2}]^{\text{BArF}} \]

To a solid mixture of complex 2a (0.08 mmol) and NaBArF (0.08 mmol), placed in a thick-wall ampoule, was added 5 mL of CH₂Cl₂. The resulting solution was stirred for 10 min at room temperature, filtered and the volatiles evaporated under reduced pressure to obtain complex 3a as an orange powder in ca. 95% yield. This species can be recrystallized by slow diffusion at -20 °C of pentane into a CH₂Cl₂ solution (2:1 by vol.).

**Anal. Calc.** for C₆₄H₅₁BF₂₄PRh: C, 54.1; H, 3.6. **Found:** C, 54.4; H, 3.4.

**¹H NMR** (400 MHz, 25 °C, CD₂Cl₂) δ: 7.82 (detected by COSY, p-C₆H₃), 7.57 (br, 1H, m’-C₆H₃), 7.30 (br, 1H, m-C₆H₃), 7.20 (br, 2H, m-Xyl), 6.80 (br, 2H, m-Xyl’), 5.88 (br, 1H, p-Xyl’), 5.53 (br, 2H, CHcod), 3.44 (s, 2H, RhCHcod), 2.44 (m, 4H, CH₂cod), 2.10 (m, 4H, CH₂cod), 2.16 (s, 6H, MeXyl’), 2.01 (s, 6H, MeXyl), 1.23 (d, 6H, ²JHP = 11.3 Hz, PMe₂).

**¹H NMR** (400 MHz, 0 °C, CD₂Cl₂) δ: 7.81 (detected by COSY, p-C₆H₃), 7.59 (m, 1H, m’-C₆H₃), 7.30 (t, ³JHH = 7.5 Hz, 1H, p-Xyl), 7.27 (dd, ³JHH = 7.4 Hz, ⁴JHP = 3.0 Hz, 1H, m-C₆H₃), 7.18 (d, ³JHH = 7.5 Hz, 2H, m-Xyl), 6.75 (d, ³JHH = 6.4 Hz, 2H, m-Xyl’), 5.81 (m, 1H, p-Xyl’), 5.55 (m, 2H, CHcod), 3.38 (m, 2H, RhCHcod), 2.43 (m, 4H, CH₂cod), 2.07 (m, 4H, CH₂cod), 2.13 (s, 6H, MeXyl’), 1.98 (s, 6H, MeXyl), 1.20 (d, ²JHP = 11.3 Hz, 6H, PMe₂).

**¹³C{¹H} NMR** (100 MHz, -10 °C, CD₂Cl₂) δ: 146.8 (o-C₆H₃), 142.6 (d, ²JCp = 21 Hz, o-C₆H₃), 137.8 (d, ¹JCp = 50 Hz, ipso-C₆H₃), 137.8 (ipso-Xyl), 136.3 (o-Xyl), 133.5 (p-C₆H₃), 132.3 (d, ²JCp = 6 Hz, m-C₆H₃), 132.3 (CHcod), 128.6 (p-Xyl), 127.8 (m-Xyl), 127.7 (d, ³JCp = 15 Hz, m’-C₆H₃), 120.5 (o-Xyl’), 116.1 (ipso-Xyl’), 112.1 (m-Xyl’), 97.1 (d, ²JCp = 10 Hz, p-Xyl’), 74.0 (d, ¹JCrh = 13 Hz, RhCHcod), 35.1 (CH₂cod), 31.7 (CH₂cod), 21.1 (MeXyl), 19.5 (MeXyl’), 13.6 (d, ¹JCp = 33 Hz, PMe₂).

**³¹P{¹H} NMR** (160 MHz, -10 °C, CD₂Cl₂) δ: 48.1 (d, ¹JPph = 192 Hz).
[Rh(cod)PMe₂ArDipp²][BARF]

To a solid mixture of complex [RhCl(cod)PMe₂ArDipp²] (0.071 mmol) and NaBARF (0.071 mmol), placed in a thick-wall ampoule, was added 6 mL of CH₂Cl₂. The resulting solution was stirred for 10 min at room temperature, filtered and the volatiles evaporated under reduced pressure to obtain [Rh(cod)PMe₂ArDipp²][BARF] as a yellow powder in ca. 85% yield.

**Anal. Calc.** for C₇₂H₆₇BF₂₄PRh : C, 56.41; H, 4.41. **Found:** C, 56.58; H, 4.22.

**¹H NMR** (400 MHz, 25 °C, CD₂Cl₂) δ: 7.75 (overlapped, 1H, p-C₆H₃), 7.73 (s, 8H, o-Ar), 7.64 (br d, 3Jₖₗₚ = 7.6 Hz, 1H, m’-C₆H₃), 7.57 (s, 4H, p-Ar), 7.45 (t, 3Jₖₗₚ = 7.8 Hz, 1H, p-Dipp), 7.39 (ddd, 3Jₖₗₚ = 7.6 Hz, 4Jₖₘₚ = 3.3 Hz, 4Jₖₖₚ = 1.1 Hz, 1H, m-C₆H₃), 7.27 (d, 3Jₖₖₚ = 7.8 Hz, 2H, m-Dipp), 6.76 (d, 3Jₖₖₚ = 6.8 Hz, 2H, m-Dipp’), 6.00 (br t, 3Jₖₖₚ = 6.8 Hz, 1H, p-Dipp’), 5.54 (br s, 2H, CH₂cod), 3.38 (br s, 2H, RhCH₂cod), 2.41 (m, 4H, CH₂cod), 2.24 (m, 2H, (CHMe₂)Dipp), 2.22 (m, 2H, (CHMe₂)Dipp’), 2.05 (m, 4H, CH₂cod), 1.36 (d, 3Jₖₖₚ = 6.9 Hz, 6H, MeDipp), 1.23 (m, 6H, MeDipp’), 1.22 (m, 6H, MeDipp’), 1.14 (dd, 2Jₖₘₚ = 11.3 Hz, 3Jₖₗₚ = 1.3 Hz, PMe₂), 1.00 (d, 3Jₖₖₚ = 6.6 Hz, 6H, MeDipp).

**¹³C{¹H} NMR** (100 MHz, 25 °C, CD₂Cl₂) δ: 162.2 (q, ¹Jₖₖₚ = 50 Hz, ipso-Ar), 147.1 (o-Dipp), 145.3 (o-C₆H₃), 141.9 (d, ²Jₖₖₚ = 21 Hz, o-C₆H₃), 140.0 (d, ¹Jₖₖₚ = 51 Hz, ipso-C₆H₃), 135.5 (ipso-Dipp), 135.2 (o-Ar), 134.2 (d, ³Jₖₖₚ = 6 Hz, m-C₆H₃), 132.0 (p-C₆H₃), 130.6 (p-Dipp), 129.6 (br, CH₂cod), 129.3 (q, ²Jₖₖₚ = 31 Hz, m-Ar), 128.6 (d, ³Jₖₖₚ = 15 Hz, m’-C₆H₃), 127.8 (br, o-Dipp’), 125.0 (q, ¹Jₖₖₚ = 272 Hz, CF₃), 123.6 (m-Dipp), 117.9 (m, p-Ar), 113.0 (br, ipso-Dipp’), 108.9 (br, m-Dipp’), 99.2 (br, p-Dipp’), 74.7 (d, ¹Jₖₖₚ = 13 Hz, RhCH₂cod), 35.7 (CH₂cod), 31.9 (CH₂cod), 31.6 ((CHMe₂)Dipp), 30.1 ((CHMe₂)Dipp’), 26.3 (MeDipp), 24.9 (MeDipp’), 23.7 (MeDipp’), 21.6 (MeDipp), 15.9 (d, ¹Jₖₖₚ = 33 Hz, PMe₂).

**³¹P{¹H} NMR** (160 MHz, 25 °C, CD₂Cl₂) δ: 48.4 (br d, ¹Jₖₖₚ = 192 Hz).

[Ir(cod)PMe₂Ar₈][BARF]

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To a solid mixture of complex [IrCl(cod)PMe$_2$Ar$^{Xyl_2}$] (0.07 mmol) and NaBAr$_F$ (0.07 mmol), placed in a thick-wall ampoule, was added 6 mL of CH$_2$Cl$_2$. The resulting solution was stirred for 10 min at room temperature, filtered and the volatiles evaporated under reduced pressure to obtain [Ir(cod)PMe$_2$Ar$^{Dipp_2}$][BAr$_F$] as a red powder in ca. 85% yield. Single crystals were grown from a saturated hexane-dichloromethane solution.

**Anal. Calcd.** for C$_{64}$H$_{51}$BF$_{24}$IrP: C, 50.91; H, 3.40. **Found:** C, 50.61; H, 3.70.

$^1$H NMR $\eta^2$-cod (500 MHz, 25 °C, CD$_2$Cl$_2$) δ: 7.76 (td, $^3$J$_{HH}$ = 7.6 Hz, $^5$J$_{HP}$ = 2.1 Hz, 1H, $p$-C$_6$H$_3$), 7.63 (m'-C$_6$H$_3$(COSY)), 7.30 (t, $^3$J$_{HH}$ = 7.6 Hz, 1H, $p$-Xyl), 7.26 (ddd, $^3$J$_{HH}$ = 7.6 Hz, $^4$J$_{HP}$ = 3.5 Hz, $^4$J$_{HH}$ = 1.2 Hz, 1H, $m$-C$_6$H$_3$), 7.17 (d, $^3$J$_{HH}$ = 7.6 Hz, 2H, $m$-Xyl), 6.63 (d, $^3$J$_{HH}$ = 6.2 Hz, 2H, $m$-Xyl'), 5.60 (m, 3H, $p$-Xyl', CH$_{cod}$), 2.93 (m, 2H, IrCH$_{cod}$), 2.41 to 2.26 (m, 4H, CH$_2$cod), 2.17 (s, 6H, Me$^{Xyl'}$), 1.98 (s, 6H, Me$^{Xyl}$), 1.76 (m, 2H, CH$_{2cod}$(COSY)), 1.28 (d, $^1$J$_{CP}$ = 11.3 Hz, 6H, PMe$_2$).

$^1$H NMR $\eta^4$-cod (400 MHz, -15 °C, CD$_2$Cl$_2$) δ: 7.60 (td, $^3$J$_{HH}$ = 7.6 Hz, $^5$J$_{HP}$ = 2.3 Hz, 1H, $p$-C$_6$H$_3$), 7.41 to 7.16 (br and overlapped, 6H, $m$-Xyl, $p$-Xyl), 7.15 ($m$-C$_6$H$_3$(COSY)), 6.68 (br, 1H, $m$-C$_6$H$_3$), 3.24 (br, 2H, trans-CH$_{cod}$), 3.18 (br, 2H, cis-CH$_{cod}$), 1.97 (s, 6H, Me$^{Xyl'}$), 1.95 (s, 6H, Me$^{Xyl}$), 1.57 (m, 2H, CH$_{2cod}$), 1.37 (d, $^1$J$_{CP}$ = 9.8 Hz, 6H, PMe$_2$).

$^{13}$C{$^1$H} NMR $\eta^2$-cod (100 MHz, -15 °C, CD$_2$Cl$_2$) δ: 140.1 (d, $^1$J$_{CP}$ = 59 Hz, ipso-C$_6$H$_3$), 129.9 (CH$_{cod}$), 127.8 (overlapped, m'-C$_6$H$_3$), 108.7 (o-Xyl'), 107.1 (d, $^2$J$_{CP}$ = 5 Hz, ipso-Xyl'), 105.0 (d, $^2$J$_{CP}$ = 3 Hz, m-Xyl'), 86.2 (d, $^2$J$_{CP}$ = 10 Hz, p-Xyl'), 52.9 (IrCH$_{cod}$), 36.1 (CH$_{2cod}$), 32.6 (CH$_{2cod}$), 21.2 (Me$^{Xyl}$), 19.1 (Me$^{Xyl'}$), 13.0 (d, $^1$J$_{CP}$ = 40 Hz, PMe$_2$).

$^{13}$C{$^1$H} NMR $\eta^4$-cod (100 MHz, -15 °C, CD$_2$Cl$_2$) δ: 134.5 (overlapped, p-C$_6$H$_3$), 130.6 (d, $^1$J$_{CP}$ = 15 Hz, m-C$_6$H$_3$), 103.7 (d, $^2$J$_{CP}$ = 11 Hz, trans-CH$_{cod}$), 62.3 (cis-CH$_{cod}$), 33.6 (CH$_{2cod}$), 28.7 (CH$_{2cod}$), 22.7 (Me$^{Xyl}$), 21.2 (Me$^{Xyl'}$), 12.0 (d, $^1$J$_{CP}$ = 37 Hz, PMe$_2$).

$^{31}$P{$^1$H} NMR (160 MHz, 25 °C, CD$_2$Cl$_2$) δ: 16.9 (59%, $\eta^4$-cod), 2.0 (41%, $\eta^2$-cod).
To a solid mixture of complex [IrCl(cod)PMe2ArDipp2] (0.06 mmol) and NaBARF (0.06 mmol), placed in a thick-wall ampoule, was added 6 mL of CH2Cl2. The resulting solution was stirred for 10 min at room temperature, filtered and the volatiles evaporated under reduced pressure to obtain [Ir(cod)PMe2ArDipp2][BARF] as an orange powder in ca. 85% yield.


**1H NMR**  ν2-cod (500 MHz, 25 °C, CD2Cl2) δ: 7.74 (overlapped m, 1H, m′-C6H3), 7.71 (td, 3JHH = 7.3 Hz, 5JHP = 1.8 Hz, 1H, p-C6H3), 7.46 (t, 3JHH = 7.7 Hz, 1H, p-Dipp), 7.37 (overlapped m, 1H, m-C6H3), 7.28 (d, 3JHH = 7.7 Hz, 2H, m-Dipp), 6.64 (d, 3JHH = 6.3 Hz, 2H, m-Dipp′), 5.77 (t, 3JHH = 6.3 Hz, 1H, p-Dipp′), 5.62 (m, 2H, CHcod), 2.96 (m, 2H, IrCHcod), 2.40 (m, 4H, CH2cod), 2.25 (h, 3JHH = 6.7 Hz, 2H, (CHMe2)Dipp), 2.13 (h, 3JHH = 6.8 Hz, 2H, (CHMe2)Dipp′), 2.06 (m, 2H, CH2cod), 1.85 (m, 2H, CH2cod). 1.32 (d, 3JHH = 6.9 Hz, 6H, MeDipp), 1.28 (d, 2JHP = 11.4 Hz, 6H, PMe2), 1.24 (m, 12H, MeDipp′, MeDipp), 1.00 (d, 3JHH = 6.6 Hz, 6H, MeDipp).

**1H NMR**  ν4-cod (500 MHz, 25 °C, CD2Cl2) δ: 3.43 (m, 2H, trans-CHcod), 3.18 (m, 2H, cis-CHcod), 2.55 (m, 2H, (CHMe2)Dipp), 2.38 ((CHMe2)Dipp(COSY)), 2.33 (CH2cod(COSY)), 2.28 (CH2cod(COSY)), 2.12 (CH2cod(COSY)), 2.05 (CH2cod(COSY)), 1.37 (d, 2JHP = 9.8 Hz, 6H, PMe2), 1.34 (MeDipp(COSY)), 1.29 (MeDipp(COSY)), 1.11 (MeDipp(COSY)), 1.07 (MeDipp(COSY)).

**13C{1H} NMR**  ν2-cod (100 MHz, 25 °C, CD2Cl2) δ: 147.2 (o-Dipp), 146.3 (o-C6H3), 142.3 (d, 1JCP = 59 Hz, ipso-C6H3), 141.2 (d, 2JCP = 18 Hz, o-C6H3), 135.5 (ipso-Dipp), 134.7 (d, 3JCP = 7 Hz, m′-C6H3), 132.0 (p-C6H3), 130.7 (p-Dipp), 130.4 (CHcod), 128.8 (d, 3JCP = 7 Hz, m′-C6H3), 123.7 (m-Dipp), 120.1 (o-Dipp′), 106.9 (d, 2JCP = 5 Hz, ipso-Dipp′), 101.7 (d, 2JCP = 4 Hz, m-Dipp′), 88.3 (d, 2JCP = 11 Hz, p-Dipp′), 53.5 (IrCHcod), 36.7 (CH2cod), 32.8 (CH2cod), 31.7 ((CHMe2)Dipp), 29.7 ((CHMe2)Dipp′), 26.3 (MeDipp), 24.7 (MeDipp′), 23.7 (MeDipp′), 21.6 (MeDipp), 15.3 (d, 1JCP = 40 Hz, PMe2).

**13C{1H} NMR**  ν4-cod (100 MHz, 25 °C, CD2Cl2) δ: 105.4 (d, 2JCP = 11 Hz, trans-CHcod), 61.0 (cis-CHcod), 13.6 (d, 1JCP = 37 Hz, PMe2).
Pyridine (0.020 mmol) was added to a dichloromethane solution of [Ir(cod)PMe₂Ar²][BArF] (0.018 mmol), which immediately turned from red to light orange. The solution was stirred for 5 min at room temperature and the solvent was removed under reduced pressure. Excess pyridine was evaporated together with pentane (2x5 mL). The finely divided orange solid was washed with pentane (5 mL) and dried under reduced pressure, affording [Ir(cod)(py)PMe₂Ar²][BArF] in 82% yield.

**Analytical Data**

Calculated for C₆₉H₅₆BF₂₄IrNP: C, 52.15; H, 3.55; N, 0.88.

Found: C, 52.46; H, 3.43; N, 0.69.

**¹H NMR (400 MHz, CD₂Cl₂, 25 ºC)**: δ: 8.06 (m, 2H, 2,6-py), 7.72 (m, 9H, o-Ar, 4-py), 7.57 (td, 3J_HH = 7.7 Hz, 5J_HP = 1.7 Hz, 1H, p-C₆H₃), 7.56 (s, 4H, p-Ar), 7.31 (m, 4H, 3,5-py, p-Xyl), 7.18 (d, 3J_HH = 7.5 Hz, 4H, m-Xyl), 7.09 (dd, 3J_HH = 7.6 Hz, 4J_HP = 3.1 Hz, 2H, m-C₆H₃), 3.98 (m, 2H, CHcod), 3.49 (br, 2H, CHcod), 2.28 to 2.18 (m, 4H, CH₂cod), 2.15 (s, 12H, MeXyl), 1.87 to 1.72 (m, 4H, CH₂cod), 0.82 (d, 2J_HP = 8.3 Hz, 6H, PMe₂).

**¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 25 ºC)**: δ: 162.2 (q, 1J_CCB = 50 Hz, ipso-Ar), 150.6 (2,6-py), 145.9 (d, 2J_CP = 10 Hz, o-C₆H₃), 141.2 (d, 3J_CP = 3 Hz, ipso-Xyl), 139.0 (4-py), 137.4 (o-Xyl), 135.2 (o-Ar), 132.3 (d, 3J_CP = 8 Hz, m-C₆H₃), 131.8 (d, 4J_CP = 2 Hz, p-C₆H₃), 129.3 (q, 2J_CF = 31 Hz, m-Ar), 129.0 (p-Xyl), 128.4 (m-Xyl), 127.4 (3,5-py), 126.8 (d, 1J_CP = 41 Hz, ipso-C₆H₃), 125.0 (q, 1J_CF = 272 Hz, CF₃), 117.9 (m, p-Ar), 89.7 (d, 2J_CP = 13 Hz, CHcod), 66.4 (CHcod), 32.7 (br, CH₂cod), 29.4 (br, CH₂cod), 22.4 (MeXyl), 14.3 (d, 1J_CP = 34 Hz, PMe₂).

**³¹P{¹H} NMR (160 MHz, CD₂Cl₂, 25 ºC)**: δ: -12.1.
A solid mixture of the rhodium dimer, \([\text{RhCl(C}_2\text{H}_2)_2]_2\), (0.2 mmol), the phosphine 1a (0.40 mmol) and NaBAR\(_F\) (0.40 mmol), placed in a Schlenk flask, was dissolved in CH\(_2\)Cl\(_2\) (6 mL). The solution was stirred for 1 hour at room temperature, and the solvent was then evaporated under reduced pressure to obtain complex 4a in ca. 90% yield. This complex can be recrystallized by slow diffusion at -20 °C of pentane into a CH\(_2\)Cl\(_2\) solution (2:1 by vol.).

**Anal. Calc.** for C\(_{58}\)H\(_{43}\)BF\(_{24}\)PRh: C, 52.0; H, 3.2. **Found:** C, 52.0; H, 3.5.

\(^1^H\) NMR (500 MHz, 25 °C, CD\(_2\)Cl\(_2\)) \(\delta\): 7.84 (td, \(^3^J_{HH} = 7.6\) Hz, \(^5^J_{HP} = 2.4\) Hz, 1H, \(p\)-C\(_6\)H\(_3\)), 7.65 (ddd, \(^3^J_{HH} = 7.7\) Hz, \(^4^J_{HP} = 2.3\) Hz, \(^4^J_{HH} = 1.3\) Hz, 1H, \(m\)'-C\(_6\)H\(_3\)), 7.31 (m, 2H, \(p\)-Xyl), 7.19 (d, \(^3^J_{HH} = 7.6\) Hz, 2H, \(m\)-Xyl), 6.96 (d, \(^3^J_{HH} = 6.6\) Hz, 2H, \(m\)-Xyl'), 5.54 (td, \(^3^J_{HH} = 6.6\) Hz, \(^3^J_{HP} = 2.3\) Hz, 1H, \(p\)-Xyl'), 2.92 (br s, 4H, C\(_2\)H\(_4\)), 2.18 (s, 6H, Me\(_{\text{Xyl'}}\)), 1.99 (s, 6H, Me\(_{\text{Xyl}}\)), 1.18 (dd, \(^2^J_{HP} = 11.5\) Hz, \(^3^J_{HRh} = 1.4\) Hz, 6H, PMe\(_2\)).

\(^{13}\)C\({}^1^H\) NMR (125 MHz, 25 °C, CD\(_2\)Cl\(_2\)) \(\delta\): 147.5 (o-C\(_6\)H\(_3\)), 142.8 (d, \(^2^J_{CP} = 20\) Hz, o-C\(_6\)H\(_3\)), 138.8 (d, \(^1^J_{CP} = 52\) Hz, ipso-C\(_6\)H\(_3\)), 137.8 (ipso-Xyl), 136.6 (o-Xyl), 133.9 (d, \(^4^J_{CP} = 2\) Hz, \(p\)-C\(_6\)H\(_3\)), 128.0 (m'-C\(_6\)H\(_3\)), 117.9 (o-Xyl'), 116.5 (ipso-Xyl'), 109.1 (m-Xyl'), 94.7 (d, \(^2^J_{CP} = 12\) Hz, \(p\)-Xyl'), 46.5 (d, \(^1^J_{CRh} = 13\) Hz, C\(_2\)H\(_4\)), 21.3 (Me\(_{\text{Xyl}}\)), 19.6 (Me\(_{\text{Xyl'}}\)), 13.9 (d, \(^1^J_{CP} = 33\) Hz, PMe\(_2\)).

\(^{31}\)P\({}^1^H\) NMR (200 MHz, 25 °C, CD\(_2\)Cl\(_2\)) \(\delta\): 48.1 (d, \(^1^J_{PRh} = 185\) Hz).

\[\text{[Rh(C}_2\text{H}_4)\text{PMe}_2\text{Ar}^{\text{Dipp2}}][\text{BAR}_F]\]

**Anal. Calc.** for C\(_{66}\)H\(_{59}\)BF\(_{24}\)PRh: C, 54.56; H, 4.09. **Found:** C, 54.65; H, 3.98.

\(^1^H\) NMR (400 MHz, 25 °C, CD\(_2\)Cl\(_2\)) \(\delta\): 7.76 (td, \(^3^J_{HH} = 7.6\) Hz, \(^5^J_{HP} = 2.3\) Hz, 1H, \(p\)-C\(_6\)H\(_3\)), 7.73 (s, 8H, o-Ar), 7.70 (ddd, \(^3^J_{HH} = 7.7\) Hz, \(^4^J_{HP} = 2.2\) Hz, \(^4^J_{HH} = 1.4\) Hz, 1H, \(m\)'-C\(_6\)H\(_3\)), 7.57 (s, 4H, p-Ar), 7.45 (t, \(^3^J_{HH} = 7.8\) Hz, 1H, \(p\)-Dipp), 7.41 (ddd, \(^3^J_{HH} = 7.5\) Hz, 1H, \(m\)-Dipp), 7.40 (ddd, \(^3^J_{HH} = 7.5\) Hz, 1H, \(p\)-Dipp).
Ethylene was bubbled through a deoxygenated pentane (15 mL, −20°C) solution of \([\text{IrCl(coe)}_2]_2\) (0.11 mmol), placed in an ampoule, until the yellow coloration fades. A red precipitate formed upon addition of the phosphine (0.22 mmol) dissolved in pentane (8 mL). NaBArF (0.22 mmol) was suspended in CH₂Cl₂ (8 mL) and added to the reaction mixture, which gradually turned pale yellow. The solution was allowed to reach room temperature and the solvent was removed under reduced pressure. The complex was extracted with CH₂Cl₂ (10 mL), the solvent was evaporated again and the complex was washed with pentane (10 mL), yielding \([\text{Ir(C}_2\text{H}_4)\text{PMe}_2\text{Ar}^{\text{Xyl}}]\)⁺BArF⁻ as a pure, pale solid in 80% yield.

**Anal. Calc.** for C₅₈H₄₃BF₂₄IrP: C, 48.72; H, 3.03. **Found:** C, 48.92; H, 3.09.
4H, p-Ar), 7.25 (t, $^3J_{HH} = 7.7$ Hz, 1H, p-Xyl), 7.21 (ddd, $^3J_{HH} = 7.5$ Hz, $^4J_{HP} = 3.4$ Hz, $^4J_{HH} = 1.1$ Hz, 1H, m-C$_6$H$_3$), 7.13 (d, $^3J_{HH} = 7.6$ Hz, 2H, m-Xyl), 6.78 (d, $^3J_{HH} = 6.2$ Hz, 2H, m-Xyl), 5.30 (td, $^3J_{HH} = 6.2$ Hz, $^3J_{HP} = 1.7$ Hz, 1H, p-Xyl), 2.93 (m, 2H, CHH=CHH), 2.18 (s, 6H, Me$_2$Xyl), 1.93 (s, 6H, Me$_2$Xyl), 1.74 (m, 2H, CHH=CHH), 1.24 (d, $^2J_{HP} = 11.4$ Hz, 6H, PMe$_2$).

$^{13}$C$^{1H}$ NMR (100 MHz, CD$_2$Cl$_2$, 25 ºC) δ: 162.3 (q, $^1J_{CB} = 50$ Hz, ipso-Ar), 148.4 (m, m-C$_6$H$_3$), 142.2 (d, $^3J_{CP} = 18$ Hz, m-C$_6$H$_3$), 141.3 (d, $^1J_{CP} = 59$ Hz, ipso-C$_6$H$_3$), 137.9 (d, $^3J_{CP} = 2$ Hz, ipso-Xyl), 136.7 (o-Xyl), 135.3 (o-Ar), 134.0 (p-C$_6$H$_3$), 133.3 (d, $^3J_{CP} = 7$ Hz, m-C$_6$H$_3$), 129.7 (p-Xyl), 129.4 (q, $^2J_{CF} = 31$ Hz, m-Ar), 128.3 (m, m'-C$_6$H$_3$, m-Xyl), 125.1 (q, $^1J_{CF} = 272$ Hz, CF$_3$), 118.0 (m, p-Ar), 110.6 (o-Xyl), 109.5 (d, $^2J_{CP} = 5$ Hz, ipso-Xyl), 102.6 (d, $^2J_{CP} = 4$ Hz, m-Xyl), 84.7 (d, $^2J_{CP} = 11$ Hz, p-Xyl), 24.5 (C$_2$H$_4$), 21.4 (Me$_2$Xyl), 19.1 (Me$_2$Xyl), 13.4 (d, $^1J_{CP} = 40$ Hz, PMe$_2$).

$^{31}$P$^{1H}$ NMR (160 MHz, CD$_2$Cl$_2$, 25 ºC) δ: 2.1.

$[\text{Ir(C}_2\text{H}_4\text{PMe}_2\text{Ar}^{\text{Dipp}}]{}^+\text{BARF}^-$

Ethylene was bubbled through a deoxygenated pentane (15 mL, −20 ºC) solution of [IrCl(coe)$_2$)$_2$ (0.11 mmol), placed in an ampoule, until the yellow coloration fades. A red precipitate formed upon addition of the phosphine (0.22 mmol) dissolved in pentane (8 mL). NaBAR$_F$ (0.22 mmol) was suspended in CH$_2$Cl$_2$ (8 mL) and added to the reaction mixture, which gradually turned pale yellow. The solution was allowed to reach room temperature and the solvent was removed under reduced pressure. The complex was extracted with CH$_2$Cl$_2$ (10 mL), the solvent was evaporated again and the complex was washed with pentane (10 mL), yielding $[\text{Ir(C}_2\text{H}_4\text{PMe}_2\text{Ar}^{\text{Dipp}}]{}^+\text{BARF}^-$ as a pure, pale solid in 80% yield.

**Anal. Calc.** for C$_{66}$H$_{460}$BF$_{24}$IrP: C, 51.37; H, 3.92. **Found:** C, 51.40; H, 4.07.

$^1$H NMR (500 MHz, CD$_2$Cl$_2$, 25 ºC) δ: 7.77 (ddd, $^3J_{HH} = 7.6$ Hz, $^4J_{HP} = 2.2$ Hz, $^4J_{HH} = 1.4$ Hz, 1H, m'-C$_6$H$_3$), 7.73 (td overlapped, $^3J_{HH} = 7.5$ Hz, $^5J_{HP} = 2.2$ Hz, 1H, p-C$_6$H$_3$), 7.72 (s, 8H, o-Ar), 7.56 (s, 4H, p-Ar), 7.46 (t, $^3J_{HH} = 7.8$ Hz, 1H, p-Dipp), 7.38 (ddd, $^3J_{HH} = 7.3$ Hz, $^4J_{HP} = 3.6$ Hz, $^4J_{HH} = 1.3$ Hz, 1H, m-C$_6$H$_3$), 7.27 (d, $^3J_{HH} = 7.8$ Hz, 2H,
m-Dipp), 6.88 (dd, $^3J_{HH} = 6.4$ Hz, $^3J_{HP} = 0.7$ Hz, 2H, m-Dipp’), 5.57 (td, $^3J_{HH} = 6.4$ Hz, $^3J_{HP} = 1.7$ Hz, 1H, p-Dipp’), 2.97 (m, 2H, CHH=CHH), 2.22 (h, $^3J_{HH} = 6.7$ Hz, 2H, (CHMe$_2$)Dipp), 2.16 (h, $^3J_{HH} = 6.9$ Hz, 2H, (CHMe$_2$)Dipp’), 1.79 (m, 2H, CHH=CHH), 1.30 (d, $^3J_{HH} = 6.9$ Hz, 6H, Me$_2$Dipp’), 1.28 (d, $^3J_{HH} = 6.8$ Hz, 6H, Me$_2$Dipp’), 1.24 (d, $^3J_{HP} = 11.4$ Hz, 6H, PMe$_2$), 1.23 (d, $^3J_{HH} = 6.7$ Hz, 6H, Me$_2$Dipp), 1.00 (d, $^3J_{HH} = 6.7$ Hz, 6H, Me$_2$Dipp). 

$^{13}$C($^1$H) NMR (100 MHz, CD$_2$Cl$_2$, 25 ºC) δ: 162.3 (q, $^1J_{CB} = 50$ Hz, ipso-Ar), 147.2 (o-Dipp), 146.5 (o-C$_6$H$_3$), 142.7 (d, $^1J_{CP} = 59$ Hz, ipso-C$_6$H$_3$), 141.2 (d, $^2J_{CP} = 18$ Hz, o-C$_6$H$_3$), 135.3 (o-Ar, ipso-Dipp (overlapped)), 134.7 (d, $^3J_{CP} = 7$ Hz, m-C$_6$H$_3$), 132.1 (p-C$_6$H$_3$), 125.1 (q, $^1J_{CF} = 272$ Hz, CF$_3$), 123.6 (m-Dipp), 121.5 (o-Dipp’), 117.9 (m, p-Ar), 108.7 (d, $^2J_{CP} = 5$ Hz, ipso-Dipp’), 98.3 (d, $^2J_{CP} = 4$ Hz, m-Dipp’), 86.0 (d, $^2J_{CP} = 11$ Hz, p-Dipp’), 31.7 ((CHMe$_2$)Dipp), 29.8 ((CHMe$_2$)Dipp’), 26.3 (Me$_2$Dipp), 24.9 (Me$_2$Dipp’), 23.9 (C$_2$H$_4$), 23.7 (Me$_2$Dipp’), 21.5 (Me$_2$Dipp), 15.3 (d, $^1J_{CP} = 40$ Hz, PMe$_2$).

$^{31}$P($^1$H) NMR (160 MHz, CD$_2$Cl$_2$, 25 ºC) δ: 2.1.

To a solid mixture of the corresponding chloride precursor 2 (0.08 mmol) and NaBAr$_F$ (0.08 mmol), placed in a thick-wall ampoule, was added 5 mL of CH$_2$Cl$_2$ and the resulting solution stirred for 10 min at room temperature under 1.5 bar of CO. After filtering, the solvent was evaporated under reduced pressure and the solid obtained washed with pentane (2×10 mL). Complexes 6a and 6b were isolated as orange powders in ca. 95% yield, which can be recrystallized by slow diffusion at -20 ºC of pentane into a CH$_2$Cl$_2$ solution (2:1 by vol.).

$$[\text{Rh(CO)}\text{PMe}_2\text{Ar}^{Xyl}_2]^+\text{[BAr}_F^-]$$

IR (Nujol): 2018 cm$^{-1}$.

**Anal. Calc.** for C$_{57}$H$_{39}$BF$_{24}$OPRh: C, 51.1; H, 2.9. **Found:** C, 51.5; H, 2.6.

$^1$H NMR (500 MHz, 25 ºC, CD$_2$Cl$_2$) δ: 7.88 (td, $^3J_{HH} = 7.6$, $^5J_{HP} = 2.6$ Hz, 1H, $p$-C$_6$H$_3$), 7.59 (d, $^3J_{HH} = 7.8$ Hz, 1H, m’-C$_6$H$_3$), 7.36 (m, 2H, $p$-Xyl, m-C$_6$H$_3$), 7.23 (d, $^3J_{HH} = 7.7$...
Hz, 2H, m-Xyl), 7.09 (d, $^3J_{HH} = 6.9$ Hz, 2H, m-Xyl’), 6.30 (t, $^3J_{HH} = 6.7$ Hz, 1H, p-Xyl’), 2.17 (s, 6H, Me$_{Xyl}$) 2.01 (s, 6H, Me$_{Xyl}$), 1.56 (d, $^2J_{HP} = 11.9$ Hz, 6H, PMe$_2$).

$^{13}$C($^1$H) NMR (125 MHz, 25 ºC, CD$_2$Cl$_2$) δ: 183.2 (dd, $^1J_{CRh} = 95$, $^2J_{CP} = 19$ Hz, CO), 148.5 (o-C$_6$H$_3$), 142.8 (d, $^2J_{CP} = 19$ Hz, o-C$_6$H$_3$), 138.4 (d, $^1J_{CP} = 49$ Hz, ipso-C$_6$H$_3$), 137.7 (o-Xyl), 135.2 (p-C$_6$H$_3$), 133.8 (d, $^3J_{CP} = 7$ Hz, m-C$_6$H$_3$), 130.5 (p-Xyl), 128.9 (m-Xyl), 128.8 (d, $^3J_{CP} = 5$ Hz, m’-C$_6$H$_3$), 126.5 (ipso-Xyl), 123.1 (o-Xyl’), 115.6 (ipso-Xyl’), 110.3 (m-Xyl’), 97.9 (d, $^1J_{CRh} = 8$ Hz, p-Xyl’), 22.0 (Me$_{Xyl}$), 20.3 (Me$_{Xyl}$), 19.1 (d, $^1J_{CP} = 37$ Hz, PMe$_2$).

$^{31}$P($^1$H) NMR (200 MHz, 25 ºC, CD$_2$Cl$_2$) δ: 49.3 (d, $^1J_{PRh} = 169$ Hz).

$$[\text{Rh(CO)PMe}_2\text{Ar}^{\text{Dipp}2}]+[\text{BAr}_4]^-$$

IR (Nujol): 2012 cm$^{-1}$.

**Anal. Calc.** for C$_{65}$H$_{55}$BF$_{24}$OPRh: C, 53.7; H, 3.8. **Found:** C, 53.2; H, 3.7.

$^1$H NMR (500 MHz, 25 ºC, CD$_2$Cl$_2$) δ: 7.83 (td, $^3J_{HH} = 7.6$, $^3J_{HP} = 2.6$ Hz, 1H, p-C$_6$H$_3$), 7.68 (d, $^3J_{HH} = 7.8$ Hz, 1H, m’-C$_6$H$_3$), 7.53 (t, $^3J_{HH} = 7.8$ Hz, 1H, p-Dipp), 7.50 (dd, $^3J_{HH} = 7.8$, $^4J_{HP} = 3.6$ Hz, 1H, m-C$_6$H$_3$), 7.34 (d, $^3J_{HH} = 7.9$ Hz, 2H, m-Dipp), 7.10 (d, $^3J_{HH} = 6.9$ Hz, 2H, m-Dipp’), 6.45 (t, $^3J_{HH} = 6.8$ Hz, 1H, p-Dipp’), 2.26 (h, $^3J_{HH} = 6.7$ Hz, 4H, (CHMe$_2$)$_{Dipp}$), 1.54 (d, $^2J_{HP} = 11.9$ Hz, 6H, PMe$_2$), 1.33 (d, $^3J_{HH} = 6.9$ Hz, 6H, Me$_{Dipp}$), 1.29 (d, $^3J_{HH} = 6.8$ Hz, 6H, Me$_{Dipp}$), 1.26 (d, $^3J_{HH} = 6.8$ Hz, 6H, Me$_{Dipp}$), 1.05 (d, $^3J_{HH} = 6.6$ Hz, 6H, Me$_{Dipp}$).

$^{13}$C($^1$H) NMR (125 MHz, 25 ºC, CD$_2$Cl$_2$) δ: 182.7 (dd, $^1J_{CRh} = 92$, $^2J_{CP} = 18$ Hz, CO), 146.8 (o-Dipp), 146.1 (o-C$_6$H$_3$), 140.7 (d, $^2J_{CP} = 20$ Hz, o-C$_6$H$_3$), 138.7 (d, $^1J_{CP} = 42$ Hz, ipso-C$_6$H$_3$), 134.1 (d, $^3J_{CP} = 7$ Hz, m’-C$_6$H$_3$), 133.1 (o-Dipp’), 132.3 (p-C$_6$H$_3$), 130.5 (p-Dipp’), 128.3 (d, $^3J_{CP} = 15$ Hz, m-C$_6$H$_3$), 127.8 (ipso-Dipp), 123.5 (m-Dipp), 113.2 (ipso-Dipp’), 104.7 (m-Dipp’), 97.7 (p-Dipp’), 31.3 ((CHMe$_2$)$_{Dipp}$), 29.8 ((CHMe$_2$)$_{Dipp}$), 25.9 (Me$_{Dipp}$), 24.5 (Me$_{Dipp}$), 23.2 (Me$_{Dipp}$), 21.0 (Me$_{Dipp}$), 20.0 (d, $^1J_{CP} = 37$ Hz, PMe$_2$).

$^{31}$P($^1$H) NMR (200 MHz, 25 ºC, CD$_2$Cl$_2$) δ: 49.2 (d, $^1J_{PRh} = 167$ Hz).
A NMR tube/Young ampoule is charged with [IrCl(CO)₂PMe₂Ar'] (ref Polyhedron) (12 mg, 0.019 mmol) and NaBArF (18.9 mg, 0.021 mmol). At -78 °C cold CD₂Cl₂ (ca. 0.7 mL) was added. The mixture was shaked and kept cold for 30 min. The solution was filtered with cannula over an NMR tube placed in a dry ice/acetone bath. The spectroscopic data for this compound were collected at -60 °C for preventing CO liberation. The yield is estimated to be quantitative based on spectroscopic data. Analytically pure samples of this compound were obtained evaporating the solvent and washing with pentane at – 60 °C.

\[
[Ir(CO)₂PMe₂Ar']^+*[BArF]^- 
\]

**Anal. Caled.** for C₅₈H₃₉BF₂₄IrO₂P: C, 47.78; H, 2.70. **Found**: C, 47.70; H, 2.26.

**IR** (CH₂Cl₂): `υ(Ir-CO) 2094, 2027 cm⁻¹.

**¹H NMR** (400 MHz, CD₂Cl₂, -60 °C) δ: 7.77 (d, 3²JHH = ca. 7.6 Hz, 2H, m-Xyl’), 7.74 (s, 8H, o-Ar), 7.68 (t, 3³JHH = 7.5 Hz, 1H, p-C₆H₃), 7.54 (s, 4H, p-Ar), 7.28 (t, 3³JHH = 7.6 Hz, 2H, p-Xyl, p-Xyl’), 7.22 (dd, 3³JHH = 7.5 Hz, 1H, m-C₆H₃), 7.16 (d, 3³JHH = 6.8 Hz, 1H, m’-C₆H₃), 2.05 (s, 6H, Me’Xyl’), 1.94 (s, 6H, MeXyl’), 1.60 (d, 2³JHP = 10.6 Hz, 6H, PMe₂).

**¹³C{¹H} NMR** (100 MHz, CD₂Cl₂, -60 °C) δ: 183.0 (d, 2³JCP = 102 Hz, trans-CO), 162.4 (d, 2³JCP = 14 Hz, cis-CO), 161.4 (q, 1³JC₆ = 49 Hz, ipso-Ar), 147.2 (o-C₆H₃), 143.9 (d, 2³JCP = 27 Hz, o-C₆H₃), 139.1 (o-Xyl’), 136.2 (ipso-Xyl, o-Xyl), 135.6 (p-C₆H₃), 134.3 (o-Ar), 134.2 (m-Xyl’), 133.2 (p-Xyl or p-Xyl’), 132.1 (d, 3³JCP = 6 Hz, m-C₆H₃), 130.7 (d, 3³JCP = 15 Hz, m’-C₆H₃), 129.7 (d, 1³JCP = 56 Hz, ipso-C₆H₃), 129.1 (p-Xyl or p-Xyl’), 128.3 (q, 2³JCF = 31 Hz, m-Ar), 127.5 (m-Xyl), 124.1 (q, 1³JCF = 272 Hz, CF₃), 117.4 (d, 2³JCP = 3 Hz, ipso-Xyl’), 117.2 (m, p-Ar), 23.6 (Me’Xyl), 21.0 (MeXyl), 14.4 (d, 1³JCP = 40 Hz, PMe₂).

**³¹P{¹H} NMR** (160 MHz, CD₂Cl₂, -60 °C) δ: 16.2.
A NMR tube/Young ampoule was charged with [IrCl(CO)2PMe2ArDipp2] (10.2 mg, 0.014 mmol) and NaBARF (14.0 mg, 0.016 mmol). At -30 ºC, cold CD2Cl2 (ca. 0.7 mL) was added. The mixture was shaked and kept cold for 30 min. The solution was filtered with cannula over an NMR tube placed in a dry ice/acetone bath. The spectroscopic data for this compound were collected at 0 ºC for preventing CO liberation. The yield is estimated to be quantitative based on spectroscopic data. Analitically pure samples of this compound were obtained evaporating the solvent and washing with pentane at 0 ºC. Single crystals suitable for X-Ray diffraction were grown through slow pentane diffusion in a dichloromethane solution of the complex at -32 ºC.


**IR** (CH2Cl2): υ(Ir-CO) 2093, 2027 cm⁻¹.

**1H NMR** (500 MHz, CD2Cl2, 25 ºC) δ: 7.99 (d, 3JHH = 7.8 Hz, 2H, m-Dipp’), 7.72 (s, 8H, o-Ar), 7.69 (m, 1H, p-C6H3), 7.59 (t, 3JHH = 7.7 Hz, 1H, p-Dipp’), 7.56 (s, 4H, p-Ar), 7.54 (t, 3JHH = 8.0 Hz, 1H, p-Dipp), 7.43 (dd, 3JHH = 7.4 Hz, 1H, m-C6H3), 7.35 (d, 3JHH = 7.8 Hz, 2H, m-Dipp), 6.79 (d, 3JHH = 7.6 Hz, 1H, m’-C6H3), 2.28 (h, 3JHH = 6.8 Hz, 4H, (CHMe2)Dipp, (CHMe2)Dipp’), 1.64 (d, 2JHP = 10.7 Hz, 6H, PMe2), 1.56 (d, 3JHH = 6.9 Hz, 6H, MeDipp’), 1.31 (d, 3JHH = 6.8, 6H, MeDipp), 1.05 (d, 3JHH = 6.6 Hz, 6H, MeDipp’), 1.03 (d, 3JHH = 6.8 Hz, 6H, MeDipp).

**13C{1H} NMR** (100 MHz, CD2Cl2, 0 ºC) δ: 183.0 (d, 2JCP = 102 Hz, trans-CO), 163.4 (d, 2JCP = 14 Hz, cis-CO), 162.0 (q, 1JCB = 50 Hz, ipso-Ar), 150.6 (o-Dipp’), 147.1 (o-Dipp), 146.5 (d, 2JCP = 2 Hz, o-C6H3), 142.5 (d, 2JCP = 26 Hz, o-C6H3), 135.0 (o-Ar), 134.6 (p-Dipp’), 134.24 (d, 3JCP = 9 Hz, m-C6H3), 134.22 (p-C6H3), 133.8 (d, 3JCP = 2 Hz, ipso-Dipp), 132.4 (d, 3JCP = 15 Hz, m’-C6H3), 132.1 (d, 1JCP = 57 Hz, ipso-C6H3), 131.3 (m-Dipp’), 130.8 (p-Dipp), 129.0 (q, 2JCF = 31 Hz, m-Ar), 124.8 (q, 1JCF = 272 Hz, CF3), 123.6 (m-Dipp), 118.1 (d, 2JCP = 3 Hz, ipso-Dipp’), 117.7 (m, p-Ar), 34.6 ((CHMe2)Dipp), 31.6 ((CHMe2)Dipp’), 26.5 (MeDipp), 26.2 (MeDipp), 24.2 (MeDipp’), 21.3 (MeDipp’), 16.0 (d, 1JCP = 40 Hz, PMe2).

**31P{1H} NMR** (160 MHz, CD2Cl2, 25 ºC) δ: 15.2.

\[\text{[Ir(CO)PMe2Ar}^{\text{Xyl}}_2]^+ [\text{BARF}]^-\]
A Young ampoule was charged with [IrCl(CO)₂PMe₂Ar¹⁺] (18.8 mg, 0.030 mmol) and NaBAR₆ (26.4 mg, 0.021 mmol). Under inert atmosphere, CH₂Cl₂ (5 mL) was added. The solution was kept under reflux and periodically opened to vacuum until CO liberation was complete. The solution was filtered with cannula over a Schlenk flask. Solvent was removed under reduced pressure and the product washed with pentane to yield an air-stable, analytically pure yellow powder (31.5 mg, 74 %). The compound was obtained quantitatively by NMR. Single crystals suitable for X-Ray diffraction were grown by means of slow pentane diffusion in a dichloromethane solution of the complex at -32 ºC. This compound was also obtained pure allowing a dichloromethane solution of complex [Ir(CO)₂PMe₂Ar¹⁺][BAR₆]⁺ to stand in an open-air NMR tube for several days.

**Anal. Calcd.** for C₅₇H₃₉BF₂₄IrOP: C, 47.88; H, 2.75. **Found**: C, 47.89; H, 2.40.

**IR** (Nujol): ν(Ir-CO) 2000 cm⁻¹.

**¹H NMR** (400 MHz, CD₂Cl₂, 25 °C) δ: 7.83 (m, 1H, p-C₆H₃), 7.73 (s, 8H, o-Ar), 7.60 (m, 1H, m'-C₆H₃), 7.57 (s, 4H, p-Ar), 7.34 (t, 3JHH = 7.7 Hz, 1H, p-Xyl), 7.31 (s, 1H, m-C₆H₃), 7.20 (d, 3JHH = 7.6 Hz, 2H, m-Xyl), 7.04 (d, 3JHH = 6.4 Hz, 2H, m'-Xyl'), 6.09 (t, 3JHH = 6.5 Hz, 1H, p-Xyl'), 2.26 (s, 6H, MeXyl'), 1.97 (s, 6H, MeXyl), 1.70 (d, 2JHP = 12.1 Hz, 6H, PMe₂).

**¹³C{¹H} NMR** (100 MHz, CD₂Cl₂, 25 °C) δ: 167.2 (d, 2JCP = 14 Hz, CO), 162.2 (q, 1JCB = 50 Hz, ipso-Ar), 148.9 (d, 2JCP = 3 Hz, o-C₆H₃), 141.3 (d, 2JCP = 18 Hz, o-C₆H₃), 139.2 (d, 1JCP = 58 Hz, ipso-C₆H₃), 136.9 (d, 3JCP = 3 Hz, ipso-Xyl), 136.7 (o-Xyl), 135.2 (o-Ar), 134.7 (d, 4JCP = 2 Hz, p-C₆H₃), 133.6 (d, 3JCP = 8 Hz, m-C₆H₃), 130.0 (p-Xyl), 129.3 (q, 2JCF = 32 Hz, m-Ar), 128.5 (m-Xyl), 128.4 (d, 3JCP = 14 Hz, m'-C₆H₃), 125.0 (q, 1JCF = 272 Hz, CF₃), 117.9 (m, p-Ar), 116.9 (d, 2JCP = 2 Hz, o-Xyl'), 109.7 (d, 2JCP = 5 Hz, ipso-Xyl'), 103.0 (d, 2JCP = 3 Hz, m-Xyl'), 89.1 (d, 2JCP = 7 Hz, p-Xyl'), 21.4 (MeXyl), 19.4 (MeXyl'), 19.3 (d, 1JCP = 43 Hz, PMe₂).

**³¹P{¹H} NMR** (160 MHz, CD₂Cl₂, 25 °C) δ: 6.7.

\[ \text{[Ir(CO)PMe₂Ar}^{\mathrm{Dipp}2}]^+\text{[BAR}_6\text{]}^- \]
A dichloromethane solution of complex $[\text{Ir(CO)}_2\text{PMe}_2\text{Ar}^{\text{dipp}}]^+\text{[BARF]}^-$ (22.0 mg, 0.014 mmol) was allowed to stand in an NMR tube until CO liberation is complete ($ca.$ 7 days). The solution is transferred to a vial, the solvent is removed under reduced pressure and the product is washed with pentane to yield an analytically pure yellow powder. The yield is estimated to be quantitative based on spectroscopic data. Single crystals suitable for X-Ray diffraction were grown through slow pentane diffusion in a dichloromethane solution of the complex at -32 °C.

**Anal. Calcd.** for C$_{65}$H$_{55}$BF$_{24}$IrOP: C, 50.63; H, 3.60. **Found:** C, 50.35; H, 3.47.

**IR** (Nujol): $\nu$(Ir-CO) 1997 cm$^{-1}$.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C) $\delta$: 7.77 (td, $^3$J$_{HH} = 7.6$ Hz, $^5$J$_{HP} = 2.4$ Hz, 1H, p-C$_6$H$_3$), 7.72 (s, 8H, o-Ar), 7.69 (ddd, $^3$J$_{HH} = 7.6$ Hz, $^4$J$_{HP} = 2.3$ Hz, $^4$J$_{HH} = 1.2$ Hz, 1H, m’-C$_6$H$_3$), 7.56 (s, 4H, p-Ar), 7.50 (t, $^3$J$_{HH} = 7.8$ Hz, 1H, p-Dipp), 7.44 (ddd, $^3$J$_{HH} = 7.5$ Hz, $^4$J$_{HP} = 3.8$ Hz, $^4$J$_{HH} = 1.1$ Hz, 1H, m-C$_6$H$_3$), 7.30 (d, $^3$J$_{HH} = 7.8$ Hz, 2H, m-Dipp), 7.04 (dd, $^3$J$_{HH} = 6.6$ Hz, $^3$J$_{HP} = 0.9$ Hz, 2H, m-Dipp’), 6.24 (t, $^3$J$_{HH} = 6.6$ Hz, 1H, p-Dipp’), 2.19 (h, $^3$J$_{HH} = 6.6$ Hz, 4H, (CHMe$_2$)$_{\text{dipp}}$, (CHMe$_2$)$_{\text{dipp}}$), 1.67 (d, $^2$J$_{HP} = 12.1$ Hz, 6H, PMe$_2$), 1.33 (d, $^3$J$_{HH} = 6.9$ Hz, 6H, Me$_{\text{Dipp}}$), 1.26 (d, $^3$J$_{HH} = 6.7$ Hz, 6H, Me$_{\text{Dipp}}$), 1.25 (d, $^3$J$_{HH} = 6.7$ Hz, 6H, Me$_{\text{Dipp}}$), 1.02 (d, $^3$J$_{HH} = 6.6$ Hz, 6H, Me$_{\text{Dipp}}$).

$^{13}$C($^1$H) NMR (100 MHz, CD$_2$Cl$_2$, 25 °C) $\delta$: 167.7 (d, $^2$J$_{CP} = 14$ Hz, CO), 162.2 (q, $^1$J$_{CB} = 50$ Hz, ipso-Ar), 147.3 (o-Dipp), 147.2 (d, $^2$J$_{CP} = 3$ Hz, o-C$_6$H$_3$), 140.6 (d, $^1$J$_{CP} = 58$ Hz, ipso-C$_6$H$_3$), 140.4 (d, $^2$J$_{CP} = 18$ Hz, o-C$_6$H$_3$), 135.3 (o-Ar), 134.9 (d, $^3$J$_{CP} = 8$ Hz, m-C$_6$H$_3$), 134.4 (d, $^3$J$_{CP} = 3$ Hz, ipso-Dipp), 132.7 (d, $^4$J$_{CP} = 2$ Hz, p-C$_6$H$_3$), 131.0 (p-Dipp), 129.3 (q, $^2$J$_{CP} = 31$ Hz, m-Ar), 128.9 (d, $^3$J$_{CP} = 14$ Hz, m’-C$_6$H$_3$), 127.7 (d, $^2$J$_{CP} = 2$ Hz, o-Dipp’), 125.1 (q, $^1$J$_{CP} = 272$ Hz, CF$_3$), 123.7 (m-Dipp), 117.9 (m, p-Ar), 108.4 (d, $^2$J$_{CP} = 5$ Hz, ipso-Xyl’), 98.4 (d, $^2$J$_{CP} = 3$ Hz, m-Dipp’), 90.0 (d, $^2$J$_{CP} = 7$ Hz, p-Dipp’), 31.8 ((CHMe$_2$)$_{\text{dipp}}$), 29.9 (CHMe$_2$)$_{\text{dipp}}$, 26.4 (Me$_{\text{Dipp}}$), 24.8 (Me$_{\text{Dipp}}$), 23.7 (Me$_{\text{Dipp}}$), 21.5 (Me$_{\text{Dipp}}$), 21.3 (d, $^1$J$_{CP} = 44$ Hz, PMe$_2$).

$^{31}$P($^1$H) NMR (160 MHz, CD$_2$Cl$_2$, 25 °C) $\delta$: 6.1.

$[\text{Ir(CO)}_2\text{PMe}_2\text{Ar}^{\text{xyl}}]^+\text{[BARF]}^-$
A CD$_2$Cl$_2$ solution of complex $[\text{Ir(CO)}_2\text{PMe}_2\text{Ar}^{Xyl_2}]^+$[$\text{BAR}_\text{F}$]$^-$ (27.2 mg, 0.019 mmol) is placed in a Young NMR tube, charged with 1.2 bar of CO and shaked for 10 min. It is transferred to a vial, the solvent removed under reduced pressure and the product washed with pentane to yield an analytically pure yellow powder. The yield is estimated to be quantitative based on spectroscopic data. Single crystals suitable for X-Ray diffraction were grown through slow pentane diffusion in a dichloromethane solution of the complex at -32 °C.

**Anal. Calcd.** for C$_{59}$H$_{39}$BF$_{24}$IrO$_3$P: C, 47.69; H, 2.65. **Found:** C, 47.66; H, 2.19.

**IR** (CH$_2$Cl$_2$): $\nu$(Ir-CO) 2126, 2027 cm$^{-1}$.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C) $\delta$: 7.74 (s, 8H, $o$-Ar), 7.71 (t, $^3$J$_{HH}$ = 7.2 Hz, 1H, $p$-C$_6$H$_3$), 7.58 (s, 4H, $p$-Ar), 7.47 (t, $^3$J$_{HH}$ = 7.6 Hz, 2H, $p$-Xyl), 7.24 (d, $^3$J$_{HH}$ = 7.5 Hz, 4H, $m$-Xyl), 6.97 (br, 2H, $m$-C$_6$H$_3$), 2.11 (s, 12H, Me$_{Xyl}$), 1.93 (d, $^2$J$_{HP}$ = 10.9 Hz, 6H, PMe$_2$).

$^{13}$C{$^1$H} NMR (100 MHz, CD$_2$Cl$_2$, 25 °C) $\delta$: 173.1 (d, $^2$J$_{CP}$ = 15 Hz, cis-CO), 168.2 (d, $^2$J$_{CP}$ = 88 Hz, trans-CO), 162.2 (q, $^1$J$_{CB}$ = 50 Hz, ipso-Ar), 147.4 (d, $^2$J$_{CP}$ = 12 Hz, $o$-C$_6$H$_3$), 140.1 ($o$-Xyl), 135.6 (d, $^4$J$_{CP}$ = 2 Hz, $p$-C$_6$H$_3$), 135.2 ($o$-Ar), 132.3 (br, ipso-Xyl), 132.1 (d, $^3$J$_{CP}$ = 10 Hz, $m$-C$_6$H$_3$), 131.0 ($p$-Xyl), 130.4 (d, $^1$J$_{CP}$ = 58 Hz, ipso-C$_6$H$_3$), 129.3 (q, $^2$J$_{CP}$ = 31 Hz, $m$-Ar), 128.7 ($m$-Xyl), 125.0 (q, $^1$J$_{CF}$ = 272 Hz, CF$_3$), 117.9 (m, $p$-Ar), 21.9 (Me$_{Xyl}$), 18.1 (d, $^1$J$_{CP}$ = 43 Hz, PMe$_2$).

$^{31}$P{$^1$H} NMR (160 MHz, CD$_2$Cl$_2$, 25 °C) $\delta$: -20.2.

$$[\text{Ir(CO)}_2\text{PMe}_2\text{Ar}^{Dipp_2}]^+[$\text{BAR}_\text{F}$]$^-$$
A CD$_2$Cl$_2$ solution of complex [Ir(CO)$_2$PMe$_2$Ar$_{Dipp}$]$^+$/[BAr$_F$]$^-$ (27.2 mg, 0.019 mmol) is placed in a Young NMR tube, charged with 1.2 bar of CO and shaked for 10 min. It is transferred to a vial, the solvent removed under reduced pressure and the product washed with pentane to yield an analytically pure yellow powder. The yield is estimated to be quantitative based on spectroscopic data. Single crystals suitable for X-Ray diffraction were grown through slow pentane diffusion in a dichloromethane solution of the complex at -32 ºC. The product can be also obtained starting from complex X (1CO) under 3 bar of CO.

**Anal. Calcd.** for C$_{67}$H$_{55}$BF$_{24}$IrO$_3$: C, 50.35; H, 3.47. **Found**: C, 50.47; H, 3.04.

**IR** (CH$_2$Cl$_2$): $\nu$(Ir-CO) 2125, 2025 cm$^{-1}$.

**$^1$H NMR** (400 MHz, CD$_2$Cl$_2$, 0 ºC) $\delta$: 7.71 (s, 8H, o-Ar), 7.64 (td, $^3$J$_{HH}$ = 7.7 Hz, $^5$J$_{HP}$ = 2.2 Hz, 1H, p-C$_6$H$_3$), 7.60 (t, $^3$J$_{HH}$ = 7.8 Hz, 2H, p-Dipp), 7.56 (s, 4H, p-Ar), 7.38 (d, $^3$J$_{HH}$ = 7.9 Hz, 4H, m-Dipp), 7.19 (dd, $^3$J$_{HH}$ = 7.7 Hz, $^4$J$_{HP}$ = 3.5 Hz, 2H, m-C$_6$H$_3$), 2.41 (h, $^3$J$_{HH}$ = 6.7 Hz, 4H, (CHMe$_2$)$_{Dipp}$), 1.83 (d, $^2$J$_{HP}$ = 11.0 Hz, 6H, PMe$_2$), 1.38 (d, $^3$J$_{HH}$ = 6.8 Hz, 12H, Me$_{Dipp}$), 0.97 (d, $^3$J$_{HH}$ = 6.6 Hz, 12H, Me$_{Dipp}$).

**$^{13}$C{$_^1$H} NMR** (100 MHz, CD$_2$Cl$_2$, 0 ºC) $\delta$: 173.2 (d, $^2$J$_{CP}$ = 14 Hz, cis-CO), 168.7 (d, $^2$J$_{CP}$ = 91 Hz, cis-CO), 161.9 (q, $^1$J$_{CB}$ = 50 Hz, ipso-Ar), 149.9 (br, o-Dipp), 144.4 (d, $^2$J$_{CP}$ = 11 Hz, o-C$_6$H$_3$), 135.0 (o-Ar), 134.0 (d, $^3$J$_{CP}$ = 10 Hz, m-C$_6$H$_3$), 132.0 (d, $^4$J$_{CP}$ = 2 Hz, p-C$_6$H$_3$), 131.9 (p-Dipp), 130.9 (d, $^1$J$_{CP}$ = 59 Hz, ipso-C$_6$H$_3$), 130.5 (br, ipso-Dipp), 129.0 (q, $^2$J$_{CP}$ = 31 Hz, m-Ar), 124.8 (q, $^1$J$_{CP}$ = 272 Hz, CF$_3$), 124.5 (m-Dipp), 117.7 (m, p-Ar), 32.4 (CHMe$_2$)$_{Dipp}$), 25.8 (Me$_{Dipp}$), 22.6 (Me$_{Dipp}$), 18.5 (d, $^1$J$_{CP}$ = 43 Hz, PMe$_2$).

**$^{31}$P{$_^1$H} NMR** (160 MHz, CD$_2$Cl$_2$, 25 ºC) $\delta$: -21.0.

$[\text{Rh(CO)}_3\text{PMe}_2\text{Ar}^{Xyl}_2]^+$/[BAr$_F$]$^-$
A CD$_2$Cl$_2$ (0.6 mL) solution of 6a (0.08 mmol), placed in a Young NMR tube, was pressurized with CO (6 bar). NMR studies carried out from 25 to -60 °C are in accord with the presence of complexes 6a and 7a (in a 1:1 ratio at -60 °C). Complex 7a is only stable under a carbon monoxide atmosphere and its removal quickly regenerated the starting material. Consequently, characterization of 7a by 1D- and 2D-NMR spectroscopy was carried out under a CO atmosphere (6 bar).

$^1$H NMR (400 MHz, 25 ºC, CD$_2$Cl$_2$) δ: 7.75 (td, $^3$J$_{HH}$ = 7.7, $^5$J$_{HP}$ = 2.2 Hz, 1H, p-C$_6$H$_3$), 7.43 (t, $^3$J$_{HH}$ = 7.6 Hz, 2H, p-Xyl), 7.31 (d, $^3$J$_{HH}$ = 7.6 Hz, 4H, m-Xyl), 7.13 (dd, $^3$J$_{HH}$ = 7.7, $^4$J$_{HP}$ = 3.5 Hz, 1H, m-C$_6$H$_3$), 2.13 (s, 12 H, Me$_{Xyl}$), 1.63 (d, $^2$J$_{HP}$ = 10.4 Hz, 6H, PMe$_2$).

$^{13}$C{${^1}$H} NMR (100 MHz, 25 ºC, CD$_2$Cl$_2$) δ: 182.1 (br s, CO), 146.5 (d, $^2$J$_{CP}$ = 11 Hz, o-C$_6$H$_3$), 138.1 (br s, ipso-Xyl), 136.9 (o-Xyl), 133.8 (br s, p-C$_6$H$_3$), 131.5 (d, $^3$J$_{CP}$ = 9 Hz, m-C$_6$H$_3$), 129.3 (p-Xyl), 128.7 (m-Xyl), 127.8 (d, $^1$J$_{CP}$ = 36 Hz, ipso-C$_6$H$_3$), 22.4 (Me$_{Xyl}$).

$^{13}$C{${^1}$H} NMR (100 MHz, -60 ºC, CD$_2$Cl$_2$): 180.6 (dd, $^1$J$_{CRh}$ = 69, $^2$J$_{CP}$ = 16 Hz, cis-CO), 178.8 (dd, $^2$J$_{CP}$ = 92 Hz, $^1$J$_{CRh}$ = 51 Hz, trans-CO), 18.6 (d, $^1$J$_{CP}$ = 37 Hz, PMe$_2$).

$^{31}$P{${^1}$H} NMR (160 MHz, 25 ºC, CD$_2$Cl$_2$) δ: -2.3 (br s).

$^{31}$P{${^1}$H} NMR (160 MHz, -60 ºC, CD$_2$Cl$_2$) δ: -1.2 (d, $^1$J$_{PRh}$ = 91 Hz).

A CD$_2$Cl$_2$ (0.6 mL) solution of [Rh(CO)PMe$_2$Ar$^{Dipp}$][BAr$_F$] (0.02 mmol), placed in a Young NMR tube, was pressurized with CO (6 bar). NMR studies carried out from 25 to -60 ºC are in accord with the presence of complexes [Rh(CO)PMe$_2$Ar$^{Dipp}$][BAr$_F$] and [Rh(CO)$_3$PMe$_2$Ar$^{Dipp}$][BAr$_F$] in a 96:4 ratio at -60 ºC. The tricarbonyl complex was not detected at -30 ºC (see SI).

$^{31}$P{${^1}$H} NMR (160 MHz, -60 ºC, CD$_2$Cl$_2$) δ: -3.5 (d, $^1$J$_{PRh}$ = 91 Hz).


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X-ray.
11a·CO + CO is found 3.2 kcal·mol⁻¹ above 11a·(CO)₂, and 11b·CO + CO lies 4.5 kcal·mol⁻¹ above 11b·(CO)₂ compared to the 8.3 kcal·mol⁻¹ found for the iridium analogs.

As a footnote/reference: CO capture by 11a·(CO)₂ yields 11a·(CO)₃ (-5.0 kcal·mol⁻¹) through a barrier of 12.7 kcal·mol⁻¹ and 11b·(CO)₂ affords 11b·(CO)₃ (+2.1 kcal·mol⁻¹) through a barrier of 6.1 kcal·mol⁻¹.