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Diverse Coordination Modes and Transformations of Allenes at Adjacent Iridium/Osmium Centers

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Supporting Information



ABSTRACT: The methylene-bridged complex, $[IrOs(CO)_3(\mu-CH_2)(dppm)_2][BF_4]$ (dppm = μ -Ph₂PCH₂PPh₂) (2), reacts with allene, resulting in C-C bond formation, to yield an equilibrium mix of two isomers of $[IrOs(CO)_3(\mu-\eta^3:\kappa^1-\eta^3)]$ $C(CH_2)_3)(dppm)_2$ [BF₄] (3/3a), in which the hapticity of the trimethylenemethane ligand with respect to the two metals, as well as the carbonyl ligand arrangement, is different in each isomer. Reaction of 2_{7} as the triflate salt (2-CF₃SO₃), with methylallene also yields two isomers, $[IrOs(CO)_3(\mu-\eta^3:\kappa^1-C(CHCH_3)(CH_2)_2)(dppm)_2][CF_3SO_3](4/4a)$; however, in this case, the binding mode of the substituted trimethylenemethane moiety is the same in each isomer and differs only in the position of the methyl group on the allylic moiety. The addition of 1,1-dimethylallene to 2-CF₃SO₃ results in loss of 4-methyl-1,3pentadiene and subsequent reaction of the remaining "[IrOs(CO)₃(dppm)₂]⁺" species with excess 1,1-dimethylallene to give $[IrOs(CO)_3(\mu-\eta^3:\kappa^1-CH_2CCMe_2)(dppm)_2][CF_3SO_3]$ (5), in which the dimethylallene moiety is κ^1 -bound to Os through the central carbon and η^3 -bound to Ir. Both allene and methylallene react with the tetracarbonyl complex, [IrOs(CO)₄(dppm)₂]- $[BF_4]$ (6), to generate analogous products, $[IrOs(CO)_3(\mu-\eta^3:\kappa^1-CH_2CCHR)(dppm)_2][BF_4]$ (R = H (7), CH₃ (8), respectively). Reaction of $\mathbf{6}$ -CF₃SO₃ with 1,1-dimethylallene yields [IrOs(CO)₄(μ -C=C(H)C(CH₃)=CH₂)(dppm)₂][CF₃SO₃] (9), the result of activation of the geminal C-H bonds of the unsubstituted end of the allene, and additional activation of a methyl C-H bond. The addition of 1,1-difluoroallene to $6-CF_3SO_3$ yields $[IrOs(CO)_4(\mu-\kappa^1:\kappa^1-F_2C=C=CH_2)(dppm)_2][CF_3SO_3]$ (10), in which this cumulene bridges both metal centers through the central carbon and the CH2 end of the substrate. These reactivities are compared to those of related Ir₂, Rh/Ru, Rh/Os, and Ir/Ru complexes.

■ INTRODUCTION

Allenes have proven to be useful substrates for the synthesis of complex target molecules that have applications as pharmaceuticals, dyes, and polymers,¹ and their reactions with nucleophiles, often catalyzed by palladium, provide facile routes to the formation of carbon–carbon and carbon–heteroatom bonds,^{1,2} via π -allyl intermediates.³ Allenes also exhibit a diverse coordination chemistry. Whereas these groups bind to a single metal almost exclusively in the η^2 -olefinic mode via one of the π bonds,⁴ the presence of a pair of adjacent metals introduces a number of additional modes, as outlined in Chart 1, for allene itself,⁵ in which either one or both sites of unsaturation can be involved in the bonding. In structure **A**, the allene is bound in a μ - κ^1 : κ^1 binding mode through one of the π bonds to form a dimetallacyclobutane moiety having exocyclic unsaturation.⁶ In the related structure **B**, the unsaturated moiety of **A** can

Chart 1.



additionally coordinate to the distal metal (in the allyl position) to give the κ^{1} : η^{3} binding mode.^{6,7} Allene can also bind in an η^{2} : η^{2} fashion in which each π bond interacts with a different metal, either in an oblique manner (C), in which the allene ligand is oblique to the metal–metal axis, or in a parallel mode (D), in which it lies parallel to the metals.^{7f,j,8} Each of these

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binding modes may or may not be accompanied by a metalmetal bond. Even in the presence of adjacent metals, the allene ligand can still interact with only one of the metals, much as observed in mononuclear complexes.^{4,9}

Allenes can also undergo a number of insertion reactions at transition-metal centers.¹⁰ Of primary interest to our group is the insertion reaction that results in the coupling of allenes and bridging methylene groups, which can yield a number of hydrocarbyl fragments, including bridging trimethylenemethane groups.¹¹ These insertion reactions can be envisioned to occur by initial allene coordination to one metal center, in one of two orientations (structures E and G, Scheme 1). Insertion of the

Scheme 1.



allene into the M–CH₂ bond can then generate C₃-bridged species (structures F or H, Scheme 1), depending on the allene orientation prior to insertion. Propanediyl species, such as structure F, have a tendency to undergo β -H elimination from the central bridging carbon;¹² however, structure H, a trimethylenemethane-like unit, lacks β -hydrogens, and is not susceptible to β -H elimination.

Previous work in our group, involving coupling of allenes with methylene-bridged, mixed-metal complexes of groups 8 and 9 yielded a variety of products depending on the metal combination and the cumulene. These Rh–M (M = Ru, Os) systems often generated trimethylenemethane-bridged complexes, presumably a result of rearrangement of the κ^1 -allylic moiety in **H** to a $\kappa^1:\eta^3$ arrangement, invariably having the η^3

Scheme 2.

interaction at the group 9 metal.^{11d} In the case of 1,1dimethylallene addition to $[RhOs(CO)_3(\mu-CH_2)(dppm)_2][X]$ $(X = BF_4, CF_3SO_3; dppm = Ph_2PCH_2PPh_2)$, the resulting product was 4-methyl-1,3-pentadiene, presumably via structure F, followed by a sequence of β -H elimination and reductive elimination steps.^{11d} The addition of allene to the analogous methylene-bridged Ir/Ru complex also resulted in β -H elimination and reductive elimination to generate 1,3butadiene, while the addition of substituted allenes yielded iridacycle products, presumably through an intermediate, such as F, in which migration of the Ru-bound end of the bridging hydrocarbyl unit to Ir occurred,¹³ a probable consequence of strain within the C_3 -bridged unit in F, and favored by the stronger Ir-C bonds. Surprisingly, the addition of a second equivalent of cumulene to the chelated complexes resulted in multiple C-H bond activation reactions,¹³ which were also observed upon addition of allenes to the related tetracarbonyl complex, $[IrRu(CO)_4(dppm)_2]^{+.14}$ The propensity for Ir to undergo facile C-H bond activation in this Ir/Ru system led us to investigate the related Ir/Os complexes in order to determine the influence of the adjacent Os center.

RESULTS AND COMPOUND CHARACTERIZATION

Reactivity of $[IrOs(CO)_3(\mu-CH_2)(dppm)_2]^+$ with Allenes. Allene. The methylene-bridged tetracarbonyl complex, [IrOs- $(CO)_4(\mu$ -CH₂)(dppm)₂][BF₄] (1), reacts over a 20 h period with propadiene (allene) to generate an equilibrium mix of two isomers of the trimethylenemethane-bridged product, [IrOs- $(CO)_{3}(\mu - \eta^{3} \cdot \kappa^{1} - C(CH_{2})_{3})(dppm)_{2}][BF_{4}](3/3a)$, in an approximate 4:3 ratio accompanied by CO loss. The same reaction, carried out using the tricarbonyl analogue, $[IrOs(CO)_3(\mu CH_2$)(dppm)₂][BF₄] (2), yields the identical isomer mix within 10 h (Scheme 2). To take advantage of the shorter reaction times, the methylene-bridged tricarbonyl complex (2) is used in subsequent reactions, in preference to the tetracarbonyl analogue (1). Differentiating between the two isomers, 3 and 3a, is challenging since neither metal displays coupling to the NMR-active nuclei in the compounds (³¹P, ¹³C, ¹H), and the chemical shifts for the respective nuclei bound to these metals are in approximately the same regions of the spectra.

Each isomer displays two resonances in the ${}^{31}P{}^{1}H{}$ NMR spectrum, consistent with an AA'BB' spin system, in which the ends of the diphosphines bound to the different metals are inequivalent, (3: δ -9.5, -27.2; 3a: δ -7.3, -19.2). Assignment of the observed NMR resonances to 3/3a is accomplished by





Figure 1. (a) Perspective view of the complex cation of $[IrOs(CO)_3(\mu-\eta^3:\kappa^1-C(CH_2)_3)(dppm)_2][CF_3SO_3]$ (3/3a-CF_3SO_3). Thermal ellipsoids are shown at the 20% probability level except for hydrogens, which are omitted for the phenyl groups but are shown arbitrarily small for the others. The atoms Ir(A) and Os(A) are refined as a combination of 50% Ir and 50% Os, so the alternate conformation (3a), composed of Ir(B) and Os(B), is equally abundant. (b) Alternate view of the cation of 3/3a-CF_3SO_3 with only the *ipso*-carbons of the phenyl rings shown. Selected parameters (distances in Å and angles in deg): Ir(A)–Os(A) = 2.9162(4), Ir(A)–C(4) = 2.278(6), Os(A)–C(7) = 2.202(6), C(4)–C(5) = 1.437(8), C(4)–C(6) = 1.449(8), C(4)–C(7) = 1.456(9), P(1)–Ir(A)–P(3) = 112.69(5); P(2)–Os(A)–P(4) = 174.91(5), C(5)–C(4)–C(6) = 110.0(6). C(6)–C(4)–C(7) = 124.1(6).

NMR experiments involving heteronuclear decoupling (³¹P, ¹³C, ¹H), and on literature precedent involving analogous mononuclear Ir and Os complexes, as outlined in what follows. ¹H NMR experiments using selective ³¹P decoupling establish that the two downfield signals represent the ³¹P nuclei bound to the metal having the κ^1 -bound methylene unit in both isomers, while the upfield signals represent the ³¹P nuclei of the metal having the η^3 -allyl-type interaction. In the ¹H NMR spectrum, the CH_2 protons of the dppm ligands appear at δ 5.04 and 4.46 (3) and δ 5.62 and 4.94 (3a), with an average mutual two-bond coupling of 15.5 Hz; however, these resonances give no significant structural insight. The protons from the η^3 -allyl-type interaction appear at δ^2 2.72 and 1.29 in **3a**, and δ 3.55 and 1.94 in **3**. These data can be compared to known allyl complexes of Os¹⁵ and Ir^{3c,9} in which the Ir-bound allyl protons are often observed at lower field than those of Osbound groups. Interestingly, the CH₂ protons of the κ^1 -bound methylene group appear at very different chemical shifts in 3 (δ 1.74, ${}^{3}J_{\text{HP}(\delta-9.5)} = 10.7 \text{ Hz}$ and 3a (δ 4.35, ${}^{3}J_{\text{HP}(\delta-7.3)} = 4.8 \text{ Hz}$) and aid in the identification of each isomer, on the basis that Os-bound κ^1 -CH₂ protons have been shown to appear upfield of Ir-bound CH₂ protons in related bridging hydrocarbyl complexes.¹⁶ Proton spin saturation transfer experiments also support the equilibrium proposed above, and irradiating the proton resonance at δ 1.74 in 3 results in a decrease in intensity of the resonance at δ 4.35, and vice versa. In a ${}^{13}CH_2$ -enriched sample of 3/3a, obtained from $[IrOs(CO)_3(\mu^{-13}CH_2)$ - $(dppm)_2$][BF₄] (2-¹³C), the ¹³C{¹H} NMR spectrum has one broad signal at δ -9.5 for the labeled carbon of the κ^1 methylene in *both* isomers; however, scrambling of the ¹³CH₂ label is also observed over the other two equivalent methylene groups of the trimethylenemethane unit in both isomers, the broad signal for which appears at δ 64.4, consistent with the exchange process suggested above. ¹³C NMR experiments on a ¹³CO-enriched sample, with selective ¹H and ³¹P decoupling, confirm that the metal with the η^3 -allyl-type

interaction has one carbonyl attached, while the other metal has two, consistent with the changing hapticity of the trimethylenemethane ligand with respect to the two metals being accompanied by migration of a carbonyl from metal to metal. In this way, each metal maintains an $18e^-$ configuration.

An X-ray structure determination of 3/3a, in which the tetrafluoroborate anion has been exchanged by triflate, is shown for the complex cation in Figure 1, and confirms the μ - η^3 : κ^1 bonding of the trimethylenemethane moiety and the accompanying carbonyl arrangement suggested above. Tables of bond lengths and angles for 3/3a-CF₃SO₃ appear in the Supporting Information. Differentiating these two metals using crystallographic methods is challenging, owing to their similar X-ray scattering amplitudes; however, the best refinement results were obtained using a 1:1 disorder of the metal positions, as described in the Experimental Section. Dissolving the crystals used for X-ray analysis in CD₂Cl₂ shows the presence of both isomers (by ${}^{31}P{}^{1}H{}$ NMR) in the same equilibrium 4:3 mix observed in earlier spectroscopy. Furthermore, as noted, both metals have saturated 18econfigurations in both isomers, so the metals cannot be distinguished on the basis of their electronic preferences.

The Ir–Os separation of 2.9162(4) Å is somewhat shorter than the intraligand P–P distances of ca. 3.09 Å, suggesting a metal–metal bonding interaction resulting in compression along the axis of the metals. However, the nature of the metal–metal bond and the corresponding metal oxidation states are uncertain. In the formulations shown in Scheme 2, an Ir(I)/Os(II) formulation is accompanied by a dative Ir \rightarrow Os bond, although an alternate formulation has an Ir(II)/Os(I) formulation and a conventional Ir–Os bond. We favor the former description since it corresponds to the favored oxidation states of the metals.

The geometry about the monocarbonyl end, Ir(A)/Os(B), can be viewed as slightly distorted trigonal-bipyramidal if the η^3 -allyl moiety is viewed as occupying a single coordination site

Scheme 3.

Scheme 4.



"[lrOs(CO)₃(dppm)₂]⁺

or as distorted octahedral if occupying two sites, while the dicarbonyl end, (Os(A)/Ir(B)) is clearly octahedral. Within the trimethylenemethane moiety, the C(4)-C(7) bond length (1.456(9) Å) is shorter than expected for a single bond, while the C(4)-C(5) and C(4)-C(6) bond lengths (1.437(8) and 1.449(8) Å, respectively) are intermediate between double and single bonds, as expected for an η^3 -allyl group.¹⁷ These bond lengths are consistent with those reported for other metalbound trimethylenemethane units.^{11c,18} The bridging diphosphines have a cis arrangement at the metal that is bound to the η^3 -allylic fragment $(P(1)-Ir(A)-P(3) = 112.69(5)^\circ)$ and a trans arrangement at the other $(P(2)-Os(A)-P(4) = 174.91(5)^\circ)$; see Figure 1b), as seen in a number of such compounds.^{9,11d}

oC

co

ဝ

Attempts to observe intermediates in the formation of 3/3a by the addition of allene to a CD_2Cl_2 solution of 2 at -78 °C resulted in the observation of several compounds at this temperature, for which the peaks in the ³¹P{¹H} NMR spectrum were broad and overlapping, preventing their characterization. Upon warming to +10 °C, the formation of 3/3a is observed in small amounts (ca. 10%) along with the aforementioned unidentified species, and warming to ambient temperature results in complete conversion to 3/3a within 10 h.

Methylallene. Compound 2-CF₃SO₃ also reacts with 1,2butadiene (methylallene) over a 10 h period, generating two isomers of $[IrOs(CO)_3(\mu-\eta^3:\kappa^1-C(CHCH_3)(CH_2)_2)(dppm)_2]$ - $[CF_3SO_3]$ (4/4a) in a 1:1 ratio, as shown in Scheme 3. In this case, isomers 4 and 4a have the same orientation of the hydrocarbyl fragment with respect to the different metals and identical orientations of CO ligands; the substituted trimethylenemethane unit differs only in the orientation of the methyl group of the η^3 -allyl-type moiety, being either syn or anti to the Os-bound CH₂ group.

The ${}^{31}P{}^{1}H$ NMR spectrum of compounds 4 and 4a contains eight resonances, representing the four chemically inequivalent ³¹P nuclei for each isomer. These resonances are often overlapping, making the differentiation of 4 and 4a difficult. The ¹H NMR spectrum for 4/4a consists of eight resonances for the dppm CH₂ protons and three signals for the four CH₂ protons of the η^3 -allyl moiety of both isomers (δ 5.20, 3.79, 2.90) in a 1:1:2 ratio, the last resulting from overlap of the two olefinic anti proton resonances of the two isomers. The methyl groups of the two isomers appear at δ 1.60 and 1.10 and their adjacent protons at δ 3.12 and 4.69, respectively, while there are two closely spaced signals for the four protons of the Os-bound CH₂ groups at δ 1.84 and 1.80. The chemical shift of these CH₂ protons supports the orientation of the η^3 -allyl-type moiety (bound to Ir as opposed to Os), as shown in Scheme 3; for the reverse orientation, the signal for the κ^1 -CH₂ protons would be expected near δ 4.¹⁶ Previous work on 1-methylsubstituted allyl groups bound to rhodium¹⁹ reports syn protons adjacent to methyl groups appearing between δ 4.06 and 5.19 and anti protons adjacent to methyl groups appearing upfield between δ 3.25 and 3.65. Related iridium complexes are reported to have upfield chemical shifts for methyl protons when the methyl group is anti, as opposed to syn.²⁰ This information suggests that the methyl resonance at δ 1.60 corresponds to the methyl group being syn, and the resonance at δ 1.10 corresponds to the anti isomer with respect to the κ^{1} -CH₂ group. The ¹³C{¹H} NMR spectrum displays five CO resonances (δ 185.4, 177.9, 177.0, 171.0, and 162.1) in a 2:1:1:1:1 ratio, consistent with each isomer having three carbonyls; however, the overlap of the ³¹P NMR signals prevents the use of selective ³¹P-decoupling experiments to accurately assign the carbonyls to a specific isomer or metal. A sample of compounds 4/4a, prepared from ¹³CH₂-enriched 2- CF_3SO_3 displays only one signal for this methylene group at δ



Figure 2. Simulated and observed ${}^{31}P{}^{1}H$ NMR spectra of 5 (in CD_2Cl_2); labeling scheme shown as inset.

-9.5 in the ${}^{13}C{}^{1}H$ NMR spectrum, consistent with it remaining on Os.

1,1-Dimethylallene. The methylene-bridged compound, 2- CF_3SO_3 , also reacts with excess 1,1-dimethylallene at ambient temperature over an 8 h period to form an unexpected μ - η^3 : κ^1 product, $[IrOs(CO)_3(\mu-\eta^3:\kappa^1-CH_2CCMe_2)(dppm)_2]$ - $[CF_3SO_3]$ (5), as shown in Scheme 4. The ³¹P{¹H} NMR spectrum of 5 displays four resonances characteristic of an ABCD spin system in which all four ³¹P nuclei are chemically inequivalent (see Figure 2 for labeling). The two-bond $P_A - P_C$ coupling constant is 254.9 Hz, typical for ³¹P nuclei in a mutually trans arrangement, whereas the smaller $P_B - P_D$ coupling constant of 23.7 Hz suggests a cis arrangement. Intraligand two-bond $P_A - P_B$ coupling (² $J_{PP} = 64.6$ Hz) and $P_C - P_D$ coupling (² $J_{PP} = 53.1$ Hz) are also observed, as well as $P_A - P_D$ coupling ($J_{PP} = 14.0 \text{ Hz}$) and $P_B - P_C$ coupling ($J_{PP} = 7.6$ Hz). A simulation of the ³¹P{¹H} NMR spectrum using the above coupling constants supports the structure proposed (see Figure 2). The ¹H NMR spectrum is as expected for the formulation shown, with four signals for the dppm CH₂ protons (δ 4.70, 4.65, 3.81, and 3.24), two signals for the methyl groups (δ 1.68 and 1.63), and two signals for the two CH₂ protons of the η^3 -allyl group (δ 3.97 (syn), 2.17 (anti)). The chemical shifts of the allylic protons are indicative of an η^3 allyl-type interaction with Ir, being downfield from those of Osbound η^3 -allylic protons (ca. δ^2 and 1, for syn and anti, respectively).^{3c,9,15} The ¹³C{¹H} NMR spectrum displays three resonances for the three carbonyls (δ 186.9, 178.0, 173.9). A crystal structure determination of an analogous complex generated from allene (vide infra) has the η^3 -allyl interaction at Ir and has similar allylic proton shifts in the ¹H NMR spectrum, also supporting the orientation of **5**, as shown in Scheme 4.

Surprisingly, this product contains the dimethylallene moiety without the original metal-bridged "CH₂" group of compound **2**. A clue regarding the fate of this "CH₂" group is the presence of 4-methyl-1,3-pentadiene, the additional product of this reaction, which has resulted from coupling of the cumulene with the methylene group of **2**, as has previously been reported.^{11d,13} This diene compound was characterized by ¹H NMR spectroscopy. In the reaction of a ¹³CH₂-enriched sample of **2** with dimethylallene, the terminal CH₂ group in this pentadiene product appears in the ¹³C{¹H} NMR spectrum at δ 115.1. We propose that the formation of 4-methyl-1,3-pentadiene results from a sequence of cumulene insertion, β -hydride elimination, and reductive elimination steps, similar to a proposal in our previous studies for the elimination of 1,3-butadiene in the reaction of [IrRu(CO)₄(μ -CH₂)(dppm)₂]⁺ with allene.¹³

The reaction of **2** with 1,1-difluoroallene yielded several unidentified products, even when carried out at low temperature. This result is puzzling, as this substrate reacted cleanly with the analogous methylene-bridged Ir/Ru complex,¹³ yielding an Ir chelate similar to the alkyl-substituted allenes.

Reactivity of [IrOs(CO)₄(dppm)₂][BF₄] with Allenes. The proposal above that the μ - η^3 : κ^1 -1,1-dimethylallene adduct (**5**) results from dimethylallene attack on the tricarbonyl species, [IrOs(CO)₃(dppm)₂]⁺, suggested that such products could also be obtained with other allenes. Since this proposed tricarbonyl complex is unstable and decomposes rapidly in solution, investigations instead focused on the reactions involving [IrOs(CO)₄(dppm)₂]⁺ (**6**).

Allene and Methylallene. The tetracarbonyl complex, $[IrOs(CO)_4(dppm)_2][BF_4]$ (6), reacts with allene and methylallene at ambient temperature over 4 h to generate the corresponding products, $[IrOs(CO)_3(\mu-\eta^3:\kappa^1-CH_2CCH_2)-(dppm)_2][BF_4]$ (7), and $[IrOs(CO)_3(\mu-\eta^3:\kappa^1-CH_2CCHCH_3)-(dppm)_2][BF_4]$ (8), respectively, accompanied by carbonyl loss. As proposed for 5, the cumulene in 7 and 8 is bound κ^1 to Os by the central carbon, and η^3 to Ir, as shown in Scheme 5.

Scheme 5.



Removal of a carbonyl from $[IrOs(CO)_4(dppm)_2][BF_4]$ (6) using trimethylamine *N*-oxide (TMNO), in the presence of allene or methylallene, instantly generates the same products.

The ³¹P{¹H} NMR spectrum of 7 displays two resonances at δ -7.4 and -19.3, consistent with the chemical inequivalence of the Ir- and Os-bound ends of the diphosphines, whereas **8** displays three resonances at δ -7.3, -16.8, and -19.9, in a 2:1:1 ratio, with the higher-intensity signal resulting from coincidental overlap of the resonances of two of the four inequivalent ³¹P nuclei. Unlike the earlier study of the methyl-

substituted trimethylenemethane complexes 4 and 4a, only one isomer of 8 is observed. As was observed earlier, both 7 and 8 display a cis/trans arrangement of disphosphines at the different metals. The ¹H NMR spectrum of 7 displays two resonances for the dppm CH₂ protons at δ 5.61 and 4.96 (²*J*_{HH} = 15.1 Hz), while the resonances for the metalaallyl protons appear at δ 4.35 (syn) and 3.55 (anti) and are similar to the resonances observed in a crystallographically characterized diiridium complex.9 The ¹H NMR spectrum of 8 has four dppm CH₂ proton signals (δ 5.64, 5.57, 5.05, and 4.84), two signals for the syn and anti CH₂ protons of the allene (δ 5.20 and 3.79, respectively), one signal for the proton adjacent to the methyl group (δ 4.61), and one signal for the methyl protons (δ 1.09), with the latter two showing mutual threebond coupling of 6.1 Hz. These data suggest that the methyl group is anti to the Os–C bond, 9,11d,19 and the chemical shifts of the olefinic CH₂ protons of the allene suggest an η^3 -binding mode to Ir.^{3c,9} The ${}^{13}C{}^{1}H$ NMR spectrum of a ${}^{13}CO$ enriched sample of 7 confirms the loss of a carbonyl ligand with only three equal-intensity signals observed (δ 185.9, 178.0, and 171.7), in which the two downfield signals couple to the set of ³¹P nuclei at δ –7.4, and the upfield signal couples to the other set of ³¹P nuclei at δ –19.3. In a ¹³CO-enriched sample of 8, the carbonyl resonances appear at δ 185.9, 178.3, and 171.5; here, the two downfield carbonyls show coupling to the ³¹P nuclei at δ –7.3, while the upfield carbonyl couples to the ³¹P nuclei at δ -16.8 and -19.9.

An X-ray structure determination of 7 verifies the geometry proposed above, in which the hydrocarbyl fragment is bound κ^1 to Os and η^3 to Ir. The complex cation of compound 7 is shown in Figure 3. Tables of selected bond lengths and angles for 7 are given in the Supporting Information. Within the bridging allene group, the C(4)–C(5) and C(5)–C(6) bond lengths (1.431(6) and 1.430(6) Å, respectively) and C(4)–C(5)–C(6) angle of 106.7(4)° are typical of an η^3 -bound allyl.^{9,17,21} Although not common, similar bridging allene coordination has been reported.^{7a–c,f,i,j,9,22} The central atom



Figure 3. (a) Perspective view of the complex cation of $[IrOs(CO)_3(\mu-\eta^3:x^1-H_2CCCH_2)(dppm)_2][BF_4]$ (7). Thermal ellipsoids are as in Figure 1. (b) Alternate view of the cation of 7 with only the *ipso*-carbons of the phenyl rings shown. Selected parameters (distances in Å and angles in deg): Ir-Os = 2.8407(2), Ir-C(5) = 2.115(4), Os-C(5) = 2.120(4), C(4)-C(5) = 1.431(6), C(5)-C(6) = 1.430(6); C(4)-C(5)-C(6) = 106.7(4), P(1)-Ir-P(3) = 111.80(4), P(2)-Os-P(4) = 170.34(4).

of the allyl fragment is essentially equidistant from both metals (Ir-C(5) = 2.115(4) Å, Os-C(5) = 2.120(4) Å), and the Ir-Os separation of 2.8407(2) Å indicates compression along the Ir-Os axis compared with the intraligand P-P separations of ca. 3.07 Å. The P(1)-Ir-P(3) angle of 111.80(4)° is acute, being bent away from the η^3 -allyl moiety in a cis arrangement, while the almost linear P(2)-Os-P(4) angle (170.34(4)°) indicates a trans arrangement at the Os, as clearly shown in Figure 3b.

1,1-Dimethylallene. Compound 6-CF₃SO₃ also reacts with excess 1,1-dimethylallene at ambient temperature over 12 h, in this case, giving a very different product, $[IrOs(CO)_4(\mu-C=C(H)C(CH_3)=CH_2)(dppm)_2][CF_3SO_3]$ (9), having a bridging 3-methyl-1,3-butadienylidene fragment, as shown in Scheme 6, resulting from the activation of the two geminal

Scheme 6.



C–H bonds of the cumulene, and one C–H bond of a methyl group, with the concomitant evolution of H₂. This reactivity is reminiscent of that observed in previous work with the related $[IrRu(CO)_4(dppm)_2]^+$ system.¹⁴

The ³¹P{¹H} NMR spectrum of **9** displays two signals, at δ -5.2 and -9.2, ruling out the formation of a μ - η^3 : κ^1 binding mode, as observed for allene and methylallene, which is expected, in this case, to give rise to four different ³¹P environments. Four signals for the vinylvinylidene fragment appear in the ¹H NMR spectrum: the methyl group is observed as a multiplet at δ 0.41, the lone vinylidene proton resonates characteristically downfield as a broad multiplet at δ 8.01, and the two geminal protons can be observed as doublets of multiplets at δ 4.69 and 4.46, with a mutual two-bond coupling of 1.6 Hz. The data obtained from the ${}^{13}C{}^{1}H$ NMR spectrum support the carbonyl arrangement shown in Scheme 6, in which three carbonyls (δ 194.9, 175.5, 171.8) are bound to one metal (Os) and one carbonyl (δ 179.9) is bound to the other (Ir). Although the most downfield chemical shift is suggestive of a semibridging interaction, there is no resolvable coupling observed between it and the Ir-bound ³¹P nuclei. This carbonyl arrangement is not surprising, given the lower tendency for third-row metals to support bridging carbonyls.²³ Two of the Os-bound carbonyls (δ 194.9 and 171.8) show mutual two-bond coupling of 26.2 Hz in a ¹³CO-enriched sample, suggesting a mutually trans arrangement, as shown in Scheme 6.

Compound 9 can be viewed as resulting from the geminal activation of both C–H bonds at the end of 2-methyl-1,3-butadiene that is γ to the methyl substituent, with the accompanying loss of H₂. However, attempts to generate 9 by reaction of 6 with this substrate does not occur in the presence of 100 equiv of the substrate over several days, even

when carried out at slightly elevated temperatures. The Ir/Ru analogue also did not react with this substrate. $^{\rm 14}$

If the reaction of **6** with 1,1-dimethylallene is attempted in the presence of the decarbonylating agent, TMNO, the resultant product obtained immediately is the cumulene adduct, $[IrOs(CO)_3(\mu-\eta^3:\kappa^1-CH_2CCMe_2)(dppm)_2][CF_3SO_3]$ (**5**), the same product observed earlier in the reaction of the methylene-bridged complex (**2**) with excess 1,1-dimethylallene.

1,1-Difluoroallene. Compound 6-CF₃SO₃ also reacts with 1,1-difluoroallene within 1 h at ambient temperature to form the adduct, $[IrOs(CO)_4(\mu-\kappa^1:\kappa^1-F_2C=C=CH_2)(dppm)_2]$ - $[CF_3SO_3]$ (10), in which the fluoroallene bridges both metals (Scheme 7). The ³¹P{¹H} NMR spectrum displays the

Scheme 7.



expected two resonances, at δ -12.0 and -19.5. In the ¹H NMR spectrum, the dppm CH_2 protons appear at δ 4.79 and 4.46, while the CH_2 protons of the fluoroallene ligand appear as a triplet at δ 1.55, coupling to the ³¹P nuclei at δ –12.0 (³ $J_{\rm HP}$ = 11.8 Hz). The observation of one allene CH₂ resonance is consistent with binding through this end of the cumulene, as is typically observed.^{8j,9,14,24} The upfield chemical shift of the CH_2 protons also suggests that they are adjacent to Os and not Ir,¹ the latter of which characteristically resonate downfield at ca. δ 4. Binding of the 1,1-difluoroallene through the "C= CH_2 " end is confirmed in the ¹⁹F NMR spectrum by the pair of resonances at δ -74.3 and -92.2 for the two chemically inequivalent fluorines, having a mutual two-bond coupling of 60.4 Hz, which is typical for such an arrangement.^{9,25} Å ¹³COenriched sample of 10 displays four resonances in the ${}^{13}C{}^{1}H$ NMR spectrum at δ 183.4, 180.2, 177.5, and 154.2, and selective ³¹P-decoupling experiments determine that two carbonyls are bound terminally to each metal.

An X-ray structure determination of **10** confirms the proposed connectivity in which the protons of the difluoroallene ligand are adjacent to Os, as shown in Figure 4. Tables of bond lengths and angles for **10** are given in the Supporting Information. Within the bridging difluoroallene unit, the C(5)–C(6) bond length of 1.511(4) Å is typical of a single bond between sp² and sp³ carbons.¹⁷ Both metals have a distorted octahedral coordination in which the sixth site is the metal–metal bond.

Rearrangement of the bridging difluoroallene to a μ - η^{3} : κ^{1} hydrocarbyl fragment, as observed with allene and methylallene, is never observed, with the κ^{1} : κ^{1} -difluoroallene arrangement being retained upon heating to 40 °C for 8 h, after which time, decomposition occurs. The η^{3} -allyl binding mode has previously been reported for 1,1-difluoroallene in only two multimetallic systems.⁸),24,26

DISCUSSION

The products obtained in the reactions of the methylenebridged compound $[IrOs(CO)_3(\mu-CH_2)(dppm)_2]^+$ (2) and the tetracarbonyl complex $[IrOs(CO)_4(dppm)_2]^+$ (6) with a



Figure 4. Perspective view of the complex cation of $[IrOs(CO)_4(\mu \kappa^1:\kappa^1-F_2C=C=CH_2)(dppm)_2][CF_3SO_3]$ (**10**). Thermal ellipsoids are as shown in Figure 1. Selected parameters (distances in Å and angles in deg): Ir–Os = 2.9095(2), Ir–C(5) = 2.111(3), Os–C(6) = 2.219(3), C(5)–C(6) = 1.511(4), C(5)–C(7) = 1.298(4), Ir–C(5)–C(6) = 112.1(2); Ir–C(5)–C(7) = 126.4(2), Os–C(6)–C(5) = 105.7(2), C(6)–C(5)–C(7) = 121.5(3).

number of allenes, as described in this paper, display a surprising structural diversity in comparison to those of the other closely related group 8/group 9 metal combinations previously studied in our group (Rh/Ru,^{11d} Rh/Os,^{11d} and Ir/Ru^{13,14}). Although the Rh-based systems display significant differences in reactivity compared with the Ir/Ru system, the current Ir/Os system demonstrates essentially all of the diverse reactions observed in the previous three metal combinations, depending on both the allene and the metal complex investigated.

Reactivity of [IrOs(CO)₃(\mu-CH₂)(dppm)₂]⁺ with Allenes. As discussed in an earlier paper,¹⁶ [IrOs(CO)₄(μ -CH₂)-(dppm)₂]⁺ (1) has a different structure than the Rh/Ru, Rh/Os, and Ir/Ru combinations of metals, having all carbonyls terminal and symmetrically distributed, two on each metal. In contrast, all the other metal combinations have two terminal carbonyls on the group 8 metal, one bridging, and only one on

Scheme 8.

the group 9 metal. The bridging carbonyl in these latter systems provides incipient unsaturation at the group 9 metal, by facile movement to a terminal position on the group 8 metal with accompanying cleavage of the metal–metal bond upon the introduction of substrates at the other metal. Without this incipient unsaturation, the reactions of $[IrOs(CO)_4(\mu-CH_2)-(dppm)_2]^+$ (1) with allenes (and also with alkynes¹⁶) are much slower than with the other metal combinations. We, therefore, investigated the reactivity of the tricarbonyl analogue, $[IrOs(CO)_3(\mu-CH_2)(dppm)_2]^+$ (2), which reacts much more readily.

As part of our strategy to generate bridging hydrocarbyl fragments, we anticipated that allene insertion into the $Ir-CH_2$ bond could occur in one of two ways, as shown earlier in Scheme 1, to give either structure F or H, depending on the allene orientation upon coordination at one metal, which we propose is dictated by steric effects. Neither insertion product F nor H is observed in this study, although a compound having a structure like F was observed in an earlier study involving the Rh/Os metal combination.^{11d} Despite our failure to observe these species, the subsequent rearranged products provide insight into the initial coordination modes and insertion pathways.

Reaction of the methylene-bridged tricarbonyl, [IrOs- $(CO)_3(\mu$ -CH₂)(dppm)₂]⁺ (2), with allene and methylallene results in the formation of the μ - η^3 : κ^1 -complexes, [IrOs- $(CO)_{3}(\mu-\eta^{3}:\kappa^{1}-C(CH_{2})_{3})(dppm)_{2}][BF_{4}]$ (3/3a) and [IrOs- $(CO)_{3}(\mu - \eta^{3}: \kappa^{1} - C(CHCH_{3})(CH_{2})_{2})(dppm)_{2}][CF_{3}SO_{3}]$ (4/ 4a), respectively (see Schemes 2 and 3). The generation of trimethylenemethane complexes (as in 3/3a) has been documented in both mononuclear^{18,27} and binuclear systems.^{11a,c-e} We propose that the μ - η^3 : κ^1 -binding mode of this group proceeds via intermediate H, having the unsaturated "C= CHR" fragment in the allyl position with respect to each metal. Facile conversion of the κ^1 - to η^3 -allyl binding is welldocumented, 29 so conversion of intermediate H to the μ - η^3 : κ^1 - binding mode is hardly surprising, representing the transformation of a κ^1 -allylic moiety (relative to both metal centers), to an η^3 -allyl bridging mode at one end of the trimethylenemethane unit. The equilibrium between isomers 3 and 3a, in which the η^3 : κ^1 -hapticity of the trimethylenemethane group alternates from metal to metal, does not appear to be unusual, having been shown to occur in other bimetallic systems.^{11c,e} This rearrangement has been confirmed by labeling



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studies in which the ¹³CH₂ group of the ¹³CH₂-labeled precursor (2) becomes incorporated into all three methylene positions of the trimethylenemethane ligand upon allene insertion. This scrambling process can be rationalized by a series of $\eta^3:\kappa^1$ to $\kappa^1:\kappa^1$ to $\eta^3:\kappa^1$ transformations, as shown (in abbreviated form) in Scheme 8 (dppm groups omitted for clarity).

Unlike isomers 3 and 3a, the isomers, $[IrOs(CO)_3(\mu-\eta^3:\kappa^1 C(CHCH_3)(CH_2)_2)(dppm)_2$ [CF₃SO₃] (4/4a), resulting from methylallene addition to 2, are static, displaying only η^3 -binding of the substituted trimethylenemethane unit to Ir. As a consequence, no ¹³CH₂ scrambling is observed in this case, and this label remains κ^{1} -bound to Os. The two isomers in this case result from syn/anti positioning of the methyl substituent on the allylic portion of the ligand. The failure of 4/4a to reverse hapticity from metal to metal, as observed for 3/3a, is somewhat puzzling, since the introduction of a single methyl substituent would not appear to introduce unusual steric demands. However, it may be that the hapticity exchange, combined with carbonyl migration from metal to metal and the concomitant realignment of the diphosphines from mutually cis at one metal to mutually trans, is inhibited by the additional substituent on the trimethylenemethane ligand.

The generation of a μ - η^{3} : κ^{1} -trimethylenemethane fragment was also observed upon reaction of allene with the methylenebridged Rh/Ru and Rh/Os analogues. However, in these systems, additional facile carbonyl loss occurred from Rh, generating a coordinatively unsaturated " $(\eta^{3}$ -allyl)RhP₂" fragment, consistent with the greater lability of Rh compared with that of Ir. The failure of this Rh-based system to undergo the κ^{1}/η^{3} isomerization observed for 3 and 3a can be rationalized on the basis that the κ^{1} : κ^{1} intermediate, analogous to that shown in Scheme 8, introduces additional coordinative unsaturation to an already unsaturated system, which is presumably unfavorable.

The reactivity observed upon the addition of allene to $[IrOs(CO)_4(\mu-CH_2)(dppm)_2]^+$ (1) or $[IrOs(CO)_3(\mu-CH_2) (dppm)_2$ ⁺ (2), in which the bridging $\eta^3:\kappa^1$ -trimethylenemethane unit is generated, is markedly different from that observed for the related Ir/Ru complex, $[IrRu(CO)_4(\mu CH_2$)(dppm)₂]⁺, which generates 1,3-butadiene through allene-methylene coupling.¹³ The loss of this diene fragment for Ir/Ru suggests that allene coordination and subsequent insertion into the Ir-CH₂ bond occurs via structures similar to E and F (Scheme 1), instead of through intermediates G and H, possibly attributable to a more crowded environment in the Ir/Ru complexes due to retention of a fourth carbonyl ligand throughout the reaction. The β -hydrogens present in this binding mode provide a route to the common decomposition pathway¹² through β -H elimination, to yield 1,3-butadiene. The apparent influence of greater steric crowding in $[IrRu(CO)_4(\mu$ - $(CH_2)(dppm)_2^{\dagger}$ was also evident in its reaction with methylallene,¹³ which again inserts via intermediates E and F, although, in this case, the hydrocarbyl fragment migrates to a chelating position on Ir, instead of undergoing the β -hydrogen elimination. The formation of the μ - η^3 : κ^1 -trimethylenemethane fragments was also observed in the reactions of allene and methylallene with the less crowded tricarbonyl Rh-based complexes, $[RhM(CO)_3(\mu-CH_2)(dppm)_2]^+$ (M = Os, Ru).^{11d}

The reaction of $[IrOs(CO)_3(\mu-CH_2)(dppm)_2]^+$ (2) with 1,1dimethylallene appears to proceed much as it does with $[RhOs(CO)_3(\mu-CH_2)(dppm)_2]^+$,^{11d} in which the dimethylallene couples with the methylene group (structures E and F, Scheme 1) and is lost as 4-methyl-1,3-pentadiene, presumably via β -H elimination and reductive elimination steps. Again, it appears that cumulene coordination as in E is favored in a more sterically congested environment, in this case, a result of double substitution on the cumulene. In the Rh/Os case, the unsaturated "[RhOs(CO)₃(dppm)₂]⁺" fragment that results from loss of the pentadiene unit decomposed immediately. However, in the current study, the resulting "[IrOs-(CO)₃(dppm)₂]⁺" fragment reacts with excess 1,1-dimethylallene to generate a μ - η^3 : κ^1 complex, [IrOs(CO)₃(μ - η^3 : κ^1 -CH₂CCMe₂)(dppm)₂][CF₃SO₃] (5). In the case of [IrRu-(CO)₄(μ -CH₂)(dppm)₂]⁺, reaction with 1,1-dimethylallene again appeared to proceed through intermediates E and F, although, in this case, migration of the Ru-end of the bridging hydrocarbyl unit to Ir was favored instead of β -H elimination, giving an Ir chelate.¹³

In the previously reported reactions of the methylenebridged Ir/Ru complex, $[IrRu(CO)_4(\mu-CH_2)(dppm)_2]^+$, with methyl- and dimethylallene, incorporation of a second equivalent of cumulene¹³ was observed, accompanied by subsequent C–H bond activations of the second substrate. No evidence of incorporation of a second cumulene or of C–H activation is observed with $[IrOs(CO)_3(\mu-CH_2)(dppm)_2]^+$ (2), even in the presence of a large excess of substrate. The related tetracarbonyl complex $[IrRu(CO)_4(dppm)_2]^{+14}$ was also shown to effect the activation of multiple C–H bonds in allenes, so we sought to investigate the analogous Ir/Os compound to test its propensity for C–H activation.

Reactivity of [IrOs(CO)₄(dppm)₂]⁺ with Allenes. The addition of allene and methylallene to the tetracarbonyl complex [IrOs(CO)₄(dppm)₂]⁺ (6) results in the formation of the η^3 : κ^1 -cumulene-bridged complexes, [IrOs(CO)₃(μ - η^3 : κ^1 -C(CH₂)₂)(dppm)₂][BF₄] (7) and [IrOs(CO)₃(μ - η^3 : κ^1 -C(CH₂)(CHCH₃)(dppm)₂][BF₄] (8), respectively, analogous to 5, accompanied by loss of a carbonyl ligand. This coordination mode of allene and methylallene has been documented in related Ir₂ complexes,^{9,30} and other multimetallic systems.^{7a-c,f,ij,22} We assume that cumulene coordination at Ir leads to migration to the bridging position, as shown for structure I in Chart 2, followed by κ^1 -to- η^3 coordination at

Chart 2.



Ir, not unlike that proposed in the transition from structure H to the μ - η^3 : κ^1 binding of the trimethylenemethane described earlier.

This reactivity with allene and methylallene, observed with Ir/Os, is completely different than that observed with the analogous $[IrRu(CO)_4(dppm)_2]^+$ complex,¹⁴ in which the activation of two geminal C–H bonds occurs with accompanying H migrations to generate the corresponding vinylidenebridged complexes, $[IrRu(CO)_4(\mu$ -C=CHR)(dppm)₂]⁺ (R = CH₃, C₂H₅, respectively). We assume that the strong M–C bonds in the Ir/Os species favor retention of the bridging hydrocarbyl unit and does not allow the activation of C–H

		0	
		NMR	
compounds	$\delta(^{31}\mathrm{P}^{\mathrm{H}})^{p}$	$\delta(^1\mathrm{H})^{c,d}$	$\delta^{(13}C^{1}H)^{c,d}$
$[IrOs(CO)_3(\mu_1\eta^3,\kappa^{1}.C(CH_2)_3)-(dppm)_2][BF_4]$ (3)	-9.5 (m, 2P), -27.2 (m, 2P)	$\begin{array}{l} \text{S.04} (\mathrm{dm},\mathrm{2H},^{J}_{\mathrm{HH}}=15.7\mathrm{Hz}),4.46(\mathrm{dm},\mathrm{2H},^{J}_{\mathrm{HH}}=15.7\mathrm{Hz}),3.55(\mathrm{b},\mathrm{2H}),1.74(\mathrm{t},\mathrm{2H},^{3}_{\mathrm{HP}}=10.7\mathrm{Hz}),1.94\\ (\mathrm{d},\mathrm{2H},^{3}_{\mathrm{J}\mathrm{He}}=2.1\mathrm{Hz}) \end{array}$	
$[IrOs(CO)_{3}(\mu_{1}\eta^{3}.\kappa^{1}.C(CH_{2})_{3})-(dppm)_{2}][BF_{4}]$ (3a)	-7.3 (m, 2P), -19.2 (m, 2P)	$\begin{array}{l} 5.62 \ (\rm dm, \ 2H, \ ^2_{\rm HH} = 15.2 \ \rm Hz), \ 4.94 \ (\rm dm, \ 2H, \ ^2_{\rm HH} = 15.2 \ \rm Hz), \ 4.35 \ (\rm t, \ 2H, \ ^2_{\rm HB} = 4.8 \ \rm Hz), \ 2.72 \ (\rm b, \ 2H), \ 1.29 \ (\rm bd, \ 2H, \ ^3_{\rm HH} = 3.9 \ \rm Hz) \end{array}$	185.5 (t, 1C, ${}^{2}f_{CP} = 9.6 \text{ Hz}$, ${}^{2}f_{CC} = 9.1 \text{ Hz}$), 177.5 (t, 1C, ${}^{2}f_{CP} = 9.1 \text{ Hz}$), 171.3 (m, 1C, ${}^{2}f_{CP} = 7.1 \text{ Hz}$), 64.4 (m, 2C), -9.5 (bm, 1C)
[IrOs(CO) ₅ (u-η ³ .x ¹ .C(CHCH ₃)- (CH ₂) ₂)(dppm) ₂][CF ₃ SO ₃] (4/4a)	$\begin{array}{l} -6.8 \ (\text{om}, 3P), -17.2 \ (\text{om}, 2P), -19.8 \ (\text{dd}, 1P, {}^3_{PP} = 49.5 \\ \text{Hz}, {}^3_{PP} = 20.8 \ \text{Hz}, {}^3_{PP} = 11.7 \ \text{Hz}, -2.84 \ (\text{dd}, 1P, {}^2_{PP} = 6.8 \\ \text{68.6 Hz}, {}^2_{PP} = 11.9 \ \text{Hz}, {}^3_{PP} = 6.3 \ \text{Hz}, -2.9.6 \ (\text{dd}, 1P, {}^2_{PP} = {}^2_{3} \\ {}^3_{PP} = 72.1 \ \text{Hz}, {}^3_{PP} = 18.9 \ \text{Hz}, {}^3_{PP} = 5.6 \ \text{Hz} \end{array}$	5.99 (dm, 1H, $^{2}_{\rm HH}$ = 15.2 Hz), 5.64 (dm, 1H, $^{2}_{\rm HH}$ = 15.5 Hz), 5.60 (dm, 1H, $^{2}_{\rm HH}$ = 15.2 Hz), 5.20 (bs, 1H), 5.16 (dm, 1H, $^{2}_{\rm HH}$ = 15.5 Hz), 5.03 (dm, 1H, $^{2}_{\rm HH}$ = 15.0 Hz), 4.82 (dm, 1H, $^{2}_{\rm HH}$ = 15.0 Hz), 4.69 (q, 1H, $^{3}_{\rm HH}$ = 60 Hz), 4.65 (dm, 1H, $^{2}_{\rm HH}$ = 15.1 Hz), 4.12 (dm, 1H, $^{3}_{\rm HH}$ = 6.4 Hz), 2.90 (o, 2H), 1.84 (o, 2H), 1.80 (o, 2H), 1.60 (dd, 3H, $^{3}_{\rm HH}$ = 6.4 Hz), $^{3}_{\rm HH}$ = 6.4 Hz), $^{2}_{\rm HH}$ = 6.4 Hz), $^{2}_{\rm HH}$ = 6.4 Hz), $^{2}_{\rm HH}$ = 6.4 Hz), $^{3}_{\rm HH}$ = 6.4 Hz), $^{3}_{\rm HH}$ = 6.4 Hz)	185.4 (om, 2C), 177.9 (t, 1C, 2]CeP = 8.0 Hz), 177.0 (t, 1C, 2]CeP = 7.1 Hz), 171.0 (t, 1C, 2]CeP = 5.4 Hz), 162.1 (t, 1C, 2]CeP = 4.6 Hz), -9.5 (om, 2C)
[IrOs(CO) ₃ (<i>µ</i> - <i>η</i> ³ : <i>x</i> ¹ .CH ₂ CCMe ₂)- (dppm) ₂][CF ₃ SO ₃] (5)	$\begin{array}{l} -4.7 \ (\mathrm{ddd}, 1P, {}^{2}_{Pp} = 254.9 \ \mathrm{Hz}, {}^{2}_{Pp} = 64.6 \ \mathrm{Hz}, {}^{p}_{Pp} = 14.0 \ \mathrm{Hz}), \\ -19.7 \ (\mathrm{ddd}, 1P, {}^{2}_{Pp} = 64.6 \ \mathrm{Hz}, {}^{2}_{Pp} = 23.7 \ \mathrm{Hz}, {}^{p}_{Pp} = 7.6 \\ \mathrm{Hz}), -21.3 \ (\mathrm{ddd}, 1P, {}^{2}_{Pp} = 254.9 \ \mathrm{Hz}, {}^{2}_{Pp} = 53.1 \ \mathrm{Hz}, {}^{p}_{Pp} = 3.1 \ \mathrm{Hz}, {}^{p}_{Pp} = 7.6 \\ \mathrm{Hz}), -21.3 \ (\mathrm{ddd}, 1P, {}^{2}_{Pp} = 254.9 \ \mathrm{Hz}, {}^{2}_{Pp} = 53.1 \ \mathrm{Hz}, {}^{p}_{Pp} = 23.7 \ \mathrm{Hz}, {}^{p}_{Pp} = 14.0 \ \mathrm{Hz}), \end{array}$	$\begin{array}{l} 4.70 \ (dm, 1H, \ ^{2}_{\rm HH} = 14.8 \ {\rm Hz}), \ 4.65 \ (dm, 1H, \ ^{2}_{\rm HH} = 14.8 \ {\rm Hz}), \ 4.65 \ (dm, 1H, \ ^{2}_{\rm HH} = 14.8 \ {\rm Hz}), \ 3.97 \ (bs, 1H), \ 3.81 \ (dm, 1H, \ ^{2}_{\rm HH} = 14.8 \ {\rm Hz}), \ 3.24 \ (dm, 1H, \ ^{2}_{\rm HH} = 14.2 \ {\rm Hz}), \ 2.17 \ (d, 1H, \ ^{3}_{\rm HP} = 5.8 \ {\rm Hz}), \ 1.68 \ (bs, 3H), \ 1.63 \ (bs, 3H), \ 1.64 \ (bs, $	$\begin{split} &186.9 \; (\mathrm{dd}, \; \mathrm{IC}, {}^{2}_{\mathrm{ICP}} = 6.5 \; \mathrm{Hz}, {}^{2}_{\mathrm{ICP}} = 6.2 \; \mathrm{Hz}), \; 178.0 \; (\mathrm{dd}, \; \mathrm{IC}, {}^{2}_{\mathrm{ICP}} = 121.8 \; \mathrm{Hz}, {}^{2}_{\mathrm{ICP}} = 9.7 \; \mathrm{Hz}), \; 173.9 \; (\mathrm{dd}, \; \mathrm{IC}, {}^{2}_{\mathrm{ICP}} = 7.9 \; \mathrm{Hz}, {}^{2}_{\mathrm{ICP}} = 7.9 \; \mathrm{Hz}, {}^{2}_{\mathrm{ICP}} = 6.8 \; \mathrm{Hz}) \end{split}$
$[IrOs(CO)_{3}(\mu \cdot \eta^{3}\kappa^{1} - CH_{2}CCH_{2}) - (dppm)_{2}][BF_{4}]$ (7)	-7.4 (m, 2P), -19.3 (m, 2P)	$\begin{array}{l} \text{5.61} \left(\text{dm}, 2\text{H}, {}^{2}\text{J}_{\text{HH}} = 15.1 \text{Hz} \right), 4.96 \left(\text{dm}, 2\text{H}, {}^{2}\text{J}_{\text{HH}} = 15.1 \text{Hz} \right), 4.35 \left(\text{dm}, 2\text{H} \right), 3.55 \left(\text{bm}, 2\text{H} \right) \end{array}$	185.9 (t, 1C, 2) _{CP} = 9.1 Hz), 178.0 (t, 1C, 2) _{CP} = 6.9 Hz), 171.7 (t, 1C, 2) _{CP} = 5.0 Hz)
[IrOs(CO) ₃ (µ-η ³ .s. ¹ .CH ₂ CCHCH ₃)- (dppm) ₂][BF ₄] (8)	$\begin{array}{l} -7.3 \ (\text{om, 2P}), -16.8 \ (\text{ddd, 1P}, {}^{2})_{\text{PP}} = 48.0 \ \text{Hz}, {}^{2}_{\text{PP}} = 25.3, \\ {}^{3}_{\text{PP}} = 12.4 \ \text{Hz}), -19.9 \ (\text{ddd, 1P}, {}^{2}_{\text{PP}} = 51.3 \ \text{Hz}, {}^{2}_{\text{PP}} = 19.7 \\ \text{Hz}, {}^{3}_{\text{PP}} = 12.4 \ \text{Hz}) \end{array}$	$\begin{array}{l} 5.64 \ (dm, 1H, \ ^{J}_{\rm HH} = 15.1 \ {\rm Hz}), \ 5.57 \ (dm, 1H, \ ^{J}_{\rm HH} = 15.1 \ {\rm Hz}), \ 5.05 \ (dm, 1H, \ ^{J}_{\rm HH} = 2.5 \ {\rm Hz}), \ 5.05 \ (dm, 1H, \ ^{J}_{\rm HH} = 2.5 \ {\rm Hz}), \ 5.05 \ (dm, 1H, \ ^{J}_{\rm HH} = 15.1 \ {\rm Hz}), \ 4.61 \ (bq, 1H, \ ^{J}_{\rm HH} = 6.1 \ {\rm Hz}), \ 3.79 \ (td, 1H, \ ^{J}_{\rm HH} = 5.3 \ {\rm Hz}), \ ^{2}_{J}_{\rm HH} = 2.5 \ {\rm Hz}), \ 1.09 \ (dm, 3H, \ ^{J}_{\rm HH} = 6.1 \ {\rm Hz}) \end{array}$	185.9 (t, IC, ${}^{2}J_{CP} = 8.9 \text{ Hz}$), 178.3 (t, IC, ${}^{2}J_{CP} = 8.6 \text{ Hz}$), 171.5 (m, IC, ${}^{2}J_{CP} = 5.4 \text{ Hz}$)
$[IrOs(CO)_4(\mu \cdot C = C(H)C(CH_3) = CH_2)(dppm)_2][CF_3SO_3]$ (9)	-5.2 (m, 2P), -9.2 (m, 2P)	8.01 (bm, 1H), 4.69 (dm, 1H), 4.46 (dm, 1H), 4.00 (dm, 2H, ${}^{2}J_{\rm HH} = 12.5 {\rm ~Hz}$), 2.91 (dm, 2H, ${}^{2}J_{\rm HH} = 12.5 {\rm ~Hz}$), 0.41 (bm, 3H)	$ \begin{array}{l} 194.9 \ (\mathrm{dt}, \ \mathrm{IC}, \ ^2\mathrm{J}_{\mathrm{CC}} = 26.2 \ \mathrm{Hz}, \ ^2\mathrm{J}_{\mathrm{CP}} = 7.2 \ \mathrm{Hz}), \ 179.9 \ (\mathrm{t}, \ \mathrm{IC}, \ ^2\mathrm{J}_{\mathrm{CP}} = 11.1 \ \mathrm{Hz}), \ 175.8 \ (\mathrm{t}, \ \mathrm{IC}, \ ^2\mathrm{J}_{\mathrm{CP}} = 7.1 \ \mathrm{Hz}), \ 171.8 \ (\mathrm{dt}, \ \mathrm{IC}, \ ^2\mathrm{J}_{\mathrm{CP}} = 7.1 \ \mathrm{Hz}), \ 171.8 \ (\mathrm{dt}, \ \mathrm{IC}, \ ^2\mathrm{J}_{\mathrm{CP}} = 26.2 \ \mathrm{Hz}, \ ^2\mathrm{J}_{\mathrm{CP}} = 7.1 \ \mathrm{Hz}), \ 171.8 \ (\mathrm{dt}, \ \mathrm{IC}, \ ^2\mathrm{J}_{\mathrm{CP}} = 7.1 \ \mathrm{Hz}), \ 171.8 \ (\mathrm{dt}, \ \mathrm{IC}, \ ^2\mathrm{J}_{\mathrm{CP}} = 7.1 \ \mathrm{Hz}), \ 171.8 \ (\mathrm{dt}, \ \mathrm{IC}, \ ^2\mathrm{J}_{\mathrm{CP}} = 7.1 \ \mathrm{Hz}), \ 171.8 \ (\mathrm{dt}, \ \mathrm{IC}, \ ^2\mathrm{J}_{\mathrm{CP}} = 7.1 \ \mathrm{Hz}), \ 171.8 \ (\mathrm{dt}, \ \mathrm{IC}, \ ^2\mathrm{J}_{\mathrm{CP}} = 7.1 \ \mathrm{Hz}), \ 171.8 \ (\mathrm{dt}, \ \mathrm{IC}, \ ^2\mathrm{J}_{\mathrm{CP}} = 7.1 \ \mathrm{Hz}), \ 171.8 \ (\mathrm{dt}, \ \mathrm{IC}, \ \mathrm{Hz}), \ 171.8 \ (\mathrm{dt}, \ \mathrm{Hz}), \ 171.8 \ (\mathrm{Hz}), \ 171.8 \ (\mathrm{dt}, \ \mathrm{Hz}), \ 171.8 \ (\mathrm{dt}, \ \mathrm{Hz}),$
$[IrOs(CO)_4(\mu, x^1; x^1, F_2C = C = CH_2)-(dppm)_2][CF_3SO_3]$ (10)	-12.0 (m, 2P), -19.5 (m, 2P)	4.79 (dm, 2H, 2 _{HH} = 14.8 Hz), 4.46 (dm, 2H, 3 _{HH} = 14.8 Hz), 1.55 (bt, 2H, 2 _{HP} = 11.8 Hz)	
"NMR abbreviations: $s = singlet, d$:	= doublet, t = triplet, q = quartet, m = multiplet, b = broad	l, o = overlapping. NMR data at $27 \degree C$ in CD_2Cl_2 unless i	otherwise indicated. $^{b31}\mathrm{P}$ chemical shifts referenced to

external 85% H₃PO₄. ^{c1}H and ¹³C chemical shifts referenced to TMS. ^dChemical shifts for phenyl hydrogens and carbons not given.

Table 1. Spectroscopic Data for the Compounds

bonds. It appears that, in these cases, the bridging modes do not result in C-H bond activation.

Surprisingly, the only case of multiple C-H bond activation with the Ir/Os metal combination occurs in the reaction of $[IrOs(CO)_4(dppm)_2]^+$ (6) with 1,1-dimethylallene. As with the Ir/Ru system,¹⁴ double, geminal C-H activation of the cumulene is accompanied by C-H activation of a methyl substituent. We propose that this sole example of C-H bond activation in this Ir/Os system is a result of steric crowding, which we assume does not favor the otherwise unreactive bridging modes, favoring instead C-H activation. The influence of steric crowding in dictating the reactivity of the allenes is clearly seen in the differing reactivities of [IrOs- $(CO)_4(dppm)_2$ ⁺ (6) and "[IrOs(CO)_3(dppm)_2]⁺" (generated in situ as shown in Scheme 4) with 1,1-dimethylallene. While the tetracarbonyl complex results in C-H activation, the less sterically crowded, coordinatively unsaturated tricarbonyl complex yields the bridged η^3 : κ^1 adduct, much as observed for allene and methylallene.

Interestingly, the 1,1-difluorallene adduct of $[IrOs(CO)_4(dppm)_2]^+$ (6), namely, $[IrOs(CO)_4(\mu-\kappa^1:\kappa^1-F_2C=C=C+2)(dppm)_2][CF_3SO_3]$ (10), displays the $\mu-\kappa^1:\kappa^1$ -binding mode as proposed above in Chart 2, except that the binding is reversed, with the central carbon of the fluoroallene bound to Ir instead of to Os. In this case, however, rearrangement to the μ - $\eta^3:\kappa^1$ -mode is not observed and the $18e^-/18e^-$ count is maintained by retention of all four carbonyls. Presumably, the failure of this complex to transform into the μ - $\eta^3:\kappa^1$ -binding mode is related to the poor donor ability of the η^3 -allyl moiety having electronegative fluorines attached, and its consequent inability to displace a carbonyl. In all cases, 9,14 when the fluoroallene bridges the metals, no C-H activation is observed, suggesting that the $\mu-\kappa^1-\kappa^1$ arrangement, like the other bridging modes, is not conducive to C-H activation.

Although the chemistry of the Ir/Os compounds with allenes, described herein, is analogous to that described previously in closely related $Ir_{2,9}^{9}$ Rh/Ru,^{11d} Rh/Os,^{11d} and Ir/Ru^{13,14} systems, the chemistry of this Ir/Os system is more diverse than that of any one of the above metal combinations, demonstrating almost the full spectrum of reactivities reported for the other four groups. In the current Ir/Os series, the comparable Ir–C and Os–C bond strengths appear to favor a bridging coordination mode for the hydrocarbyl fragment, which appears to be unreactive to subsequent transformations, such as C–H bond cleavage.

EXPERIMENTAL SECTION

General Comments. All solvents were dried using appropriate desiccants, distilled before use, and stored under a nitrogen atmosphere. Reactions were performed under an argon atmosphere using standard Schlenk techniques unless otherwise noted. Diazomethane was generated from Diazald, which was purchased from Aldrich, as was the ¹³C-enriched Diazald. ¹³C-enriched *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide was also prepared by using a modified version of the procedure for synthesizing the ¹⁴C-enriched radio-labeled analogue.³¹ The trimethylamine *N*-oxide dihydrate was also purchased from Aldrich and was dried according to the literature procedure,³² and the ¹³CO was purchased from Cambridge Isotopes. The methylene-bridged complex [IrOs(CO)₃(μ -CH₂)(dppm)₂][BF₄] (**2**) and the tetracarbonyl complex [IrOs(CO)₄(dppm)₂][BF₄] (**6**) were prepared according to the published procedures.¹⁶

The methylallene was purchased from Organic Technologies; allene from Matrix Scientific; 1,1-dimethylallene from Aldrich; and 2-methyl-1,3-butadiene from Alfa Aesar. 1,1-Difluoroallene was prepared using a modification of the published procedures,^{9,33} in which a solution of 100 μ L of 2-bromo-3,3,3-trifluoro-1-propene (purchased from Aldrich) in 3 mL of diethyl ether was cooled to -90 °C in an acetone/liquid N₂ bath. To this was added dropwise 385 μ L of a 2.5 M solution of *n*-butyllithium in hexanes (purchased from Aldrich), followed by stirring of the solution at this temperature for 30 min. The -90 °C bath was replaced by an acetonitrile/CO_{2(s)} bath (ca. -40 °C), and the solution was stirred for 15 min. The solution was then slowly warmed over 15 min to -20 °C, resulting in the evolution of 1,1-difluoroallene gas.

The ¹H and ³¹P{¹H} NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 399.9 and 161.8 MHz, respectively. All low-temperature spectra and the heteronuclear decoupling experiments ($^{13}C{^{1}H}$ and $^{13}C{^{1}H, ^{31}P}$) were recorded on a Varian Unity spectrometer operating at 161.9 MHz for ¹³C, 202.3 MHz for ³¹P, and 499.8 MHz for ¹H. Mass spectrometry was performed on a Micromass ZabSpec TOF spectrometer by the mass spectrometry facility of this department, and elemental analyses were also carried out in the departmental facility.

Preparation of Compounds. Spectroscopic data for the compounds are presented in Table 1.

[$lrOs(CO)_3(\mu-\eta^3:\kappa^3-C(CH_2)_3)(dppm)_2$][BF_4] (3/3a). Under an argon atmosphere, allene was passed through a stirred red solution of 2 (42 mg, 0.031 mmol) in 10 mL of CH₂Cl₂ for 1 min at a rate of approximately 0.1 mL/s, resulting in an immediate color change of the solution to yellow. The solution was left to stir under an allene atmosphere for 10 h, after which time 30 mL of diethyl ether and 10 mL of pentane were added to a yellow/orange solution to precipitate a light yellow solid. This solid was recrystallized from CH₂Cl₂/diethyl ether, washed with 2 × 5 mL of diethyl ether, and dried in vacuo (85% yield). HRMS: m/z calcd for C₅₈H₅₀IrO₃OsP₄ (M⁺), 1291.1949; found, 1291.1941 (M⁺). Anal. Calcd for C₅₈F₃H₅₀IrO₆OsP₄S (3/3a-CF₃SO₃): C, 48.43; H, 3.50. Found: C, 48.14; H, 3.61.

 $[IrO_5(CO)_3(\mu-\eta^3:\kappa^1-C(CHCH_3)(CH_2)_2)(dppm)_2][CF_3SO_3]$ (4/4a). Under an argon atmosphere, methylallene was passed through a stirred red solution of 2-CF₃SO₃ (33 mg, 0.024 mmol) in 10 mL of CH₂Cl₂ for 1 min at a rate of approximately 0.1 mL/s, resulting in an immediate color change of the solution to yellow. The solution was left to stir under a methylallene atmosphere for 10 h, after which time 30 mL of diethyl ether and 10 mL of pentane were added to the yellow/orange solution to precipitate a light yellow solid. This solid was recrystallized from CH₂Cl₂/diethyl ether, washed with 2 × 5 mL of diethyl ether, and dried in vacuo (83% yield). HRMS: *m/z* calcd for C₅₉H₅₂IrO₃OsP₄ (M⁺), 1215.1493; found, 1215.1534 (M⁺). Anal. Calcd for C₅₉F₃H₅₂IrO₆OsP₄S: C, 48.79; H, 3.61. Found: C, 48.58; H, 3.96.

 $[IrOs(CO)_{3}(\mu - \eta^{3}:\kappa^{1}-CH_{2}CCMe_{2})(dppm)_{2}][CF_{3}SO_{3}]$ (5). Compound 2- CF_3SO_3 (47 mg, 0.034 mmol) was dissolved in 10 mL of CH_2Cl_2 to afford a red solution to which was added 1,1-dimethylallene (1.2 equiv, 0.042 mmol, 4.1 μ L). The solution turned light yellow immediately and then darkened to yellow-orange within 5 min. The solution was left to stir under an argon atmosphere for 8 h, after which time 30 mL of diethyl ether and 10 mL of pentane were added to the orange solution to precipitate a light orange solid. This solid was recrystallized from CH_2Cl_2 /diethyl ether, washed with 2 × 5 mL of diethyl ether, and dried in vacuo (86% yield). HRMS: m/z calcd for C₅₈H₅₂IrO₃OsP₄ (M⁺), 1305.2105; found, 1305.2085 (M⁺). Anal. Calcd for C₅₉F₃H₅₂IrO₆OsP₄S (5·0.61CH₂Cl₂): C, 47.60; H, 3.57. Found: C, 47.31; H, 3.70. ¹H NMR spectroscopy in CDCl₃ confirmed the presence of dichloromethane of crystallization. The gas formed from the reaction was condensed into another NMR tube and characterized by ¹H NMR. ¹H NMR data for 4-methyl-1,3-pentadiene $(+27 \text{ °C in } \text{CD}_2\text{Cl}_2)$: 1.77 (b, 6H), 4.94 (dd, 1H, $^3J_{\text{HH}} = 9.9 \text{ Hz}$, $^2J_{\text{HH}} =$ 1.9 Hz), 5.09 (dd, 1H, ${}^{3}J_{\rm HH}$ = 16.5 Hz, ${}^{2}J_{\rm HH}$ = 1.9 Hz), 5.92 (m, 1H),

6.44 (dd, 1H, ${}^{3}J_{HH} = 16.5 \text{ Hz}$, ${}^{3}J_{HH} = 9.9 \text{ Hz}$). [$lrOs(CO)_{3}(\mu-\eta^{3}\kappa^{1}-CH_{2}CCH_{2})(dppm)_{2}$][BF_{4}] (7). Under an argon atmosphere, allene was passed through a stirred yellow/orange solution of compound 6 (39 mg, 0.029 mmol) in 10 mL of CH₂Cl₂ for 1 min at a rate of approximately 0.1 mL/s. The solution was left to stir under an allene atmosphere for 4 h at ambient temperature, during which time the solution lightened to yellow. After stirring, the solution volume was reduced to 3 mL, and to this was added 30 mL of diethyl ether to precipitate a yellow solid that was washed with 2 × 5 mL of diethyl ether and dried in vacuo (88% yield). HRMS: m/z calcd for $C_{56}H_{48}IrO_3OsP_4$ (M⁺), 1277.1792; found, 1277.1770 (M⁺). Anal. Calcd for $BC_{56}F_4H_{48}IrO_3OsP_4$: C, 49.38; H, 3.55. Found: C, 48.98; H, 3.64.

[*IrOs*(*CO*)₃(μ - η^3 : κ^1 -*CH*₂*CCHCH*₃)(*dppm*)₂][*BF*₄] (**8**). Under an argon atmosphere, methylallene gas was passed through a stirring yellow/ orange solution of compound **6** (33 mg, 0.024 mmol) in 5 mL of CH₂Cl₂ for 1 min at a rate of approximately 0.1 mL/s. The solution was left to stir under a methylallene atmosphere for 4 h at ambient temperature, during which time the solution lightened to yellow. After stirring, the solution volume was reduced to 2 mL, and to this was added 30 mL of diethyl ether to precipitate a yellow solid that was washed with 2 × 5 mL of diethyl ether and dried in vacuo (85% yield). HRMS: *m/z* calcd for C₅₇H₅₀IrO₃OsP₄ (M⁺), 1291.1949; found, 1291.1929 (M⁺). Anal. Calcd for BC₅₇F₄H₅₀IrO₃OsP₄: C, 49.75; H, 3.66. Found: C, 49.52; H, 3.74.

[*IrOs*(*CO*)₄(μ -*C*=*C*(*H*)*C*(*CH*₃)=*CH*₂)(*dppm*)₂][*CF*₃*SO*₃] (9). Compound 6-*CF*₃*SO*₃ (39 mg, 0.028 mmol) was dissolved in 5 mL of CH₂Cl₂ to afford a yellow/orange solution to which was added 1,1-dimethylallene (10 equiv, 0.29 mmol, 28.4 μ L) by microsyringe. The solution was left to stir at ambient temperature for 12 h, after which time the solution had lightened to yellow. The solvent volume was reduced to 3 mL, and 30 mL of diethyl ether was added to precipitate a light yellow solid that was washed with 2 × 5 mL of diethyl ether and dried in vacuo (82% yield). HRMS: *m/z* calcd for C₅₉H₅₀IrO₄OsP₄ (M⁺), 1331.1898; found, 1331.1883 (M⁺). Anal. Calcd for BC₅₉F₄H₅₀IrO₄OsP₄: C, 50.04; H, 3.56. Found: C, 50.02; H, 3.67. [*IrOs*(*CO*)₄(μ - κ^{1} : κ^{1} -*CF*₂=*C*=*CH*₂)(*dppm*)₂][*CF*₃SO₃] (10). Com-

[*IrOs*(*CO*)₄(μ - κ' : κ' -*CF*₂=*C*=*CH*₂)(*dppm*)₂][*CF*₃SO₃] (**10**). Compound **6-CF**₃SO₃ (35 mg, 0.025 mmol) was dissolved in 0.7 mL of CD₂Cl₂ in an NMR tube fitted with a J. Young valve to afford an orange/yellow solution. The solution was cooled to -78 °C, and the headspace was evacuated and replaced with 1,1-difluoroallene, generated as described above. The NMR tube was warmed over 30 min to ambient temperature and left to react at ambient temperature for 1 h, after which time 20 mL of diethyl ether and 5 mL of pentane were added to the yellow solution to precipitate a light yellow solid. This solid was recrystallized from CH₂Cl₂/diethyl ether, washed with 2 × 5 mL of diethyl ether, and dried in vacuo (90% yield). ¹⁹F NMR of **10** (+27 °C in CD₂Cl₂): δ -74.3 (bd, 1F, ²J_{FF} = 60.4 Hz), δ -92.2 (bd, 1F, ²J_{FF} = 60.4 Hz). HRMS: *m/z* calcd for C₅₇F₂H₄₆IrO₄OsP₄ (M⁺), 1341.1553; found, 1341.1560 (M⁺). Anal. Calcd for C₅₈F₅H₄₆IrO₇OsP₄S: C, 46.80; H, 3.12. Found: C, 46.82; H, 3.22.

Attempted Reaction of $[IrOs(CO)_4(dppm)_2][CF_3SO_3]$ (**6-CF_3SO**₃) with 2-Methyl-1,3-butadiene. To a stirring yellow/orange solution of **6-CF_3SO**₃ (24 mg, 0.018 mmol) was added 2-methyl-1,3-butadiene (100 equiv, 0.18 mmol, 180 μ L) by microsyringe. The solution was left at ambient temperature for 1 week, and after this time, the ³¹P{¹H} NMR spectrum revealed compound **6-CF_3SO**₃ as the only phosphorus-containing product. Slightly elevated temperatures did not result in a reaction.

X-ray Structure Determinations. General. Crystals were grown via layered-solvent slow diffusion using the following solvent systems: CH_2Cl_2 /pentane (3/3a), acetonitrile/Et₂O (7), and CH_2Cl_2 /Et₂O (10). Data were collected using a Bruker APEX II CCD detector/ PLATFORM diffactometer³⁴ (3/3a, 10) or with a Bruker APEX II CCD detector/D8 diffractometer³⁴ (7); all data were collected using Mo K α radiation (λ = 0.71073 Å) and with the crystals cooled to -100 °C. The data were corrected for absorption via a multiscan method (3/3a) or through Gaussian integration from indexing of the crystal faces (7, 10). Structures were solved using Patterson search/structure expansion (DIRDIF-2008³⁵) (3/3a, 10) or direct methods (SHELXS- 97^{36}) (7), and least-squares refinements were completed using the program SHELXL-97.36 Hydrogen atoms attached to carbons were assigned positions based on the sp²- or sp³-hybridization geometries of their attached carbons and were given thermal parameters 20% greater than those of their parent atoms.

Special Refinement Conditions. (i) 3/3a: The exact identities of the metals at each position could not be unambiguously assigned from the structure refinement alone. Values of R_1 , wR_2 , and the goodness-offit were extremely similar (to the fourth decimal place) regardless of whether the iridium atom was singly or triply coordinated to the trimethylenemethane ligand. Refinement of the relative occupancies of each metal was attempted, but this was unsuccessful, as the refinement became unstable during these calculation cycles. Satisfactory results were obtained by setting the occupancy factors to be 50% Ir and 50% Os at each metal atom position, suggesting a disordered mix of isomers in the crystals, which would be consistent with the solution-phase spectroscopic data for 3/3a. The Cl-C distances (d(Cl(1S)-C(1S)), d(Cl(2S)-C(1S)) within the disordered solvent CH_2Cl_2 molecule were restrained to be 1.75(1) Å during refinement. (ii) 10: The Cl-C distances within the minor (30%) component of the disordered solvent CH₂Cl₂ molecule were restrained during refinement: d(Cl-(3S)-C(2S) = d(Cl(4S)-C(2S)) = 1.75(1) Å. (iii) For each of the complexes in which the metals have dissimilar coordination environments, the final models were tested by switching the identities of the metal atom centers (Ir for Os and vice versa) and refining these to completion. In each case, the final indices became subtly, but noticeably, worse for the "reversed-metals" models (7: from R_1 = 0.0289, $wR_2 = 0.0619$ to $R_1 = 0.0293$, $wR_2 = 0.0639$; **10**: from $R_1 =$ 0.0204, $wR_2 = 0.0564$ to $R_1 = 0.0207$, $wR_2 = 0.0577$).

ASSOCIATED CONTENT

S Supporting Information

Tables of crystallographic experimental details and selected bond lengths and angles for compounds 3/3a-CF₃SO₃, 7, and 10 in pdf format and atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for these compounds in a CIF file. 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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