Diverse Reactivity of Alkynes with the Binuclear Methyl and Incipient Methyl Complexes [RhIr(CH₃)(CO)₃(Ph₂PCH₂PPh₂)₂][CF₃SO₃] and [Ir₂H(CO)₃(μ-CH₂)(Ph₂PCH₂PPh₂)₂][CF₃SO₃]

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The binuclear diiridium complex, [Ir₂H(CO)₃(μ-CH₂)(dppm)₂][CF₃SO₃] (**2**), reacts with acetylene and phenylacetylene to give the alkyne- and vinylidene-bridged complexes, [Ir₂(CH₃)(CO)₃(μ-HC≡CR)(dppm)₂][CF₃SO₃] and [Ir₂(CH₃)(CO)₃(μ-C=C(H)R)(dppm)₂][CF₃SO₃] (R = H, Ph), respectively, in each case. At −78 °C in the acetylene reaction an intermediate acetylide−hydride, [Ir₂(H)(CH₃)(CO)₃(μ-C≡CH)(dppm)₂][CF₃SO₃], is observed, which transforms into the vinylidene product at higher temperature. The reaction of the related mixed-metal species [RhIr(CH₃)(CO)₃(dppm)₂][CF₃SO₃] (**1**) with acetylene at −78 °C gives an acetylene-bridged intermediate analogous to that observed in the diiridium system, but warming to ambient temperature results in dissociation of the rhodium end of one of the diphosphines, which undergoes nucleophilic attack at the Rh end of the alkyne to yield [RhIr-(CH₃)(μ-η¹:η²:η¹-HC=C(H)PPh₂CH₂PPh₂)(dppm)][CF₃SO₃]. The reaction of **1** with phenylacetylene at −78 °C yields a methyl−hydrido−phenylacetylide intermediate analogous to that observed in diiridium−acetylene chemistry; however, upon warming reductive elimination of methane occurs to give the phenylacetylide-bridged species [RhIr(CO)₃(μ-C≡CPh)-(dppm)₂][CF₃SO₃], which reacts with excess phenylacetylene to give the diacetylide−hydride product [RhIr(C≡CPh)(CO)₂(μ-H) (μ-C≡CPh)(dppm)₂][CF₃SO₃]. Monitoring of the reaction at various temperatures by multinuclear NMR allows the characterization of the observed intermediates. Both compounds **1** and **2** react with dimethyl acetylenedicarboxylate (DMAD) to give the respective products [MIr(C(R)=C(CH₃)R)(CO)₃(dppm)₂][CF₃SO₃] (M = Rh, Ir; R = CO₂Me) resulting from alkyne insertion into the metal−methyl bond. Also observed in the diiridium chemistry is the alkyne-bridged product [Ir₂(CH₃)(CO)₃(μ-DMAD)(dppm)₂][CF₃-SO₃]. The structure of [RhIr(C≡CPh)(CO)₂(μ-H)(μ-C≡CPh)(dppm)₂][CF₃SO₃] was determined by X-ray crystallography. This compound crystallizes with 2 equiv of CH₂Cl₂ in the monoclinic space group $P2_1/c$ in a cell having $a = 17.821(3)$ Å, $b = 24.780(5)$ Å, $c = 17.892(3)$ Å, $\beta = 117.56(1)°$, $V = 7004(2)$ Å³, and $Z = 4$. On the basis of 8365 unique observations the structure has been refined to $R = 0.064$ and $R_w = 0.083$. Both acetylides are σ-bound to Ir in a mutually trans orientation, with one also engaging in a weak π-interaction with Rh. The hydride ligand bridges both metals on the face opposite the bridging acetylide group.

Introduction

The alkyne molecule can display a wealth of chemistry in its reactions with transition metal complexes.[1] Not only can it bind in the η^2-fashion, in which it can function as either a two- or a four-electron donor,[1,2] but it can also undergo a variety of transformations, yielding acetylide[3] or vinylidene[4] ligands, as well as products of alkyne condensation with substrates such as CO,[5] CS₂,[6] olefins,[7] or other alkyne molecules.[8] Alkynes can also undergo migratory insertion reactions into metal−carbon,[9,10] metal−hydride,[1,11] or metal−heteroatom[12] bonds. Although examples of alkyne insertions into metal−hydride bonds are not as well-documented as those involving olefins,[11] they are nevertheless rather common. In contrast, insertions of alkynes into metal−alkyl or related bonds are not still common,[9f,10] in spite of their obvious significance in C−C-bond-forming processes.

Binuclear complexes add an additional dimension to the chemistry of alkynes since, in addition to reactivity at either one of the metal centers, the involvement of both metals is also possible. This is readily seen in the two alkyne bridging modes that are possible, in which the alkyne orients itself either parallel or perpendicular to the metal−metal axis.[13] The reactivity of bridging alkyne groups continues to be a topic of interest[14] in efforts to determine the possible effects of adjacent metals on the chemistry.

As part of an ongoing interest in alkyne reactivity at two adjacent metals,[15−17] we have been investigating the migratory insertions of alkynes into metal−hydrogen[16]

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or metal−carbon bonds, with the aim of yielding vinyl complexes, and the transformations of alkyne molecules to vinylidene ligands,[17] again with the aim of effecting carbon−hydrogen or carbon−carbon bond formation. As part of this study, we undertook an investigation into the reactivity of the related compounds, $[RhIr(CH_3)(CO)_3(dppm)_2][CF_3SO_3]$ (**1**) and $[Ir_2H(CO)_3(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**2**),[18] with alkynes. Although at a glance these compounds appear substantially different, one being a methyl complex and the other being a methylene-bridged hydride, they are in fact more closely related than these ground state formulations suggest. In compound **2** it has been shown that facile scrambling of the hydride ligand and the methylene hydrogens occurs via a labile methyl intermediate,[18,19] which is presumed to be rather similar to **1**. It was reasoned that in **1**, and in the methyl intermediate involved in the rearrangement of **2**, the coordinative unsaturation at one metal could serve as a site of alkyne coordination, leading to species that might be capable of C−C-bond-forming reactions. In addition, the diiridium species **2** presents the additional possibilities of alkyne insertions involving the hydride or bridging methylene group.

In this paper we report the results of an investigation into the reactivities of compounds **1** and **2** with a number of alkyne molecules, demonstrating an interesting diversity in reactivities that is alkyne- and metal-dependent.

Experimental Section

General Considerations. All solvents were dried using the appropriate drying agents, distilled before use, and stored under argon. Deuterated solvents used for NMR experiments were degassed and stored under argon over molecular sieves. Reactions were carried out at room temperature unless otherwise noted by using standard Schlenk procedures, and compounds obtained as solids were purified by recrystallization. A flow rate of *ca.* 0.2 mL s^{-1} was employed for all reactions that involved purging a solution with a gas. Acetylene was obtained from Matheson, while ^{13}C-labeled acetylene was purchased from Cambridge Isotopes and ^{13}CO (99%) was supplied by Isotec Inc. All gases were used as received. The hydrated rhodium(III) and iridium(III) chlorides were purchased from Engelhard Scientific or Vancouver Island Precious Metals, whereas dimethyl acetylenedicarboxylate (DMAD) and phenylacetylene were obtained from Aldrich. The compounds $[RhIr(CH_3)(CO)_3(dppm)_2][CF_3SO_3]$ (**1**) and $[Ir_2H(CO)_3(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**2**) were prepared as previously reported.[18]

Routine NMR spectra were recorded on a Bruker AM-400 spectrometer at 400.1 MHz for ^1H, 161.9 MHz for $^{31}P\{^1H\}$, and 100.6 MHz for $^{13}C\{^1H\}$ spectra. The $^{13}C\{^1H\}\{^{31}P\}$ NMR experiments were obtained on a Bruker WH-200 spectrometer operating at 50.32 MHz. All ^{13}C NMR spectra were obtained with use of ^{13}C-enriched samples unless otherwise noted. Infrared spectra were run on a Nicolet 7199 FT interferometer or a Perkin-Elmer 883 IR spectrometer either as Nujol mulls on KBr plates or as solutions in KCl cells with 0.5 mm path lengths. Unless otherwise noted, IR spectra were carried out on samples containing the isotopes in their natural abundance.

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Spectroscopic parameters for the compounds prepared are found in Table 1. Elemental analyses were performed by the microanalytical service within the department.

Preparation of Compounds. (a) [Ir$_2$(CH$_3$)(CO)$_3$(μ-C=CH$_2$)(dppm)$_2$][CF$_3$SO$_3$] (4). The compound [Ir$_2$(H)(CO)$_3$(μ-CH$_2$)(dppm)$_2$][CF$_3$SO$_3$] (2) (60 mg, 0.043 mmol) was dissolved in 7 mL of CH$_2$Cl$_2$ in a round-bottomed flask. The solution was then cooled to −78 °C by immersing the flask in a dry ice/acetone bath. Acetylene was then passed through the solution for 1 min, after which time the mixture was stirred under a static atmosphere of the gas for 30 min at −78 °C and then warmed to room temperature. After the solution was stirred for 2 h at this temperature, during which time the color changed from orange to yellow, the solvent was removed under vacuum and the solid was recrystallized from CH$_2$Cl$_2$/Et$_2$O, yielding a yellow product in 84% yield. Anal. Calcd for Ir$_2$SP$_4$F$_3$O$_4$C$_{59}$H$_{49}$: C, 47.96; H, 3.46. Found: C, 47.76; H, 3.36.

(b) [Ir$_2$(H)(CH$_3$)(CO)$_3$(μ-η^1:η^2-C≡CH)(dppm)$_2$][CF$_3$SO$_3$] (5). Excess acetylene (20 mL) was added, by means of a gas-tight syringe, to a solution of compound 2 (30 mg, 0.021 mmol) in 0.6 mL of CD$_2$Cl$_2$ at −78 °C in an NMR tube capped with a rubber septum. NMR spectra obtained at −80 or −40 °C showed the presence of compound 5, which was not isolated as a solid.

(c) [Ir$_2$(CH$_3$)(CO)$_3$(μ-PhC$_2$H)(dppm)$_2$][CF$_3$SO$_3$] (7). Compound 2 (60 mg, 0.043 mmol) was dissolved in 10 mL of CH$_2$Cl$_2$. After the solution was cooled to −78 °C, 1 equiv (4.7 μL, 0.043 mmol) of phenylacetylene was added. The orange mixture was stirred for 1 h at that temperature. It was then warmed to room temperature and stirred for another 1 h, during which time the color slowly changed to brown. The solvent was then removed under vacuum, and the residue was recrystallized from CH$_2$Cl$_2$/Et$_2$O to give a brown product (76% yield). Anal. Calcd for Ir$_2$SP$_4$F$_3$O$_6$C$_{63}$H$_{53}$: C, 50.32; H, 3.55. Found: C, 49.52; H, 3.36.

(d) [RhIr(CH$_3$)(CO)$_3$(μ-C$_2$H$_2$)(dppm)$_2$][CF$_3$SO$_3$] (9). Compound 1 (30 mg, 0.023 mmol) was dissolved in 0.6 mL of CD$_2$Cl$_2$ in an NMR tube capped by a rubber septum and then cooled to −78 °C. Excess acetylene (*ca.* 20 mL) was then slowly added to the solution by means of a gas-tight syringe. Warming the sample to −40 °C yielded compound 9, which was characterized by its NMR spectra (compound 9 was not isolated as a solid).

(e)[RhIr(CH$_3$)(CO)$_3$(dppm)(HC=C(H)P(Ph)$_2$CH$_2$PPh$_2$)]-[CF$_3$SO$_3$] (10). Acetylene was passed through a solution of compound 1 (60 mg, 0.046 mmol) in 10 mL of CH$_2$Cl$_2$, which had been cooled to −78 °C, for 1 min. The solution was stirred under a static atmosphere of the gas at this temperature for about 10 min and then warmed to room temperature. To obtain NMR spectra, the reaction was carried out in CD$_2$Cl$_2$ solution under the same conditions, and the spectra were obtained after keeping the solution at room temperature for about 5 min. Attempts to precipitate the product as a solid resulted in several decomposition products.

(f) [RhIr(μ-η^1:η^2-C≡CPh)(CO)$_3$(dppm)$_2$][CF$_3$SO$_3$]·¹/₂-CH$_2$Cl$_2$ (11). To a solution of compound 1 (60 mg, 0.046 mmol) in 10 mL of CH$_2$Cl$_2$ was added 1 equiv (5.0 μL, 0.046 mmol) of phenylacetylene. The mixture was stirred for 2 h under a slow stream of argon, during which time the color changed from orange to red. The solvent volume was then reduced to about 5 mL, and the red solid was precipitated and washed with ether. The solid was collected and dried under a stream of argon. After recrystallization from CH$_2$Cl$_2$/Et$_2$O, the product was dried again under an argon stream and then under vacuum (75% yield). Anal. Calcd for IrRhClSP$_4$F$_3$O$_6$C$_{62.5}$H$_{50}$: C, 52.06; H, 3.50. Found: C, 52.12; H, 3.61.

(g) [RhIr(C≡CPh)$_2$(CO)$_2$(μ-H)(dppm)$_2$][CF$_3$SO$_3$]·¹/₂CH$_2$Cl$_2$ (12). The procedure for preparing compound 12 was the same as that described for compound 11, except that an excess (*ca.* 3 equiv) instead of 1 equiv of phenylacetylene was used, and the solution color changed from orange to yellow and then to

orange again. The orange product was obtained in 70% yield. Anal. Calcd for IrRhClSP$_4$F$_3$O$_5$C$_{69.5}$H$_{56}$: C, 55.10; H, 3.72; Cl, 2.34. Found: C, 54.38; H, 3.70; Cl, 2.00.

(h) [RhIr(RC=C(CH$_3$)R)(CO)$_3$(dppm)$_2$][CF$_3$SO$_3$] (R = CO$_2$Me) (16). Compound 1 (60 mg, 0.046 mmol) was dissolved in 5 mL of CH$_2$Cl$_2$, and 1 equiv (5.6 μL, 0.046 mmol) of DMAD was added. The solution was then stirred for 1 h, after which time the solvent was removed under vacuum. The residue was then recrystallized from CH$_2$Cl$_2$/Et$_2$O, giving a yellow product (75% yield). Anal. Calcd for IrRhSP$_4$F$_3$O$_{10}$C$_{61}$H$_{53}$: C, 50.38; H, 3.67. Found: C, 49.42; H, 3.44.

Reaction of Compound 2 with Acetylene at Room Temperature. The procedure was the same as that used for the preparation of compound 4 as stated earlier, except that the entire reaction was carried out at room temperature for 1 h, yielding a mixture of compound 4 and [Ir$_2$(CH$_3$)(CO)$_3$(μ-C$_2$H$_2$)(dppm)$_2$][CF$_3$SO$_3$] (3) as products.

Reaction of Compound 2 with Phenylacetylene at Room Temperature. The procedure was the same as that used for the preparation of compound 7 as stated earlier, except that the entire reaction was carried out at room temperature for 1 h, yielding a mixture of compound 7 and [Ir$_2$(CH$_3$)(CO)$_3$(μ-C=C(H)Ph)(dppm)$_2$][CF$_3$SO$_3$] (8) as products.

Reaction of Compound 2 with DMAD. The procedure was the same as that used for the preparation of compound 16, except that compound 2 was used instead of compound 1 and the mixture was stirred for 2 h instead of 1 h. A mixture of the compounds [Ir$_2$(RC=C(CH$_3$)R)(CO)$_3$(dppm)$_2$][CF$_3$SO$_3$] (R = CO$_2$Me) (17) and [Ir$_2$(CH$_3$)(CO)$_3$(μ-DMAD)(dppm)$_2$][CF$_3$SO$_3$] (18) was obtained, as shown by the NMR spectra. The reaction was repeated using a procedure similar to that employed for the preparation of compound 7, except that DMAD was used instead of phenylacetylene and the color of the solution changed from orange to yellow. This reaction yielded the same products as those obtained from the reaction carried out at room temperature.

Reaction of Compound 4 with PMe$_3$. To a solution of compound 4 (60 mg, 0.042 mmol) dissolved in 5 mL of THF was added a solution of 1 equiv of PMe$_3$ (42.0 μL of a 1 M solution in THF) in 5 mL of THF. The solution was then stirred for 2 h, during which time its color changed to lighter yellow. The solvent was then removed under vacuum, and the yellow solid was recrystallized from CH$_2$Cl$_2$/Et$_2$O. The NMR spectra showed that the product was the compound [Ir$_2$-(CH$_3$)(CO)$_2$(PMe$_3$)(μ-C=CH$_2$)(dppm)$_2$][CF$_3$SO$_3$] (6).

Characterization of Intermediates in the Reaction of Compound 1 with Excess Phenylacetylene. Compound 1 (30 mg, 0.023 mmol) was dissolved in 0.6 mL of CD$_2$Cl$_2$ in an NMR tube, capped with a rubber septum, and cooled to −78 °C. Phenylacetylene (7.5 μL, 0.069 mmol) was then added, and NMR spectra of the reaction mixture were obtained at temperatures starting from −80 to +25 °C by warming the probe to the desired temperature, with the sample in place, and allowing the sample to stand for 20 min before recording the spectra.

X-ray Data Collection. Orange crystals of [RhIr(C≡CPh)$_2$-(CO)$_2$(μ-H)(dppm)$_2$][CF$_3$SO$_3$]·2CH$_2$Cl$_2$ (12) were obtained by slow diffusion of ether into a concentrated CH$_2$Cl$_2$ solution of the compound. Several suitable crystals were mounted and flame-sealed in glass capillaries under solvent vapor to minimize decomposition or deterioration due to solvent loss. Data were collected on an Enraf-Nonius CAD4 diffractometer by using graphite-monochromated Mo Kα radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range 20.0° ≤ 2θ ≤ 24.0°. The monoclinic diffraction symmetry and the systematic absences (*h0l*, *l* = odd; 0*k*0, *k* = odd) were consistent with the space group *P*2$_1$/*c*.

Intensity data were collected at 22 °C by using the θ/2θ scan technique to a maximum 2θ = 50.0°, collecting reflections with indices of the form +*h*, +*k*, ±*l*. Backgrounds were scanned for 25% of the peak width on either side of the peak scan. Three

reflections were chosen as intensity standards and were re-measured at 120 min intervals of X-ray exposure time. There was no significant systematic decrease in the intensities of these standards; thus, no decomposition correction was applied. A total of 12 976 unique reflections was measured and processed in the usual way using a value of 0.04 for p[20] to downweight intense reflections; of these, 8365 were considered to be observed $[F_o^2 \geq 3\sigma(F_o^2)]$ and were used in subsequent calculations. Absorption corrections were applied to the data by using the method of Walker and Stuart.[21,22] See Table 2 for crystal data and further information on X-ray data collection.

Structure Solution and Refinement. The structure was solved in the space group $P2_1/c$ by using standard Patterson and Fourier techniques. Full-matrix, least-squares refinements minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$. All non-hydrogen atoms ultimately were located. In addition, two molecules of CH_2Cl_2 per formula unit of complex were also located. Atomic scattering factors[23,24] and anomalous dispersion terms[25] were taken from the usual tabulations. Hydrogen atoms, with the exception of the methylene chloride hydrogens, were included as fixed contributions but not refined. Their idealized positions were calculated from the geometries about the attached carbon atoms, using a C−H bond length of 0.95 Å, and they were assigned thermal parameters 20% greater than the equivalent isotropic B values of their attached C atoms.

The final model, with 575 parameters refined, converged to values of $R = 0.064$ and $R_w = 0.083$. In the final difference Fourier map, the 10 highest residuals (1.7−1.2 e/Å³) were found in the vicinity of the metal atoms, phenyl rings, and solvent molecules. A typical carbon atom in an earlier synthesis had an electron density of *ca.* 5.0 e/Å³. The positional and isotropic thermal parameters of the non-hydrogen atoms are given in Table 3.

Results and Compound Characterization

The reaction of $[Ir_2(H)(CO)_3(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**2**) with acetylene at ambient temperature gives a mixture of the alkyne- and vinylidene-bridged products $[Ir_2(CH_3)(CO)_3(\mu\text{-}HC_2H)(dppm)_2][CF_3SO_3]$ (**3**) and $[Ir_2(CH_3)(CO)_3(\mu\text{-}C\!=\!CH_2)(dppm)_2][CF_3SO_3]$ (**4**), respectively, in a typical ratio of about 1.7:1. The ^1H NMR spectrum of the mixture shows the methyl resonance of **3** as a broad signal at δ −0.14 and the proton resonances of the coordinated acetylene as multiplets at δ 10.25 and 9.15, in the appropriate ratios. The $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample shows broad resonances for **3** at δ 198.7 and 181.3 and a triplet at δ 194.4, and the IR spectrum[26] shows CO stretches at 2007, 1970, and 1911 cm⁻¹, suggesting the presence of three terminally bound CO ligands. Also in the IR spectrum, the peak at 1632 cm⁻¹ is assigned to the C≡C stretch of the coordinated acetylene.[27] This is within the range of 1530−1642 cm⁻¹ observed in closely related dppm-bridged binuclear complexes, in which the alkyne

bridges the two metals parallel to the metal−metal axis,[15c,e,i,28] and contrasts with the lower values of *ca.* 1425 cm⁻¹ reported for $[Rh_2(CO)_2(\mu\text{-}\eta^2\!:\!\eta^2\text{-}PhC_2H)(dppm)_2]$ and $[Rh_2(CO)_2(\mu\text{-}\eta^2\!:\!\eta^2\text{-}PhC_2Ph)(dppm)_2]$, in which the alkyne bridges the metals perpendicular to the metal−metal bond.[29] The $^{13}C\{^1H\}$ NMR spectrum of compound **3**, prepared by using acetylene that was ^{13}C-enriched at both positions, shows two doublets of multiplets at δ 160.7 and 147.1 ($^1J_{C-C} = 50.8$ Hz) due to the two carbon nuclei of the coordinated acetylene. These chemical shifts are close to those in related systems in which the alkyne bridges in an orientation parallel to the metal−metal axis,[17] suggesting such a bridging mode in compound **3**. The ^1H NMR spectrum of this ^{13}C-enriched sample shows the proton resonances of the bridging acetylene as two doublets of multiplets ($^1J_{C-H} \approx 160$ Hz for each of the protons). In a sample of compound **3** in which all of the carbon nuclei of the bridging acetylene and CO ligands were ^{13}C-enriched, each of the carbonyl resonances at δ 194.4 and 181.3 shows strong coupling (21.0 Hz) to one of the carbon nuclei of the coordinated acetylene, suggesting a trans arrangement of the carbon atoms of the acetylene and two of the CO ligands,[29a] as shown in Scheme 1.

The ^1H NMR spectrum of compound **4** shows the methyl resonance as a triplet at δ −0.55 and the vinylidene proton resonances as singlets at δ 6.40 and 5.72. The $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample shows a broad resonance at δ 181.2 and triplets at δ 175.1 and 172.3, indicating the presence of three CO ligands in compound **4**. Although none of these resonances is at low enough field to unequivocally indicate the presence of a symmetrically bridging carbonyl ligand, the CO stretch at 1790 cm⁻¹ in the IR spectrum suggests the presence of some form of bridging carbonyl ligand, presumably that giving rise to the broad, low-field resonance at δ 181.2. However, since this resonance is broad and the ^{31}P resonances for **4** are quite close, as shown in Table 1, $^{13}C\{^{31}P\}\{^1H\}$ NMR experiments (using the ^{13}CO-enriched sample) do not give much information about the nature of the bridging interaction. The $^{13}C\{^1H\}$ NMR spectrum of **4**, prepared using ^{13}C-enriched acetylene, shows a doublet of quintets at δ 198.4 and a doublet at δ 123.5 ($^1J_{C-C} = 67.0$ Hz), due to the α- and β-carbon atoms of the bridging vinylidene ligand. In the ^1H NMR spectrum of this sample, the vinylidene proton resonances appear as doublets ($^1J_{C-H} = 160$ Hz for each of the protons). Although the carbon resonance at δ 198.4 is unusually high-field for a vinylidene α-carbon, it is very close to that of another vinylidene-bridged compound, $[Ir_2I_2(CO)_2(\mu\text{-}C\!=\!CH_2)(dppm)_2]$ (δ 194.3), previously characterized by an X-ray structure determination.[17a] In addition, the bridging vinylidene formulation for **4**, as shown in Scheme 1, is substantiated by $^{13}C\{^{31}P\}\{^1H\}$

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(22) Programs used were those of the Enraf-Nonius Structure Determination Package by B. A. Frenz, adapted for use on the SUN SPARC station 1⁺ by R. G. Ball, in addition to local programs by R. G. Ball.

(23) Cromer, D. T.; Waber, J. T. *International Tables for Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(24) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(25) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(26) IR spectra are of samples with natural abundance carbon.

(27) Compounds such as **3**, with an alkyne bridging two metals parallel to the metal−metal axis, are sometimes referred to as dimetalated olefin compound, in which case reference is made to the C=C stretch.

(28) See, for example: (a) Vaartstra, B. A. Ph.D. Thesis, University of Alberta, Edmonton, AB, 1989. (b) Mague, J. T. *Organometallics* **1986**, *5*, 918. (c) Mague, J. T.; Klein, C. L.; Majeste, R. J.; Stevens, E. D. *Organometallics* **1984**, *3*, 1860. (d) Cowie, M.; Dickson, R. S.; Hames B. W. *Organometallics* **1984**, *3*, 1879. (e) Puddephatt, R. J.; Thomson, M. A. *Inorg. Chem.* **1982**, *21*, 725. (f) Puddephatt, R. J.; Thomson, M. A. *Inorg. Chim. Acta* **1980**, *45*, L281.

(29) (a) Berry, D. H.; Eisenberg, R. *Organometallics* **1987**, *6*, 1796. (b) Berry, D. H.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 7181.

Scheme 1
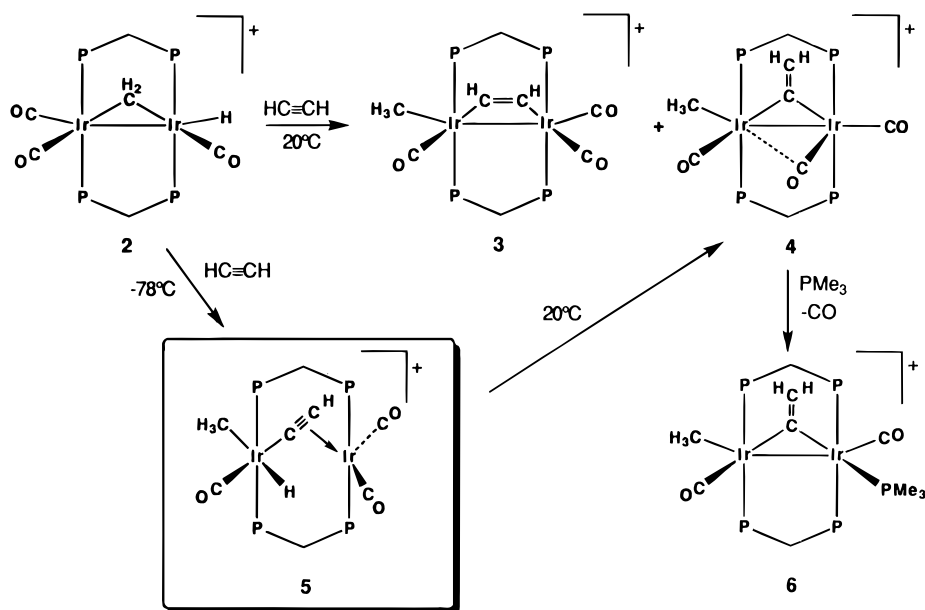
experiments (using the sample prepared with ^{13}C-enriched acetylene) that indicate that the α-carbon shows essentially equal coupling to all four phosphorus nuclei, whereas the β-carbon shows no phosphorus coupling. In this experiment, decoupling of either phosphorus resonance leads to the collapse of the signal at δ 198.4 into a doublet of triplets, while it collapses into a doublet upon broadband ^{31}P decoupling. The signal at δ 123.5 remains a doublet in all of these decoupling experiments, as expected. In samples that are ^{13}C-enriched at both the carbonyl and vinylidene carbon atoms, the carbonyl resonance at δ 175.1 shows strong coupling (23.3 Hz) to the vinylidene α-carbon nucleus, while the carbonyl resonance at δ 172.3 shows weaker coupling (13.0 Hz) to the same vinylidene carbon nucleus. This suggests a trans arrangement of the vinylidene α-carbon and one of the terminal CO ligands and an orientation with respect to the other terminal CO ligand that deviates significantly from trans.[17a] The ^{13}C{^{31}P}{^{1}H} and ^{1}H{^{31}P} NMR experiments show that the CO ligand that is trans to the vinylidene α-carbon is bound to the same metal as the methyl group, while the carbonyl group that shows a weaker coupling to the α-carbon is bound to the other metal, together with the third CO ligand.

When the reaction of compound **2** with acetylene is carried out at −78 °C, a hydrido−acetylide intermediate, [Ir$_2$(H)(CH$_3$)(CO)$_3$(μ-η^1:η^2-C≡CH)(dppm)$_2$][CF$_3$SO$_3$] (**5**), is observed, which is converted quantitatively to the vinylidene product **4** upon warming to room temperature. (In all schemes, intermediates observed only at low temperatures are highlighted within a box enclosure.) The ^{1}H NMR spectrum of compound **5** shows the acetylide proton resonance as a broad signal at δ 8.06, the methyl resonance as a triplet at δ −0.40, and the hydride resonance as a multiplet at δ −9.83. Selective ^{31}P decoupling experiments show that the methyl group and the hydride are terminally bound to the same metal. The ^{13}C{^{1}H} NMR spectrum of a ^{13}CO-enriched sample shows broad resonances at δ 181.8 and 179.1, as well as a triplet at δ 154.7, suggesting the presence of three terminal CO ligands, and the ^{13}C{^{1}H} NMR spectrum of a sample prepared using ^{13}C$_2$H$_2$ shows two doublets

of multiplets at δ 127.2 and 102.4 ($^1J_{C-C}$ = 55.3 Hz), which are assigned to the acetylide β- and α-carbons, respectively. These resonances are in a range similar to those of other acetylides.[30−32] Appropriate ^{13}C{^{1}H}-{^{31}P} NMR experiments show that the acetylide resonances are actually doublets of triplets of triplets, indicating that both acetylide ^{13}C nuclei couple to the phosphorus nuclei bound to both metals. However, the α-carbon shows stronger coupling to the phosphorus nuclei that are bound to the Ir bearing the methyl ligand than to the other set, while the β-carbon nucleus shows stronger coupling to the phosphorus nuclei on the other Ir. This suggests a σ,π-mode of coordination for the acetylide. The assignment of the α- and β-carbon resonances is based on the stronger P−C coupling that is assumed to occur with the σ-bound α-carbon. The proposed σ,π-coordination mode is consistent with the magnitude of the C−C coupling, which is close to that of the coordinated alkyne in compound **3** and other related compounds and substantially less than that expected for a triple bond.[17a] It is also consistent with the low-field signal of the acetylide hydrogen noted earlier. The ^{1}H NMR spectrum of the sample having the ^{13}C-enriched ligand shows the acetylide proton resonance as a broad doublet ($^1J_{C-H}$ ≈ 160 Hz). A trans orientation of the methyl and hydride ligands is proposed as the factor inhibiting methane loss, which does not occur upon warming **5**; instead, hydrogen transfer to the β-carbon of the acetylide ligand occurs to give the vinylidene-bridged product **4**.

Attempts to induce C−C coupling via migratory insertion of the vinylidene and methyl groups in compound **4** by reaction with PMe$_3$ instead resulted in the substitution of a CO by PMe$_3$ to give [Ir$_2$-(CH$_3$)(CO)$_2$(PMe$_3$)(μ-C=CH$_2$)(dppm)$_2$][CF$_3$SO$_3$] (**6**). The

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Table 1. Spectroscopic Data for the Compounds[a]

compound	IR[b,c] (cm^{-1})	δ(^{31}P{^{1}H})[e]	δ(^{1}H)[f,g]	δ(^{13}C{^{1}H})
[Ir$_2$(CH$_3$)(CO)$_3$(μ-C$_2$H$_2$)(dppm)$_2$][CF$_3$SO$_3$] (**3**)	2007(s), 1970(vs), 1911(b), 1632(med)[j]	11.4(m), −19.9(m)	10.25(m, 1H), 9.15 (m, 1H), 4.20(m, 2H), 3.18(m, 2H), −0.14(b, 3H)	198.7(b, CO),194.4(t, CO), 181.3(b, CO),160.7(dm, $^1J_{C-C}$ = 50.8 Hz), 147.1(dm)
[Ir$_2$(CH$_3$)(CO)$_3$(μ-C=CH$_2$)(dppm)$_2$][CF$_3$SO$_3$] (**4**)	2004(s), 1964(vs), 1790(s)	−1.0(m), −6.5(m)	6.40(s, 1H), 5.72(s, 1H), 3.90(m, 2H), 2.93(m, 2H), −0.55(t, 3H)	198.4(dm, $^1J_{C_\alpha-C_\beta}$ = 67.0 Hz), 181.2(b, CO), 175.1(t, CO), 172.3(t, CO), 123.5(d, C$_\beta$)
[Ir$_2$(H)(CH$_3$)(CO)$_3$(μ-η^1:η^2-C≡CH)(dppm)$_2$][CF$_3$SO$_3$] (**5**)		−13.1(m), −26.8(m)	8.06(b, 1H), 4.67(m, 2H), 4.03(m, 2H), −0.40(t, 3H), −9.83(m, 1H)	181.8(b, CO), 179.1(b, CO), 154.7(t, CO), 127.2(dm, C≡CH, $^1J_{C-C}$ = 55.3 Hz, $^2J_{P-C}$ = 13.6 Hz), 102.4(dm, C≡CH, $^2J_{P-C}$ = 11.2 Hz)
[Ir$_2$(CH$_3$)(CO)$_2$(PMe$_3$)(μ-C=CH$_2$), (dppm)$_2$][CF$_3$SO$_3$] (**6**)[h]	2010(s), 1971(vs)[d]	−12.6(m), −19.3(m), −76.9(b)	6.49(b, 2H), 6.10(d,b, 2H), $^4J_{P-H}$ = 9.0 Hz), 0.01(t, 3H)	184.3(t, 1C), 183.8(dt, $^2J_{P-C}$ = 15.0 Hz)
[Ir$_2$(CH$_3$)(CO)$_3$(μ-PhC$_2$H)(dppm)$_2$][CF$_3$SO$_3$] (**7**)	2011(vs), 1970(vs), 1785(w), 1640(med)[j]	13.8(m), −21.6(m)	9.51(m, 1H), 4.08(m, 2H), 3.08(m, 2H), 0.02(b, 3H)	198.7(b, 1C), 191.5(t, 1C), 182.9(b,1C)
[Ir$_2$(CH$_3$)(CO)$_3$(μ-C=C(H)Ph)(dppm)$_2$][CF$_3$SO$_3$] (**8**)	1960(vs), 1920(sh), 1780(s), 1655(w)[j]	−2.6(m), −8.0(m)	3.91(m, 2H), 2.70(m, 2H), −0.58(t, 3H)	182.9(b, 1C), 179.6(t, 1C), 168.0(t, 1C)
[RhIr(CH$_3$)(CO)$_3$(μ-C$_2$H$_2$)(dppm)$_2$][CF$_3$SO$_3$] (**9**)		22.1(dm, $^1J_{Rh-P}$ = 151.1 Hz), −0.3(m)	9.12(dt, $^1J_{Rh-H}$ = 6.4 Hz, 1H), 7.63(m, 1H), 4.35(m, 2H), 2.83(m, 2H), −1.00(t, 3H)	210.2(dt, $^1J_{Rh-C}$ = 19.0 Hz, CO), 191.0(dt, $^1J_{Rh-C}$ = 55.3 Hz, CO), 172.8(t, CO), 162.9(dm, $^1J_{Rh-C}$ = 20.6 Hz), 147.0(dm, $^1J_{C-C}$ = 53.0 Hz)
[RhIr(CH$_3$)(CO)$_3$(HC=C(H)P(Ph)$_2$CH$_2$PPh$_2$)(dppm)][CF$_3$SO$_3$] (**10**)	2056(s), 2017(vs), 1975(s)	29.9(m), 18.1(ddd, $^1J_{Rh-P}$ = 152 Hz), −11.7(m), −22.6(m)	8.58(t, 1H), 5.60(dm, $^3J_{P-H}$ = 40.0 Hz, 1H), 4.12(m, 1H), 3.95(m, 1H), 3.72(m, 1H), 2.88(m, 1H), 0.46(t, 3H)	191.1(dm, $^1J_{Rh-C}$ = 45.1 Hz, CO), 186.4(dm, $^1J_{Rh-C}$ = 63.9 Hz, CO), 171.5(m, CO), 42.1(dm, $^1J_{Rh-C}$ = 8.4 Hz, $^1J_{C-C}$ = 36.5, IrC=C), 33.1(dm, $^1J_{P-C}$ = 76.0 Hz, $^1J_{Ir-C}$ = 11.8 Hz, C=CP)
[RhIr(μ-η^1:η^2-C≡CPh)(CO)$_3$(dppm)$_2$][CF$_3$SO$_3$] (**11**)[h]	2000(sh), 1955(s), 1825(m)	26.6(dm, $^1J_{Rh-P}$ = 94.2 Hz), −6.0(m)	3.82(m, 2H), 3.32(m, 2H)	196.0(dm, $^1J_{Rh-C}$ = 22.1 Hz, 1C), 194.6(dt, $^1J_{Rh-C}$ = 80.3 Hz, 1C), 181.7(t, 1C)
[RhIr(C≡CPh)$_2$(CO)$_2$(μ-H)(dppm)$_2$][CF$_3$SO$_3$] (**12**)	2134(w), 2090(s),[k] 2015(med), 1958(vs)	24.1(dm, $^1J_{Rh-P}$ = 106.1 Hz), −22.7(m)	4.12(m, 2H), 3.49(m, 2H), −8.70(m, $^1J_{Rh-H}$ = 12.7 Hz, 1H)	191.1(dt, $^1J_{Rh-C}$ = 82.5 Hz), 162.7(t, 1C)
[RhIr(H)(CH$_3$)(CO)$_3$(μ-η^1:η^2-C≡Ph)(dppm)$_2$][CF$_3$SO$_3$] (**13**)		24.2(dm, $^1J_{Rh-P}$ = 102.7 Hz), −13.6(m)	4.00(m, 2H), 3.22(m, 2H), 0.33(t, 3H), −8.87(t, 1H)	193.1(b, 1C), 192.8(dt, $^1J_{Rh-C}$ = 80.5 Hz, 1C), 186.0(dt, $^1J_{Rh-C}$ = 72 Hz, 1C)
[RhIr(CH$_3$)(CO)$_3$(HC$_2$Ph)(dppm)$_2$][CF$_3$SO$_3$] (**14**)[h]		20.1(dm, $^1J_{Rh-P}$ = 123.3 Hz), −18.2(m)	8.53(t, 1H), 4.10(m, 2H), 3.33(m, 2H), 0.27(b, 3H)	200.6(dm, $^1J_{Rh-C}$ = 5.0 Hz, 1C), 193.8(dt, $^1J_{Rh-C}$ = 54.3 Hz, 1C), 180.8(b,1C)
[RhIr(H)(CH$_3$)(CO)$_2$(μ-C=CPh)(dppm)$_2$][CF$_3$SO$_3$] (**15**)		19.0(dm, $^1J_{Rh-P}$ = 160 Hz), 0.5(m)	−0.52(s ,3H), −8.75((t, 1H)	197.0(dt, $^1J_{Rh-C}$ = 56 Hz), 168.6(t)
[RhIr(RC=C(CH$_3$)R)(CO)$_3$(dppm)$_2$][CF$_3$SO$_3$] (**16**)[h] (R = CO$_2$Me)	2022(s), 1995(sh), 1720(sh), 1698(b),[i] 1641(med)[j]	16.8(dm, $^1J_{Rh-P}$ = 119.9 Hz), −19.4(m)	4.35(m,2H), 3.65(m, 2H), 3.33(s, 3H, OCH$_3$), 2.22(s, 3H, OCH$_3$), 0.81(s, 3H, CH$_3$)	197.9(dm, $^1J_{Rh-C}$ = 4.0 Hz, 1C), 194.4(dt, $^1J_{Rh-C}$ = 55.3 Hz, 1C), 176.8(t, 1C)
[Ir$_2$(RC=C(CH$_3$)R)(CO)$_3$(dppm)$_2$][CF$_3$SO$_3$] (**17**)[h] (R = CO$_2$Me)	2015(vs), 1998(sh), 1717(sh), 1695(b),[i] 1642(med)[j]	7.5(m), −21.8(m)	4.43(m, 2H), 3.60(m, 2H), 3.27(s, 3H, OCH$_3$), 2.23(s, 3H, OCH$_3$), 0.68(s, 3H, CH$_3$)	194.7(b, 1C), 192.0(t, 1C), 179.5(t, 1C)
[Ir$_2$(CH$_3$)(CO)$_3$(μ-DMAD)(dppm)$_2$][CF$_3$SO$_3$] (**18**)	2029(s), 2001(vs), 1982(vs), 1690(b),[i] 1635(med)[j]	−10.7(m), −28.9(m)	4.78(m, 2H), 4.25(m, 2H), 3.45(s, 3H, OCH$_3$), 2.13(s, 3H, OCH$_3$), −0.52(t, 3H, CH$_3$)	182.2(t, 1C), 175.9(t, 1C), 152.5(t, 1C)

[a] Abbreviations used: med, medium; s, strong; vs, very strong; d, doublet; t, triplet; m, multiplet; dt, doublet of triplets; dm, doublet of multiplets; b, broad. [b] Nujol mull on KBr disk unless otherwise stated. [c] Values are ν(CO) unless otherwise noted. [d] IR in CH$_2$Cl$_2$. [e] Vs 85% H$_3$PO$_4$, −40 °C in CD$_2$Cl$_2$ solvent unless otherwise stated. [f] Vs TMS, −40 °C in CH$_2$Cl$_2$. [g] Resonances for dppm phenyl group protons appear in the range δ 6.90−8.10 for all compounds. [h] NMR data at 25 °C. [i] ν(CO) of DMAD. [j] ν(C=C). [k] ν(C≡C).

**Table 2. Crystallographic Data for
$[RhIr(C{\equiv}CPh)_2(CO)_2(\mu\text{-}H)(dppm)_2][CF_3SO_3]\cdot2CH_2Cl_2$
(12)**

formula	$C_{71}H_{59}Cl_4F_3IrO_5P_4RhS$
formula weight	1642.14
crystal shape	monoclinic prism
crystal dimensions (mm)	$0.39 \times 0.47 \times 0.62$
space group	$P2_1/c$ (No. 14)
temperature (°C)	22
radiation (λ, Å)	graphite-monochromated Mo Kα (0.710 69)
unit cell parameters	
a (Å)	17.821(3)
b (Å)	24.780(5)
c (Å)	17.892(3)
β (deg)	117.56(1)
V (Å^3)	7004(2)
Z	4
ρ(calcd) (g cm^{-3})	1.557
linear absorption coefficient (μ) (cm^{-1})	24.497
range of transmission factors	0.884–1.095
detector aperture (mm)	$(3.00 + \tan\theta)$ wide $\times$ 4.00 high
take-off angle (deg)	3.0
maximum 2θ (deg)	50.0
crystal–detector distance (mm)	173
scan type	$\theta/2\theta$
scan rate (deg/min)	between 1.43 and 6.71
scan width (deg)	$0.60 + 0.347 \tan\theta$
total unique reflections	12 976 ($+h, +k, \pm l$)
total observations (NO)	8365 ($F_o^2 \geq 3\sigma(F_o^2)$)
final no. params varied (NV)	575
error in obs of unit weight (GOF)^a	2.544
R^b	0.064
$R_w{}^c$	0.083

^{a} GOF = $[\sum\omega(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where $\omega = 4F_o^2/\sigma^2(F_o^2)$. ^{b} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{c} $R_w = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega F_o^2]^{1/2}$.

spectroscopic data for compound **6**, given in Table 1, are consistent with the assigned structure shown in Scheme 1.

The reaction of compound **2** with phenylacetylene also occurs readily, yielding a mixture of the alkyne- and phenylvinylidene-bridged products $[Ir_2(CH_3)(CO)_3(\mu\text{-}PhC_2H)(dppm)_2][CF_3SO_3]$ (**7**) and $[Ir_2(CH_3)(CO)_3(\mu\text{-}C{=}C(H)Ph)(dppm)_2][CF_3SO_3]$ (**8**), which are analogous to those obtained in the reaction with acetylene. Their structural assignments (see Scheme 2) are largely based on their NMR data, which resemble those of **3** and **4**. The ^{1}H NMR spectrum of compound **7** shows the proton resonance of the coordinated alkyne as a multiplet at δ 9.51 and the methyl resonance as a broad signal at δ 0.02. The $^{13}C\{^1H\}$ NMR spectrum[33] shows two broad carbonyl resonances at δ 198.7 and 182.9, as well as a triplet at δ 191.5, and the IR spectrum shows CO stretches at 2011, 1970, and 1785 cm^{-1}, suggesting that one CO ligand is semibridging. The peak at 1640 cm^{-1} in the IR spectrum is assigned to the C$\equiv$C stretch of the coordinated phenylacetylene and is consistent with the alkyne lying parallel to the metal–metal axis. The orientation of the alkyne, in terms of which metal the phenyl substituent is closer to, is assigned on the basis of steric arguments, with the bulky phenyl group lying closer to the less cluttered metal. This could not be determined from the NMR spectra; even NOE experiments did not yield information on this orientation.

The ^{1}H NMR spectrum of compound **8** shows the methyl resonance as a triplet at δ −0.58, but does not

(33) $^{13}C\{^1H\}$ NMR spectra are of ^{13}CO-enriched samples, unless otherwise stated.

**Table 3. Positional and Thermal Parameters for
the Atoms of
$[RhIr(C{\equiv}CPh)_2(CO)_2(\mu\text{-}H)(dppm)_2][CF_3SO_3]\cdot2CH_2Cl_2$
(12)^a**

| atom	x	y	z	B (Å^2)^b
Ir	0.24240(2)	0.15084(2)	0.26946(2)	2.59(1)*
Rh	0.25265(5)	0.24799(4)	0.37922(5)	2.72(2)*
P(1)	0.0983(2)	0.1483(1)	0.2297(2)	3.01(8)*
P(2)	0.1071(2)	0.2550(1)	0.3192(2)	2.97(8)*
P(3)	0.3900(2)	0.1508(1)	0.3387(2)	2.70(7)*
P(4)	0.3966(2)	0.2575(1)	0.4269(2)	2.83(8)*
O(1)	0.2204(6)	0.1164(4)	0.0946(5)	6.2(3)*
O(4)	0.2728(6)	0.2845(4)	0.5454(5)	6.2(3)*
C(1)	0.2273(7)	0.1331(5)	0.1573(8)	4.1(4)*
C(2)	0.2420(6)	0.0690(4)	0.2826(6)	3.0(3)*
C(3)	0.2376(6)	0.0214(4)	0.2758(6)	3.1(3)*
C(4)	0.2631(7)	0.2701(5)	0.4781(7)	3.8(3)
C(5)	0.2417(6)	0.2323(4)	0.2520(5)	2.9(3)*
C(6)	0.2450(6)	0.2809(5)	0.2429(6)	3.6(3)*
C(7)	0.0557(6)	0.2165(5)	0.2210(6)	2.8(3)*
C(8)	0.4330(6)	0.2182(4)	0.3632(6)	2.7(3)*
C(91)	0.2321(6)	−0.0361(4)	0.2632(7)	3.5(3)*
C(92)	0.2663(9)	−0.0616(5)	0.2173(8)	6.1(5)*
C(93)	0.261(1)	−0.1156(7)	0.206(1)	8.7(6)*
C(94)	0.222(1)	−0.1451(6)	0.241(1)	9.7(8)*
C(95)	0.188(1)	−0.1225(6)	0.279(1)	9.3(8)*
C(96)	0.1955(9)	−0.0689(6)	0.293(1)	6.2(5)*
C(101)	0.2554(6)	0.3365(4)	0.2181(6)	2.7(3)*
C(102)	0.2811(8)	0.3414(5)	0.1565(8)	5.2(4)*
C(103)	0.291(1)	0.3895(7)	0.1279(8)	7.3(5)*
C(104)	0.273(1)	0.4336(6)	0.162(1)	8.7(6)*
C(105)	0.247(1)	0.4296(5)	0.220(1)	8.4(6)*
C(106)	0.2389(9)	0.3807(6)	0.2482(9)	7.4(5)*

^{a} Numbers in parentheses are estimated standard deviations in the least significant digits in this and all subsequent tables. ^{b} Starred B values are for atoms refined anisotropically. Displacement parameters for the anisotropically refined atoms are given in the form of the equivalent isotropic Gaussian displacement parameter, defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. Atoms of the triflate anion, the solvent molecules, and the phenyl groups of the dppm ligands are given as supporting information.

Scheme 2
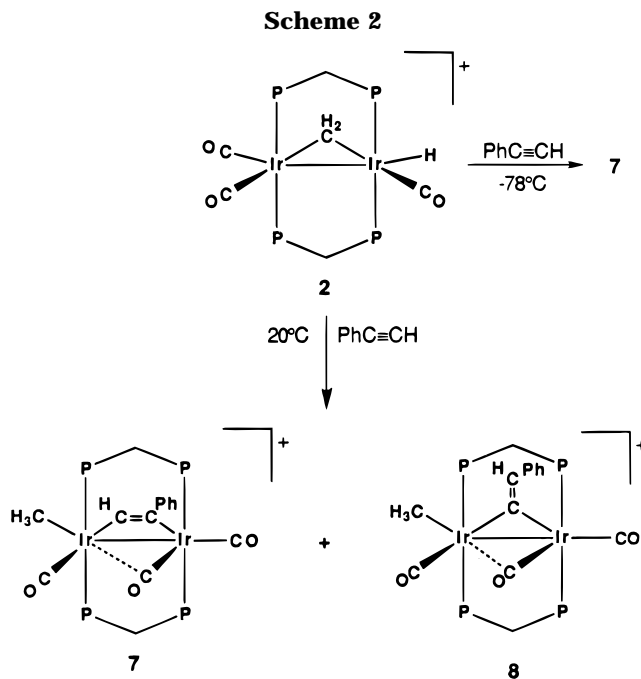
show the vinylidene proton resonance, which is presumably obscured by the phenyl resonances. The $^{13}C\{^1H\}$ NMR spectrum shows a broad resonance at δ 182.9 and two triplets at δ 179.6 and 168.0 for the three carbonyls, while the IR spectrum shows CO stretches at 1960,

Scheme 3
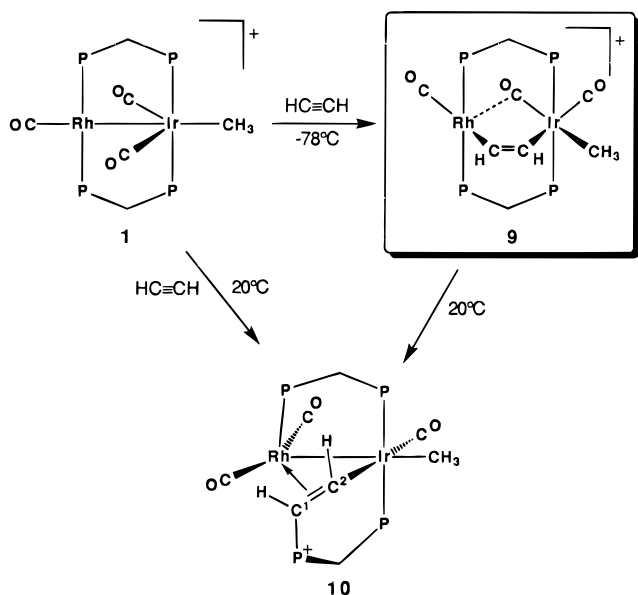
1920, and 1780 cm^{-1}, indicating the presence of two terminally bound CO ligands and a third one that is presumed to be semibridging. The IR spectrum of **8** also shows a low-intensity peak at 1655 cm^{-1}, which is assigned to the C=C stretch of the vinylidene. The orientation of the vinylidene ligand shown, having the hydrogen adjacent to the methyl group, again is proposed on steric grounds.

In contrast to the chemistry of compound **2** with acetylene, the reaction with phenylacetylene at -78 °C, followed by warming to room temperature, does not yield the phenylvinylidene product **8**. Instead, the alkyne-bridged product **7** is obtained. When this reaction is monitored by NMR at low temperature, only compounds **2** and **7** are observed.

The closely related mixed-metal species, [RhIr-(CH$_3$)(CO)$_3$(dppm)$_2$][CF$_3$SO$_3$] (**1**), also reacts with acetylene, as shown in Scheme 3. But in this case, the reaction proceeds very differently from that involving **2**, yielding instead [RhIr(CH$_3$)(CO)$_3$(HC=C(H)P(Ph)$_2$CH$_2$-PPh$_2$)(dppm)][CF$_3$SO$_3$] (**10**), the unusual product of formal insertion of acetylene into one of the Rh–P bonds of **1**. The ^{31}P NMR spectrum of compound **10** shows a pattern diagnostic of an ABCDX spin system in which only one of the phosphorus nuclei shows strong coupling to Rh, consistent with a direct Rh–P bond. This spectrum displays a multiplet at δ 29.9 (showing a maximum coupling of about 9 Hz), a doublet of doublets at δ 18.1 for the Rh-bound P nucleus ($^1J_{Rh-P} = 152.0$ Hz, $^2J_{P-P} = 48.0$ Hz), and two doublets of doublets at δ -11.7 ($^2J_{P-P} = 406.0$ Hz, $^2J_{P-P} = 9.3$ Hz) and -22.6 ($^2J_{P-P} = 406.0$ Hz, $^2J_{P-P} = 48.0$ Hz). The last two resonances are due to the phosphorus nuclei bound to Ir, and the large coupling between them shows that they maintain a trans orientation with respect to each other.[34] The ^{1}H NMR spectrum of compound **10** shows one proton resonance of the inserted acetylene as an apparent triplet at δ 8.58 ($^3J_{H-H} \approx {}^2J_{P-H} \approx 6.5$ Hz) and the other as a doublet of multiplets at δ 5.60 ($^3J_{P-H} \approx$

40.0 Hz). These resonances are assigned to H^1 and H^2, respectively (see Scheme 3 for the numbering scheme; acetylenic protons have the same number as their attached carbon), on the basis of the coupling constants. The magnitude of the P–H coupling displayed by the latter resonance suggests that the unsaturated ligand in **10** has a trans configuration of H^2 and phosphorus, as shown.[35] The methyl resonance appears as a triplet at δ 0.46, while the four dppm protons, which are all inequivalent, give rise to multiplets at δ 4.12, 3.95, 3.72, and 2.88. The ^{13}C{^{1}H} NMR spectrum of a ^{13}CO-enriched sample of compound **10** shows two doublets of multiplets at δ 191.1 ($^1J_{Rh-C} = 45.1$ Hz) and 186.4 ($^1J_{Rh-C} = 63.9$ Hz) and a multiplet at δ 171.5. Although the Rh–C coupling constant for the low-field resonance is smaller than expected for a CO ligand that is terminally bound to Rh, the IR spectrum of compound **10** shows stretches at 2056, 2017, and 1975 cm^{-1}, none of which is in the range typical for symmetrically bridging or semibridging CO ligands. The possibility that this coupling of 45.1 Hz was due to carbon–carbon coupling between two CO ligands, as was proposed for [RhIr(CO)$_2$(μ-CO)(μ-DMAD)(dppm)$_2$][BF$_4$],[15i] was rejected since neither of the other two CO resonances shows coupling of this magnitude.

The ^{13}C{^{1}H} NMR spectrum of **10**, prepared using ^{13}C-enriched acetylene, shows a doublet of multiplets at δ 42.1 ($^1J_{C-C} = 36.5$ Hz, $^1J_{Rh-C} = 8.4$ Hz) and a doublet of doublets of multiplets at δ 33.1 ($^1J_{P-C} = 76.0$ Hz, $^1J_{C-C} = 36.5$ Hz, $^1J_{Rh-C} = 11.8$ Hz). The latter resonance is assigned to C^1, the carbon atom of the inserted acetylene that is directly bound to one of the phosphorus atoms, because it shows a large P–C coupling, while the former resonance is assigned to C^2. These ^{13}C NMR chemical shift values for C^1 and C^2 are close to those of the coordinated olefins in [Rh(C$_2$H$_4$)-Cl(P(p-tolyl)$_3$)$_2$] (δ 44.6),[36] [Rh(acac)(C$_2$H$_4$)$_2$] (δ 39.6),[37] [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] (δ 36.3),[37] and [Pt(C$_2$H$_4$)$_2$(PMePh$_2$)] (δ 36.3, 42.0),[38] while the Rh–C coupling constants (for both C^1 and C^2) compare well with values in the range of 10–16 Hz observed for the olefinic carbon nuclei in related Rh–olefin complexes.[36,38,39] In the ^{31}P{^{1}H} NMR spectrum of the ^{13}C$_2$H$_2$-enriched sample of compound **10**, the resonance at δ 29.9 shows an additional coupling of 76.0 Hz, which is consistent with it being directly bound to C^1. Also, the ^{1}H NMR spectrum of this sample shows the resonances for H^1 and H^2 as a doublet of triplets ($^1J_{C-H} = 131$ Hz) and a doublet of doublets of multiplets ($^1J_{C-H} \approx 148$ Hz), respectively. These C–H coupling constants are lower than those expected for sp^2-hybridized carbon atoms[40,41] and suggest a change in hybridization of the carbon atoms of the inserted

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(35) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon Press: Oxford, 1969; p 352.

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(38) Harrison, N. C.; Murray, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1337.

(39) See, for example: (a) Mann, B. E.; Taylor, B. F. *^{13}C Data for Organometallic Compounds*; Academic Press: London, 1981; p 188. (b) Bodner, G. M.; Storhoff, B. N.; Doddrell, D.; Todd, L. J. *J. Chem. Soc., Chem. Commun.* **1970**, 1530. (c) Jesse, A. C.; Gijben, H. P.; Stufkens, D. J.; Vrieze, K. *Inorg. Chim. Acta* **1978**, *31*, 203. (d) Maisonnat, A.; Poilblanc, R. *Inorg. Chim. Acta* **1978**, *29*, 203.
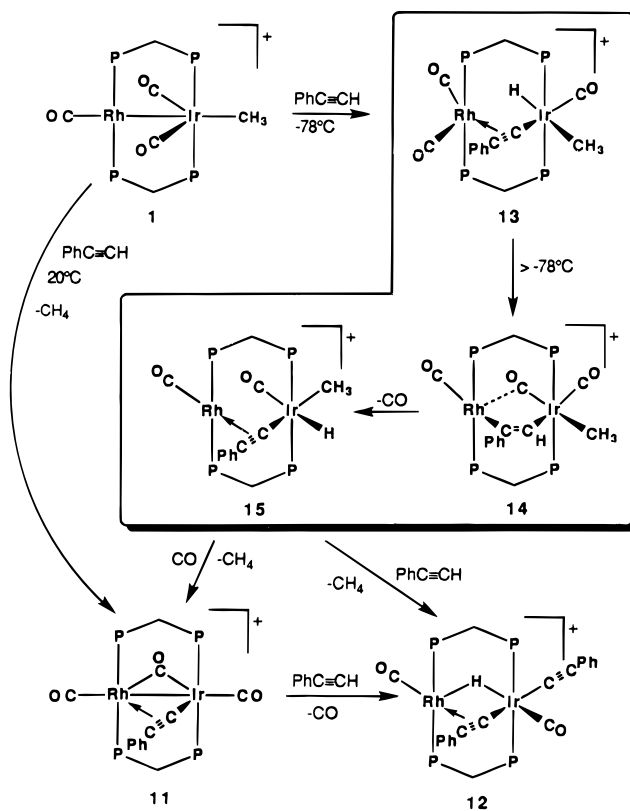
(40) Kegley, S. E.; Pinhas, A. R. *Problems and Solutions in Organometallic Chemistry*; University Science Books: Mill Valley, CA, 1986; p 11.

acetylene in compound **10** toward sp³. Moreover, the C–C coupling constant ($^1J_{C-C} = 36.5$ Hz) is significantly lower than that expected for carbon atoms linked by a C=C double bond between sp² carbons, such as those of the coordinated alkynes (resulting in dimetalated olefins) in compounds **3** and **9** (*vide infra*), and is close to that of ethane (34.6 Hz).[41] On the basis of these observations, it is proposed that there is interaction of the C=C bond of the inserted acetylene with Rh as shown, reducing the C=C bond order. All of the NMR data are consistent with the structure proposed for compound **10**, as shown in Scheme 3. In addition, this structure is reminiscent of that determined for [CpRh-(μ-η^1:η^2-HC=C(H)PMe₃)(μ-CO)Os(CO)₃],[42] which resulted from migration of a PMe₃ ligand from Rh to a bridging acetylene moiety, much as proposed here for one of the dppm ligands (*vide infra*). Although formulation of a structure for **10** is not unambiguous, we favor one in which Rh has a tetrahedral ligand geometry, reminiscent of a [Rh(CO)₂(olefin)PR₃]⁻ fragment, and Ir has an octahedral geometry. The sixth coordination site at the latter metal is occupied by a Rh–Ir bond. This geometry at Rh is not unlike that at one of the metal centers in the related mixed-valence species [MM′(CO)₃(dppm)₂] (M,M′ = Rh, Ir),[43] and is favored over a square-planar geometry, for which model building could not easily accommodate binding of Rh to the olefinic fragment within the 6-membered iridacycle. Unfortunately, suitable single crystals of compound **10** could not be obtained due to facile decomposition.

Although the final product in the reaction of acetylene with compound **1** is vastly different from those obtained in the reaction with compound **2**, an analogous alkyne-bridged intermediate [RhIr(CH₃)(CO)₃(μ-HC₂H)(dppm)₂]-[CF₃SO₃] (**9**) is observed at −78 °C. This intermediate is converted to **10** upon warming to room temperature. Characterization of **9** by NMR was relatively straightforward. Its ¹H NMR spectrum shows the proton resonances of the coordinated acetylene as a doublet of triplets at δ 9.12 ($^2J_{Rh-H} = 6.4$ Hz) and a multiplet at δ 7.63 and the methyl resonance as a triplet at δ −1.00. The ¹³C{¹H} NMR spectrum of a sample prepared with ¹³C₂H₂ shows the carbon resonances of the coordinated acetylene as a doublet of doublets of multiplets at δ 162.9 ($^1J_{Rh-C} = 20.6$ Hz, $^1J_{C-C} = 53.0$ Hz) and a doublet of multiplets at δ 147.0 (coupling to the phosphorus nuclei was complex in both cases). Selective ³¹P decoupling experiments indicate that each carbon nucleus shows larger coupling to a different set of phosphorus nuclei. The chemical shifts of the carbon nuclei of the coordinated acetylene in compound **9** are very close to those of **3** (δ 160.7 and 147.1), and this observation, together with the fact that only one of the carbon nuclei of the coordinated acetylene in **9** shows coupling to Rh, is consistent with the assignment of an acetylene ligand bridging the two metals. The ¹H NMR spectrum of this sample shows the proton resonances of the coordinated acetylene as a doublet of doublets of triplets and a doublet of multiplets ($^1J_{C-H} \approx 152$ Hz for each of the

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(42) Takats, J.; Washington, J.; Santarsiero, B. D. *Organometallics* **1994**, *13*, 1078.
(43) (a) Woodcock, C.; Eisenberg, R. *Inorg. Chem* **1985**, *24*, 1285. (b) McDonald, R; Cowie, M. *Inorg. Chem.* **1990**, *29*, 1564.
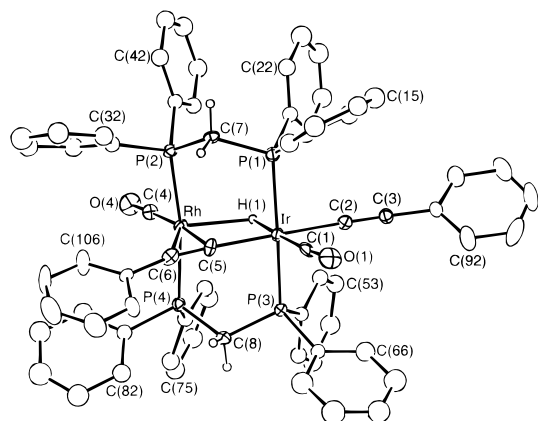
Scheme 4

protons). The ¹³C{¹H} NMR spectrum of a ¹³CO-enriched sample shows a doublet of multiplets at δ 210.2 ($^1J_{Rh-C} = 19.0$ Hz), a doublet of triplets at δ 191.0 ($^1J_{Rh-C} = 55.3$ Hz), and a triplet at δ 172.8, indicating the presence of one semibridging carbonyl ligand (inferred from the Rh–C coupling of 19 Hz[18]) and a terminally bound carbonyl ligand each on Rh and Ir. The transformation of **9** to **10** can be seen as resulting from dissociation of the Rh-bound end of a diphosphine, followed by nucleophilic attack by this phosphorus at the Rh end of the bridged alkyne.

The reaction of compound **1** with phenylacetylene again differs from any of the previous reactions of compound **1** or **2** with acetylene or of **2** with phenylacetylene. At room temperature, compound **1** reacts with 1 equiv of phenylacetylene to give the monoacetylide product [RhIr(CO)₃(μ-η^1:η^2-C≡CPh)(dppm)₂][CF₃-SO₃] (**11**), accompanied by methane loss, whereas with excess phenylacetylene it gives the diacetylide–hydride product [RhIr(C≡CPh)₂(CO)₂(μ-H)(dppm)₂][CF₃SO₃] (**12**), with the evolution of methane and CO (see Scheme 4). The ¹H NMR spectrum of compound **11** shows only dppm methylene proton resonances as multiplets at δ 3.82 and 3.32, apart from the phenyl and solvent resonances, which is consistent with the loss of methane at some stage in the formation of this compound. The ¹³C{¹H} NMR spectrum of a ¹³CO-enriched sample shows a doublet of multiplets at δ 196.0 ($^1J_{Rh-C} = 22.1$ Hz), a doublet of triplets at δ 194.6 ($^1J_{Rh-C} = 80.3$ Hz), and a triplet at δ 181.7, indicating the presence of a bridging CO ligand and a terminally bound CO ligand on each metal. The peak at 1825 cm⁻¹ in the IR spectrum is consistent with a bridging CO, while those at 2000 and 1955 cm⁻¹ arise from the two terminally bound CO ligands. The presence of the acetylide ligand is inferred from the disappearance of the methyl group

Figure 1. ORTEP diagram of the complex cation [RhIr-(C₂Ph)(CO)₂(μ-H)(μ-C₂Ph)(dppm)₂]⁺ (**12**) showing the numbering scheme. Thermal parameters are shown at the 20% level except for hydrogens, which are either omitted or shown artificially small. Numbering of the phenyl carbons starts at the ipso carbon and works sequentially around the ring.

of **1** and the formation of **12** upon reaction with an additional equivalent of phenylacetylene (the acetylide stretch could not be unambiguously assigned in the IR spectrum of **11**).

The ¹H NMR spectrum of compound **12** shows the hydride resonance as a multiplet at δ −8.70. Selective and broadband ³¹P decoupling experiments show that this signal is actually a doublet of triplets of triplets ($^1J_{Rh-H}$ = 12.7 Hz, $^2J_{P(Ir)-H}$ = 12.0 Hz, $^2J_{P(Rh)-H}$ = 3.3 Hz) and the magnitudes of the two P−H coupling constants show that the hydride ligand couples more strongly to the Ir-bound phosphorus nuclei than to those bound to Rh. This observation, together with the relatively small Rh−H coupling constant,[44] suggests that the hydride ligand interacts more strongly with Ir than with Rh. The ¹³C{¹H} NMR spectrum shows a doublet of triplets at δ 191.1 ($^1J_{Rh-C}$ = 82.5 Hz) and a triplet at δ 162.7, indicating the presence of a terminal CO ligand each on Rh and Ir. The IR spectrum shows CO stretches at 2015 and 1958 cm⁻¹, as well as stretches at 2134 and 2090 cm⁻¹, assigned to the C≡C stretches of the two acetylide ligands. Although the NMR data do not unambiguously establish the structure of compound **12**, the structure shown in Scheme 4 was established by an X-ray structure determination.

Figure 1 shows a perspective view of the cation of compound **12**, with the dppm ligands bridging the metal nuclei in a typical manner. Relevant bond lengths and angles are given in Tables 4 and 5. While both molecules of CH₂Cl₂ of crystallization are disordered, the triflate anion is well-behaved. The diphosphine groups are oriented approximately trans to each other about the metal centers [P(1)−Ir−P(3) = 167.53(6)° and P(2)−Rh−P(4) = 168.61(7)°] and are both cis to the other atoms coordinated to the metal nuclei. The geometry about Rh is tetragonal-pyramidal (with the hydride ligand occupying the apical site), if the interaction between this metal and the acetylide C≡C bond is considered to occupy one of the basal coordination sites, while the CO and the two dppm phosphines occupy the other sites. About Ir, the geometry is approximately octahedral. The hydride ligand was not refined, but was

(44) Vaartstra, B. A.; Cowie, M. *Inorg. Chem.* **1989**, *28*, 3138.

Table 4. Selected Distances (Å) in [RhIr(C≡CPh)₂(CO)₂(μ-H)(dppm)₂][CF₃SO₃]·2CH₂Cl₂ (12)

(a) Bonded			
Ir−P(1)	2.326(2)	P(2)−C(31)	1.822(8)
Ir−P(3)	2.332(2)	P(2)−C(41)	1.801(8)
Ir−C(1)	1.95(1)	P(3)−C(8)	1.805(7)
Ir−C(2)	2.042(7)	P(3)−C(51)	1.824(7)
Ir−C(5)	2.041(8)	P(3)−C(61)	1.815(8)
Ir−H(1)	1.69ᵃ	P(4)−C(8)	1.831(7)
Rh−P(2)	2.310(2)	P(4)−C(71)	1.818(8)
Rh−P(4)	2.310(2)	P(4)−C(81)	1.801(8)
Rh−C(4)	1.778(8)	O(1)−C(1)	1.15(1)
Rh−C(5)	2.228(6)	O(4)−C(4)	1.190(9)
Rh−C(6)	2.515(7)	C(2)−C(3)	1.185(9)
Rh−H(1)	2.07ᵃ	C(3)−C(91)	1.44(1)
P(1)−C(7)	1.830(7)	C(5)−C(6)	1.22(1)
P(1)−C(11)	1.811(7)	C(6)−C(101)	1.49(1)
P(1)−C(21)	1.827(8)		
P(2)−C(7)	1.829(7)		

(b) Nonbonded			
Ir−Rh	3.0582(8)	P(3)−P(4)	3.053(3)
P(1)−P(2)	3.056(3)		

ᵃ Ir−H(1) and Rh−H(1) distances are approximate since the H(1) position was not refined.

Table 5. Selected Angles (deg) in [RhIr(C≡CPh)₂(CO)₂(μ-H)(dppm)₂][CF₃SO₃]·2CH₂Cl₂ (12)

P(1)−Ir−P(3)	167.53(6)	Rh−P(2)−C(31)	111.1(3)
P(1)−Ir−C(1)	94.1(2)	Rh−P(2)−C(41)	120.5(2)
P(1)−Ir−C(2)	86.9(2)	C(7)−P(2)−C(31)	104.1(3)
P(1)−Ir−C(5)	93.0(2)	C(7)−P(2)−C(41)	103.9(3)
P(1)−Ir−H(1)	83ᵃ	C(31)−P(2)−C(41)	104.4(4)
P(3)−Ir−C(1)	97.5(2)	Ir−P(3)−C(8)	112.1(2)
P(3)−Ir−C(2)	90.1(2)	Ir−P(3)−C(51)	117.4(2)
P(3)−Ir−C(5)	90.4(2)	Ir−P(3)−C(61)	114.9(2)
P(3)−Ir−H(1)	85ᵃ	C(8)−P(3)−C(51)	104.1(3)
C(1)−Ir−C(2)	83.6(3)	C(8)−P(3)−C(61)	104.0(3)
C(1)−Ir−C(5)	94.4(3)	C(51)−P(3)−C(61)	102.7(3)
C(1)−Ir−H(1)	177ᵃ	Rh−P(4)−C(8)	111.7(2)
C(2)−Ir−C(5)	178.0(3)	Rh−P(4)−C(71)	117.2(3)
C(2)−Ir−H(1)	95ᵃ	Rh−P(4)−C(81)	113.2(3)
C(5)−Ir−H(1)	87ᵃ	C(8)−P(4)−C(71)	106.5(3)
P(2)−Rh−P(4)	168.61(7)	C(8)−P(4)−C(81)	104.5(3)
P(2)−Rh−C(4)	91.0(2)	C(71)−P(4)−C(81)	102.7(3)
P(2)−Rh−C(5)	89.4(2)	Ir−C(1)−O(1)	171.7(8)
P(4)−Rh−C(4)	90.8(3)	Ir−C(2)−C(3)	168.7(7)
P(4)−Rh−C(5)	87.3(2)	C(2)−C(3)−C(91)	176.9(9)
C(4)−Rh−C(5)	172.1(3)	Rh−C(4)−O(4)	178.0(7)
Ir−P(1)−C(7)	110.9(2)	Ir−C(5)−Rh	91.4(3)
Ir−P(1)−C(11)	113.8(3)	Ir−C(5)−C(6)	177.2(7)
Ir−P(1)−C(21)	117.9(2)	Rh−C(5)−C(6)	88.7(5)
C(7)−P(1)−C(11)	103.8(3)	C(5)−C(6)−C(101)	167.4(7)
C(7)−P(1)−C(21)	104.4(3)	P(1)−C(7)−P(2)	113.3(4)
C(11)−P(1)−C(21)	104.7(3)	P(3)−C(8)−P(4)	114.2(4)
Rh−P(2)−C(7)	111.3(2)	Rh−H(1)−Ir	109ᵃ

ᵃ Angles involving H(1) are approximate since this atom was not refined.

fixed in the position obtained from the Fourier map; therefore, no significance should be attached to the derived Rh−H and Ir−H distances. The Ir−C(1) distance (1.95(1) Å), which is opposite H(1), is significantly longer than the Rh−C(4) distance (1.778(8) Å), consistent with the high trans influence of a hydride ligand, but otherwise the geometries of these carbonyls are normal. The Rh−Ir distance of 3.0582(8) Å is almost exactly equal to the intraligand P−P separations [P(1)−P(2) = 3.056(3) Å, P(3)−P(4) = 3.053(3) Å], suggesting that there is no formal metal−metal bond. Instead, the Ir−H(1) bond is viewed as functioning as an agostic interaction with Rh, much as that observed in [RhIr-(H)₂(CO)₂(μ-Cl)(dppm)₂][BF₄] (3.0651(5) Å), which also was formulated as having no formal metal−metal

bond.[44] Both of the acetylide groups are σ-bound to Ir, with Ir–C(2) and Ir–C(5) bond lengths of 2.042(7) and 2.041(8) Å, respectively. One of these mutually trans groups is directed away from Rh, while the other appears to interact weakly with this second metal. This orientation of the two acetylides is similar to that found in $[Pt_2(C≡CPh)(\mu-\eta^1:\eta^2-C≡CPh)(\mu-SiMe_2)(PR_3)_2]$ (R = cyclo-C_6H_{11}).[45] The bending of the phenyl group on C(6) away from Rh [C(5)–C(6)–C(101) = 167.4(7)°], and the proximity of the acetylide carbons to Rh [Rh–C(5) = 2.228(6) Å, Rh–C(6) = 2.515(7) Å], suggest that there is a π-interaction between Rh and the C(5)–C(6) acetylide bond. However, the small difference in the C≡C distances of the two acetylide ligands [C(2)–C(3) = 1.185(9) Å, C(5)–C(6) = 1.22(1) Å] suggests that the π-interaction of the latter is weak. A similar bending of the phenyl group of one of the acetylide ligands was observed in $[Pt_2(C≡CPh)_2(\mu-\eta^1:\eta^2-C≡CPh)(dppm)_2]$-$[ClO_4]$.[46] There is a slight bending of the Ir–C(2)–C(3) moiety [Ir–C(2)–C(3) = 168.7(7)°], probably due to interactions with rings 2 and 5 of the dppm groups, while the Ir–C(5)–C(6) moiety is almost linear (177.2-(7)°). Bending of the same magnitude was observed in the acetylide ligands of $[Rh_2(CO)_2(\mu-\eta^1:\eta^2-C≡C^tBu)-(dppm)_2][ClO_4]$[47] and $[Mn_2(\mu-H)(\mu-\eta^1:\eta^2-C≡CPh)(CO)_6-(\mu-dppm)]$.[31]

When the reaction of compound **1** with phenylacetylene is started at −78 °C, and monitored by NMR while gradually warming the reaction mixture, three additional intermediates are observed (as shown in the enclosure in Scheme 4). At −78 °C, the NMR spectra of the reaction mixture, using 1 equiv of phenylacetylene, show the presence of **1** as the major compound, together with $[RhIr(CH_3)(H)(CO)_3(\mu-\eta^1:\eta^2-C≡CPh)-(dppm)_2][CF_3SO_3]$ (**13**) and a small amount of another species, $[RhIr(CH_3)(CO)_3(\mu-HC≡CPh)(dppm)_2][CF_3SO_3]$ (**14**). Increasing the temperature at a rate of approximately 15 °C h^{-1} results in increasing concentrations of intermediates **13** and **14** at the expense of **1**, such that by −20 °C little of **1** remains, while the acetylide-bridged species **11** and a new intermediate **15** also begin to appear. Further increases in temperature result in the total disappearance of **1** and increasing concentrations of **11** and **15**, while **13** disappears (compound **14** remains until **13** is depleted). Intermediate **15** is a minor species and is never present in greater than 10% concentration. If more than 1 equiv of phenylacetylene is present, the diacetylide product **12** also begins to appear near 0 °C.

The ¹H NMR spectrum of compound **13** shows the hydride resonance as a triplet at δ −8.87 and the methyl resonance as a triplet at δ 0.33. Selective ³¹P decoupling experiments show that both the methyl and the hydride ligands are bound to Ir, since they couple only to the phosphorus nuclei bound to this metal. The ¹³C{¹H} NMR spectrum shows a doublet of triplets at δ 192.8 ($^1J_{Rh–C}$ = 80.5 Hz), a broad resonance at δ 193.1, and a doublet of triplets at δ 186.0 ($^1J_{Rh–C}$ = 72 Hz) all having equal intensities, indicating that there are two CO ligands terminally bound to Rh and one terminally bound to Ir in compound **13**. The presence of the acetylide ligand in this compound is inferred from the

presence of the hydride ligand. A trans orientation of the hydride and methyl ligands is proposed as the factor inhibiting methane loss in **13**, however, the stereochemistry at Ir is not known with certainty. The proposed $\mu-\eta^1:\eta^2$-bonding mode of the acetylide in **11** and **13** is based on analogies with several related compounds[31,45−48] (also see compound **5**).

The next species observed (**14**) is proposed to be a phenylacetylene-bridged complex. The ¹H NMR spectrum of compound **14** shows the alkyne proton resonance as a triplet at δ 8.53 and also shows a broad resonance at δ 0.27 due to the methyl protons. Selective ³¹P decoupling experiments show that the methyl group is still bound to Ir and that the alkyne proton couples to the phosphorus nuclei bound to Ir, suggesting the alkyne orientation shown in which the large phenyl substituent is close to the less congested Rh center. The ¹³C{¹H} NMR spectrum of **14** shows a doublet of multiplets at δ 200.6 ($^1J_{Rh–C}$ = 5.0 Hz), a doublet of triplets at δ 193.8 ($^1J_{Rh–C}$ = 54.3 Hz), and a broad resonance at δ 180.8, indicating the presence of a CO ligand on Ir that interacts very weakly with Rh (inferred from the small Rh–C coupling of 5 Hz), as well as a terminally bound CO ligand each on Rh and Ir.

The final intermediate observed before conversion to **11** is complete is **15** and is formulated as the dicarbonyl species $[RhIr(H)(CH_3)(CO)_2(\mu-C≡CPh)(dppm)_2)][CF_3-SO_3]$, in which the methyl and hydrido groups are now proposed to be mutually cis. Only two carbonyl resonances are observed with only the low-field signal showing Rh coupling (56 Hz), indicating that each CO is terminally bound to a different metal. We cannot rule out the possibility that a third carbonyl resonance is buried under the signals for the more abundant products, but this seems unlikely since the spectra were monitored over widely changing concentrations of all species. The ¹H NMR spectra clearly show the methyl and hydrido groups as triplets at δ −0.52 and −8.75, respectively, and selective ³¹P decoupling indicates that they are both coordinated to Ir.

Although compounds **1** and **2** react quite differently with the nonactivated alkynes, PhC≡CH and HC≡CH, as described earlier, their reactions with the activated alkyne, DMAD, yield similar products: $[MIr(RC=C-(CH_3)R)(CO)_3(dppm)_2][CF_3SO_3]$ [R = CO₂Me; M = Rh (**16**), Ir (**17**)], in which the alkyne apparently has inserted into the M–C(alkyl) bonds of the precursor complexes (as shown in Schemes 5 and 6).

The ¹H NMR spectrum of the RhIr compound **16** shows the dppm methylene proton resonances as multiplets at δ 4.35 and 3.65. It also shows three singlets at δ 3.33, 2.22, and 0.81, which are assigned to the two DMAD methyl groups and the methyl group that has undergone migratory insertion. The shifting of the methyl resonance from a triplet at δ −0.08 in compound **1** to a singlet at lower field (δ 0.81) in compound **16** is consistent with the formal insertion of DMAD into the Ir–CH₃ bond. The ¹³C{¹H} NMR spectrum shows two doublets of triplets at δ 197.9 ($^1J_{Rh–C}$ = 4.0 Hz) and 194.4 ($^1J_{Rh–C}$ = 55.3 Hz) and a triplet at δ 176.8,

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(46) Yam, V. W.; Chan, L.; Lai, T. *Organometallics* **1993**, *12*, 2197.
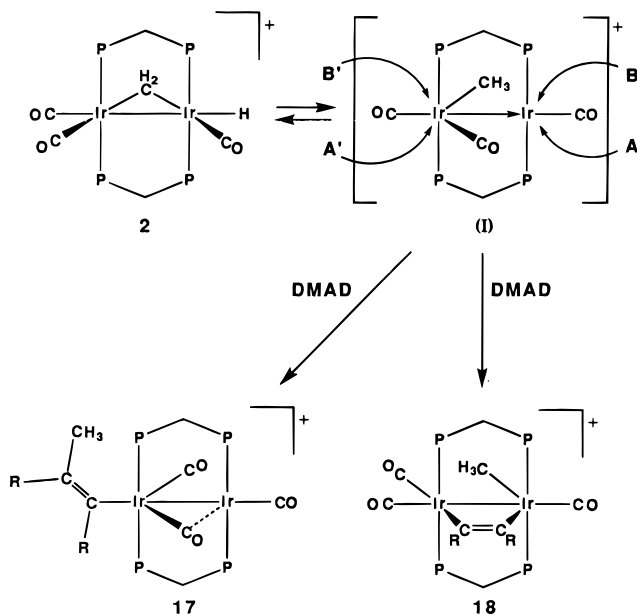(47) Cowie, M.; Loeb, S. J. *Organometallics* **1985**, *4*, 852.

(48) See, for example: (a) Esteruelas, M. A.; Lahuerta, O.; Modrego, J.; Nurnberg, O.; Oro, L. A.; Rodriguez, L.; Sola, E.; Werner, H. *Organometallics* **1993**, *12*, 266. (b) McEwan, D. M.; Markham, D. P.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1986**, 1809. (c) Hutton, A.; Langrick, C. R.; McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 2121.

Scheme 5
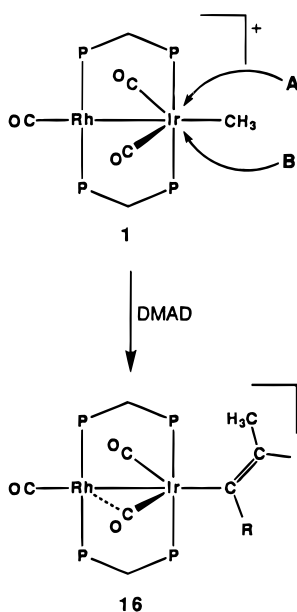
Scheme 6

indicating that there is one semibridging CO ligand showing a very weak interaction with Rh, as well as a terminally bound CO ligand each on Rh and Ir. The IR spectrum of this product shows a peak at 1720 cm^{-1}, which is consistent with the presence of a semibridging CO ligand, as well as peaks at 2022 and 1995 cm^{-1} due to the terminal CO ligands. In addition to these stretches, bands at 1698 cm^{-1}, due to the CO stretch of the inserted DMAD, and at 1641 cm^{-1}, assigned to the C=C stretch of the same ligand, are observed.

The ^{1}H NMR spectrum of the diiridium analogue **17** shows two multiplets at δ 4.43 and 3.60, representing the dppm methylene proton resonances, as well as three singlets at δ 3.27, 2.23, and 0.68, which are assigned to the two methyl groups of the inserted DMAD and the methyl group bound to the DMAD as a result of the insertion. The ^{13}C{^{1}H} NMR spectrum shows a broad resonance at δ 194.7 and two triplets at δ 192.0 and 179.5 while the IR spectrum shows stretches at 2015, 1998, and 1717 cm^{-1}, indicating the presence of two

terminally bound and one semibridging CO ligand in compound **17**. The identification of one CO as semibridging is based on the low CO stretch in the IR spectrum and the ^{13}C chemical shift in the NMR spectrum that is not unlike those of the terminal groups. Analogies with compound **16** also support this assignment. The CO stretch of the inserted DMAD ligand appears at 1695 cm^{-1} in the IR spectrum, while the band at 1642 cm^{-1} is assigned to the C=C stretch of the same ligand. The similarities in the spectroscopic data for **16** and **17** support the assignment of similar structures to both compounds.
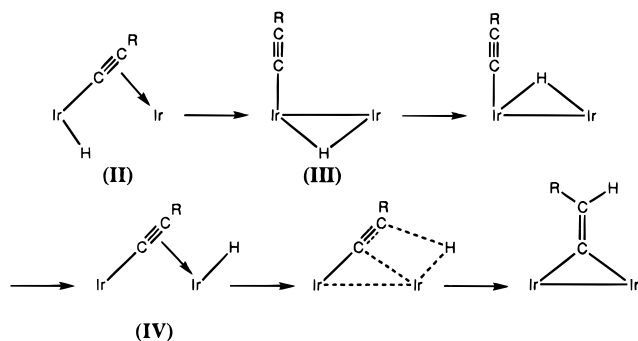
In addition to compound **17**, the reaction of **2** with DMAD also gives [Ir$_2$(CH$_3$)(CO)$_3$(μ-DMAD)(dppm)$_2$][CF$_3$-SO$_3$] (**18**), typically in about half the concentration of compound **17**. The ^{1}H NMR spectrum of **18** shows the dppm methylene proton resonances as multiplets at δ 4.78 and 4.25, the methyl resonances of the coordinated DMAD as singlets at δ 3.45 and 2.13, and the metal-bound methyl resonance as a triplet at δ −0.52. The ^{13}C{^{1}H} NMR spectrum shows triplets at δ 182.2, 175.9, and 152.5 and the IR spectrum shows CO stretches at 2029, 2001, and 1982 cm^{-1}, indicating the presence of three terminal CO ligands. The IR spectrum also shows the CO stretch of the coordinated DMAD at 1690 cm^{-1}, and the band at 1635 cm^{-1} in this spectrum is assigned to the C≡C stretch of the same ligand. Compound **18** is analogous to the acetylene and phenylacetylene adducts **3** and **7**, described earlier. Although the location of the methyl group in **18** is shown opposite the bridging alkyne, we cannot rule out an arrangement like that shown in **3** and **7**, in which the methyl is adjacent to the bridging alkyne.

Discussion

As indicated earlier, the methyl complex [RhIr-(CH$_3$)(CO)$_3$(dppm)$_2$][CF$_3$SO$_3$] (**1**) and the methylene-bridged hydride species [Ir$_2$H(CO)$_3$(μ-CH$_2$)(dppm)$_2$][CF$_3$-SO$_3$] (**2**) are more similar than they first appeared. The latter, coordinatively saturated species can be viewed as an incipient methyl complex since it has been shown[19] to be in equilibrium with the labile, coordinatively unsaturated methyl complex [Ir$_2$(CH$_3$)(CO)$_3$-(dppm)$_2$][CF$_3$SO$_3$] (shown as **I** in Scheme 6), the similarity of which to compound **1** is obvious. Due to the unsaturation at one metal in this proposed species, it was felt that reactions of **2** with small molecules would proceed *via* attack at this unsaturated center. The reactivities of **1** and **2** with acetylene, phenylacetylene, and dimethyl acetylenedicarboxylate therefore were investigated to compare the reactivities involving either a RhIr or Ir$_2$ core. In all cases it appears that our assumption that **2** would react as a methyl complex, much like **1**, was justified, since all products obtained are methyl species or, in one case, resulted from methane elimination. Nevertheless, the two species do show some interesting contrasts in reactivity that relate to the replacement of one Ir center in **2** by Rh. With the two terminal alkynes investigated, two basic types of reactivity have been noted: reaction at the alkyne triple bond yields the alkyne-bridged products, whereas reaction at the alkyne C−H bond yields acetylide-hydride products. In each of these cases, the ultimate product depends on the metal centers involved. In the diiridium system, the alkyne-bridged products

[Ir$_2$(CH$_3$)(CO)$_3$(μ-HC≡CR)(dppm)$_2$][CF$_3$SO$_3$] [R = H (**3**), Ph (**7**)] are stable and do not react further under the relatively mild temperatures (ambient or subambient) investigated. In this metal system, the presumed acetylide–hydride intermediates (only observed for the acetylene reaction at low temperatures) transform to the vinylidene and phenylvinylidene products [Ir$_2$(CH$_3$)(CO)$_3$-(μ-CC(H)R)(dppm)$_2$][CF$_3$SO$_3$] [R = H (**4**), Ph (**8**)]. In each case, reaction at −78 °C followed by slow warming to ambient temperature yields only one product; however, interestingly, these products differ for the two alkynes, yielding exclusively the vinylidene species **4** in the acetylene reaction but the alkyne-bridged **7** with phenylacetylene. This was of some surprise to us since we had initially assumed that oxidative addition of the alkyne–H bond in phenylacetylene would occur more readily than in acetylene, in which case formation of the phenylvinylidene product should have a lower kinetic barrier. It also seemed that coordination of the more bulky phenylacetylene group through the C≡C bond should be less favored on steric grounds. Clearly these ideas are not the determining factors since the opposite occurs.

The transformation of a 1-alkyne into a vinylidene group is shown, in this and other studies,[49] to occur readily in the presence of adjacent metal centers. We propose that the facility of this transformation, at least in related dppm-bridged complexes, results from the abilities of the acetylide and hydride ligands in the intermediates to function as either terminal or bridging groups and from the mobilities of both of these groups over the bimetallic core. The hydride ligand can readily migrate from one metal to the other and from one face of an M$_2$P$_4$ unit to the other,[44,50] and the acetylide group can also move from metal to metal in a "windshield wiper" motion.[51] It is proposed that a pivotal step in the conversion of the acetylide and hydride groups to a vinylidene group, in the presence of adjacent metals, is the alignment of the hydride ligand adjacent to the π-bound acetylide moiety, as shown for intermediate **IV**, since such an orientation can facilitate transfer of the hydride to the β-carbon atom in a concerted manner, as diagrammed.

Although it is difficult to establish the exact stereochemistry at a metal in these intermediates, the mobilities of the hydride and acetylide groups can usually generate the proposed acetylide–hydride precursor **IV**. Even for compound **5** (Scheme 1), in which the hydride and acetylide groups are suggested to be on opposite faces of the complex, as shown by species **II**, the necessary intermediate **IV** can be obtained from the hydride-bridged species **III** via rotation about both P$_2$-Ir units, bringing the hydride ligand between the metals. It should be recalled that an alternate, but convenient, valence-bond representation of the 3-center, 2-electron M(μ-H)M interaction, as shown for **III**, is one in which a terminal M−H bond on one metal forms an agostic interaction with the second metal.[52] In this description, it becomes clear that the loss of the π-interaction of the μ-η^1:η^2-acetylide group with the second Ir center in **II** is compensated for by the agostic interaction involving the Ir−H bond, forming the hydride-bridged intermediate **III** while maintaining the valence electron counts at both metals. It must also be pointed out that the ancillary ligands, not shown in the preceding generic scheme, can also migrate from metal to metal. Such migrations, accompanied in some cases by metal−metal bond formation or breakage, allows the metals to maintain favorable electron counts. Intermediate **IV** can be generated from a number of other geometries by variations of the preceding rearrangements of the hydride and acetylide groups. By the same token, complex **5**, having the geometry shown, presumably derives from an original species in which the hydride and acetylide groups were adjacent on the same face of the complex, following oxidative addition of the alkyne, by movement of the hydride between the metals.

Although the RhIr system ultimately reacts very differently with acetylene and phenylacetylene than the Ir$_2$ system, the initial products seen at −78 °C are analogous to those noted earlier. The reaction of **1** with acetylene at −78 °C first yields the acetylene-bridged [RhIr(CH$_3$)(CO)$_3$(μ-HC≡CH)(dppm)$_2$][CF$_3$SO$_3$] (**9**), not unlike the diiridium analogues **3** and **7**. However, upon warming, a much different product, [RhIr(CH$_3$)(CO)$_3$(μ-η^1:η^2:η^1-HC=C(H)PPh$_2$CH$_2$PPh$_2$)(dppm)][CF$_3$SO$_3$] (**10**), the apparent result of acetylene insertion into one of the Rh−P bonds, is obtained. Formation of this product can be rationalized by the greater lability at Rh, giving rise to dissociation of the Rh-bound end of a diphosphine with subsequent nucleophilic attack of this group at the bridging alkyne and concomitant cleavage of the Rh−alkyne bond (see Scheme 3). In the resulting product, the 6-membered IrC=CPCP iridacycle has maintained the original iridium−olefin σ-bond and the Ir−P bond from the original dppm group, while being simultaneously π-bonded to Rh through the olefinic linkage. We suggest that Rh has an 18-electron configuration on the basis of a [Rh(CO)$_2$(olefin)(PR$_3$)]$^-$ formulation and that donation of a pair of nonbonding Rh electrons to the Ir (+3) center occurs, giving this metal an octahedral geometry typical of this oxidation state. The proposal that **10** results from the dissociation of one end of a bridging diphosphine group (that bound to Rh) followed by nucleophilic attack at a bridging acetylene unit is unusual, but has precedent. As noted earlier, nucleo-

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philic attack of a *monodentate* PMe₃ group on a bridging acetylene ligand to yield a μ-η^1:η^2-hydrocarbyl moiety has been reported,[42] and even more closely related to the present study, dissociation of one end of a *bridging* diphosphine ligand in a phenylacetylene-bridged dicobalt complex, followed by attack at the alkyne, has also resulted in the formation of a bridging hydrocarbyl unit,[53] not unlike that reported for **10**. The only other example of attack of dppm on a coordinated alkyne, of which we are aware, occurs in a mononuclear Ru species, in which the free end of a dangling dppm ligand apparently attacks an alkyne carbon of a coordinated hexafluoro-2-butyne, followed by proton transfer from dppm to the other acetylenic carbon.[54]

As in the reaction of **2** with acetylene to give the acetylide–hydride species **5**, compound **1** reacts with phenylacetylene to give a phenylacetylide–hydride species **13**, which is observed at low temperature. This species does not, however, yield a vinylidene species as in the Ir₂ system, but instead gives an alkyne-bridged intermediate [RhIr(CH₃)(CO)₃(μ-HC≡CPh)(dppm)₂][CF₃SO₃] (**14**), which goes on to lose methane, yielding the phenylacetylide-bridged species [RhIr(CO)₃(μ-C≡CPh)(dppm)₂][CF₃SO₃] (**11**). The involvement of **14** as an intermediate in methane elimination is puzzling, although it may serve as a route to species **15** (preceding reductive elimination) in which the hydride and methyl groups are adjacent. As in the diiridium species **5**, it is proposed that the hydrido and methyl groups in **13** do not have a cis disposition so do not eliminate readily. Intermediate **14** undergoes a subsequent oxidative addition of the alkyne–hydrogen bond accompanied by CO loss to yield the new hydrido-methyl complex **15**, which is now assumed to have these groups mutually cis, facilitating the reductive elimination of methane. In the absence of excess phenylacetylene, methane loss is followed by recoordination of the liberated CO to yield **11**, whereas in the presence of excess phenylacetylene oxidative addition of this substrate competes, yielding **12**. In support of the dicarbonyl formulation for **15**, the generation of **12** at subambient temperatures appears to occur more readily from **15** in the presence of PhC≡CH than from reaction of **11** with this alkyne. Subsequent studies have shown[55] that carbonyl loss from **11** is necessary before oxidative addition of phenylacetylene occurs.

The actual geometry at Ir in **13** is not known; however the transformations of **1** (+PhC≡CH) to **13** and of **13** to **14** are reasonable when it is recalled that movement of a hydride ligand from one face of an MM′P₄ unit to the other is a facile process[44,50] which, in combination with the known ability of bridging acetylides to undergo a windshield wiper movement from one metal to the other,[51] could easily give rise to such rearrangements. We had considered that reductive elimination might be occurring from Rh since this process might be expected to be more facile from a second- rather than a third-row metal, due to the stronger M–H and M–CH₃ bonds with the latter[56] and due to the greater kinetic lability

of the second-row metal.[57] However, we see no evidence of migration of the hydride or methyl groups to Rh preceding the reductive elimination step. It instead may be that the more labile Rh center serves to facilitate rearrangements that allow these groups to attain a mutually cis orientation on Ir, from which elimination is possible.

One goal of this study was to induce migratory insertion of an alkyne and a methyl group, leading to a substituted vinyl moiety. This has been achieved for both metal systems studied, but only with the strongly electrophilic alkyne, dimethyl acetylenedicarboxylate; other alkynes having strongly electron-withdrawing substituents were not investigated. That insertion occurs with DMAD but not with acetylene or phenylacetylene possibly is not surprising since it has previously been noted that most alkyne insertions occur with activated alkynes.[10] It is unfortunate that no intermediates were observed in this migratory insertion since several questions arise about the mechanism. Although one might expect alkyne attack to occur at the unsaturated (Rh) center in the RhIr precursor **1**, the resulting alignment of the DMAD and methyl groups is unsuitable for insertion, due to an intervening carbonyl group, and instead might be expected to generate an alkyne-bridged product analogous to the diiridium species **18**. The absence of such a product suggests an alternate site of alkyne coordination. Attack at a saturated metal has been proposed via a dipolar pathway, in which nucleophilic attack by the metal on the electrophilic alkyne occurs.[10] This being the case, alkyne coordination on Ir at either site A or B would be expected to generate the observed product, as shown in Scheme 5.

In the related reaction of the diiridium precursor **2** with DMAD, two products are obtained as shown in Scheme 6; in addition to the alkenyl product **17** resulting from migratory insertion, an alkyne-bridged product was also obtained. As noted earlier, the reactive intermediate in this diiridium species is presumed to be a methyl complex, suggested to resemble intermediate **I** shown in Scheme 6. If, in this intermediate, reaction occurs via a dipolar species resulting from alkyne coordination at the saturated metal, the two different products can be rationalized on the basis of whether DMAD approaches from the front or the back of the complex (routes A′ and B′). Alternately, even if alkyne attack occurs at the unsaturated metal (routes A and B), the same products might be expected on the basis of the resulting positions of the methyl and alkyne groups.

Conclusions

Alkyne molecules display a rich chemistry with the binuclear methyl complexes described, in which three basic reactivities are initially observed. With all alkynes, the common reactivity mode for late metal binuclear complexes, leading to species having the alkyne group bridging both metals, is again observed. In the second reactivity type, 1-alkynes can oxidatively add to give hydrido–acetylide species; and finally, the third reactivity is observed with DMAD, in which insertion of this

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alkyne into the metal−alkyl bond occurs to give alkenyl species. In all three reactivity modes, the diiridium system is well-behaved, and only the hydrido−acetylide species reacts further, in what is becoming a common transformation in these binuclear systems,[49] to give vinylidene-bridged products. The unexpected subsequent reactivities occur when one iridium is substituted by the more labile rhodium. In one case involving a bridging acetylene ligand, the Rh center is directly involved in the transformation, which results from phosphine dissociation from this center followed by nucleophilic attack at the coordinated acetylene, giving an unusual unsaturated metallacycle involving iridium. However, in the case in which the RhIr complex reacts with phenylacetylene, subsequent reductive elimination of methane from a hydrido−methyl−acetylide species occurs. In this case there is no direct evidence of methane elimination from Rh; instead, it may be that the involvement of this more labile metal center may result from its ability to facilitate rearrangements, which in the present case allows the methyl and hydride ligands to adopt a cis arrangement at Ir preceding elimination.

Although reactivity of these 16-/18-electron binuclear systems often appears to be initiated at the unsaturated metal, the reactions with DMAD may occur at the saturated metal, initiated by electron transfer from the metal to the electrophilic alkyne. We also cannot rule out facile carbonyl transfer from the saturated to the unsaturated metal, exchanging the site of unsaturation prior to reaction. Further work is required to obtain detailed information (where possible) on the involvement of the adjacent metals in the chemistry.

Supporting Information Available: Tables of positional and thermal parameters for the dppm phenyl carbons, solvent atoms, and atoms of the anion, anisotropic thermal parameters, idealized hydrogen parameters, and complete listings of bond distances and angles (12 pages). Ordering information is given on any current masthead page.

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