

Carbon–Carbon Bond Formation by Cumulene Insertion into “Rh(μ -CH₂)M” Moieties (M = Ru, Os): Roles of the Cumulenes and the Metals in Product Formation

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The reactions of allene, methylallene, and 1,1-dimethylallene with [RhM(CO)₄(μ -CH₂)-(dppm)₂][X] (M = Os, X = BF₄ (**1**); M = Ru, X = CF₃SO₃ (**3**); dppm = μ -Ph₂PCH₂PPh₂) in the presence of 1 equiv of trimethylamine oxide yield a variety of products. Under these conditions compounds **1** and **3** react with allene to yield the trimethylenemethane-bridged products [RhM(CO)₂(μ - η^3 : η^1 -C(CH₂)₃)(dppm)₂][X] (M = Os (**5**), Ru (**6**)), in which the trimethylenemethane fragment is η^1 -bound to the group 8 metal by one methylene group and η^3 -bound to Rh by the rest of the fragment. These compounds react with CO and PMe₃ to yield [RhM(CO)₂L(μ - η^3 : η^1 -C(CH₂)₃)(dppm)₂][X] (L = CO, PMe₃), in which L is coordinated to Rh and the η^3 : η^1 -binding mode of trimethylenemethane is retained. Although attack of L occurs at Rh for the Rh/Ru species, carbonyl attack in the Rh/Os compound initially occurs at Os with subsequent scrambling throughout the three carbonyl sites; attack of PMe₃ on the Rh/Os compound occurs at Rh. Methylallene reacts with **1** and Me₃NO to give a species analogous to **5** and **6**, having the methyl substituent on one of the terminal carbons of the allylic functionality. This methyl group is involved in an agostic interaction with Rh, which can be displaced by CO. The tricarbonyl complex [RhOs(CO)₃(μ -CH₂)(dppm)₂][CF₃SO₃] (**2**) reacts with 1,1-dimethylallene at –10°C to give [RhOs(CO)₃(μ - η^1 : η^1 -(CH₃)₂CCCH₂CH₂)(dppm)₂][CF₃SO₃], in which the dimethylvinyl group is adjacent to Rh, exo to the RhCCH₂CH₂Os dimetallacycle. At ambient temperature this species decomposes to give 1,1-dimethyl-1,3-butadiene. Compound **3** reacts with 1,1-dimethylallene in the presence of Me₃NO to yield [RhRu(CO)₂((CH₃)₂CCCH₂CH₂CO)(dppm)₂][CF₃SO₃] (**14**), in which [2+1+1] coupling of the allene, the bridging methylene group, and a coordinated carbonyl has occurred. The dative bond from the bridging acyl moiety of **14** to Ru is displaced in reactions with H₂ and CO to give [RhRu(CO)₂(C(O)CH₂CH₂C(=C(CH₃)₂)(μ -H)₂(dppm)₂][CF₃SO₃] and [RhRu(CO)₃(C(O)CH₂-CH₂C(=C(CH₃)₂)(dppm)₂][CF₃SO₃], respectively. A rationalization of this chemistry is presented.

Introduction

The coupling of unsaturated C₂ fragments with surface-bound methylene groups has been suggested as an important part of the chain-propagating steps of the Fischer–Tropsch reaction.^{1–3} In the proposal by Maitlis and co-workers¹ this C₂ fragment is suggested to be a

surface-bound alkenyl group, in the proposal by Basset^{2a} and later by Dry^{2b} it is proposed to be a surface-bound olefin, whereas others have suggested the involvement of surface-bound vinylidenes.³ A recent study from our laboratory, in which diazomethane-generated methylene groups couple to yield either allyl or butanediyl fragments at a Rh/Os core,⁴ appears consistent with the proposal of Basset and Dry, at least in the early stages of methylene coupling. In our study⁴ the stepwise transformations of a bridging methylene group to a bridging ethylene to a bridging propanediyl group were proposed before divergence to the allyl or butanediyl products occurred, either by β -hydrogen elimination from the C₃H₆-bridged intermediate or insertion of a fourth methylene group, respectively. The propanediyl-bridged intermediate is pivotal to this scheme of methylene coupling, observed in the Rh/Os system,⁴ as well as to the Basset/Dry scheme, so we set out to learn more

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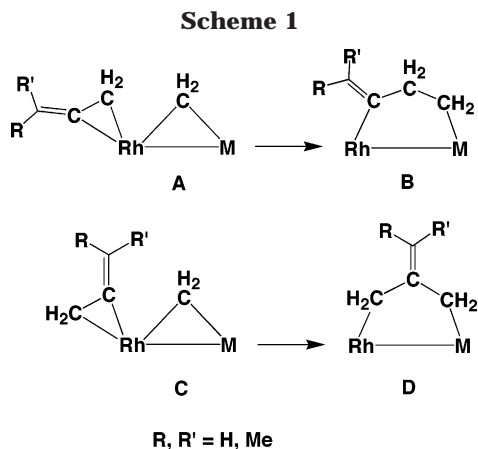
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about such species. Propanediyl-bridged complexes have been observed⁵ and are also proposed as unstable intermediates in the coupling of ethylene with methylene-bridged units to give propene.⁶ The probable mechanism for propene formation in the latter example is via a sequence of β -hydrogen-elimination and reductive-elimination steps, the facility of which also explains the paucity of propanediyl-bridged species.

Attempts by us to generate propanediyl-bridged products through ethylene insertion into a series of "Rh(μ -CH₂)M"-containing species (M = Ru, Os) were unsuccessful, leading either to no reaction or to propene formation.^{4,7} We therefore sought to model these C₃-bridged species by insertions of other unsaturated substrates such as alkynes or cumulenes. Although alkyne insertions into the Rh(μ -CH₂)M-based complexes worked well to give model C₃-bridged products,^{8,9} these products differed from the propanediyl-bridged targets in having unsaturation within the C₃ framework. We reasoned that cumulenes could yield insertion products as diagrammed in Scheme 1, in which the unsaturation was *exo* to the C₃ fragment, possibly leading to better models of the propanediyl-bridged targets.

For cumulenes having substitution at only one end, coordination to Rh (the site of unsaturation) should be favored at the unsubstituted end, leading to two product types, in which insertion into the Rh-CH₂ bond has occurred to give a vinylic group adjacent to Rh (structure **B**) or having an allylic group in a symmetric position between the two methylene groups (structure **D**). Allene, having no substituents, can give rise to two analogous products. In product **D** the absence of β -hydrogens eliminates the decomposition route proposed for propanediyl-bridged species.⁶

In this paper we report the reactions of allene, methylallene, and 1,1-dimethylallene with methylene-

bridged complexes of Rh/Os and Rh/Ru in attempts to generate models for the above-mentioned propanediyl-bridged intermediates. By investigating this series of cumulenes and these two metal combinations we hoped to gain information about the functions of the cumylene substituents and the different metals in the carbon-carbon bond formation leading to C₃-bridged complexes.

Experimental Section

General Comments. All solvents were dried using the appropriate desiccants, distilled before use, and stored under argon. Reactions were carried out under an argon atmosphere using standard Schlenk techniques. Allene gas was purchased from Praxair, while methylallene and dimethylallene were purchased from Fluka Chemicals. The trimethylphosphine was purchased from Aldrich as a 1.0 M solution in toluene. The ¹³CO (99% enrichment) was purchased from Isotech, Inc. The complexes [RhOs(CO)_x(μ -CH₂)(dppm)₂][BF₄] (*x* = 4 (**1**), 3 (**2**))⁴ and [RhRu(CO)_x(μ -CH₂)(dppm)₂][CF₃SO₃] (*x* = 4 (**3**), 3 (**4**))¹⁰ (dppm = μ -Ph₂PCH₂PPh₂) were prepared as previously reported.

The ¹H, ¹³C{¹H}, ¹H-¹H COSY, and ³¹P{¹H} NMR spectra were recorded on a Varian iNova-400 spectrometer operating at 399.8 MHz for ¹H, 161.8 MHz for ³¹P, and 100.6 MHz for ¹³C{¹H}. Infrared spectra were obtained on a Nicolet Magna 750 FTIR spectrometer with a NIC-Plan IR microscope either in the solid state or as a solution. The elemental analyses were performed by the microanalytical service within the department. Electrospray ionization mass spectra were run on a Micromass ZabSpec spectrometer by the staff in the mass spectrometry service laboratory. In all cases, the distribution of isotope peaks for the appropriate parent ion matched that calculated for the formula given. Spectroscopic data for all compounds are given in Table 1.

Preparation of Compounds. (a) [RhOs(CO)₂(μ - η^3 : η^1 -C(CH₂)₃)(dppm)₂][BF₄] (**5**). [RhOs(CO)₄(μ -CH₂)(dppm)₂][BF₄] (**1**) (50 mg, 0.039 mmol) was dissolved in 15 mL of CH₂Cl₂. Allene was passed through this solution at a rate of 2 mL/min for 2 min. At this stage, no reaction was observed. Addition of 5 mL of a CH₂Cl₂ solution of Me₃NO (3.5 mg, 1.2 equiv) via cannula to the solution of **1** and allene resulted in a color change from yellow to dark red. The solution was stirred for 30 min and filtered, and a red-orange solid was isolated by the slow addition of 10 mL of ether followed by 20 mL of pentane. The isolated solid was washed with ether and dried under a stream of argon (yield 87%). Anal. Calcd for C₅₆H₅₀F₄O₂P₄RhOsB: C, 51.78; H, 3.89. Found: C, 52.20; H, 3.75 MS: *m/z* 1173 (M⁺ - BF₄).

(b) [RhRu(CO)₂(μ - η^3 : η^1 -C(CH₂)₃)(dppm)₂][CF₃SO₃] (**6**). A Schlenk flask was charged with the compound [RhRu(CO)₄(μ -CH₂)(dppm)₂][CF₃SO₃] (**3**) (85 mg, 0.068 mmol) and Me₃-NO (8.70 mg, 0.116 mmol, 1.7 equiv). The flask was cooled to -8 °C using a saltwater/ice bath, evacuated, then back-filled to ca. 1 atm with allene. Then 5 mL of acetone was added to the flask, causing the solution color to change immediately from red to yellow-orange. The ice bath was removed, and the solution was stirred for 1 h, after which it was filtered over Celite. The filtrate was concentrated to ca. 2 mL, and subsequent dropwise addition of Et₂O caused the formation of an orange solid. The supernatant was removed, and the solid was washed with 2 × 15 mL of Et₂O and dried in vacuo (yield: 54 mg, 65%). Anal. Calcd for C₅₇H₅₀F₃O₅P₄RhRuS: C, 55.52; H, 4.09. Found: C, 55.69; H, 4.09.

(c) [RhOs(CO)₃(μ - η^3 : η^1 -C(CH₂)₃)(dppm)₂][BF₄] (**7**). Compound **5** (30 mg, 0.026 mmol) was dissolved in 10 mL of CH₂-Cl₂, and carbon monoxide was passed over the solution for 5

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Table 1. Spectroscopic Data for Compounds

compound	IR (cm ⁻¹) ^{a-c}	NMR ^{d,e}		
		³¹ P{ ¹ H} (ppm) ^f	¹ H (ppm) ^{g,h}	¹³ C{ ¹ H} (ppm) ^{h,i}
[RhOs(CO) ₂ (μ-η ³ :η ¹ -C(CH ₂) ₃ -(dppm) ₂][BF ₄] (5)	2003 (s), 1929 (s)	40.6 (dm, ¹ J _{RhP} = 152 Hz), -1.4 (m)	4.39 (m, 2H, dppm), 4.10 (s, 2H), 4.01 (m, 2H, dppm), 1.95 (d, ³ J _{PH} = 8 Hz, 2H), 1.79 (t, ³ J _{PH} = 12 Hz, 2H)	181.6 (t, ² J _{PC} = 8 Hz, 1C), 172.4 (t, ² J _{PC} = 7 Hz, 1C), 73.5 (t, ² J _{PC} = 7 Hz), 7.27 (s, br)
[RhRu(CO) ₂ (μ-η ³ :η ¹ -C(CH ₂) ₃ -(dppm) ₂][CF ₃ SO ₃] (6)	2021 (m), 1951 (s)	30.9 (om)	4.30 (m, 2H, dppm), 3.90 (m, 2H, dppm), 4.02 (s, 2H), 1.98 (d, ³ J _{PH} = 8 Hz, 2H), 1.49 (t, ³ J _{PH} = 8 Hz, 2H)	194.5 (m, 1C), 191.7 (m, 1C), 13.8 (s, 1C)
[RhOs(CO) ₃ (μ-η ³ :η ¹ -C(CH ₂) ₃ -(dppm) ₂][BF ₄] (7)		13.8 (dm, ¹ J _{RhP} = 137 Hz), -8.1 (m)	4.74 (m, 2H, dppm), 4.31 (m, 2H, dppm), 2.63 (d, ³ J _{PH} = 9 Hz, 2H), 2.03 (s, 2H), 1.69 (t, ³ J _{PH} = 9 Hz, 2H)	194.7(dt, ¹ J _{RhC} = 60 Hz, 1C), 185.9 (m, 1C), 177.3 (m, 1C)
[RhRu(CO) ₃ (μ-η ³ :η ¹ -C(CH ₂) ₃ -(dppm) ₂][CF ₃ SO ₃] (8)	2010 (m), 1980 (m), 1935 (m)	30.4 (m), 13.2 (dm)	4.16 (m, 2H, dppm), 4.06 (m, 2H, dppm), 2.64 (d, ³ J _{PH} = 9 Hz, 2H), 1.79 (s, 2H), 1.52 (t, ³ J _{PH} = 9 Hz, 2H)	205.2 (m, 1C), 198.7 (m, 1C), 184.2 (dm, ¹ J _{RhC} = 57 Hz, 1C)
[RhOs(CO) ₂ (PMe ₃)(μ-η ³ :η ¹ -C(CH ₂) ₃)(dppm) ₂][BF ₄] (9)		14.3 (dm, ¹ J _{RhP} = 140 Hz), -13.7 (m), -49.8 (d, ¹ J _{RhP} = 104 Hz)	4.87 (m, 2H, dppm), 4.55 (m, 2H, dppm), 3.21 (s, 2H), 2.07 (t, ³ J _{PH} = 11 Hz, 2H), 1.87 (d, ³ J _{PH} = 8 Hz, 2H), 1.76 (d, ² J _{PH} = 13 Hz, 9H)	
[RhRu(CO) ₂ (PMe ₃)(μ-η ³ :η ¹ -C(CH ₂) ₃)(dppm) ₂][CF ₃ SO ₃] (10)		26.3 (m), 13.3 (dm), -34.6 (dm) ^j	4.32 (m, 2H, dppm), 4.12 (m, 2H, dppm), 1.86 (s, br, 2H), 1.73 (m, br, 2H), 1.50 (s, br, 2H), 0.39 (d, ² J _{PH} = 7 Hz, 9H) ^j	
[RhOs(CO) ₂ (μ-η ³ :η ¹ -CH(CH ₃)-C(CH ₂) ₂)(dppm) ₂][BF ₄] (11)	2001 (s), 1923 (s)	42.8 (m), 36.9 (m), -0.1 (m), -7.2 (m)	4.41 (om, 3H, dppm; 1H, CHCH ₃), 3.9 (m, 1H, dppm), 3.61 (s, 1H, C(CHH)CHCH ₃), 2.12 (d, 1H, ³ J _{PH} = 8 Hz CHHCHCH ₃), 2.01 (m, 1H, ¹ J _{CH} = 130 Hz, Os-CH ₂), 1.90 (m, 1H, ¹ J _{CH} = 130 Hz, Os-CH ₂), -0.22 (dd, 3H, ⁴ J _{PH} = 6 Hz, CHCH ₃ , ³ J _{HH} = 6 Hz)	181.2 (m, 1C), 172.7 (m, 1C), 81.9 (dd, 1C, ¹ J _{RhC} = 29 Hz, ² J _{PC} = 6 Hz, CHCH ₃), 64.6 (dd, 1C, ¹ J _{RhC} = 32 Hz, ² J _{PC} = 7 Hz, C(CH ₂)CHCH ₃), 15.6 (s, 1C, CH ₃), 9.52 (s, 1C, Os-CH ₂)
[RhOs(CO) ₃ (μ-η ³ :η ¹ -CH(CH ₃)-C(CH ₂) ₂)(dppm) ₂][BF ₄] (12)		11.3 (om), -3.2 (m), -16.2 (m)	5.35 (m, 1H, dppm), 4.82 (m, 1H, dppm), 4.59 (m, 1H, dppm), 4.21 (m, 1H, CHCH ₃), 4.10 (m, 1H, dppm), 1.35 (m, 3H, CHCH ₃)	184.9 (m), 183.9 (m), 177.1(m), -4.1 (s)
[RhOs(CO) ₃ (μ-η ¹ :η ¹ -(CH ₃) ₂ C-CH ₂ CH ₂)(dppm) ₂][CF ₃ SO ₃] (13)		24.3 (dm, ¹ J _{RhP} = 121 Hz), -3.2 (m)	4.90 (m, dppm, 2H), 4.07 (m, dppm, 2H), 2.41 (s, br, CH ₂ , 2H), 1.63 (t, br, Os-CH ₂ , 2H), 0.78 (t, ² J _{PC} = 6 Hz, CH ₃ , 3H), 0.10 (s, br, CH ₃ , 3H)	191.4 (dt, ¹ J _{RhC} = 48 Hz, ² J _{PC} = 11 Hz), 182.5 (s, br, Os(CO)), 172.8 (t, ² J _{PC} = 8 Hz, Os(CO)), 2.69 (t, ² J _{PC} = 8 Hz), 250.7 (dt, ¹ J _{RhC} = 33 Hz, ² J _{PC} = 8 Hz, 1C), 220.2 (m, 1C), 202.4 (t, ² J _{PC} = 23 Hz, 1C)
[RhRu(CO) ₂ ((CH ₃) ₂ CCH ₂ -CH ₂ CO)(dppm) ₂][CF ₃ SO ₃] (14)	1975 (m), 1910 (s)	35.5 (m), 20.4 (dm)	3.58 (m, 2H, dppm), 3.41 (m, 2H, dppm), 2.73 (m, 2H), 1.31 (s, 3H), 0.96 (s, 3H), 0.37 (m, 2H)	220.2 (m, 1C), 202.4 (t, ² J _{PC} = 23 Hz, 1C)
[RhRu(CO) ₂ (μ-H) ₂ (η ¹ :η ¹ -C(O)CH ₂ CH ₂ C(=C(CH ₃) ₂)-(dppm) ₂][CF ₃ SO ₃] (15)	2053 (m), 2001 (s), 1683 (w)	31.9 (m), 22.3 (dm)	3.94 (m, 2H, dppm), 3.60 (m, 2H, dppm), 1.99 (s, 3H), 1.73 (m, 2H), 1.16 (s, 3H), 0.93 (m, 2H), -7.89 (m, 1H), -10.01 (m, 1H)	236.3 (dt, ¹ J _{RhC} = 28 Hz, ² J _{PC} = 7 Hz, 1C), 196.8 (m, 1C), 190.7 (t, ² J _{PC} = 11 Hz, 1C)
[RhRu(CO) ₃ (η ¹ :η ¹ -C(O)-CH ₂ CH ₂ C(=C(CH ₃) ₂)-(dppm) ₂][CF ₃ SO ₃] (16)	2025 (m), 1975 (m), 1951 (m), 1687 (w)	31.9 (m), 17.9 (dm)	4.40 (m, 2H, dppm), 3.99 (m, 2H, dppm), 1.98 (t, 2H), 1.69 (s, 3H), 1.17 (s, 3H), 1.08 (br, 2H)	231.9 (dt, ¹ J _{RhC} = 30 Hz, ² J _{PC} = 8 Hz, 1C), 207.6 (m, 1C), 206.4 (m, 1C), 195.6 (t, ² J _{PC} = 12 Hz, 1C)

^a IR abbreviations: s = strong, m = medium, w = weak, sh = shoulder. ^b CH₂Cl₂ solutions unless otherwise stated, in units of cm⁻¹. ^c Carbonyl stretches unless otherwise noted. ^d NMR abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, dm = doublet of multiplets, om = overlapping multiplets, br = broad, dt = doublet of triplets. ^e NMR data at 25 °C for Rh/Ru compounds and at -80 °C for Rh/Os compounds in CD₂Cl₂ unless otherwise stated. ^f ³¹P chemical shifts referenced to external 85% H₃PO₄. ^g Chemical shifts for the phenyl hydrogens are not given. ^h ¹H and ¹³C chemical shifts referenced to TMS. ⁱ ¹³C{¹H} NMR performed with ¹³C enrichment of both carbonyls and methylene groups. ^j NMR data at -60 °C.

min at a rate of 1 mL/min. The solution slowly turned from red-orange to yellow. The solution was stirred for 30 min and filtered, and then a yellow solid was precipitated by the slow addition of 10 mL of ether and 20 mL of pentane. The solid

was washed with ether and dried under a stream of argon (yield 78%). Satisfactory elemental analyses for this compound could not be obtained due to facile CO loss. Characterization was based on spectroscopic studies.

(d) [RhRu(CO)₃(μ-η³:η¹-C(CH₂)₃)(dppm)₂][CF₃SO₃] (8). Compound **6** (100 mg, 0.081 mmol) was dissolved in 4 mL of CH₂Cl₂, and carbon monoxide gas was passed over the solution for ca. 5 min. The solution slowly turned from yellow-orange to orange. After 0.5 h of stirring, the solution was concentrated to ca. 3 mL using a stream of Ar gas. Slow addition of 15 mL of Et₂O resulted in the precipitation of orange microcrystals. The supernatant was removed, and the crystals were dried in vacuo (yield: 80 mg, 78%). Anal. Calcd for C₅₈H₅₀F₃O₆P₄RhRuS: C, 55.24; H, 4.00. Found: C, 55.23; H, 3.87.

(e) [RhOs(CO)₂(PMe₃)(μ-η³:η¹-C(CH₂)₃)(dppm)₂][BF₄] (9). Compound **5** (30 mg, 0.026 mmol) was dissolved in 0.7 mL of CD₂Cl₂ and cooled to -78 °C. An excess of 1.0 M trimethylphosphine in toluene (40 μL, 0.040 mmol, 1.6 equiv) was added at this temperature. Although no color change was observed, NMR characterization at -80 °C revealed complete conversion to a new product. This product was stable up to -20 °C. However at higher temperatures, facile PMe₃ loss occurred, necessitating its characterization at low temperature using NMR spectroscopy.

(f) [RhRu(CO)₂(PMe₃)(μ-η³:η¹-C(CH₂)₃)(dppm)₂][CF₃SO₃] (10). Compound **6** (10 mg, 0.008 mmol) was dissolved in 0.7 mL of CD₂Cl₂ and cooled to -78 °C. To this was added 9 μL of a 1.0 M solution of PMe₃ in THF (0.009 mmol, 1.1 equiv), causing no noticeable color change. However, monitoring the solution at -80 °C by NMR spectroscopy showed essentially quantitative conversion into a new compound, **10**. This was the only product formed between -80 and -40 °C; however, at temperatures higher than -40 °C this product began to decompose into several unidentified products. As a result, characterization of **10** was achieved by ³¹P{¹H} and ¹H NMR spectroscopy at the lower temperatures.

(g) Attempted Reactions of 5 and 6 with CH₂N₂. In separate experiments compounds **5** and **6** (20 mg) were each dissolved in 0.7 mL of CD₂Cl₂ and cooled to -78 °C. An excess of diazomethane was passed through the solution at a rate of 10 mL/min for 2 min. The reaction was stirred for 20 min at low temperature. In both cases the NMR spectra of the solutions at -80 °C showed a mixture of unidentifiable products. The same results were obtained if compounds **5** and **6** were reacted with diazomethane at ambient temperature.

(h) [RhOs(CO)₂(μ-η³:η¹-CH(CH₃)C(CH₂)₂)(dppm)₂][BF₄] (11). Compound **1** (30 mg, 0.024 mmol) was dissolved in 10 mL of CH₂Cl₂, and methylallene was slowly passed through the solution at a rate of 0.5 mL/min. No reaction was observed. A 2 mL solution of Me₃NO (2.1 mg, 1.2 equiv) was added via cannula to the solution containing both compound **1** and methylallene. The resultant orange solution was stirred for 30 min and then filtered. An orange solid was precipitated by the slow addition of 15 mL of pentane, and the isolated solid was washed with 20 mL of ether and dried under a stream of argon (yield 86%). Anal. Calcd for C₅₇H₅₀F₄O₂P₄RhOsB: C, 52.17; H, 3.93. Found: C, 51.88, H, 3.90. MS: *m/z* 1187 (M⁺ - BF₄).

(i) [RhOs(CO)₃(μ-η³:η¹-CH(CH₃)C(CH₂)₂)(dppm)₂][BF₄] (12). Compound **11** (30 mg, 0.025 mmol) was dissolved in 10 mL of CH₂Cl₂, and carbon monoxide was passed through the solution at a rate of 2 mL/min for 2 min. This caused an immediate color change from orange to yellow. The solution was stirred for 20 min and precipitated by the slow addition of 20 mL of ether followed by 10 mL of pentane, filtered, and dried under a stream of argon. This compound was prone to facile CO loss, and thus it was characterized using NMR techniques.

(j) Attempted Reaction of 11 with PMe₃. An NMR tube charged with compound **11** (15 mg, 0.013 mmol) was dissolved in 0.7 mL of CD₂Cl₂ and cooled to -78 °C. A 25 μL portion of PMe₃ (0.025 mmol, 1.25 equiv) was added to the solution via syringe. No color change was observed, and the ³¹P {¹H} NMR

spectrum of this solution showed only compound **11** and unreacted PMe₃, between temperatures of -80 °C and ambient.

(k) Reaction of 1 with (CH₃)₂C=C=CH₂. To an NMR tube containing [RhOs(CO)₄(μ-CH₂)(dppm)₂][BF₄] (**1**) (10 mg, 0.008 mmol) dissolved in 0.5 mL of CD₂Cl₂, was added Me₂C=C=CH₂ (4 μL, 0.04 mmol). After approximately 12 h, a small amount of the compound [RhOs(CO)₄(dppm)₂][BF₄]¹¹ was observed by NMR spectroscopy. After 3 days all of **1** had disappeared, leaving [RhOs(CO)₄(dppm)₂][BF₄] as the only phosphorus-containing product observed. 1,1-Dimethyl-1,3-butadiene was also identified on the basis of its ¹H NMR spectrum.

(l) [RhOs(CO)₃(μ-η¹:η¹-((CH₃)₂CCCH₂CH₂CO)(dppm)₂][CF₃SO₃] (13). The tricarbonyl complex [RhOs(CO)₃(μ-CH₂)(dppm)₂][CF₃SO₃] (**2**) (20 mg, 0.015 mmol) was dissolved in 0.7 mL of CD₂Cl₂ and cooled to -10 °C. To the cooled solution, 1.8 μL (1.2 equiv) of dimethylallene was added and stirred for 5 min. The resultant dark red solution could be characterized only by NMR spectroscopy, as the compound rapidly decomposed at ambient temperature. Compound **13** could also be generated as the BF₄⁻ salt from the tetracarbonyl (**1**) in the presence of Me₃NO; however the route described above gave a sample having a cleaner ¹H NMR spectrum without the presence of N(CH₃)₃ and Me₃NO.

(m) [RhRu(CO)₂((CH₃)₂CCCH₂CH₂CO)(dppm)₂][CF₃SO₃]·0.5CH₂Cl₂ (14). A Schlenk flask was charged with 115 mg (0.092 mmol) of [RhRu(CO)₄(μ-CH₂)(dppm)₂][CF₃SO₃] (**3**), 9.5 μL of dimethylallene (0.096 mmol, 1.04 equiv), and 6 mL of acetone. The solution then was cooled to -10 °C, and 6 mL of a 0.025 M solution of Me₃NO in acetone (0.150 mmol, 1.7 equiv) was added dropwise, causing the immediate color change from yellow to dark red to orange. The solution was stirred for 1 h, after which it was warmed to ambient temperature and then filtered over Celite. The solvent was removed in vacuo, and the orange residue was dissolved in 2 mL of CH₂Cl₂. Orange microcrystals precipitated after dropwise addition of 17 mL of Et₂O. The supernatant was removed, and the crystals were dried in vacuo (yield: 70 mg, 57%). Anal. Calcd for C_{60.5}H₅₅-ClF₃O₆P₄RhRuS: C, 54.62; H, 4.17; Cl, 2.66. Found: C, 54.80; H, 4.16; Cl, 2.16.

(n) [RhRu(CO)₂(C(O)CH₂CH₂C(=C(CH₃)₂))(μ-H)₂(dppm)₂][CF₃SO₃] (15). Compound **14** (67 mg, 0.052 mmol) was dissolved in 5 mL of CH₂Cl₂. Hydrogen gas was passed over the solution for ca. 5 min, after which no noticeable color change occurred. The solution was stirred under H₂ for 1 h, the solvent was removed in vacuo, and the orange residue was dissolved in 2 mL of CH₂Cl₂. Slow addition of 10 mL of Et₂O caused formation of a dark orange solid. The supernatant was removed, and the solid was washed with 2 × 10 mL of Et₂O and dried in vacuo (yield: 52 mg, 77%). Anal. Calcd for C₆₀H₅₆F₃O₆P₄RhRuS: C, 55.86; H, 4.38. Found: C, 55.23; H, 4.29.

(o) [RhRu(CO)₃(C(O)CH₂CH₂C(=C(CH₃)₂))(dppm)₂][CF₃SO₃] (16). A Schlenk flask was charged with 15 mg (0.011 mmol) of [RhRu(CO)₂(C(O)CH₂CH₂C(=C(CH₃)₂))(dppm)₂][CF₃SO₃] (**14**) and ca. 1 atm of CO. To this, 10 mL of CH₂Cl₂ was added, causing the formation of a yellow solution. The mixture was stirred for 30 min, after which it was concentrated via an Ar stream to 2 mL. Dropwise addition of 25 mL of Et₂O afforded a dark yellow solid, which was washed with 2 × 10 mL of Et₂O after the supernatant was removed. Satisfactory elemental analysis could not be obtained for **16**, perhaps owing to the air-sensitive nature of this compound.

X-ray Data Collection. Orange crystals of [RhRu(CO)₂((CH₃)₂CCCH₂CH₂CO)(dppm)₂][CF₃SO₃]·(CH₃)₂CO (**14**) were obtained by slow diffusion of diethyl ether into an acetone solution of the compound. Data were collected on a Bruker

(11) Hilts, R. W.; Franchuk, R. A.; Cowie, M. *Organometallics* **1991**, *10*, 304.

Table 2. Crystallographic Data for Compound 14

formula	[RhRu(CO) ₂ ((CH ₃) ₂ CCCH ₂ CH ₂ CO)-(dppm) ₂][CF ₃ SO ₃]·(CH ₃) ₂ CO (14)
fw	C ₆₃ H ₆₀ F ₃ O ₇ P ₄ RhRuS
cryst dimens, mm	0.17 × 0.16 × 0.14
cryst syst	triclinic
space group	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> , Å	13.228(1) ^a
<i>b</i> , Å	15.403(2)
<i>c</i> , Å	15.544(2)
α , deg	75.761(2)
β , deg	74.776(2)
γ , deg	72.884(2)
<i>V</i> , Å ³	2871.1(5)
<i>Z</i>	2
<i>d</i> _{calcd} , g cm ⁻³	1.557
μ , mm ⁻¹	0.762
radiation (λ , Å)	graphite-monochromated Mo K α (0.71073)
<i>T</i> , °C	-80
scan type	ω scans (0.2°) (25 s exposures)
2 θ (max), deg	52.70
no. of unique reflns	11 377 (<i>R</i> _{int} = 0.053)
no. of observns	11 148 [<i>F</i> _o ² ≥ 2 σ (<i>F</i> _o ²)]
range of transmn factors	0.9008–0.8813
no. of data/restraints/params	18 118 [<i>F</i> _o ² ≥ -3 σ (<i>F</i> _o ²)]/0/724
residual density, e/Å ³	1.104 to -1.353
<i>R</i> ₁ (<i>F</i> _o ² > 2 σ (<i>F</i> _o ²)) ^b	0.0560
<i>wR</i> ₂ [<i>F</i> _o ² ≥ -3 σ (<i>F</i> _o ²)] ^b	0.1377
GOF (<i>S</i>) ^c	0.953 [<i>F</i> _o ² ≥ -3 σ (<i>F</i> _o ²)]

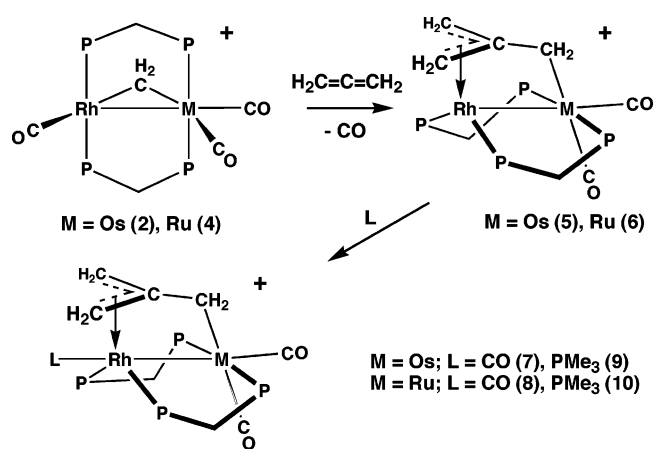
^a Cell parameters obtained from least-squares refinement of 3998 centered reflections. ^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$. Refinement on *F*_o² for all reflections (having *F*_o² ≥ -3 σ (*F*_o²)). *wR*₂ and *S* based on *F*_o²; *R*₁ based on *F*_o, with *F*_o set to zero for negative *F*_o². The observed criterion of *F*_o² > 2 σ (*F*_o²) is used only for calculating *R*₁ and is not relevant to the choice of reflections for refinement. ^c $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (*n* = number of data, *p* = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0638P)^2]^{-1}$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$).

PLATFORM/SMART 1000 CCD diffractometer¹² using Mo K α radiation at -80 °C. Preliminary crystallographic experiments indicated that the crystal used for data collection displayed nonmerohedral twinning. Both components of the twin were indexed with the program GEMINI¹³ on reflections extracted from four sets of 200 frames. The first twin component can be related to the second component by 180° rotation about the [141] axis in reciprocal space and the [010] axis in direct space. The integrated intensities for the reflections for the two components were extracted from the frames data using the program SAINT,¹² corrected for absorption using the Gaussian integration (face-indexed) method, and written into a single SHELXL-93 HKLF 5 reflection file with the program GEMINI using all reflection data (exactly overlapped, partially overlapped, and nonoverlapped). Unit cell parameters were obtained from a least-squares refinement of the setting angles of 3998 reflections from the data collection. The space group was determined to be *P* $\bar{1}$ [No. 2]. 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.

Structure Solution and Refinement. The structure for compound **14** was solved by automated Patterson location of the heavy metal atoms and structure expansion via the DIRDIF-99¹⁴ program system, using a partial HKLF reflection file containing only the nonoverlapping reflections from the major component of the twinned crystal. Refinement was

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

(13) *Gemini Twinning Solution Program Suite*, Version 1.0; Bruker-AXS: Madison, WI, 1999.

Scheme 2

completed using the HKLF 5 reflection file (containing all the reflection data: exactly overlapped, partially overlapped, and nonoverlapped) and the program SHELXL-93.¹⁵ 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. The final model for **14** refined to values of *R*₁(*F*) = 0.0560 (for 11 148 data with *F*_o² ≥ 2 σ (*F*_o²)) and *wR*₂(*F*²) = 0.1377 (for all 18 118 data).

Results and Compound Characterization

Attempts to react a series of cumulenes with the methylene-bridged tetracarbonyl complexes [RhM(CO)₄(μ -CH₂)(dppm)₂][X] (M = Os, X = BF₄ (**1**); M = Ru, X = CF₃SO₃ (**3**)) failed except in the case of **1** and dimethylallene, which react over a period of several days at ambient temperature, as described later. All other combinations of compounds **1** and **3** with allene, methylallene, and 1,1-dimethylallene gave no reaction after several days under the same conditions. However, all of these cumulenes react instantly with the above complexes in the presence of 1 equiv of trimethylamine oxide. Previous studies have shown that the reactions of **1** and **3** with Me₃NO yield the respective tricarbonyl complexes [RhM(CO)₃(μ -CH₂)(dppm)₂][X] (M = Os (**2**), Ru (**4**)),^{4,10} which are presumably the species reacting with the cumulenes. However it usually proved most convenient and reproducible to carry out these reactions by generating the tricarbonyl compounds in situ from their tetracarbonyl precursors in the presence of the cumulene of interest by the addition of Me₃NO. In all schemes involving carbonyl removal from **1** and **3** the respective tricarbonyls **2** and **4** are shown as the precursors.

(a) Allene Reactions. Under the above conditions, compounds **2** and **4** react with allene at subambient temperatures to yield the trimethylenemethane-bridged products [RhM(CO)₂(μ - η^3 : η^1 -C(CH₂)₃)(dppm)₂]⁺ (M = Os (**5**), Ru (**6**)), as shown in Scheme 2. The spectral parameters for both species are closely comparable and in agreement with the formulation shown, in which one methylene group of the trimethylenemethane unit is η^1 -

(14) Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Israel, R.; Gould, R. O.; Smits, J. M. M. *DIRDIF-99 program system*; Crystallography Laboratory, University of Nijmegen: The Netherlands, 1999.

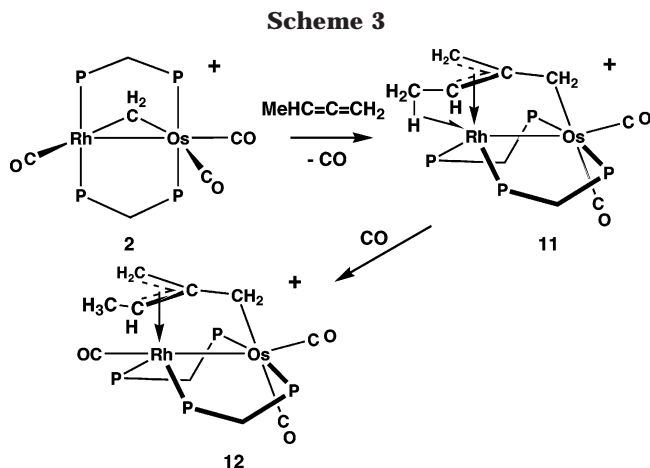
(15) Sheldrick, G. M. *SHELXL-93*: Program for crystal structure determination; University of Göttingen: Göttingen, Germany, 1993.

bound to the group 8 metal while the rest of this unit is η^3 -bound to Rh. For compound **5**, as an example, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows two resonances, typical for such species in which the low-field signal displays 152 Hz coupling to Rh. In the ^1H NMR spectrum, in addition to the phenyl resonances, the dppm methylenes appear at δ 4.39 and 4.01 and three additional signals corresponding to the trimethylenemethane moiety appear as a triplet at δ 1.79, a doublet at δ 1.95, and a broad singlet at δ 4.10. The high-field triplet corresponds to the methylene group that is σ -bound to Os, displaying 12 Hz coupling to the phosphorus nuclei on this metal. The mid-field doublet corresponds to a pair of protons on the η^3 -allyl portion of the trimethylenemethane unit that are *anti* to the Os-bound CH_2 group; this pair displays 8 Hz coupling to one of the Rh-bound phosphines. Finally, the broad singlet corresponds to the *syn* protons of the allyl moiety. The two resonances for the allyl functionality are very similar to those reported for the 2-methylallyl ligand in a series of compounds, $[\text{Rh}(\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2)\text{L}_2]^+$ ($\text{L}_2 =$ disphosphine),¹⁶ in which the *syn* protons appear as broad singlets at lower field (between δ 3.20 and 4.00) and the *anti* protons appear as doublets at somewhat higher field (between δ 2.36 and 2.71), showing coupling to one of the ^{31}P nuclei of the diphosphine ligands.

A sample of **5** in which the carbonyls are ^{13}C enriched displays two carbonyl resonances at δ 181.6 and 172.4; selective phosphorus-decoupling experiments and the absence of Rh coupling establishes that both carbonyls are bound to Os. The IR spectrum of an unenriched sample shows the carbonyl stretches at 2003 and 1929 cm^{-1} , which together with the high-field chemical shifts of these groups in the NMR spectrum, establishes that both carbonyls are terminally bound.

When compound **5** is generated using a $^{13}\text{CH}_2$ -enriched sample of **2**, the label is found to be uniquely situated in the site that is σ -bound to Os (at δ 7.27 in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum); no scrambling of this label is observed over the other two sites of the trimethylenemethane unit. The unique placement of the labeled CH_2 group adjacent to Os indicates that allene insertion into the Rh– CH_2 bond of the precursor occurs. Similarly no scrambling was observed for the $^{13}\text{CH}_2$ -labeled Rh/Ru analogue **6**. Although not initially observed in the ^{13}C NMR experiment of **5**, the methylene carbons of the allylic fragment in this species were identified at δ 73.5 in 2-D HMBC and HMQC experiments.¹⁷ Attempts to assign the central carbon of the trimethylenemethane unit in an HMBC experiment failed, as it did not show the appropriate correlation.

The addition of CO or PMe_3 to compounds **5** and **6** yields the respective adducts $[\text{RhM}(\text{CO})_3(\mu\text{-}\eta^3\text{-}\eta^1\text{-C}(\text{CH}_2)_3\text{-}(\text{dppm})_2)]^+$ ($\text{M} = \text{Os}$ (**7**), Ru (**8**)) and $[\text{RhM}(\text{PMe}_3)(\text{CO})_2(\mu\text{-}\eta^3\text{-}\eta^1\text{-C}(\text{CH}_2)_3)(\text{dppm})_2]^+$ ($\text{M} = \text{Os}$ (**9**), Ru (**10**)). In all cases, the ^1H NMR spectra display the singlet, doublet, triplet pattern for the trimethylenemethane unit, as observed for compounds **5** and **6**, suggesting that this moiety has remained η^1 -bound to the group 8 metal and η^3 -bound to Rh. Although all products appear analogous, now having a terminal ligand (CO or PMe_3) bound to



Rh, an interesting difference in the site of ligand attack is observed in the Rh/Os complex. The addition of PMe_3 to **5** at -80°C gives rise to a doublet for the coordinated PMe_3 group at δ -49.8 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, displaying 104 Hz coupling to Rh. The magnitude of the Rh–P coupling clearly identifies that the added phosphine is bound to Rh, and the appearance of this product as the sole species at -80°C suggests initial attack at this metal. Warming to ambient temperature does not lead to rearrangement. In contrast, addition of ^{13}CO to **5** at -80°C shows that initial carbonyl attack occurs at Os with the labeled ^{13}CO appearing at δ 185.9 in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum and displaying no coupling to Rh. Upon warming to ambient temperature, scrambling of the label over all carbonyl sites (δ 194.7, 185.9, and 177.3) is observed, with the low-field signal displaying typical Rh coupling of 60 Hz.

In the case of ^{13}CO and PMe_3 addition to the Rh/Ru analogue **6**, low-temperature addition at Rh occurs in both cases with no scrambling detected upon warming the sample to ambient temperature. Another curious difference in the reactivity of the Rh/Os (**5**) and the Rh/Ru (**6**) compounds is that whereas reaction of the former with CO and PMe_3 is reversible, with the added ligand being labile, the CO ligand is bound irreversibly in **8** while the PMe_3 adduct (**10**) is unstable, decomposing to unidentified products.

Attempts to incorporate additional methylene groups into the trimethylenemethane fragments by reactions of compounds **5** and **6** with diazomethane did not yield isolable products. Although these reactions occurred readily, even at -80°C , a complex mixture of products was obtained in each case, from which none of the species could be identified.

(b) Methylallene Reactions. The reaction of methylallene with **1** in the presence of Me_3NO yields $[\text{RhOs}(\text{CO})_2(\mu\text{-}\eta^3\text{-}\eta^1\text{-CH}(\text{CH}_3)\text{C}(\text{CH}_2)_2)(\text{dppm})_2][\text{BF}_4]$ (**11**), shown in Scheme 3. This product appears to be analogous to the allene-insertion products **5** and **6** except having a methyl substituent at one end of the allyl moiety. Methyl substitution at this end lowers the symmetry of the product, leading to the inequivalence of all four phosphorus nuclei. As a result, four signals are seen in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum; the low-field pair of resonances at δ 42.8 and 36.9 correspond to the ^{31}P nuclei bound to Rh, and those at δ -0.1 and -7.2 correspond to the Os-bound pair.

(16) Fryzuk, M. D. *Inorg. Chem.* **1982**, *21*, 2134.

(17) Braun, S.; Kalinowski, H.-O.; Berger, S. In *100 and More Basic NMR Experiments: A Practical Course*; VCH Publ.: New York, 1996; Chapter 10.

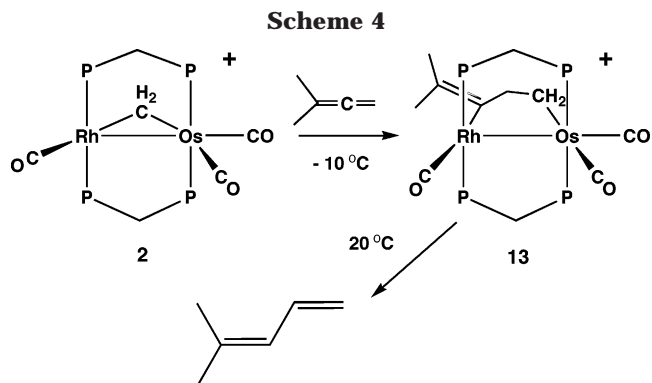
In the ^1H NMR spectrum the *syn* protons (at δ 3.61 and 4.41) appear at low field, while the sole *anti* proton (δ 2.12) is at higher field, as was observed for compounds **5–10** and in the similarly substituted $[\text{Rh}(\eta^3\text{-allyl})\text{L}_2]$ series of compounds.¹⁶ Furthermore, as is also typical of this substitution pattern, the observed *syn* proton signal appears as a broad singlet, while the *anti* proton is a doublet displaying typical 8 Hz coupling to one of the Rh-bound phosphines. The signal for the *syn* proton that is adjacent to the methyl substituent was found buried beneath one of the dppm methylene signals at δ 4.41 through ^1H COSY experiments. The methyl protons appear as a doublet of doublets ($^4J_{\text{PH}} = ^3J_{\text{HH}} = 6$ Hz) at δ -0.22 . Formulation of this signal as resulting from identical coupling to a Rh-bound phosphine and to the adjacent proton was confirmed by selective ^{31}P decoupling resulting in its collapse to a doublet with only H–H coupling remaining. The above information indicates that the methyl substituent occupies one of the sites on the allyl moiety *anti* to the Os-bound methylene group.

Again, the use of $^{13}\text{CH}_2$ -enriched compound **1** confirms that the original metal-bound methylene group remains bound to Os with no scrambling to the other methylene site. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum this group in **11** appears as a broad unresolved signal at δ 9.52. Also analogous to compounds **5** and **6**, the two carbonyls in **11** are established as being bound to Os on the basis that no Rh coupling is observed.

The unusually high-field chemical shift for the methyl resonance in the ^1H NMR spectrum of **11** leads us to propose that this group is involved in an agostic interaction with Rh, in which rapid exchange between the agostic hydrogen and the other two is occurring. Facile exchange of the three protons of a methyl group when one of the C–H bonds is involved in an agostic interaction is common.¹⁸ In this compound the agostic interaction proposed would give Rh an 18e configuration. We anticipated that this agostic interaction might be displaced by another ligand. Accordingly, CO addition to **11** yields the carbonyl adduct $[\text{RhOs}(\text{CO})_3(\mu\text{-}\eta^3\text{:}\eta^1\text{-CH}(\text{CH}_3)\text{C}(\text{CH}_2)_2)(\text{dppm})_2][\text{BF}_4]$ (**12**), which displays one Rh-bound carbonyl and two on Os. Consistent with the suggestion that CO addition has displaced the agostic interaction involving the methyl group, the ^1H signal for this group has shifted substantially downfield to δ 1.35, a value that is more characteristic of a normal methyl group. Attempts to determine the initial site of CO attack were unsuccessful since no reaction is seen at low temperatures. At temperatures at which reaction occurs, the labeled carbonyl is observed scrambled over all three sites in the complex.

No reaction of **11** with PMe_3 was observed over a range of temperatures. Presumably, coordination of the larger phosphine ligand at Rh is inhibited by the methyl substituent on the allyl moiety. It is also surprising that no product analogous to **11** was observed for the Rh/Ru system. Reaction of **4** with methylallene over a range of temperatures gave only mixtures of unidentified products.

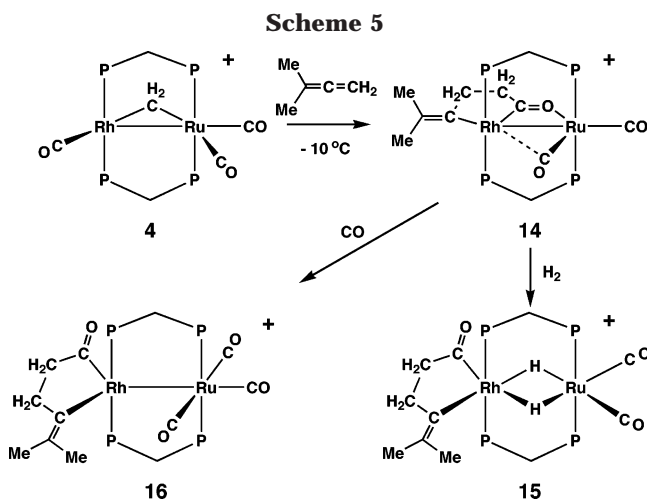
(c) 1,1-Dimethylallene Reactions. As noted earlier, 1,1-dimethylallene is the only cumulene investigated



that reacts with one of the tetracarbonyl precursors. In this reaction involving compound **1** the products obtained after several days are $[\text{RhOs}(\text{CO})_4(\text{dppm})_2][\text{BF}_4]$ ¹¹ and 1,1-dimethyl-1,3-butadiene. No other species is observed at intermediate times. However, the addition of 1,1-dimethylallene to $[\text{RhOs}(\text{CO})_3(\mu\text{-CH}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**2-CF₃SO₃**) results in an instantaneous reaction yielding $[\text{RhOs}(\text{CO})_3(\mu\text{-}\eta^1\text{:}\eta^1\text{-}(\text{CH}_3)_2\text{CCCH}_2\text{CH}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**13**) as shown in Scheme 4. This product is unstable upon workup, decomposing within hours at ambient temperature, yielding 1,1-dimethyl-1,3-butadiene, $[\text{RhOs}(\text{CO})_4(\text{dppm})_2][\text{CF}_3\text{SO}_3]$, and unidentified decomposition products, which presumably are the source of the additional carbonyl in the binuclear product. Owing to its instability, characterization of **13** was carried out by NMR at low temperatures. In addition to the dppm resonances in the ^1H NMR spectrum, two other methylene resonances are observed; a broad triplet at δ 1.63, having 8 Hz coupling to the osmium-bound phosphines, is consistent with an Os-bound methylene group, while the other appears as a broad singlet at δ 2.41. ^{31}P decoupling experiments support these assignments, with only the former signal displaying coupling to phosphorus. 2-D proton COSY experiments show coupling between the two adjacent methylene groups. The methyl signals appear at δ 0.78 and 0.10; the lower-field signal is a triplet with 6 Hz coupling to the Rh-bound phosphines, while the other is a broad unresolved singlet. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a ^{13}CO -enriched sample three resonances are observed (δ 191.4, 182.5, 172.8) with only the low-field signal displaying Rh coupling. It is significant that whereas the initial $\eta^1\text{:}\eta^3$ -trimethylenemethane products are dicarbonyls, having no Rh-bound carbonyl, complex **13**, having the $\eta^1\text{:}\eta^1$ -bound ligand, has a Rh-bound carbonyl ligand. This additional carbonyl ligand is required in order to give Rh a 16e configuration.

Reaction of dimethylallene with the Rh/Ru precursor (**3**) in the presence of Me_3NO (generating **4** in situ) gives a very different result, yielding $[\text{RhRu}(\text{CO})_2((\text{CH}_3)_2\text{CCCH}_2\text{CH}_2\text{CO})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**14**), as diagrammed in Scheme 5. In the ^1H NMR spectrum two methyl resonances (singlets) are observed at δ 1.31 and 0.96, while four multiplets for the methylene groups are observed at δ 3.58, 3.41, 2.73, and 0.37. The former two are identified as dppm methylene groups by their characteristic appearance as an AB quartet upon broadband ^{31}P decoupling experiments. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a ^{13}CO -enriched sample one resonance appears at δ 250.7 as a doublet of triplets with coupling to Rh (33 Hz) and to the Rh-bound phosphorus nuclei.

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The low-field chemical shift of this species suggests an acyl carbonyl group.¹⁹ Two other carbonyl resonances, at δ 220.2 and 202.4, are assigned as a semibridging carbonyl, having no resolved Rh coupling, and a terminal Ru-bound carbonyl, respectively. The IR spectrum shows carbonyl bands at 1975 and 1910 cm^{-1} consistent with this assignment. No stretch for the acyl carbonyl is observed. Failure to observe the carbonyl stretch for a μ - η^1 : η^1 acyl group, of the type diagrammed in Scheme 5, has been noted previously¹⁹ and presumably results from some contribution by an oxycarbene resonance structure, which shifts this stretch to lower frequency, where it can become obscured by other bands. In one acetyl-bridged complex, $\text{Cp}_2\text{Zr}(\mu\text{-CH}_3\text{CO})\text{Mo}(\text{CO})_2\text{Cp}$, the acyl carbonyl stretch was observed at 1339 cm^{-1} .²⁰

An unambiguous structural assignment is based on the X-ray structure determination of **14**, and a representation of the complex cation is shown in Figure 1, with relevant bond lengths and angles appearing in Table 3. The X-ray structure confirms that a [2+1+1] condensation of the dimethylallene, methylene, and carbonyl groups has occurred, yielding the metallacycle proposed in Scheme 5. Within the five-membered metallacycle the bond lengths and angles appear normal for the formulation proposed, and the unit is quite planar, with the largest out-of-plane deviation (0.051(7) Å) being that of C(4). The bonding parameters involving the acyl group are intermediate between acyl and oxycarbene formulations. Therefore, the Rh–C(3) distance (1.915(5) Å) is short, suggesting some carbene character in this bond, and can be compared with the Rh–C(6) bond (2.077(5) Å) involving the vinylic group. Despite the short “carbene-like” Rh–C(3) distance, the C(3)–O(3) distance of 1.234(6) Å is normal for a double bond²¹ and is somewhat shorter than the range observed (1.24–1.29 Å) in related species.^{19a,d,e,20,22} Furthermore, the ¹³C chemical shift for this acyl carbon in the NMR

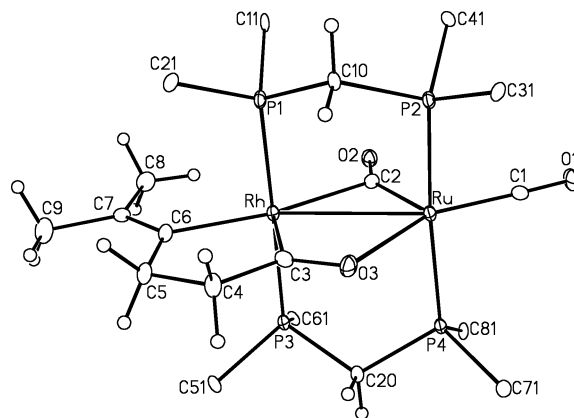


Figure 1. Perspective view of the complex cation of $[\text{RhRu}(\text{CO})_2((\text{CH}_3)_2\text{CCCH}_2\text{CH}_2\text{CO})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$ (**14**) showing the atom-labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Only the *ipso* carbons of the dppm phenyl rings are shown.

spectrum is also at slightly higher field than previous examples.¹⁹

The acyl carbonyl is clearly oriented toward Ru in such a way as to give rise to a bonding interaction with this metal, although this distance (2.449(4) Å) is long,²³ suggesting that this interaction is weak. We suggest that the weakness of the O(3)–Ru bond arises because of strain within the bridging acyl moiety; the Ru–O(3)–C(3) angle (107.5(3)°) is significantly more acute than the 120° predicted on the basis of the sp^2 hybridization of an acyl group, again being more consistent with the oxycarbene formulation. It is suggested that the optimum overlap between the acyl oxygen and Ru cannot be achieved without further elongation of the Rh–Ru bond, which at 2.9833(6) Å is already unusually long; the parameters observed are a compromise between the conflicting needs for the Rh–Ru and Ru–O(3) bonds.

Reaction of **14** with H_2 yields the dihydride product $[\text{RhRu}(\eta^1\text{-}\eta^1\text{-C}(\text{O})\text{CH}_2\text{CH}_2\text{C}=\text{C}(\text{CH}_3)_2(\text{CO})_2(\mu\text{-H})_2(\text{dppm})_2)]\text{-}[\text{CF}_3\text{SO}_3]$ (**15**) as shown in Scheme 5. Both hydride resonances are complex multiplets, consistent with their bridging environments in which they couple to all four phosphorus nuclei, Rh, and each other. Selective ³¹P decoupling experiments confirm coupling of these hydride signals to both sets of chemically inequivalent phosphorus nuclei, and broadband ³¹P decoupling allows observation of 10 Hz coupling of the low-field hydride and 18 Hz coupling of the high-field hydride to Rh and additional 8 Hz mutual coupling. ¹³C{¹H} NMR spectra clearly demonstrate that both terminal carbonyls are bound to Ru, while the low-field acyl resonance (δ 236.3) displays 28 Hz coupling to Rh, confirming that it remains bound to this metal. Location of the hydrides, bridging the metals, indicates that the acyl fragment must have moved from the bridging site it occupied in the precursor **14**, so is shown in Scheme 5 bound solely to Rh. The ¹H NMR resonances for the acyl ligand are

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(21) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans 2* **1987**, 51.

(22) (a) Lindley, P. F.; Mills, O. S. *J. Chem. Soc., A* **1969**, 1279. (b) Blickensderfer, J. R.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 2686. (c) Hendrick, K.; Iggo, J. A.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1984**, 209. (d) Shafiq, F.; Kramarz, K. W.; Eisenberg, R. *Inorg. Chim. Acta* **1993**, *213*, 111.

(23) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, 51.

Table 3. Selected Distances (Å) and Angles (deg) for Compound 14

atom 1	atom 2	distance	atom 1	atom 2	distance
Rh	Ru	2.9833(6)	P1	P2	3.089(2) ^a
Rh	P1	2.368(2)	P3	P4	3.090(2) ^a
Rh	P3	2.363(2)	O1	C1	1.160(6)
Rh	C2	2.238(5)	O2	C2	1.162(5)
Rh	C3	1.915(5)	O3	C3	1.234(6)
Rh	C6	2.077(5)	C3	C4	1.497(7)
Ru	P2	2.361(2)	C4	C5	1.536(7)
Ru	P4	2.341(2)	C5	C6	1.510(7)
Ru	O3	2.449(4)	C6	C7	1.329(7)
Ru	C1	1.837(5)	C7	C8	1.488(7)
Ru	C2	1.919(5)	C7	C9	1.520(7)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Ru	Rh	P1	90.23(4)	O3	Ru	C2	108.2(2)
Ru	Rh	P3	89.56(4)	C1	Ru	C2	104.0(2)
Ru	Rh	C2	40.0(1)	Ru	O3	C3	107.5(3)
Ru	Rh	C3	73.6(2)	C6	C7	C8	122.8(5)
Ru	Rh	C6	158.1(1)	C6	C7	C9	121.5(5)
P1	Rh	P3	175.71(5)	C8	C7	C9	115.7(4)
C2	Rh	C3	113.6(2)	C5	C6	C7	125.8(5)
C2	Rh	C6	161.8(2)	Rh	C6	C5	112.3(3)
C3	Rh	C6	84.6(2)	Rh	C6	C7	122.0(4)
Rh	Ru	P2	92.31(4)	C3	C4	C5	112.3(4)
Rh	Ru	P4	93.01(4)	C4	C5	C6	112.6(4)
Rh	Ru	O3	59.59(8)	Rh	C3	O3	119.3(4)
Rh	Ru	C1	152.6(2)	Rh	C3	C4	118.0(4)
Rh	Ru	C2	48.6(2)	C4	C3	O3	122.7(4)
P2	Ru	P4	169.51(5)	Rh	C2	O2	120.5(4)
O3	Ru	C1	147.8(2)	Ru	C2	O2	148.0(4)

^a Nonbonded distance.

also consistent with this ligand fragment remaining intact. The IR spectrum of **15** shows two terminal carbonyl stretches in addition to a weak stretch due to the acyl group at 1683 cm⁻¹.

Reaction of **14** with CO yields the tricarbonyl complex [RhRu(η¹:η¹-C(O)CH₂CH₂C=C(CH₃)₂)(CO)₃(dppm)₂][CF₃-SO₃] (**16**). Again, all carbonyl ligands are shown, by ¹³C-¹H NMR studies, to be terminally bound to Ru, while the acyl carbonyl is bound to Rh (¹J_{RhC} = 30 Hz). Three stretches in the IR spectrum correspond to the terminal carbonyl groups, while the acyl stretch is observed at 1687 cm⁻¹. The ¹H resonances of the acyl ligand are very similar to those of **15**, indicating that this ligand fragment has remained intact and is presumably bound to Rh as suggested for **15**. Both **15** and **16** can be thought of as resulting from displacement of the oxygen–ruthenium dative bond from the bridging acyl group in **14** by H₂ or CO, respectively.

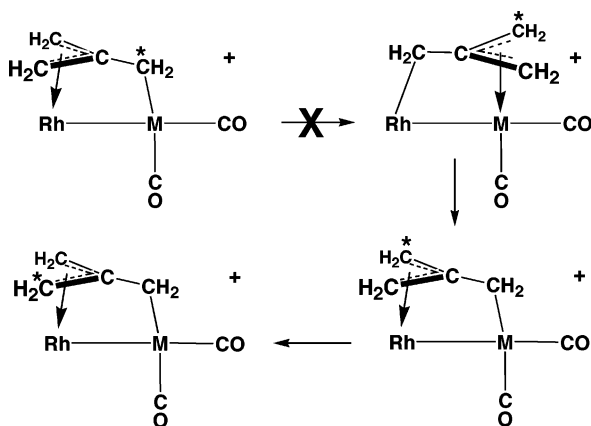
Discussion

As noted earlier, one goal of this study was to effect cumulene insertion into the Rh–CH₂ bond of the methylene-bridged precursors [RhM(CO)₄(μ-CH₂)(dppm)₂][X] (M = Os (**1**), Ru (**3**)) in attempts to generate models for the C₃H₆-bridged species that was proposed to be a pivotal intermediate in the coupling of diazomethane-generated methylene groups, promoted by a Rh/Os complex.⁴ Such C₃-containing products could also model surface-bound species that had been suggested² in Fischer–Tropsch chemistry. Furthermore, by comparing the chemistries of both the Rh/Os and Rh/Ru combinations of metals a better understanding of the roles of the different metals in this chemistry was anticipated. Although both compounds were found to be unreactive

with the cumulenes studied (only **1** reacted very slowly with dimethylallene), facile reactions were observed in all cases by the removal of a carbonyl ligand using Me₃NO. As part of our strategy to generate C₃-bridged ligands, we had anticipated that cumulene insertion could occur in one of two ways, as shown in Scheme 1. Of all reactions studied, only the reaction of **2** and 1,1-dimethylallene gives one of the anticipated products. However, we suggest in what follows that in all cases initial insertion of the cumulene molecule into the Rh–CH₂ bond occurs to give either structure **B** or **D**, but that in all but one example these intermediates are not observed, instead rearranging to the products observed. It appears that whether intermediate **B** or **D** is obtained is determined by the steric demands of the cumulene molecule; in the cases of allene and methylallene, initial cumulene coordination at Rh occurs as shown in **C**, subsequently leading to **D**, whereas for 1,1-dimethylallene, coordination as shown for **A** occurs, which upon insertion leads to **B**. As noted, in most cases both **B** and **D** undergo further transformations to give the observed products. We assume that the orientation of the cumulene molecule upon coordination to Rh and the subsequent nature of the insertion product are dictated by the nonbonded contacts between the cumulene substituents and the phenyl groups of the dppm ligands.

The reactions of compounds **2** and **4** (generated in situ from the reactions of **1** and **3** with Me₃NO) with allene give the analogous trimethylenemethane-bridged products [RhM(CO)₂(μ-η³:η¹-C(CH₂)₃)(dppm)₂]⁺ (M = Os (**5**), Ru (**6**)), in which the trimethylenemethane unit is σ-bound to the group 8 metal through one methylene group while binding as an η³-allylic fragment to Rh through the remainder of the ligand. The retention of the labeled methylene group from the precursors (**2**, **4**)

Scheme 6



as the one that is σ -bound to Os or Ru in the products (**5**, **6**) confirms that cumulene insertion into the Rh–CH₂ bond has occurred. In the case of the reaction of **2** with methylallene, the nonbonded contacts noted above favor a product, [RhOs(CO)₂(μ - η^3 : η^1 -CH(CH₃)C(CH₂)₂)-(dppm)₂]⁺ (**11**), that is exactly analogous to compounds **5** and **6**, except having a methyl substituent on one of the terminal allylic carbons.

Trimethylenemethane complexes of mononuclear²⁴ and binuclear²⁵ complexes are known, and in the latter cases the μ - η^3 : η^1 -binding mode proposed herein has also been proposed or observed. Although some mononuclear trimethylenemethane complexes have been shown to be fluxional by rotation about the ligand–metal axis,^{24a} this fluxionality has been reported with only one bridged complex.^{25d} Certainly in compounds **5** and **6**, prepared from ¹³CH₂-labeled compounds **2** and **4**, no scrambling of the label over the three methylene sites of the ligand is observed; the label remains bound to Os or Ru. For the Os species (**5**) we might argue that this results from the stronger Os–CH₂ bond;²⁶ however, this argument is less compelling for the Ru analogue given the presumed similarity in Rh–C and Ru–C bond strengths.²⁶ If scrambling of the trimethylenemethane moiety were to occur, this would presumably take place as diagrammed in Scheme 6 (dppm ligands above and below the plane of the drawing are omitted), through an intermediate in which the η^3 -allylic fragment is bound to the group 8 metal. We propose that such an intermediate would be unstable owing to the greater steric crowding at this metal by virtue of its higher coordination number.

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(25) (a) Wolfe, S.; Hason, S. K.; Campbell, J. R. *Chem. Commun.* **1970**, 1420. (b) Whitesides, T. H.; Slaven, R. W. *J. Organomet. Chem.* **1974**, *67*, 99. (c) Fildes, M. J.; Knox, S. A. R.; Orpen, A. G.; Turner, M. L.; Yates, M. I. *J. Chem. Soc., Chem. Commun.* **1989**, 1680. (d) Chetcuti, M. J.; Fanwick, P. E.; Grant, B. E. *Organometallics* **1991**, *10*, 3003.

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Although the η^3 : η^1 coordination mode for the trimethylenemethane unit is not that of our original target, we assume that it derives readily from the targeted structure **D**, in which the exocyclic allyl moiety that is β to both Rh and the group 8 metal rearranges to an η^3 -allylic moiety with concomitant CO loss from Rh. The stability of the η^3 -allyl binding mode over the η^1 -mode is well documented.^{27a} Clearly, the reverse binding mode, having the allylic fragment bound to the group 8 metal, is also possible. However, as already noted, it is assumed that the greater steric crowding in this case is destabilizing, favoring instead the observed species. In the case of the Os complexes (**5** and **11**), retention of the strong Os–CH₂ σ -bond would also favor the structures observed.

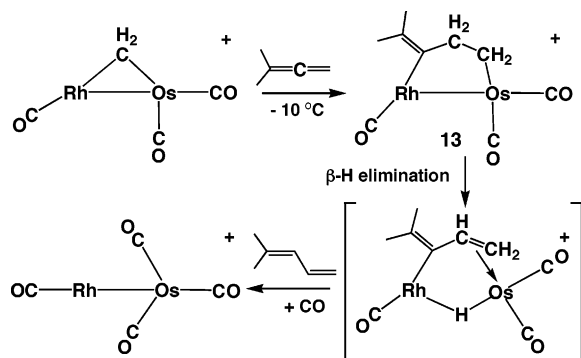
Since the rearrangement of **D** to the η^3 -allyl product was assumed to occur with concomitant CO loss, it seemed likely that ligand (CO or PMe₃) addition to **5** or **6** would reverse this rearrangement, allowing us to observe the targeted η^1 : η^1 -binding mode. However in all cases ligand attack leading to species **7**–**10** and having either CO or PMe₃ bound to Rh resulted in retention of the η^3 -binding mode of the allylic fragment. In the precursors **5** and **6** the Rh center is coordinatively unsaturated, so additional ligand coordination can occur without transformation to an η^1 -allylic binding mode. Surprisingly, the initial site of attack on the Rh/Os compound **5** differs for CO and PMe₃. Whereas at –80 °C PMe₃ attacks, as expected, at the coordinatively unsaturated Rh, initial carbonyl attack at this temperature occurs at Os, with scrambling occurring at higher temperatures. Although the Os center in **5** is saturated, transfer of a carbonyl to Rh can give rise to unsaturation at Os. Presumably, the larger PMe₃ group cannot readily gain access at the more crowded Os, so attacks instead at Rh. In the Rh/Ru analogue, there is no evidence of either attack at Ru or carbonyl scrambling.

With the methylallene analogue **11**, the coordinative unsaturation at Rh is alleviated by an agostic interaction involving a C–H bond of the methyl substituent, but this interaction is readily displaced by a carbonyl generating the tricarbonyl analogue of **7**.

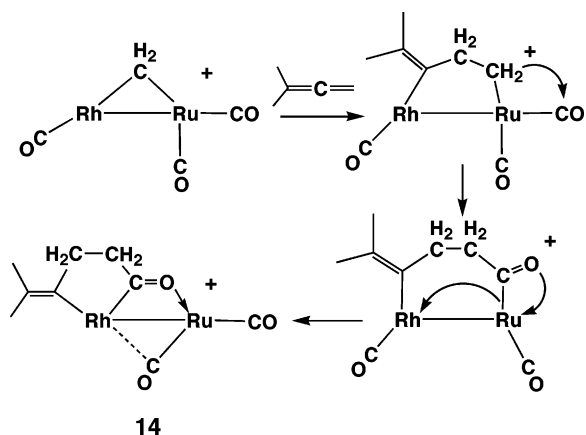
1,1-Dimethylallene appears to coordinate to the Rh centers in both the Rh/Os and Rh/Ru analogues, as shown in structure **A**, which upon insertion into the Rh–CH₂ bond yields **B**. In each case, however, an additional transformation occurs. In the reaction of **1** with dimethylallene, no complex containing this substrate is observed, but **1** is quantitatively consumed over several days, yielding 1,1-dimethyl-1,3-butadiene and [RhOs(CO)₄(dppm)₂]⁺. A species analogous to the presumed intermediate in this transformation, [RhOs(CO)₃(μ - η^1 : η^1 -(CH₃)₂CCCH₂CH₂)(dppm)₂]⁺ (**13**), is observed at low temperature when the reaction is carried out with compound **2**. This product is unstable at ambient temperature, decomposing to the 1,1-dimethylbutadiene and the above tetracarbonyl products, together with other decomposition products, which presumably give rise to the additional carbonyl group. We assume that this transformation results as outlined in Scheme 7 (dppm ligands omitted). β -Hydrogen elimination from

(27) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 3. (b) Chapter 6.

Scheme 7



Scheme 8



the central carbon of the C₃-bridged unit and reductive elimination, in which hydrogen transfer to the vinylic Rh-bound carbon occurs, would yield the butadiene molecule. We had anticipated that allene insertion into the Rh(μ -CH₂)M units might give rise to better models of propanediyl-bridged species than the products of alkyne insertion. The above proposed sequence, leading to dimethylbutadiene formation, supports this contention since it parallels the conversion of the bridging propanediyl fragment to propene.⁶

In the case of the Rh/Ru complex the only product observed in its reaction with 1,1-dimethylallene is the acyl-containing **14**, which has resulted from 2+1+1 coupling of dimethylallene, the bridging methylene unit, and a carbonyl. We propose that this also proceeds via an intermediate like **B**. In this case however, substitution of Os by Ru leads to a greater tendency for carbonyl migratory insertion,^{27b} so migration of the Ru-bound methylene group to an adjacent carbonyl, as diagrammed in Scheme 8 (dppm groups omitted), yields a Ru-bound acyl, and subsequent migration of the acyl to Rh to give a favorable five-membered metallacycle, accompanied by coordination of the acyl oxygen at Ru and carbonyl migration from Rh to Ru, yields the product **14**.

The observation that the Ru–O distance of the bridging acyl unit in **14** was long, presumably indicating a weak interaction, suggested that displacement of this Ru–acyl interaction could be induced by ligand addition. This has been confirmed by the addition of either H₂ or CO, as shown earlier in Scheme 5. We had anticipated that, in the case of H₂ addition, hydrogenolysis of the Rh–C bonds might occur, yielding the appropriate

aldehyde. However, reductive elimination from the dihydride product **15** is not observed even upon mild heating.

Conclusions

The products obtained in the reactions of methylene-bridged complexes of Rh/Os and Rh/Ru with a series of cumulenes are consistent with insertion of cumulenes into the Rh–CH₂ bond and depend both on the cumulene substituents and on the combinations of metals. Although the initial products of cumulene insertion are not all observed, the observed final products are consistent with insertion occurring such that the uncoordinated “C=CRR” moiety is *exo* to the resulting five-membered dimetallacycle, either adjacent to the original metal-bound methylene group or adjacent to Rh. The nature of the initial product depends on the degree of substitution of the cumulene. Therefore, the unsubstituted allene initially yields an $\eta^1:\eta^1$ -trimethylenemethane unit having the allylic “C=CH₂” group in a symmetrical site between the two metal-bound methylene groups, while the bulkier 1,1-dimethylallene yields an initial species in which the dimethylvinyl group is adjacent to Rh. In the first case, both metal combinations (Rh/Os and Rh/Ru) behave identically and the presumed $\eta^1:\eta^1$ -trimethylenemethane intermediate rearranges to an $\eta^3:\eta^1$ -binding mode having one methylene group σ -bound to the group 8 metal and the remainder of the fragment η^3 -bound to Rh. This transformation reflects the well-documented preference for η^3 - over η^1 -allyls.^{27a}

In the second case the differing reactivity of the two metal combinations becomes obvious. Both metal combinations give similar initial products in which the metals are bridged by an $\eta^1:\eta^1$ -(CH₃)₂C=CCH₂CH₂ fragment. However, with the Rh/Os metal combination, β-hydrogen elimination occurs followed by reductive elimination of 1,1-dimethyl-1,3-butadiene. With the Rh/Ru combination, migration of the Ru-bound end of the hydrocarbyl fragment to a Ru-bound carbonyl occurs, yielding an acyl group. The difference in these latter two products is consistent with the greater tendency of the second-row metal (Ru) to undergo migratory insertion compared to the third-row Os^{27b} and with the greater propensity of the third-row metal for C–H bond activation.²⁸

The stated goal of this study was to obtain models for C₃-bridged species, proposed as intermediates in a methylene-coupling sequence.⁴ In this regard, the study was only partially successful; only 1,1-dimethylallene with the Rh/Os complex yielded the anticipated product as an observable species. The subsequent transformation of this product was consistent with transformations of related C₃ products containing β-hydrogens.^{4,6} In all other cases, products different from those anticipated were obtained. Under these conditions, these products are certainly not useful models for Fischer–Tropsch chemistry. Nevertheless, the different products obtained demonstrate how small modifications to the system can result in significant reactivity differences. In particular, it is significant that although reactivity is initiated at

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the Rh center in all cases, the identity of the final product can depend on the nature of the adjacent metal. It is important to gain an understanding of such reactivity trends in heterobinuclear complexes in order to fully appreciate the roles of different metals in bimetallic catalysts.

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this research and NSERC for funding the Bruker PLATFORM/SMART 1000-CCD diffractometer.

Supporting Information Available: Tables of X-ray experimental details, atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for compound **14**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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