

C–H Bond Activation and C–C Bond Formation in the Reactions of the Methyl Complex $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2][\text{CF}_3\text{SO}_3]$ with Alkynes

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The methyl complex $[\text{Ir}_2(\text{CH}_3)(\text{CO})(\mu\text{-CO})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**1**) reacts readily with a variety of alkyne molecules. With alkynes containing electron-withdrawing substituents ($\text{RC}\equiv\text{CR}'$; $\text{R} = \text{R}' = \text{CO}_2\text{Me}$, CF_3 ; $\text{R} = \text{CO}_2\text{Me}$, $\text{R}' = \text{H}$), the alkyne-bridged products, $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\mu\text{-alkyne})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$, result. With other 1-alkynes ($\text{HC}\equiv\text{CR}$, $\text{R} = \text{Me}$, Ph) reaction at -80°C results in oxidative addition to give acetylide hydrides $[\text{Ir}_2\text{H}(\text{CH}_3)(\text{CO})_2(\mu\text{-C}_2\text{R})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$, which upon warming undergo transfer of the hydride ligand to the β -carbon of the acetylide to give the vinylidene-bridged products. At ambient temperature methane elimination occurs, yielding the acetylide-bridged "A-frames", $[\text{Ir}_2(\text{CO})_2(\mu\text{-C}_2\text{R})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$. Reaction of **1** with 1 equiv of acetylene proceeds through analogous acetylide and vinylidene intermediates; however under carbon monoxide exchange of a vinylidene hydrogen and the methyl ligand occurs to give a methylvinylidene-bridged hydride $[\text{Ir}_2(\text{H})(\text{CO})_3(\mu\text{-CCHMe})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$. Reaction of **1** with an excess of acetylene results in the incorporation of two acetylene molecules, giving $[\text{Ir}_2(\text{CH}_3)(\text{C}_2\text{H})(\text{CO})_2(\mu\text{-H})(\mu\text{-CCH}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$, containing terminal methyl and acetylide ligands and bridging hydride and vinylidene groups. Reaction of **1** with a number of internal, nonactivated alkynes results first in the formation of the alkyne-bridged products, which slowly rearrange to the unusual species $[\text{Ir}_2\text{H}(\text{CO})_2(\mu\text{-CHCRC}(\text{H})\text{R})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$, in which cleavage of two C–H bonds of the methyl group has occurred accompanied by condensation of the resulting methyne group at one end of alkyne linkage and transfer of a hydrogen to the other end. The resulting hydrocarbyl moiety can be viewed as a vinylcarbene. The X-ray structures of three representative products are reported, including one of these vinylcarbenes ($\text{R} = \text{C}_2\text{H}_5$).

Introduction

We have recently demonstrated that the methyl complex $[\text{Ir}_2(\text{CH}_3)(\text{CO})(\mu\text{-CO})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**1**) ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) undergoes facile and, in some cases, reversible C–H bond cleavage of the methyl group upon addition of a number of substrates ($\text{L} = \text{CO}$, SO_2 , PR_3 , and CNR), yielding the methylene-bridged hydride products $[\text{Ir}_2\text{H}(\text{L})(\text{CO})_2(\mu\text{-CH}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$.¹ As an extension of this study we have sought to utilize this conversion in the formation of C–C bonds through reactions of **1** with unsaturated organic substrates such as alkynes. If the above transformation of a methyl ligand into methylene and hydride groups also occurs upon coordination of alkynes, two subsequent pathways become available for C–C bond formation. Migration of the coordinated alkyne to the bridging methylene group would yield a vinylcarbene, as has previously been observed,² and migratory insertion of the alkyne and hydrido groups could occur to give a vinyl moiety, a common transformation involving these fragments.³

Although this latter reaction does not lead directly to C–C bond formation, subsequent coupling of the resulting vinyl and methylene groups would yield an allyl ligand, a transformation known to occur in binuclear complexes⁴ and proposed to be of significance in Fischer–Tropsch (FT) chemistry.⁵

In the absence of C–H bond cleavage of the methyl group, other routes to C–C bond formation involving the reaction of **1** and alkynes are also available. Although less favorable than insertions involving metal hydrides,⁶ insertions of alkynes into metal–alkyl bonds have been observed.⁷ Particularly relevant to this study,

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the closely related species $[\text{Ir}_2\text{H}(\text{CO})_3(\mu\text{-CH}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ and $[\text{RhIr}(\text{CH}_3)(\text{CO})_3(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ were shown to yield the substituted-vinyl products $[\text{M}(\text{R})\text{C}(\text{R})=\text{C}(\text{Me})\text{R}(\text{CO})_3(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ ($\text{M} = \text{Rh}, \text{Ir}$; $\text{R} = \text{CO}_2\text{Me}$), through migratory insertion involving dimethyl acetylenedicarboxylate and the methyl ligand.^{7g} Furthermore, in reactions involving 1-alkynes, the formation of acetylide⁸ and vinylidene⁹ groups must also be considered, since C–C bond formation involving migratory insertion of these fragments has also been observed.^{10,11}

In this article we report the results of the reactions of **1** with a variety of alkyne molecules, leading in a number of cases to C–C bond formation.

Experimental Section

General Comments. Acetylene was obtained from Matheson, ¹³C-labeled acetylene was purchased from Cambridge Isotopes, and ¹³CO (99%) was supplied by Isotec Inc. Propyne and hexafluoro-2-butyne (HFB) were purchased from Farchan Laboratories Ltd.; all other alkynes and trimethylphosphine were purchased from Aldrich. Two-dimensional NMR experiments were performed on a Varian Unity 500 MHz spectrometer. All ¹³C{¹H} NMR spectra were obtained using ¹³CO-, ¹³C-acetylene-, or ¹³CH₃-enriched samples (the latter obtained from ¹³C-methyl triflate) unless otherwise stated. The compound $[\text{Ir}_2(\text{CH}_3)(\text{CO})(\mu\text{-CO})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**1**) was prepared by the published procedure.¹ The ³¹P{¹H} and ¹H NMR and IR spectroscopic data for all compounds are given in Table 1, while selected ¹³C{¹H} and ¹⁹F NMR data are given, where appropriate, with the details on the preparation of the compounds.

Preparation of Compounds. (a) $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\mu\text{-DMAD})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**2**). The compound $[\text{Ir}_2(\text{CH}_3)(\text{CO})(\mu\text{-CO})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**1**) (40 mg, 0.029 mmol) was dissolved in 5 mL of CH₂Cl₂, and dimethyl acetylenedicarboxylate (DMAD) (3.65 μL, 0.029 mmol) was added by syringe. The solution was stirred for 1 h, by which time the color had changed from red to dark red. The solvent was evaporated to ca. 2 mL, and the product was precipitated and washed with Et₂O (2 × 10 mL) and dried under vacuum, yielding a brown powder in 79% yield. Recrystallization was from CH₂Cl₂/Et₂O. ¹³C{¹H} NMR: δ 193.6 (t, ²J_{PC} = 9.6 Hz, CO), 182.4 (t, ²J_{PC} = 8.3 Hz, CO). Anal. Calcd for Ir₂SP₄F₃O₉C₆₀H₅₃: C, 47.55; H, 3.53. Found: C, 47.16; H, 3.26.

(b) $[\text{Ir}_2(\text{CH}_3)(\text{CO})_3(\mu\text{-DMAD})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**3**). Compound **2** (50 mg, 0.033 mmol) was dissolved in 5 mL of CH₂Cl₂. Carbon monoxide gas was passed over the dark red

solution for 30 s, producing a color change to yellow followed by stirring of the solution under a static atmosphere of the gas for 5 min. The bright yellow solution was worked up in the same manner as described for compound **2**, yielding a yellow powder in 78% yield. ¹³C{¹H} NMR: δ 183.7 (t, ²J_{PC} = 6.3 Hz, CO), 177.7 (t, ²J_{PC} = 7.6 Hz, CO), 176.4 (t, ²J_{PC} = 24 Hz, CO). Anal. Calcd for Ir₂SP₄F₃O₁₀C₆₁H₅₃: C, 47.46; H, 3.47. Found: C, 46.99; H, 3.22.

(c) $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\mu\text{-DMAD})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**4**). Compound **2** (50 mg, 0.033 mmol) was dissolved in 5 mL of CH₂Cl₂, and trimethylphosphine (3.7 μL, 0.033 mmol) was added, giving a bright yellow solution. The solution was stirred for 1 h and then worked up as described for compound **2**, yielding a bright yellow powder in 91% yield. Anal. Calcd for Ir₂ClSP₅F₃O₉C_{63.5}H₆₃: C, 46.67; H, 3.89. Found: C, 46.70; H, 3.63. The compound was crystallized as the hemisolvate **4**.

(d) $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\mu\text{-HFB})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**5**). Compound **1** (34 mg, 0.025 mmol) was dissolved in 5 mL of CH₂Cl₂, and HFB was passed through the solution for 30 s, resulting in an immediate color change from red to orange. The solution was stirred under a static atmosphere of the gas for 10 min and then worked up as described for compound **2**, yielding a light orange powder in 95% yield. Anal. Calcd for Ir₂SP₄F₉O₅C₅₈H₄₇: C, 45.37; H, 3.09. Found: C, 45.55; H, 3.06. ¹⁹F NMR: δ -44.4 (qu, ⁵J_{F-F} = 14 Hz, 3F), -50.9 (qu, 3F). Abbreviations as given in Table 1.

(e) $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\mu\text{-HC}\equiv\text{CC}(\text{O})\text{OMe})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**6**). Compound **2** (34 mg, 0.025 mmol) was dissolved in 5 mL of CH₂Cl₂ and cooled to -78 °C. Methyl propiolate (2.2 μL, 0.026 mmol) was added, producing a yellow solution that was stirred at -78 °C for 1 h. The solution was then warmed to room temperature and worked up as described for compound **2**, yielding a yellow powder in 89% yield. Anal. Calcd for Ir₂SP₄F₃O₇C₅₈H₅₁: C, 47.80; H, 3.53. Found: C, 47.57; H, 3.35.

(f) $[\text{Ir}_2(\text{CO})_2(\mu\text{-C}\equiv\text{CMe})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**9**). Compound **1** (30 mg, 0.022 mmol) was dissolved in 5 mL of CH₂Cl₂ and cooled to -78 °C. Propyne (1 mL) was added via a gastight syringe, causing a color change from red to yellow, followed by stirring -78 °C for 1 h. Upon slowly warming, the solution darkened to a light brown at ca. -20 °C. After stirring at room temperature for 1 h the solvent was evaporated to ca. 2 mL, and a light brown powder was precipitated and washed with Et₂O (2 × 10 mL), followed by drying under vacuum. Intermediates in the reaction, observed at low temperature ($[\text{Ir}_2(\text{H})(\text{CH}_3)(\text{CO})_2(\mu\text{-C}\equiv\text{CMe})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**7**) and $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\mu\text{-C}\equiv\text{C}(\text{H})\text{Me})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**8**)), were characterized by NMR spectroscopy, as described later.

(g) $[\text{Ir}_2(\text{CO})_2(\mu\text{-C}\equiv\text{CPh})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**11**). The procedure used was the same as that used for the preparation of compound **9** except that 1 equiv of phenyl acetylene was used. Yield: 83%. Anal. Calcd for Ir₂SP₄F₃O₃C₆₁H₁₉: C, 50.20; H, 3.39. Found: C, 50.10; H, 3.28. Low-temperature intermediates in the reaction, $[\text{Ir}_2(\text{H})(\text{CH}_3)(\text{CO})_2(\mu\text{-C}\equiv\text{CPh})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**10**) and $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\mu\text{-C}\equiv\text{C}(\text{H})\text{Ph})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**11**), were characterized by NMR spectroscopy, as described later.

(h) **Low-Temperature Reaction of Compound 1 with 1 equiv of Acetylene.** The procedure used is as described below for the characterization of low-temperature intermediates. The compound $[\text{Ir}_2(\text{H})(\text{CH}_3)(\text{C}\equiv\text{CH})(\text{CO})_2(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**13**) was formed at -78 °C by addition of ca. 1 equiv of acetylene by gastight syringe to compound **1** and persisted in solution until ca. 0 °C. ¹³C{¹H} NMR for **13**: δ 124.4 (dt, ¹J_{CC} = 78.7 Hz, ²J_{PC} = 12.6 Hz, C≡CH), 76.2 (d, ¹J_{CC} = 78.7 Hz, C≡CH), 179.8 (b, CO), 178.3 (b, CO). Upon warming **13** to ca. 0 °C $[\text{Ir}_2(\text{CH}_3)(\mu\text{-C}=\text{CH}_2)(\text{CO})_2(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**14**) began to appear and persisted in solution until room temperature along with other minor uncharacterized products. ¹³C{¹H} NMR for **14**: δ 218.2 (dq, ¹J_{CC} = 63.0 Hz, ²J_{PC} = 8.3 Hz, μ-C=CH₂), 119.7 (d, ¹J_{CC} = 63.0 Hz, μ-C=CH₂). After stirring at room temperature for 1 day, CO gas was added to the mixture of

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Table 1. Spectroscopic Data for the Compounds^a

compound	NMR ^{f,g}		δ ¹ H ^{h,i}	δ ³¹ P{ ¹ H} ^j
	IR, cm ⁻¹ b,c			
[Ir ₂ (CH ₃)(CO) ₂ (<i>u</i> -DMAD)(dppm) ₂]-[CF ₃ SO ₃] (2)	2009 s, 1980 m, 1702 m, b, ^d 1682 m, b ^d		4.28 (m, 2H), 3.37 (m, 2H), 2.91 (s, 3H), 2.27 (s, 3H), 0.65 (t, 3H, ³ J _{PH} = 5.6 Hz)	7.7 (m), -9.3 (m)
[Ir ₂ (CH ₃)(CO) ₃ (<i>u</i> -DMAD)(dppm) ₂]-[CF ₃ SO ₃] (3)	2041 s, 1995 vs, 1967 s, 1709 s, ^d 1682 m ^d		4.87 (m, 2H), 4.28 (m, 2H), 3.55 (s, 3H), 2.22 (s, 3H), -0.39 (t, 3H, ³ J _{PH} = 5.7 Hz)	-11.2 (m), -28.9 (m)
[Ir ₂ (CH ₃)(CO) ₂ (PMe ₃)(<i>u</i> -DMAD)(dppm) ₂][CF ₃ SO ₃] (4)	1986 vs, 1967 vs, 1695 vs ^d		5.03 (bm, 2H), 4.55 (bm, 2H), 3.56 (bs, 3H), 1.87 (bs, 3H), 0.71 (bs, 3H), 0.40 (d, ² J _{PH} = 9 Hz, 9H)	-22.6 (b, 2P), -24.3 (b, 2P), -89.3 (b, 1P)
[Ir ₂ (CH ₃)(CO) ₂ (<i>u</i> -HFB)(dppm) ₂]-[CF ₃ SO ₃] (5)	2018 vs, 1992 vs, 1547 w ^e		4.12 (m, 2H), 3.64 (m, 2H), 0.98 (tm, 3H, ³ J _{PH} = 5.5 Hz)	5.9 (m), -15.5 (m)
[Ir ₂ (CH ₃)(CO) ₂ (<i>u</i> -HC≡CC(O)OMe)(dppm) ₂][CF ₃ SO ₃] (6)	2002 vs, 1982 sh, 1678 s ^d		9.9 (tt, ³ J _{PH} = 4.7 Hz, ⁴ J _{PH} = 2.5 Hz, 1H), 3.89 (m, 2H), 3.19 (m, 2H), 2.31 (s, 3H), 0.45 (t, 3H, ³ J _{PH} = 6.7 Hz)	12.3 (m), -11.7 (m)
[Ir ₂ (H)(CH ₃)(CO) ₂ (<i>u</i> -C≡CMe)(dppm) ₂]-[CF ₃ SO ₃] (7) ^k			3.62 (m, 2H), 3.01 (m, 2H), 0.62 (s, 3H), 0.19 (t, 3H, ³ J _{PH} = 5.5 Hz), -9.52 (t, 1H, ² J _{PH} = 33.6 Hz)	2.1 (m), -10.4 (m)
[Ir ₂ (CH ₃)(CO) ₂ (<i>u</i> -C≡C(H)Me)(dppm) ₂]-[CF ₃ SO ₃] (8) ^l			5.79 (qu, 1H, ³ J _{HH} = 3.0 Hz), 4.51 (m, 2H), 2.95 (m, 2H), 1.73 (t, 3H, ³ J _{PH} = 7.5 Hz), 0.95 (bd, 3H, ³ J _{HH} = 3.0 Hz)	24.8 (m), -6.7 (m)
[Ir ₂ (CO) ₂ (<i>u</i> -C≡CMe)(dppm) ₂][CF ₃ SO ₃] (9)	1971 s, 1945 vs		4.28 (m, 2H), 3.99 (m, 2H), 1.02 (q, ⁴ J _{PH} = 1.5 Hz, 3H)	8.3 (s)
[Ir ₂ (H)(CH ₃)(CO) ₂ (<i>u</i> -C≡CPh)(dppm) ₂]-[CF ₃ SO ₃] (10) ^k			3.73 (m, 2H), 2.94 (m, 2H), 0.26 (bt, 3H, ³ J _{PH} = 5.0 Hz), -9.17 (t, 1H, ² J _{PH} = 17.4 Hz)	-0.9 (m), -12.4 (m)
[Ir ₂ (CH ₃)(CO) ₂ (<i>u</i> -HC≡CPh)(dppm) ₂]-[CF ₃ SO ₃] (11) ^l			3.61 (m, 2H), 2.96 (m, 2H), 1.74 (t, 3H, ³ J _{PH} = 7.0 Hz)	23.0 (m), -10.6 (m)
[Ir ₂ (CO) ₂ (<i>u</i> -C≡CPh)(dppm) ₂]-[CF ₃ SO ₃] (12)	1970 sh, 1953 vs, b		4.21 (m, 2H), 3.92 (m, 2H)	7.9 (s)
[Ir ₂ (H)(CH ₃)(CO) ₂ (<i>u</i> -C≡CH)(dppm) ₂]-[CF ₃ SO ₃] (13) ^k			4.39 (m, 2H), 4.15 (s, 1H, ¹ J _{CH} = 229 Hz), ^h 3.40 (m, 2H), 0.68 (t, 3H, ³ J _{PH} = 6.0 Hz), -10.06 (t, 1H, ² J _{PH} = 13.2 Hz)	-16.1 (s)
[Ir ₂ (CH ₃)(CO) ₂ (<i>u</i> -C=CH ₂)(dppm) ₂]-[CF ₃ SO ₃] (14) ^m			6.26 (s, ¹ J _{CH} = 160 Hz, 1H), ^h 6.24 (s, ¹ J _{CH} = 160 Hz, 1H), ^h 4.42 (m, 2H), 2.99 (m, 2H), -0.20 (t, 3H, ³ J _{PH} = 5.3 Hz)	13.3 (m), 3.7 (m)
[Ir ₂ (H)(CO) ₃ (<i>u</i> -C=CHMe)(dppm) ₂]-[CF ₃ SO ₃] (15)	2045 s, 1992 vs, 1963 sh		6.50 (b, ¹ J _{CH} = 155 Hz, 1H), ^h 4.08 (m, 2H), 3.59 (m, 2H), 0.84 (b, ¹ J _{CH} = 126 Hz, 3H), ^h -10.62 (t, 1H, ² J _{PH} = 13.1 Hz)	-7.8 (m), -14.3 (m)
[Ir ₂ (CH ₃)(C≡CH)(CO) ₂ (<i>u</i> -H)(<i>u</i> -C=CH ₂)(dppm) ₂][CF ₃ SO ₃] (16)	2064 s, 2000 vs, 1574 m ⁿ		6.23 (s, ¹ J _{CH} = 156 Hz, 1H), ^h 6.21 (s, ¹ J _{CH} = 156 Hz, 1H), ^h 4.12 (m, 2H), 3.10 (m, 2H), 1.87 (t, ³ J _{PH} = 1.9 Hz, ¹ J _{CH} = 228 Hz, 1H), ^h -0.35 (t, 3H, ³ J _{PH} = 6.6 Hz), -14.01 (tt, ² J _{PH} = 10 Hz, 5 Hz, 1H)	-7.99 (m), -24.58 (m)
[Ir ₂ (CH ₃)(CO) ₂ (<i>u</i> -CH ₃ C≡CCH ₃)(dppm) ₂]-[CF ₃ SO ₃] (17)	1982 vs, b, 1959 vs, b		3.91 (m, 2H), 3.24 (m, 2H), 1.33 (b, 3H), 0.76 (b, 3H), 0.47 (t, 3H, ³ J _{PH} = 6.0 Hz)	10.4 (m), -9.4 (m)
[Ir ₂ (H)(CO) ₂ (<i>u</i> - η^1 : η^3 -HCC(Me)=CHMe)(dppm) ₂][CF ₃ SO ₃] (18)	1969 s, b		8.79 (m, 1H, ¹ J _{CH} = 155.4 Hz), ^h 7.12 (m, 1H), 5.83 (m, 1H), 4.60 (m, 1H), 3.78 (m, 1H), 3.29 (m, 1H), 2.72 (d, 3H, ⁴ J _{HH} = 3.9 Hz), 1.42 (bm, 3H), -11.25 (m, 1H)	-5.8 (m), -6.0 (m), -34.3 (m), -37.8 (m)
[Ir ₂ (H)(CO) ₂ (<i>u</i> - η^1 : η^3 -HCC(Et)=CHEt)(dppm) ₂][CF ₃ SO ₃] (19)	1980 s, sh, 1964 vs		8.83 (m, 1H), 5.83 (m, 1H), 4.52 (m, 1H), 3.68 (bm, 1H), 3.23 (m, 1H), 2.97 (dqu, 1H, ³ J _{HH} = 14.0, 7.8 Hz), 2.56 (dqu, 1H, ³ J _{HH} = 14.8, 7.8 Hz), 1.88 (dqu, 1H, ³ J _{HH} = 11.8, 7.8 Hz), 1.43 (t, 3H, ³ J _{HH} = 7.8 Hz), 1.32 (b, 1H), 0.89 (t, 3H, ³ J _{HH} = 7.5 Hz), -11.2 (m, 1H)	-5.4 (m), -7.7 (m), -35.1 (m), -38.4 (m)
[Ir ₂ (H)(CO) ₂ (<i>u</i> - η^1 : η^3 -HCC(Me)=CHEt)(dppm) ₂][CF ₃ SO ₃] (20a , 20b) ^p	1971 s, b		8.80 (m, 2H), 5.85 (m, 2H), 4.57 (m, 2H), 3.73 (m, 2H), 3.28 (m, 2H), 2.98 (m, 1H), 2.73 (d, 3H, <i>J</i> = 3.6 Hz), 2.52 (m, 1H), 1.82 (m, 1H), 1.43 (t, 3H, <i>J</i> = 6.3 Hz), 1.40 (t, 3H, <i>J</i> = 7.5 Hz), 1.32 (m, 1H), 0.96 (t, 3H, <i>J</i> = 7.5 Hz), -11.2 (m, 2H)	-5.7 (m), -6.8 (m), -34.7 (m), -38.4 (m)
[Ir ₂ (H)(CO) ₂ (<i>u</i> - η^1 : η^3 -HCC(Me)=CHPh)(dppm) ₂][CF ₃ SO ₃] (21a)	1972 vs, b		8.91 (m, 1H), 5.95 (m, 1H), 4.60 (m, 1H), 3.45 (m, 1H), 2.92 (s, 3H), -11.10 (b) ^q	-5.7 (m, 2P), -32.7 (m), -38.0 (m)
[Ir ₂ (H)(CO) ₂ (<i>u</i> - η^1 : η^3 -HCC(Ph)=CHMe)(dppm) ₂][CF ₃ SO ₃] (21b)			9.22 (m, 1H), 5.70 (m, 1H), 4.80 (m, 1H), 3.20 (m, 1H), 2.92 (s, 3H), -11.10 (b) ^q	0.1 (m), -8.4 (m), -33.7 (m), -43.2 (m)
[Ir ₂ (H)(CO) ₂ (<i>u</i> - η^1 : η^3 -HCC(<i>n</i> Pr)=CH <i>n</i> Pr)(dppm) ₂][CF ₃ SO ₃] (22)	1968 s, b		8.78 (dm, 1H, ³ J _{PH} = 10.8 Hz), 7.40 (m, 1H), 5.85 (m, 1H), 4.58 (m, 1H), 3.25 (m, 1H), 2.15 (t, 3H, ³ J _{HH} = 7.8 Hz), 0.70 (t, 3H, ³ J _{HH} = 6.0 Hz), -11.19 (m, 1H) ^q	-5.0 (m), -7.4 (m), -34.8 (m), -38.1 (m)

^a The ¹³C{¹H} and ¹⁹F NMR spectral data for some compounds are given in the Experimental Section. ^b IR abbreviations (ν (CO) unless otherwise stated): vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, b = broad. ^c Nujol mull or CH₂Cl₂ cast unless otherwise stated. ^d ν (C=O ester). ^e ν (C≡C). ^f NMR abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, q = quintet, qu = quartet, dm = doublet of multiplets, dqu = doublet of quartets, b = broad, bd = broad doublet. ^g NMR data at 25 °C in CD₂Cl₂ unless otherwise stated. ^h ¹J_{CH} coupling values for ¹³C-labeled compounds. ⁱ Chemical shifts for the phenyl hydrogens are not given in the ¹H NMR data. ^j ³¹P{¹H} chemical shifts are referenced vs external 85% H₃PO₄. ^k NMR data at -80 °C. ^l NMR data at -20 °C. ^m NMR data at 0 °C. ⁿ ν (C=C). ^p Signals for both isomers (1:1 abundance) listed together; some signals coincident, some distinct. ^q Some signals obscured by impurities.

compound **14** and uncharacterized products, and the solution was stirred for 2 h, after which, NMR spectra on the complex reaction mixture showed production of $[\text{Ir}_2(\text{H})(\mu\text{-C}=\text{C}(\text{H})\text{CH}_3)(\text{CO})_3(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**15**) in ca. 35% yield. $^{13}\text{C}\{^1\text{H}\}$ NMR for **15**: δ 192.0 (dq, $^1J_{\text{CC}} = 65.9$ Hz, $^2J_{\text{PC}} = 8.0$ Hz, $\mu\text{-C}=\text{CHCH}_3$), 137.1 (dd, $^1J_{\text{CC}} = 65.9$, 42.0 Hz, $\mu\text{-C}=\text{CHCH}_3$), 24.6 (d, $^1J_{\text{CC}} = 42.0$ Hz, $\mu\text{-C}=\text{CHCH}_3$).

(i) $[\text{Ir}_2(\text{CH}_3)(\text{C}\equiv\text{CH})(\text{CO})_2(\mu\text{-H})(\mu\text{-C}=\text{CH}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**16**). Compound **1** (30 mg, 0.022 mmol) was dissolved in 5 mL of CH_2Cl_2 . Acetylene was passed through the solution for 10 min, causing a color change from red to orange and then to yellow. The solution was stirred under a static atmosphere of the gas for 1 h and then worked up as described for compound **2**, giving a yellow powder in 83% yield. Anal. Calcd for $\text{Ir}_2\text{Cl}_{0.566}\text{SP}_4\text{F}_3\text{O}_5\text{C}_{58.283}\text{H}_{51.566}$: C, 48.29; H, 3.59. Found: C, 48.18; H, 3.34. The amount of CH_2Cl_2 present (0.283 mol/mol complex) in the elemental analysis was confirmed by ^1H NMR spectroscopy in CDCl_3 . $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 193.6 (dm, $^1J_{\text{CC}} = 64.9$ Hz, $\text{C}=\text{CH}_2$), 173.8 (t, $^2J_{\text{PC}} = 10.2$ Hz, CO), 166.3 (t, $^2J_{\text{PC}} = 8.4$ Hz, CO), 120.2 (d, $^1J_{\text{CC}} = 64.9$ Hz, $\text{C}=\text{CH}_2$), 103.7 (d, $^1J_{\text{CC}} = 119.1$ Hz, $\text{C}\equiv\text{CH}$), 61.6 (ddt, $^1J_{\text{CC}} = 119.1$ Hz, $^2J_{\text{PC}} = 15$ Hz, $^2J_{\text{CC}} = 15$ Hz, $\text{C}=\text{CH}$), -5.2 (bs, CH_3).

(j) $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\mu\text{-CH}_3\text{C}\equiv\text{CCH}_3)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**17**). Compound **1** (40 mg, 0.029 mmol) was dissolved in 5 mL of CH_2Cl_2 . Excess 2-butyne (3.5 μL , 0.045 mmol) was added, causing an immediate color change from red to dark red. The solution was stirred for 1 h and then worked up in a manner similar to that described for compound **2**, giving a reddish brown powder in 86% yield. Anal. Calcd for $\text{Ir}_2\text{SP}_4\text{F}_3\text{O}_5\text{C}_{58}\text{H}_{53}$: C, 48.80; H, 3.75. Found: C, 49.02; H, 3.74.

(k) $[\text{Ir}_2(\text{H})(\text{CO})_2(\mu\text{-}\eta^1\text{-}\eta^3\text{-HCC}(\text{CH}_3)=\text{CHCH}_3)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**18**). Compound **17** was prepared in situ as above and stirred for a period of 24 h, during which time the color changed from dark red to yellow. The solvent was evaporated to ca. 2 mL, and a yellow powder was precipitated and washed with Et_2O (2×10 mL) and then dried under vacuum, yield 84%. Anal. Calcd for $\text{Ir}_2\text{SP}_4\text{F}_3\text{O}_5\text{C}_{59}\text{H}_{55}$: C, 48.80; H, 3.75. Found: C, 48.30; H, 3.58. $^{13}\text{C}\{^1\text{H}\}$ NMR (natural abundance): δ 170.9 (m, CO), 168.2 (m, CO), 138.4 (dm, $^2J_{\text{PC}} = 63.0$ Hz, $\mu\text{-}\eta^1\text{-}\eta^3\text{-HCC}(\text{CH}_3)=\text{CHCH}_3$), 110.2 (s, $\mu\text{-}\eta^1\text{-}\eta^3\text{-HC}(\text{CH}_3)=\text{CHCH}_3$), 64.1 (t, $^1J_{\text{PC}} = 28.2$ Hz, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$), 56.2 (m, $\mu\text{-}\eta^1\text{-}\eta^3\text{-HCC}(\text{CH}_3)=\text{CHCH}_3$), 42.3 (t, $^1J_{\text{PC}} = 28.2$ Hz, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$), 23.4 (s, $\mu\text{-}\eta^1\text{-}\eta^3\text{-HCC}(\text{CH}_3)=\text{CHCH}_3$), 18.1 (s, $\mu\text{-}\eta^1\text{-}\eta^3\text{-HCC}(\text{CH}_3)=\text{CHCH}_3$).

(l)–(o) $[\text{Ir}_2(\text{H})(\text{CO})_2(\mu\text{-}\eta^1\text{-}\eta^3\text{-HCC}(\text{R})=\text{CHR}')(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**R** = **R'** = **Et** (**19**); **R** = **Me**, **R'** = **Et** (**20**); **R** = **Me**, **R'** = **Ph** (**21**); **R** = **R'** = **nPr** (**22**)). Compounds **19**–**22** were prepared by adding 1.1 equiv of the appropriate alkyne (3-hexyne (yielding product **19**), 2-pentyne (**20**), 1-phenyl-2-propyne (**21**), 4-octyne (**22**)) to a CH_2Cl_2 solution of compound **1**, stirring for 24 h, and then working up the same as was done with compound **18** except that pentane was used for precipitation and washing. In each case the color of the solution changed from red to dark red upon addition of the alkyne and then over 24 h changed to yellow. For **19**, yield, 83%. Anal. Calcd for $\text{Ir}_2\text{SP}_4\text{F}_3\text{O}_5\text{C}_{59}\text{H}_{57}$: C, 49.51; H, 3.96. Found: C, 49.66; H, 3.55. For **20**, yield, 71%. Anal. Calcd for $\text{Ir}_2\text{SP}_4\text{F}_3\text{O}_5\text{C}_{58}\text{H}_{55}$: C, 49.16; H, 3.85. Found: C, 48.89; H, 3.38. Satisfactory elemental analyses were not obtained for compounds **21** (yield, 75%) and **22** (yield, 82%) since they could not be separated from minor impurities, and characterization is based on similarities in the $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra compared to compounds **18** and **20**. (see Table 1).

General Procedure for Characterization of Low-Temperature Intermediates. Compound **1** (ca. 20 mg, 0.015 mmol) was dissolved in 0.6 mL of CD_2Cl_2 in an NMR tube, capped with a rubber septum, and cooled to -78 °C. Approximately 1 equiv of the appropriate alkyne was added to the NMR tube via gastight syringe, and NMR spectra of the reaction mixture were obtained at temperatures starting from -80 °C to $+25$ °C by warming the probe to the desired

temperature, with the sample in place, and allowing the sample to stand at that temperature for 20 min before recording the spectra.

X-ray Data Collection. For compounds **4** and **16**, crystals suitable for X-ray diffraction were grown via slow diffusion of diethyl ether into a concentrated CH_2Cl_2 solution of the compound. For compound **19**, crystals were grown by diffusing Et_2O into a concentrated 1:1 CH_2Cl_2 /toluene solution of the compound. Crystals of each compound were mounted and flame-sealed in glass capillaries under solvent vapor to minimize decomposition or deterioration resulting from solvent loss. Data collection details are given in Table 2 together with crystal parameters. For each compound, three reflections were chosen as intensity standards and were remeasured every 120 min of X-ray exposure time; in no case was decay evident. Absorption corrections to **19** were applied by the method of Walker and Stuart,¹² while for **4** and **16** the crystal faces were indexed and measured, with absorption corrections being carried out using Gaussian integration.

Structure Solution and Refinement. For each structure, the positions of the iridium and phosphorus atoms were found using the direct-methods program *SHELXS-86*;¹³ the remaining atoms were found using a succession of least-squares and difference Fourier maps. Refinement of each structure proceeded using the program *SHELXL-93*.¹⁴ Hydrogen atom positions (except for hydride ligands as noted below) were calculated by assuming idealized sp^2 or sp^3 geometries about their attached carbon atoms (as appropriate) and were given thermal parameters 120% of the equivalent isotropic displacement parameters of their attached carbons. For compound **19** the hydride ligand (H(2)) was located and refined with a fixed Ir(2)–H(2) distance of 1.70 Å and position to minimize non-bonded contacts. Further details of structure refinement (other than described below) and final residual indices may be found in Table 2.

Location of all atoms in $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\text{PMe}_3)(\mu\text{-DMAD})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**4**)· $3/4\text{CH}_2\text{Cl}_2\cdot\text{H}_2\text{O}$ proceeded smoothly; however, the triflate ion and the water molecule did not behave well, so bond distances were constrained.¹⁵ All atoms were refined isotropically except the iridium and phosphorus atoms, which were refined anisotropically.

For the compound $[\text{Ir}_2(\text{CH}_3)(\text{C}\equiv\text{CH})(\text{CO})_2(\mu\text{-C}=\text{CH}_2)(\mu\text{-H})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**16**)· CH_2Cl_2 all nonhydrogen atoms were located. The hydride ligand (H(1)) was not located from a difference Fourier map so on the basis of spectroscopic data was placed in an idealized position bridging the two metals. The triflate anion and the dichloromethane solvent molecule were not well behaved so were constrained to idealized geometries by fixing the bond distances. The same distance restraints were applied to the triflate ion as for compound **4**,¹⁵ and the following restraints were applied to enforce an idealized geometry upon the dichloromethane solvent mol-

(12) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158–166.

(13) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(14) Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination; University of Göttingen: Germany, 1993. Refinement on F_o^2 for all reflections having $F_o^2 \geq -3\sigma(F_o^2)$. Weighted R -factors (wR_2) and all goodness of fit parameters (S) are based on F_o^2 ; conventional R -factors (R_1) are based on F_o , with F_o set to zero for negative F_o^2 . The observed criteria of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1 and is not relevant to the choice of reflections for refinement. R -factors based on F_o^2 are statistically about twice as large as those based on F_o , and R -factors based on all data will be even larger.

(15) The following distance restraints were applied to enforce an idealized geometry upon the triflate ion ($d(\text{S}-\text{C}(98)) = 1.80(1)$ Å; $d(\text{S}-\text{O}(91)) = d(\text{S}-\text{O}(92)) = d(\text{S}-\text{O}(93)) = 1.45(1)$ Å; $d(\text{F}(91)-\text{C}(98)) = d(\text{F}(92)-\text{C}(98)) = d(\text{F}(93)-\text{C}(98)) = 1.35(1)$ Å; $d(\text{F}(91)\cdots\text{F}(92)) = d(\text{F}(91)\cdots\text{F}(93)) = d(\text{F}(92)\cdots\text{F}(93)) = 2.20(1)$ Å; $d(\text{O}(91)\cdots\text{O}(92)) = d(\text{O}(91)\cdots\text{O}(93)) = d(\text{O}(92)\cdots\text{O}(93)) = 2.37(1)$ Å; $d(\text{F}(91)\cdots\text{O}(92)) = d(\text{F}(91)\cdots\text{O}(93)) = d(\text{F}(92)\cdots\text{O}(91)) = d(\text{F}(92)\cdots\text{O}(93)) = d(\text{F}(93)\cdots\text{O}(91)) = d(\text{F}(93)\cdots\text{O}(92)) = 3.04(1)$ Å) and to the hydrogen atoms of the water molecule ($d(\text{O}(99)-\text{H}(99\text{C})) = d(\text{O}(99)-\text{H}(99\text{D})) = 1.00(1)$ Å; $d(\text{H}(99\text{C})\cdots\text{H}(99\text{D})) = 1.00(1)$ Å; $d(\text{O}(91)\cdots\text{H}(99\text{C})) = d(\text{O}(91)\cdots\text{H}(99\text{D})) = 1.86(2)$ Å).

Table 2. Crystallographic Data for Compounds 4, 16, and 19

	[Ir ₂ (CH ₃)(CO) ₂ (PMe ₃) ₂](<i>μ</i> -DMAD)(dppm) ₂][CF ₃ SO ₃] (4)·3/4CH ₂ Cl ₂ ·H ₂ O	[Ir ₂ (CH ₃)(C≡CH)(CO) ₂](<i>μ</i> -C≡CH ₂)(<i>μ</i> -H)(dppm) ₂][CF ₃ SO ₃] (16)·CH ₂ Cl ₂	[Ir ₂ H(CO) ₂ (<i>μ</i> -η ³ :η ¹ -HCCEtCHET)(dppm) ₂][CF ₃ SO ₃] (19)·2PhMe
A. Crystal Data			
formula	C _{63.75} H _{65.5} Cl _{1.5} F ₃ Ir ₂ O ₁₀ P ₅ S	C ₅₉ H ₅₃ Cl ₂ F ₃ Ir ₂ O ₅ P ₄ S	C ₇₄ H ₇₃ Ir ₂ O ₅ P ₄ S
fw	1673.15	1510.25	1639.66
crystal dimens (mm)	0.40 × 0.15 × 0.05	0.42 × 0.24 × 0.08	0.43 × 0.19 × 0.08
color	dark red	yellow	yellow
crystal system	monoclinic	monoclinic	triclinic
space group	<i>P2</i> ₁ / <i>c</i> (No. 14)	<i>P2</i> ₁ / <i>c</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)
unit cell params			
<i>a</i> (Å)	12.9605(15) ^a	12.5041(9) ^b	12.599(2) ^c
<i>b</i> (Å)	39.912(6)	21.7598(15)	14.284(3)
<i>c</i> (Å)	13.224(2)	21.5316(15)	18.871(4)
α (deg)	90.0	90.0	88.50(2)
β (deg)	109.610(10)	99.522(5)	84.946(15)
γ (deg)	90.0	90.0	89.16(2)
<i>V</i> (Å ³)	6444.0(15)	5777.7(7)	3381.4(12)
<i>Z</i>	4	4	2
ρ_{calcd} (g cm ⁻³)	1.725	1.736	1.610
μ (mm ⁻¹)	4.410	11.50	4.116
B. Data Collection and Refinement Conditions			
diffractometer	Enraf-Nonius CAD4 ^d	Siemens P4A/RA ^e	Enraf-Nonius CAD4 ^d
radiation (λ [Å])	graphite-monochromated Mo K α (0.71073)	graphite-monochromated Cu K α (1.54178)	graphite-monochromated Mo K α (0.71073)
temp (°C)	-50	-60	-50
scan type	ω	$\theta-2\theta$	$\theta-2\theta$
data collection	50.0	113.50	50.0
2θ limit (deg)			
total no. of data collected	7137 ($-15 \leq h \leq 14$, $0 \leq k \leq 34$, $0 \leq l \leq 15$)	8144 ($0 \leq h \leq 13$, $0 \leq k \leq 23$, $-23 \leq l \leq 23$)	12231 ($-14 \leq h \leq 14$, $-16 \leq k \leq 16$, $0 \leq l \leq 22$)
no. of indep reflns	6801	7730	11827
no. of observations (NO)	3394 ($F_o^2 \geq 2\sigma(F_o^2)$)	5472 ($F_o^2 \geq 2\sigma(F_o^2)$)	8426 ($F_o^2 \geq 2\sigma(F_o^2)$)
range of abs corr factors	0.7996–0.3593	0.4240–0.1714	1.223–0.892
no. of data/restraints/ params	6784 [$F_o^2 \geq -3\sigma(F_o^2)$]/ 24/446	7716 [$F_o^2 \geq -3\sigma(F_o^2)$]/ 24/663	11827 [$F_o^2 \geq -3\sigma(F_o^2)$]/ 4/808
largest diff peak and hole (e Å ⁻³)	1.268 and -1.277	2.179 and -1.202	1.290 and -1.362
final <i>R</i> indices ^f			
<i>R</i> ₁ [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0627	0.0640	0.0364
<i>wR</i> ₂ [$F_o^2 \geq -3\sigma(F_o^2)$]	0.1579	0.1755	0.0958
GOF (<i>S</i>) ^g	1.002 [$F_o^2 \geq -3\sigma(F_o^2)$]	1.041 [$F_o^2 \geq -3\sigma(F_o^2)$]	1.050 [$F_o^2 \geq -3\sigma(F_o^2)$]

^a Obtained from least-squares refinement of 24 reflections with $19.9^\circ < 2\theta < 23.6^\circ$. ^b Obtained from least-squares refinement of 46 reflections with $57.0^\circ \leq 2\theta \leq 58.9^\circ$. ^c Obtained from least-squares refinement of 24 reflections with $20.9^\circ < 2\theta < 23.9^\circ$. ^d Programs for diffractometer operation, data collection, and processing were those supplied by Enraf-Nonius. ^e Programs for diffractometer operation, data collection, and data processing were those of the XSCANS system supplied by Siemens. ^f $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$. ^g $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (a_0P)^2 + a_1P]^{-1}$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$). For compound **4** $a_0 = 0.0507$, $a_1 = 34.2392$; for compound **16** $a_0 = 0.0725$, $a_1 = 101.6339$; for compound **19** $a_0 = 0.0481$, $a_1 = 0.0$.

ecule: $d(\text{C}(99)-\text{Cl}(1)) = d(\text{C}(99)-\text{Cl}(2)) = 1.80(1)$ Å; $d(\text{Cl}(1)-\text{Cl}(2)) = 2.90(1)$ Å. Owing to the structural similarities between the acetylide and carbonyl groups, the atoms C(5) and O(1) were interchanged. However, least-squares refinement resulted in an abnormally large thermal parameter for O(1) and an unusually small thermal parameter for C(5), confirming the original assignment.

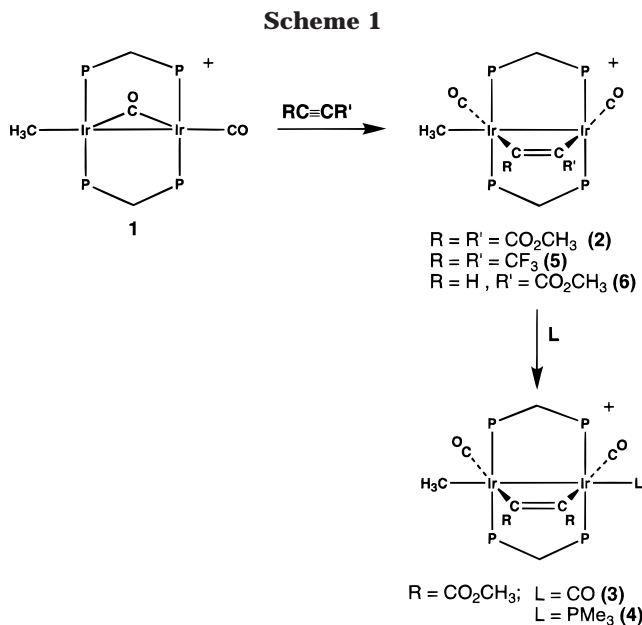
For the compound [Ir₂H(CO)₂(*μ*-η³:η¹-HCC(Et)C(H)Et)(dppm)₂][CF₃SO₃] (**19**)·2C₆H₅CH₃ all nonhydrogen atoms were located; even the hydride ligand (H(2)) was located on a difference Fourier map and refined with a fixed Ir(2)–H(2) distance of 1.70 Å while minimizing nonbonded contacts with the carbonyl carbon (C(2)), the vinyl carbene hydrogen (H(7)), and the dppm phenyl hydrogen (H(46)). The restraints are as follows: H2···H7, H2···H46 (both not less than 2.0 Å) and H2···C2 (not less than 2.2 Å).

Results and Characterization of Compounds

Compound **1** reacts with dimethyl acetylenedicarboxylate (DMAD) to produce the alkyne-bridged product

[Ir₂(CH₃)(CO)₂(*μ*-DMAD)(dppm)₂][CF₃SO₃] (**2**), as outlined in Scheme 1, in which the alkyne lies parallel to the metals as is often observed.¹⁶ The ¹H NMR resonance for the Ir-bound methyl group appears as a triplet at δ 0.65 and the coupling (³*J*_{PH} = 5.6 Hz) to two adjacent phosphorus nuclei demonstrates that this group has remained bound to one metal. Addition of CO to **2** in attempts to yield the previously characterized product of migratory insertion of the alkyne and methyl

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groups^{7g} yields only the carbonyl adduct, $[\text{Ir}_2(\text{CH}_3)(\text{CO})_3(\mu\text{-DMAD})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**3**). Similarly, phosphine addition also does not induce migration but yields the phosphine adduct $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\text{PMe}_3)(\mu\text{-DMAD})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**4**). Although the ¹H NMR spectrum of **3** at ambient temperature shows a triplet for the methyl resonance, displaying coupling to the two ³¹P nuclei on one metal, as expected for a terminally bound methyl ligand, the resonances of **4** are broad and unresolved. At –60 °C the ¹H NMR signals for **4** sharpen and the methyl resonance appears as a doublet, displaying 9.0 Hz coupling to the coordinated PMe_3 , as established by selective ³¹P-decoupling experiments. Coupling to the *dppm* ³¹P nuclei is not resolved. The coupling between the methyl and PMe_3 groups is consistent with the geometry established in the X-ray study, in which these groups are opposite the Ir–Ir bond (vide infra). Strong coupling through a metal–metal bond has been observed previously.^{16h,i,k} A spin-saturation transfer experiment at ambient temperature establishes that the broad signals result from exchange of free and coordinated PMe_3 . Irradiation at the ³¹P frequency for free PMe_3 (carried out in the presence of a 3-fold excess of the ligand) results in a drop in intensity of the coordinated PMe_3 to one-quarter of its original value. The X-ray structure of **4** was carried out in order to determine whether the alkyne and methyl groups were mutually *cis* and therefore capable of migratory insertion without significant rearrangement, or whether their positions were unfavorable for migration. A representation of the molecule is shown in Figure 1, with selected distances and angles given in Table 3. The structure confirms the alkyne-bridged formulation with the methyl ligand bound terminally to Ir(2) *cis* to one end of the alkyne. The overall geometry is best described as octahedral at each metal having the carbonyls essentially opposite the bridging alkyne group, with the PMe_3 and methyl ligands *trans* to each other across the metal–metal bond, almost bisecting the angles between the respective $\mu\text{-DMAD}$ and terminal carbonyl groups. The metal–metal separation of 3.022(2) Å is long for an iridium–iridium single bond, but electron counting suggests its presence, giving each

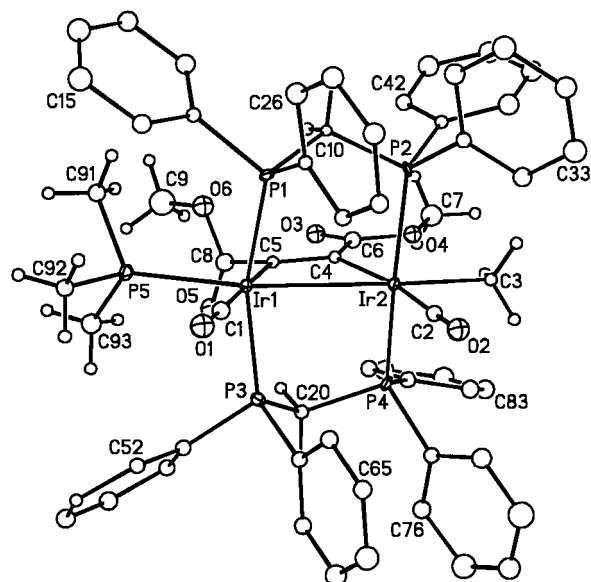


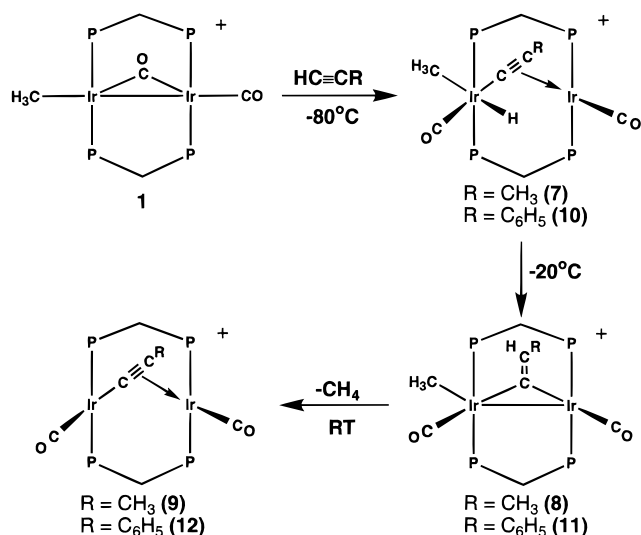
Figure 1. Perspective view of the $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\mu\text{-DMAD})(\text{dppm})_2]^+$ cation of compound **4**. Thermal ellipsoids are shown at the 20% probability level except for hydrogens, which are shown artificially small. Phenyl hydrogens are omitted.

Table 3. Selected Interatomic Distances and Angles for Compound 4

(a) Distances (Å)							
atom1	atom2	distance	atom1	atom2	distance		
Ir(1)	Ir(2)	3.022(2)	O(1)	C(1)	1.10(4)		
Ir(1)	P(1)	2.348(9)	O(2)	C(2)	1.14(4)		
Ir(1)	P(3)	2.342(9)	O(3)	C(6)	1.21(4)		
Ir(1)	P(5)	2.453(11)	O(4)	C(6)	1.32(4)		
Ir(2)	P(2)	2.336(9)	O(4)	C(7)	1.46(4)		
Ir(2)	P(4)	2.357(10)	O(5)	C(8)	1.22(4)		
Ir(1)	C(1)	1.91(4)	O(6)	C(8)	1.32(4)		
Ir(1)	C(5)	2.14(3)	O(6)	C(9)	1.46(5)		
Ir(2)	C(2)	1.87(4)	C(4)	C(5)	1.33(4)		
Ir(2)	C(3)	2.16(3)	C(4)	C(6)	1.49(5)		
Ir(2)	C(4)	2.11(3)	C(5)	C(8)	1.49(5)		
(b) Angles (deg)							
atom1	atom2	atom3	angle	atom1	atom2	atom3	angle
Ir(2)	Ir(1)	P(5)	156.6(3)	P(2)	Ir(2)	P(4)	160.5(4)
Ir(2)	Ir(1)	C(1)	115.5(12)	C(2)	Ir(2)	C(3)	89.0(15)
Ir(2)	Ir(1)	C(5)	64.1(10)	C(2)	Ir(2)	C(4)	168.4(17)
P(1)	Ir(1)	P(3)	161.2(4)	C(3)	Ir(2)	C(4)	102.5(14)
P(1)	Ir(1)	P(5)	97.2(3)	C(6)	O(4)	C(7)	118.1(31)
P(3)	Ir(1)	P(5)	100.3(4)	C(8)	O(6)	C(9)	115.9(33)
P(5)	Ir(1)	C(1)	87.8(12)	Ir(1)	C(1)	O(1)	177.0(39)
P(5)	Ir(1)	C(5)	92.6(10)	Ir(2)	C(2)	O(2)	176.1(34)
C(1)	Ir(1)	C(5)	179.3(15)	Ir(2)	C(4)	C(5)	109.1(27)
Ir(1)	Ir(2)	C(2)	99.5(12)	Ir(2)	C(4)	C(6)	130.8(30)
Ir(1)	Ir(2)	C(3)	171.5(9)	C(5)	C(4)	C(6)	120.0(36)
Ir(1)	Ir(2)	C(4)	69.0(11)	Ir(1)	C(5)	C(4)	117.6(28)
Ir(1)	C(5)	C(8)	121.6(27)	O(4)	C(6)	C(4)	113.9(35)
C(4)	C(5)	C(8)	120.0(35)	O(5)	C(8)	O(6)	125.1(39)
O(3)	C(6)	O(4)	122.5(39)	O(5)	C(8)	C(5)	123.0(35)
O(3)	C(6)	C(4)	123.5(42)	O(6)	C(8)	C(5)	111.9(33)

metal an 18-electron configuration. Compound **4** resembles related complexes having unusually long M–M single bonds, most probably resulting from the almost eclipsed octahedral coordinations at both metals, which result in strong ligand–ligand repulsions and a concomitant lengthening of the M–M bond.^{3b,17} Both ends of the diphosphine ligands are bent significantly from a *trans* alignment owing to repulsions involving the

Scheme 2



PMe_3 group and the large alkyne substituents, $\text{P}(1)-\text{Ir}(1)-\text{P}(3) = 161.2(4)^\circ$ and $\text{P}(2)-\text{Ir}(2)-\text{P}(4) = 160.5(4)^\circ$. The bonding of the alkyne, which can be considered as a cis-dimetalated olefin, is supported by the $\text{C}(4)-\text{C}(5)$ distance of 1.33(4) Å, which is consistent with a carbon-carbon double bond, and by the angles at these carbons, which suggest sp^2 hybridization. The $\text{Ir}(2)-\text{C}(4)$ and $\text{Ir}(1)-\text{C}(5)$ distances (2.11(3) and 2.14(3) Å) are not significantly different from the $\text{Ir}(2)-\text{C}(3)$ distance of 2.16(3) Å, even though the former pair involves sp^2 carbons, while the latter involves an sp^3 carbon. The $\text{Ir}-\text{P}$ distances for the dppm ligands are all quite consistent (2.348(9), 2.342(9), 2.336(9), 2.357(10) Å); however, the $\text{Ir}(1)-\text{P}(5)$ distance (2.453(11) Å) involving the PMe_3 group is ca. 0.1 Å longer, possibly owing to the trans influence of the metal-metal bond.¹⁸

The reaction of compound **1** with other activated alkynes such as hexafluorobutyne (HFB) and methylpropiolate gives the products $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\mu\text{-HFB})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**5**) and $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\mu\text{-HC}\equiv\text{CC}(\text{O})\text{OMe})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**6**), respectively, which, on the basis of the similarity of their spectral parameters with those of **2**, are assigned similar structures (see Scheme 1). For compound **6**, the ^1H NMR spectrum with selective phosphorus decoupling shows that the terminal acetylenic carbon having the small hydrogen substituent is bound to the more crowded iridium center, bearing the methyl ligand, as expected on the basis of steric arguments.

Compound **1** also reacts with nonactivated 1-alkynes. However, alkyne adducts similar to those described above are not observed; instead, the products result from oxidative addition of the acetylenic $\text{C}-\text{H}$ bond. At -78°C compound **1** reacts with propyne yielding the acetylide hydride methyl compound $[\text{Ir}_2(\text{H})(\text{CH}_3)(\text{CO})_2(\mu\text{-C}\equiv\text{CMe})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**7**) (see Scheme 2). The ^1H NMR at -80°C shows the acetylide methyl protons as a singlet at δ 0.62, the Ir-bound methyl resonance as a triplet at δ 0.19, and the terminal hydride signal as a triplet at δ -9.52. ^1H NMR experiments with selective ^{31}P decoupling indicate that the methyl and hydride

ligands are terminally bound to the same metal. On the basis that methane elimination is not observed from **7**, even upon warming (vide infra), the compound is assumed to have the structure shown in which the hydride and methyl ligands are separated by a carbonyl. Upon warming to -20°C , compound **7** begins to rearrange to **8**, in which the hydride signal in the ^1H NMR spectrum has disappeared. On the basis of this observation two structures seem possible for compound **8**, having either a bridging alkyne or a bridging vinylidene functionality. The vinylidene formulation, $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\mu\text{-C}=\text{C}(\text{H})\text{Me})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$, is proposed based on the 3 Hz coupling observed between the vinylidene hydrogen (δ 5.79) and methyl (δ 0.95) substituents, which compares favorably with that observed (5 Hz) between the vinylidene hydrogen and benzyl hydrogens in $[\text{RhIr}(\text{CH}_3)(\text{CO})_2(\mu\text{-C}=\text{C}(\text{H})\text{CH}_2\text{Ph})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$.¹⁹ Furthermore, vinylidene products are unambiguously identified in the analogous reaction of **1** with acetylene (vide infra). The Ir-bound terminal methyl group appears as a triplet at δ 1.73 displaying coupling to the two adjacent ^{31}P nuclei. Warming compound **8** results in reductive elimination of methane with formation of the bridging acetylide species, $[\text{Ir}_2(\text{CO})_2(\mu\text{-C}\equiv\text{CMe})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**9**). The $\mu\text{-}\eta^1\text{:}\eta^2$ -bridging mode proposed for the acetylide group in compound **9** is common,²⁰ and this compound is analogous to the related acetylide-bridged A-frames $[\text{Rh}_2(\text{CO})_2(\mu\text{-C}_2\text{R})(\text{dppm})_2]^+$ ^{20e,21} and $[\text{RhIr}(\text{CO})_2(\mu\text{-C}_2\text{Ph})(\text{dppm})_2]^+$,²² previously studied. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for **9**, at ambient temperature, shows a singlet at δ 8.3, indicative of a symmetrical species. However this can also be explained by a fluxional windshield-wiper motion of the acetylide ligand in which it transfers back and forth between the two metals. This type of fluxionality is common in homobimetallic complexes with bridging acetylide ligands,^{21,23} for which the low-temperature limiting spectra were also not obtained, even at -80°C . The ^1H NMR spectrum of **9** shows the acetylide methyl protons at δ 1.02 as a quintet ($^4J_{\text{H-P}} = 1.5$ Hz) coupling equally to all four phosphorus nuclei. If the acetylide were bridging the two metals in a symmetric fashion, binding only via the α -carbon, we would not expect the methyl protons to show 5-bond coupling to the phosphorus nuclei.

Compound **1** reacts with phenyl acetylene in much the same way, first yielding an acetylide hydride species $[\text{Ir}_2(\text{H})(\text{CH}_3)(\text{CO})_2(\mu\text{-C}\equiv\text{CPh})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**10**) at low temperature, which upon warming transforms into a vinylidene-bridged intermediate $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\mu\text{-C}=\text{CHPh})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**11**), which at ambient

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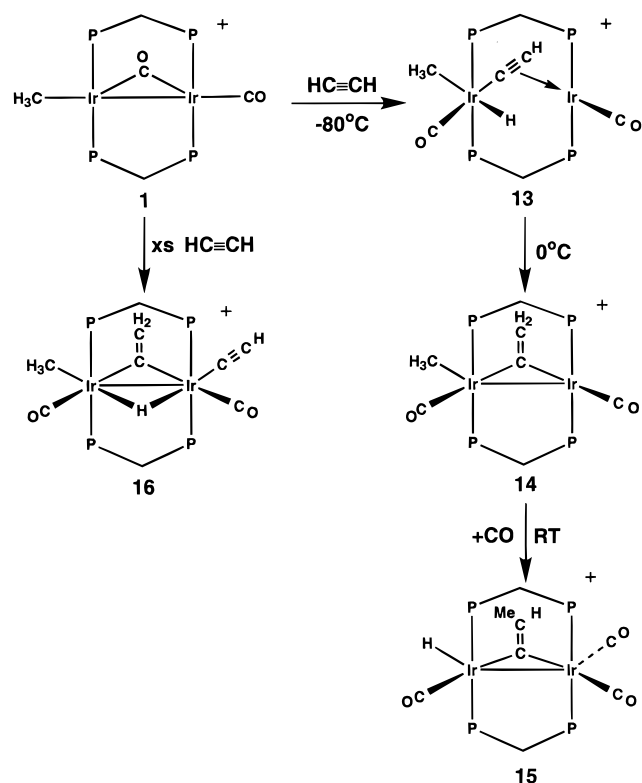
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Scheme 3



temperature eliminates methane, yielding $[\text{Ir}_2(\text{CO})_2(\mu\text{-C}\equiv\text{CPh})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**12**). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for the three compounds **10**, **11**, and **12** are very similar to the analogous products of the propyne reaction (**7**, **8**, **9**) and by analogy are assumed to have the same structures.

The reaction of compound **1** with 1 equiv of acetylene at -80°C initially proceeds much like the reactions with propyne and phenylacetylene, producing an acetylide hydride species, $[\text{Ir}_2(\text{H})(\text{CH}_3)(\text{CO})_2(\mu\text{-C}\equiv\text{CH})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**13**), as outlined in Scheme 3. Although the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at -80°C , there is actually a coincidental overlap of two signals that upon warming begin to separate, demonstrating the expected AA'BB' pattern. The ^1H NMR spectrum at this temperature shows the bridging acetylide proton as a singlet at δ 4.15 and the terminal methyl and hydride signals as triplets at δ 0.68 and -10.06 , respectively. Selective ^{31}P decoupling experiments could not be done on this compound because of the close proximity of the phosphorus resonances, but the proposed trans arrangement of the hydride and methyl ligands is based on similarities between the spectral data of compounds **7** and **10** as well as the previously characterized tricarbonyl species $[\text{Ir}_2(\text{H})(\text{CH}_3)(\text{CO})_3(\mu\text{-C}\equiv\text{CH})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$.^{7g} The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **13**, which was prepared using ^{13}C -enriched acetylene, shows the acetylide α -carbon as a doublet of triplets at δ 124.4 ($^1J_{\text{CC}} = 78.7$ Hz) with the β -carbon appearing as a doublet at δ 76.2. These chemical shifts and coupling constant appear typical of bridging acetylide groups.^{7g,24} However the triplet coupling of the α -carbon to one set

of phosphorus nuclei, the lack of phosphorus coupling to the β -carbon, and the relatively large carbon–carbon coupling suggest a weaker η^2 -interaction with the second metal than often observed. The presence of the weak η^2 -interaction is proposed on the basis of differences in the chemical shifts when compared to terminal acetylides (see compound **16** below). Upon warming to 0°C the vinylidene compound $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\mu\text{-C}=\text{CH}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**14**) begins to appear in solution. The ^1H NMR spectrum of compound **14** shows the vinylidene protons at δ 6.26 and 6.24 as broad signals with the Ir-bound methyl protons appearing at δ -0.20 as a triplet. When **14** is prepared using ^{13}C -enriched acetylene, the vinylidene protons show coupling of 160 Hz to the β -carbon, consistent with one-bond C–H coupling of an sp^2 -hybridized carbon.²⁵ The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows the vinylidene α -carbon as a doublet of quintets at δ 218.2 with $^1J_{\text{CC}} = 63.0$ Hz and the β -carbon as a doublet at δ 119.7. In this case the α -carbon shows approximately equal coupling to all phosphorus nuclei. Compound **14** decomposes after a period of 3 days in solution. However, under CO, **14** yields the methylvinylidene compound $[\text{Ir}_2(\text{H})(\text{CO})_3(\mu\text{-C}=\text{CHMe})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**15**) in about 35% yield, as determined by NMR spectroscopy. The many other products remain uncharacterized. Compound **15** is an unusual example of carbon–carbon bond formation in which the methyl group and one of the vinylidene hydrogens in the precursor have exchanged positions. If **15** is prepared from $^{13}\text{CH}_3$ -labeled compound **1** and ^{13}C -enriched acetylene, and purified by recrystallization, its ^1H NMR spectrum shows the vinylidene proton as a broad signal at δ 6.50 with the typical one-bond C–H coupling of 155 Hz,²⁵ the methyl protons as a broad signal at δ 0.84 showing one-bond C–H coupling of 126 Hz, consistent for a sp^3 -hybridized carbon,²⁵ and the terminal hydride as a triplet at δ -10.62 . In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum the α -carbon of the vinylidene appears as a doublet of quintets at δ 192.0, showing coupling to the β -carbon (65.9 Hz) and the four phosphorus nuclei, the β -carbon appears as a doublet of doublets at δ 137.1, and the methyl substituent of the vinylidene appears as a doublet at δ 24.6, showing coupling of 42.0 Hz to the β -carbon.

If compound **1** is reacted with a large excess of acetylene at room temperature, 2 equiv of acetylene are incorporated, producing the compound $[\text{Ir}_2(\text{CH}_3)(\text{C}\equiv\text{CH})(\text{CO})_2(\mu\text{-H})(\mu\text{-C}=\text{CH}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**16**), as shown in Scheme 3. The bridging vinylidene protons appear as singlets in the ^1H NMR at δ 6.23 and 6.21, showing the typical $^1J_{\text{CH}}$ values for a vinylidene when prepared using ^{13}C -enriched acetylene. The terminal acetylide proton resonance appears at δ 1.87 as a triplet with 1.9 Hz coupling to one set of phosphorus nuclei and 228 Hz coupling to the β -carbon for the ^{13}C -enriched sample. The Ir-bound methyl resonance appears as a triplet at δ -0.35 in the ^1H NMR spectrum, and the bridging hydride appears at δ -14.01 as an apparent septet, which upon selective phosphorus decoupling is better described as a triplet of triplets showing 5 and 10 Hz coupling to the two different sets of phosphorus

(24) Average values for $^1J_{\text{C-C}}$ (Hz) for different hybridizations: acetylene ($\text{sp} = 172$), ethylene ($\text{sp}^2 = 68$), ethane ($\text{sp}^3 = 35$). From: Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH Publishers: New York and Weinheim, Germany, 1991; p 99.

(25) Average values for $^1J_{\text{C-H}}$ (Hz) for different hybridizations: acetylene ($\text{sp} = 249$), ethylene ($\text{sp}^2 = 156$), ethane ($\text{sp}^3 = 125$). From: Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH Publishers: New York and Weinheim, Germany, 1991; p 95.

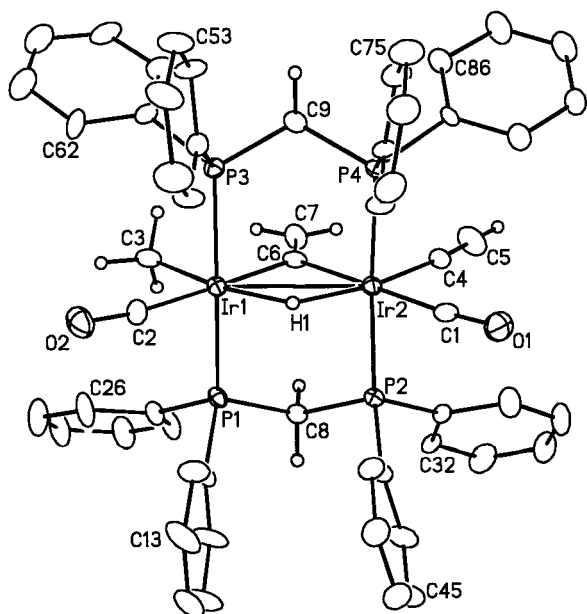


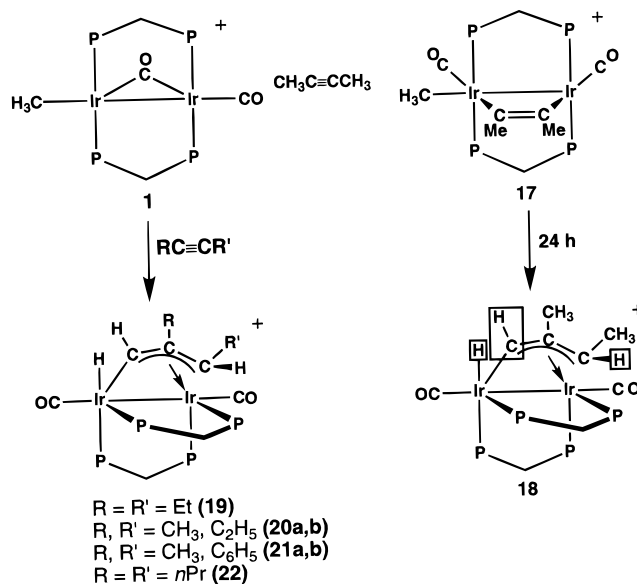
Figure 2. Perspective view of the $[\text{Ir}_2(\text{CH}_3)(\text{C}\equiv\text{CH})(\text{CO})_2-(\mu\text{-H})(\mu\text{-C}\equiv\text{CH})(\text{dppm})_2]^+$ cation of compound **16**. Thermal ellipsoids as for Figure 1.

nuclei. The infrared spectrum displays a stretch at 1574 cm^{-1} for the bridging vinylidene and stretches at 2064 and 2000 cm^{-1} that are assigned to the terminal acetylide and carbonyl groups, respectively. A labeling experiment using a ^{13}C -enriched sample of compound **16** confirmed the assignment for the acetylide and carbonyl bands, showing a lowering of the carbonyl stretch to 1956 cm^{-1} with no change in the acetylide band. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum the α -carbon of the bridging vinylidene appears as a broad doublet at δ 193.6 and the β -carbon as a doublet at δ 120.2 ($^1J_{\text{CC}} = 64.9\text{ Hz}$). The acetylide α -carbon appears at δ 61.6 as a doublet of doublets of triplets coupling to the β -carbon ($^1J_{\text{CC}} = 119.1\text{ Hz}$), the vinylidene α -carbon, and the dppm phosphines, with the β -acetylide carbon appearing at δ 103.7 as a doublet.²⁴ The iridium-bound methyl carbon appears at δ -5.2 as a broad, unresolved singlet. The structure proposed is supported by the X-ray structure determination, a representation of which is shown in Figure 2. A compilation of important bond lengths and angles is given in Table 4. Although the metal–metal bond length of $2.9460(9)\text{ \AA}$ is longer than typically observed for an Ir–Ir single bond, this lengthening is in line with the presence of a bridging hydride ligand,²⁶ which was not located but was fixed in the position shown, based upon ^1H NMR data. Both carbonyl ligands are terminally bound, one to each metal in the sites opposite the bridging vinylidene group, with the methyl and acetylide ligands on the opposite face, trans to the bridging hydride. The vinylidene group symmetrically bridges the two metals with Ir–C(6) distances of $2.07(2)$ and $2.09(1)\text{ \AA}$ and an Ir(1)–C(6)–Ir(2) angle of $90.0(6)^\circ$, in good agreement with the parameters observed in a number of vinylidene-bridged complexes,^{11b,27} and the C(6)–C(7) bond distance of $1.31-$

Table 4. Selected Interatomic Distances and Angles for Compound **16**.

(a) Distances (\AA)							
atom1	atom2	distance	atom1	atom2	distance		
Ir1	Ir2	2.9460(9)	Ir2	C1	1.94(2)		
Ir1	P1	2.354(4)	Ir2	C4	2.01(2)		
Ir1	P3	2.345(4)	Ir2	C6	2.09(1)		
Ir1	C2	1.90(2)	O1	C1	1.15(2)		
Ir1	C3	2.13(2)	O2	C2	1.14(2)		
Ir1	C6	2.07(2)	C4	C5	1.13(2)		
Ir2	P2	2.340(4)	C6	C7	1.31(2)		
Ir2	P4	2.337(4)					
(b) Angles (deg)							
atom1	atom2	atom3	angle	atom1	atom2	atom3	angle
Ir2	Ir1	C2	137.0(5)	P2	Ir2	P4	176.7(1)
Ir2	Ir1	C3	132.2(5)	C1	Ir2	C4	93.7(7)
Ir2	Ir1	C6	45.4(4)	C1	Ir2	C6	178.7(6)
P1	Ir1	P3	176.2(1)	C4	Ir2	C6	87.6(6)
C2	Ir1	C3	90.8(7)	Ir2	C1	O1	170.7(15)
C2	Ir1	C6	177.5(7)	Ir1	C2	O2	167.8(17)
C3	Ir1	C6	86.8(6)	Ir2	C4	C5	174.1(18)
Ir1	Ir2	C1	134.1(5)	Ir1	C6	Ir2	90.0(6)
Ir1	Ir2	C4	132.2(5)	Ir1	C6	C7	135.0(13)
Ir1	Ir2	C6	44.6(4)	Ir2	C6	C7	135.0(13)

Scheme 4



(2) \AA corresponds to a normal double bond in an olefinic unit.²⁸ The acetylide ligand is σ -bound to Ir(2) with a metal–carbon bond length of $2.01(2)\text{ \AA}$, similar to the distance seen for the terminal acetylide in $[\text{RhIr}(\text{C}\equiv\text{CPh})(\text{CO})_2(\mu\text{-H})(\mu\text{-C}\equiv\text{CPh})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$,^{7g} and the short C(4)–C(5) distance ($1.13(2)\text{ \AA}$) is consistent with the triple-bond order.²⁸

Reaction of the internal alkyne, 2-butyne, with **1** initially occurs much as described for HFB and DMAD, initially giving a product $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\mu\text{-CH}_3\text{C}\equiv\text{CCH}_3)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**17**) (see Scheme 4), in which the alkyne group bridges the two metals. The assignment of this structure is based upon similarities with the $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR data for compound **2**. However, upon stirring for 24 h at ambient temperature, compound **17** disappears, being replaced by the unusual vinylcarbene compound $[\text{Ir}_2(\text{H})(\text{CO})_2(\mu\text{-}\eta^1\text{:}\eta^3\text{-HCC}(\text{Me})=$

(26) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 83.

(27) (a) Xiao, J.; Cowie, M. *Organometallics* **1993**, *12*, 463. (b) Wang, L.-S.; Cowie, M. *Organometallics* **1995**, *14*, 3040.

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CHMe)(dppm)₂][CF₃SO₃] (**18**). The ³¹P{¹H} NMR spectrum shows a complex pattern with four individual resonances at δ –5.8, –6.0, –34.3, and –37.8, indicating an ABCD spin system, and the ¹H NMR spectrum shows the bridgehead or carbene proton as a multiplet at δ 8.79,²⁹ the methyl groups on the vinyl substituent appearing as a doublet and a broad multiplet at δ 2.72 and 1.42, respectively, and the hydride resonance as a complex multiplet at δ –11.25. Two-dimensional ¹H–¹³C correlation NMR data help in establishing the dppm methylene proton resonances at δ 7.12, 5.83, 4.60, and 3.78, with the vinylic hydrogen resonance appearing at δ 3.29. Both carbonyls are terminally bound, appearing in the ¹³C{¹H} NMR spectrum as multiplets at δ 170.9 and 168.2. The carbene carbon appears as a doublet of multiplets at δ 138.4, displaying 63.0 Hz coupling to one phosphine (presumably in a trans or almost-trans location) and unresolved coupling to the other phosphorus nuclei, with the vinyl resonances appearing as a singlet at δ 110.2 for the α-carbon and as a multiplet at δ 56.2 for the β-carbon. The α and β methyl-substituents on the vinyl moiety appear as singlets at δ 23.4 and 18.1, respectively. If ¹³CH₃-labeled **1** is used in the preparation of **18**, the ¹³C{¹H} NMR spectrum shows that the methyl carbon has been incorporated only into the carbene or bridgehead position, and in this case the attached proton is shown to have coupling to this carbon of 155.4 Hz. The fragments of the original Ir-bound methyl group are shown in boxes in Scheme 4.

Compound **1** reacts similarly with other internal alkynes, producing the vinylcarbene compounds [Ir₂(H)(CO)₂(μ-η¹:η³-HCC(R)=CHR')(dppm)₂][CF₃SO₃] (R = R' = Et (**19**); R, R' = Me, Et (**20**); R, R' = Me, Ph (**21**); R = R' = nPr (**22**)) (outlined in Scheme 4), and their characterization is based on similarities with the spectral data of compound **18**. All show similar ABCD patterns in the ³¹P{¹H} NMR spectra and have a characteristic downfield shift in the ¹H NMR spectra between δ 8.79 to 9.22 for the proton on the bridgehead carbon. Positive assignment of some ¹H NMR resonances proved to be very difficult due to the number, overlap, and complexity of the signals, and so is incomplete. In most cases the low-field resonance for one of the dppm methylene hydrogens is buried under the phenyl resonances and is not identified; it was identified in compounds **18** and **22** by 2-D NMR experiments. In **19** all methylene hydrogens are inequivalent (they are diastereotopic), and those on the ethyl groups couple equivalently in the ¹H NMR spectrum to their adjacent methyl hydrogens, giving apparent triplets for the latter. Compounds **20** and **21**, prepared using unsymmetrical alkynes, each yielded two isomers, differing by the relative positions of the two substituents. The isomers of compound **20** were produced in a 1:1 ratio, while those of **21** appeared in a 4:1 ratio, as determined by NMR experiments.

The proposed structures for these products are supported by the X-ray structure determination of **19**, a representation of which is shown in Figure 3. A com-

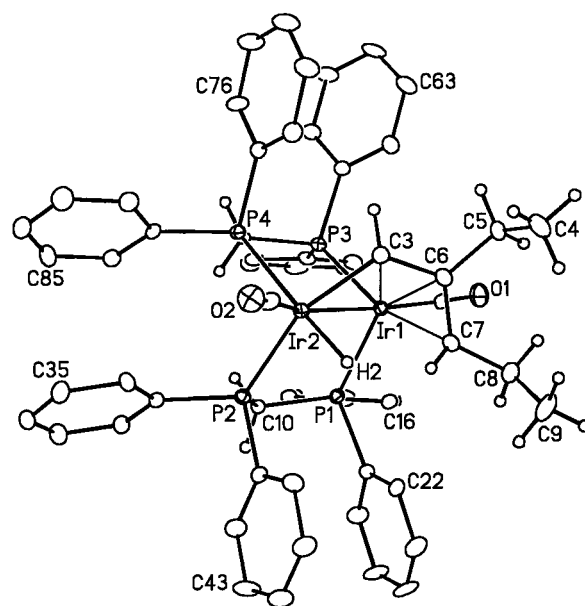


Figure 3. Perspective view of the [Ir₂H(CO)₂(μ-η¹:η³-HCCEtC(H)Et)(dppm)₂]⁺ cation of compound **19**. Thermal parameters as for Figure 1.

Table 5. Selected Interatomic Distances and Angles for Compound 19

(a) Distances (Å)							
atom1	atom2	distance	atom1	atom2	distance		
Ir1	Ir2	2.7623(7)	Ir2	C3	2.064(7)		
Ir1	P1	2.329(2)	O1	C1	1.164(8)		
Ir1	P3	2.361(2)	O2	C2	1.141(8)		
Ir1	C1	1.864(7)	C3	C6	1.440(10)		
Ir1	C3	2.207(6)	C4	C5	1.505(10)		
Ir1	C6	2.233(6)	C5	C6	1.520(9)		
Ir1	C7	2.220(7)	C6	C7	1.431(9)		
Ir2	P2	2.322(2)	C7	C8	1.497(10)		
Ir2	P4	2.372(2)	C8	C9	1.503(11)		
Ir2	C2	1.869(7)					
(b) Angles (deg)							
atom1	atom2	atom3	angle	atom1	atom2	atom3	angle
Ir2	Ir1	C1	168.8(2)	Ir2	C2	O2	175.5(7)
Ir2	Ir1	C3	47.5(2)	Ir1	C3	Ir2	80.5(2)
Ir2	Ir1	C6	76.9(2)	Ir1	C3	C6	72.1(4)
Ir2	Ir1	C7	83.1(2)	Ir2	C3	C6	126.0(5)
P1	Ir1	P3	96.79(6)	C4	C5	C6	111.6(6)
C1	Ir1	C3	122.3(3)	Ir1	C6	C3	70.1(4)
C1	Ir1	C6	91.9(3)	Ir1	C6	C5	127.5(5)
C1	Ir1	C7	88.3(3)	Ir1	C6	C7	70.7(4)
C3	Ir1	C6	37.9(2)	C3	C6	C5	119.8(6)
C3	Ir1	C7	67.1(2)	C3	C6	C7	116.9(6)
C6	Ir1	C7	37.5(2)	C5	C6	C7	123.3(6)
Ir1	Ir2	C2	159.6(2)	Ir1	C7	C6	71.8(4)
Ir1	Ir2	C3	52.0(2)	Ir1	C7	C8	123.9(5)
P2	Ir2	P4	98.39(6)	C6	C7	C8	124.2(6)
C2	Ir2	C3	109.3(3)	C7	C8	C9	112.6(7)
Ir1	C1	O1	175.8(6)				

pilation of important bond lengths and angles is given in Table 5. The diphosphine groups are in a cis orientation, with angles of 96.79 (6)° and 98.39 (6)° for P(1)–Ir(1)–P(3) and P(2)–Ir(2)–P(4), respectively, and the Ir–Ir distance of 2.7623 (7) Å is typical of a metal–metal bond.³⁰ The carbonyls are terminally bound to each metal, and the vinylcarbene moiety asymmetrically

(29) For typical comparisons see: (a) Sumner, C. E., Jr.; Collier, J. A.; Pettit, R. *Organometallics* **1982**, *1*, 1350. Examples for ¹³C{¹H} NMR: (b) Chetcuti, M. J.; McDonald, S. R.; Rath, N. P. *Organometallics* **1989**, *8*, 2077. (c) Howard, J. A. K.; Knox, S. A. R.; Terrill, N. J.; Yates, M. I. *J. Chem. Soc., Chem. Commun.* **1989**, 640. (d) Eisenstadt, A.; Efraty, A. *Organometallics* **1982**, *1*, 1100.

(30) (a) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2733. (b) Sutherland, B. R.; Cowie, M. *Organometallics* **1984**, *3*, 1869. (c) Sutherland, B. R.; Cowie, M. *Inorg. Chem.* **1984**, *23*, 2324. (d) Sutherland, B. R.; Cowie, M. *Organometallics* **1985**, *4*, 1801. (e) Xiao, J.; Cowie, M. *Organometallics* **1993**, *12*, 463.

bridges the metals, being η^1 -bound to Ir(2) (Ir(2)–C(3) = 2.064(7) Å) and η^3 -bound to Ir(1) (Ir(1)–C distances: 2.207(6), 2.233(6), 2.220(7) Å). The C(3)–C(6) and C(6)–C(7) bonds of the resulting fragment (1.440(10), 1.431(9) Å) are typical of an η^3 -bound allyl group.³¹ In this geometry the vinylcarbene unit can equally well be considered as a metallaallyl moiety, and both formulations have previously been considered.³² Both formulations are diagrammed below.



Discussion

We had anticipated that alkyne coordination to [Ir₂(CH₃)(CO)(μ -CO)(dppm)₂][CF₃SO₃] (**1**) might result in C–H bond cleavage of the methyl group, as observed in reactions of **1** with a number of other substrates, and that this might be followed at some stage by C–C bond formation between the two hydrocarbyl fragments on the metals. Instead, a range of reactivities is observed, depending upon the class of alkyne investigated, although internal, nonactivated alkynes do appear to react as anticipated, as will be discussed later. Reactions with the activated alkynes, DMAD, HFB, and methylpropiolate, were the most disappointing, yielding the simple alkyne adducts [Ir₂(CH₃)(CO)₂(μ - η^1 : η^1 -alkyne)(dppm)₂][CF₃SO₃], in which the methyl group has remained intact and the alkynes occupy a bridging position parallel to the metals, much as observed in the majority of dppm- and alkyne-bridged complexes.¹⁶ Although the methyl ligand was shown to lie *cis* to the bridging DMAD group, reaction with CO and PMe₃ has not resulted in migratory insertion of the methyl and DMAD ligands, yielding instead only the ligand adducts. These observations are somewhat surprising in view of the observed insertion of DMAD into an Ir–CH₃ bond in the tricarbonyl analogue to give [Ir₂(C(R)=C(Me)R)(CO)₃(dppm)₂][CF₃SO₃] (R = CO₂Me). The idea that migratory insertion for the CO and PMe₃ adducts (**3** and **4**) did not occur owing to unfavorable arrangements of the alkyne and methyl groups was eliminated by the structural determination of **4**, which showed a mutually *cis* arrangement. These results suggest that reaction of the tricarbonyl precursor with DMAD results in migratory insertion *before* the DMAD ligand enters the bridging site. The inertness of activated alkynes when bridging two metals as *cis*-dimetalated olefins has previously been noted,^{16i,j,33} suggesting that in this case migration may involve an η^2 -bound alkyne intermediate at a single metal.

(31) (a) Wakefield, J. B.; Stryker, J. M. *Organometallics* **1990**, *9*, 2428 (Supporting Information). (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 176. (c) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 6, Sections 37.6, 38.7, and 39.9. (d) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 3252.

(32) See for example "allylidene (vinylcarbene)": (a) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 803. (b) Eisenstadt, A.; Efraty, A. *Organometallics* **1982**, *1*, 1100. "Metallaallyl": (c) Chetcuti, M. J.; McDonald, S. R.; Rath, N. P. *Organometallics* **1989**, *8*, 2077. (d) Muller, J.; Passon, B.; Pickardt, J. *J. Organomet. Chem.* **1982**, *236*, C11.

The reactions of terminal alkynes such as propyne, phenylacetylene, and acetylene with **1** to give acetylide-containing intermediates which subsequently undergo hydrogen migration to give the vinylidene-bridged species, [Ir₂(CH₃)(CO)₂(μ -CC(R)H)(dppm)₂][CF₃SO₃] (R = CH₃, Ph, H), are also not unexpected outcomes. However, the subsequent elimination of methane from the above methyl- and phenylvinylidene, methyl intermediates was unexpected to us. Apparently the acetylide-to-vinylidene transformation is reversible, and at the higher temperatures the intermediate containing the hydrido and methyl groups eliminates methane.

For the vinylidene-bridged species, [Ir₂(CH₃)(CO)₂(μ -CCH₂)(dppm)₂][CF₃SO₃] (**14**), the transformation into the methylvinylidene hydride product [Ir₂(H)(CO)₃(μ -CC(H)CH₃)(dppm)₂][CF₃SO₃] (**15**) upon reaction with CO was even more surprising, with the obvious question arising as to how exchange between a vinylidene hydrogen and the methyl ligand occurred. On the basis of analogies with the previous reactions of propyne and phenylacetylene, we propose a reversible vinylidene to acetylide hydride transformation, converting **14** back to **13**, or to an isomer thereof. At higher temperatures we assume that this is followed by methyl, rather than hydride, migration to the acetylide ligand to give the product **15**. It appears that the hydride migration yields the kinetically favored product (**14**), whereas methyl migration to give **15** is the thermodynamically favored transformation. In any case, although this reaction did not proceed as anticipated, it did give rise to C–C bond formation, as originally targeted. Although hydride migration to the β -carbon of an acetylide to give a vinylidene is common,^{9,22,34} we are aware of only two examples involving migration of a σ -bound hydrocarbyl fragment to the β -carbon of an acetylide; the first involves migration of an aryl group,^{10d} and the second involves allyl migration,^{10b,c} giving a bridging vinylidene in each case. We are unaware of any previous examples of methyl migration to the β -carbon of acetylides.

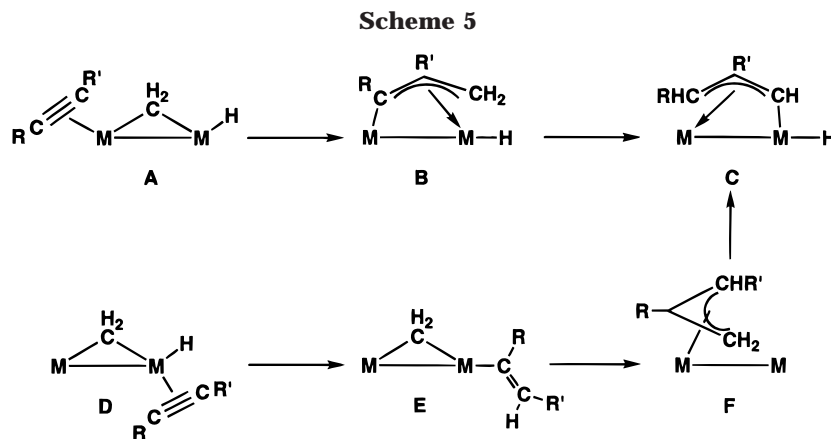
The product of addition of two acetylene molecules to **1**, [Ir₂(CH₃)(CCH)(CO)₂(μ -H)(μ -CCH₂)(dppm)₂][CF₃SO₃] (**16**), in which a bridging vinylidene is flanked by a methyl ligand on one side and an acetylide on the other, suggests the possibility of C–C bond formation involving the vinylidene ligand and either of the adjacent hydrocarbyl anions. However, no C–C bond formation was observed; presumably the coordinative saturation at both metals and the strong Ir–C bonds inhibit any subsequent reactivity. Species such as **16**, having adjacent vinylidene and alkynyl groups, are of interest owing to the involvement of vinylidene/alkynyl complexes or iron, ruthenium, and osmium in the coupling of 1-alkynes.³⁵

Without doubt, the most unusual transformation in the reactions described herein is that involving **1** with the internal alkynes RC \equiv CR', in which the alkyne substituents are various combinations of alkyl and phenyl groups (see Scheme 4). The vinylcarbene prod-

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(35) Bianchini, C.; Innocenti, P.; Peruzzini, M.; Romerosa, A.; Zanolini, F. *Organometallics* **1996**, *15*, 272, and references therein.



ucts obtained, $[\text{Ir}_2\text{H}(\text{CO})_2(\mu-\eta^1:\eta^3\text{-CHCRCHR}')(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**18–22**), have resulted from formal cleavage of two C–H bonds of the methyl ligand, accompanied by addition of the methyne fragment to one of the alkyne carbons and hydrogen transfer to the other. A preliminary report of this work has appeared.³⁶ Vinylcarbenes are typically formed by the addition of alkynes to methylene-bridged complexes,^{32,37} suggesting the involvement of a methylene-bridged moiety in these reactions of **1**. As suggested earlier, compound **1** is known to react with substrates to generate the methylene-bridged hydrides $[\text{Ir}_2\text{H}(\text{CO})_2\text{L}(\mu\text{-CH}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$. If this occurs with alkynes, two routes to the vinylcarbene products can be proposed, as presented in Scheme 5, in which the ancillary ligands are not shown. If the alkyne coordinates adjacent to the methylene group as in species **A**, insertion into the adjacent Ir–CH₂ bond would yield the vinylcarbene **B**. A metal-mediated, 1,3-shift of one of the methylenic hydrogens in **B** would yield the isomeric vinylcarbene **C**, as observed in products **18–22**. An alternate proposal, which we find particularly intriguing, is that depicted by transformations **D–C** in Scheme 5. If the alkyne coordinates adjacent to the hydride ligand as in **D**, migratory insertion to give the vinyl-containing species **E** should occur, which can then give the allyl product **F**. Transformations of vinyl and methylene groups to give allyl groups have been documented⁴ and are proposed to be pivotal in Fischer–Tropsch chemistry.⁵ The conversion of **F** to **C** would occur by C–H activation at the less crowded end of the allyl group by the adjacent metal. Although we have no evidence supporting either proposed route at this time, we are investi-

gating both possibilities via reactions of related methylene-bridged species, not containing hydride ligands, with internal alkynes and with vinyl sources such as vinyl Grignards.

The two isomers obtained when unsymmetrical alkynes are used result from one end or the other binding to the methyne carbon and are readily rationalized in the “vinyl route” (steps **D–C**) by the steric considerations that would favor the bulkier substituent at the β -position of the vinyl moiety.

The kinetic products in these reactions of **1** with internal alkynes are again the simple alkyne-bridged species. We assume that these products are reversibly formed and that alkyne loss is followed by coordination as shown in either **A** or **D** of Scheme 5 to give the thermodynamic products. The failure of the activated alkyne adducts (**2–6**) to react in a manner analogous to the nonactivated alkyne adducts (e.g., **17**), even though they are structurally analogous, adds further support to the idea that once in the $\mu-\eta^1:\eta^1$ -binding mode the activated alkynes in this system are rather unreactive, binding essentially irreversibly to the metals. Certainly metal–carbon σ -bonds are known to be strong when the α -carbon has electron-withdrawing substituents.³⁸

Conclusions

Although alkynes react with the binuclear methyl complex $[\text{Ir}_2(\text{CH}_3)(\text{CO})(\mu\text{-CO})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**1**) in a variety of ways, the most interesting transformations result from the reactions of **1** with internal, nonactivated alkynes, in which a series of vinylcarbenes are obtained. These transformations result from the activation of the methyl C–H bonds in **1** upon addition of substrate molecules and demonstrate the utility of this process in the formation of C–C bonds, by reaction of unsaturated hydrocarbons (in this case alkynes) with either the methylene or hydrido ligands generated in the C–H bond-cleavage step. Studies are currently under way to determine the extent of this reactivity with a number of other unsaturated substrates and to elaborate the mechanism(s) of these transformations.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (NSERC)

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(38) (a) Reger, D. L.; McElligot, P. J. *J. Organomet. Chem.* **1981**, *216*, C12. (b) Elschenbroich, C.; Salzer, A. *Organometallics: A Concise Introduction*; VCH Publishers: New York, 1989; Chapter 13. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 99.

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Supporting Information Available: Tables of X-ray experimental details, atomic coordinates, interatomic dis-

tances and angles, anisotropic thermal parameters, and hydrogen parameters for compounds **4**, **16**, and **19**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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