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Bis(diethylphosphino)methane As a Bridging Ligand in Complexes of Ir_2, Rh_2, and IrRh: Geminal C−H Activation of α-Olefins

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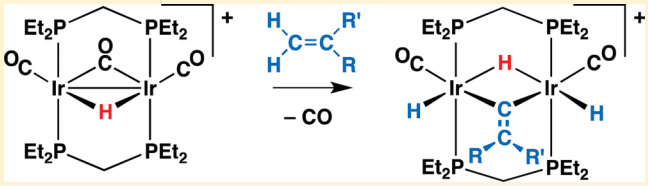
Supporting Information

ABSTRACT: Bis(diethylphosphino)methane (depm, $Et_2PCH_2PEt_2$) is used as a new bridging ligand for the syntheses of a series of diiridium, dirhodium, and iridium/rhodium complexes, starting from *trans*-$[MM'Cl_2(CO)_2(depm)_2]$ (M = M′ = Ir (**1**); M = M′ = Rh (**11**); M = Ir, M′ = Rh (**19**)). The reduction of all three chloro compounds in aqueous KOH under an atmosphere of CO produces the neutral tricarbonyl complexes $[MM'(CO)_3(depm)_2]$ (M = M′ = Ir (**2**); M = M′ = Rh (**12**); M = Ir, M′ = Rh (**20**)). Protonation of these tricarbonyl complexes by triflic acid (HOTf) or Brookhart's acid ($HBAr^F_4$) yields the hydride-bridged tricarbonyl complexes $[MM'(CO)_3(\mu\text{-}H)(depm)_2][X]$ (M = M′ = Ir (**9**); M = M′ = Rh (**16**); M = Ir, M′ = Rh (**25**); X = SO_3CF_3 or $B(3,5\text{-}(CF_3)_2C_6H_3)_4$). Reaction of **2** with methyl triflate yields the methylene/hydride product $[Ir_2(H)(CO)_3(\mu\text{-}CH_2)(depm)_2][OTf]$ (**4**), while the same reaction with the dirhodium analogue (**12**) produces the methyl complex $[Rh_2(CH_3)(CO)_3(depm)_2][OTf]$ (**14**) at below −20 °C, which upon warming to above −20 °C results in migratory insertion to yield an acetyl-bridged species, $[Rh_2(CO)_2(\mu\text{-}C(CH_3)O)(depm)_2][OTf]$ (**14a**). The analogous Rh/Ir species (**20**) reacts with methyl triflate to give the methyl-tricarbonyl product $[IrRh(CH_3)(CO)_3(depm)_2][OTf]$ (**22**). Removal of a carbonyl from **4** and **22** yields $[MIr(CH_3)(CO)_2(depm)_2][OTf]$ (M = Ir (**5**); M = Rh (**23**)), which are highly susceptible to hydrolysis; however the dirhodium species **14** and **14a** are not susceptible to CO loss under the conditions investigated. The reaction of $[Ir_2(CO)_3(\mu\text{-}H)(depm)_2][BAr^F_4]$ (**9**) with a number of α-olefins results in double C−H bond activation of the geminal hydrogens to give the vinylidene-bridged trihydride products of the form $[Ir_2(H)_2(CO)_2(\mu\text{-}H)(\mu\text{-}C{=}CRR')(depm)_2][BAr^F_4]$.



INTRODUCTION

Interest in the reactivity of binuclear complexes[1] containing either pairs of identical metals[2−18] or two metals that differ[19−33] has primarily been driven by the idea that these metals may act together in some way, either in a cooperative manner,[18,26−36] whereby the pair of adjacent metals give rise to reactivity that differs from that observed at single-metal sites, or in tandem, whereby one metal performs one transformation, followed by a second transformation at the other metal.[37−40] A binuclear compound studied by us, namely, $[Ir_2(CH_3)(CO)_2(dppm)_2][X]$ (dppm = μ-$Ph_2PCH_2PPh_2$, X = anion), has demonstrated a wealth of reactivity including C−H[41,42] and C−F[36,43,44] bond activation, in which the pair of adjacent metals play a pivotal role. In addition to the interesting reactivity displayed by this species, its simplicity and the fact that each ligand present has one or more convenient NMR-active nuclei (^{31}P, ^{13}C, ^{1}H) have often allowed the stepwise transformations to be conveniently followed by multinuclear and variable-temperature NMR studies, giving us an appreciation of the roles of the adjacent metals in the chemistry.

One transformation of interest to us, which could make use of the cooperative involvement of pairs of metals, is the double activation of pairs of geminal C−H bonds in α-olefins. Although the activation of single olefinic C−H bonds is common,[45−55] double, geminal C−H activation is rare, with only a few examples having been reported.[41,56−63] Of these, all but one[62] involve pairs of metals at some stage in the activation process.

In a previous study we observed the unusual double activation of a pair of geminal C−H bonds in 1,3-butadiene by the above diiridium complex and proposed the cooperative involvement of the pair of metals in this transformation.[41] However, this reaction is extremely slow (48 h at 22 °C), and the binding of the butadiene, in a presumed intermediate, is extremely weak and only observed at temperatures below ca. −50 °C. Furthermore, this reactivity was limited to 1,3-butadiene, with no C−H activation observed for other α-olefins investigated. Seeking to improve the scope of double, geminal C−H activation, we considered replacing the bridging dppm groups by smaller, more basic alkyl diphosphines to allow better substrate access to the metals and to increase metal basicity, respectively. The obvious diphosphine of choice for this replacement was bis(dimethylphosphino)methane (dmpm), the smallest of the fully alkyl-substituted diphosphines. Furthermore, the dmpm analogue of the above methyl complex, namely, $[Ir_2(CH_3)(CO)_2(dmpm)_2]^+$, had been reported.[11] Unfortunately, our attempts to duplicate the reported synthesis were unsuccessful,

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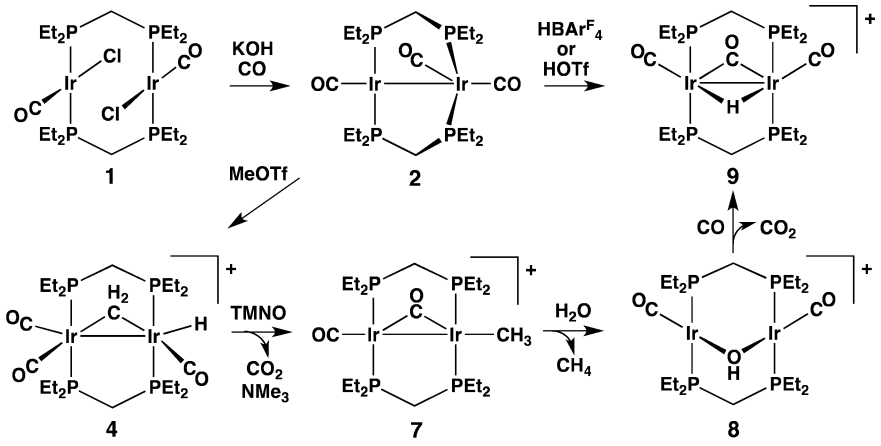
Scheme 1



and in general we found that the dmpm chemistry deviated significantly from that of dppm in rather unpredictable ways.[64]

The capricious nature of this dmpm chemistry (in our hands) led us to instead investigate the closely related depm ($Et_2PCH_2PEt_2$) ligand, the chemistry of which, we find, parallels that of dppm in a rational manner. Surprisingly, the use of depm as a bridging ligand has received little attention, with the majority of examples involving group 10 metals.[65−69] In this paper we report the synthesis and characterization of a series of depm-bridged complexes of Ir_2, Rh_2, and RhIr and investigate their reactivity toward a series of α-olefins. Although the Rh/Ir and Rh_2 analogues of $[Ir_2(CH_3)(CO)_2(dppm)_2]^+$ were unreactive toward 1,3-butadiene, we were also interested in determining whether these Rh-containing analogues, incorporating a pair of more basic depm groups, might display reactivity toward olefin C−H activation, not previously observed with the dppm system.

RESULTS AND DISCUSSION

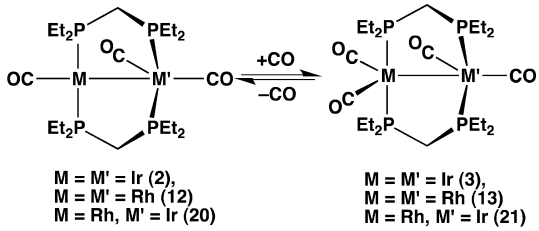
a. Synthesis of Ir_2, Rh_2, and IrRh Complexes.

Diiridium Complexes. The addition of $[IrCl(COD)]_2$ to a CH_2Cl_2 solution of bis(diethylphosphino)methane (depm) followed by a slow CO purge results in the formation of *trans*-$[Ir_2Cl_2(CO)_2(depm)_2]$ (**1**) in modest yields (the structure of **1** is diagrammed in Scheme 1 and has been determined by an X-ray study, which appears as Supporting Information). Compound **1** displays a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ 8.3, indicating the chemical equivalence of all four ^{31}P nuclei, and the ^1H NMR spectrum also displays a single resonance at δ 2.52 for the backbone-methylene protons of depm, consistent with "front/back" symmetry in the species; this signal appears as a quintet owing to virtual coupling to all ^{31}P nuclei. The chemical equivalence of both carbonyls also gives rise to a single resonance in the $^{13}C\{^1H\}$ spectrum at δ 168.3. In all cases described herein, carbonyl resonances in the ^{13}C NMR spectra are obtained using ^{13}CO-enriched compounds.

Compound **1** is the precursor for all other Ir_2 compounds reported in this paper and is readily reduced under an atmosphere of CO in aqueous KOH to yield $[Ir_2(CO)_3(depm)_2]$ (**2**). More conventional reduction methods such as the reaction with sodium borohydride or zinc powder under carbon monoxide were also investigated; however, these methods resulted in mixtures of products that were difficult to separate and consequently gave substantially lower yields of **2**, making aqueous KOH/CO the preferred method. At ambient temperature, compound **2** has spectroscopic characteristics similar to those of **1** and its dppm congener,[7] displaying a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ = −11.0 a quintet for the backbone-methylene group ($Et_2PCH_2PEt_2$) in the ^1H NMR spectrum at δ 2.67 and one carbonyl signal in the $^{13}C\{^1H\}$ NMR spectrum at δ 185.6. However, upon cooling to −80 °C, the $^{31}P\{^1H\}$ NMR spectrum displays two signals at δ −8.9 and −28.0, consistent with the chemically inequivalent environments, and although there is no noticeable change in the ^1H NMR spectrum at this temperature, three unique CO resonances are observed in the $^{13}C\{^1H\}$ NMR at δ 179.8, 189.3, and 193.8, indicating that a fluxional process is occurring at higher temperatures. This fluxionality most likely involves a "merry-go-round" exchange of the carbonyls, accompanied by the alternating exchange of cis-to-trans phosphine arrangement at the different metals, as was also proposed in both the dppm and dmpm analogues.[7,12] The similarities in the low-temperature NMR spectra of **2** compared to those of $[Rh_2(CO)_3(dppm)_2]$,[8] $[RhIr(CO)_3(dppm)_2]$,[22] and $[Ir_2(CO)_3(dppm)_2]$[7] suggest similar structures, which were established for the Rh-containing dppm species by X-ray structure determinations, in which they are shown to have a trans arrangement of diphosphines at one metal and a cis arrangement at the other.

In the presence of CO, compound **2** is converted to the tetracarbonyl complex $[Ir_2(CO)_4(depm)_2]$ (**3**) (Scheme 2), while removal of the CO atmosphere causes compound **3** to revert to **2** within minutes in solution. Again at ambient temperature a singlet is observed for **3** in the $^{31}P\{^1H\}$ NMR, while only a

Scheme 2



single ^{13}CO resonance is observed in the $^{13}C\{^1H\}$ NMR spectrum. However, cooling a solution of **3** to −80 °C results in similar behavior to that of compound **2**, with two distinct $^{31}P\{^1H\}$ signals observed (δ −19.6 and −41.1), along with four distinct carbonyl resonances in the $^{13}C\{^1H\}$ NMR at δ 181.2, 191.8, 194.2, and 195.2, again indicating fluxionality, presumably

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analogous to that of **2**. Compound **3** is similar to the dmpm analogue, the structure of which was reported by Reinking and shown to have the unsymmetrical structure diagrammed below for our species.[70]

In parallel with the analogous dppm-bridged diiridium species,[18] reaction of **2** with methyl trifluoromethanesulfonate (MeOTf) results in the formation of $[Ir_2(H)(CO)_3(\mu\text{-}CH_2)(depm)_2][OTf]$ (**4**; Scheme 1), in which the methyl group has undergone C−H bond activation to produce a methylene/hydride species. For all cationic species the accompanying anion is triflate, unless otherwise noted. The $^{31}P\{^1H\}$ NMR spectrum displays two broad resonances at δ −8.9 and −19.5, which sharpen into pseudotriplets upon cooling to −80 °C. The ^1H NMR spectrum at this temperature confirms the methylene/hydride formulation with the metal-bridged methylene protons appearing at δ 3.95 and the hydride resonance at δ −12.42. In the reaction of **2** with carbon-13-labeled MeOTf, the resulting $^{13}C\{^1H\}$ resonance appears in the methylene region at δ 44.2. Also observed in the $^{13}C\{^1H\}$ NMR spectrum for the ^{13}CO-labeled product is a single resonance at δ 177.2 for the three carbonyls, and cooling to −80 °C results in its separation into three signals (δ 166.3, 178.7, and 180.2). A spin-saturation transfer experiment on the methylene and hydride protons at ambient temperature confirms that the fluxionality at elevated temperatures involves the reversible transformation of the methylene and hydride groups to a methyl ligand, much as reported for the dppm analogue.[18]

An X-ray structure determination of **4** confirms the ligand orientation proposed by spectroscopy, as displayed in Figure 1.

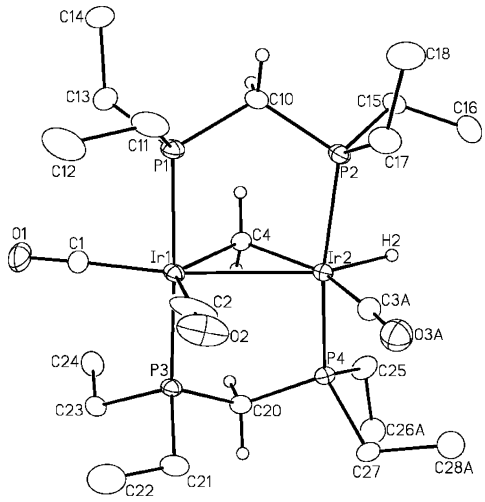

Figure 1. Perspective view of the complex cation of $[Ir_2(H)(CO)_3(\mu\text{-}CH_2)(depm)_2][OTf]$ (**4**) showing the atom-labeling scheme. Thermal parameters are shown at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters for the hydride, bridging methylene, and depm methylene groups, but are not shown for the Et groups. Only one pair of disordered methyl substituents of the ethyl groups on P(4), along with the disordered carbonyl on Ir(2), are shown for clarity. Relevant bond distances (Å) and angles (deg): Ir(1) − Ir(2) = 2.7887(3); Ir(1)−C(4) = 2.163(5); Ir(2)−C(4) = 2.075(5); P(1)−P(2) = 3.049(2); P(3)−P(4) = 3.015(2); Ir(1)−C(4)−Ir(2) = 82.3(2).

The Ir(1)−Ir(2) separation of 2.7887(3) Å indicates the presence of a metal−metal bond, displaying significant compression compared to the nonbonded P(1)−P(2) and P(3)−P(4) distances of 3.049(2) and 3.015(2) Å, respectively, within the depm groups. The bridging methylene group is unsymmetrically bound, being slightly closer to the less crowded Ir(2) center (Ir(2)−C(4) = 2.075(5) Å) than to Ir(1) (Ir(1)−C(4) = 2.163(5) Å). There is a 50/50 disorder of the ethyl groups on P(4), with two different orientations forcing the neighboring carbonyl (C(3) and O(3)) to also be disordered over two positions. Placing compound **4** under a CO atmosphere results in the formation of two other compounds, identified as $[Ir_2(CH_3)(CO)_4(depm)_2][OTf]$ (**5**) and $[Ir_2(CO)_4(C(O)CH_3)(depm)_2][OTf]$ (**6**), the result of sequential CO uptake (Scheme 3). Both compounds are susceptible to CO loss upon CO removal, resulting in reversion to **4**. In the ^1H NMR spectrum of **5**, a triplet appears at δ 0.68 ($^3J_{HP}$ = 5.4 Hz) for the Ir-bound methyl group, while for **6** the methyl group appears as a singlet at δ 2.60, consistent with migration of this group to a carbonyl. In the $^{13}C\{^1H\}$ NMR spectrum two carbonyl signals (δ 187.4 and 191.1) appear for **5** in a 2:2 ratio, while for **6** three resonances appear in a 2:2:1 ratio at δ 187.8, 195.0, and 221.2; the downfield signal is typical of an Ir-bound acyl carbonyl.[71] Additional coupling of the methyl group to the acyl carbonyl ($^1J_{CC}$ = 28.0 Hz; $^{13}CH_3/^{13}CO$-enriched sample) also supports the migratory insertion product. The similarities in the spectral parameters of **5** and **6** are consistent with their similar geometries.

Reacting compound **4** with trimethylamine-*N*-oxide (TMNO) at ambient temperature produces the dicarbonyl product $[Ir_2(CH_3)(CO)_2(depm)_2][OTf]$ (**7**), as shown earlier in Scheme 1. Compound **7** displays a single broad resonance at ambient temperature in the $^{31}P\{^1H\}$ NMR spectrum at δ 23.2, similar to the methyl dicarbonyl analogues of dppm and dmpm.[11,18] The ^1H NMR spectrum displays a quintet at δ 0.57 ($^3J_{HP}$ = 4.4 Hz) for the methyl ligand, and the $^{13}C\{^1H\}$ NMR spectrum also displays a single carbonyl resonance at δ 174.2, suggesting a symmetric, methyl-bridged structure as reported for the dmpm analogue.[11] However, cooling to −80 °C gives rise to the separation of the $^{31}P\{^1H\}$ signal into two distinct resonances at δ 26.1 and 19.8 and the appearance of two carbonyl resonances, δ 179.9 and 168.3, in the $^{13}C\{^1H\}$ NMR spectrum, suggesting an unsymmetrical structure, such as that shown in Scheme 1, and analogous to that observed for the dppm analogues $[IrRh(CH_3)(CO)_2(dppm)_2]^+$ and $[Ir_2(CH_3)(CO)_2(dppm)_2]^+$.[18,25] The symmetrical structure suggested by the ambient temperature spectra is presumably the result of migration of the methyl group from metal to metal on one face of the Ir_2P_4 plane, in conjunction with the two CO ligands migrating across the opposite face of the metals. A merry-go-round migration of these ligands is ruled out owing to the appearance of two ^1H resonances for the methylene linkers of the depm ligands, indicating front/back asymmetry in the time-averaged structure.

Unfortunately, compound **7** is unstable in solution at ambient temperature, transforming to $[Ir_2(CO)_2(\mu\text{-}OH)(depm)_2][OTf]$ (**8**; Scheme 1) within 5 min, owing to its reaction with adventitious water that results from either the earlier aqueous KOH/CO reduction step or the use of trimethylamine-*N*-oxide, which is difficult to obtain fully dried.[72] In both cases, an azeotropic distillation in benzene or dimethylformamide, respectively, was performed in attempts to minimize residual water. However, the transformation of **7** to **8** in solution could not be prevented by these precautions, having still occurred after 45 min. Compound **8** displays spectral parameters similar to its dppm analogue[7] and, therefore, is not discussed here (refer to Experimental Section for NMR data).

Reaction of compound **8** with CO generates the hydride-bridged species $[Ir_2(CO)_3(\mu\text{-}H)(depm)_2][OTf]$ (**9-OTf**), as

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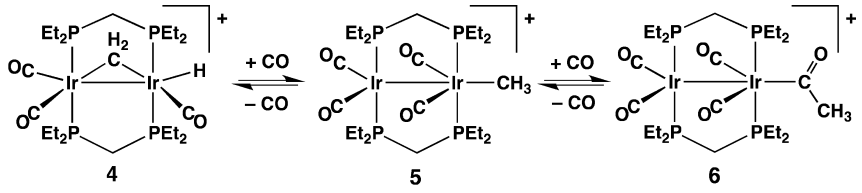
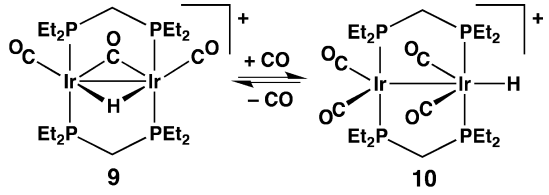
Scheme 3



shown in Scheme 1, which was obtained more directly by protonation of **2**. Compound **9**, as either the triflate or $BAr^{F}_{4}^{-}$ salt, displays a singlet in the $^{31}P\{^{1}H\}$ NMR spectrum, while the ^{1}H NMR spectrum displays a single, upfield resonance at δ −10.40, appearing as a quintet with equal coupling to all four phosphorus nuclei ($^{2}J_{HP}$ = 9.8 Hz). At ambient temperature, the $^{13}C\{^{1}H\}$ NMR spectrum shows a single, broad resonance at δ 183.7, which upon cooling to −80 °C resolves into two resonances at δ 185.3 and 183.3, in a 1:2 intensity ratio, respectively; at low temperature the $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra remain unchanged, appearing to rule out a fluxional process at higher temperatures.

Under a CO atmosphere, compound **9** generates $[Ir_2(H)(CO)_4(depm)_2]^+$ (**10**), in which the hydride ligand is now terminally bound to one Ir center (Scheme 4), as shown by the

Scheme 4



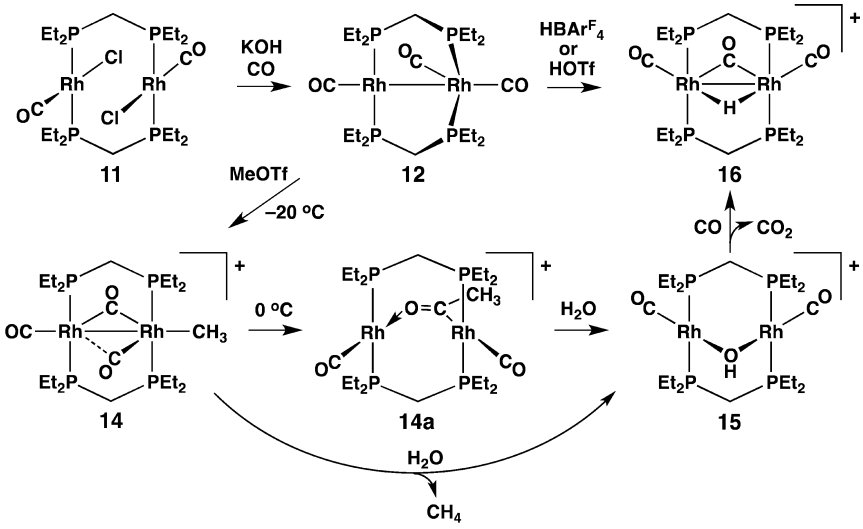
triplet in the ^{1}H NMR spectrum at δ −8.80, displaying coupling to only one pair of ^{31}P nuclei ($^{2}J_{HP}$ = 14.4 Hz). The appearance of only two equal-intensity carbonyl resonances in the carbon-13 NMR spectrum, in conjunction with only one signal for the backbone-methylene protons, suggests that compound **10** has a similar geometry to those of compounds **5** and **6**, with front/back symmetry about the metal−phosphine plane.

b. Dirhodium Complexes. Reacting $[Rh_2Cl_2(COD)_2]$ with depm under a CO purge results in the formation of *trans*-$[Rh_2Cl_2(CO)_2(depm)_2]$ (**11**; Scheme 5) much as described for the Ir_2 analogue. The $^{31}P\{^{1}H\}$, ^{1}H, and $^{13}C\{^{1}H\}$ spectral parameters are all as expected, including rhodium−phosphorus coupling observed in the $^{31}P\{^{1}H\}$ NMR spectrum ($^{1}J_{RhP}$ = 117.2 Hz) and rhodium−carbon coupling for the carbonyls in the $^{13}C\{^{1}H\}$ NMR spectrum ($^{1}J_{RhC}$ = 74.8 Hz). An X-ray structure determination of compound **11** reveals a near superimposable structure to that of the diiridium analogue (**1**) and is given as Supporting Information.

As described earlier for the Ir_2 complex, compound **11** can also be reduced under a CO atmosphere in the presence of aqueous KOH, resulting in the formation of $[Rh_2(CO)_3(depm)_2]$ (**12**). Multinuclear NMR spectra show similarities to compound **2** at ambient temperature, with the exception of additional rhodium−phosphorus coupling ($^{1}J_{RhP}$ = 137.7 Hz). Cooling **12** to −110 °C shows separation of the single $^{31}P\{^{1}H\}$ signal into two doublets of pseudotriplets at δ 22.5 and 8.5, with rhodium−phosphorus couplings of 117.1 and 152.6 Hz, respectively, along with mutual phosphorus−phosphorus coupling of 69.7 Hz. At −110 °C, the broad carbonyl resonance observed at ambient temperature resolves into three signals at δ 209.1, 206.8, and 183.4 ($^{1}J_{RhC}$ = 77.0 Hz, 71.2, and 67.9 Hz, respectively). Selective $^{13}C\{^{31}P\}$ decoupling establishes that the upfield carbonyl is coupled to one end of the diphosphines (δ 22.5), while the two downfield signals are coupled to the other end, consistent with the structure proposed in Scheme 5 and in agreement with the structures determined for the dppm analogues, $[Rh_2(CO)_3(dppm)_2]$[2] and $[IrRh(CO)_3(dppm)_2]$.[22]

As shown earlier in Scheme 2, compound **12** reacts under an atmosphere of CO, producing $[Rh_2(CO)_4(depm)_2]$ (**13**), which is highly susceptible to CO loss. Multinuclear NMR

Scheme 5



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spectroscopy displays broad resonances at ambient temperature; however cooling the sample to −80 °C produces the pattern expected for an AA′BB′XY spin system in the $^{31}P\{^{1}H\}$ NMR spectrum and, in conjunction with two $^{13}C\{^{1}H\}$ resonances at δ 214.3 and 204.1 in a 1:3 ratio, confirms the presence of a fourth carbonyl (refer to Experimental Section for full spectroscopic characterization). This intensity ratio is not the 1:1:1:1 ratio expected and appears to indicate coincidental overlap of three resonances masked by the breadth of the resulting signal.

The addition of MeOTf to compound **12** at −20 °C produces the tricarbonyl methyl species $[Rh_2(CH_3)(CO)_3(depm)_2][OTf]$ (**14**), as shown in Scheme 5. Unlike the diiridium analogue (**4**), the methyl moiety does not undergo C−H activation to give a methylene/hydride isomer, but remains intact, as confirmed by both ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy at −80 °C, with the methyl protons appearing as a broad multiplet at δ 0.63 and the methyl carbon appearing as a broad, unresolved resonance at δ −0.7. The $^{13}C\{^{1}H\}$ NMR spectrum also displays two carbonyl resonances at δ 214.3 (2C) and 199.3 (1C), with the downfield signal suggesting two bridging carbonyls, while the upfield signal indicates one terminal carbonyl. The $^{13}C\{^{1}H, ^{31}P\}$ NMR spectrum shows the downfield multiplet as a triplet due to coupling to rhodium (32.7 Hz), while the upfield signal resolves to a doublet from coupling to rhodium (74.9 Hz). Although the single low-field resonance for the pair of carbonyls suggests two symmetrically bridging groups, the static structure more likely resembles that depicted in Scheme 5, with one bridging carbonyl and one semibridging carbonyl, which are rapidly exchanging on the NMR time scale, as seen in a similar Rh/Os system.[73]

Warming compound **14** to 0 °C results in its transformation to $[Rh_2(CO)_2(\mu\text{-}C(CH_3)O)(depm)_2][OTf]$ (**14a**) by the migratory insertion of the CH_3 and a CO ligand, as outlined in Scheme 5. The ^{1}H NMR spectrum displays the methyl protons as a singlet with no observable coupling to phosphorus, and the $^{13}C\{^{1}H\}$ NMR spectrum displays a broad, downfield signal at δ 319.9, similar to its dppm counterpart,[15] indicative of a bridging acetyl moiety, as shown in Scheme 5. Unfortunately, **14a** readily decomposes above 0 °C, with the major product (ca. 50%), $[Rh_2(CO)_2(\mu\text{-}OH)(depm)_2][OTf]$ (**15**), resulting from reaction with adventitious H_2O. Compound **15** can be prepared in near quantitative yield by reacting **14** or **14a** with water, resulting in the elimination of methane. The spectral parameters for **15** are as expected and are given in the Experimental Section.

Attempts to produce the rhodium analogue of compound **7**, $[Rh_2(CH_3)(CO)_2(depm)_2][OTf]$, proved unsuccessful, with TMNO failing to react with compound **14** below −20 °C. Increasing the temperature to near 0 °C yields only **14a**, which is unreactive to TMNO below this temperature, while at higher temperatures the irreversible conversion to **15** and numerous unidentified decomposition products was observed. Our failure to remove a carbonyl is consistent with the lower lability of the carbonyl ligands in the presence of the smaller, more basic depm group. Also consistent with the more basic depm compared to dppm is the observation of the methyl complex **14**, the dppm analogue of which was not observed; the more basic depm groups disfavor migratory insertion owing to the resulting lower electrophilicity of the carbonyls, resulting from increased π-back-donation.

As observed in the Ir_2 analogue, the hydroxide-bridged Rh_2 complex (**15**) reacts with CO to produce the hydride-bridged complex $[Rh_2(CO)_3(\mu\text{-}H)(depm)_2][OTf]$ (**16-OTf**), which is also obtained as either the OTf^- or $BAr^F{}_4^-$ salt by protonation of **12** by the appropriate acid, as shown in Scheme 5. Compound **16** contains a symmetrically bridged hydride, as shown by the complex multiplet in the ^{1}H NMR at δ −10.34, displaying couplings to both rhodium atoms ($^{1}J_{RhH}$ = 24.3 Hz) and all four phosphorus nuclei ($^{2}J_{HP}$ = 12.2 Hz). The $^{13}C\{^{1}H\}$ NMR spectrum displays three overlapped carbonyl signals at δ 194.3 and, upon cooling to −80 °C, shows slight separation of the signal into two broad resonances at δ 195.1 and 194.0 in a 1:2 ratio; interestingly, the $^{13}C\{^{1}H\}$ chemical shifts for the bridging and terminal CO ligands do not differ significantly, much as observed earlier for the diiridium analogue.

An X-ray structure determination of **16-BAr$^F{}_4$** confirms the structure proposed, revealing a symmetrically bridged hydrido ligand with two terminal carbonyls and one bridging on the face opposite the hydride, as shown in Figure 2. The rhodium−rhodium separation (Rh(1)−Rh(2) = 2.7613(3) Å) is significantly shorter than the nonbonding P−P distances within the diphosphine backbones (P(1)−P(2) = 3.046(1), P(3)−P(4) = 3.051(1) Å), indicating significant contraction along the Rh−Rh vector, consistent with a strong metal−metal interaction. Other crystallographic parameters are as expected and are in close agreement to those reported for the dppm analogue, $[Rh_2(CO)_3(\mu\text{-}H)(dppm)_2]^+$.[2]

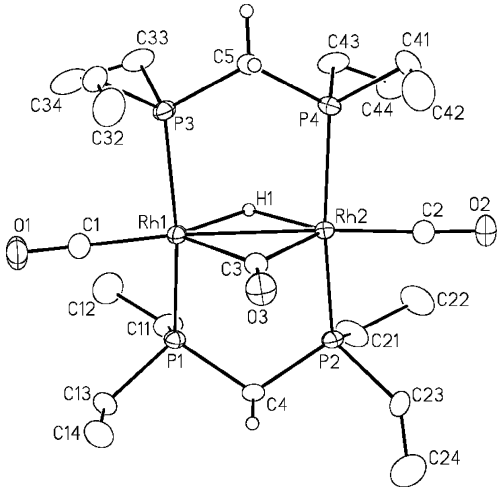

Figure 2. Perspective view of the complex cation of $[Rh_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(depm)_2][BAr^F{}_4]$ (**16-BAr$^F{}_4$**) showing the atom-labeling scheme. Thermal parameters are as described in Figure 1. Relevant bond distances (Å) and angles (deg): Rh(1)−Rh(2) = 2.7613(3); P(1)−P(2) = 3.046(1); P(3)−P(4) = 3.051(1); Rh(1)−C(1) = 1.842(4); Rh(1)−C(3) = 2.143(3); Rh(2)−C(2) = 1.850(3); Rh(2)−C(3) = 2.119(3); Rh(1)−C(3)−Rh(2) = 80.8(1); P(1)−Rh(1)−P(3) = 162.52(3); P(2)−Rh(2)−P(4) = 163.54(3).

Compound **16** reacts with additional acid, producing the dicationic complex $[Rh_2(CO)_3(depm)_2]^{2+}$ (**17**), accompanied by H_2 evolution (Scheme 6), and this product takes up two additional carbonyl ligands under a CO atmosphere to yield $[Rh_2(CO)_5(depm)_2]^{2+}$ (**18**), which readily reverts to **17** in the absence of CO. Both compounds **17** and **18** are fluxional at ambient temperatures; however the nature of the fluxionality was not investigated by low-temperature NMR. Compound **18** is analogous to the diiridium complex $[Ir_2(CO)_4(\mu\text{-}CO)(dppm)_2]^{2+}$,[7] which was shown to have fluxional behavior similar to that observed for **18** at ambient temperature.

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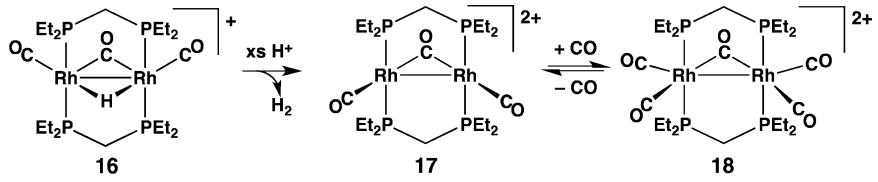
Scheme 6



The structure proposed for compound **18** has been confirmed crystallographically for the ditriflate salt and is shown in the ORTEP representation of the cation in Figure 3. The structure shows a symmetrical arrangement of carbonyls with both metals having nearly identical geometries. The carbonyls oriented along the Rh−Rh bond have significantly shorter Rh−C distances (1.904(3), 1.924(3) Å) than those that are pseudo trans to the bridging carbonyl (1.992(3), 1.998(3) Å); the bridging carbonyl displays Rh−C bond lengths that are elongated relative to the terminal ligands and is unsymmetrically bound (Rh(1)−C(3) = 2.195(3) Å; Rh(2)−C(3) = 2.025(3) Å), presumably a result of nonbonded contacts involving the depm ethyl groups, which are in different orientations at each end of the depm ligands, as shown in Figure 3.

c. Iridium/Rhodium Complexes. The addition of depm to Vaska's complex, $[IrCl(CO)(PPh_3)_2]$, followed by 0.5 equiv of $[Rh(Cl)(CO)_2]_2$ produces a dark orange solution of *trans*-$[IrRhCl_2(CO)_2(depm)_2]$ (**19**). As is the case with related dppm-bridged mixed-metal Ir/Rh systems, the $^{31}P\{^1H\}$ NMR displays two signals, corresponding to an AA′BB′X spin system, with the downfield signal displaying rhodium coupling along with the expected phosphorus coupling, while the upfield signal, corresponding to the iridium-bound phosphines, shows only phosphorus coupling. All other spectral parameters for compound **19** closely match those already discussed for compounds **1** and **11**.

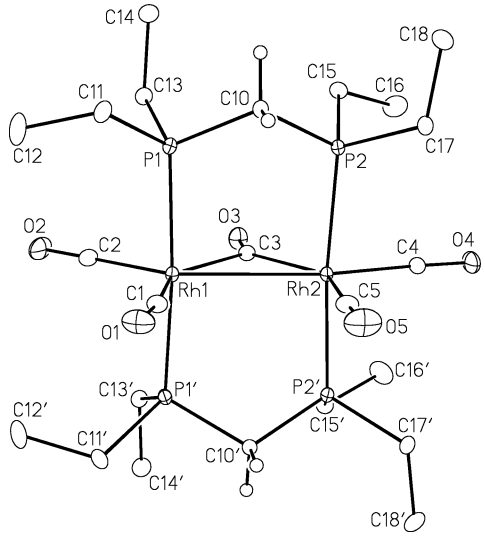


Figure 3. Perspective view of the complex cation of $[Rh_2(CO)_4(\mu\text{-}CO)(depm)_2][OTf]_2$ (**18**) showing the atom-labeling scheme. Thermal parameters are as described in Figure 1. Relevant bond distances (Å) and angles (deg): Rh(1)−Rh(2) = 2.8373(3); Rh(1)−C(1) = 1.992(3); Rh(1)−C(2) = 1.904(3); Rh(1)−C(3) = 2.195(3); Rh(2)−C(3) = 2.025(3); Rh(2)−C(4) = 1.924(3); Rh(2)−C(5) = 1.998(3); C(1)−Rh(1)−C(2) = 117.2(1); C(1)−Rh(1)−C(3) = 146.8(1); C(2)−Rh(1)−C(3) = 96.0(1); C(3)−Rh(2)−C(4) = 111.1(1); C(3)−Rh(2)−C(5) = 141.6(1); C(4)−Rh(2)−C(5) = 107.3(1).

As with the homobimetallic analogues, compound **19** is readily reduced (Scheme 7), producing a 1:1 mixture of the neutral tricarbonyl and tetracarbonyl compounds, $[IrRh(CO)_3(depm)_2]$ (**20**) and $[IrRh(CO)_4(depm)_2]$ (**21**), upon the addition of aqueous KOH under a CO atmosphere. A CO purge converts **20** to **21** (Scheme 2), which reverts to **20** in the absence of a CO atmosphere. At ambient temperature, the NMR spectra of compound **20** differ from those of its homobimetallic congeners, displaying two signals in the $^{31}P\{^1H\}$ NMR spectrum, while the $^{13}C\{^1H\}$ NMR spectrum shows two signals: broad singlet at δ 189.0 (2C) and a doublet at δ 185.7 (1C); the additional coupling of the latter signal is due to rhodium. Interestingly, cooling to −80 °C shows separation of the downfield signal in the $^{13}C\{^1H\}$ NMR spectrum into two broad singlets at δ 192.6 (1C) and 188.9 (1C), while the upfield signal remains unchanged. Although there is no evidence of exchange of the Rh- and Ir-bound carbonyls, the pair of Ir-bound carbonyls are exchanging, presumably accompanied by movement of the Ir-bound ends of the diphosphines from above the plane of the drawing in Scheme 7 to below.

At ambient temperature **21** displays broad resonances in the $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectra; however cooling to −80 °C yields two sharp signals in the $^{31}P\{^1H\}$ spectrum and four carbonyl resonances in the $^{13}C\{^1H\}$ spectrum, the two downfield signals of which display additional coupling to rhodium ($^1J_{CRh}$ = 73.5 Hz, 72.4 Hz). We propose a structure for **21** similar to the homobimetallic analogues and much like that of the dmpm-bridged diiridium species reported by Reinking.[70]

Addition of MeOTf to **20** yields $[IrRh(CH_3)(CO)_3(depm)_2][OTf]$ (**22**), as shown in Scheme 7, resembling the dirhodium analogue (**14**), in which the methyl group remains intact, and in contrast to the Ir_2 analogue, which undergoes intramolecular C−H activation to give the methylene/hydride compound **4**. Unlike compound **14**, which is proposed to contain a bridging and a semibridging CO (see above), only one carbonyl shows coupling to rhodium, suggesting that the other two carbonyls are bound solely to iridium.

An X-ray structure confirms the proposed geometry for **22** (Figure 4), although the structure is disordered such that the metals are found to have 60/40 occupancy across the two sites (refer to the Experimental Section for an overlapped view of disorder). The relatively long Rh(A)−C(2A) and Rh(A)−C(3A) distances (2.70(1) and 2.71(1) Å) and the close-to-linear Ir(A)−C(2A)−O(2A) and Ir(A)−C(3A)−O(3A) angles (175(1)°, 170(4)°) indicate that any interaction with rhodium is weak, consistent with the absence of Rh coupling in the $^{13}C\{^1H\}$ NMR spectrum.

Compound **22** reacts with TMNO to give the dicarbonyl complex $[IrRh(CH_3)(CO)_2(depm)_2][OTf]$ (**23**; Scheme 7), in which the methyl group remains terminally bound to iridium, as demonstrated by $^1H\{^{31}P\}$ and $^{13}C\{^1H\}$ NMR experiments; in particular, the absence of rhodium coupling in the $^{13}CH_3$ resonance confirms its binding to Ir. Two equal-intensity carbonyl signals are observed in the $^{13}C\{^1H\}$ NMR spectrum, with only the

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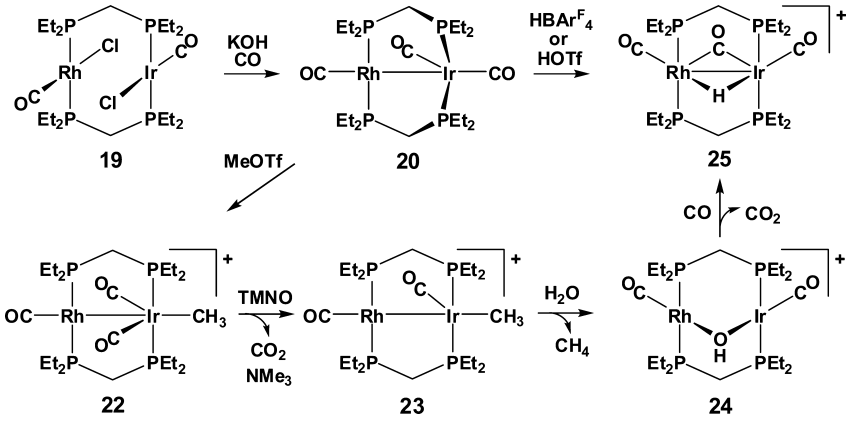
Scheme 7



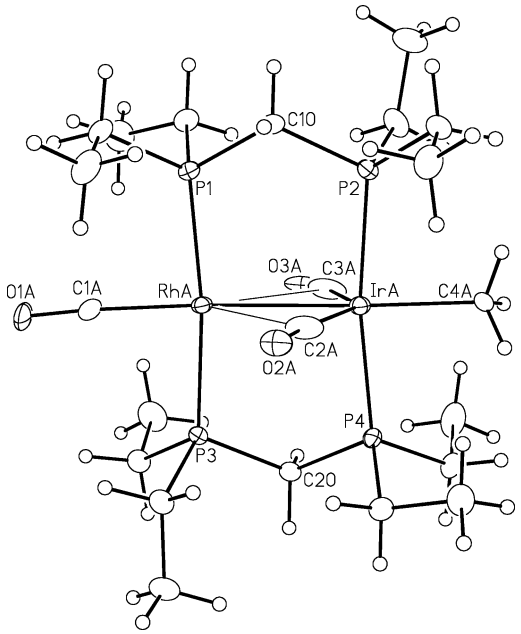


Figure 4. Perspective view of the complex cation of [RhIrMe(CO)$_3$(depm)$_2$][OTf] (**22**) showing the atom-labeling scheme. Only the major orientation of the disordered "RhIr(CO)$_3$(CH$_3$)" fragment (IrA, RhA, O1A, O2A, O3A, C1A, C2A, C3A, C4A) is shown. Thermal parameters are as described in Figure 1, except that all hydrogen atoms are shown, having arbitrarily small thermal parameters. Relevant bond distances (Å) and angles (deg) for the major orientation: Ir(A)−Rh(A) = 2.7282(7); Ir(A)−C(4A) = 2.10(2); Rh(A)−C(1A) = 1.93(2); Ir(A)−C(2A) = 1.95(1); Ir(A)−C(3A) = 2.02(2), Rh(A)−C(2A) = 2.70(1); Rh(A) − C(3A) = 2.71(1); Ir(A)−Rh(A)−C(1A) = 173.3(9); Rh(A)−Ir(A)−C(4A) = 177.6(9); Ir(A)−C(2A)−O(2A) = 175(1); Ir(A)−C(3A)−O(3A) = 170(4).

upfield signal displaying coupling to rhodium, suggesting two terminal carbonyls with one on each metal. Unfortunately, compound **23** is transient and, within 30 min, decomposes to [IrRh(CO)$_2$(μ-OH)(depm)$_2$][OTf] (**24**), again due to adventitious water.

Compound **24** is readily converted to [IrRh(CO)$_3$(μ-H)(depm)$_2$][OTf] (**25-OTf**) upon the addition of a CO purge, the latter of which can also be formed by protonation of **20** (refer to Scheme 7). As for the homobimetallic congeners, the hydride ligand appears to be symmetrically bridging the two metals, displaying coupling to all four phosphorus nuclei ($^2J_{HP}$ = 9.8 Hz) and to rhodium ($^1J_{HRh}$ = 21.1 Hz).

2. Geminal C−H Activation of Olefins. Compound **9**, as either the OTf$^-$ or BAr$^F_4{}^-$ salt, reacts with a variety of α-olefins (ethylene, vinylfluoride, propylene, 3,3,3-trifluoropropene, 1,3-butadiene, and styrene) under a variety of conditions to give the vinylidene-bridged trihydride products [Ir$_2$(H)$_2$(CO)$_2$(μ-H)(μ-C=CRR′)(depm)$_2$][BAr$^F_4$] (R = R′ = H (**26**); R = H, R′ = F (**27**); R = H, R′ = CH$_3$ (**28**); R = H, R′ = CF$_3$ (**29**); R = H, R′ = C(H)CH$_2$ (**30**); R = H, R′ = C$_6$H$_5$ (**31**)), in which a pair of geminal C−H bonds in the α-olefin have been cleaved. Although most of the above reactions take place over the course of several hours at ambient temperature, the reaction with styrene required elevated temperatures (40 °C) for several days, while the reaction with vinyl fluoride yielded **27** in only 5% yield (the major product resulting from geminal C−H and C−F bond activation).[69] However, all products (**26**−**31**) were obtained in a fraction of the time (10−30 min) at ambient temperature upon the addition of TMNO to solutions of **9** and the olefin (Scheme 8). In addition, isobutylene, which was unreactive with **9**, yielded the dimethylvinylidene-bridged product [Ir$_2$(H)$_2$(CO)$_2$(μ-H)(μ-C=CMe$_2$)(depm)$_2$][BAr$^F_4$] (**32**) in 30 min upon reaction with TMNO, and the fluorovinylidene-bridged **27** was obtained as the sole product upon inclusion of TMNO. The activation of a pair of geminal C−H bonds in α-olefins has precedent, but is not common.[41,56−63] In attempts to obtain a difluorovinylidene analogue, compound **9** was exposed to 1,1-difluoroethylene in the presence of TMNO; however decomposition to numerous unidentified products occurred, with no indication of geminal C−H activation occurring.

Compounds **26** and **32** each display a singlet in their ^{31}P{^{1}H} NMR spectra due to the symmetrical nature of each bridging vinylidene unit, while compounds **27**−**31**, formed from the unsymmetrical α-olefins (R ≠ R′), display two multiplets as a result of the unsymmetrical vinylidene group generating different chemical environments at the two metals. These symmetry differences are also evident in the ^{1}H NMR spectra with two hydride signals, in a 2:1 ratio for the two symmetric products (**26** and **32**), while compounds **27**−**31** each show three hydride signals (two relatively downfield signals for the terminal hydrides and an upfield signal arising from the bridging hydride). Interestingly, no trans H−H coupling between the bridging and terminal hydrides is observed in any of these species; the analogous vinylvinylidene-bridged/dppm species, which was crystallographically characterized,[41] also did not exhibit this coupling. However, the nonsymmetric compounds (**27**−**31**) display long-range coupling between the two terminal hydrides, typically on the order of 9.0 Hz. Compounds **26** and

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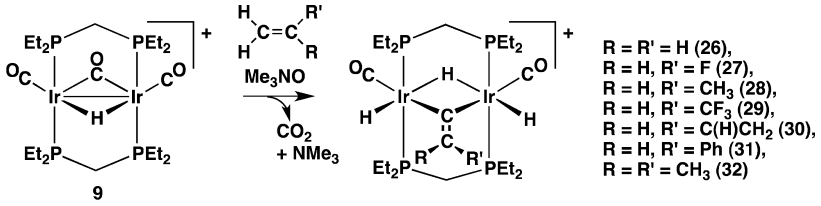
Scheme 8



32 display a single proton resonance for the vinylidene moiety: a singlet for the vinylidene hydrogens at δ 6.57 for compound **26** and a singlet for the methyl protons at δ 1.40 for compound **32**. The bridging fluorovinylidene unit (**27**) shows a doublet ($^2J_{HF}$ = 108.2 Hz) at δ 6.61 in the ^{1}H NMR spectrum, with a matching doublet found at δ −72.1 in the ^{19}F NMR spectrum, while the bridging trifluoromethylvinylidene moiety shows no coupling between the proton and fluorines, each appearing as singlets in their ^{1}H and ^{19}F NMR spectra. The vinylvinylidene unit in **30**, formed from the double C−H activation of 1,3-butadiene, displays four proton resonances at δ 6.82, 6.28, 4.93, and 4.82, all showing mutual couplings ($^3J_{HHvicinal}$ = 9.9 Hz, $^3J_{HHcis}$ = 9.9 Hz, $^3J_{HHtrans}$ = 17.1 Hz) that are in close agreement with the values reported for $[Ir_2(CH_3)(H)(CO)_2(\mu\text{-}H)(\mu\text{-}C{=}C(H)C(H){=}CH_2)(dppm)_2]^+$ ($^3J_{HHvicinal}$ = 10.0 Hz, $^3J_{HHcis}$ = 10.0 Hz, $^3J_{HHtrans}$ = 16.5 Hz).[41] Finally, the $^{13}C\{^1H\}$ NMR spectra display a single carbonyl resonance for the symmetric complexes, while the nonsymmetric compounds each show two signals. The addition of $^{13}C_2H_4$ to **9** produced two additional signals in the $^{13}C\{^1H\}$ NMR spectrum: a doublet of triplets of triplets at δ 190.1 and a doublet at δ 130.4. Each displays mutual coupling of 64.9 Hz, while the downfield resonance, corresponding to the α-carbon, also displays coupling to both sets of chemically inequivalent ^{31}P nuclei. Although we were unsuccessful in obtaining X-ray structures of these vinylidene species, their spectroscopy clearly defines their formulations; in particular, the above $^{13}C\{^1H\}$ NMR data clearly identify the bridging vinylidene fragment by the coupling of the α-carbon to the four ^{31}P nuclei and the absence of ^{31}P coupling to the β-carbon and rule out the acetylene-bridged isomer, for which ^{31}P coupling to both carbons would be observed. The presence of two unique resonances also supports the proposed bridging-vinylidene moiety, with a bridging acetylene group expected to have only a single resonance due to symmetry. Furthermore, the spectroscopic parallels between compound **30** and the crystallographically determined dppm analogue[42] convincingly support this proposed structure.

Labeling the bridging hydride position in the starting material **9** with deuterium (**9-D**) proved to be challenging due to its propensity for H/D exchange with adventitious water remaining from earlier transformations. However, the addition of D_2O to **9** gave conversion to **9-D** and **9** in a 4:1 ratio after 24 h. Repeating the experiment shown in Scheme 8 with either 1,3-butadiene or vinyl fluoride and this **9-D**/**9** mix of isotopologues results in the original D/H ratio in the bridging hydride position of the products, with no deuterium incorporation into the terminal hydride sites, whereas the reaction with ethylene results in scrambling of deuterium across all three hydride sites, along with deuterium incorporation into the bridging vinylidene ligand. However, repeating the ethylene reaction in the presence of TMNO produces **26**, having the original D/H ratio in the bridging hydride position and no deuterium in the terminal sites or in the vinylidene positions. The scrambling in the absence of TMNO is presumably the result of reversible ethylene insertion into the Ir−D−Ir unit of **9-D**, whereas in the presence of TMNO, carbonyl loss and subsequent C−H bond activation are favored. The reaction of **9** with 1,1-dideuteroethylene ($D_2C{=}CH_2$) in the absence of TMNO again shows deuterium scrambling across all hydride and vinylidene positions of **26**, presumably a result of reversible olefin insertion, while in the presence of TMNO no deuterium incorporation into the bridging hydride position is observed, although the terminal hydride and vinylidene sites are partially deuterated, owing to competing C−H and C−D bond activation.

Attempts to bring about geminal C−H activation of the above α-olefins in reactions with $[MM'(CO)_3(depm)_2]$ (M = M′ = Ir (**2**), Rh (**12**); M = Rh, M′ = Ir (**20**)), formally M(0)/M′(0) complexes, gave no reaction over a range of conditions, even in the presence of TMNO. Similarly, neither of the rhodium hydride species $[RhIr(CO)_3(\mu\text{-}H)(depm)_2]^+$ (**25**) or $[Rh_2(CO)_3(\mu\text{-}H)(depm)_2]^+$ (**16**) reacts with these olefins, either in the presence or absence of TMNO. Furthermore, attempts to react the dppm species $[Ir_2(CO)_3(\mu\text{-}H)(dppm)_2]^+$ with the above α-olefins under identical conditions yielded only starting materials.

DISCUSSION

As noted in the Introduction of this paper, the advantage of depm over dmpm in this chemistry is that although both bridging groups contain small alkyl substituents that result in greater basicity over the more commonly used dppm ligand and better substrate access to the metals, the depm chemistry is much better behaved than that of dmpm, allowing rational modifications to the well-studied dppm system. The parallels between depm and dppm are clearly seen in the similarities between the series of Ir_2, Rh/Ir, and Rh_2 complexes involving both diphosphines, as described earlier. Nevertheless, substituting dppm by depm has had the targeted effect on the reactivity, and the depm complexes are much more reactive than the dppm analogues. One unfortunate consequence of this increased reactivity is the extreme sensitivity of the methyl dicarbonyl species $[MM'(CH_3)(CO)_2(depm)_2]^+$ (MM′ = Ir_2 (**7**) and RhIr (**23**)) to adventitious water, resulting in hydrolysis of these species to hydroxide-bridged products accompanied by methane elimination. Although none of the precautions taken in this paper to minimize water were taken in previous studies with dppm,[7,15,18,25] the analogous dppm complexes showed no adverse affects of water; in fact the dppm complexes were stable to the deliberate addition of water. In any future attempts to study the methyl dicarbonyl complexes of depm, other methods for reduction of the dihalide precursors, and the use of scrupulously dried TMNO for carbonyl removal will have to be employed, since the targeted methyl complexes are intolerant of water. Otherwise, other routes to these targets will have to be devised.

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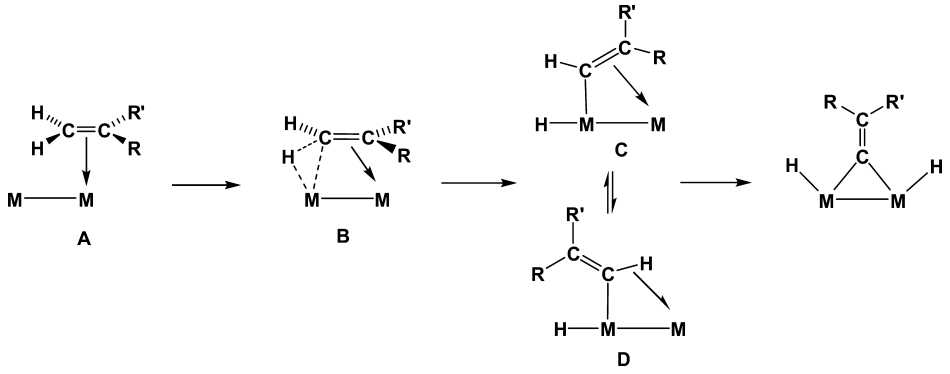
Chart 1



Addition of methyl triflate to the complexes $[MM'(CO)_3(depm)_2]$ (MM′ = Ir_2 (**2**), Rh_2 (**12**), RhIr (**20**)) led to reactivity that very much parallels that of the dppm analogues with some minor variations. As a consequence, both depm and dppm Ir_2 systems give rise to C−H activation of the added methyl group at the pair of adjacent Ir centers, consistent with the greater tendency of the third-row metal for oxidative addition. In the Rh/Ir complexes involving either dppm or depm, the methyl group binds to Ir, having the stronger metal−carbon bond, and although we had considered the possibility of C−H activation by Rh in the depm system, as a consequence of the greater basicity of this ligand, this is not observed. Similarly in the Rh_2 systems, both depm and dppm systems yield the acetyl product, the result of facile migratory insertion at this metal. However, here the greater basicity of depm over dppm is evident in two ways. First, although the methyl tricarbonyl product was never observed in the dppm chemistry, this precursor to migratory insertion is observed with depm, presumably owing to the lower electrophilicity of the carbonyls in this more electron-rich system, which inhibits migratory insertion. In addition, although a carbonyl could be removed from the acetyl-bridged dicarbonyl under reflux in the dppm system,[15] we were unable to remove a carbonyl in the depm analogue, consistent with the increased π-back-donation in this species (of course in the depm complex its instability does not allow refluxing, and only TMNO addition was attempted).

However, the most significant consequence of replacement of dppm by depm is seen in the reactivity of $[Ir_2(CO)_3(\mu\text{-}H)(depm)_2]^+$ with α-olefins. Although the analogous dppm complex is inert to α-olefins under the conditions investigated, even in the presence of TMNO, the depm complex reacts readily with a number of α-olefins to give the corresponding vinylidene-bridged trihydride products from activation of the pair of geminal C−H bonds on the olefin. Furthermore, in the presence of TMNO these activations are extremely facile, requiring only minutes for completion at ambient temperature. Few examples of this type of reactivity were previously known,[41,56−63] and this system represents (by far) the most reactive system to date, reacting under very mild conditions with a number of α-olefins.

Although C−H bond activation in unsaturated substrates by mononuclear species can proceed via prior π-coordination of the substrate, Bergman et al. have demonstrated that this is not always necessary.[46,48] In binuclear complexes a third mechanism that essentially combines these two mononuclear pathways is also possible, whereby π-coordination at one metal positions the olefin for σ-complex formation with the adjacent metal, leading to C−H bond cleavage,[74] as shown in structure **B** in Chart 1. In structure **D** of the resulting vinyl complex the second metal can be involved in an agostic interaction with the second olefinic C−H bond, leading to the second activation. Although the involvement of the second metal in the second activation step seems clear, initial coordination of the olefin at one metal (structure **A**) preceding C−H activation at the adjacent metal is more speculative.

We had hoped that the increased reactivity noted above in the "$Ir_2(depm)_2$" system over that of "$Ir_2(dppm)_2$" might also be reflected in the chemistry of the Rh-containing congeners, either in allowing C−H activation at this metal or at least in allowing the Rh-containing species to model key intermediates in the double C−H activation observed for the Ir_2 system. Even in the event that the Rh center was unreactive toward C−H activation, we anticipated that the mixed-metal species $[RhIr(CO)_3(\mu\text{-}H)(depm)_2]^+$ (particularly in the presence of TMNO) might still result in a single C−H activation at Ir, allowing us to obtain information about the first C−H activation product. Furthermore, we anticipated that although unreactive to C−H bond cleavage, the Rh_2 systems might yield an olefin adduct, giving information about the adduct prior to C−H activation. Unfortunately, none of this is observed with the least encumbered olefin, ethylene. Although this is surprising and disappointing, it does demonstrate the cooperative nature of these activations, whereby the proximity of the unreactive Rh also deactivates the Ir center to oxidative addition. This lack of reactivity may in fact support the "prior coordination" model, whereby C−H activation at Ir requires prior coordination at Rh, which is apparently not effective enough in this role.

The steric differences between dppm and depm are evident in the range of olefins activated by the depm system, in which even the disubstituted isobutylene and the bulky styrene react readily in the presence of TMNO. Finally, this study reaffirms the pronounced synergic effect that two metal centers can have in giving rise to reactivity that is not commonly observed in single-metal complexes. This example of *geminal* C−H activation of olefins represents one of the few of its kind[41,56−61,63,75,76] and appears to be the most reactive, requiring only TMNO addition to initiate facile activation and being reactive for a range of α-olefins, even those having reasonably bulky substituents.

EXPERIMENTAL SECTION

General Comments. All solvents were dried (using appropriate drying agents), distilled before use, and stored under dinitrogen. Deuterated solvents used for NMR experiments were freeze−pump−thaw degassed (three cycles) and stored under nitrogen or argon over molecular sieves. Reactions were carried out under argon using standard

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Schlenk techniques, and compounds that were obtained as solids were purified by recrystallization. Prepurified argon and nitrogen were purchased from Praxair, and carbon-13-enriched CO (99%) was supplied by Isotec Inc. All purchased gases were used as received. Bis(diethylphosphino)methane,[77,78] $[IrCl(COD)]_2$,[79] $[IrCl(CO)(PPh_3)_2]$,[80] $[RhCl(COD)]_2$,[81] $[RhCl(CO)_2]_2$[82] and $[H(Et_2O)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ ($HBAr^F_4$)[83] were all prepared as previously described. Trimethylamine-*N*-oxide dihydrate was dried by azeotropic distillation as described in the literature.[72] All other reagents were obtained from Aldrich and were used as received (unless otherwise stated).

Proton NMR spectra were recorded on Varian Unity 400 or 500 spectrometers or on a Bruker AM400 spectrometer. Carbon-13 NMR spectra were recorded on Varian Unity 400 or 500 or Bruker AM300 spectrometers. Phosphorus-31 and fluorine-19 NMR spectra were recorded on Varian Unity 400 or 500 or Bruker AM400 spectrometers. Two-dimensional NMR experiments (COSY, NOESY, and $^1H-^{13}C$ HMQC) were obtained on Varian Unity 400 or 500 spectrometers.

a. Preparation of Compounds. *trans-$[Ir_2Cl_2(CO)_2(depm)_2]$ (**1**).* To a solution of $[Ir(Cl)(COD)]_2$ (200 mg, 0.30 mmol) in 25 mL of dichloromethane was quickly added, via cannula, 100 μL (0.60 mmol) of bis(diethylphosphino)methane (depm) in 5 mL of dichloromethane, causing the solution to change from orange-red to yellow-orange. The solution was stirred for 15 min and then placed under a slow CO purge for 5 min. The CO was replaced by an argon purge, and the solution was set to reflux for 0.5 h. Reducing the solution to dryness left an oily orange residue, which was redissolved into 25 mL of THF. This solution was set to reflux again for 1.5 h, with a continuing argon purge, resulting in a color change to dark red-purple. The solution was reduced to ~5 mL, and Et_2O (40 mL) was added to precipitate a deep red-purple solid, which was isolated, washed twice with Et_2O (2 × 10 mL), and dried to yield 150 mg (60%) of **1**. HRMS *m*/*z* calcd for $Ir_2P_4O_2C_{20}H_{44}Cl$: 860.3804. Found: 860.3805. ^1H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 2.52 (quin, 4H, depm). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 27 °C): δ 168.3 (s, 2C, Ir−*C*O). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ 8.3 (s, 4P). Anal. Calcd (%) for $Ir_2P_4Cl_2O_2C_{20}H_{44}$ (895.80): C 26.82, H 4.95. Found: C 26.87, H, 5.02.

*b. $[Ir_2(CO)_3(depm)_2]$ (**2**).* **Method i.** **1** (100 mg, 0.090 mmol) was dissolved in 10 mL of THF, giving a turbid, deep scarlet-purple solution. This was placed under an atmosphere of CO, resulting in a series of color changes, through red, and finally to clear orange. The addition of 2.5 mL of 1 M KOH/H_2O yielded a dark orange solution, which was stirred (closed under CO) at room temperature for 0.5 h. The solution was stripped to dryness, extracted with 3 × 10 mL of benzene, and filtered through Celite. A further 50 mL of benzene was added, and the resulting solution was distilled for 2 h to remove residual water by azeotropic distillation, after which time it could be carried forward as such or stripped again to dryness to give a dark brown-orange residue. (98%). **Method ii.** Compound **1** (54 mg, 0.049 mmol) was dissolved in 10 mL of acetone. Excess $NaBH_4$ (0.200 mmol) was added directly to the solution, which was allowed to stir for 1 h. The solvent was removed, and the product redissolved in 10 mL of benzene. Filtration through Celite gave a clear orange-brown solution, which was purged with CO for 5 min followed by argon for 10 min. The solvent was reduced to dryness, affording the complex as a viscous orange-brown oil. However, samples obtained via this method were always less pure, spectroscopically, and were generally obtained in poorer yields compared to the first method. **Method iii.** Compound **1** (30 mg, 0.027 mmol) was dissolved in 20 mL of acetonitrile. Excess zinc (0.500 mmol) was added directly to the solution, producing a gray slurry, which was allowed to stir for 1 h under a CO purge. The mixture was filtered through Celite, and the clear orange solution was reduced to dryness under vacuum. The residue was redissolved in CD_2Cl_2, and the purity of the product was verified by NMR spectroscopy. This method also resulted in a product that is less pure, spectroscopically, and generally in poorer yields compared to the first method. Due to compound **2** not being isolated as a solid, an elemental analysis could not be obtained; however $^{31}P\{^1H\}$ and ^1H NMR spectra showing the purity can be found in the Supporting Information. ^1H NMR (400 MHz, C_6D_6, 27 °C): δ 2.67 (quin., 4H, depm). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 27 °C): δ 185.6 (s, 3C, Ir−CO). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 27 °C): δ −11.0 (s, 4P). Low-temperature data: $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, −80 °C): δ 193.8 (bs, 1C, Ir−CO), 189.3 (bs, 1C, Ir−*C*O), 179.8 (bs, 1C, Ir−CO). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, −80 °C): δ −8.9 (b, 2P), −28.0 (b, 2P).

*c. $[Ir_2(CO)_4(depm)_2]$ (**3**).* Compound **2** (50 mg, 0.058 mmol) was dissolved in 10 mL of benzene and stirred under a dynamic atmosphere of CO for 0.5 h, causing the color to change from orange to bright yellow. The solvent was removed, giving an oily, dark yellow-orange residue containing a mixture of **2** and **3** in variable proportions, as gauged by NMR spectroscopy, revealing the susceptibility of **3** to CO loss. The lability of this carbonyl has limited the characterization to NMR spectroscopy. ^1H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 2.71 (quin., 4H, depm). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 27 °C): δ 189.8 (bs, 4C, Ir−CO). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ −31.4 (bs, 4P). Low-temperature data: $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, −80 °C): δ 195.2 (bs, 1C, Ir−CO), 194.2 (bs, 1C, Ir−CO), 191.8 (bs, 1C, Ir−CO), 181.2 (bs, 1C, Ir−CO). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, −80 °C): δ −19.6 (bt, 2P, $^2J_{PP}$ = 53.7 Hz), −41.1 (bt, 2P, $^2J_{PP}$ = 53.7 Hz).

*d. $[Ir_2(H)(CO)_3(\mu\text{-}CH_2)(depm)_2][CF_3SO_3]$ (**4**).* Neat methyl trifluoromethanesulphonate (MeOTf) (11 μL, 1.00 mmol) was slowly added dropwise to a solution of **2** (75 mg, 0.088 mmol) in 15 mL of benzene. The resulting turbid, dark orange mixture was stirred for 1 h, whereupon it was reduced to ~2 mL, followed by the dropwise addition of pentane (10 mL) to precipitate a yellow-orange solid. This solid was further washed with pentane (2 × 10 mL) and dried, giving 80 mg of a pale orange powder (89% yield). HRMS *m*/*z* calcd for $Ir_2P_4O_3C_{22}H_{47}$: 867.9729. Found: 867.9732. ^1H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 3.95 (bs, 2H, Ir−C*H*$_2$−Ir), 2.75 (m, 4H, depm), −12.42 (t, 1H, $^2J_{HP}$ = 4.3 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 27 °C): δ 177.2 (s, 3C, Ir−CO), 44.2 (m, 1C, Ir−*C*H$_2$−Ir). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ −8.9 (bm, 2P), −19.5 (bm, 2P). Low-temperature data: $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, −80 °C): δ 180.2 (bs, 1C, Ir−CO), 178.7 (bs, 1C, Ir−CO), 166.3 (bs, 1C, Ir−CO), 45.3 (m, 1C, Ir−*C*H$_2$−Ir). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, −80 °C): δ −8.9 (t, 2P, $^2J_{PP}$ = 32.4 Hz), −19.5 (t, 2P, $^2J_{PP}$ = 32.4 Hz). Anal. Calcd (%) for $Ir_2SP_4F_3O_6C_{23}H_{47}$ (1017.00): C 27.16, H 4.66. Found: C 26.82, H, 4.55.

*e. $[Ir_2(CH_3)(CO)_4(depm)_2][CF_3SO_3]$ (**5**) and $[Ir_2(CO)_4(C(O)CH_3)(depm)_2][CF_3SO_3]$ (**6**).* Excess carbon monoxide (3 mL, 0.131 mmol) was transferred via gastight syringe onto a solution of 50 mg (0.037 mmol) of compound **3** in 0.7 mL of CD_2Cl_2. Under these conditions both complexes were identified and characterized through NMR spectroscopy. However, we were unable to isolate either compound due to the regeneration of **3** upon the removal of the CO atmosphere. Compound **5**: ^1H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 2.75 (quin., 4H, depm), 0.68 (t, $^3J_{HP}$ = 5.4 Hz, Ir−C*H*$_3$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 27 °C): δ 191.1 (t, 2C, $^2J_{CP}$ = 11.2 Hz, Ir−CO), 187.4 (t, 2C, $^2J_{CP}$ = 12.9 Hz, Ir−CO), −39.9 (t, 1C, $^2J_{CP}$ = 5.8 Hz, Ir−*C*H$_3$). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ −14.9 (m, 2P), −18.6 (m, 2P). Compound **6**: ^1H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 3.35 (quin., 4H, depm), 2.60 (s, 3H, Ir−C(O)C*H*$_3$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 27 °C): δ 221.2 (t, 1C, $^2J_{CP}$ = 6.3 Hz, Ir−C(O)CH$_3$), 195.0 (t, 2C, $^2J_{CP}$ = 10.3 Hz, Ir−CO), 187.8 (t, 2C, $^2J_{CP}$ = 12.9 Hz, Ir−CO), 53.2 (m, 1C, Ir−C(O)CH$_3$). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ −15.7 (m, 2P), −20.9 (m, 2P).

*f. $[Ir_2(CH_3)(CO)_2(depm)_2][CF_3SO_3]$ (**7**).* To a solution of compound **3** (55 mg, 0.63 mmol) in 0.5 mL of CD_2Cl_2 was added, dropwise, trimethylamine-*N*-oxide (4 mg, 0.53 mmol) in 0.3 mL of CD_2Cl_2. The resulting solution was mixed, and the reaction was monitored via NMR. The product was found to be extremely moisture-sensitive and was susceptible to further reaction in solution, at ambient temperature, resulting in the formation compound **8** after 30 min. Therefore, compound **7** was characterized via solution spectroscopy, through comparison of its spectral parameters to those of its dppm analogue $[Ir_2(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$.[18] ^1H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 2.80

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(m, 2H, depm), 2.30 (dm, 2H, depm), 0.57 (quin., 3H, $^3J_{HP}$ = 4.4 Hz, Ir−CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 27 °C): δ 174.2 (bs, 2C, Ir−CO), 19.5 (bs, 1C, Ir−CH_3). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ 23.2 (s, 4P). Low-temperature data: $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, −80 °C): δ 179.9 (bs, 1C, Ir−CO), 168.3 (bs, 1C, Ir−CO). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, −80 °C): δ 26.1 (b, 2P), 19.8 (b, 2P).

*g. [Ir$_2$(CO)$_2$(μ-OH)(depm)$_2$][CF$_3$SO$_3$] (**8**).* To a solution of compound **7** (50 mg, 0.050 mmol), generated *in situ* at −20 °C in 5 mL of dichloromethane, was added 5 μL (0.277 mmol) of water, and the resultant mixture stirred while warming to room temperature over the course of 0.5 h. The solvent was removed, and the product recrystallized from dichloromethane and pentane, affording a bright yellow powder (70% yield). ^1H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 3.60 (bs, 1H, Ir−O*H*−Ir), 2.85 (m, 4H, depm). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 27 °C): δ 184.7 (s, 2C, Ir−CO). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ 16.5 (s, 4P). Anal. Calcd (%) for $Ir_2SP_4F_3O_6C_{21}H_{45}$ (990.97): C 25.45, H 4.58. Found: C 25.65, H, 4.59.

*h. [Ir$_2$(CO)$_3$(μ-H)(depm)$_2$][X] (X = OTf (**9-OTf**), BAr$^F{}_4$ (**9-BAr$^F{}_4$**)).* **9-OTf: Method i.** To a solution of compound **2** (100 mg, 0.118 mmol) in 25 mL of CH_2Cl_2 was slowly added neat HOTf (11 μL, 0.124 mmol) via microsyringe. The solution was stirred for 1 h, whereupon it was reduced to dryness. The solid was recrystallized from THF and pentane to afford a dark brown solid (74% yield). **Method ii.** To a solution of **8** was added a CO purge at a rate of 1 cm^3/s. After 15 min, the CO purge was removed and an argon purge was added for 15 min to remove excess carbon monoxide, resulting in **9-OTf**. **9-BAr$^F{}_4$:** To a solution of **2** (125 mg, 0.147 mmol) in 30 mL of CH_2Cl_2 was slowly added dropwise (170 mg, 0.170 mmol) $[H(Et_2O)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ in 10 mL of CH_2Cl_2. The resulting mixture was stirred for 1 h, whereupon it was reduced to dryness. The resulting residue was redissolved in ∼5 mL of diethyl ether, and 10 mL of pentane was added to precipitate a dark red solid, which was isolated, further washed with pentane (2 × 10 mL), and dried, giving 115 mg of **9** (78% yield). ^1H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 2.45 (quin., 4H, depm), −10.40 (quin., 1H, $^2J_{HP}$ = 9.8 Hz, Ir−*H*−Ir). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 27 °C): δ 183.7 (s, 3C, Ir−CO). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ 14.3 (s, 4P). Low-temperature data: ^1H NMR (400 MHz, CD_2Cl_2, −80 °C): δ 2.45 (b, 4H, depm), −10.40 (b, 1H, Ir−*H*−Ir). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, −80 °C): δ 185.3 (b, 1C, Ir−CO), 183.3 (b, 2C, Ir−CO). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, −80 °C): δ 14.4 (b, 4P). Anal. Calcd (%) for $Ir_2SP_4F_3O_6C_{22}H_{45}$ (**9-OTf**, 1002.98): C 26.35, H 4.52. Found: C 26.45, H, 4.50.

*i. [Ir$_2$(H)(CO)$_4$(depm)$_2$][BAr$^F{}_4$] (**10**).* A solution of **9** dissolved in 0.7 mL of CD_2Cl_2 was placed under an atmosphere of CO, resulting in the generation of **10**, as determined spectroscopically. This species was characterized only in solution, since removal of the CO atmosphere resulted in quantitative conversion to **9**. ^1H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 3.40 (m, 4H, depm), −8.80 (t, $^2J_{HP}$ = 14.4 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 27 °C): δ 192.3 (t, 2C, $^2J_{CP}$ = 11.2 Hz, Ir−CO), 186.9 (t, 2C, $^2J_{CP}$ = 12.9 Hz, Ir−CO). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ −9.5 (t, 2P, $^2J_{PP}$ = 29.8 Hz), −11.2 (t, 2P, $^2J_{PP}$ = 29.8 Hz).

*j. trans-[Rh$_2$Cl$_2$(CO)$_2$(depm)$_2$] (**11**).* A solution of $[Rh_2Cl_2(COD)_2]$ (110 mg, 0.223 mmol) in 20 mL of acetone was placed under an atmosphere of CO and stirred for 10 min. To this solution was added dropwise, over a 5 min period, 100 μL (0.441 mmol) of depm in 10 mL of acetone, causing the color to change from yellow to orange. The solution was then refluxed for 0.5 h, whereupon it was cooled to room temperature and reduced to dryness. The residue was redissolved into 5 mL of THF, and Et_2O (20 mL) was added to precipitate an orange solid, which was further washed with Et_2O (2 × 5 mL) and dried, yielding 85 mg (53% yield) of spectroscopically pure **11**. HRMS *m*/*z* calcd for $Rh_2P_4O_2C_{20}H_{44}Cl$: 681.0088. Found: 681.0090. ^1H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 2.37 (quin., 4H, depm). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 27 °C): δ 189.1 (d, 2C, $^1J_{CRh}$ = 74.8 Hz, Rh−CO). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ 17.9 (dm, 4P, $^1J_{RhP}$ = 117.2 Hz). Anal. Calcd (%) for $Rh_2P_4Cl_2O_2C_{20}H_{44}$ (717.17): C 33.49, H 6.18. Found: C 33.22, H, 5.85.

*k. [Rh$_2$(CO)$_3$(depm)$_2$] (**12**).* Compound **11** (65 mg, 0.091 mmol) was dissolved in 20 mL of THF and stirred under a static atmosphere of CO. Two milliliters of aqueous 1 M KOH was transferred dropwise, via a syringe, onto the stirred solution, and the resulting mixture left to stir for 1.5 h. The solvent was removed to give an oily brown residue, which was then extracted with benzene (3 × 10 mL). Filtration through Celite gave a clear orange-brown solution, which was reduced to dryness to afforded 55 mg of the spectroscopically pure **12** as a viscous orange-brown oil (90% yield). ^1H NMR (400 MHz, C_6D_6, 27 °C): δ 2.17 (quin., 4H, depm). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 27 °C): δ 198.8 (bs, 3C, Rh−CO). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 27 °C): δ 15.1 (d, 4P, $^1J_{RhP}$ = 137.7 Hz). Low-temperature data: $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, −110 °C): δ 209.1 (bd, 1C, $^1J_{RhC}$ = 77.0 Hz, Rh−CO), 206.8 (bd, 1C, $^1J_{RhC}$ = 71.2 Hz, Rh−CO), 183.4 (bd, 1C, $^1J_{RhC}$ = 67.9 Hz, Rh−CO). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, −110 °C): δ 22.5 (bd, 2P, $^1J_{RhP}$ = 117.1 Hz), 8.5 (bd, 2P, $^1J_{RhP}$ = 152.6 Hz).

*l. [Rh$_2$(CO)$_4$(depm)$_2$] (**13**).* Compound **12** (50 mg, 0.072 mmol) was dissolved in 7 mL of CD_2Cl_2 and placed under an atmosphere of CO, causing the color of the solution to change from orange to yellow. The conversion of **12** to **13** was determined to be quantitative via NMR spectroscopy. However, removal of the CO atmosphere resulted in complete reversion back to **12**. Therefore, **13** has only been characterized *in situ* via NMR spectroscopy. ^1H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 2.60 (bm, 4H, depm). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 27 °C): δ 206.7 (bs, 4C, Rh−CO). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ 12.4 (bd, $^1J_{RhP}$ = 133.2 Hz, 4P). Low-temperature data: $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, −80 °C): δ 214.3 (dt, 1C, $^1J_{RhP}$ = 90.2 Hz, $^2J_{CP}$ = 29.7 Hz, Rh−CO), 204.1 (bs, 3C, Rh−CO). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, −80 °C): δ 24.3 (m, 2P), −1.3 (m, 2P).

*m. [Rh$_2$(CH$_3$)(CO)$_3$(depm)$_2$][CF$_3$SO$_3$] (**14**) and [Rh$_2$(CO)$_2$(μ-κ^1:κ^1-C(CH$_3$)O)- (depm)$_2$][CF$_3$SO$_3$] (**14a**).* To a solution of **12** (35 mg, 0.052 mmol) in 0.8 mL of CD_2Cl_2, cooled in a dry ice/acetone ice bath to −80 °C, was slowly added 6 μL (0.054 mmol) of neat methyl trifluoromethanesulphonate (MeOTf). The reaction was then monitored via low-temperature NMR at −40 °C, showing the formation of compound **14**. Upon warming to −20 °C, **14** slowly converted to compound **14a** after 1 h. Warming to above 0 °C resulted in the decomposition of **14** to **15**, along with numerous unidentified products. Compound **14**: ^1H NMR (400 MHz, C_3D_6O, −80 °C): δ 2.35 (quin., 4H, depm), 0.63 (bm, 3H, Rh−C*H*$_3$). $^{13}C\{^1H\}$ NMR (101 MHz, C_3D_6O, −80 °C): δ 214.3 (bt, 2C, $^1J_{CRh}$ = 32.7 Hz, Rh−CO), 199.3 (bd, 1C, $^1J_{CRh}$ = 74.9 Hz, Rh−CO), −0.7 (bm, 1C, Rh−CH_3). $^{31}P\{^1H\}$ NMR (162 MHz, C_3D_6O, −80 °C): δ 35.6 (bm, 4P). Compound **14a**: ^1H NMR (400 MHz, C_3D_6O, −20 °C): δ 2.55 (quin., 4H, depm), 2.42 (s, 3H, Rh−C(C*H*$_3$)O). $^{13}C\{^1H\}$ NMR (101 MHz, C_3D_6O, −20 °C): δ 319.9 (bm, 1C, Rh−C(CH_3)O), 199.8 (m, 1C, Rh−CO), 194.1 (d, 1C, $^1J_{RhC}$ = 76.3 Hz), 44.2 (s, 1C, Rh−C(CH_3)O). $^{31}P\{^1H\}$ NMR (162 MHz, C_3D_6O, −20 °C): δ 22.5 (bm, 2P), 17.2 (bm, 2P).

*n. Addition of TMNO to **14**.* To a 0.5 mL solution of **14** (32 mg, 0.038 mmol) in CD_2Cl_2, cooled to −40 °C, was added trimethylamine-*N*-oxide (3 mg, 0.040 mmol) dissolved in 0.3 mL of CD_2Cl_2. The mixture was monitored by variable-temperature NMR. Below −20 °C, no observable reaction was observed. Warming the solution to −10 °C resulted in the formation of **14a** as described above, but there was no indication of reaction with TMNO. Warming the mixture above 0 °C resulted in decomposition to compound **15** along with various unidentified products.

*o. [Rh$_2$(CO)$_2$(μ-OH)(depm)$_2$][CF$_3$SO$_3$] (**15**).* To a solution of **14** (34 mg, 0.041 mmol) in 0.8 mL of d_6-acetone cooled to −20 °C was added 5 μL (0.277 mmol) of water, causing the solution to lighten in color. Maintaining this temperature for 0.5 h, while stirring, caused the color to become bright yellow. The solvent was subsequently removed, and the residue extracted three times into 5 mL of ether. The extraction solvent was removed, and the product was isolated as a yellow, oily material. ^1H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 2.65 (quin., 4H, depm). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 27 °C): δ 192.3 (dt, 2C, $^1J_{RhC}$ = 70.3 Hz, $^2J_{CP}$ = 15.8 Hz, Rh−CO). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ 21.7 (dm, 4P, $^1J_{RhP}$ = 120.3 Hz).

*p. [$Rh_2(CO)_3(\mu$-H)(depm)$_2$][X] (X = OTf (**16-OTf**), $BAr^F{}_4$ (**16-$BAr^F{}_4$**)).* **16-OTf: Method i.** To a solution of compound **12** (140 mg, 0.207 mmol) in 30 mL of CH_2Cl_2 was slowly added neat triflic acid (18 μL, 0.203 mmol) via microsyringe. The solution was stirred for 1 h, whereupon it was reduced to dryness. The solid was recrystallized from THF and pentane to afford a dark brown solid (81% yield). **Method ii.** To a solution of **15** was added a CO purge at a rate of 1 cm^3/s. After 15 min, the CO purge was replaced by a brief argon purge to remove excess carbon monoxide. **16-$BAr^F{}_4$:** To a solution of **12** (100 mg, 0.148 mmol) in 30 mL of CH_2Cl_2 was slowly added dropwise 150 mg (0.150 mmol) of $[H(Et_2O)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$. The resulting mixture was stirred for 1 h, whereupon it was reduced to dryness and redissolved in ∼2 mL of ether. Pentane (10 mL) was added to precipitate a dark orange-red solid, which was isolated and further washed with pentane (2 × 10 mL), then dried, giving 155 mg of spectroscopically pure **16** (75% yield). HRMS *m*/*z* calcd for $Rh_2P_4O_2C_{20}H_{45}$ [M^+ − CO]: 647.0473. Found: 647.0475. ^{1}H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 2.23 (quin., 4H, depm), −10.34 (m, 1H, $^1J_{RhH}$ = 24.3 Hz, $^2J_{HP}$ = 12.2 Hz, Rh−*H*−Rh). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 27 °C): δ 194.3 (bm, 3C, Rh−CO). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ 35.2 (dm, 4P, $^1J_{RhP}$ = 97.4 Hz). Low-temperature data: ^{1}H NMR (400 MHz, CD_2Cl_2, −80 °C): δ 2.25 (b, 4H, depm), −10.39 (b, 1H, Rh−*H*−Rh). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, −80 °C): δ 195.1 (b, 1C, Rh−CO), 194.0 (b, 2C, Rh−CO). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ 35.2 (b, 4P). Anal. Calcd (%) for $Rh_2P_4F_{24}O_3C_{53}H_{37}B$ (1538.50): C 41.38, H 3.73. Found: C 41.17, H, 3.95.

*q. [$Rh_2(CO)_3$(depm)$_2$][CF_3SO_3]$_2$ (**17**).* To a solution of **12** (95 mg, 0.089 mmol), in 10 mL of acetone at 0 °C, was added a large excess of neat triflic acid (85 μL, 0.960 mmol), and the solution stirred for 3 h while warming to ambient temperature. The solvent was subsequently removed, and the isolated orange solid was recrystallized from acetone and pentane, affording a yellow residue. ^{1}H NMR (400 MHz, C_3D_6O, 27 °C): δ 2.70 (quin., 4H, depm). $^{13}C\{^1H\}$ NMR (101 MHz, C_3D_6O, 27 °C): δ 188.6 (s, 3C, Rh−CO). $^{31}P\{^1H\}$ NMR (162 MHz, C_3D_6O, 27 °C): δ 29.0 (bd, 4P, $^1J_{RhP}$ = 93.1 Hz).

*r. [$Rh_2(CO)_5$(depm)$_2$][CF_3SO_3]$_2$ (**18**).* To an NMR-scale solution (50 mg, 0.037 mmol) of **17** in 0.7 mL of d_6-acetone was added excess CO, producing a clear yellow solution. The sample was subsequently investigated via multinuclear NMR spectroscopy. X-ray quality crystals of **18** were obtained by diffusion of diethyl ether into a CH_2Cl_2 solution of **18**, under a CO atmosphere; however removal of the CO atmosphere resulted in reversion to starting material. ^{1}H NMR (400 MHz, C_3D_6O, 27 °C): δ 3.00 (quin., 4H, depm). $^{13}C\{^1H\}$ NMR (101 MHz, C_3D_6O, 27 °C): δ 191.7 (b, 5C, Rh−CO). $^{31}P\{^1H\}$ NMR (162 MHz, C_3D_6O, 27 °C): δ 32.0 (bs, 4P).

*s. trans-[IrRhCl_2(CO)$_2$(depm)$_2$] (**19**).* To a solution of Vaska's complex, $[Ir(Cl)(CO)(PPh_3)_2]$ (250 mg, 0.320 mmol), in 15 mL of THF was added 150 μL (0.66 mmol) of bis(diethylphosphino)-methane, which caused the solution to change from yellow to red-purple. Leaving the solution to stir for 1 h resulted in a cloudy yellow slurry, signifying the formation of $[IrCl(CO)(depm)_2]$. The solvent was removed, and the faint yellow solid was redissolved in 10 mL of CH_2Cl_2, while in a separate flask, $[Rh(Cl)(CO)_2]_2$ (75 mg, 0.197 mmol) was dissolved in 7 mL of CH_2Cl_2. The $[IrCl(CO)$-$(depm)_2]$ solution was then added to the $[Rh(Cl)(CO)_2]_2$ solution, and the resulting orange mixture was stirred for 2 h. The solvent was removed, and the residue redissolved in 7 mL of THF, followed by the addition of pentane (30 mL) to precipitate a dark orange solid. The solid was further washed with pentane (2 × 10 mL) and dried, giving 200 mg (67% yield). HRMS *m*/*z* calcd for $IrRhP_4O_2C_{20}H_{44}Cl$: 771.0659. Found: 771.0658. ^{1}H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 2.42 (quin., 4H, depm). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 27 °C): δ 190.0 (bs, 1C, Rh−CO), 171.8 (s, 1C, Ir−CO). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ 18.0 (dt, 2P, $^1J_{RhP}$ = 118.3 Hz, $^2J_{PP}$ = 63.9 Hz), 9.6 (t, 2P, $^2J_{PP}$ = 63.9 Hz), Anal. Calcd (%) for $IrRhP_4Cl_2O_2C_{20}H_{44}$ (806.49): C 29.79, H 5.50. Found: C 29.72, H, 5.34.

*t. [IrRh$(CO)_3$(depm)$_2$] (**20**).* **Method i.** Compound **19** (275 mg, 0.341 mmol) was dissolved in 20 mL of THF and stirred under a dynamic atmosphere of CO. Eight milliliters of aqueous 1 M KOH was transferred dropwise, via syringe, to the stirred solution, and the resulting mixture was stirred for 1.5 h. The solvent was removed under vacuum, and the product extracted into 3 × 20 mL of benzene. Filtration through Celite gave a clear orange-brown solution, which was purged with CO for 5 min followed by argon for 10 min. The solvent was reduced to dryness, affording the complex as a spectroscopically pure, viscous orange-brown oil. **Method ii.** Compound **19** (37 mg, 0.046 mmol) was dissolved in 10 mL of acetone. Excess $NaBH_4$ (0.200 mmol) was added directly to the solution, which was stirred for 1 h. The solvent was removed, and the product redissolved in 10 mL of benzene or THF. Filtration through Celite gave a clear orange-brown solution, which was purged with CO for 5 min followed by argon for 10 min. The solvent was reduced to dryness, affording the complex as a viscous orange-brown oil. Samples obtained via this method were always less pure, spectroscopically, and were generally obtained in poorer yields compared to the first method (76% yield). HRMS *m*/*z* calcd for $IrRhP_4O_2C_{20}H_{45}$ [M + H^+ − CO]: 737.1054. Found: 737.1049. ^{1}H NMR (400 MHz, C_6D_6, 27 °C): δ 2.67 (quin., 4H, depm). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 27 °C): δ 189.0 (bs, 2C), 185.7 (d, 1C, $^1J_{RhC}$ = 70.1 Hz, Rh−CO). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 27 °C): δ 17.1 (dt, 2P, $^1J_{RhP}$ = 124.0 Hz, $^2J_{PP}$ = 64.3 Hz), −28.8 (t, 2P, $^2J_{PP}$ = 64.3 Hz).

*u. [IrRh$(CO)_4$(depm)$_2$] (**21**).* Compound **20** (275 mg, 0.341 mmol) was dissolved in 20 mL of CH_2Cl_2 and stirred under a dynamic atmosphere of CO for 1 h. NMR spectroscopy confirmed the formation of **21**; however subsequent removal of the CO atmosphere resulted in the loss of a CO, with quantitative reversion back to the starting compound. Thus, the characterization of **21** has been limited to solution $^{31}P\{^1H\}$ and ^{1}H NMR spectroscopy. ^{1}H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 2.79 (bs, 4H, depm). $^{13}C\{^1H\}$ NMR (101 MHz. CD_2Cl_2, 27 °C): δ 197.5 (b, 4C). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ −0.6 (b, 2P), −17.2 (b, 2P). Low-temperature data: ^{1}H NMR (400 MHz, CD_2Cl_2, −80 °C): δ 3.15 (bs, 4H, depm). $^{13}C\{^1H\}$ NMR (101 MHz. CD_2Cl_2, −80 °C): δ 210.2 (dt, 1C, $^1J_{CRh}$ = 73.5 Hz, $^2J_{CP}$ = 48.6 Hz), 200.6 (dt, 1C, $^1J_{CRh}$ = 72.4 Hz, $^2J_{CP}$ = 10.5 Hz), 194.6 (m, 1C, $^2J_{CC}$ = 10.5 Hz, $^2J_{CP}$ = 13.7 Hz), 192.7 (m, 1C, $^2J_{CC}$ = 10.5 Hz, $^2J_{CP}$ = 11.1 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, −80 °C): δ −2.4 (m, 2P, $^1J_{PRh}$ = 140.1 Hz, $^2J_{PP}$ = 57.5 Hz), −14.5 (t, 2P, $^2J_{PP}$ = 57.5 Hz).

*v. [IrRh$(CH_3)(CO)_3$(depm)$_2$][CF_3SO_3] (**22**).* To a solution of **20** (75 mg, 0.098 mmol) in 10 mL of benzene was slowly added dropwise, over a 5 min period, neat MeOTf (11 μL, 0.098 mmol). The resulting mixture was stirred for 1 h, whereupon it was reduced to dryness and redissolved in a minimum volume of THF (∼2 mL). Pentane (10 mL) was added to precipitate a dark yellow-brown solid, which was isolated and further washed with pentane (2 × 10 mL), then dried under vacuum. ^{1}H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 3.00 (m, 4H, depm), 0.20 (t, $^3J_{HP}$ = 6.2 Hz, Ir−C*H*$_3$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 27 °C): δ 185.4 (s, 2C, Ir−CO), 184.2 (dt, $^1J_{RhC}$ = 71.1 Hz, $^2J_{CP}$ = 22.3 Hz, Rh−CO), −34.8 (s, 1C, Ir−*C*H$_3$). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ 33.0 (dt, 2P, $^1J_{RhP}$ = 110.3 Hz, $^2J_{PP}$ = 41.8 Hz), −11.0 (t, 2P, $^2J_{PP}$ = 39.5 Hz). Anal. Calcd (%) for $IrRhSP_4F_3O_6C_{23}H_{47}$ (927.69): C 29.78, H 5.11. Found: C 29.64, H, 5.15.

*w. [IrRh$(CH_3)(CO)_2$(depm)$_2$][CF_3SO_3] (**23**).* To a solution of **21** (45 mg, 0.049 mmol) in 0.8 mL of CD_2Cl_2 was slowly added 100 μL of 0.5 M TMNO in CD_2Cl_2. The reaction was monitored by NMR, which verified the formation of compound **23** after 10 min. Much like its homobinuclear congeners, this product was unstable and extremely moisture-sensitive; subsequent recrystallization attempts from various dried solvents resulted only in decomposition or hydrolysis products; thus **23** has been characterized via NMR spectroscopy. ^{1}H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 2.70 (m, 2H, depm), 2.40 (m, 2H, depm), 0.58 (t, 3H, $^3J_{HP}$ = 9.2 Hz, Ir−C*H*$_3$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 27 °C): δ 183.2 (t, 1C, $^2J_{CP}$ = 7.2 Hz, Ir−CO), 177.4 (dt, $^2J_{RhC}$ = 73.1 Hz, $^2J_{CP}$ = 16.7 Hz, Rh−CO), 9.9 (s, 1C, Ir−*C*H$_3$). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ 22.5 (dt, $^1J_{RhP}$ = 107.1 Hz, $^2J_{PP}$ = 47.2 Hz, 2P), 19.8 (t, $^2J_{PP}$ = 47.2 Hz, 2P).

*x. [IrRh$(CO)_2(\mu$-OH)(depm)$_2$][CF_3SO_3] (**24**).* To a solution of **23** (90 mg, 0.097 mmol), prepared *in situ* in 7 mL of CH_2Cl_2, was added water (5 μL, 0.277 mmol). The solution was stirred at room tem-

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perature for 0.5 h, during which time the color lightened to a pale orange. The solvent was removed, and the product recrystallized from dichloromethane and pentane, affording an orange, oily material. ^{1}H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 3.33 (s, 1H, Ir−O*H*−Rh), 2.70 (m, 2H, depm), 2.05 (m, 2H, depm). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 27 °C): δ 191.2 (dt, 1C, $^1J_{RhC}$ = 72.4 Hz, $^2J_{CP}$ = 16.6 Hz, Rh−*C*O), 174.9 (t, $^2J_{CP}$ = 11.2 Hz, Ir−*C*O). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ 20.6 (dm, 2P, $^1J_{RhP}$ = 116.6 Hz), 17.2 (t, 2P, $^2J_{PP}$ = 14.3 Hz).

y. [IrRh(CO)$_3$(μ-H)(depm)$_2$][X] (X = OTf (25-OTf), BAr$^F_4$ (25-BAr$^F_4$)). **25-OTf: Method i.** To a solution of compound **20** (124 mg, 0.162 mmol) in 25 mL of CH_2Cl_2 was slowly added neat triflic acid (15 μL, 0.169 mmol) via microsyringe. The solution was stirred for 1 h, whereupon it was reduced to dryness. The solid was recrystallized from THF and pentane to afford a dark brown solid (71% yield). **Method ii.** To a solution of **24** was added a CO purge at a rate of 1 cm^3/s. After 15 min, the CO purge was replaced by a brief argon purge to remove excess carbon monoxide. **25-BAr$^F_4$:** To a solution of compound **20** (100 mg, 0.131 mmol) in 30 mL of CH_2Cl_2 was slowly added a solution of $[H(Et_2O)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ (170 mg, 0.170 mmol) in 10 mL of CH_2Cl_2. The resulting mixture was stirred for 1 h, whereupon it was reduced to dryness. The solid was recrystallized from ether and pentane, affording a dark brown solid, which, after isolation and further washing with pentane (2 × 10 mL), was dried under vacuum (75% yield). HRMS *m*/*z* calcd for $RhIrP_4O_3C_{21}H_{45}$: 913.6678. Found: 913.6676. ^{1}H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 2.85 (quin., 4H, depm), −11.32 (m, $^1J_{RhH}$ = 21.1 Hz, $^2J_{HP}$ = 9.8 Hz, Ir−*H*−Rh). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 27 °C): δ 187.2 (dt, 1C, $^1J_{CRh}$ = 74.6 Hz, $^2J_{CP}$ =16.2 Hz, Rh−*C*O), 180.3 (t, 2C, $^2J_{CP}$ = 9.3 Hz, Ir−*C*O). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 27 °C): δ 27.7 (dt, 2P, $^1J_{RhP}$ = 106.9 Hz, $^2J_{PP}$ = 45.5 Hz), −5.5 (t, 2P, $^2J_{PP}$ = 45.5 Hz). Anal. Calcd (%) for $IrRhSP_4F_3O_6C_{22}H_{45}$ (913.67): C 28.92, H 4.96. Found: C 29.14, H, 4.97.

z. [Ir$_2$(H)$_2$(CO)$_2$(μ-H)(μ-C═CH$_2$)(depm)$_2$][BAr$^F_4$] (26). **Method i.** In an NMR tube containing **9** (38 mg, 0.022 mmol) dissolved in 0.8 mL of CD_2Cl_2 was added ethylene (5 mL, 0.219 mmol) via a gastight syringe to the headspace. The solution was mixed, and the reaction was monitored by multinuclear NMR. After 2 h, complete conversion to **26** was observed. **Method ii.** In an NMR tube containing **9** (42 mg, 0.024 mmol) dissolved in 0.6 mL of CD_2Cl_2 was added TMNO (2 mg, 0.027) dissolved in 0.2 mL of CD_2Cl_2, followed by the addition of ethylene (5 mL, 0.219 mmol) to the headspace. The reaction was mixed and monitored by multinuclear NMR, which showed complete conversion after 15 min. Attempts to isolate the product as a solid for crystallization were unsuccessful due to its solubility in both polar and nonpolar solvents. HRMS *m*/*z* calcd for $IrP_4O_2C_{22}H_{49}$: 855.1936. Found: 855.1901. ^{1}H NMR (498 MHz, CD_2Cl_2, 27 °C): δ 6.57 (s, 2H, C═C*H*$_2$), 2.85 (m, 2H, depm), 1.75 (m, 2H, depm), −12.66 (m, 2H, Ir−*H*), −14.69 (m, 1H, Ir−*H*−Ir). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 27 °C): δ 190.1 (dtt, 1C, $^1J_{CC}$ = 64.9 Hz, $^2J_{CP}$ = 10.0 Hz, $^2J_{CP}$ = 10.0 Hz, μ-*C*═CH$_2$), 172.4 (m, 2C, Ir−*C*O), 130.4 (d, 1C, $^1J_{CC}$ = 64.9 Hz, μ-C═*C*H$_2$). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 27 °C): δ −6.9 (s, 4P).

aa. [Ir$_2$(H)$_2$(CO)$_2$(μ-H)(μ-C═CHF)(depm)$_2$][BAr$^F_4$] (27). In an NMR tube containing **9** (43 mg, 0.025 mmol) dissolved in 0.5 mL of CD_2Cl_2 was added TMNO (2 mg, 0.027 mmol) in 0.3 mL of CD_2Cl_2, along with 5 mL of vinylfluoride (0.0219 mmol) via a gastight syringe to the headspace. The solution was mixed, and the reaction was monitored by multinuclear NMR. After 30 min, complete conversion to **27** was observed. Attempts to isolate the product as a solid for crystallization were unsuccessful due to its solubility in both polar and nonpolar solvents. Performing the same reaction in the absence of TMNO still produced **27**; however the yield was <10% based on NMR integration after 2 h. ^{1}H NMR (498 MHz, CD_2Cl_2, 27 °C): δ 6.61 (d, 1H, $^2J_{HF}$ = 108.2 Hz, C═C*H*F), 2.77 (m, 2H, depm), 1.67 (m, 2H, depm), −12.54 (m, 1H, Ir−*H*), −13.09 (m, 1H, Ir−*H*), −15.48 (m, 1H, Ir−*H*−Ir). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 27 °C): δ 171.1 (m, 2C, Ir−*C*O). ^{19}F NMR (469 MHz, CD_2Cl_2, 27 °C): δ −72.1 (d, 1F, $^2J_{HF}$ = 108.2 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 27 °C): δ −7.1 (m, 2P), −9.1 (m, 2P).

bb. [Ir$_2$(H)$_2$(CO)$_2$(μ-H)(μ-C═C(H)CH$_3$)(depm)$_2$][BAr$^F_4$] (28). **Method i.** In an NMR tube containing **9** (24 mg, 0.014 mmol) dissolved in 0.8 mL of CD_2Cl_2 was added 5 mL of propylene (0.0219 mmol) via a gastight syringe. The solution was mixed, and the reaction was monitored by multinuclear NMR. After 2.5 h, complete conversion to **28** was observed. **Method ii.** In an NMR tube containing **9** (33 mg, 0.019 mmol) dissolved in 0.6 mL of CD_2Cl_2 was added TMNO (1 mg, 0.014) dissolved in 0.2 mL of CD_2Cl_2, followed by the addition of propylene (5 mL, 0.219 mmol). The reaction was mixed and monitored by multinuclear NMR, which showed complete conversion after 15 min. Attempts to isolate the product as a solid for crystallization were unsuccessful due to its solubility in both polar and nonpolar solvents. HRMS *m*/*z* calcd for $IrP_4O_2C_{23}H_{51}$: 869.2092. Found: 869.2082. ^{1}H NMR (498 MHz, CD_2Cl_2, 27 °C): δ 6.00 (m, 2H, C═C(*H*)CH$_3$), 2.58 (m, 2H, depm), 1.88 (m, 3H, C═C(H)C*H*$_3$), 1.63 (m, 2H, depm), −12.37 (m, 1H, $^4J_{HH}$ = 8.2 Hz, Ir−*H*), −12.63 (m, 1H, $^4J_{HH}$ = 8.2 Hz, Ir−*H*), −14.80 (m, 1H, Ir−*H*−Ir). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 27 °C): δ 171.9 (m, 2C, Ir−*C*O). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 27 °C): δ −6.2 (m, 2P), −7.5 (m, 2P).

cc. [Ir$_2$(H)$_2$(CO)$_2$(μ-H)(μ-C═C(H)CF$_3$)(depm)$_2$][BAr$^F_4$] (29). **Method i.** In an NMR tube containing **9** (42 mg, 0.025 mmol) dissolved in 0.8 mL of CD_2Cl_2 was added 5 mL of 3,3,3-trifluoropropylene (0.0219 mmol) via a gastight syringe. The solution was mixed, and the reaction was monitored by multinuclear NMR. After 2 h, complete conversion to **29** was observed. **Method ii.** In an NMR tube containing **9** (39 mg, 0.024 mmol) dissolved in 0.6 mL of CD_2Cl_2 was added TMNO (2 mg, 0.027) dissolved in 0.2 mL of CD_2Cl_2, followed by the addition of 3,3,3-trifluoropropylene (5 mL, 0.219 mmol) to the headspace via a gastight syringe. The reaction was mixed and monitored by multinuclear NMR, which showed complete conversion after 15 min. Attempts to isolate the product as a solid for crystallization were unsuccessful due to its solubility in both polar and nonpolar solvents. ^{1}H NMR (498 MHz, CD_2Cl_2, 27 °C): δ 6.70 (s, 1H, C═C(*H*)CF$_3$), 2.08 (m, 2H, depm), 1.74 (m, 2H, depm), −12.33 (m, 1H, Ir−*H*), −12.61 (m, 1H, Ir−*H*), −14.84 (m, 1H, Ir−*H*−Ir). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 27 °C): δ 172.3 (t, 1C, $^2J_{CP}$ = 8.7 Hz, Ir−*C*O), 171.7 (t, 1C, $^2J_{CP}$ = 8.2 Hz, Ir−*C*O). ^{19}F NMR (469 MHz, CD_2Cl_2, 27 °C): δ −59.9 (s, 3F). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 27 °C): δ −8.6 (t, 2P, $^2J_{PP}$ = 28.4 Hz), −9.4 (t, 2P, $^2J_{PP}$ = 28.4 Hz).

dd. [Ir$_2$(H)$_2$(CO)$_2$(μ-H)(μ-C═C(H)C(H)═CH$_2$)(depm)$_2$][BAr$^F_4$] (30). **Method i.** To the headspace above an NMR tube containing **9** (46 mg, 0.027 mmol) dissolved in 0.8 mL of CD_2Cl_2 was added 5 mL of 1,3-butadiene (0.0219 mmol) via a gastight syringe. The solution was mixed, and the reaction was monitored by multinuclear NMR. After 5 h, complete conversion to **30** was observed. **Method ii.** In an NMR tube containing **9** (51 mg, 0.030 mmol) dissolved in 0.6 mL of CD_2Cl_2 was added TMNO (2 mg, 0.027) dissolved in 0.2 mL of CD_2Cl_2, followed by the addition of 1,3-butadiene (5 mL, 0.219 mmol) via a gastight syringe to the headspace. The reaction was mixed and monitored by multinuclear NMR, which showed complete conversion after 15 min. Attempts to isolate the product as a solid for crystallization were unsuccessful due to its solubility in both polar and nonpolar solvents. HRMS *m*/*z* calcd for $IrP_4O_2C_{24}H_{51}$: 881.2092. Found: 881.2084. ^{1}H NMR (498 MHz, CD_2Cl_2, 27 °C): δ 6.82 (d, 1H, $^3J_{HH}$ = 9.9 Hz, C═C(*H*)C(H)═C(H)H), 6.28 (ddd, 1H, $^3J_{HH}$ = 17.1 Hz, $^3J_{HH}$ = 9.9 Hz, $^3J_{HH}$ = 9.9 Hz, C═C(H)C(*H*)═C(H)H), 4.93 (d, 1H, $^3J_{HH}$ = 17.1 Hz, C═C(H)C(H)═C(*H*)H), 4.82 (d, 1H, $^3J_{HH}$ = 9.9 Hz, C═C(H)C(H)═C(H)*H*), 2.57 (m, 2H, depm), 1.65 (m, 2H, depm), −12.31 (m, 1H, Ir−*H*), −12.56 (m, 1H, Ir−*H*), −14.70 (m, 1H, Ir−*H*−Ir). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 27 °C): δ 171.5 (t, 1C, $^2J_{CP}$ = 7.9 Hz, Ir−*C*O), 171.3 (t, 1C, $^2J_{CP}$ = 7.8 Hz, Ir−*C*O). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 27 °C): δ −6.6 (m, 2P), −7.1 (m, 2P).

ee. [Ir$_2$(H)$_2$(CO)$_2$(μ-H)(μ-C═C(H)Ph)(depm)$_2$][BAr$^F_4$] (31). **Method i.** In a round-bottom flask containing **9** (89 mg, 0.052 mmol) dissolved in 15 mL of CH_2Cl_2 was added neat styrene (200 μL, 1.746 mmol). The solution was brought to reflux for 48 h, after which the solution was cooled to ambient temperature. The solvent was removed, and the yellow residue was dried under reduced pressure. **Method ii.** In an NMR tube charged with **9** (44 mg, 0.025 mmol) dissolved in 0.6 mL

of CD_2Cl_2 was added neat styrene (100 μL, 0.873 mmol), followed immediately by TMNO (2.5 mg, 0.033 mmol) dissolved in 0.2 mL of CD_2Cl_2. The solution was mixed, and the reaction monitored by NMR, after which quantitative conversion to **31** was observed after 10 min. Attempts to isolate the product as a solid for crystallization were unsuccessful due to its solubility in both polar and nonpolar solvents. ^{1}H NMR (498 MHz, CD_2Cl_2, 27 °C): δ 7.67 (d, 2H, $^3J_{HH}$ = 7.9 Hz, *-ortho*), 7.66 (s, 1H, C═C(*H*)Ph), 7.28 (t, 2H, $^3J_{HH}$ = 7.9 Hz, *-meta*), 7.17 (t, 1H, $^3J_{HH}$ = 7.9 Hz, *-para*), 2.26 (m, 2H, depm), 1.65 (m, 2H, depm), −11.90 (dt, 1H, $^2J_{HP}$ = 15.7 Hz, $^4J_{HH}$ = 9.0 Hz, Ir−*H*), −12.36 (dt, 1H, $^2J_{HP}$ = 14.9 Hz, $^4J_{HH}$ = 9.0 Hz, Ir−*H*), −14.64 (m, 1H, Ir−*H*−Ir). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 27 °C): δ 171.2 (m, 2C, Ir−CO). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 27 °C): δ −8.7 (m, 2P), −9.2 (m, 2P).

*ff. [Ir$_2$(H)$_2$(CO)$_2$(μ-H)(μ-C═C(CH$_3$)$_2$)(depm)$_2$][BAr$^F_4$] (**32**).* In an NMR tube containing **9** (52 mg, 0.030 mmol) dissolved in 0.8 mL of CD_2Cl_2 and cooled to −80 °C was added TMNO (2.5 mg, 0.033 mmol) followed by isobutylene (25 μL, 0.262 mmol), which had also been cooled to −80 °C. The solution was mixed and slowly allowed to warm to ambient temperature. Once ambient temperature was reached, the reaction was monitored by multinuclear NMR. Attempts to isolate the product as a solid for crystallization were unsuccessful due to its solubility in both polar and nonpolar solvents. ^{1}H NMR (400 MHz, CD_2Cl_2, 27 °C): δ 2.42 (m, 2H, depm), 1.52 (m, 2H, depm), 1.40 (s, 6H, C═C(C*H*$_3$)$_2$), −13.73 (m, 3H, Ir−*H*), −15.88 (m, 1H, Ir−*H*−Ir). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 27 °C): δ 167.6 (m, 2C, Ir−CO). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 27 °C): δ −6.2 (m, 4P).

*gg. Reaction of **25** with Ethylene.* In an NMR tube containing **25-OTf** (36 mg, 0.039 mmol) dissolved in 0.8 mL of CD_2Cl_2 and cooled to −80 °C was added TMNO (3 mg, 0.040 mmol) followed by ethylene (5 mL, 0.219 mmol). The solution was mixed and slowly allowed to warm to ambient temperature. Once ambient temperature was reached, the reaction was monitored by multinuclear NMR. Decomposition of **25-OTf** was observed, leading to multiple unidentified products.

a. X-ray Structure Determinations. *General.* Crystals were grown via slow diffusion using the following solvent combinations: CH_2Cl_2/Et_2O (**1**, **18**); THF/*n*-pentane (**4**); THF/Et_2O (**11**); Et_2O/*n*-pentane (**16**); CH_2Cl_2/*n*-pentane (**22**). Data were collected using a Bruker SMART 1000 CCD detector/PLATFORM diffactometer with the crystals cooled to −80 °C (**1**, **4**, **11**, **18**, **22**) or with a Bruker APEX II CCD detector/D8 diffractometer[84] with the crystal cooled to −100 °C (**16**); all data were collected using Mo Kα radiation (λ = 0.71073 Å). The data were corrected for absorption via a multiscan method (**1**, **11**, **18**, **22**) or through Gaussian integration from indexing of the crystal faces (**4**, **16**). Structures were solved using direct methods (SHELXS-97[85] for **1**, **4**, **11**, **18**, and **22**) or Patterson search/structure expansion (DIRDIF-2008[86] for **16**). Refinements were completed using the program SHELXL-97.[85] Non-hydridic hydrogen atoms were assigned positions based on the sp^2 or sp^3 hybridization geometries of their attached carbon atoms and were given isotropic displacement parameters 20% greater than those of their parent atoms. See Supporting Information for a listing of crystallographic experimental data.

b. Special Refinement Conditions. (i) **1**: The chloro and carbonyl ligands attached to iridium were disordered, thus refined as two sets of positions (Cl(A), C(1A), O(1A) with an occupancy factor of 0.6 and Cl(B), C(1B), O(1B) with an occupancy factor of 0.4). (ii) **4**: The Ir(2)−H(2) distance was restrained to be 1.65(1) Å. The C(25)−C(26A) and C(25)−C(26B) distances (within a disordered phosphine ethyl group) were restrained to be 1.53(1) Å. (iii) **11**: The chloro and carbonyl ligands attached to rhodium were disordered, thus refined as two sets of positions ({Cl(A), C(1A), O(1A)} and {Cl(B), C(1B), O(1B)}, each with an occupancy factor of 0.5). (iv) **16**: The atomic coordinates and isotropic displacement parameter for the bridging hydrido ligand (H(1)) were allowed to refine without restraints. (v) **22**: Bond distances and angles within the minor (40%) component of the disordered "RhIr(CO)$_3$(CH$_3$)" fragment (Ir(B), Rh(B), O(1B), O(2B), O(3B), C(1B), C(2B), C(3B), C(4B)) were restrained to have the same values as the corresponding ones for the major orientation, as shown in Figure 5. In cases involving partial occupancy for atoms, the occupancy factors were refined in initial refinements, but were fixed in the final refinements.

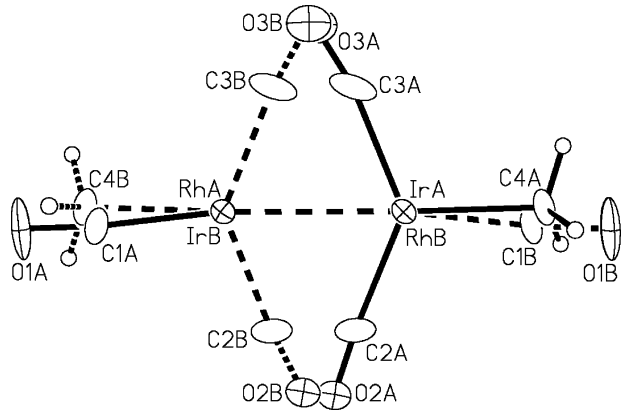

Figure 5. Perspective view of the disordered "IrRhMe(CO)$_3$" fragment in the cation of compound **22**. The depm atoms have been omitted for clarity. The atoms of one disordered form are connected by solid bonds, while the others are connected by dashed bonds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables of crystallographic experimental details for **1**, **4**, **11**, **16**, **18**, and **22**; ORTEP diagrams for the complex cations of **1** and **11**, showing all non-hydrogen atoms of phenyl groups. Atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for **1**, **4**, **11**, **16**, **18**, and **22** in a CIF file. The ^{31}P{^{1}H} and ^{1}H NMR spectra are given for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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