An Unusual Example of Allyl-to-Alkynyl Migration in a Phenylacetylide-Bridged Heterobinuclear Complex of Rhodium and Iridium

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The reactivity of the alkynyl-bridged complex $[RhIr(CO)_2(\mu_2\text{-}\eta^1{:}\eta^2\text{-}C_2Ph)(dppm)_2][X]$ (X = BF_4 (**1a**), SO_3CF_3 (**1b**); dppm = $Ph_2PCH_2PPh_2$) with electrophiles has been demonstrated. Protic acids HX (X = BF_4, SO_3CF_3) first yield the oxidative-addition products $[RhIr(X)(CO)_2\text{-}(\mu\text{-}H)(\mu\text{-}C_2Ph)(dppm)_2][X]$, which under carbon monoxide result in displacement of the weakly coordinating BF_4^- or $SO_3CF_3^-$ anions and subsequent conversion to the vinylidene-bridged $[RhIr(CO)_4(\mu\text{-}CC(H)Ph)(dppm)_2][X]_2$. Reaction of **1** with allyl halides yields the allyl vinylidene-bridged compounds $[RhIr(Y)(CO)(\mu\text{-}CC(Ph)CH_2CH{=}CH_2)(\mu\text{-}CO)(dppm)_2][X]$ (Y = Br (**5**), Cl (**6**)), by coupling of the alkynyl and allyl groups at the β-position of the alkynyl moiety. NMR studies at low temperatures show coordination of allyl halide at Ir at −80 °C, followed by allyl halide loss and subsequent oxidative addition at −50 °C. The oxidative-addition intermediates, $[RhIr(\eta^1\text{-}CH_2CH{=}CH_2)(CO)_2(\mu\text{-}Y)(\mu\text{-}C_2Ph)(dppm)_2][X]$ (Y = Br (**9**), Cl (**10**)), rearrange to the allylvinylidene products (**5** and **6**) at ambient temperature. Although halide removal from compounds **5** and **6**, using $AgBF_4$, does not result in destabilization of the allylvinylidene fragment, resulting instead in replacement of halide by fluoborate ion, the reaction of **1** with allyl halide in the presence of a silver salt does not lead to coupling of the allyl and alkynyl moieties, but gives $[RhIr(\eta^3\text{-}C_3H_5)(CO)(\mu\text{-}C_2Ph)(\mu\text{-}CO)(dppm)_2][X]_2$ (**13**). Addition of halide ion to this η^3-allyl complex at ambient temperature again leads to formation of **5** or **6**. On the basis of these results a mechanism is proposed for the allyl/alkynyl coupling reaction.

Introduction

The alkynyl (or acetylide) group is a versatile ligand in organometallic chemistry.[1] Not only does it serve as a common precursor to vinylidenes,[2] themselves versatile ligands in carbon−carbon bond formation,[3] but alkynyl complexes have also been implicated in a number of carbon−carbon bond-forming processes such as alkyne oligomerization and polymerization[4] and cycloaddition reactions.[5] As part of an ongoing effort to determine how adjacent metals can influence the reactivity of hydrocarbyl ligands,[6] we have undertaken a study of bridging alkynyl groups in binuclear complexes.[7]

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The most common alkynyl bonding mode is the terminal one (**A**) in which this group is η^1-bound to a single metal.[1a,8] In this geometry the alkynyl group has
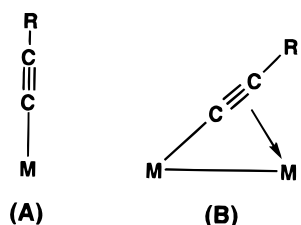
been shown to be susceptible to electrophilic attack at the β-carbon to yield vinylidene ligands.[5d,8a,9] When it bridges two metals, it usually adopts the μ-η^1:η^2-binding mode (**B**), in which it is σ-bound to one metal while π-bound to the adjacent metal.[8b,10] As might be expected, this bonding mode results in a modified reactivity compared to that of the η^1-alkynyl, with bridging groups being susceptible to *nucleophilic* attack.[11,12] Furthermore, Carty[11] and others[12] have shown that nucleophilic attack can occur at either the α- or β-positions. We have also shown, in an alkynyl-bridged, heterobinuclear Rh/Ir complex, that nucleophilic attack occurs first at Ir and that in the case of the hydride group this is followed

by migration to the alkynyl β-carbon,[7] raising the possibility that other cases of alkynyl reactivity may also proceed via initial attack at the metal. One goal of this study was to extend the reactivity of bridging alkynyl groups to include electrophilic attack, through initial involvement of the electron-rich group 9 metals.

Alkynyl groups have also been implicated as intermediates in the transformation of 1-alkynes to vinylidenes.[13] Certainly, in binuclear late-metal complexes we have shown that this transformation is extremely facile and have proposed that it is facilitated by the μ-η^1:η^2-alkynyl binding mode, in which migration of the hydride ligand from an intermediate such as **C** to the alkynyl β-carbon occurs readily, as diagrammed in eq 1.[6h,14]

$$(1)$$
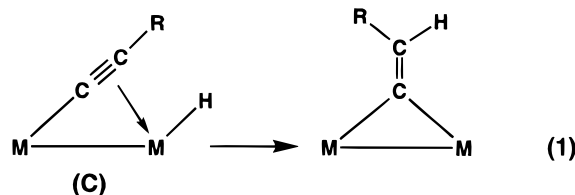
Intermediate **C** can be considered as containing a metal-substituted alkyne moiety (RC≡CM), which is π-bound to the second metal, with the process shown in eq 1 being analogous to migratory insertion involving mutually cis hydride and alkyne ligands. We sought to extend this analogy to carbanionic ligands in efforts to induce migration of an alkyl or related group from one metal to the adjacent β-carbon of an μ-η^1:η^2-alkynyl group. Certainly the analogous migrations of alkyls to coordinated alkynes are well-known.[14d,15] Although most previous examples of C−C bond formation involving alkynyl groups occur at the alkynyl α-carbon,[1f,o,q,4a,b,8b,3l] we are aware of two examples of apparent migration to the β-carbon of a bridging alkynyl group to generate vinylidene-bridged complexes. In the first case, migration of an aryl group in a Ti/Cu complex occurs,[16] whereas in the second, migration of a methyl ligand in a diiridium complex was observed.[6h] In this report we describe our studies aimed at probing this uncommon mode of carbon−carbon bond formation.

Experimental Section

All solvents were distilled over appropriate drying agents (sodium/benzophenone for THF, ether, benzene, and pentane; phosphorus pentoxide for halogenated solvents) before use. Reactions were done at ambient temperature using standard Schlenk techniques (under either dinitrogen or argon) unless otherwise stated. Prepurified dinitrogen, argon, and carbon monoxide were purchased from Praxair Products, Inc., and

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were used as received. Ammonium hexachloroiridate(IV) and potassium hexachlororhodate(III) were obtained from Vancouver Island Precious Metals; hydrated rhodium trichloride was purchased from Colonial Metals. The compounds [IrAgCl-(CCPh)(CO)(dppm)$_2$],[17] [Rh$_2$(CO)$_4$Cl$_2$],[18] and [Rh$_2$(COD)$_2$Cl$_2$][19] were prepared by literature methods. Deuterated solvents (obtained from Cambridge Isotope Laboratories) were distilled and stored over molecular sieves under argon. The compound [RhIr(CO)$_2$(CCPh)(dppm)$_2$][SO$_3$CF$_3$] (**1b**) was prepared as previously reported.[7b] The silver salts (AgBF$_4$, AgO$_3$SCF$_3$) were obtained from Aldrich and were stored and used in an argon-filled glovebox. All other compounds were obtained from Aldrich and used as received. Spectroscopic data for all new compounds are given in Table 1.

NMR spectra were obtained on either a Bruker 400 or 200 MHz spectrometer. Infrared spectra were run on either a Perkin-Elmer Model 1600 FTIR or a Nicolet Magna-IR 750 spectrometer as either solids (Nujol mulls on KBr disks) or solutions (KCl cell with 0.5 mm window path length). Elemental analyses were conducted by the microanalytical service within the department.

Preparation of Compounds. (a) [RhIr(CO)$_2$(μ-CCPh)-(dppm)$_2$][BF$_4$] (1a). A solid sample of [IrAgCl(CO)(CCPh)-(dppm)$_2$] (1.000 g, 810.7 μmol) was placed in a flask with [Rh$_2$(COD)$_2$Cl$_2$] (180.0 mg, 409.9 μmol), NaBF$_4$ (90.0 mg, 820 μmol), and 30 mL of CH$_2$Cl$_2$, yielding a brown-red mixture, which was stirred for 1 h, followed by the introduction of 1 atm of carbon monoxide. The solution was filtered after a further 3 h of stirring, then the solvent was removed in vacuo. The resulting solid was recrystallized from 1:3 CH$_2$Cl$_2$/ether and washed three times with 10 mL aliquots of pentane. The product was dissolved in 10 mL of CH$_2$Cl$_2$ and the solution refluxed for 1 h. THF (20 mL) was added, and the reflux continued for 5 h, after which time the solvent was reduced to 10 mL and the product was precipitated by the addition of diethyl ether (60 mL). The red product was then washed three times with 10 mL aliquots of ether and then recrystallized from CH$_2$Cl$_2$/Et$_2$O (1:1) at room temperature, affording [RhIr(CO)$_2$-(μ-CCPh)(dppm)$_2$][BF$_4$]·1.5CH$_2$Cl$_2$ (0.8850 g, 76%) as burgundy crystals. Anal. Calcd for C$_{61.5}$H$_{52}$O$_2$P$_4$Cl$_3$RhIrBF$_4$: C, 51.47; H, 3.65; Cl, 8.88. Found: C, 51.13; H, 3.56, Cl, 8.42.

(b) [RhIr(FBF$_3$)(CO)$_2$(μ-H)(μ-CCPh)(dppm)$_2$][BF$_4$] (2a). An NMR tube was charged with **1a** (20.2 mg, 15.4 μmol) and 0.4 mL of CD$_2$Cl$_2$. Excess HBF$_4$·OEt$_2$ (5.1 μL, 37 μmol) was added, resulting in a color change from red-brown to yellow-brown. The product was spectroscopically characterized as [RhIr(FBF$_3$)(CO)$_2$(μ-H)(μ-CCPh)(dppm)$_2$][BF$_4$] (**2a**) but could not be isolated pure due to facile loss of HBF$_4$ to give the starting material.

(c) [RhIr(OSO$_2$CF$_3$)(CO)$_2$(μ-H)(μ-CCPh)(dppm)$_2$][BF$_4$] (2b). An NMR tube was charged with **1b** (20.2 mg, 15.4 μmol) and 0.4 mL of CD$_2$Cl$_2$. Excess HBF$_4$·OEt$_2$ (5.1 μL, 37 μmol) was added, resulting in a color change from red-brown to yellow-brown. This was shown to contain [RhIr(OSO$_2$CF$_3$)-(CO)$_2$(μ-H)(μ-CCPh)(dppm)$_2$][BF$_4$] (**2b**) as the only organometallic compound; however, this compound could not be isolated pure due to facile loss of free acid to give **1** and so was characterized in solution only.

(d) Reaction of 2a with CO. An NMR tube was charged with **1a** (20.2 mg, 15.4 mmol) and 0.4 mL of CD$_2$Cl$_2$. Excess HBF$_4$·OEt$_2$ was added, forming a brown-yellow solution. This was placed under an atmosphere of CO, causing a color change to yellow. The NMR spectra of this sample showed complete conversion to [RhIr(CO)$_3$(μ-H)(μ-CCPh)(dppm)$_2$][BF$_4$]$_2$ (**3**). Upon standing under CO, this converted to the vinylidene complex [RhIr(CO)$_4$(μ-CCHPh)(dppm)$_2$][BF$_4$]$_2$ (**4**). Neither compound

could be isolated free from [RhIr(CO)$_3$(μ-CCPh)(dppm)$_2$][BF$_4$], which is formed via loss of HBF$_4$, and were characterized in solution only.

(e) [RhIrBr(CO)(μ-CCPhCH$_2$CH=CH$_2$)(μ-CO)(dppm)$_2$]-[BF$_4$] (5a). A sample of **1a** (140.0 mg, 107.0 μmol) was placed in a flask with 15 mL of CH$_2$Cl$_2$, forming a red-purple solution. Allyl bromide (9.3 μL, 107.5 μmol) was added via gastight syringe, causing a color change to brown. After stirring for 3 h, the solution had turned a deep cherry red. The solvent volume was then reduced to 2 mL under nitrogen flow, and the product precipitated by the addition of 40 mL of diethyl ether. The product was recrystallized from 1:1:4 CH$_2$Cl$_2$/THF/ether, then washed three times with ether. Yield: 110.0 mg (72%). Anal. Calcd for C$_{63}$H$_{54}$BrO$_2$P$_4$RhIrBF$_4$: C, 52.95; H, 3.81. Found: C, 52.85; H, 3.94.

(f) [RhIrBr(CO)(μ-CCPhCH$_2$CH=CH$_2$)(μ-CO)(dppm)$_2$]-[SO$_3$CF$_3$] (5b). A sample of **1b** (50.5 mg, 36.9 μmol) was placed in a flask with 5 mL of benzene and 7 mL of THF. Allyl bromide (3.2 μL, 44 μmol) was added via gastight syringe, causing a slow color change to brown. After stirring for 1 h, the solution was allowed to stand undisturbed overnight, yielding a crop of dark purple crystals. The red-brown supernatant was removed, and the product was dried under vacuum. Yield: 28.1 mg (51% yield). Anal. Calcd for C$_{64}$H$_{54}$BrO$_5$P$_4$RhIrF$_3$S: C, 51.55; H, 3.65; Br, 5.36. Found: C, 51.56; H, 3.54; Br, 5.64.

(g) [RhIrCl(CO)(μ-CCPhCH$_2$CH=CH$_2$)(μ-CO)(dppm)$_2$]-[BF$_4$] (6a). A sample of **1a** (29.4 mg, 22.5 μmol) was placed in a flask with 5 mL of CH$_2$Cl$_2$, forming a red-purple solution. Allyl chloride (1.8 μL, 22 μmol) was added via gastight syringe, causing a color change to brown. After stirring overnight, the solution had turned a deep cherry red. The solvent volume was then reduced to 1 mL under nitrogen flow, and the product precipitated by the addition of 10 mL of ether. The product was recrystallized from 1:5 CH$_2$Cl$_2$/ether, then washed twice with 5 mL of ether, affording [RhIrCl(CO)(μ-CCPhCH$_2$CH= CH$_2$)(μ-CO)(dppm)$_2$][BF$_4$](**6a**)·1.75CH$_2$Cl$_2$ as cherry-red crystals. Yield: 15.3 mg (44%). Anal. Calcd for C$_{64.75}$H$_{57.5}$Cl$_{4.5}$O$_2$P$_4$-RhIrBF$_4$: C, 50.73; H, 3.78; Cl, 10.41. Found: C, 51.09; H, 3.69; Cl, 10.49.

(h) [RhIrCl(CO)(μ-CCPhCH$_2$CH=CH$_2$)(μ-CO)(dppm)$_2$]-[SO$_3$CF$_3$] (6b). Compound **1b** (0.200 g, 145 μmol) was placed in a 100 mL flask along with 30 mL of CH$_2$Cl$_2$, affording a red-purple solution. Allyl chloride (12 μL, 146 μmol) was added by microliter syringe, and the mixture was stirred overnight at ambient temperature, during which time the solution color changed from burgundy to cherry red. The solvent volume was reduced to ca. 3 mL in vacuo, and 30 mL of diethyl ether was added, causing the product to precipitate as a red crystalline solid. Recrystallization from CH$_2$Cl$_2$/diethyl ether (1:1) at ambient temperature afforded red crystals of [RhIrCl(CO)(μ-CCPhCH$_2$CH=CH$_2$)(μ-CO)(dppm)$_2$][SO$_3$CF$_3$] (**6b**)·0.5CH$_2$Cl$_2$. Yield: 0.085 g (39%). Anal. Calcd for C$_{64.5}$H$_{55}$O$_5$Cl$_2$P$_4$RhIrF$_3$S: C, 52.02; H, 3.72; Cl, 4.76; S, 2.15. Found: C, 52.44; H, 3.65; Cl, 3.60; S, 2.51.

(i) Low-Temperature Reaction of 1b with CH$_2$= CHCH$_2$Br or CH$_2$=CHCH$_2$Cl. An NMR tube was charged with **1b** (17.5 mg, 12.8 μmol) and 0.4 mL of CD$_2$Cl$_2$. The sample was cooled to -90 °C and treated with allyl bromide (1.1 μL, 13 μmol). The NMR spectra of this sample showed the formation of the olefin adduct [RhIr(CO)$_2$(η^2-CH$_2$CHCH$_2$Br)-(μ-CCPh)(dppm)$_2$][SO$_3$CF$_3$] (**7**). Warming to -30 °C resulted in complete conversion to the oxidative addition product [RhIrBr(η^1-CH$_2$CHCH$_2$)(CO)$_2$(μ-CCPh)(dppm)$_2$][SO$_3$CF$_3$] (**9**). Upon warming to room temperature, this compound reacted further, slowly giving the allylvinylidene bromo complex **5b** as the major product. The same procedure was used to monitor the reaction of **1b** with allyl chloride. Analogous intermediates **8** and **10** were observed before formation of the final product **6b**.

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Table 1. Spectral Data[a]

compound	NMR $\delta(^{31}P\{^1H\})$[b]	$\delta(^{13}C\{^1H\})$[c]	$\delta(^1H)$[c]	IR, cm^{-1} [d]
[RhIr(BF$_4$)(CO)$_2$(μ-CCPh)(μ-H)-(dppm)$_2$][BF$_4$] (**2a**)	21.8 (dm, $^1J_{RhP}$ = 91.7 Hz), −4.5 (m)	186.7 (dt, Rh-*C*O, $^1J_{RhC}$ = 81.8 Hz, $^2J_{PC}$ = 15.5 Hz), 170.6 (t, Ir-*C*O, $^2J_{PC}$ = 9.6 Hz)	4.65 (m, PC*H*$_2$P), 3.40 (m, PC*H*$_2$P), −19.00 (bd, μ-H, $^1J_{RhH}$ = 6 Hz)	2068 1985
[RhIr(O$_3$SCF$_3$)(CO)$_2$(μ-CCPh)(μ-H)-(dppm)$_2$][BF$_4$] (**2b**)	22.7 (dm, $^1J_{RhP}$ = 109.2 Hz), −6.0 (m)		4.75 (m, PC*H*$_2$P), 3.55 (m, PC*H*$_2$P), −19.42 (m, μ-H, $^1J_{RhH} \approx {}^2J_{PH} \approx$ 6 Hz)	
[RhIr(CO)$_3$(μ-H)(μ-CCPh)(dppm)$_2$]-[BF$_4$]$_2$ (**3**)	22.0 (dm, $^1J_{RhP}$ = 105.1 Hz), −19.1 (m)	188.1 (dt, Rh-*C*O, $^1J_{RhC}$ = 83.0 Hz, $^2J_{PC}$ = 16.7 Hz), 161.4 (t, Ir-*C*O, $^2J_{PC}$ = 7.7 Hz), 154.9 (t, Ir-*C*O, $^2J_{PC}$ = 4.4 Hz)	4.45 (m, PC*H*$_2$P), 3.70 (m, PC*H*$_2$P), −7.78 (m, μ-H, $^1J_{RhH}$ = 11.7 Hz, $^2J_{PH}$ = 8.0, 2.4 Hz)	2018 1996 1984
[RhIr(CO)$_4$(μ-CCHPh)(dppm)$_2$]-[BF$_4$]$_2$ (**4**)	9.5 (dm, $^1J_{RhP}$ = 79.1 Hz), −20.9 (m)	210.6 (dm, μ-*C*=CHPh, $^1J_{RhC}$ = 28.2 Hz), 188.7 (dm, Rh-*C*O, $^1J_{RhC}$ = 51.0 Hz), 176.1 (dm, Rh-*C*O, $^1J_{RhC}$ = 60.6 Hz), 168.1 (t, Ir-*C*O, $^2J_{PC}$ = 9.9 Hz), 161.7 (s, Ir-*C*O)	4.45 (m, PC*H*$_2$P), 4.55 (m, PC*H*$_2$P), 6.94 (b, 1H)	2105 2092 2059 1987
[RhIrBr(CO)(μ-CCPhCH$_2$CH=CH$_2$)(μ-CO)(dppm)$_2$][BF$_4$] (**5a**)	6.2 (dm, $^1J_{RhP}$ = 105.4 Hz), −0.96 (m)	185.8 (dm, μ-*C*O, $^1J_{RhC}$ = 39.6 Hz), 178.9 (t, Ir-*C*O, $^2J_{PC}$ = 10.4 Hz)	6.20 (b, H$_c$), 4.15 (d, H$_e$, $^3J_{HH}$ = 16 Hz), 4.05 (d, H$_d$, $^3J_{HH}$ = 9 Hz), 3.80 (m, PC*H*$_2$P), 3.40 (m, H$_a$ + H$_b$), 3.20 (m, PC*H*$_2$P)	1998 1803
	6.3 (dm, $^1J_{RhP}$ = 105.3 Hz),[e] 1.7 (dm, $^2J_{PP}$ = 260.7 Hz), −2.4 (dm, $^2J_{PP}$ = 260.7 Hz)	186.4 (dm, μ-*C*O, $^1J_{RhC}$ = 38.6 Hz),[e] 178.8 (t, Ir-*C*O, $^2J_{PC}$ = 9.9 Hz)	5.90 (b, H$_c$),[e] 3.90 (b, H$_a$ + H$_d$ + H$_e$), 3.60, 2.80 (m, PC*H*$_2$P), 3.40 (b, H$_b$)	
[RhIrBr(CO)(μ-CCPhCH$_2$CH=CH$_2$)(μ-CO)(dppm)$_2$][O$_3$SCF$_3$] (**5b**)	6.5 (dm, $^1J_{RhP}$ = 105.4 Hz), −0.5 (m)	186.0 (dm, μ-*C*O, $^1J_{RhC}$ = 41.1 Hz), 179.1 (t, Ir-*C*O, $^2J_{PC}$ = 10.3 Hz), 200.4 (m, μ-*C*=CRPh, $^1J_{RhC}$ = 18.7 Hz), 157.4 (t, μ-C=*C*RPh, $^3J_{PC}$ = 3.8 Hz), 38.5 (s, C=CPh*C*H$_2$-CH=CH$_2$), 123.5 (s, C=CPhCH$_2$-*C*H=CH$_2$), 99.1 (s, C=CPhCH$_2$-CH=*C*H$_2$)	6.20 (b, H$_c$), 4.20 (d, H$_e$, $^3J_{HH}$ = 16 Hz), 4.05 (d, H$_d$, $^3J_{HH}$ = 8 Hz), 3.85 (m, PC*H*$_2$P), 3.40 (m, H$_a$ + H$_b$), 3.30 (m, PC*H*$_2$P)	1986 1802
	6.4 (dm, $^1J_{RhP}$ = 105.4 Hz),[e] 2.1 (dm, $^2J_{PP}$ = 261.3 Hz), −1.96 (dm, $^2J_{PP}$ = 261.3 Hz)	186.4 (dm, μ-*C*O, $^1J_{RhC}$ = 39.4 Hz),[e] 178.9 (t, Ir-*C*O, $^2J_{PC}$ = 10.0 Hz)		
[RhIrCl(CO)(μ-CCPhCH$_2$CH=CH$_2$)(μ-CO)(dppm)$_2$][BF$_4$] (**6a**)	6.2 (dm, $^1J_{RhP}$ = 105.1 Hz), −0.7 (m)	186.1 (dm, μ-*C*O, $^1J_{RhC}$ = 39.6 Hz), 178.9 (t, Ir-*C*O, $^2J_{PC}$ = 10.5 Hz)	6.22 (b, H$_c$), 4.37 (d, H$_e$, $^3J_{HH}$ = 16 Hz), 4.02 (d, H$_d$, $^3J_{HH}$ = 9 Hz), 3.77 (m, PC*H*$_2$P), 3.40 (m, H$_a$ + H$_b$), 3.25 (m, PC*H*$_2$P)	2001 1810
[RhIrCl(CO)(μ-CCPhCH$_2$CH=CH$_2$)(μ-CO)(dppm)$_2$][CF$_3$SO$_3$] (**6b**)	6.3 (dm, $^1J_{RhP}$ = 105 Hz), −0.5 (m)		6.21 (b, H$_c$), 4.27 (d, H$_e$, $^3J_{HH}$ = 17 Hz), 4.01 (d, H$_d$, $^3J_{HH}$ = 9 Hz), 3.78 (m, PC*H*$_2$P), 3.41 (m, H$_a$ + H$_b$), 3.29 (m, PC*H*$_2$P)	2015 1794

Table 1 (Continued)

compound	δ(^{31}P{^{1}H})^b	δ(^{13}C{^{1}H})^c	δ(^{1}H)^c	IR, cm^{-1} ^{d}
[RhIr(CO)$_2$(CH$_2$CHCH$_2$Br)(μ-CCPh)-(dppm)$_2$][O$_3$SCF$_3$] (**7**)	16.7 (ddm, $^1J_{RhP}$ = 92.7 Hz, $^2J_{PP}$ = 316.4 Hz),^{e} 14.8 (ddm, $^1J_{RhP}$ = 103.8 Hz, $^2J_{PP}$ = 316.4 Hz), −11.7 (m)	190.0 (dt, Rh-CO, $^2J_{PC}$ = 13.9 Hz, $^1J_{RhC}$ = 83.6 Hz),^{e} 180.2 (d, Ir-CO, $^1J_{RhC}$ = 17.6 Hz)	5.2 (b, H$_a$ + H$_b$),^{e} 2.0 (b, 1H), 0.0 (b, 1H), −0.8 (b, 1H), 4.20, 4.00 (b, PCH$_2$P)	
[RhIr(CO)$_2$(CH$_2$CHCH$_2$Cl)-(μ-CCPh)(dppm)$_2$][O$_3$SCF$_3$] (**8**)	17.8 (ddm, $^1J_{RhP}$ = 94 Hz, $^2J_{PP}$ = 314 Hz), 14.8 (ddm, $^1J_{RhP}$ = 94 Hz, $^2J_{PP}$ = 314 Hz), −11.6 (m)		5.1 (b, H$_a$ + H$_b$), 2.0 (b, 1H), 0.7 (b, 1H), 4.2, 4.0 (b, PCH$_2$P)	
[RhIr(η^1-CH$_2$CH=CH$_2$)(μ-Br)(CO)$_2$-(μ-CCPh)(dppm)$_2$][O$_3$SCF$_3$] (**9**)	22.1 (d, $^1J_{RhP}$ = 104.8 Hz), −24.3 (s)	186.3 (dt, Rh-CO, $^2J_{PC}$ = 15.2 Hz, $^1J_{RhC}$ = 83.3 Hz),^{f} 167.7 (t, Ir-CO, $^2J_{PC}$ = 7.6 Hz)	4.90 (H$_c$, ddt, $^3J_{HH}$ = 16, 11, 8 Hz),^{f} 4.15 (H$_d$, dd, $^3J_{HH}$ = 11, 2 Hz), 3.65 (H$_e$, dd, $^3J_{HH}$ = 16, 2 Hz), 2.40 (H$_a$, H$_b$, dt, $^3J_{PH}$ = 9 Hz, $^3J_{HH}$ = 8 Hz) 4.65, 4.50 (m, PCH$_2$P)	
[RhIr(η^1-CH$_2$CH=CH$_2$)(μ-Cl)(CO)$_2$-(μ-CCPh)(dppm)$_2$][O$_3$SCF$_3$] (**10**)	22.5 (d, $^1J_{RhP}$ = 106.2 Hz),^{g} −19.5 (s)		4.58 (H$_c$, ddt, $^3J_{HH}$ = 16,11,8 Hz),^{g} 4.18 (H$_d$, dd, $^3J_{HH}$ = 10, 2 Hz), 3.28 (H$_c$, dd, $^3J_{HH}$ = 16, 2 Hz), 2.01 (H$_a$, H$_b$, dt, $^3J_{PH}$ = 9 Hz, $^3J_{HH}$ = 8 Hz), 4.59, 4.14 (m, PCH$_2$P, $^2J_{HH}$ = 7 Hz)	
[RhIr(BF$_4$)(CO)(μ-CCPhCH$_2$CH=CH$_2$)(μ-CO)(dppm)$_2$][BF$_4$] (**11**)	11.9 (dm, $^1J_{RhP}$ = 115.3 Hz), 1.14 (m)	188.1 (dm, μ-CO, $^1J_{RhC}$ = 40.1 Hz), 176.8 (t, Ir-CO, $^2J_{PC}$ =10.3 Hz), 190.0 (m, μ-C=CRPh, $^1J_{RhC}$ = 22.6 Hz), 151.5 (t, μ-C=CRPh, $^3J_{PC}$ = 3.8 Hz), 38.7 (s, C=CPhCH$_2$-CH=CH$_2$), 96.4 (s, C=CPhCH$_2$-CH=CH$_2$)	6.15 (m, H$_c$), 4.56 (m, H$_e$, $^3J_{HH}$ = 16 Hz), 4.39 (m, H$_d$, $^3J_{HH}$ = 9 Hz), 3.57 (m, H$_a$, $^2J_{HH}$ = 14 Hz), 2.95 (m, H$_b$, $^3J_{HH}$ = 11, 14 Hz), 3.90, 3.85 (m, PCH$_2$P), 3.45, 3.25 (m, PCH$_2$P)	2023 (s) 1814 (s)
[RhIr(CO)$_3$(μ-CCPhCH$_2$CH=CH$_2$)(dppm)$_2$][BF$_4$]$_2$ (**12**)	23.70 (m, $^1J_{RhP}$ = 84.47 Hz, $^2J_{AB}$ = 386.9 Hz, $^XJ_{AC}$ = 14.95 Hz, $^2J_{AD}$ = 46.96 Hz), 13.58 (m, $^1J_{RhP}$ = 87.8 Hz, $^2J_{BC}$ = 43.50 Hz, $^XJ_{BD}$ = 11.0 Hz), −23.96(m, $^2J_{CD}$ = 302.6 Hz), −29.21 (m)	194.6 (dt, Rh-CO, $^1J_{RhC}$ = 53.0 Hz, $^2J_{PC}$ = 18.5 Hz), 173.6 (t, Ir-CO, $^2J_{PC}$ = 6.9 Hz), 160.0 (m, Ir-CO), 225.3 (m, μ-C=CRPh, $^1J_{RhC}$ = 21.0 Hz), 161.7 (m, μ-C=CRPh), 42.2 (s, C=CPhCH$_2$-CH=CH$_2$), 113.1 (s, C=CPhCH$_2$-CH=CH$_2$), 82.9 (s, C=CPhCH$_2$-CH=CH$_2$)	6.40 (m, H$_c$), 4.90 (m, PCH$_2$P), 4.55 (m, H$_e$), 4.40 (m, H$_d$), 4.05 (m, PCH$_2$P), 3.80 (m, PCH$_2$P + H$_b$), 3.60 (m, PCH$_2$P), 3.25 (d, H$_a$)	2019 2037 2086
[RhIr(CO)$_2$(η^3-CH$_2$CHCH$_2$)-(μ-CCPh)(dppm)$_2$][BF$_4$]$_2$ (**13a**)	17.2 (m, $^1J_{RhP}$ = 95.6 Hz, $^2J_{PP}$ = 318.1 Hz), 15.5 (ddm, $^1J_{RhP}$ = 95.5 Hz, $^2J_{PP}$ = 318.1 Hz), −12.1 (m)		4.98 (d, H$_d$), 4.60 (m, H$_c$ + PCH$_2$P), 4.18 (m, PCH$_2$P), 3.60 (m, 2 PCH$_2$P), 3.45 (m, H$_e$), 2.10 (m, H$_a$), 1.00 (m, H$_b$)	2025 (s) 1880 (s)

Table 1 (Continued)

compound	NMR			IR, cm^{-1} ^{d}
	$\delta(^{31}P\{^1H\})^b$	$\delta(^{13}C\{^1H\})^c$	$\delta(^1H)^c$	
[RhIr(CO)$_2$(η^3-CH$_2$CHCH$_2$)-(μ-CCPh)(dppm)$_2$][O$_3$SCF$_3$]$_2$ (13b)	17.5 (m, $^1J_{RhP}$ = 95.4 Hz, $^2J_{PP}$ = 316.7 Hz), 15.5 (m, $^1J_{RhP}$ = 5.0 Hz, $^2J_{PP}$ = 316.7 Hz), −11.6 (dm, $^2J_{PP}$ = 335.3 Hz), −12.2 (dm, $^2J_{PP}$ = 335.3 Hz)	190.6 (dt, Rh-CO, $^1J_{RhC}$ = 83.5 Hz, $^2J_{PC}$ = 15.0 Hz), 180.3 (dt, Ir-CO, $^1J_{RhC}$ = 17.0 Hz, $^2J_{PC}$ ≈ 6 Hz), 106.1 (s, Ir−C≡CPh, $^1J_{RhC}$ = 3.7 Hz), 100.0 (s, CH$_2$$CHCH_2$), 64.6 (m, Ir-$C$≡CPh, $^1J_{RhC}$ = 5.1 Hz, $^2J_{PC}$ = 15.0 Hz), 58.0 (s, CH$_2$CHCH$_2$), 48.4 (s, CH$_2$CHCH$_2$)	4.98 (d, H$_d$), 4.55 (m, H$_c$ + PCH$_2$P), 4.12 (m, PCH$_2$P), 3.78 (m, 2 PCH$_2$P), 3.45 (m, H$_e$), 2.06 (m, H$_a$), 1.00 (m, H$_b$)	2013 1882

^{a} Abbreviations used: NMR, m = multiplet, dm = doublet of multiplets, s = singlet; d = doublet, t = triplet, q = quartet, dt = doublet of triplets, ddt = doublet of doublets of triplets, dtt = doublet of triplets of triplets, ddm = doublet of doublets of multiplets, b = broad, bd = broad doublet; IR, w = weak, m = medium, s = strong, b = broad. ^{b} Vs 85% H$_3$PO$_4$ in CD$_2$Cl$_2$ at 25 °C unless otherwise stated. ^{c} Vs TMS in CD$_2$Cl$_2$ at 25 °C unless otherwise stated. Labeling scheme for carbons and protons is given in ref 31. ^{d} Nujol mull on KBr disks unless otherwise noted, ν_{CO} unless otherwise noted. ^{e} −80 °C. ^{f} −60 °C. ^{g} 0 °C.

(j) [RhIr(BF$_4$)(CO)(μ-CCPhCH$_2$CH=CH$_2$)(μ-CO)(dppm)$_2$]-[BF$_4$] (11). Compound **1a** (140.0 mg, 107.0 μmol) was placed in a flask and dissolved in 20 mL of CH$_2$Cl$_2$. Allyl bromide (9.2 μL, 106 μmol) was added via gastight syringe, causing a color change from red-purple to brown. This solution was stirred for 3 h, over which time the solution changed to a deep cherry red. A solution of AgBF$_4$ (21.0 mg, 107.9 μmol) in 10 mL of THF was added via cannula, resulting in the formation of a red-orange suspension. This was stirred 1 h, filtered through Celite, and taken to dryness in vacuo. The residue was recrystallized from 1:15 CH$_2$Cl$_2$/ether and then again from 1:3:25 CH$_2$Cl$_2$/THF/ether. Yield: 122.0 mg (79%). Anal. Calcd for C$_{63}$H$_{54}$O$_2$P$_4$RhIrB$_2$F$_8$: C, 52.70; H, 3.79. Found: C, 52.53; H, 3.62.

(k) [RhIr(CO)$_3$(μ-CCPhCH$_2$CH=CH$_2$)(dppm)$_2$][BF$_4$]$_2$ (12). An NMR tube was charged with **11** (10.2 mg, 7.1 μmol) and 0.4 mL of CD$_2$Cl$_2$. An atmosphere of CO was placed over the sample, resulting in a color change from red-orange to yellow. The ^{31}P{^{1}H} NMR spectrum of this sample at −20 °C showed complete conversion to **12**. This compound was not isolated in the solid state, due to facile loss of CO, and was characterized in solution only.

(l) [RhIr(η^3-CH$_2$CHCH$_2$)(CO)$_2$(μ-CCPh)(dppm)$_2$][BF$_4$]$_2$ (13a). Silver fluoborate (28.0 mg, 144 μmol) and **1a** (181.0 mg, 138.3 μmol) were dissolved in 20 mL of CH$_2$Cl$_2$, forming a purple solution. Allyl bromide (12.0 μL, 139 μmol) was added, causing a rapid color change to brown. After stirring for 2 h, the suspension was filtered to give a clear yellow solution and the solvent removed under vacuum. The brown residue was dissolved in 2 mL of CH$_2$Cl$_2$ and 4 mL of THF, and the product precipitated by the slow addition of 25 mL of ether. The yellow solid was washed three times with 15 mL of ether and dried. Yield: 160.4 mg (81%). Anal. Calcd for C$_{63}$H$_{54}$O$_2$P$_4$RhIrB$_2$F$_8$: C, 52.70; H, 3.79. Found: C, 52.62; H, 3.79.

(m) [RhIr(η^3-CH$_2$CHCH$_2$)(CO)$_2$(μ-CCPh)(dppm)$_2$][SO$_3$CF$_3$]$_2$ (13b). Silver triflate (27.1 mg, 106 μmol) and **1b** (140.6 mg, 102.6 μmol) were dissolved in 8 mL of CH$_2$Cl$_2$, forming a purple solution. Allyl bromide (8.9 μL, 103 μmol) was added, causing a rapid color change to brown. After stirring for 1 h, the suspension was filtered to give a clear yellow solution. The solution was then reduced to 1 mL, diluted with 3 mL of THF, and precipitated by the slow addition of 25 mL of ether. The yellow solid was washed three times with 10 mL of ether and dried. Yield: 131.0 mg (80%). Anal. Calcd for C$_{65}$H$_{54}$O$_8$S$_2$P$_4$-RhIrF$_6$: C, 50.04; H, 3.49. Found: C, 50.47; H, 3.50.

(n) Low-Temperature Reaction of 1a with AgO$_3$SCF$_3$ and CH$_2$=CHCH$_2$Br. Compound **1a** (23.0 mg, 17.6 μmol) was placed in a flask with AgO$_3$SCF$_3$ (14.5 mg, 56.4 μmol) and 0.6

mL of CD$_2$Cl$_2$ and stirred for 5 min. The purple solution was then transferred to an NMR tube and cooled to −80 °C. The ^{31}P{^{1}H} NMR spectrum of this sample showed the presence of one new compound (^{31}P{^{1}H}, 23.6 (dm, $^1J_{RhP}$ = 101.3 Hz), 7.5 (b); ^{1}H, 4.55 (b), 4.00 (b), each 2H) in addition to small amounts of **1a**. Upon addition of allyl bromide (1.5 μL, 17 μmol) to this solution at −80 °C, the color changed form purple to brown. This solution was shown to contain a mixture of **13** and two new species (**A**, ^{31}P{^{1}H}: 28.3 (dm, $^1J_{RhP}$ = 107.9 Hz), −24.2 (b); **B** 27.8 (dm, $^1J_{RhP}$ = 109.3 Hz), −24.2 (b)). Even at −80 °C, these compounds rapidly transformed into **13**.

(o) Reaction of 13 with Chloride Anion. An NMR tube was charged with **13a** (10.8 mg, 7.5 μmol) and PPNCl (11.0 mg, 19.2 μmol). This was cooled to −80 °C, and 0.4 mL of CD$_2$-Cl$_2$ was added, forming a red solution. This was shown by ^{31}P-{^{1}H} NMR spectroscopy to contain a mixture of **13** and **1** in a 5:1 ratio. Warming to −60 °C caused nearly complete conversion to **1**. Upon warming to ambient temperature, the allyl-vinylidene chloride **6a** was formed, which reacted further to give the dichloro species [RhIrCl$_2$(CO)(μ-CCPhCH$_2$CH=CH$_2$)-(dppm)$_2$].[7a,20]

(p) Attempted Reaction of 1 with CH$_3$O$_3$SCF$_3$. An NMR tube was charged with **1b** (24.0 mg, 17.5 μmol) and 0.4 mL of CD$_2$Cl$_2$. Methyl triflate (2.0 μL, 16 μmol) was added, resulting in no change in the ^{31}P{^{1}H} spectrum.

(q) Attempted Reaction of 1 with PhCH$_2$Br. An NMR tube was charged with **1b** (20.0 mg, 14.6 μmol) and 0.4 mL of CD$_2$Cl$_2$. Benzyl bromide (1.3 μL, 11 μmol) was added. NMR spectroscopy showed no reaction. The same result was obtained after the addition of AgO$_3$SCF$_3$ (2.7 mg, 11 μmol).

(r) Attempted Reaction of 1 with CH$_3$I. An NMR tube was charged with **1b** (19.9 mg, 14.5 μmol) and 0.4 mL of CD$_2$-Cl$_2$. Methyl iodide (0.9 μL, 15 μmol) was added, resulting in no change in the ^{31}P{^{1}H} NMR spectrum.

X-ray Data Collection and Structure Solution. Deep red crystals of [RhIrCl(CO)$_2$(μ-C≡C(Ph)CH$_2$CH=CH$_2$)(dppm)$_2$]-[SO$_3$CF$_3$]·1.5CH$_2$Cl$_2$ were obtained from layering Et$_2$O onto a CH$_2$Cl$_2$ solution of the compound. Data were collected on a Bruker P4/RA/SMART 1000 CCD diffractometer using Mo Kα radiation at −80 °C. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 8192 reflections from the data collection. The systematic absences indicated the space group to be $P2_1/c$ (No. 14). The data were corrected for absorption through use of the SADABS proce-

(20) [RhIrCl$_2$(CO)(μ-CCPhCH$_2$CH=CH$_2$)(dppm)$_2$]·CH$_2$Cl$_2$: Anal. Calcd for C$_{63}$H$_{56}$OCl$_4$P$_4$RhIr: C, 54.44; H, 4.06; Cl, 10.20. Found: C, 54.40; H, 3.91; Cl, 10.52. IR: ν(CO) = 1991 cm^{-1}.

**Table 2. Crystal Data and Summary of Data
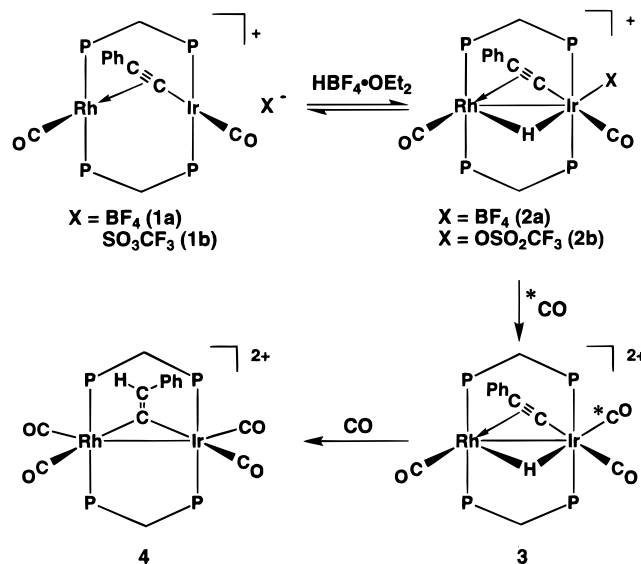Collection and Refinement for Compound
6b·1.5CH$_2$Cl$_2$**

formula	C$_{65.5}$H$_{57}$Cl$_4$F$_3$IrO$_5$P$_4$RhS
cryst size (mm)	0.28 × 0.24 × 0.22
fw	1573.96
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a, Å	23.707(2)
b, Å	22.365(2)
c, Å	24.030(2)
β, deg	91.715(1)
V, Å^3	12735(1)
Z	8
D_{calcd}, Mg/M^3	1.642
diffractometer	Bruker P4/RA/SMART 1000 CCD
radiation (λ), Å	Mo Kα (0.71073)
max 2θ, deg	51.60
μ, mm^{-1}	2.706
$F(000)$	6264
T, K	193
no. of indep reflns	24280
no. of obsd reflns ($I > 2\sigma(I)$)	15567
no. of params refnd	1505
goodness of fit	1.043
R_1 ($F_o^2 \geq 2\sigma(F_o^2)$)	0.0574
wR_2 (all data)	0.1538
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e/Å^3	2.27, −1.80

dure.[21] See Table 2 for a summary of crystal data and X-ray data collection information.

The structure was solved using the DIRDIF-96 program system,[22] and refinement was completed using the program SHELXL-93.[23] Hydrogen atoms were assigned positions based on the geometries of their attached carbon atoms and were given thermal parameters 20% greater than those of the attached carbons. There are two crystallographically independent formula units in the asymmetric unit. One of the two crystallographically independent triflate anions was found to be disordered over two orientations occupying the same region of space, necessitating the use of the following distance restraints within orientation: d(S−O) = 1.45 Å; d(S−C) = 1.80 Å; d(F−C) = 1.35 Å; d(F···F) = 2.20 Å; d(O···O) = 2.37 Å; d(F···O)(gauche) = 3.04 Å. Distance restraints were also applied to achieve idealized geometries within two of the solvent CH$_2$Cl$_2$ molecules (d(Cl−C) = 1.80 Å; d(Cl···Cl) = 2.95 Å). The final model refined to values of $R_1(F)$ = 0.0574 (for 15567 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2)$ = 0.1538 (for all 24280 independent data).[24]

Results and Compound Characterization

Reaction of the phenylacetylide-bridged A-frame [RhIr(CO)$_2$(μ-CCPh)(dppm)$_2$][BF$_4$] (**1a**) with an excess of HBF$_4$ leads to the formation of the hydride-bridged product [RhIr(BF$_4$)(CO)$_2$(μ-H)(μ-CCPh)(dppm)$_2$][BF$_4$] (**2a**), for which the structure shown in Scheme 1 is proposed, resulting from formal oxidative addition of HBF$_4$ to the iridium center. Coordination of the fluoborate ion to a

(21) Programs for diffractometer operation, data collection, data reduction, and absorption were those supplied by Bruker.

(22) Beurskens, P. T.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Garcia Granda, S.; Gould, R. O.; Israel, R.; Smits, J. M. M. The *DIRDIF-96* program system; Crystallography Laboratory, University of Nijmegen: The Netherlands, 1996.

(23) Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination; University of Göttingen: Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted R-factors wR_2 and all goodnesses of fit 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 criterion 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.

(24) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Scheme 1

late transition metal is not common but is well documented.[25] The hydride signal of **2a** appears in the ^{1}H NMR spectrum at δ −19.00, and the small observed coupling to rhodium (6 Hz) is consistent with an iridium-bound hydride having a weak bridging interaction with rhodium, as was found for other products of HX addition to **1**.[7a,b] The IR spectrum shows only terminal carbonyls (ν_{CO} = 2068, 1985 cm^{-1}), in agreement with the ^{13}C-{^{1}H} NMR spectrum, which shows a terminal carbonyl on rhodium (δ 186.7, $^1J_{RhC}$ = 81.8 Hz) and another on iridium (δ 170.6). A trans arrangement of the hydride and fluoborate groups is proposed based on analogies with the trans addition of other polar reagents to square planar Ir(I) complexes.[26] Furthermore, it has been shown that in many [Ir(H)L$_5$]-type complexes, the ^{1}H NMR chemical shift of the hydride ligand depends strongly upon the identity of the ligand in the trans position.[27] Compounds in which the trans ligand is a weakly coordinating σ-donor display the hydride at high field (cf. [Ir(H)(Cl)(X)(CO)(PPh$_3$)$_2$] (X = BF$_4$, δ −26.5; X = O$_3$SCF$_3$, δ −21.8; X = AlCl$_4$, δ −20.8),[28a] [Ir(H)(Cl)(L)(CO)(PPh$_3$)$_2$][BF$_4$] (L = CH$_3$C(O)CH$_3$, δ −21.4; L = H$_2$O, δ −21.1),[28a] and [Ir(H)(Cl)(BF$_4$)(N$_2$)(PPh$_3$)$_2$] (δ −24.8)).[28b] In complexes in which the hydride is trans to a carbonyl, the hydride signal appears at much lower field (cf. [Ir(H)(L)(CO)$_2$(PPh$_3$)$_2$][X] (L = Cl, X = BF$_4$, δ −8.6; L = CCPh, X = PF$_6$, δ −8.8)[28b,29] and [RhIr(X)(CO)$_2$(μ-H)(μ-CCR)(dppm)$_2$][O$_3$SCF$_3$] (X = CCPh, R = CH$_3$, δ −8.5; X = H, R = Ph, δ −9.9).[7a,b]

Although the fluxionality of **2a** made it difficult to confirm the coordination of fluoborate to the metal without a crystal structure, the proposed structure is based on analogies with the mononuclear complexes

(25) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405, and references therein.

(26) Collman, J. P.; Sears, C. T. *Inorg. Chem.* **1968**, *7*, 27.

(27) (a) Chatt, J.; Coffey, R. S.; Shaw, B. L. *J. Chem. Soc.* **1965**, 7391. (b) Vaska, L. *J. Am. Chem. Soc.* **1966**, *88*, 5325. (c) Taylor, R. C.; Young, I. F.; Wilkinson, G. *Inorg. Chem.* **1966**, *5*, 20. (d) Singer, H.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2516.

(28) (a) Olgemöller, B.; Beck, W. *Inorg. Chem.* **1983**, *22*, 997. (b) Olgemöller, B.; Bauer, H.; Beck, W. *J. Organomet. Chem.* **1981**, *213*, C57.

(29) Walter, R. H.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1978**, 381.

$[Ir(H)(Cl)(BF_4)(L)(PPh_3)_2]$ (L = CO, N_2)[28b] and on the protonation of the triflate salt, compound **1b**, by HBF_4, which yields $[RhIr(O_3SCF_3)(CO)_2(\mu\text{-}H)(\mu\text{-}CCPh)(dppm)_2]$-$[BF_4]$ (**2b**), in which the coordinated fluoborate anion is replaced by triflate. This triflate-containing compound is less susceptible to deprotonation than **2a**, requiring a smaller excess of acid to effect 100% conversion to the hydride complex, and the two compounds show significant differences in their $^{31}P\{^1H\}$ NMR spectra for the iridium-bound phosphines. Not only are the signals for the two compounds separated by 1.5 ppm, but the signals for **2b** are much sharper than those of **2a**, suggesting that the coordinating anion in **2a** is more labile than that in the triflate analogue. This is consistent with previous reports that have shown triflate to be a more strongly coordinating ligand than fluoborate.[25,30] Replacing both anions with triflate (by adding triflic acid to **1b**) gives $[RhIr(O_3SCF_3)(CO)_2(\mu\text{-}H)(\mu\text{-}CCPh)(dppm)_2][SO_3CF_3]$, which is indistinguishable from **2b** by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. Although ^{19}F NMR spectroscopy would be expected to confirm the coordination of the fluoborate ion, the broad signals from the excess HBF_4 in solution mask any potentially informative signals in this case.

Addition of carbon monoxide to a solution of **2a** results in the immediate formation of $[RhIr(CO)_3(\mu\text{-}H)(\mu\text{-}CCPh)$-$(dppm)_2][BF_4]_2$ (**3**). The IR spectrum of this compound shows only terminal carbonyl stretches (ν_{CO} = 2018, 1996, 1984 cm^{-1}), while the $^{13}C\{^1H\}$ NMR spectrum shows three carbonyl signals, one due to a terminal carbonyl on rhodium (δ 188.1, $^1J_{RhC}$ = 83.0 Hz) and two on iridium (δ 161.4, 154.9). The ^1H NMR spectrum shows a hydride signal at δ −7.78, with coupling to rhodium ($^1J_{RhH}$ = 11.7 Hz) and to both sets of ^{31}P nuclei ($^2J_{P(Rh)H}$ = 2.4 Hz, $^2J_{P(Ir)H}$ = 8.0 Hz). The lower-field chemical shift is consistent with the hydride ligand being trans to a carbonyl. Labeling experiments in which unenriched **2a** is reacted with ^{13}CO have shown that the newly introduced carbonyl ligand is bound to iridium, giving rise to the signal at 154.9 ppm. The large coupling seen between this carbonyl and the hydride in the $^1H\{^{31}P\}$ NMR spectra ($^2J_{CH}$ = 44 Hz) indicates that these ligands are mutually trans, with the carbonyl occupying the coordination site previously occupied by the labile fluoborate ion. In contrast, labeling the other carbonyl positions (by adding ^{12}CO to an ^{13}CO-enriched sample of **2a**) gives rise to only small (≈2 Hz) coupling between the hydride and the labeled carbonyls, indicating that the carbonyls originally in the complex remain trans to the alkynyl ligand on each metal.

Under excess carbon monoxide, **3** slowly converts to complex **4**, in which the hydride ligand has migrated from the metals to the C_β of the alkynyl ligand, forming a bridging vinylidene group. The C_α of the vinylidene appears in the $^{13}C\{^1H\}$ NMR spectrum at δ 210.6 ($^1J_{RhC}$ = 28.2 Hz), which is diagnostic for a bridging vinylidene,[2] and is similar to those seen in the other vinylidenes described herein. Also apparent are four carbonyl signals, two resulting from carbonyls terminally bound to rhodium (δ 188.7, $^1J_{RhC}$ = 51.0 Hz; δ 176.1, $^1J_{RhC}$ = 60.6 Hz) and two due to carbonyls terminally bound to iridium (δ 168.1, 161.7). The hydride signal of **3** has disappeared from the ^1H NMR

Scheme 2
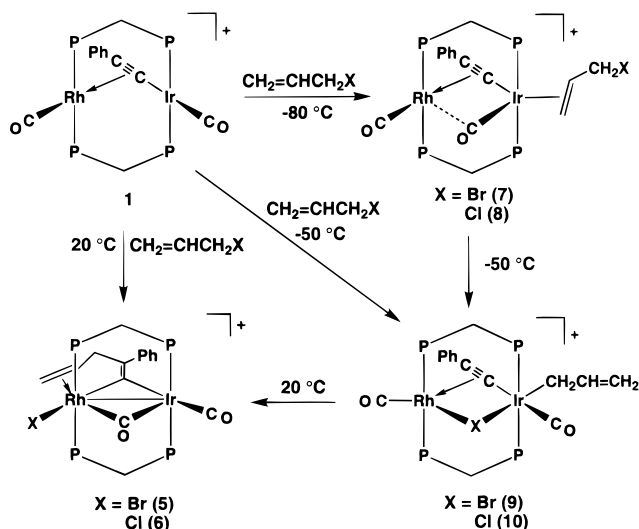
spectrum and is replaced by a new broad signal at δ 6.94, which is in the range expected for a vinylidene hydrogen.[2a,e]

Attempts to effect the oxidative addition of methyl iodide, methyl triflate, and benzyl bromide to compound **1** failed, with no reaction being observed in either case. However, allyl bromide reacts with compound **1** at room temperature to give $[RhIrBr(CO)(\mu\text{-}CO)(\mu\text{-}C=C(Ph)CH_2\text{-}CH=CH_2)(dppm)_2][X]$ (X = BF_4, **5a**; X = O_3SCF_3, **5b**), in which the allyl fragment has condensed with the alkynyl moiety to give a bridging allylvinylidene ligand, as outlined in Scheme 2. The $^{13}C\{^1H\}$ NMR spectrum of **5b** shows the signals for C_α and C_β at δ 200.4 and δ 157.4, respectively, within the expected range for vinylidenes in analogous systems.[2] The observed coupling of C_α to the rhodium nucleus ($^1J_{RhC}$ = 18.7 Hz) and to both sets of phosphines confirms that the vinylidene is in the bridging position. This spectrum also shows the presence of two carbonyls, one of which is terminally bound to iridium (δ 179.1) and one that bridges the two metals (δ 186.0, $^1J_{RhC}$ = 41.1 Hz). The $^{13}C\{^1H\}$ NMR signals for the olefinic carbons of the allyl fragment (δ 123.5 (C_δ) and 99.1 (C_ϵ); see ref 31 for the numbering scheme for these carbons) are closer to the expected range for an uncoordinated olefin ($RC_aH=C_bH_2$, $\delta_{C_a} \simeq$ 120−140; $\delta_{C_b} \simeq$ 105−120)[32] than for that expected for typical olefins coordinated to rhodium or iridium, which give rise to $^{13}C\{^1H\}$ NMR signals in the range δ 40−85.[33] Similarly, the signals for the olefin moiety in the ^1H NMR spectrum (δ 6.20, 4.20, 4.05) fall closer to the range expected for a noncoordinated alkene (δ 4.5−7.0)[32] than for a typical coordinated olefin (which, for electron-rich metals, normally are shifted to higher field by 1−5 ppm[34]). In addition, no coupling of either the olefinic

(30) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

(31) The labeling scheme for the carbons and hydrogens of the allylvinylidene complexes is as follows: C_α and C_β refer to the two carbons of the alkynyl ligand (C_α being directly bound to iridium), C_γ, C_δ, and C_ϵ are those derived from the allyl group with C_γ bound to the original β-carbon of the acetylide (C_β). H_a and H_b are the hydrogens bound to C_γ; H_c is bound to C_δ; H_d and H_e are bound to C_ϵ.
(32) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH Publishers: New York, 1993.
(33) Mann, B. E.; Taylor, B. F. *$^{13}C\{^1H\}$ NMR Data For Organometallic Compounds*; Academic Press: London, 1981.
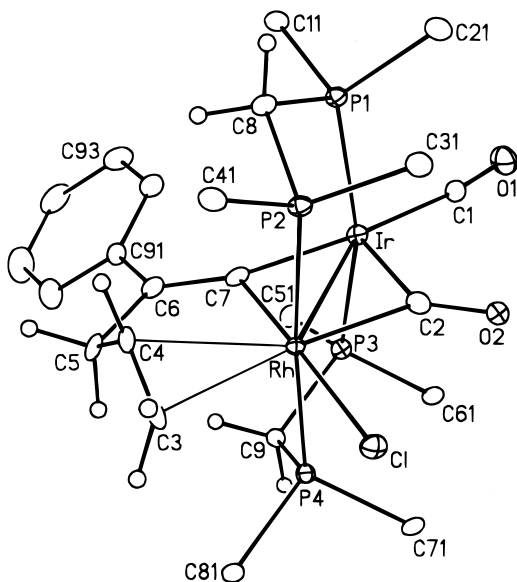(34) Herberhold, M. *Metal π-Complexes*; Elsevier Scientific Publishers: Amsterdam, 1974; Vol. II, Part 2.

Figure 1. Perspective view of one of the two crystallographically independent [RhIrCl(CO)(μ-CC(Ph)CH$_2$CH=CH$_2$)(μ-CO)(dppm)$_2$]$^+$ cations of compound **6b** (molecule A) showing the atom-labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Only the ipso carbons of the dppm phenyl rings are shown. Hydrogen atoms are shown with arbitrarily small thermal parameters.

carbons or protons to rhodium or to phosphorus is observed. This suggests that any bonding between the olefin and either metal center is weak.

The ^{31}P{^{1}H} NMR spectra of **5a** and **5b** at room temperature show typical AA′BB′X patterns, although the signals for the iridium-bound phosphines are broad. For example, cooling a sample of **5a** to −80 °C results in the two iridium-bound phosphines becoming inequivalent, causing the peak at δ −0.96 to split into a second-order set of doublets of multiplets, due to two strongly coupled (260.7 Hz) nuclei at δ 1.7 and −2.4. The signal for the rhodium-bound phosphines, in contrast, does not change significantly with temperature. Reaction of **1a** or **1b** with allyl chloride gives the analogous chloro complexes **6a** and **6b**, having very similar spectral parameters to those of **5**.

To confirm the proposed geometry, the X-ray structure of **6b** was determined and is shown in Figure 1, with selected bond lengths and angles shown in Tables 3 and 4, respectively. This determination confirms that the allyl fragment from the allyl chloride has added to the β-carbon of the alkynyl ligand, forming an allylvinylidene group. In addition, it shows that the olefinic moiety of this ligand is coordinated to rhodium, resulting in an octahedral geometry around this metal (if the Rh−Ir bond is ignored), with the olefinic and vinylidene functionalities of the allyl vinylidene ligand occupying two mutually cis coordination sites, with the remaining four occupied by the mutually trans dppm phosphines, the chloride, and the bridging carbonyl. The significance of the allyl-group coordination to rhodium will be made obvious later. At iridium, the coordination is best described (again ignoring the metal−metal bond) as a tetragonal pyramid, with the dppm phosphines, the bridging vinylidene, and the terminal carbonyl occupying the basal sites and the bridging carbonyl occupying

Table 3. Selected Interatomic Distances (Å) in Compound 6b

atom 1	atom 2	molecule A distance	molecule B distance
Ir	Rh	2.9840(7)	2.9700(7)
Ir	P(1)	2.347(2)	2.350(2)
Ir	P(3)	2.347(2)	2.345(2)
Ir	C(1)	1.906(9)	1.902(10)
Ir	C(2)	2.041(9)	2.069(9)
Ir	C(7)	2.043(9)	2.036(8)
Rh	Cl	2.527(2)	2.507(2)
Rh	P(2)	2.361(2)	2.362(2)
Rh	P(4)	2.399(2)	2.397(2)
Rh	C(2)	2.040(9)	2.046(8)
Rh	C(3)	2.389(8)	2.385(9)
Rh	C(4)	2.403(8)	2.413(8)
Rh	C(7)	2.108(8)	2.116(8)
O(1)	C(1)	1.129(11)	1.138(12)
O(2)	C(2)	1.163(10)	1.158(10)
C(3)	C(4)	1.351(13)	1.369(13)
C(4)	C(5)	1.507(13)	1.462(12)
C(5)	C(6)	1.513(12)	1.492(12)
C(6)	C(7)	1.340(12)	1.336(12)
C(6)	C(91)	1.486(13)	1.487(13)

Table 4. Selected Interatomic Angles (deg) in Compound 6b

atom 1	atom 2	atom 3	molecule A angle	molecule B angle
Rh	Ir	C(1)	143.2(3)	142.4(3)
Rh	Ir	C(2)	43.0(2)	43.5(2)
Rh	Ir	C(7)	44.9(2)	45.4(2)
P(1)	Ir	P(3)	163.13(8)	162.07(8)
C(1)	Ir	C(2)	100.2(4)	98.9(4)
C(1)	Ir	C(7)	171.9(4)	172.2(4)
C(2)	Ir	C(7)	87.9(3)	88.9(3)
Ir	Rh	Cl	137.10(6)	136.77(6)
Ir	Rh	C(2)	43.0(3)	44.1(3)
Ir	Rh	C(3)	145.3(2)	145.9(2)
Ir	Rh	C(4)	113.6(2)	113.9(2)
Ir	Rh	C(7)	43.2(2)	43.3(2)
Cl	Rh	C(2)	94.1(3)	92.7(3)
Cl	Rh	C(3)	77.6(2)	77.3(2)
Cl	Rh	C(4)	108.7(2)	108.8(2)
Cl	Rh	C(7)	177.7(2)	178.5(2)
P(2)	Rh	P(4)	174.64(8)	174.61(8)
C(2)	Rh	C(3)	171.6(4)	170.0(3)
C(2)	Rh	C(4)	155.4(3)	156.4(3)
C(2)	Rh	C(7)	86.2(4)	87.3(3)
C(3)	Rh	C(4)	32.7(3)	33.2(3)
C(3)	Rh	C(7)	102.1(3)	102.6(3)
C(4)	Rh	C(7)	71.4(3)	71.4(3)
Ir	C(1)	O(1)	170.9(9)	171.5(10)
Ir	C(2)	Rh	94.0(4)	92.4(4)
Ir	C(2)	O(2)	127.3(7)	126.9(7)
Rh	C(2)	O(2)	138.6(7)	140.7(7)
Rh	C(3)	C(4)	74.2(5)	74.5(5)
Rh	C(4)	C(3)	73.0(5)	72.3(5)
Rh	C(4)	C(5)	104.5(5)	104.7(5)
C(3)	C(4)	C(5)	125.7(9)	129.3(9)
C(4)	C(5)	C(6)	107.7(8)	111.2(7)
C(5)	C(6)	C(7)	115.2(8)	114.6(8)
C(5)	C(6)	C(91)	119.0(8)	118.9(7)
C(7)	C(6)	C(91)	125.7(8)	126.4(8)
Ir	C(7)	Rh	91.9(3)	91.3(3)
Ir	C(7)	C(6)	144.5(7)	145.1(7)
Rh	C(7)	C(6)	122.3(6)	122.3(6)

the apical site. Consistent with this geometry description, the basal ligands are clearly bent away from the bridging carbonyl (P(1)−Ir−P(3) = 163.13(8)°, 162.07(8)°; C(1)−Ir−C(7) = 171.9(4)°, 172.2(4)°).[35] This combination of geometries (octahedral around one metal; tetragonal

(35) The two values given for each parameter are for the two independent molecules.

pyramidal around the other) is fairly common in these heterobinuclear systems and has been observed in $[RhMn(CO)_4(\mu\text{-}S)(dppm)_2]$,[36] $[RhMo(CO)_4(\mu\text{-}Cl)(dppm)_2]$,[37] and $[RhIr(CCPh)(CO)_2(\mu\text{-}CCPh)(\mu\text{-}H)(dppm)_2][O_3SCF_3]$.[14d]

One carbonyl of **6b** bridges the two metals in an essentially symmetric fashion ($Rh\text{-}C(2) = 2.040(9)$, 2.046(8) Å, $Ir\text{-}C(2) = 2.041(9)$, 2.069(9) Å; $Rh\text{-}C(2)\text{-}O(2) = 138.6(7)°$, $140.7(7)°$, $Ir\text{-}C(2)\text{-}O(2) = 127.3(7)°$, $126.9(7)°$). Despite the long metal–metal separation of 2.9840(7), 2.9700(7) Å, the compound is best formulated with a metal–metal bond, to satisfy the electron count at each metal. This abnormally long separation may result from the presence of the chelating allylvinylidene ligand, in which the pendent allyl moiety appears to pull the rhodium center away from Ir. Consistent with this, the $Rh\text{-}C(7)$ distance (2.108(8), 2.116(8) Å) is somewhat longer than the $Ir\text{-}C(7)$ distance (2.043(9), 2.036(8) Å) and is notably longer than the rhodium–carbon bonds in comparable vinylidene complexes such as $[Rh_2(CO)_2(PCy_3)_2(\mu\text{-}O_2CCH_3)(\mu\text{-}C=CHPh)][BF_4]$ ($Rh\text{-}C = 2.015(5)$, 1.984(5) Å).[38] Similarly, the vinylidene moiety is bent toward rhodium, with the $Rh\text{-}C(7)\text{-}C(6)$ angle being significantly smaller (122.3(6)°, 122.3(6)°) than the $Ir\text{-}C(7)\text{-}C(6)$ angle (144.5(7)°, 145.1(7)°), showing the strain within the chelate.

Despite the movement of Rh toward the olefinic moiety, the Rh–olefin bonds ($Rh\text{-}C(3)$, $Rh\text{-}C(4)$) are still long, ranging from 2.385(9) to 2.413(8) Å (compared to 2.16 and 2.02 Å found in $[CpRh(CH_2=CH_2)(CF_2=CF_2)]$[39] and between 2.09 and 2.19 Å for a number of "normal" Rh(I) olefin complexes[40]), a further indication that the coordination is strained. The olefinic carbon–carbon bond length (1.35(1), 1.37(1) Å) is not substantially lengthened from that in the free olefin, further suggesting a weak coordination to Rh.

Although the X-ray study on **6b** supports the conclusions from the NMR studies of **5** and **6** that the olefin moiety is only weakly coordinated to Rh, it is significant that these compounds do not react with CO, indicating that the olefin is not displaced by this ligand. Further reactivity studies of **5** and **6** are underway and will be the subject of a future paper.

The observed fluxionality of **5** and **6** can be rationalized on the basis of a consideration of the structure determined in the solid state for **6b**. The coordination of the olefinic fragment to rhodium causes the vinylidene to twist out of the equatorial plane. This results in the phenyl ring of the allylvinylidene ligand being thrust into the vicinity of the dppm phenyl rings on one of the iridium-bound phosphines (toward C(51) in Figure 1), as diagrammed in Chart 1. As a result, the magnetic environments of the phosphorus atoms bound to iridium are inequivalent in the static structure. At room temperature, however, the two iridium-bound phosphines can become equivalent on the NMR time scale by a

Chart 1
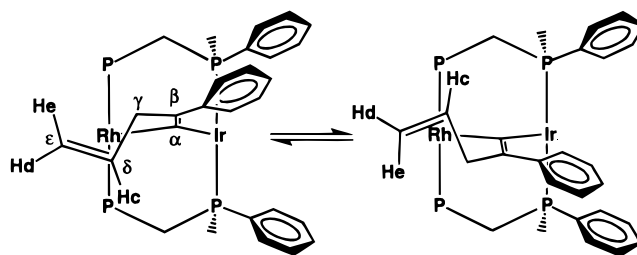
process in which the olefin dissociates, twists around the $C_\gamma\text{-}C_\delta$ single bond, and recoordinates via the other face of the olefin. This causes the vinylidene to bend in the other direction, resulting in effective exchange of the phosphine environments. At lower temperatures, the up-and-down motion of the allylvinylidene group is sufficiently slow to allow the different environments to be detected. The top–bottom asymmetry apparently has a much reduced effect upon the rhodium-bound phosphines, which appear degenerate at all temperatures between ambient temperature and −80 °C.

In an attempt to determine how the allyl fragment migrated to the alkynyl group, we sought to observe intermediates in this transformation by monitoring the low-temperature addition of allyl bromide to compound **1b**. The first intermediate, observed at −80 °C, is proposed to be $[RhIr(CO)_2(\eta^2\text{-}CH_2=CHCH_2Br)(\mu\text{-}CCPh)(dppm)_2][O_3SCF_3]$ (**7**), as shown in Scheme 2. This species contains a semibridging carbonyl and the olefin coordinated to iridium in an arrangement similar to that suggested previously for a number of olefin adducts of **1** and confirmed crystallographically for the dimethylallene adduct.[7b] The olefin signals in the ^1H NMR spectrum have shifted substantially, from between δ 6.2 and 5.0 in free allyl bromide to δ 2.0, 0.0, and −0.8, consistent with the upfield shift expected upon coordination to a metal center.[34] Unfortunately, these signals are broad, even at very low temperature (−90 °C), and thus reveal very little structural information. As a result, exact assignments of these signals could not be made.

When compound **7** is warmed to −50 °C, it transforms into a mixture of **1** and the oxidative-addition product $[RhIr(\eta^1\text{-}CH_2CHCH_2)(CO)_2(\mu\text{-}CCPh)(\mu\text{-}Br)(dppm)_2][O_3SCF_3]$ (**9**). The observation of **1** in the reaction mixture indicates that the allyl bromide ligand does not remain coordinated at higher temperatures. The structural formulation of **9**, in which an η^1-allyl group is bound to iridium, is based on the ^1H NMR spectrum, which shows the characteristic signals;[41] the signal for the hydrogens on the α-carbon appears as a multiplet at δ 2.40, showing coupling to the iridium-bound phosphines, and the three olefinic protons appear at δ 4.90, 4.15, and 3.65, showing no coupling to rhodium or to phosphorus. The equivalence of the hydrogens on the α-carbon also indicates that the allyl is σ-bound. In an η^3-allyl species all five protons would be expected to couple to the adjacent phosphines. Although the exact arrangement of the ligands at iridium is equivocal, the arrangement shown, containing the bridging bromide trans to the η^1-allyl, is assumed on the basis that the addition of organic halides to the analogous mononuclear complex

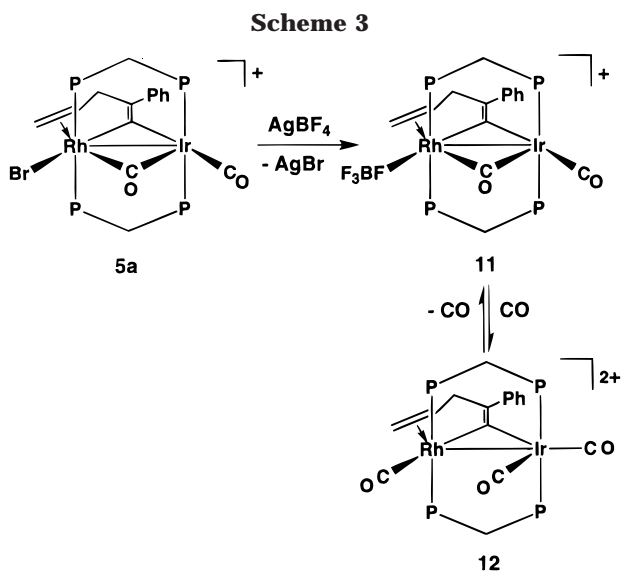(36) Wang, L.-S.; McDonald, R.; Cowie, M. *Inorg. Chem.* **1994**, *33*, 3735.

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Scheme 3

for the weakly coordinating BF_4^- group in $[Ru(BF_4)(NO)(CO)(PPh_3)_2]$.[44] This can be contrasted to the ^{19}F NMR spectrum expected for a strongly coordinated BF_4^- anion,[45] for which two signals for the coordinated (δ -250 to -420) and noncoordinated fluorines (δ -153 to -159) are observed. Addition of 1 equiv of $[Bu_4N][BF_4]$ causes this signal to sharpen ($W_{1/2} = 113$ Hz) and move slightly downfield to δ -150.8, consistent with the proposed exchange.

Compound **11** reacts reversibly with carbon monoxide, forming **12**, in which the coordinating fluoborate ion is replaced by a carbonyl ligand. This exchange is accompanied by the movement of the bridging carbonyl of **11** to a terminal position on the iridium center of **12**, as demonstrated by the IR and $^{13}C\{^1H\}$ NMR spectra. Upon broad-band ^{31}P decoupling, the iridium-bound carbonyl multiplet at δ 160.0 appears as a doublet with 6.2 Hz coupling to Rh, probably as a result of trans coupling through the metal–metal bond. Upon conversion of **11** to **12**, binding of the olefinic fragment to Rh appears to have been strengthened by the addition of the carbonyl, as seen in the slight high-field shift of the $^{13}C\{^1H\}$ NMR signals of the olefinic carbons. The $^{31}P\{^1H\}$ NMR spectrum of this compound at low temperature shows that all four phosphorus nuclei are inequivalent, displaying a pattern typical of an ABCDX spin system (X = Rh). The top–bottom asymmetry is more pronounced in this compound than in the dicarbonyl complex **11**; this is probably due to the stronger coordination of the olefinic group to rhodium, which should cause a more pronounced bending of the vinylidene out of the equatorial plane. The strong P–P coupling between the two rhodium-bound phosphines (387 Hz) and between the two iridium-bound phosphines (303 Hz) indicates that the trans arrangement of the dppm ligands has been retained. The ^{19}F NMR spectrum of this compound clearly shows that the fluoborate has been displaced by the carbonyl ($W_{1/2} = 6.5$ Hz). Under vacuum or dinitrogen purge, compound **12** readily loses CO, reforming **11**.

If the addition of allyl bromide to **1a** or **1b** is carried out in the presence of either $AgBF_4$ or AgO_3SCF_3, the condensation of the alkynyl and allyl fragments does not occur. Rather, the η^3-allyl complexes $[RhIr(\eta^3\text{-}CH_2CHCH_2)(CO)_2(\mu\text{-}CCPh)(dppm)_2][X]_2$ (X = BF_4, **13a**; X = SO_3CF_3, **13b**) are formed, as shown in Scheme 4. The $^1H\{^{31}P\}$ NMR spectrum of **13b** shows a pattern consistent with an asymmetrically bound η^3-allyl group with two high-field signals at δ 1.00 and 2.06 for protons H_b and H_a (see Chart 2 for labeling) and the other three protons at significantly lower field (δ 3.45–4.98). These assignments have been confirmed by $^{13}C–^1H$ NMR correlation experiments. The observed pattern suggests that the bonding of the allyl ligand approaches the σ,π-coordination mode, as is found for $[RhM(\eta^3\text{-}C_3H_5)(CO)_3(dppm)_2]$ (M = Os, Ru).[6b,43b] Although the chemical shifts are also consistent with an η^1-allyl group, which normally gives rise to signals at δ 2.0–3.5 for the methylene protons and δ 3.5–5.5 for the olefinic hydro-

$[IrCl(CO)(PPh_3)_2]$ has been found to result in trans addition to the metal center.[42] Furthermore, the unusually small intraligand coupling within the dppm ligands ($^2J_{PP} < 2$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum has been previously associated with the presence of a bridging halide in these systems.[40,43a] The chemical shift of the iridium-bound carbonyl (δ 167.7) in the $^{13}C\{^1H\}$ NMR spectrum is also more consistent with a carbonyl angled away from rhodium. As described previously,[7a,b] iridium-bound carbonyls angled toward rhodium appear at lower field than those angled away, presumably indicating a weak interaction with Rh in the former case. Warming a solution of **9** results in transformation to the allylvinylidene product **5**, along with small quantities ($\approx$10–15%) of unidentified decomposition products. No other intermediate was observed. The reaction of **1** with allyl chloride at low temperatures parallels that of the allyl bromide, with analogous intermediates **8** and **10** being observed (see Scheme 2).

Reaction of **5a** with $AgBF_4$ gives $[RhIr(BF_4)(CO)(\mu\text{-}CO)(\mu\text{-}C=C(Ph)CH_2CH=CH_2)(dppm)_2][BF_4]$ (**11**), in which the bromide ligand has been replaced by a coordinating fluoborate, with all other ligands maintaining the same geometries as in the precursor (see Scheme 3). The $^{13}C\{^1H\}$ NMR signals for the carbonyl and allylvinylidene ligands are very similar to those of **5**, indicating a similar structure, and the IR spectrum shows carbonyl stretches at 2023 and 1814 cm^{-1}, indicating the presence of both terminal and bridging CO ligands; the shift to higher frequency is consistent with the replacement of the good donor bromide by the weakly coordinating fluoborate anion. At both ambient temperature and -80 °C, only one, very broad peak ($W_{1/2} = 217$ Hz) is seen at δ -150.3 in the ^{19}F NMR spectrum, indicating that the coordinating fluoborate is exchanging with free fluoborate, equilibrating all eight fluorine nuclei. A similar broad ^{19}F NMR signal at δ -160.7, with half-width of 321 Hz, was observed

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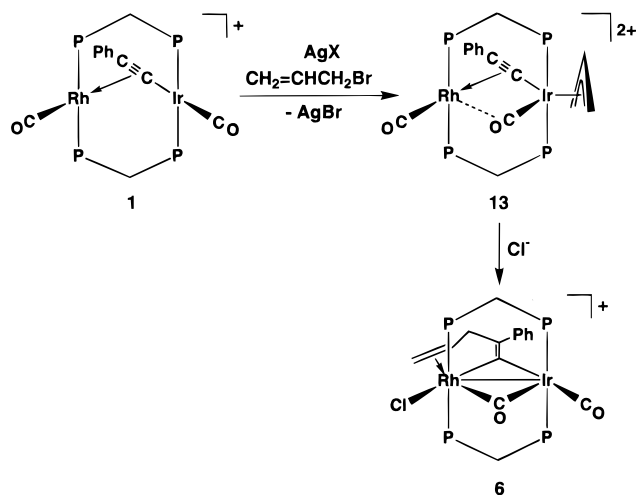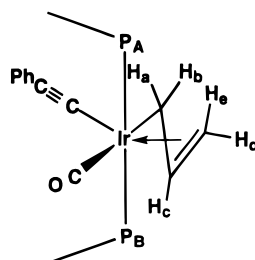
Scheme 4

Chart 2

gens,[41] coupling observed between the iridium-bound phosphines and all five hydrogens on the allyl ligand is consistent with η^3-coordination. In addition, the high-field protons (H_aH_b) would be expected to be equivalent in an η^1-allyl. In **13**, not only are the two protons inequivalent, but H_b has a greater coupling to H_c ($^3J_{bc} \approx 9$ Hz) than does H_a ($^3J_{ac} \approx 5$ Hz), indicating that H_b is anti to H_c. The $^{13}C\{^1H\}$ NMR spectrum shows that the Ir-bound carbonyl is semibridging to rhodium ($^1J_{RhC} = 17.0$ Hz), an observation supported by the IR spectrum ($\nu_{CO} = 1882$ cm^{-1}), and the alkynyl ligand remains in the bridging position, as shown by the coupling of the α- and β-carbons to rhodium (C_α, δ 64.6, $^1J_{RhC} = 5.1$ Hz; C_β, δ 106.1, $^1J_{RhC} = 3.7$ Hz).

The $^{31}P\{^1H\}$ NMR spectrum of **13b** indicates that this compound displays top−bottom asymmetry, and the P−P coupling constants (316.7 and 335.3 Hz for the rhodium- and iridium-bound phosphines) indicate that the diphosphine ligands are still mutually trans at the metals. This arrangement of the phosphines is unexpected, since the comparable mononuclear [IrCl(η^3-C$_3$H$_5$)(CO)(PPh$_3$)$_2$][46] and the binuclear [RhM(η^3-C$_3$H$_5$)(CO)$_3$(dppm)$_2$] (M = Os, Ru)[6b,43b] compounds have cis phosphines at the allyl-bound metal, presumably to minimize steric interactions with the allyl group.

In attempts to probe the steps involved in the formation of **13**, low-temperature addition of allyl bromide to a solution of **1a** and silver triflate was monitored by ^{31}P-$\{^1H\}$ NMR spectroscopy. Prior to the addition of allyl bromide, the purple solution of **1a** and AgO$_3$SCF$_3$ shows the presence of one main compound, which gives rise to broad signals in the $^{31}P\{^1H\}$ NMR spectrum at δ 23.6

($^1J_{RhP} = 101$ Hz) and δ 7.5, which are only slightly shifted from the signals of compound **1a** (δ 21.0 and δ 6.2). Although it seems clear that this compound is formed through the interaction of the silver ion with **1a**, the actual structure is uncertain, since this intermediate could not be isolated or further characterized. No coupling was observed in the $^{31}P\{^1H\}$ NMR spectrum to either ^{107}Ag or ^{109}Ag (52% and 48% natural abundance, respectively).[47] Upon addition of allyl bromide to this solution at −80 °C, a mixture is formed that contains **13** and two new compounds, which give rise to overlapping peaks at δ 27.9 ($^1J_{RhP} = 111$ Hz) and δ 27.6 ($^1J_{RhP} = 111$ Hz) for the Rh-bound phosphines and exactly overlapping peaks at δ −24.1 for the Ir-bound nuclei. Although the nature of these intermediates is also uncertain, their almost identical ^{31}P spectral parameters suggest that they are isomers (although the nature of the isomerism is unclear). Furthermore, these ^{31}P NMR signals are very similar to those seen for the oxidative-addition product [RhIr(η^1-CH$_2$CH=CH$_2$)Br-(CO)$_2$(CCPh)(dppm)$_2$][O$_3$SCF$_3$] (**9**), so it is suggested that these intermediates also have an η^1-allyl group bound to Ir. Unfortunately the spectral data yield no information pertaining to the bromo, silver, or triflate moieties, and the instability of these species, even at low temperature, precluded their characterization. Upon warming or with time these intermediates transform into **13**.

Compound **13** is susceptible to nucleophilic attack, and addition of chloride ion causes migration of the allyl fragment to the alkynyl group, yielding the allylvinylidene chloride **6**. At low temperature, the initial product of chloride addition to **13** is compound **1** and free allyl chloride, formed either through halide attack on the terminal carbon of the allyl ligand or through halide attack at iridium, followed by reductive elimination. At higher temperatures the reactions leading to compound **6** occur, as previously described.

The reaction of **13** with other nucleophiles (PMe$_3$, H$^-$, CN$^-$) does not result in migration of the allyl group to the alkynyl ligand and results instead in attack directly at the allyl moiety.[7a]

Discussion

As noted earlier, π coordination of an alkynyl group to a second metal, as observed in the doubly bridged, μ-η^1:η^2-binding mode, has a substantial effect on its reactivity. Whereas η^1-alkynyl groups are susceptible to *electrophilic* attack at the β-carbon,[5d,8a,9] μ_2-η^1:η^2-alkynyls are susceptible to attack by *nucleophiles*, at either the α- or the β-carbon.[11,12] This reactivity difference can be partially rationalized as resulting from π donation to the second metal, thereby rendering the alkynyl group more electron deficient. Surprisingly perhaps, little else is known about the functions of the two metals in influencing alkynyl reactivity in the doubly bridging mode. We have previously demonstrated, in this alkynyl-bridged Rh/Ir system, that nucleophilic attack occurs preferentially at Ir and that when the nucleophile is the hydride ligand subsequent migration to the β-carbon of the alkynyl group occurs,

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Scheme 5
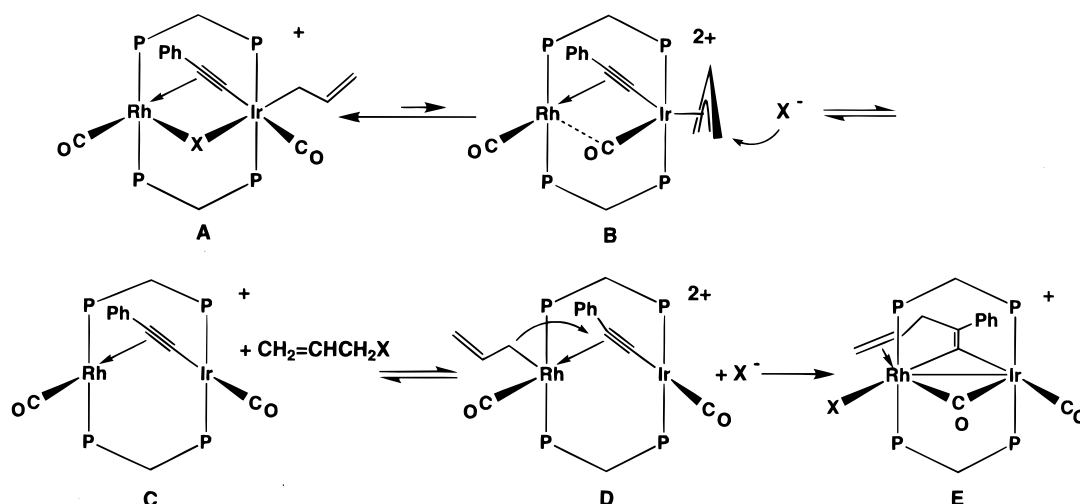
yielding a bridging vinylidene group.[7] We reasoned that these low-valent, late metals should also be susceptible to coordination of electrophiles and that similar migration of the electrophile to the alkynyl group may subsequently occur. This has been verified in the reaction of $[RhIr(CO)_2(\mu-\eta^1:\eta^2-CCPh)(dppm)_2][X]$ (X = BF_4 (**1a**), SO_3CF_3 (**1b**)) with fluoboric acid, which initially yields the oxidative-addition products $[RhIr-(X)(CO)_2(\mu-H)(\mu-\eta^1:\eta^2-C_2Ph)(dppm)_2][BF_4]$ (X = BF_4 (**2a**), SO_3CF_3 (**2b**)). Although hydrogen transfer from the metals to the alkynyl ligand is not observed in **2**, replacement of the weakly coordinating BF_4^- or $SO_3CF_3^-$ anions by CO does lead subsequently to migration, yielding the vinylidene-bridged $[RhIr(CO)_4(\mu-CC(H)Ph)-(dppm)_2]^{2+}$. This demonstration of metal-mediated electrophile transfer to the alkynyl group suggested that carbon–carbon bond formation at the alkynyl β-carbon could result if organic electrophiles were used.

Initial attempts to induce carbon–carbon bond formation by the addition of methyl iodide, methyl triflate, or benzyl bromide to **1** failed with no reaction observed in either case. However, reaction of **1** with either allyl bromide or chloride occurs readily, yielding $[RhIrX(CO)-(\mu-CO)(\mu-CC(Ph)CH_2CH=CH_2)(dppm)_2]^+$ (X = Br (**5**), Cl (**6**)), in which carbon–carbon bond formation has occurred by coupling of the allyl group with the alkynyl β-carbon to give an allylvinylidene ligand (Scheme 2). A series of reactions at low temperatures has established that, analogous to the reactions with acids, this coupling is metal mediated and does not result from direct electrophilic attack at the alkynyl group. Monitoring the above reaction of **1** with the allyl halide at -80 °C shows initial conversion to the olefin adducts $[RhIr(CO)(\eta^2-CH_2=CHCH_2X)(\mu-CCPh)(\mu-CO)(dppm)_2]^+$, in which the allyl halide molecules are bound to Ir. These species are not believed to be directly involved in the transformations to the final allylvinylidene products, since upon warming, allyl halide dissociation, regenerating starting materials, is first observed. Presumably, at -80 °C olefin coordination is the only accessible pathway. Upon further warming (-50 °C), oxidative addition of the allyl halide occurs, yielding $[RhIr(\eta^1-CH_2CH=CH_2)(CO)_2(\mu-X)(\mu-CCPh)(dppm)_2]^+$, which has the allyl fragment η^1-bound to Ir and the alkynyl moiety in its original bridging position.

Further warming generates the final allyl–vinylidene-bridged products by apparent migration of the η^1-allyl group to the alkynyl β-carbon, with no other species being observed. We suggest, in fact, that direct migration of the allyl group from Ir to the alkynyl group does not occur. Not only is the alkynyl group oriented unfavorably for such a direct transfer, but this direct transfer should yield an isomer of the observed product, in which the allyl moiety was adjacent to Ir (and π-bound to this metal) with the phenyl substituent adjacent to Rh. On the basis of the stronger Ir–olefin bond,[48] this should be the favored isomer. Although isomerism via rotation about the vinylidene C=C bond is known,[14b] we observe no isomerism in this system, presumably because of the bulk of the vinylidene substituents in **5** and **6**.

The observation that allyl addition in the absence of halide ion (complexed by Ag$^+$) does *not* lead to alkynyl/allyl coupling, but instead yields an η^3-allyl complex (Scheme 4), clearly demonstrates the importance of halide ion in this transformation. Significantly, the addition of halide ion to the η^3-allyl complex at ambient temperature then leads to alkynyl/allyl coupling, which is irreversible, since halide removal *after* formation of the allylvinylidene product does not lead to destabilization of this moiety (Scheme 3). A significant observation is that halide ion addition to the η^3-allyl product at low temperature results first in loss of allyl halide and regeneration of starting materials.

On the basis of the above observations we propose a mechanism for generation of the alkynyl–allyl-coupled product as shown in Scheme 5 (ignoring the η^2-allyl halide adduct). At low temperature the favored species is the oxidative-addition product (**A**) in which the η^1-allyl group is coordinated to Ir. We propose that this is in equilibrium with small (undetected) amounts of the η^3-allyl product (**B**) resulting from halide loss. The conversion of an η^1- to an η^3-allyl upon loss of a two-electron donor (X$^-$) is a well-precedented transformation.[49] Species **B** differs from compound **13** only by the presence of halide in the former. In the presence of halide ion, nucleophilic attack of the halide at the allyl

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group can occur regenerating the starting materials, **C** and allyl halide. This is the reverse of nucleophilic displacement of the halide ion by the Ir center in the oxidative-addition step that initially yields **A**. Although the thermodynamically favored oxidative addition is at Ir, regenerating **A**, oxidative addition can also occur at Rh yielding **D**, in which the η^1-allyl fragment is bound to Rh. This species is not observed and either loses allyl halide regenerating **C** or reacts irreversibly at higher temperatures by transfer of the allyl group to the alkynyl β-carbon yielding the allylvinylidene product (**E**). Although we have no direct evidence of this last transformation (**D → E**), it is consistent with geometry of the product observed in which the allyl moiety is adjacent to and π-bound to Rh. Furthermore, the geometry in **D** is favorable for allyl migration to the β-position in the alkynyl group, and our failure to observe such an intermediate is consistent with the greater lability of Rh compared to Ir.[50] Although this transformation (**D** to **E**) involving allyl and alkynyl groups has not been previously reported, the closely related migration of an aryl group to a μ_2-η^1:η^2-alkynyl ligand in a Ti/Cu complex[16] and the migration of a methyl ligand to a bridging acetylide in a diiridium complex[6h] have been proposed to rationalize the formation of vinylidene-bridged products in each case. Despite their apparent rarity, we suggest that migrations of alkyl or related hydrocarbyl groups to the β-carbon of bridging alkynyls may be more common than imagined, on the basis of the similarities between an alkyne and a metalloalkynyl moiety, in which the metal can be viewed as one of the alkyne substituents. In this analogy the Ir−C≡CPh moiety in structure **D** can be considered as an alkyne that is π-bound to Rh. Migration of an alkyl group to the alkynyl β-carbon is analogous to the well-documented alkyl-to-alkyne migrations in mononuclear complexes.[14d,15] Even more closely related to the transformation **D** to **E** is the allyl/alkyne coupling on single metals[51] that has found recent applications in cycloaddition reactions to generate five-, six-, and seven-membered carbocycles.[52]

Certainly, another possibility that must be considered for the generation of the allylvinylidene compounds **5** and **6** from **1** is the direct electrophilic attack at the alkynyl β-carbon. However, the failure of **1** to react with either methyl triflate or benzyl bromide under the same conditions indicates that the alkynyl group is not very nucleophilic. In addition, we would expect direct attack on the alkynyl group to occur on the face *away from* Rh, thereby generating the other isomer of **5** or **6** in which the allyl fragment is adjacent to Ir.

There are two recent reports of related metal-mediated coupling reactions involving alkynyl and allyl ligands, although both involve coupling at the alkynyl α-carbon.[53,54] In the first case, coupling was initiated in the presence of silica gel, possibly by initial protonation of the alkynyl group yielding a vinylidene, which underwent subsequent coupling with the allyl ligand.[53] This proposal receives support from the study by Chin and co-workers[54] in which the coupling of alkynyl and allyl ligands was shown to be initiated by electrophiles, again through initial formation of vinylidene ligands, followed by subsequent coupling. Also in the first report,[53] allyl condensation at the β-carbon of an alkynyl ligand was proposed, although this apparently occurs by direct electrophilic attack by allyl halides, and is not metal mediated.

Conclusions

This and our previous study[7a,b] have shown that either nucleophiles or electrophiles can react with bridging alkynyl groups via a metal-mediated process in which attack at a metal first occurs, followed by transfer to the β-carbon of the alkynyl group. It appears that transfer occurs from the metal that is π-bound to the alkynyl group and is therefore analogous to the migratory insertion involving transfer of a hydride or alkyl group to a coordinated alkyne. Although metal-mediated coupling of a hydrocarbyl fragment to the β-carbon of an alkynyl group is rare, the above analogy with alkyne chemistry suggests that this should be a general phenomenon.

Supporting Information Available: Tables of X-ray experimental details, atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for compound **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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