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Carbon−Carbon Bond Formation Promoted by Adjacent Metal Centers: Regioselective Alkyne Insertions into a “Rh(μ-CH_2)Ru” Moiety Yielding C_3- and C_5-Bridged Fragments

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The heterobinuclear complex $[RhRu(CO)_3(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**2**) (dppm = $Ph_2PCH_2PPh_2$), generated in situ from the tetracarbonyl precursor, reacts with the alkynes, dimethyl acetylenedicarboxylate, hexafluoro-2-butyne, and diethyl acetylenedicarboxylate to give the C_3-bridged products $[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(R){=}C(R)CH_2)(dppm)_2][CF_3SO_3]$ (R = CO_2CH_3 (**3**), CF_3 (**4**), $CO_2CH_2CH_3$ (**5**)), in which the alkynes have inserted into the Rh−C bond of the bridging methylene group. Compound **2** also reacts with 2-butyn-1-al diethylacetal and 2-butyn-1-ol, producing the insertion products $[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CH_3){=}C(R)CH_2)(dppm)_2][CF_3SO_3]$ (R = $CH(OEt)_2$ (**6**), CH_2OH (**7**)) analogous to compounds **3**−**5**. The regiochemistry of alkyne insertion in both cases has been established by 2-D NMR spectroscopy; the methyl substituent is adjacent to Rh, and the oxygen-containing substituent is adjacent to the methylene group. Attempts to generate an isomer of **3** by the reverse sequence of methylene insertion into the Rh−C bond of the alkyne-bridged species $[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CO_2CH_3){=}C(CO_2CH_3))(dppm)_2][X]$ (X = BF_4 (**8a**), CF_3SO_3 (**8b**)) failed with no reaction occurring, although reaction of the dicarbonyl analogue, $[RhRu(OSO_2CF_3)(CO)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CO_2CH_3){=}C(CO_2CH_3))(dppm)_2]$, with CH_2N_2 results in methylene insertion into the Rh−Ru bond to give $[RhRu(OSO_2CF_3)(CO)_2(\mu\text{-}CH_2)(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CO_2CH_3){=}C(CO_2CH_3))(dppm)_2]$ (**10**). Reaction of **3** with trimethylamine-*N*-oxide results in loss of a carbonyl and a rearrangement of the C_3-bridged group, affording $[RhRu(CO)_2(\mu\text{-}\eta^1{:}\eta^3\text{-}CHC(CO_2CH_3){=}CH(CO_2CH_3))(dppm)_2][CF_3SO_3]$ (**11**). Propargyl alcohol reacts with **2**, affording a double-insertion product $[RhRu(CO)_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CH{=}C(CH_2OH)CH{=}C(CH_2OH)CH_2)(dppm)_2][CF_3SO_3]$ (**12**) with incorporation of two propargyl alcohol units in a head-to-tail arrangement. The structures of compounds **4**, **8a**, and **12** were determined by X-ray methods.

Introduction

The Fischer−Tropsch (FT) process, in which synthesis gas (CO + H_2) is converted into a variety of hydrocarbons over group 8 and 9 transition-metal catalysts,[1] has enormous implications for the conversion of underutilized carbon resources, such as coal and natural gas, into chemical feedstocks.[2] Although it is recognized that the formation of carbon−carbon bonds in this process occurs by the coupling of methylene groups, the mechanisms for coupling these groups are not clearly understood, and several proposals have been presented.[1,3−6]

The recent interest in bimetallic Fischer−Tropsch catalysts,[7] in which two different group 8 and 9 metals are used as catalysts, led us to study a series of methylene-bridged complexes involving the Rh/Os,[8] Rh/Ru,[9] and Ir/Ru[10] metal combinations as models for these bimetallic systems. To date, the Rh/Os system has proven to be the most promising, showing selective coupling of either three or four methylene groups to give allyl or butanediyl fragments, respectively.[8] Although no intermediates in the formation of these C_3 and C_4 products were observed beyond the methylene-bridged species, we proposed stepwise methylene insertions to

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give first a C_2H_4-bridged followed by a C_3H_6-bridged intermediate, the latter of which yielded the allyl or butanediyl groups by β-H elimination or an additional CH_2-insertion step, respectively. Our failure to observe the proposed C_2- or C_3-bridged intermediates led us to attempt to synthesize models for these species using alkynes and methylene groups as the C_2 and C_1 fragments, respectively, which could be combined to yield C_3 species. A recent report by Dry has alluded to the possible importance of surface-bound C_3 units in the FT process,[6a] produced by the condensation of bridging methylene groups and surface-bound olefins as the C_2 fragments.

In this paper we report our attempts to synthesize C_3-bridged complexes via the coupling of methylene groups and alkynes promoted by the Rh/Ru combination of metals.

Experimental Section

General Comments. All solvents were dried (using appropriate desiccants), distilled before use, and stored under a dinitrogen atmosphere. Reactions were performed under an argon atmosphere using standard Schlenk techniques. Diazomethane was generated from Diazald, which was purchased from Aldrich, as was dimethyl acetylenedicarboxylate, diethyl acetylenedicarboxylate, propargyl alcohol, 2-butyn-1-al diethyl acetal, and 2-butyn-1-ol. The ^{13}C-enriched Diazald was purchased from Cambridge Isotopes, and ^{13}CO was purchased from Isotech, Inc. The complexes $[RhRu(CO)_4(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**1**) and $[RhRu(CO)_3(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**2**) were prepared by the published procedures.[9] In all cases compound **2** was generated in situ from **1** in the presence of Me_3NO and filtered over Celite.

The ^1H, $^{13}C\{^1H\}$, $^1H-^1H$ COSY, $^{31}P-^{31}P$ COSY, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian iNova-400 spectrometer operating at 399.8 MHz for ^1H, 161.8 MHz for ^{31}P, and 100.6 MHz for ^{13}C. The HMBC experiments were performed on a Varian Unity 500 MHz spectrometer, and infrared spectra were obtained on a Bomem MB-100 spectrometer. Elemental analyses were performed by the microanalytical service within the department. In a number of cases, elemental analyses are less satisfactory than desired owing to facile yet incomplete loss of CH_2Cl_2 of crystallization upon removal of the crystals from the mother liquor. In all cases, however, the compounds were shown to be spectroscopically pure on the basis of NMR spectroscopy. The $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR and IR spectroscopic data are given in Table 1, while other relevant NMR data are provided in the text.

Preparation of Compounds. $[RhRu(CO)_3(\mu,\eta^1{:}\eta^1\text{-}C(CO_2CH_3){=}C(CO_2CH_3)CH_2)(dppm)_2][CF_3SO_3]$ (3). Method i. A 10 mL portion of acetone was added to a mixture of compound **1** (135 mg, 0.111 mmol) and Me_3NO (13.75 mg, 0.185 mmol, 1.70 equiv), resulting in a rapid color change from orange to dark red. Dimethyl acetylenedicarboxylate (14 μL, 0.11 mmol, 1.0 equiv) was added, causing an immediate color change from dark red to orange. The solution was filtered over Celite, after which the solvent was removed in vacuo. The orange residue was recrystallized from CH_2Cl_2/ether/pentane (1:3:1), and the orange solid was washed with 2 × 10 mL of ether and dried in vacuo, yielding 130.0 mg (0.0955 mmol, 86%) of product. The fractional CH_2Cl_2 of crystallization was established by elemental analysis and by ^1H NMR spectroscopy. Anal. Calcd for $C_{61.1}H_{52.2}Cl_{0.2}F_3O_{10}P_4RhRuS$ (**2**$\cdot 0.1CH_2Cl_2$): C, 53.55; H, 3.84; Cl, 0.52. Found: C, 53.12; H, 3.76; Cl, 0.43.

Method ii. Dimethyl acetylenedicarboxylate (2.6 μL, 0.021 mmol) was added to a solution of $[RhRu(CO)_4(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**1**) (25 mg, 0.020 mmol) in 0.7 mL of CD_2Cl_2 in an NMR tube. The complete conversion to **3** was confirmed by ^1H and ^{31}P NMR spectroscopy in less than 1 h at ambient temperature.

$[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CF_3){=}C(CF_3)CH_2)(dppm)_2][CF_3SO_3]$ (4). Compound **2** was generated from a mixture of compound **1** (120 mg, 0.0962 mmol) and Me_3NO (12.30 mg, 0.164 mmol, 1.70 equiv) in 15 mL of acetone as described above. Hexafluoro-2-butyne was passed through the headspace of the flask containing the solution of **2** for 1 min at a rate of ca. 10 mL/min, causing a slow color change from dark red to dull orange. The solution was filtered over Celite and the solvent was removed in vacuo, yielding 70.5 mg (0.0510 mmol, 53%) of product. The orange residue was recrystallized from CH_2Cl_2/ether, and the orange solid was washed with 2 × 10 mL of ether and 1 × 10 mL of pentane and dried in vacuo. Anal. Calcd for $C_{59}H_{46}F_9O_6P_4RhRuS$ (**4**): C, 51.28; H, 3.36. Found: C, 50.45; H, 3.29.

$[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CO_2CH_2CH_3){=}C(CO_2CH_2CH_3)CH_2)(dppm)_2][CF_3SO_3]$ (5). Compound **2** (125 mg, 0.103 mmol) was prepared, as noted above, in 10 mL of acetone. Diethyl acetylenedicarboxylate (18 μL, 0.113 mmol, 1.1 equiv) was added, causing an immediate color change from dark red to orange. The solution was filtered over Celite, after which the solvent was removed in vacuo, affording 107.4 mg (0.0773 mmol, 75%) of product. The orange residue was recrystallized from CH_2Cl_2/ether, and the orange solid was washed with 2 × 10 mL of ether and dried in vacuo. Anal. Calcd for $C_{63}H_{56}F_3O_{10}P_4RhRuS$ (**5**): C, 54.44; H, 4.06. Found: C, 54.01; H, 3.99.

$[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CH_3){=}C(CH(OCH_2CH_3)_2)CH_2)(dppm)_2][CF_3SO_3]$ (6). Compound **2** (156 mg, 0.128 mmol) was prepared in 10 mL of acetone and cooled to −10 °C. 2-Butyn-1-al diethylacetal (22 μL, 0.140 mmol, 1.1 equiv) was added, causing a slow color change from dark red to orange over the course of 5 min. The solution was stirred at −10 °C for 2 h, after which the solution was warmed to room temperature and filtered over Celite. The solvent was then removed in vacuo, the dull orange residue was recrystallized from CH_2Cl_2/ether, and the orange-red solid was washed with 3 × 15 mL of ether and dried in vacuo, yielding 104.6 mg (0.0768 mmol, 60%) of product. Anal. Calcd for $C_{63.2}H_{60.4}Cl_{0.4}F_3O_8P_4RhRuS$ (**6**$\cdot 0.2CH_2Cl_2$): C, 55.04; H, 4.42; Cl, 1.05. Found: C, 54.54; H, 4.39; Cl, 0.71.

$[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CH_3){=}C(CH_2OH)CH_2)(dppm)_2][CF_3SO_3]$ (7). Compound **2** (113 mg, 0.093 mmol) was prepared in 10 mL of acetone. 2-Butyn-1-ol (8 μL, 0.107 mmol, 1.2 equiv) was added, causing an immediate color change from dark red to orange. The solution was stirred for 1 h, after which the solution was filtered over Celite and the solvent was removed in vacuo. The bright orange residue was recrystallized from CH_2Cl_2/ether/pentane (1:3:2), washed with 2 × 10 mL of ether, and dried in vacuo, yielding 103.2 mg (0.0800 mmol, 86%) of product. Anal. Calcd for $C_{60}H_{56}F_3O_6P_4RhRuS$ (**7**): C, 54.88; H, 4.06. Found: C, 54.60; H, 4.03.

$[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CO_2CH_3){=}C(CO_2CH_3))(dppm)_2][X]$, $X = BF_4^-$ (8a), $X = CF_3SO_3$ (8b). Dimethyl acetylenedicarboxylate (20 μL, 0.126 mmol) was added to a solution of $[RhRu(CO)_4(dppm)_2][X]$ (110 mg, 0.089 mmol) at 20 °C, dissolved in 10 mL of CH_2Cl_2. No noticeable color change resulted; however, NMR spectroscopy showed complete conversion to a new product. The solvent was removed in vacuo, and the bright orange residue was recrystallized from CH_2Cl_2/Et_2O. The orange solid was washed with 2 × 15 mL of ether and dried in vacuo, yielding 114.0 mg (0.0730 mmol, 82%) of **8a**$\cdot 2CH_2Cl_2$. Anal. Calcd for $C_{61}H_{58}BCl_4F_4O_7P_4RhRu$ (**8a**$\cdot 2CH_2Cl_2$): C, 50.33; H, 3.73; Cl, 9.74. Found: C, 49.82; H, 3.35; Cl, 9.33.

$[RhRu(OSO_2CF_3)(CO)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CO_2CH_3){=}C(CO_2CH_3))(dppm)_2]$ (9). A Schlenk flask was charged with compound **8b** (40 mg, 0.0297 mmol) and trimethylamine-*N*-oxide (3.9 mg, 0.0519 mmol, 1.75 equiv). The flask was cooled to approximately 0 °C, and 10 mL of acetone was added slowly. After 20

Table 1. Spectroscopic Data for the Compounds

		NMR[d,e]		
compound	IR[a,b,c]	δ ($^{31}P\{^1H\}$)[f]	δ (^1H)[g,h]	δ ($^{31}C\{^1H\}$)[h,i]
$[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CO_2CH_3)=C(CO_2CH_3)CH_2)(dppm)_2][CF_3SO_3]$ (**3**)	2039 (s), 2018 (s), 1968 (m), 1705 (br, m), 1574 (w)[j]	28.4 (m), 24.6 (dm)	4.58 (m, 2H), 3.72 (m, 2H), 3.15 (s, 3H), 2.65 (s, 3H), 1.48 (br, t, 2H)	194.0 (t, $^2J_{PC}$ = 15 Hz, 1C), 193.2 (t, $^2J_{PC}$ = 15 Hz, 1C), 191.1 (dt, $^2J_{PC}$ = 12 Hz, $^1J_{RhC}$ = 50 Hz, 1C), 15.3 (t, $^2J_{PC}$ = 9 Hz, 1C)
$[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CF_3)=C(CF_3)CH_2)(dppm)_2][CF_3SO_3]$ (**4**)	2049 (s), 2019 (s), 1968 (s), 1574 (w)[j]	27.3 (m), 22.7 (dm)	4.37 (m, 2H), 4.55 (m, 2H), 1.82 (m, 2H)	194.0 (m, 1C), 193.1 (t, $^2J_{PC}$ = 14 Hz, 1C), 191.3 (dt, $^2J_{PC}$ = 12 Hz, $^1J_{RhC}$ = 50 Hz, 1C), 13.8 (t, $^2J_{PC}$ = 8 Hz, 1C)[k]
$[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CO_2Et)=C(CO_2Et)CH_2)(dppm)_2][CF_3SO_3]$ (**5**)	2042 (m), 2016 (s), 1953 (m), 1695 (br, m), 1574 (m)[j]	28.3 (m), 25.0 (dm)	5.06 (m, 2H), 4.23 (m, 2H), 3.40 (q, 2H), 3.17 (q, 2H), 1.53 (m, 2H), 1.07 (t, 3H), 0.81 (t, 3H)	204.7 (t, $^2J_{PC}$ = 13 Hz, 1C), 194.4 (td, $^2J_{PC}$ = 13 Hz, $^2J_{RhC}$ = 4 Hz, 1C) 190.9 (dt, $^2J_{PC}$ = 13 Hz, $^1J_{RhC}$ = 51 Hz, 1C)
$[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CH_3)=C(CH(OEt)_2)CH_2)(dppm)_2][CF_3SO_3]$ (**6**)	2024 (s), 1977 (sh), 1951 (s)	28.4 (m), 22.9 (dm)	4.97 (s, 1H), 4.75 (m, 2H), 4.41 (m, 2H), 3.70 (q, 2H), 3.59 (q, 2H), 1.45 (m, 2H), 1.33 (t, 6H), 0.07 (s, 3H)	201.4 (t, $^2J_{PC}$ = 6 Hz, 1C), 193.8 (t, $^2J_{PC}$ = 15 Hz, $^2J_{RhC}$ = 7 Hz, 1C), 193.2 (dt, $^2J_{PC}$ = 12 Hz, $^1J_{RhC}$ = 52 Hz, 1C)
$[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CH_3)=C(CH_2OH)CH_2)(dppm)_2][CF_3SO_3]$ (**7**)	2024 (s), 1995 (m), 1950 (s)	28.3 (m), 22.4 (dm)	4.64 (m, 2H), 3.92 (d, 2H), 3.73 (m, 2H), 1.98 (s, 1H), 1.36 (m, 2H), 0.11 (s, 3H)	
$[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CO_2CH_3)=C(CO_2CH_3))(dppm)_2][CF_3SO_3]$ (**8b**)[l]	2038 (s), 2019 (s), 1969 (s), 1726 (m)[k]	19.9 (om)	4.04 (m, 2H), 3.29 (m, 2H), 2.71 (s, 3H), 2.32 (s, 3H)	197.5 (m, 1C), 192.4 (t, $^2J_{PC}$ = 13 Hz, 1C), 190.5 (m)
$[RhRu(OSO_2CF_3)(CO)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CO_2CH_3)=C(CO_2CH_3)(dppm)_2]$ (**9**)	2003(s), 1945(s), 1356 (m)[k]	22.7 (m), 17.0 (dm)[k]	3.89 (m, 2H), 3.67 (m, 2H), 3.23 (s, 3H), 2.18 (s, 3H)[k]	206.9 (m, 1C), 192.2 (m, 1C)[k]
$[RhRu(OSO_2CF_3)(CO)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CO_2CH_3)=C(CO_2CH_3)(\mu\text{-}CH_2)(dppm)_2]$ (**10**)	2027 (s), 1964 (s), 1703 (s), 1575 (w)[j,k]	26.2 (d, $^1J_{RhP}$= 142 Hz), 15.3 (s)[k]	4.42 (m, 2H), 3.66 (m, 2H), 3.34 (s, 3H), 2.74 (m, 2H), 1.70 (s, 3H)[k]	199.4 (m, 1C), 193.1 (m, 1C)[k]
$[RhRu(CO)_2(\mu\text{-}\eta^1{:}\eta^3\text{-}CHC(CO_2CH_3)=CH(CO_2CH_3))(dppm)_2][CF_3SO_3]$ (**11**)	1998 (s), 1969 (s)[k]	45.3 (m), 43.5 (m), 24.8 (cm), 29.4 (cm)[k]	5.90 (m, 1H), 4.90 (m, 1H), 4.35 (m, 1H), 3.79 (s, 3H), 3.52 (m, 1H), 3.32 (m, 1H), 2.82 (s, 3H)[k]	205.0 (t, $^2J_{PC}$ = 13 Hz, 1C), 193.3 (dt, $^2J_{PC}$ = 15 Hz, $^1J_{RhC}$ = 67 Hz, 1C), 110.2 (dm, $^1J_{RhC}$ = 21 Hz, 1C)[k]
$[RhRu(CO)_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CH=C(CH_2OH)CH=C(CH_2OH)CH_2)(dppm)_2][CF_3SO_3]$ (**12**)	1995 (s), 1957 (s)	66.7 (dd, J = 21, 124 Hz), 39.7 (ddd, J = 16, 84, 140 Hz), 27.8 (dd, J = 22, 46 Hz), 0.62 (ddd, J = 16, 46, 104 Hz)	6.03, (s, 1H), 5.03 (m, 1H), 4.36 (m, 1H), 3.71 (m, 1H), 3.60 (m, 1H), 3.44 (m, 1H), 3.24 (m, 1H), 2.86 (m, 1H), 2.80 (om, 2H), 2.55 (m, 1H), 2.03 (m, 1H), 0.77 (m, 1H)	200.3 (m, 1C), 192.2 (dm, $^1J_{RhC}$ = 67 Hz, 1C), 3.6 (ddd, $^1J_{RhC}$ = 16 Hz, $^2J_{PC(trans)}$ = 64 Hz, $^2J_{PC(cis)}$ = 5 Hz, 1C)

[a] IR abbreviations: s = strong, m = medium, br = broad, sh = shoulder. [b] CD_2Cl_2 solutions; in units of cm^{-1}. [c] Carbonyl stretches unless otherwise noted. [d] NMR abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, cm = complex multiplet, om = overlapping multiplet, dm = doublet of multiplets, ddd = doublet of doublet of doublets, br = broad, dt = doublet of triplets, td = triplet of doublets. [e] NMR data at 25 °C in CD_2Cl_2 unless otherwise indicated; in units of ppm. [f] ^{31}P chemical shifts referenced to external 85% H_3PO_4. [g] Chemical shifts for the phenyl hydrogens not given. [h] ^1H and ^{13}C chemical shifts referenced to TMS. [i] $^{13}C\{^1H\}$ NMR performed with ^{13}CO enrichment. [j] ν (C=C). [k] In acetone-d_6. [l] Spectroscopic parameters for the cation of **8a** are identical to those of **8b**.

min the reaction changed color from orange to orange-red. The reaction was stirred for another 15 min, after which the solution was slowly warmed to room temperature and filtered over Celite. The solvent was removed in vacuo, and the orange-red residue was recrystallized from acetone/ether/pentane (1:5:1), washed with 3 × 10 mL ether, and dried in vacuo, yielding 29.4 mg (0.0223 mmol, 75%) of product. Anal. Calcd for $C_{59}H_{50}F_3O_9P_4RhRuS$ (**9**): C, 53.68; H, 3.82. Found: C, 53.21; H, 3.92.

$[RhRu(OSO_2CF_3)(CO)_2(\mu\text{-}CH_2)(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CO_2CH_3)=C(CO_2CH_3))(dppm)_2]$ (10). Compound **9** (70.8 mg, 0.0520 mmol) was dissolved in 10 mL of acetone. Diazomethane was bubbled through the solution vigorously for 10 min, causing no noticeable color change. The solution was concentrated down to 5 mL and filtered over Celite to remove any polymethylene that may have formed. The solvent was removed in vacuo, and the orange residue was recrystallized from acetone/ether/pentane (1:5:1), washed with 2 × 10 mL ether, and dried in vacuo, yielding 46.5 mg (0.0348 mmol, 67%) of product. Owing to the air sensitivity of compound **10**, satisfactory elemental analyses could not be obtained.

$[RhRu(CO)_2(\mu\text{-}\eta^1{:}\eta^3\text{-}CHC(CO_2CH_3)=CH(CO_2CH_3))(dppm)_2][CF_3SO_3]$ (11). A 0.7 mL sample of acetone-d_6 was added to a mixture of compound **3** (35 mg, 0.026 mmol) and

Me_3NO (3.23 mg, 0.043 mmol, 1.67 equiv) at 20 °C in an NMR tube. An immediate color change from orange to dark orange occurred immediately upon mixing. Compound **11** was characterized entirely by ^1H, ^2H, and ^{31}P spectroscopy; elemental analyses were not obtained owing to its high air-sensitivity.

$[RhRu(CO)_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CH{=}C(CH_2OH)CH{=}C(CH_2OH)CH_2)(dppm)_2][CF_3SO_3]$ (12). Compound **2** (134 mg, 0.110 mmol) was prepared in 15 mL of acetone. The solution was cooled to −78 °C, and propargyl alcohol (14 μL, 0.241 mmol, 2.2 equiv) was added, causing a gradual color change from dark red to light orange over the course of 2 min. The solution was brought to room temperature and filtered over Celite followed by removal of the solvent in vacuo. The orange residue was recrystallized from CH_2Cl_2/ether, and the orange-red solid was washed with 2 × 10 mL of ether and dried in vacuo, yielding 120.5 mg (0.0924 mmol, 84%) of product. Anal. Calcd for $C_{60.1}H_{54.2}Cl_{0.2}F_3O_7P_4RhRuS$ ($\mathbf{12}\cdot 0.1CH_2Cl_2$): C, 54.99; H, 4.16. Found: C, 54.20; H, 4.13.

Reaction of 2 with Acetylene. An NMR tube was charged with 45 mg (0.0361 mmol) of **1** and 4.60 mg (0.0612 mmol) of trimethylamine-*N*-oxide along with 0.7 mL of acetone-d_6. The resulting red solution was filtered over Celite, then cooled to −78 °C with a dry ice/acetone bath, and acetylene was passed through the headspace for ca. 5 min. VT NMR analysis showed that even at −80 °C numerous unidentified ^{31}P-containing products were obtained.

Reaction of 2 with Propyne. A Teflon-valved NMR tube was charged with 0.7 mL of a 0.05 M solution of **2** and was degassed by two freeze/pump/thaw cycles. Once the solution was frozen in liquid nitrogen, the tube was back-filled using a 5 mL flask previously filled with ca. 1 atm propyne. The solution was then warmed to −78 °C for VT NMR analysis. Monitoring the $^{31}P\{^1H\}$ NMR between −78 °C and ambient temperature showed the presence of a large number of unidentified species.

Reaction of 2 with 2-Butyne. A Teflon-valved NMR tube was charged with 0.7 mL of a 0.025 M solution of **2** and was degassed by two freeze/pump/thaw cycles. A 5 mL flask was charged with the room-temperature vapor pressure of 2-butyne (ca. 0.8 atm). The solution of **2** was frozen in liquid nitrogen, and the tube was back-filled using the flask containing the 2-butyne. The solution was then warmed to −78 °C for VT NMR analysis. Monitoring the $^{31}P\{^1H\}$ NMR spectrum between −78 °C and ambient temperature showed the presence of a large number of unidentified species.

Reaction of 12 with H_2. Compound **12** (25 mg, 0.0192 mmol) was dissolved in 0.7 mL of CD_2Cl_2 in an NMR tube. Hydrogen gas was bubbled through the headspace of the tube, with no noticeable color change. ^1H and $^{31}P\{^1H\}$ NMR spectroscopy detected the presence of $[RhRu(\mu\text{-}H)_2(CO)_3(dppm)_2][CF_3SO_3]$[9] as well as several unidentified organic products.

Attempted Reaction of 12 with $[(Cp)_2Fe][PF_6]$. Compound **12** (20 mg, 0.0153 mmol) and $[(Cp)_2Fe][PF_6]$ (10.1 mg, 0.0302 mmol, 1.97 equiv) were placed in an NMR tube and dissolved in 0.7 mL of acetone, forming a green solution. $^{31}P\{^1H\}$ NMR spectroscopy after 14 h detected only the presence of **12**.

Attempted Reaction of 12 with $[NH_4]_2[IrCl_6]$. Compound **12** (15 mg, 0.0115 mmol) and $[NH_4]_2[IrCl_6]$ (10.1 mg, 0.0229 mmol, 1.99 equiv) were placed in an NMR tube and dissolved in 0.6 mL of acetonitrile and 0.1 mL of D_2O. After sitting overnight, only starting material was observed by $^{31}P\{^1H\}$ NMR.

X-ray Data Collection. (a) Pale yellow crystals of $[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CF_3){=}C(CF_3)CH_2)(dppm)_2][CF_3SO_3]\cdot 1.5CH_2Cl_2$ (**4**) were obtained via slow diffusion of pentane into a dichloromethane-d_2 solution of the compound. Data were collected on a Bruker PLATFORM/SMART 1000 CCD diffractometer[11] using Mo Kα radiation at −80 °C. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 5957 reflections from the data collection. The space group was determined to be $P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14]). The data were corrected for absorption through use of the SADABS procedure. See Table 2 for a summary of crystal data and X-ray data collection information.

(b) Red-orange crystals of $[RhRu(CO)_3(\mu\text{-}CO)(\mu\text{-}CH_3O_2CC{=}CCO_2CH_3)(dppm)_2][BF_4]$ (**8a**) were obtained via slow diffusion of diethyl ether into a dichloromethane solution of the compound. Data were collected as for **4** above (see Table 2), and data were corrected for absorption via Gaussian integration (crystal dimensions measured and faces indexed). Unit cell parameters were obtained from a least-squares refinement of the setting angles of 7423 reflections from the data collection, and the space group was determined to be $P\bar{1}$ (No. 2).

(c) Orange crystals of $[RhRu(CO)_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CH{=}C(CH_2OH)CH{=}C(CH_2OH)CH_2)(dppm)_2][CF_3SO_3]\cdot CH_2Cl_2$ (**12**) were obtained via slow diffusion of diethyl ether into a dichloromethane solution of the compound. Data were collected and corrected for absorption as for **4** above (see Table 2). Unit cell parameters were obtained from a least-squares refinement of the setting angles of 3321 reflections from the data collection. The space group was determined to be $P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14]).

Structure Solution and Refinement. The structure of **4** was solved using direct methods (SHELXS-86[12]). Refinement was completed using the program SHELXL-93.[13] Hydrogen atoms were assigned positions on the basis of the geometries of their attached carbon atoms and were given thermal parameters 20% greater than those of the attached carbons. Although the presence of 1.5 equiv of CD_2Cl_2 in the crystals was confirmed by ^2H NMR, the atoms of these solvent molecules could not be unambiguously located in difference Fourier syntheses; only smeared out regions of electron density were found, for which suitable disorder models could not be found. These solvent molecules were therefore handled using the SQUEEZE routine as implemented in the PLATON[14] program system, in which the contribution of the disordered solvent electron density to the intensity data was calculated, and the refinement continued using data with this contribution removed. The final model for **4** was refined to values of $R_1(F) = 0.0398$ (for 10 314 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.1031$ (for all 12464 independent data).

The structure of **8a** was solved using the direct-methods program SHELXS-86, and refinement was completed using the program SHELXL-93, during which the hydrogen atoms were treated as for **4**. One of the chlorine atoms of a solvent dichloromethane molecule was found to be disordered; this atom was split into two positions, which were assigned occupancy factors of 0.75 and 0.25 and were allowed to refine independently. The final model for **8a** was refined to values of $R_1(F) = 0.0496$ (for 10 311 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.1423$ (for all 12744 independent data).

The structure of **12** was solved using the direct-methods program SHELXS-86, and refinement was completed using the program SHELXL-93, during which the hydrogen atoms were treated as for **4**. The final model for **12** was refined to values of $R_1(F) = 0.0699$ (for 6446 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.1770$ (for all 11 524 independent data).

Results and Compound Characterization.

Reaction of the methylene-bridged, tetracarbonyl species $[RhRu(CO)_3(\mu\text{-}CH_2)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**1**) with

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[11] Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by Bruker.

[12] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

[13] Sheldrick, G. M. *SHELXL-93*, Program for crystal structure determination; University of Göttingen: Germany 1993.

[14] Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34. PLATON−a multipurpose crystallographic tool. Utrecht University, Utrecht, The Netherlands.

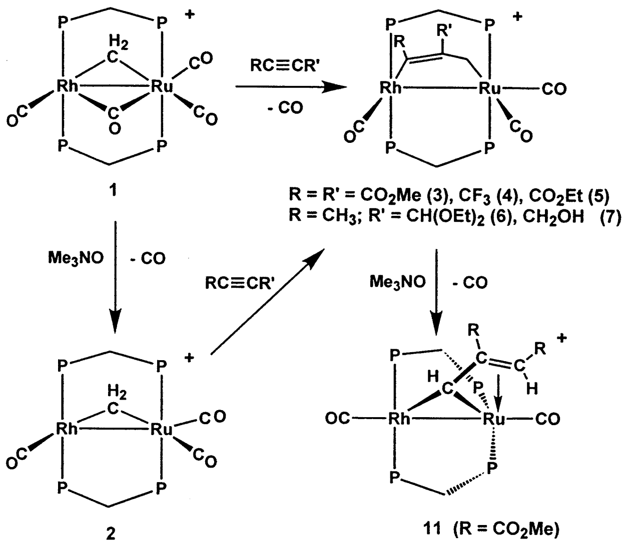
Table 2. Crystallographic Experimental Details for Compounds 4, 8a, and 12

	4	8a	12
formula	$C_{60.5}H_{49}Cl_3F_9O_6P_4RhRuS$	$C_{61}H_{54}BCl_4F_4O_7P_4RhRu$	$C_{61}H_{56}Cl_2F_3O_7P_4RhRuS$
fw	1509.27	1455.51	1388.88
cryst dimens (mm)	0.34 × 0.24 × 0.20	0.44 × 0.37 × 0.36	0.32 × 0.14 × 0.03
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])	$P\bar{1}$ (No. 2)	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters[a]			
a (Å)	12.4541 (7)	11.5463 (8)	11.988 (1)
b (Å)	19.1183 (11)	14.731 (1)	22.217 (2)
c (Å)	25.8616 (14)	19.101 (1)	22.280 (2)
α (deg)	90.0	87.334 (1)	90.0
β (deg)	97.6146 (11)	76.823 (1)	104.662 (2)
γ (deg)	90.0	85.017 (1)	90.0
V (Å^3)	6103.4 (6)	3150.2 (4)	5740.9 (8)
Z	4	2	4
ρ_{calcd} (g cm^{-3})	1.642	1.534	1.607
μ (mm^{-1})	0.866	0.835	0.855
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)	graphite-monochromated Mo Kα (0.71073)	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	−80	−80	−80
scan type	ω scans (0.2°) (25 s exposures)	ω scans (0.2°) (20 s exposures)	ω scans (0.2°) (30 s exposures)
data collection 2θ limit (deg)	52.76	52.76	52.88
total data collected	37 974 ($-13 \le h \le 15$, $-23 \le k \le 23$, $-32 \le l \le 32$)	21 548 ($-14 \le h \le 12$, $-18 \le k \le 18$, $-23 \le l \le 23$)	25 993 ($-14 \le h \le 11$, $-27 \le k \le 27$, $-25 \le l \le 27$)
no. of ind reflns	12464 ($R_{int} = 0.0462$)	12744 ($R_{int} = 0.0272$)	11524 ($R_{int} = 0.1008$)
no. of obsd reflns	10 314 [$F_o^2 \ge 2\sigma(F_o^2)$]	10 311 [$F_o^2 \ge 2\sigma(F_o^2)$]	6446 [$F_o^2 \ge 2\sigma(F_o^2)$]
range of transmn factors	0.8458−0.7571	0.7987−0.7112	0.9748−0.7714
no. of data/restraints/params	12 464 [$F_o^2 \ge -3\sigma(F_o^2)$]/0/730	12 744 [$F_o^2 \ge -3\sigma(F_o^2)$]/0/754	11 524 [$F_o^2 \ge -3\sigma(F_o^2)$]/0/723
goodness-of-fit (S)[b]	1.037 [$F_o^2 \ge -3\sigma(F_o^2)$]	1.054 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.985 [$F_o^2 \ge -3\sigma(F_o^2)$]
final R indices[c]			
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0398	0.0496	0.0699
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.1031	0.1423	0.1770
largest diff peak and hole (e Å^{-3})	1.212 and −2.058	1.979 and −1.031	1.162 and −0.739

[a] Obtained from least-squares refinement of 5957 reflections for compound **4**, 7423 reflections for compound **8a** and 3321 reflections for compound **12**. [b] $S = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0603P)^2 + 0.8779P]^{-1}$ for compound **4**, $w = [\sigma^2(F_o^2) + (0.00822P)^2 + 3.9605P]^{-1}$ for compound **8a**, and $w = [\sigma^2(F_o^2) + (0.0808P)^2]^{-1}$ for compound **12** where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$). [c] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$. Refinement on F_o^2 for all reflections (having $F_o^2 \ge -3\sigma(F_o^2)$. wR_2 and S based on F_o^2; R_1 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.

a number of alkynes has been attempted. Although this reaction proceeds readily with dimethyl acetylenedicarboxylate (DMAD), yielding $[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CO_2Me){=}C(CO_2Me)CH_2)(dppm)_2][CF_3SO_3]$ (**3**), the reactions with other alkynes proceed sluggishly, requiring hours or days to reach completion at ambient temperature. However, removal of a carbonyl from **1**, using trimethylamine-*N*-oxide to give the tricarbonyl $[RhRu(CO)_3(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**2**)[9] in situ, results in instantaneous reaction with a number of alkynes to give the same products as with **1**, as shown in Scheme 1. With the symmetric alkynes RC≡CR (R = CO_2Me, CF_3, CO_2Et), reaction with **2** yields the products $[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(R){=}C(R)CH_2)(dppm)_2][CF_3SO_3]$ (R = CO_2Me (**3**), CF_3 (**4**), CO_2Et (**5**)), in which alkyne insertion into the Rh−CH_2 bond of the precursor has occurred. All products display very similar $^{31}P\{^1H\}$ NMR spectra (see Table 1), having two complex multiplet patterns between δ 22 and 29, in which the higher field signal in each case displays coupling to Rh. In all cases, the presence of three terminally bound carbonyls is confirmed by the $^{13}C\{^1H\}$ NMR spectra of ^{13}CO-enriched products in which the high-field resonance in each case shows coupling to Rh of ca. 50 Hz, confirming this signal as resulting from the Rh-bound carbonyl. In the case of compound **5**, one of the Ru-bound carbonyls also displays 4 Hz coupling to Rh. This carbonyl is assigned as opposite the Rh−Ru bond, since such coupling has been observed when Rh and a carbonyl are mutually trans at an intervening metal.[15] The IR spectra of the three compounds confirm the terminal binding for all carbonyl ligands and also display the C=C stretch of the dimet-

Scheme 1



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[15] George, D. S. A.; Hilts, R. W.; McDonald, R.; Cowie, M. *Organometallics* **1999**, *18*, 5330.

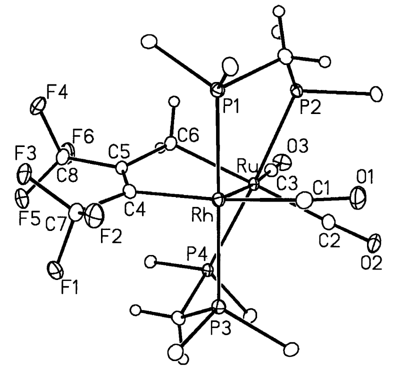
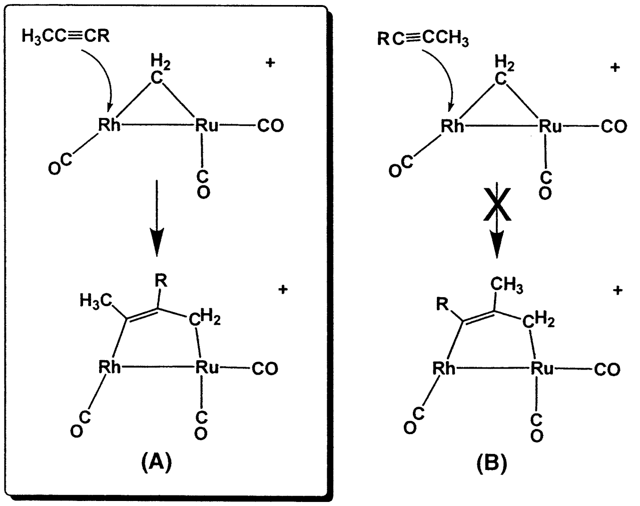


Figure 1. Perspective view of the complex cation of compound **4**, showing the numbering scheme. Thermal ellipsoids are drawn at the 20% level except for methylene hydrogens, which are drawn arbitrarily small. Phenyl groups, except for ipso carbons, are omitted. Relevant bond lengths (Å) and angles (deg): Rh−Ru = 2.7771(3), Rh−C(4) = 2.095(3), Ru−C(6) = 2.171(3), C(4)−C(5) = 1.344(4), C(5)−C(6) = 1.505(4); Ru−Rh−C(4) = 84.80(8), Rh−C(4)−C(5) = 123.3(2), C(4)−C(5)−C(6) = 122.2(3), C(5)−C(6)−Ru = 114.2(2), Rh−Ru−C(6) = 83.64(7).

allacyclopentene moiety at 1574 cm^{-1}. A broad carbonyl stretch at 1705 cm^{-1} is observed for the carboxylate group of **3**, while that of **5** appears at 1695 cm^{-1}. In all cases, the ^{1}H NMR spectra of compounds **3**−**5** display the dppm-methylene resonances in the range δ 3.7−5.1 and the metal-bound methylene group between approximately δ 1.5 and 1.8. The two dppm resonances are consistent with different environments on either side of the "$RhRuP_4$" plane and have the typical appearance, which simplifies to an AB quartet upon broadband ^{31}P decoupling. The metal-bound methylene group in each case appears as a triplet, showing coupling to the Ru-bound ^{31}P nuclei, consistent with alkyne insertion having occurred into the $Rh-CH_2$ bond. In addition to the above ^{1}H resonances, compound **3** displays two separate resonances for the methyl groups of the inserted DMAD molecule, and **5** shows the corresponding resonances for the two inequivalent ethyl groups. The inequivalence of the two methyl groups of **3** and the two ethyl groups of **5** is consistent with the insertion products diagrammed in Scheme 1. By the same token, the ^{19}F NMR spectrum of **4** displays two broad singlets at δ −46.7 and −61.9 for the inequivalent CF_3 groups. Additional support for alkyne insertion into the $Rh-CH_2$ bond comes from the $^{13}C\{^{1}H\}$ NMR spectra of $^{13}CH_2$-enriched samples of **3** and **4**, which show the methylene resonances as triplets at δ 15.3 and 13.8, respectively, displaying coupling to only the Ru-bound ^{31}P nuclei. In contrast, the methylene resonance in the precursor (**2**-$^{13}CH_2$) appears at δ 97.0 and shows coupling to all four ^{31}P nuclei and to Rh (25 Hz).[9]

Support for the structures proposed for complexes **3**−**5** comes from the X-ray structure determination of compound **4**. A representation of the complex cation is diagrammed in Figure 1. Although both dppm ligands are bridging the metals in the common manner, in which these groups are essentially trans on each metal, there is significant twisting of the two coordination geometries about the metal−metal vector, to give an average torsion angle of approximately 26°. This staggering of the ligands on adjacent metals may occur to minimize nonbonded contacts, which otherwise would be quite severe because of the short Rh−Ru distance (2.7771(3) Å), and may also result from the strain imposed by the bridging C_3 fragment. As deduced from the spectral data, alkyne insertion into the $Rh-CH_2$ bond of **2** has occurred, leaving the $Ru-CH_2$ bond intact. Within the resulting C_3-bridged fragment the bond lengths and angles are as expected. The C(4)−C(5) distance (1.344(4) Å) is typical of a double bond,[16] while the C(4)−C(7), C(5)−C(6), and C(5)−C(8) bond lengths (1.499(4), 1.505(4), 1.513(4) Å, respectively) are typical of single bonds between sp^2 and sp^3 carbons.[16,17] Similarly, the angles at C(4) and C(5) are also consistent with sp^2 hybridization of these atoms, while the smaller Ru−C(6)−C(5) angle (114.2(2)°) is consistent with sp^3 hybridization at C(6). The shorter Rh−C(4) bond compared to Ru−C(6) (2.095(3) vs 2.171(3) Å) also probably reflects the hybridization difference of these two carbon atoms.

Scheme 2



The unsymmetrical alkynes 2-butyn-1-al dimethylacetal (BDA) and 2-butyn-1-ol also react readily with **2**, giving the products $[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(R){=}C(R')CH_2)(dppm)_2][CF_3SO_3]$ ($R = CH_3$; $R' = CH(CO_2Et)_2$ (**6**), CH_2OH (**7**)), in which alkyne insertion into the $Rh-CH_2$ bond has again occurred. These products are analogous to compounds **3**−**5** and show spectroscopic parameters (see Table 1) very similar to these products. Although compounds **6** and **7** could, in principle, give rise to two isomers resulting from alkyne insertion into the $Rh-CH_2$ bond, in which either the methyl substituent or the oxygen-containing substituent ends up adjacent to the methylene group, as shown in Scheme 2, only the latter is observed. The regiochemistry in each of compounds **6** and **7** was established on the basis of 2-D NMR techniques. In a heteronuclear multiple bond correlation (HMBC) experiment, two- and three-bond carbon−hydrogen coupling is observed, while four-bond carbon−hydrogen coupling is not. In these experiments, coupling between the carbon of the methylene group and the single hydrogen of the adjacent $CH(CO_2Et)_2$ group in **6** or the pair of $CH_2(OH)$ hydrogens of **7** was observed, while coupling of the metal-bound methylene group with the methyl group on the bound alkyne of each compound

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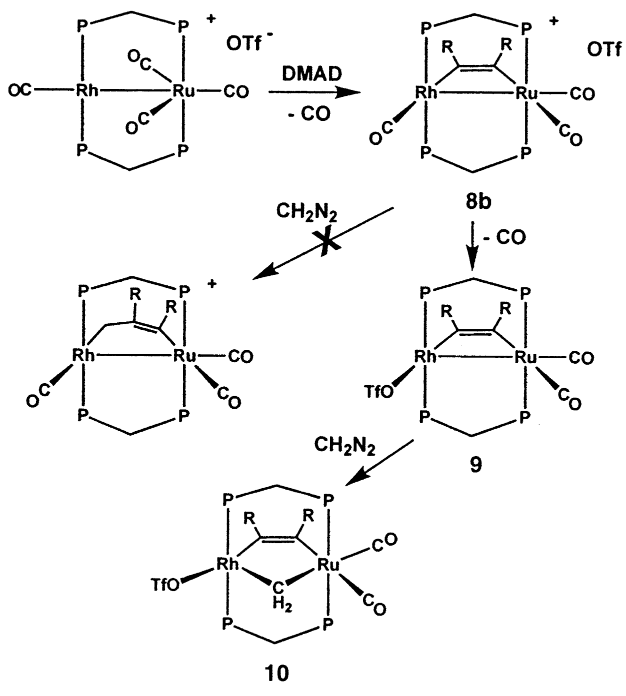
(16) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, 51.

(17) $r_c(sp^3) = 0.77$ Å; $r_c(sp^2) = 0.74$ Å.

Scheme 3



was not observed. This clearly establishes the geometry as **A** and not **B**.

The nonactivated alkynes, acetylene, propyne, and 2-butyne, apparently do not give the analogous insertion products but yield a complex mixture of unidentified products over a range of temperatures between −80 and 20 °C. We have not pursued this chemistry further.

The C_2-bridged species $[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CO_2Me){=}C(CO_2Me))(dppm)_2][X]$ ($X = BF_4$ (**8a**), CF_3SO_3 (**8b**)) were obtained by the reaction of dimethyl acetylenedicarboxylate with $[RhRu(CO)_4(dppm)_2][X]$, accompanied by CO loss. In solution, the spectral characteristics of the cations of **8a** and **8b** are identical, although complete spectral data were obtained only for **8b**. The methyl protons appear as two singlets in the ^1H NMR spectrum (δ 2.71 and 2.32), indicating two chemically inequivalent methyl environments, consistent with the structure shown in Scheme 3. In addition, the presence of two dppm-methylene resonances indicates "front-back" asymmetry in the complex. Both ^{31}P resonances in the $^{31}P\{^1H\}$ NMR spectrum are overlapping, giving rise to a complex pattern centered at δ 19.9, while the $^{13}C\{^1H\}$ NMR data and the IR spectrum indicate that the three carbonyls are terminally bound (see Table 1).

The structure of **8a** was confirmed by an X-ray structure determination, and a representation of the complex cation is diagrammed in Figure 2. The alkyne moiety bridges the metals in a parallel arrangement in which the C(4)−C(5) axis is almost parallel to the metal−metal axis. However, the alkyne is not symmetrically bound to both metals but is offset slightly toward Ru. As a result, the Ru−C(5)−C(4) angle (100.7(3)°) is substantially smaller than the expected value of near 120°, while the Ru−C(5)−C(8) angle (133.5(3)°) has opened up substantially from the expected value. By contrast, the angles at C(4) appear quite normal and are close to 120°. This asymmetry also manifests itself in a difference in Rh−C(4) and Ru−C(5) distances (2.110(4) vs 2.070(3) Å). Apart from the asymmetric binding of the alkyne, other parameters within this bound hydrocarbyl unit are normal. Therefore, the C(4)−C(5) separation (1.332(5) Å) is typical for a double bond,[16] and the C(6)−C(4)−C(5) and C(4)−C(5)−C(8) angles are all near the expected 120°. The metal−metal separation (2.8627(4) Å) is typical of a single bond, showing significant contraction relative to the intraligand nonbonded P−P distances of 3.015(1) and 3.011(1) Å.

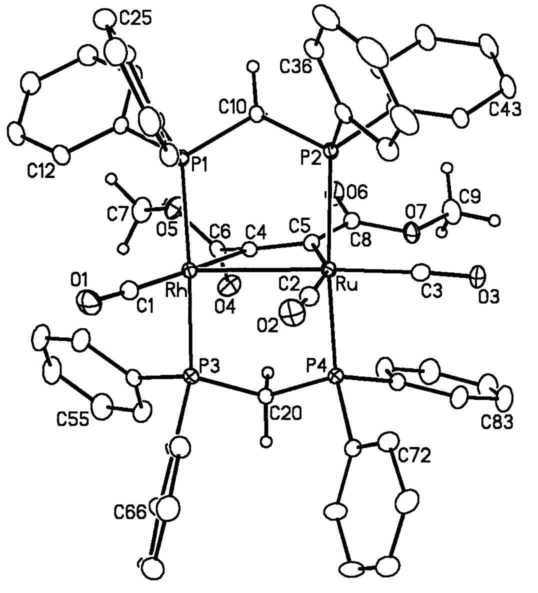


Figure 2. Perspective view of the complex cation of compound **8a**. Thermal ellipsoids are as described in Figure 1. Each phenyl ring carbon is numbered from C(*n*1) to C(*n*6) starting at the ipso carbon, where *n* = 1 to 8 for the eight phenyl rings. Relevant bond lengths (Å) and angles (deg): Rh−Ru = 2.8627(4), Rh−C(4) = 2.110(4), Ru−C(5) = 2.070(3), C(4)−C(5) = 1.332(5); Ru−Rh−C(4) = 62.6(1), Rh−Ru−C(5) = 74.1(1), Rh−C(4)−C(5) = 122.3(3), Ru−C(5)−C(4) = 100.7(3), Rh−C(4)−C(6) = 114.9(3), Ru−C(5)−C(8) = 133.5(3).

Surprisingly, the C_2-bridged **8** fails to react with diazomethane to yield a C_3-bridged product analogous to compounds **3**−**7**. The targeted species would be an isomer of compound **3**, in which the methylene group was adjacent to Rh rather than Ru. However, reaction with diazomethane could be induced upon CO removal from **8b** (vide infra).

Removal of a carbonyl from **8b**, using Me_3NO, yields a dicarbonyl product, $[RhRu(OSO_2CF_3)(CO)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CO_2Me){=}C(CO_2Me))(dppm)_2]$ (**9**). The dicarbonyl formulation is supported by the two carbonyl stretches in the IR spectrum (2003, 1945 cm^{-1}) and the carbonyl resonances in the $^{13}C\{^1H\}$ NMR spectrum, at δ 206.9 and 192.2. Neither of these carbonyls displays coupling to Rh, indicating that both are bound to Ru, and the absence of one of these carbonyls on Rh suggests that the coordination site vacated by the carbonyl is now occupied by the triflate anion; anion coordination at Rh upon CO loss was observed in a related RhOs compound.[18] Although the triflate anion is generally weakly coordinating, its coordination is common and has been observed in numerous Rh compounds.[18−22] The possibility that a solvent molecule is coordinated to Rh instead

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(18) Chokshi, A.; Graham, T. W.; McDonald, R.; Cowie, M. Manuscript in preparation.

of the triflate anion was excluded on the basis that the spectral parameters for **9** are essentially identical (apart from slight chemical shift differences) in CH_2Cl_2 and in acetone. In addition, the IR spectrum of **9** in CH_2Cl_2 shows an S−O stretch for the triflate group at 1356 cm^{-1}, consistent with coordination of this group.[20] The parallel coordination mode of the alkyne is supported by the appearance of two methyl resonances in the ^1H NMR spectrum, which shows the asymmetry expected based on the two different metals. All other spectroscopic parameters are similar to those of **8b**, adding further support to our proposal that no gross geometry change has occurred on transformation of **8b** to **9**.

Treatment of **9** with diazomethane results in methylene group insertion into the Rh−Ru bond to give the methylene- and alkyne-bridged complex $[RhRu(OSO_2CF_3)(CO)_2(\mu\text{-}CH_2)(\mu\text{-DMAD})(dppm)_2]$ (**10**), as shown in Scheme 3. Again, the $^{13}C\{^1H\}$ NMR spectrum shows no coupling of either carbonyl resonance to Rh, indicating that both remain bound to Ru. In the ^1H NMR spectrum the dppm methylene groups (δ 4.42, 2.74) have their usual appearance, which simplifies to an AB quartet upon broadband ^{31}P decoupling. The metal-bridged methylene group appears as a pseudoquintet at δ 3.66, displaying coupling to all four ^{31}P nuclei. Selective ^{31}P decoupling of either ^{31}P resonance results in simplification of the ^1H resonance of the bridging methylene group to a triplet, and broadband ^{31}P decoupling yields a singlet. The absence of Rh coupling is not unusual since two-bond Rh−H coupling in hydrocarbyl fragments is usually less than 3 Hz.[8,18,23]

The $^{31}P\{^1H\}$ NMR spectrum of **10** is atypical, appearing as a singlet (δ 26.2) for the Ru end of the diphosphines and a doublet (δ 15.3, $^1J_{Rh-P} = 142$ Hz) for the Rh end. A similar, unusually simple spectrum has been observed previously;[24] in the present case the simplified spectrum appears to result from small intraligand P−P coupling, presumably a consequence of opening up of the dppm P−C−P angles upon cleavage of the Rh−Ru bond. We have previously noted a significant decrease in intraligand P−P coupling on cleavage of the metal−metal bond in related compounds.[25]

Carbonyl removal from **3** using Me_3NO results in a hydrogen shift within the C_3 moiety and subsequent rearrangement to yield $[RhRu(CO)_2(\mu\text{-}\eta^1{:}\eta^3\text{-}CHC(CO_2CH_3){=}CH(CO_2CH_3))(dppm)_2][CF_3SO_3]$ (**11**) as diagrammed in Scheme 1. This rearrangement is accompanied by a dramatic change in the $^{31}P\{^1H\}$ NMR spectrum from an AA′BB′X spin system in which there are two pairs of chemically inequivalent ^{31}P nuclei to an ABCDX spin system in which all four ^{31}P nuclei are chemically inequivalent. The appearance of only two carbonyls (one on each metal) in the $^{13}C\{^1H\}$ NMR spectrum confirms the loss of one carbonyl. In the ^1H NMR spectrum four resonances are observed for the four dppm-methylene protons and two signals appear for the inequivalent methyl groups of the DMAD ligand. Only one of the hydrogens that originated from the methylene group of **3** was unambiguously identified in the ^1H NMR spectrum (at δ 5.90). However, the ^2H NMR spectrum of a deuterium isotopomer of **11**, $[RhRu(CO)_2(\mu\text{-}\eta^1{:}\eta^3\text{-}C(D)\text{-}C(CO_2Me){=}CD(CO_2Me))(dppm)_2][CF_3SO_3]$, prepared from the μ-CD_2 isotopomer of **3**, revealed the missing resonance of the vinylic deuterium at δ 3.90, typical for such a species.[26] The presence of this proton was confirmed by HMQC NMR experiments on compound **11**, in which the proton at δ 3.90 correlated with a carbon resonance at δ 55.0, also typical of such an arrangement.[27] If a sample of **11** is prepared from $^{13}CH_2$-enriched **1**, the single hydrogen at δ 5.90 shows 175 Hz coupling to the ^{13}C nucleus, confirming that these nuclei are mutually bonded. That this ^{13}C nucleus has only one proton attached was confirmed by both the presence of a positive signal in the $^{13}C\{^1H\}$ APT NMR spectrum and the appearance of a doublet of doublet of multiplets in the ^{13}C NMR spectrum with coupling of 175 Hz to only a single hydrogen nucleus. In the $^{13}C\{^1H\}$ NMR spectrum this carbon, at δ 110.2, appears as a doublet of multiplets. The large splitting of 73 Hz was confirmed to be due to coupling to phosphorus, based on ^{31}P decoupling experiments, and the magnitude of this coupling suggests a trans arrangement of the CH moiety and one end of the diphosphine unit. Selective ^{31}P decoupling experiments show that this large coupling is due to a Ru-bound phosphine. In the $^{13}C\{^1H,^{31}P\}$ NMR spectrum the resonance due to the CH group displays 23 Hz coupling to Rh, consistent with this unit occupying a bridging position. On the basis of these NMR data the structure shown in Scheme 1 is proposed, which is very similar to that confirmed in an X-ray study for $[Ir_2H(CO)_2(\mu\text{-}\eta^1{:}\eta^3\text{-}HCC(Et)C(H)Et)(dppm)_2][CF_3SO_3]$, previously studied in our group.[26] Unfortunately, we were unable to obtain crystals of **11** suitable for an X-ray study, to confirm the proposed geometry.

The reaction of **2** with propargyl alcohol ($HC{\equiv}CCH_2OH$) occurs very differently than with the previously noted alkynes, yielding a product that has incorporated two alkyne molecules. Even if less than 2 equiv of the alkyne is utilized, only the “double-insertion” product $[RhRu(CO)_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CH{=}C(CH_2OH)CH{=}(CH_2OH)\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**12**) is obtained, together with unreacted starting material. The structure of this compound has been established by X-ray crystallography, and a representation of the complex cation of **12** is shown in Figure 3. This structure determination clearly confirms that two alkynes have coupled in a head-to-tail manner with the methylene group, to form a rhodacyclohexadiene fragment. Both olefinic bonds of this rhodacyclohexadiene unit are also π-bonded to Ru,

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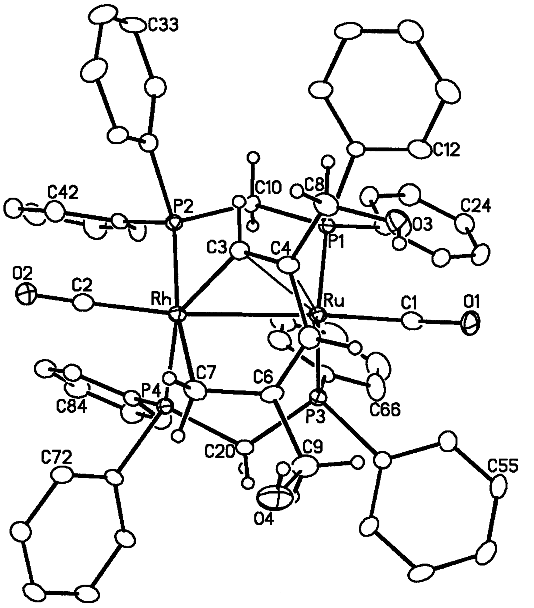


Figure 3. Perspective view of the complex cation of compound **12**. Thermal ellipsoids and numbering are as described in Figure 2, except that the hydroxyl protons are also shown arbitrarily small. Relevant bond lengths (Å) and angles (deg): Rh−Ru = 2.7722(8), Rh−C(3) = 2.043(7), Rh−C(7) = 2.116(8), Ru−C(3) = 2.202(7), Ru−C(4) = 2.270(7), Ru−C(5) = 2.227(8), Ru−C(6) = 2.395(8), C(3)−C(4) = 1.39(1), C(4)−C(5) = 1.43(1), C(5)−C(6) = 1.39(1), C(6)−C(7) = 1.48(1); P(2)−Rh−P(4) = 105.61(7), P(1)−Ru−P(3) = 98.27(8), C(3)−Rh−C(7) = 86.1(3), Rh−C(3)−C(4) = 129.9(6), C(3)−C(4)−C(5) = 119.3(7), C(4)−C(5)−C(6) = 123.1(7), C(5)−C(6)−C(7) = 121.1(7), C(6)−C(7)−Rh = 108.6(5).

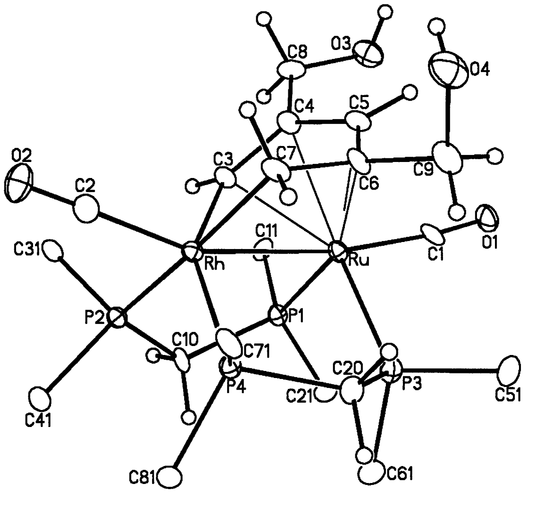


Figure 4. Alternate view of the cation of **12** in which the phenyl carbons, except for the ipso carbons, are omitted.

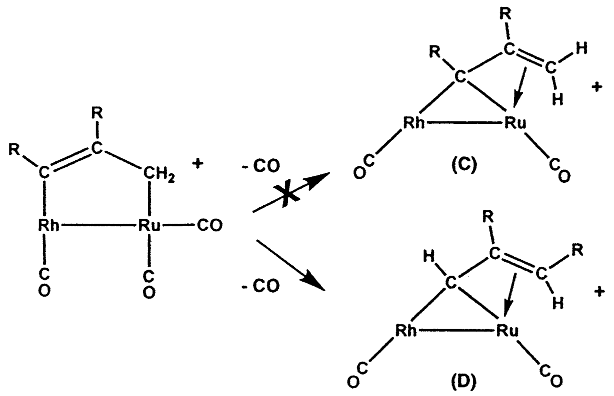
with Ru−C distances varying from 2.202(7) to 2.395(8) Å. As a consequence of the binding of this diolefin to Ru, the C(3)−C(4) and C(5)−C(6) bonds (1.39(1) and 1.39(1) Å) are somewhat elongated compared to normal double bonds.[16] Although the Rh−C(3)−C(4)−C(5)−C(6) fragment is very close to planar, the methylene carbon (C(7)) lies 0.85(1) Å out of this plane. This is shown clearly in the alternate view of **12** shown in Figure 4. Both diphosphine ligands are bent back, away from the bridging hydrocarbyl group, with P(2)−Rh−P(4) and P(1)−Ru−P(3) angles of 105.61(7)° and 98.27(8)°, respectively. The geometry at both metals can be described as octahedral. At Rh, the hydrocarbyl group resulting from coupling of the methylene group and two alkynes occupies two cis positions, as do the two ends of the diphosphines; the carbonyl on this metal is opposite the metal−metal bond. Ruthenium has a rather similar geometry except that two of the mutually cis coordination sites are occupied by the two π interactions involving the metallacyclohexadienyl fragment. Although both Rh−C bonds of the metallacycle are normal, that involving the vinylic fragment (Rh−C(3) = 2.043(7) Å) is significantly shorter than the Rh−alkyl bond (Rh−C(7) = 2.116(8) Å) at the other end. This difference presumably reflects (in part) the differences in hybridization of both carbon atoms;[17] however, additional shortening of the Rh−vinyl bond may be due to π back-bonding from the metal.

NMR spectroscopic studies suggest that the structure described above is maintained in solution. For example, the $^{31}P\{^1H\}$ NMR spectrum shows four separate phosphorus resonances and the ^1H NMR spectrum shows a separate resonance for each of the four dppm methylene hydrogens. In addition, the protons on the methylene group of the hydrocarbyl fragment are chemically distinct (δ 2.03 and 0.77) and display coupling to the Rh-bound ^{31}P nuclei. The resonance for the vinylic proton of C(5) of the diolefin fragment is observed at δ 6.03 as a singlet, showing no coupling to Rh or to its bound phosphine ligands. That of the proton on C(3) is not observed, but is shown by a ^1H COSY NMR experiment to be at δ 7.60 on the basis of its very weak coupling to the proton on C(5). Similarly, both alcoholic protons are coincident at δ 2.80, and ^1H COSY experiments show coupling of these protons to the pairs of adjacent methylene protons at δ 3.71 and 3.60 and at δ 3.24 and 2.55. The $^{13}C\{^1H\}$ NMR and IR spectra show that both carbonyls are terminally bound, and the former spectrum establishes that one is bound to each metal on the basis of the 67 Hz coupling to Rh.

Discussion

Our earlier observation of facile coupling of diazomethane-derived methylene groups at a Rh/Os core[8] to yield either allyl or butanediyl fragments suggested to us the intermediacy of a C_3H_6-bridged propanediyl species. Elimination of a β-hydrogen from the central carbon of this C_3 intermediate would yield the allyl group, whereas insertion of an additional methylene group would yield the butanediyl fragment. We have attempted to model this putative C_3-bridged species by insertion of alkynes into one of the metal−CH_2 bonds of $[RhRu(CO)_4(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**1**). Although this reaction proceeds with varying degrees of success, depending on the alkyne, the anticipated products are obtained much more readily by first converting **1** into the tricarbonyl, $[RhRu(CO)_3(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**2**), followed by the reactions with alkynes. The resulting products, $[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}RC{=}C(R')CH_2)(dppm)_2][CF_3SO_3]$ (R = R′ = CO_2Me (**3**), CF_3 (**4**), CO_2Et (**5**); R = Me, R′ = $CH(OEt)_2$ (**6**), R′ = CH_2OH (**7**)), have the so-formed C_3 fragment bridging the metals with the vinylic end of this fragment bound to Rh and the alkyl end bound to Ru. This arrangement is analogous to that proposed for the putative C_3H_6 fragment in the Rh/Os

Scheme 4



system.[8] Although insertion of the nonactivated alkynes, acetylene, propyne, and 2-butyne, into the Rh−CH_2 bond of **1** or **2** would have given rise to better models for the above C_3H_6-bridged intermediate,[8] these simple insertion products did not result. Instead, mixtures of unidentified products resulted.

The products of alkyne insertion in this report are in contrast to the products previously obtained from alkyne insertion in "$Fe_2(\mu\text{-}CH_2)$",[27a,28] "$Ru_2(\mu\text{-}CH_2)$",[29] "$FeRu(\mu\text{-}CH_2)$",[27b] and "$Rh_2(\mu\text{-}CH_2)_2$"[30] units, in which the resulting C_3 fragments could be viewed as vinyl carbenes. Unlike our bridging "RC═C(R′)CH_2" unit, which functions as a neutral two-electron donor, the vinyl carbene functions as a four-electron donor. We therefore anticipated that removal of a carbonyl from our dimetallacyclopentene unit could lead to a transformation of the bridging hydrocarbyl group to a vinyl carbene (**C**) with the two-electron deficiency resulting from CO loss being alleviated by the ligand transformation shown in Scheme 4 (dppm groups above and below the plane of the page are omitted for the sake of clarity). Surprisingly, carbonyl loss from **3** does not generate the anticipated product, but instead yields compound **11**, corresponding to the isomer **D**, in which a 1,3-hydrogen shift and an accompanying rearrangement has occurred, moving the fragment originating from the alkyne molecule from the Rh end to the Ru end of the complex. The reason for this isomerization is not clear, although having a hydrogen on the bridging carbene carbon, as observed in **11**, rather than a larger CO_2Me group, as in the anticipated product, is sterically favored. Analogous hydrogen migrations have previously been observed in related chemistry in which the vinyl carbene products, $[Fe_2(CO)_7(\mu\text{-}\eta^1{:}\eta^3\text{-}C(H)C(H)C(H)Ph)]$[28] and $[Ir_2H(CO)_2(\mu\text{-}\eta^1{:}\eta^3\text{-}C(H)C(R)C(H)R)(dppm)_2][CF_3SO_3]$ ($R = C_2H_5$),[26] were obtained. In these examples, as for compound **11** in this report, the products have a less substituted carbene carbon than would have resulted without hydrogen migration. Although the origin of the above diiridium species appears to differ, having resulted from alkyne attack at a methyl complex, we now believe that it also proceeded via a methylene-bridged alkyne adduct and that subsequent alkyne insertion and hydrogen migration occurred much as proposed for the above Fe_2 system and for the RhRu system reported herein.

In the case of the unsymmetrical alkynes, MeC≡$CCH(OEt)_2$ and MeC≡CCH_2OH, insertion occurs to yield the products having the bulkier $CH(OEt)_2$ and CH_2OH groups adjacent to the methylene group. This is in contrast to the regiochemistry demonstrated for the insertion of unsymmetrical alkynes into the methylene bridges of the complexes $[Ru_2(NCMe)(CO)_2(Cp)_2(\mu\text{-}CH_2)]$,[29e] $[Ru_2(NCMe)(CO)Cp_2(\mu\text{-}CH_2)_2]$,[29d] and $[FeRu(CO)_3Cp_2(\mu\text{-}CH_2)]$,[27b] in which the less sterically crowded alkyne carbon usually ended up bonded to the methylene group. In the case of 3-phenyl-2-propyn-1-ol (PhC≡CCH_2OH), insertion gave both isomers.[29e] Clearly the steric demands of the dppm-bridged system differs substantially from those of the above Cp complexes.

In all alkyne-insertion reactions reported herein, insertion has occurred into the Rh−CH_2 bond rather than the Ru−CH_2 bond. This presumably reflects the coordinative unsaturation at Rh, allowing alkyne coordination at this metal, followed by insertion into the adjacent Rh−CH_2 bond.

We attempted to obtain the isomeric C_3-bridged species $[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}CH_2C(R){=}C(R))(dppm)_2][CF_3SO_3]$, in which the methylene group was adjacent to Rh instead of Ru, by reaction of the alkyne-bridged product $[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}C(CO_2Me){=}C(CO_2Me))(dppm)_2][CF_3SO_3]$ (**8b**) with diazomethane. We had assumed that diazomethane coordination and activation would occur at the unsaturated Rh center with subsequent CH_2 insertion into the Rh−alkyne bond. Formation of the C_3-bridged product by this route would more closely model the formation of the putative C_3H_6-bridged intermediate from the ethylene-bridged precursor in the Rh/Os chemistry.[8] Furthermore, this would also model a key step in the Dry mechanism for carbon−carbon chain growth in FT chemistry.[6a] However, the alkyne-bridged product **8b** proved to be unreactive toward diazomethane. Either diazomethane coordination at Rh is blocked by the CO_2Me group adjacent to this metal, or insertion into the stronger bond between Rh and the sp^2 carbon is not favored. This bond is presumably further strengthened by the adjacent electron-withdrawing CO_2Me substituent.[31] Methylene insertion into a metal−carbon bond of an alkyne-bridged complex has been observed;[29a] however, in this case the alkyne bridged the metals in an arrangement perpendicular to, rather than parallel to, the metal−metal bond. We have previously noted reactivity differences between isomeric complexes in which the alkyne was bound in either a perpendicular or parallel arrangement,[32,33] so we have attempted to generate a perpendicular alkyne complex from **8b**. In the parallel mode the alkyne functions as a neutral two-electron donor, whereas in the perpendicu-

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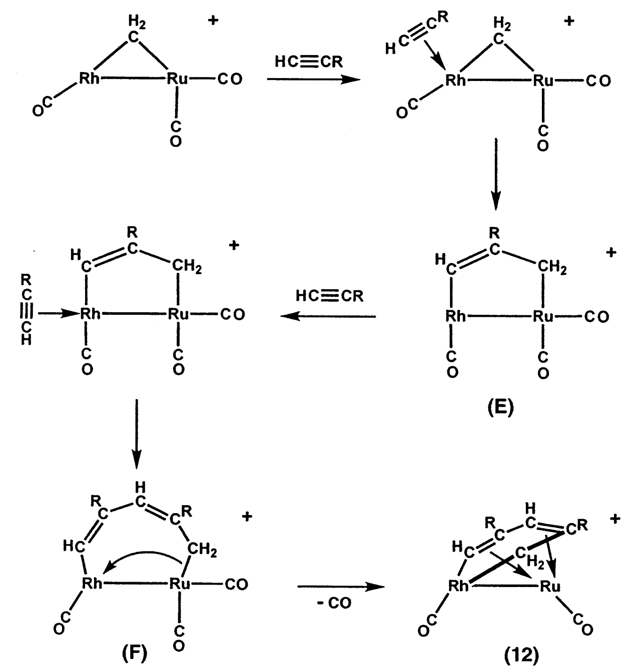
Scheme 5



lar mode it is a four-electron donor. Removal of a carbonyl should induce a rotation of the alkyne group to perpendicular in order to alleviate the resulting electron deficiency. Instead however, carbonyl loss is accompanied by coordination of the triflate anion at Rh, thereby alleviating the resulting unsaturation and yielding a product (**9**), shown in Scheme 3, very much like the precursor, in which the alkyne group remains parallel to the metals. Nevertheless, this product does react with diazomethane, although not to give a product of methylene insertion into the Rh−alkyne bond. Instead, methylene insertion into the Rh−Ru bond has occurred, to give the methylene- and alkyne-bridged **10**. This product is analogous to a dirhodium compound, $[Rh_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}CF_3C{=}CCF_3)(dppm)_2]$, previously prepared by us by reaction of the alkyne-bridged precursor with diazomethane.[34]

With the terminal alkyne, propargyl alcohol, the single-insertion product analogous to compounds **3**−**7** was not observed. Instead, reaction with 2 equiv occurred to give the C_5-bridged $[RhRu(CO)_2(\mu\text{-}\eta^2{:}\eta^4\text{-}CH{=}C(CH_2OH)CH{=}C(CH_2OH)CH_2)(dppm)_2][CF_3SO_3]$ (**12**). Stepwise insertion of both alkynes into the Rh−CH_2 bond in a head-to-tail manner has occurred with the more bulky substituent (CH_2OH) ending up adjacent to the methylene group. We propose that this double insertion occurs as diagrammed in Scheme 5 (dppm groups omitted for clarity). Coordination of the first alkyne at Rh leads to insertion into the Rh−CH_2 bond to give the C_3-bridged product **E**. This proposed intermediate has a geometry like those of **6** and **7**, with the bulkier alkyne substituent adjacent to the methylene group. The small hydrogen substituent on the carbon bound to Rh presumably allows for coordination of a second alkyne at this metal, leading to the second insertion reaction which gives a C_5-bridged species. We assume that strain within this initially formed seven-membered dimetallacycle (**F**) leads to migration of the CH_2 end to Rh, giving a rhodacyclohexadiene moiety, which forms two π interactions with Ru, accompanied by carbonyl loss. Double insertions involving the internal alkynes described earlier do not occur owing to the inability of the second alkyne to coordinate to Rh in the monoinsertion products **3**−**7** because of steric repulsions involving the substituent on the carbon bound to Rh. Double insertions of alkyne into a single bridging methylene unit to give C_5-bridged moieties have been observed,[28,29b] and in a couple of these cases coupling of internal alkynes was observed. Presumably, the steric demands of these "$Fe_2(CO)_x$" and "Ru_2Cp_2" core frameworks are lower than for the "$RhRu(dppm)_2$" framework reported herein, for which a second insertion was observed only for the terminal alkyne, propargyl alcohol. A double insertion was also reported for the bismethylene-bridged complex $[Cp^*Rh(NCMe)(\mu\text{-}CH_2)]_2$,[30] in which stepwise alkyne insertion involving *both* methylene units, accompanied by coupling of the two resulting C_3 fragments, was proposed.

Compound **12** seems ideally suited to either reductive elimination via C−C bond formation yielding a cyclopentadiene fragment or hydrogenolysis of the Rh−C bonds to give a substituted pentadiene. Attempts to induce reductive elimination by mild heating (refluxing THF) or by oxidation by ferricinium hexafluorophosphate or ammonium hexachloroiridate(IV)[35] failed; no reaction was observed in either case. Reaction of **12** with H_2 does yield the expected binuclear hydride product, $[RhRu(CO)_3(\mu\text{-}H)_2(dppm)_2][CF_3SO_3]$;[9] however the other expected product, $H_2C{=}C(CH_2OH)C(H){=}C(CH_2OH)\text{-}CH_3$, or the fully hydrogenated $H_3CCH(CH_2OH)CH_2CH\text{-}(CH_2OH)CH_3$ was not detected; the complex mixture of organic products observed in the ^1H NMR spectrum of the reaction mixture was not analyzed.

Conclusions

The insertion of a variety of alkynes into the Rh−CH_2 group of the methylene-bridged species $[RhRu(CO)_3(\mu\text{-}CH_2)(dppm)_2][CF_3SO_3]$ (**2**) occurs readily. In all cases studied the first product is either observed or assumed to be the single-insertion product in which the resulting "RC=C(R′)CH_2" moiety bridges the metals with the terminal vinylic carbon bound to Rh and the methylene group bound to Ru. This is consistent with all previous studies from our group on "Rh(μ-CH_2)M" complexes (M = Ru, Os), in which coordinative unsaturation at Rh allows substrate coordination at this metal and subsequent substrate insertion into the Rh−CH_2 bond.[8,9,18,36] Surprisingly, the reverse process of methylene insertion into the Rh−C bond of the alkyne-bridged product $[RhRu(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}(CO_2Me)C{=}C(CO_2Me))(dppm)_2][X]$ (**8**) did not occur. Whether the alkyne substituent blocked diazomethane attack at Rh or whether the strength of the Rh−C bond in **8** prevented insertion is not known.

In the cases in which the alkyne substituents (R,R′) were not the same, regioselective insertion occurred, giving the product in which the larger substituent was adjacent to the methylene group. For propargyl alcohol

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the small hydrogen on one end of the alkyne appears to allow subsequent coordination of a second propargyl alcohol molecule at Rh followed by a second insertion to give a C_5-bridged product.

The C_3-bridged products containing the μ-η^1:η^1-RC═C(R′)CH_2 groups are effective models for the proposed C_3H_6-bridged intermediates obtained by coupling of three methylene groups in a related Rh/Os system. Our success at isolating the alkyne-insertion products, where the C_3H_6-bridged species could not be observed, probably relates to the absence of hydrogens on the β-carbon atom in the former, eliminating the possibility of β-hydrogen elimination as a decomposition pathway.

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Supporting Information Available: Tables of X-ray experimental details, atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for compounds **4**, **8a**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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