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Heterobinuclear Vinyl, Allyl, and Related Complexes of Rhodium/Osmium from Terminal Alkynes and Allenes, Vinyl to Carbene Transformations, and the Structures of $[RhOs(C(CH_3){=}CH_2)(CO)_3(Ph_2PCH_2PPh_2)_2]$ and $[RhOs(C(CH_3){=}C(CH_3)_2)(CH_3)(CO)_3(Ph_2PCH_2PPh_2)_2][CF_3SO_3]$

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This paper reports the synthesis and characterization of a series of vinyl, vinyl−hydride, vinyl−alkyl, and related heterobimetallic complexes of Rh and Os. Reductive elimination reactions of the vinyl−hydride products and the transformations of vinyl groups to carbenes are also reported. Reaction of $[RhOs(H)(CO)_3(dppm)_2]$ (**1**, dppm = $Ph_2PCH_2PPh_2$) with propyne yields $[RhOs(C(CH_3){=}CH_2)(CO)_3(dppm)_2]$ (**3**), and reaction with $(CH_3)_2C{=}C{=}CH_2$ yields $[RhOs(C(CH_3){=}C(CH_3)_2)(CO)_3(dppm)_2]$ (**5**). Reaction of **1** with allene yields **3** as the major product, together with small amounts of $[RhOs(\eta^3\text{-}C_3H_5)(CO)_3(dppm)_2]$ (**4**). Compound **4** can be independently synthesized via reaction of $(CH_2CHCH_2)_2Mg$ with $[RhOs(CO)_4(dppm)_2][BF_4]$ (**2**). Compound **3** reacts with CO to form the isopropenoyl complex $[RhOs(C(O)C(CH_3){=}CH_2)(CO)_3(dppm)_2]$ (**6**). Both vinyl complexes **3** and **5** react with $CH_3SO_3CF_3$ to form $[RhOs(C(CH_3){=}CR_2)(CH_3)(CO)_3(dppm)_2][CF_3SO_3]$ (**7a**,**b** R = H; **8a**,**b** R = CH_3) and with $HBF_4{\cdot}Me_2O$ to form $[RhOs(C(CH_3){=}CR_2)(H)(CO)_3(dppm)_2][BF_4]$ (**9a**,**b** R = H; **10a**,**b** R = CH_3). The isopropenoyl complex **6** reacts with $HBF_4{\cdot}Me_2O$ to form $[RhOs(C(O)C(CH_3){=}CH_2)(\mu\text{-}H)(CO)_3(dppm)_2]$ $[BF_4]$ (**11**). The vinyl−hydride compounds **9** and **10** rearrange under a CO atmosphere to form hydride-bridged isomers $[RhOs(C(CH_3){=}CR_2)(\mu\text{-}H)(CO)_3(dppm)_2][BF_4]$ (**12a**,**b** R = H; **13a**,**b** R = CH_3), which subsequently reductively eliminate the alkene. Protonation of $[RhOs(C(CH_3){=}CH_2)(CH_3)(CO)_3(dppm)_2][CF_3SO_3]$ (**7**) or $[RhOs(C(CH_3){=}CH_2)(H)(CO)_3(dppm)_2][BF_4]$ (**9**) at low temperature results in formation of the carbene complexes $[RhOs({=}C(CH_3)_2)(R)(CO)_3(dppm)_2][X][Y]$ (**14** R = H, X = Y = BF_4; **15** R = CH_3, X = BF_4, Y = CF_3SO_3) in which the carbene is terminally bound to Rh. Protonation of $[RhOs(C(O)C(CH_3){=}CH_2)(\mu\text{-}H)(CO)_3(dppm)_2][BF_4]$ (**11**) yields the carbene complex $[RhOs({=}C(OH)C(CH_3){=}CH_2)(\mu\text{-}H)(CO)_3(dppm)_2][BF_4]_2$ (**16**). The structures of **3** and **8** have been established by X-ray crystallography. In compound **3**, the isopropenyl group is terminally bound to Rh and three carbonyls are bound to Os, with one of them forming a semibridging interaction with Rh. The trimethylvinyl group in compound **8** is also bound terminally to Rh, while three carbonyls and the methyl group are on Os. Two of the carbonyls form semibridging interactions with Rh.

Introduction

Currently there is considerable interest in the development of heterogeneous catalysts that employ two or more different metals.[1] Mixed-metal catalysts already find use in a wide range of industrial processes, including synthesis gas chemistry, coal hydrodesulfurization, methane or olefin oxidation, and gasoline reforming, and even find everyday common use in automobile catalytic converters, which employ group 9 and 10 combinations, such as Rh/Pt. In spite of extensive work in the development of these catalysts, little is understood about the functions of the different metals in the respective processes. The prospects of obtaining mechanistic information about processes occurring under heterogeneous conditions are difficult enough;[2] attempting to elucidate the functions of the different metals under these conditions is even more daunting. Transition-metal complexes containing two or more adjacent metals can, therefore, function as valuable models for heterogeneous processes, owing to the ease of studying such systems in solution under homogeneous conditions. In binuclear (or polynuclear) complexes, as in heterogeneous systems, in which metals are in close proximity, the involvement of bridged bonding modes for the substrate molecules or substrate-derived ligands must be considered. These bridging coordination modes might be expected to substantially influence any transformations of these groups[3] and are relevant to their mobilities,[4] since transfer of these groups from metal to metal, presumably, occurs via a bridged intermediate.

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In this paper, we extend the organometallic chemistry of our previously studied "Rh/Os" systems[5] to include σ-bound organic groups having unsaturation within their framework. Two such groups are the vinyl ($-CH{=}CH_2$) and allyl ($-CH_2CH{=}CH_2$) moieties and their substituted analogues. The unsaturation in these groups means that in addition to being σ-bound to one metal, simultaneous π-donation to an adjacent metal is also possible. How this μ_2-η^1,η^2-interaction can modify the reactivity of the group or its ability to influence the chemistry at a metal by stabilizing coordinatively unsaturated intermediates was of interest to us.

In addition, the proposed involvement of vinyl groups in Fisher−Tropsch chemistry[6] has permitted an explanation of the propagation steps that successfully accounts not only for the lower than expected amounts of C_2 products obtained, but also for the formation of small amounts of branched-chain hydrocarbons. A key part of this proposal involves the isomerization of substituted allyl groups to the corresponding vinyl groups on the metal surface. An investigation of allyl and vinyl ligands in the presence of our mixed Rh/Os system was, therefore, of interest to us, particularly as it relates to C−C bond formation,[7] and is reported herein. Related studies on binuclear ruthenium complexes had previously shown an extensive chemistry of bridging vinyl groups,[8] suggesting tremendous potential for our heterobinuclear species.

Experimental Section

General Comments. All solvents were dried and deoxygenated immediately before use. Sodium benzophenone ketyl was used as the drying agent for all the solvents except dichloromethane, which was distilled over P_2O_5. Rhodium(III) chloride trihydrate was purchased from Johnson Matthey Ltd., $Os_3(CO)_{12}$ was purchased from Sudtek, and $Ph_2PCH_2PPh_2$ (dppm), $HBF_4{\cdot}Me_2O$, $CH_3SO_3CF_3$, 3-methyl-1,2-butadiene, and $[(Ph_3P)_2N]Cl$ were obtained from Aldrich. The 99% carbon-13-enriched carbon monoxide was purchased from Isotec, Inc. The compounds $[RhOs(H)(CO)_3(dppm)_2]$ (**1**)[9] and $[RhOs(CO)_4(dppm)_2][BF_4]$ (**2**)[5a] were prepared by the published procedures.

The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AM-400 spectrometer operating at 400.1, 162.0, and 100.6 MHz for the respective nuclei, whereas $^{13}C\{^{31}P,^1H\}$ spectra were recorded on a Bruker AM-200 spectrometer operating at 50.3 MHz. All NMR spectra were recorded in CD_2Cl_2 or THF-d_8, with the deuterated solvent serving as a lock for the spectrometer. The infrared spectra were run on a Nicolet Magna 750 FTIR spectrometer as solids in Nujol on KBr plates. Elemental analyses were performed by the microanalytical service within the department. Spectroscopic data for all compounds are given in Table 1.

Preparation of the Compounds. (a) $[RhOs(C(CH_3){=}CH_2)(CO)_3(dppm)_2]$ (3). Allene or propyne was passed over a solution of $[RhOs(H)(CO)_3(dppm)_2]$ (**1**; 200 mg, 0.174 mmol) in 20 mL of CH_2Cl_2 for 3 min, causing an immediate color change from yellow-orange to orange. The solution was then stirred under allene or propyne for 30 min, and the solvent was removed in vacuo. The dark orange residue was recrystallized from CH_2Cl_2/Et_2O, washed with 3 × 20 mL of Et_2O, and dried in vacuo, yielding a bright orange powder. Yield: 0.155g, 0.131 mmol, 75%. Anal. Calcd for $C_{56}H_{59}O_3OsP_4Rh$: C, 56.67; H, 4.16. Found: C, 56.41; H, 3.93. If the allene reaction was carried out without recrystallization, the sample was found to contain approximately 10% of compound **4**.

(b) $[RhOs(\eta^3\text{-}C_3H_5)(CO)_3(dppm)_2]$ (4). Diallylmagnesium was prepared by addition of 1 mL of 2.0 M allylmagnesium chloride in THF to 9 mL of dioxane. Five milliliters of the resulting solution (0.5 mmol) was filtered and added to $[RhOs(CO)_4(dppm)_2][BF_4]$ (**2**; 95 mg, 0.075 mmol), suspended in 100 mL of THF, causing gradual dissolution of the yellow crystals and a color change to orange. After the reaction mixture was stirred for 2.5 h, the solvent was removed in vacuo and the residue washed with 2 × 10 mL of pentane, extracted into THF/Et_2O (10 mL/20 mL), and filtered. The solvent was removed in vacuo, and the bright orange residue was crystallized by slow addition of Et_2O to a saturated THF solution to form a bright orange powder. Yield: 0.035 mg, 0.029 mmol, 39%. Satisfactory elemental analyses could not be obtained due to difficulties in separating **4** from $Mg(BF_4)_2$.

(c) $[RhOs(C(CH_3){=}C(CH_3)_2)(CO)_3(dppm)_2]$ (5). 3-Methyl-1,2-butadiene (9.4 μL, 0.096 mmol) was added to a solution of **1** (110 mg, 0.096 mmol) in 5 mL of CH_2Cl_2, causing a darkening of the orange solution. After the reaction mixture was stirred for 2 h, the solvent was reduced to 2 mL. Slow addition of 20 mL of Et_2O resulted in the formation of a yellow-orange microcrystalline solid. The pale orange supernatant was discarded, and the solid was washed with 3 × 20 mL of Et_2O and dried in vacuo. Yield: 0.88 g, 0.072 mmol, 76%. Anal. Calcd for $C_{58}H_{53}O_3OsP_4Rh$: C, 57.33; H, 4.40. Found: C, 57.15; H, 4.58.

(d) $[RhOs(C(O)C(CH_3){=}CH_2)(CO)_3(dppm)_2]$ (6). $[RhOs(C(CH_3){=}CH_2)(CO)_3(dppm)_2]$ (**3**; 150 mg, 0.126 mmol) was dissolved in 20 mL of CH_2Cl_2, and CO gas was passed over the solution for 3 min, causing a darkening of the orange solution. The solution was stirred under CO for 1 h, and the solvent was removed in vacuo. The dark orange residue was recrystallized from CH_2Cl_2/Et_2O/hexanes to yield a dark orange powder. Yield: 118 mg, 0.097 mmol, 77%.

(e) $[RhOs(C(CH_3){=}CH_2)(CH_3)(CO)_3(dppm)_2][CF_3SO_3]$ (7a,b). *Method (i):* Methyl triflate (4.8 μL, 6.9 mg, 0.042 mmol) was added to a stirred solution of $[RhOs(C(CH_3){=}CH_2)(CO)_3(dppm)_2]$ (**3**; 50 mg, 0.042 mmol) in 10 mL of CH_2Cl_2 at −80 °C. The solution was stirred at −80 °C for 30 min and allowed to slowly warm to ambient temperature. The solvent was removed in vacuo, and the residue was recrystallized from CH_2Cl_2/Et_2O. Yield: 36 mg, 63%. *Method ii*: Methyl triflate (12 μL, 17 mg, 0.104 mmol) was added to a solution of $[RhOs(H)(CO)_3(dppm)_2]$ (**1**; 120 mg, 0.104 mmol) in 30 mL of CH_2Cl_2 at −80 °C, and the solution was warmed to −40 °C and stirred for 1 h. Allene gas was then passed over the solution for 2 min. The solution was stirred under allene and gradually allowed to return to ambient temperature. The solution volume was then reduced to 5 mL, and 30 mL of Et_2O was added, causing precipitation of a fine, pale yellow powder, which was washed with 3 × 10 mL of Et_2O and dried in vacuo. The residue was then recrystallized from CH_2Cl_2/Et_2O. Yield: 70 mg, 50%. Anal. Calcd for $C_{58}H_{52}F_3O_6OsP_4RhS$: C, 51.56; H, 3.88. Found: C, 51.21; H, 3.91.

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(f) $[RhOs(C(CH_3){=}C(CH_3)_2)(CH_3)(CO)_3(dppm)_2][CF_3SO_3]\cdot 2CH_2Cl_2$ (8a,b). Methyl triflate (3.5 μL, 5 mg, 0.031 mmol) was added to a cloudy, yellow-orange solution of $[RhOs(C(CH_3){=}C(CH_3)_2)(CO)_3(dppm)_2]$ (**5**; 35 mg, 0.029 mmol) in 10 mL of CH_2Cl_2. Over 15 min, the cloudiness disappeared and the color changed to yellow. After 1 h of stirring, the solvent was removed in vacuo and the residue was recrystallized from CH_2Cl_2/Et_2O to give a yellow, microcrystalline solid. Yield: 25 mg, 0.018 mmol, 63%. Anal. Calcd for $C_{61.25}H_{56.25}Cl_{0.25}F_3O_6OsP_4RhS$: C, 51.96; H, 4.08; Cl, 0.64. Found: C, 51.72; H, 3.71; Cl, 0.69. Note: Crystals desolvated rapidly. Analysis sample contained 0.125 mol equiv of cocrystallized CH_2Cl_2.

(g) $[RhOs(C(CH_3){=}CH_2)(H)(CO)_3(dppm)_2][BF_4]$ (9a,b). $HBF_4\cdot Et_2O$ (4.5 μL, 5.34 mg, 0.33 mmol) was added to a stirred solution of $[RhOs(C(CH_3){=}CH_2)(CO)_3(dppm)_2]$ (**3**; 39 mg, 0.033 mmol) at −80 °C, causing the color to change from orange to yellow. The solution was stirred at −80 °C for 30 min and then allowed to warm to ambient temperature. The solvent was removed in vacuo, and the residue was recrystallized from CH_2Cl_2/Et_2O, washed with 3 × 10 mL of Et_2O, and dried in vacuo, resulting in a pale yellow powder. Yield: 25 mg, 0.020 mmol, 60%.

(h) $[RhOs(C(CH_3){=}C(CH_3)_2)(H)(CO)_3(dppm)_2][BF_4]$ (10a,b). $HBF_4\cdot Me_2O$ (4.4 μL, 4.8 mg, 0.036 mmol) was added to a solution of **5** (44 mg, 0.036 mmol) in 15 mL of CH_2Cl_2, causing an immediate change from cloudy orange to clear yellow. After 1 h, the solvent was removed in vacuo and the residue was recrystallized from CH_2Cl_2/Et_2O to yield a yellow microcrystalline solid. Yield: 33 mg, 0.025 mmol, 70%. Anal. Calcd for $C_{58}H_{54}BF_4O_3OsP_4Rh$: C, 53.47; H, 4.18. Found: C, 52.97; H, 4.18.

(i) $[RhOs(C(O)C(CH_3){=}CH_2)(\mu\text{-}H)(CO)_3(dppm)_2][BF_4]$ (11). $HBF_4\cdot Me_2O$ (5.0 μL, 5.5 mg, 0.041 mmol) was added to a stirred solution of **6** (50 mg, 0.041 mmol) in 10 mL of CH_2Cl_2 at −80 ° C, causing an immediate color change from orange to yellow-orange. The solution was stirred at −80 °C for 30 min and then allowed to warm to ambient temperature. The solvent was removed in vacuo, and the residue was recrystallized from CH_2Cl_2/Et_2O to give a pale yellow powder. Yield: 37 mg, 0.028 mmol, 69%.

(j) $[RhOs({=}C(CH_3)_2)(H)(CO)_3(dppm)_2][BF_4]_2$ (14). The compound $[RhOs(C(CH_3){=}CH_2)(CO)_3(dppm)_2]$ (**3**; 13 mg, 0.011 mmol) was dissolved in 0.5 mL of CD_2Cl_2 and cooled to −80 °C. $HBF_4\cdot Me_2O$ (3.3 μL, 3.7 mg, 0.027 mmol) was added, and NMR spectra at −80 °C showed quantitative conversion to **14**. At temperatures above 0 °C, compound **14** was unstable, decomposing into **9a,b** and other unidentified products.

(k) $[RhOs({=}C(CH_3)_2)(CH_3)(CO)_3(dppm)_2][BF_4][CF_3SO_3]$ (15). The compound $[RhOs(C(CH_3){=}CH_2)(CH_3)(CO)_3(dppm)_2][CF_3SO_3]$ (**7a,b**; 4 mg, 0.003 mmol) was dissolved in 0.5 mL of CD_2Cl_2 and cooled to −40 °C. $HBF_4\cdot Me_2O$ (2 μL, 2.2 mg, 0.016 mmol) was added, and NMR spectra showed quantitative conversion to **15** at −40 °C. At temperatures above 0 °C, the sample was unstable, decomposing into **7a,b** and other unidentified products.

(l) $[RhOs({=}C(OH)C(CH_3){=}CH_2)(\mu\text{-}H)(CO)_3(dppm)_2][BF_4]_2$ (16). The compound $[RhOs(C(O)C(CH_3){=}CH_2)(CO_3)(dppm)_2]$ (**6**; 20 mg, 0.016 mmol) was dissolved in 0.5 mL of CD_2Cl_2 and cooled to −80 °C. $HBF_4\cdot Me_2O$ (4 μL, 4.4 mg, 0.33 mmol) was added, and the reaction was monitored by NMR. At −80 °C, compound **11** formed quantitatively. At temperatures above −40 °C, **11** transformed into **16**, which persisted in solution at ambient temperature for up to 2 h, but decomposed upon workup.

Reactions. (a) Reaction of $[RhOs(C(CH_3){=}CH_2)(H)(CO)_3(dppm)_2][BF_4]$ (9a,b) with CO. (i) Compound **9** (10 mg, 0.0078 mmol) was dissolved in 0.5 mL of CD_2Cl_2 in an NMR tube, which was then evacuated and refilled with ^{13}CO to approximately 1.2 atm. ^1H, ^{31}P, and ^{13}C NMR spectra showed complete conversion to two isomeric intermediates $[RhOs(C(CH_3){=}CH_2)(\mu\text{-}H)(CO)_3(dppm)_2][BF_4]$ (**12a,b**). The intermediates ultimately yielded $[RhOs(CO)_4(dppm)_2][BF_4]$ and $H_2C{=}C(H)CH_3$, with **12a** reacting slowly, over a 20 h period, while **12b** disappeared within 2 h. (ii) The reaction was repeated as above, but the CO was removed by evacuating the tube and refilling with Ar after 2 min. NMR spectra showed complete conversion to **12a,b**. In the absence of CO, **12a,b** reacted slowly over 48 h to form a mixture of $[RhOs(CO)_4(dppm)_2][BF_4]$ and $[RhOs(CO)_3(\mu\text{-}H)(\mu^2\text{-}\eta^3\text{-}(o\text{-}C_6H_4)PhPCH_2PPh_2)(dppm)][BF_4]$, along with decomposition products.

(b) Reaction of $[RhOs(C(CH_3){=}C(CH_3)_2)(H)(CO)_3(dppm)_2][BF_4]$ (10a,b) with CO. Compound **10** (10 mg, 0.0077 mmol) was dissolved in 0.5 mL of CD_2Cl_2 in an NMR tube, which was then evacuated and refilled with ^{13}CO to approximately 1.2 atm. ^1H, ^{31}P, and ^{13}C NMR spectra showed slow formation of two isomeric intermediates $[RhOs(C(CH_3){=}C(CH_3)_2)(\mu\text{-}H)(CO)_3(dppm)_2][BF_4]$ (**13a,b**), with the starting materials completely disappearing in approximately 2 h. The intermediates ultimately yielded $[RhOs(CO)_4(dppm)_2][BF_4]$ and $(CH_3)_2C{=}C(H)CH_3$; **13a** reacted slowly, persisting for days in solution, but **13b** disappeared within 2 h, once the starting compounds were depleted.

(c) Reaction of $[RhOs(C(O)C(CH_3){=}CH_2)(CO)_3(dppm)_2]$ (6) with $CH_3SO_3CF_3$. Compound **6** (20 mg, 0.016 mmol) was dissolved in 0.5 mL of CD_2Cl_2 and cooled to −80 °C. Methyl triflate (1.8 μL, 2.7 mg, 0.016 mmol) was added, and the reaction was monitored by NMR. No reaction was observed up to −30 °C. At this temperature, three products began to form simultaneously, and conversion to these products, along with several minor products, was complete at ambient temperature. The mixture of products could not be separated, but spectroscopic evidence suggests that a mixture of $[RhOs({=}C(OMe)C(CH_3){=}CH_2)(CO)_3(dppm)_2][CF_3SO_3]$ and two isomers of $[RhOs(C(O)C(CH_3){=}CH_2)(CH_3)(CO)_3(dppm)_2][CF_3SO_3]$ were formed.

X-ray Data Collection. (a) $[RhOs(C(CH_3){=}CH_2)(CO)_3(dppm)_2]$ (3). Diffusion of ether into a concentrated CH_2Cl_2 solution of complex **3** yielded deep red-orange crystals, which were mounted and flame-sealed in glass capillaries under N_2 and solvent vapor to minimize decomposition and/or solvent loss. Data were collected on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation at 22 °C. Unit-cell parameters were obtained from a least-squares refinement of the setting angles of 24 reflections in the range 17.3° ≤ 2θ ≤ 25.6°. The cell parameters indicated a triclinic space group, and the lack of systematic absences indicated either $P1$ or $P\bar{1}$ with $Z = 1$. The centrosymmetric space group $P\bar{1}$ was confirmed as the correct choice by the successful solution and refinement of the structure, with the molecule being inversion-disordered (vide infra). Intensity data were collected as outlined in Table 2. Three reflections were chosen as intensity standards and were remeasured every 120 min of X-ray exposure time; no decay was evident.

(b) $[RhOs(C(CH_3){=}C(CH_3)_2)(CH_3)(CO)_3(dppm)_2][CF_3SO_3]\cdot 2CH_2Cl_2$ (8a,b). Yellow crystals of **8** were grown by slow diffusion of ether into a concentrated CH_2Cl_2 solution and mounted as for compound **3**. Data collection for compound **8** proceeded as for **3**, except at −50 °C. Unit-cell parameters, obtained from 20 reflections in the range 20° ≤ 2θ ≤ 25°, and the systematic absences uniquely defined the space group as $P2_1/c$.

Structure Solution and Refinement. (a) $[RhOs(C(CH_3){=}CH_2)(CO)_3(dppm)_2]$ (3). Initial attempts to solve and refine the structure of complex **3** in the space group $P1$ were unsuccessful, however, solution in $P\bar{1}$ proceeded well, with the molecule disordered about an inversion center. Similar disorder had been observed in a number of related compounds.[5b,9] The position of the disordered Os/Rh atom was obtained through use of the direct-methods program SHELXS-86.[10] The remaining non-hydrogen atoms were located using successive difference Fourier maps. The positions of the atoms

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Table 1. Spectroscopic Parameters for the Compounds[a]

		NMR[d]		
compound	IR,[b] $\mathrm{cm^{-1}}$	$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$
$[\mathrm{RhOs(C(CH_3){=}CH_2)(CO)_3(dppm)_2}]$ (**3**)	1910 (ss), 1861 (ss), 1725 (ss)	RhP: 31.23 ($^1J_{\mathrm{Rh-P}} =$ 158 Hz) OsP: 5.54	PCH_2P: (25 °C) 3.44 (b, 4H); (0 °C) 3.25 (m, 2H), 3.19 (m, 2H); (75 °C) 3.46 (pq, 4H, $J = 5$ Hz)[h] RhC=CH_2: 3.73 (bs), 4.77 (bs) RhC−CH_3: 0.76 (s, 3H)	OsCO: 195.46 (t, $^2J_{\mathrm{P-Os-C}}$ = 14 Hz), 212.24 (bs), 229.41 (bs) RhC: 181.37 (dt, $^1J_{\mathrm{RhC}} = 29$ Hz, $^2J_{\mathrm{PC}}$ = 12 Hz) RC=CH$_2$: 115.29 (t, $^3J_{\mathrm{PC}} = 6$ Hz); CH$_3$: 31.02 (t, $^3J_{\mathrm{PC}} = 4$ Hz)
$[\mathrm{RhOs(CH_2CH{=}CH_2)(CO)_3(dppm)_2}]$ (**4**)[e] (a) 20 °C	1910 (sb), 1852 (sb), 1715 (sb)	RhP: 27.34 (vb) OsP: 1.32	PCH_2P: 4.05 (bs)	OsCO: 226.5 (bs, 2C) 189.6 (bs, 1C)
(b) −80 °C		P_A 36.80, P_B 9.80, P_C 4.73, P_D −5.20 ($J(P_AP_B)$ = 22 Hz, $J(P_AP_C)$ = 112 Hz, $J(P_AP_D) = 35$ Hz, $J(P_BP_C) = 28$ Hz, $J(P_BP_D) = 119$ Hz, $J(P_CP_D) = 242$ Hz, $J(\mathrm{Rh}P_A) = 157$ Hz, $J(\mathrm{Rh}P_B) = 125$ Hz)	CH_C: 5.55 PCH_2P: 4.46, 4.12, 3.85, 3.07 CH_S: 2.53, 1.30 CH_A: 0.99, 0.22	OsCO: 188.3 (bs); 204.7 (bs); 253.4 (bs)
$[\mathrm{RhOs(C(CH_3){=}C(CH_3)_2)(CO)_3(dppm)_2}]$ (**5**)	1924 (ss), 1875(ss), 1707(ss)	RhP: 28.52 ($^1J_{\mathrm{Rh-P}} =$ 160 Hz) OsP: 4.79	PCH_2P: 3.4 (m, 2H), 3.5 (m, 2H) RhC−CH_3: 0.95 (s, 3H) RhC=C(CH_3)$_2$: 0.80 (bs, 3H), 0.40 (bs, 3H)	OsCO: 196.7 (tm, $^2J_{\mathrm{OsP-C}} = 15$ Hz), 216.7 (bm), 228.2 (bs)
$[\mathrm{RhOs(C(O)C(CH_3){=}CH_2)(CO)_3(dppm)_2}]$ (**6**)	1934(m), 1882(ss), 1720(m), 1555(ms)[c]	RhP: 27.20 ($^1J_{\mathrm{Rh-P}} =$ 164 Hz) OsP: 4.56	PCH_2P: 3.45 (bm, 4H) RhC=CH_2: 5.04 (bs), 6.07 (bs) RhC−CH_3: 0.66 (s, 3H)	OsCO: 194.10 (m), 206.38 (bs), 230.47 (bs) RhCO: 271.93 (dt, $^1J_{\mathrm{Rh-C}}$ = 31 Hz, $^2J_{\mathrm{RhP-C}}$ = 5 Hz)
$[\mathrm{RhOs(C(CH_3){=}CH_2)(CH_3)(CO)_3(dppm)_2}][\mathrm{CF_3SO_3}]$ (**7a**)	2032 (sb), 1840 (mb), 1805 (sb) (both isomers)	RhP: 21.74 ($^1J_{\mathrm{Rh-P}} =$ 150 Hz) OsP: −5.07	PCH_2P: 3.38 (m, 2H), 3.26 (m, 2H) RhC=CH_2: 5.11 (s, 1H), 4.18 (s, 1H) RhC−CH_3: 1.05 (s, 3H) OsCH_3: −0.23 (t, 3H, $^3J_{\mathrm{OsP-H}} = 6.5$ Hz)	OsCO: 179.4 (m), 201.9 (s), 230 (m)
7b		RhP: 22.24 ($^1J_{\mathrm{Rh-P}} =$ 158 Hz) OsP: −5.93	PCH_2P: 3.45 (bm, 4H) RhC=CH_2: 5.11 (bs, 1H), 4.58 (bs, 1H) RhC−CH_3: 0.88 (s, 3H) OsC$H_{3:}$ −0.12 (t, 3H, $^3J_{\mathrm{OsP-H}} = 6.5$ Hz)	OsCO: 179.4 (m), 203.5 (s), 230 (m)
$[\mathrm{RhOs(C(CH_3){=}C(CH_3)_2)(CH_3)(CO)_3(dppm)_2}][\mathrm{CF_3SO_3}]$ (**8a**)	2041 (ss), 1860 (w), 1808 (ss)	RhP: 19.31 ($^1J_{\mathrm{Rh-P}} =$ 154 Hz) OsP: −4.79	PCH_2P: 3.35 (m, 4H) RhC−CH_3: 1.15 (s, 3H) RhC=C(CH_3)$_2$: 0.90 (bs, 3H), 0.40 (bs, 3H) OsC$H_{3:}$ −0.3 (t, 3H $^3J_{\mathrm{OsP-H}} = 6.5$ Hz)	OsCO: 180.8 (m); 204.4 (t, $^2J_{\mathrm{OsP-C}} = 5$ Hz); 231.5 (bm)
8b	2032 (sh), 1832 (w), 1789 (ms)	RhP: 19.80 ($^1J_{\mathrm{Rh-P}} =$ 152 Hz) OsP: −6.29	PCH_2P: 3.44 (m, 4H) RhC−CH_3: 1.05 (s, 3H) RhC=C(CH_3)$_2$: 0.90 (bs), 0.50 (bs) OsC$H_{3:}$ −0.1 (t, $^3J_{\mathrm{OsP-H}} = 7$ Hz)	OsCO: 180.1 (m); 201.6 (bm); 233.0 (m)
$[\mathrm{RhOs(C(CH_3){=}CH_2)(H)(CO_3)(dppm)_2}][\mathrm{BF_4}]$ (**9a**)	2033 (ms), 1984 (ss), 1942 (ms), 1799 (mb), 1770(sb) (both isomers)	RhP: 22.88 ($^1J_{\mathrm{Rh-P}} =$ 149 Hz) OsP: −1.24	PCH_2P: 3.3 (m, 4H) RhC=CH_2: 5.2 (s, 1H), 4.55 (s, 1H) RhC−CH_3: 0.75 (s, 3H) OsH: −6.8 (t, 1H, $^2J_{\mathrm{OsP-H}} = 18$ Hz)	
9b		RhP: 24.40 ($^1J_{\mathrm{Rh-P}} =$ 149 Hz) OsP: −1.24	PCH_2P: 3.4 (m, 4H) RhC=CH_2: 5.1 (s, 1H), 3.9 (s, 1H) RhC−CH_3: 1.15 (s, 3H) OsH: −6.7 (t, 1H, $^2J_{\mathrm{OsP-H}} = 18$ Hz)	
$[\mathrm{RhOs(C(CH_3){=}C(CH_3)_2)(H)(CO)_3(dppm)_2}][\mathrm{BF_4}]$ (**10a**)	2027 (ss), 1859 (w), 1815 (mb)	RhP: 21.19 ($^1J_{\mathrm{Rh-P}} =$ 153 Hz) OsP: −1.70	PCH$_2$P: 3.45 (m, 2H), 3.3 (m, 2H) RhC−CH_3: 0.93 (t, 3H, $^4J_{\mathrm{RhP-H}} < 2$ Hz) RhC=C(CH_3)$_2$: 0.83 (s, 3H), 0.65 (s, 3H) OsH: −7.02 (t, 1H, $^2J_{\mathrm{OsP-H}} = 16$ Hz)	OsCO: 178.6 (dm, $^1J_{\mathrm{C-C}} =$ 24 Hz), 208.5 (dm, $^1J_{\mathrm{Rh-C}} = 13$ Hz), 223.7 (ddm, $^1J_{\mathrm{Rh-C}} = 25$ Hz, $^2J_{\mathrm{C-C}} = 24$ Hz)
10b	2044 (ms), 1888 (w), 1793 (ms)	RhP: 20.49 ($^1J_{\mathrm{Rh-P}} =$ 132 Hz) OsP: −1.57	PCH_2P: 3.45 (m, 2H), 3.3 (m, 2H) RhC−CH_3: 0.89 (t, 3H, $^4J_{\mathrm{RhP-H}} < 2$ Hz) RhC=C(CH_3)$_2$: 1.29 (s, 3H), 0.17 (s, 3H) OsH: −6.55 (t, 1H, $^2J_{\mathrm{OsP-H}} = 17$ Hz)	OsCO: 178.1 (dm, $^1J_{\mathrm{C-C}} =$ 24 Hz); 203.7 (dm, $^1J_{\mathrm{Rh-C}} = 8$ Hz); 224.5 (ddm, $^1J_{\mathrm{Rh-C}} = 29$ Hz, $^2J_{\mathrm{C-C}} = 24$ Hz)

Table 1 (Continued)

compound	IR,[b] cm^{-1}	NMR[d] $\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$
$[RhOs(C(O)C(CH_3){=}CH_2)(\mu\text{-}H)(CO)_3(dppm)_2][BF_4]$ (**11**)	2044 (ss), 1981 (ss), 1755 (ss), 1587 (ss)[c]	Rh*P*: 17.33 ($^1J_{Rh-P}$ = 153 Hz) Os*P*: −3.89	PC*H*$_2$P: 3.34(m, 2H), 3.07(m, 2H) RhC=C*H*$_2$: 5.88 (s, 1H), 4.95 (s, 1H) RhC−C*H*$_3$: 0.52 (s, 3H) Os*H*Rh: −8.82 (bm)	Os*C*O: 174.17 (s); 179.97 (dt, $^2J_{CC}$ = 22 Hz, $^2J_{PC}$ = 9 Hz); 234.26 (dd, $^2J_{CC} = {}^1J_{RhC}$ = 22 Hz) Rh*C*O: 254.05 (d, $^1J_{Rh-C}$ = 31 Hz)
$[RhOs(C(CH_3){=}CH_2)(\mu\text{-}H)(CO)_3(dppm)_2][BF_4]$ (**12a**)		Rh*P*: 26.23 ($^1J_{Rh-P}$ = 149 Hz) Os*P*: −4.64	PC*H*$_2$P: 3.34(m, 2H), 3.07(m, 2H) RhC=C*H*$_2$: 5.84 (bs, 1H), 4.64 (m, 1H) RhC−C*H*$_3$: 1.58 (s, 3H) Os*H*Rh: −8.90 (bm)	
12b		Rh*P*: 24.47 ($^1J_{Rh-P}$ = 114 Hz) Os*P*: −5.75	PC*H*$_2$P: 3.34(m, 2H), 3.07(m, 2H) RhC=C*H*$_2$: 6.59 (bs, 1H), 5.02 (m, 1H) RhC−C*H*$_3$: 1.15 (s, 3H) Os*H*Rh: −12.41 (bm)	
$[RhOs(C(CH_3){=}C(CH_3)_2)(\mu\text{-}H)(CO)_3(dppm)_2][BF_4]$ (**13a**)		Rh*P*: 23.59 ($^1J_{Rh-P}$ = 153 Hz) Os*P*: −5.96	PC*H*$_2$P: 3.4 (bm) RhC−C*H*$_3$: 1.67 (t, 3H, $^4J_{RhP-H}$ < 2 Hz) RhC=C(C*H*$_3$)$_2$: 1.60 (s, 3H), 1.01 (s, 3H) Os*H*Rh: −8.38 (bm)	Os*C*O: 175.1 (s); 180.6 (m), 233.7 (dm, $^1J_{Rh-C}$ = 35 Hz)
13b		Rh*P*: 23.5 ($^1J_{Rh-P}$ = 153 Hz) Os*P*: −6.25	PC*H*$_2$P: 3.4 (bm) RhC−C*H*$_3$: 0.77 (t, 3H, $^4J_{RhP-H}$ = 2 Hz) RhC=C(C*H*$_3$)$_2$: 0.86 (s, 3H), 0.57 (s, 3H) Os*H*Rh: −8.8 (bm)	Os*C*O: 175.5 (s); 179.9 (m); 233.7 (dm, $^1J_{Rh-C}$ = 23 Hz)
$[RhOs({=}C(CH_3)_2(H)(CO)_3(dppm)_2][BF_4]_2$ (**14**)		Rh*P*: 19.0 ($^1J_{Rh-P}$ = 135 Hz) Os*P*: −4.80	PC*H*$_2$P: 3.7 (m, 2H), 3.6 (m, 2H) RhC−C*H*$_3$: 2.65 (s, 3H), 2.18 (s, 3H) Os*H*: −6.21 (t, $^2J_{P-H}$ = 13 Hz)	Os*C*O: 172.8 (t, $^2J_{P-C}$ = 9 Hz); 193.1 (bs); 204.0 (dt, $^1J_{Rh-C}$ = 10 Hz, $^2J_{P-C}$ = 3 Hz) Rh=*C*(CH$_3$)$_2$: 377.9 (dt, $^1J_{Rh-C}$ = 35 Hz, $^2J_{P-C}$ = 5 Hz) Rh=C(*C*H$_3$)$_2$: 63.6 (s), 60.6 (s)
$[RhOs({=}C(CH_3)_2)(CH_3)(CO)_3(dppm)_2][BF_4][CF_3SO_3]$ (**15**)		Rh*P*: 17.67 ($^1J_{Rh-P}$ = 136 Hz) Os*P*: −8.00	PCH$_2$P: 3.66 (m, 4H) RhC−C*H*$_3$: 2.62 (s, 3H), 2.38 (s, 3H) OsC*H*$_3$: −0.10 (t, $^3J_{P-H}$ = 8 Hz)	
$[RhOs({=}C(OH)C(CH_3){=}CH_2)(\mu\text{-}H)(CO)_3(dppm)_2][BF_4]$ (**16**)	2060(ss), 2002(ss), 1756(wb)[f]	Rh*P*: 24.80 ($^1J_{Rh-P}$ = 115 Hz) Os*P*: −5.84	PC*H*$_2$P: 4.14 (m, 2H), 3.85(m, 2H) C=C*H*$_2$: 5.61 (s), 4.30 (s) C−C*H*$_3$: 1.06 (s, 3H) Os*H*Rh: −9.85 (bm) O*H*: 9.56 (s)[g]	Os*C*O: 172.5 (s); 175.7 (dt, $^2J_{C-C}$ = 27 Hz, $^2J_{P-C}$ = 9 Hz); 234.8 (dd, $^1J_{Rh-C} = {}^2J_{P-C}$ = 27 Hz) Rh=*C*: 301.2 (dt, $^1J_{Rh-C}$ = 49 Hz, $^2J_{P-C}$ = 8 Hz)

[a] IR abbreviations: ss = strong sharp, ms = medium sharp, ws = weak sharp, sb = strong broad, mb = medium broad, wb = weak broad, m = medium, w = weak, sh = shoulder. NMR abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dm = doublet of multiplets, ddm = doublet of doublets of multiplets, tm = triplet of multiplets, bs = broad singlet, bm = broad multiplet. [b] Nujol mull. Values quoted are ν(CO) except as indicated. [c] ν(C=C). [d] $^{31}P\{^1H\}$ chemical shifts are referenced vs external 85% H_3PO_4, while ^1H and $^{13}C\{^1H\}$ are referenced vs external TMS. Chemical shifts for the phenyl hydrogens are not given in the ^1H NMR data. Spectra were recorded in CD_2Cl_2 except as indicated. [e] Spectra recorded in THF-d_8. [f] Recorded in CH_2Cl_2 solution. [g] Observed only in the triflate analogue. [h] Recorded in benzene-d_6.

of the carbonyl and isopropenyl ligands were resolved without difficulty, despite the disorder; the carbon atom C(1) (belonging to the osmium-bound carbonyl C(1)O(1) and the isopropenyl ligand $H_3C(4){-}C(1'){=}C(5)H_2$) and the oxygen atom O(2) (belonging to the carbonyl groups C(2)O(2) and C(3)O(2′)) were included at full occupancy, while the other atoms (O(1), C(2), C(3), C(4), and C(5)) were refined at half occupancy. A view of the equatorial plane of the complex showing the atom positions corresponding to the two superimposed molecules is shown in Figure 1. Refinement was completed using the program SHELXL-93.[11] The diphosphine unit was well-behaved. Hydrogen atom positions were calculated by assuming idealized sp^2 or sp^3 geometries about their attached carbons as appropriate; these hydrogens were given thermal parameters equal to 120% of the equivalent isotropic displacement parameters of their attached carbons. After all of the atoms had been located and the structure was refined to convergence, using isotropic displacement parameters, the data were corrected for absorption using the method of Walker and Stuart.[12] The structure was further refined with all non-hydrogen atoms having anisotropic thermal parameters. The final model for complex **3**, with 316 parameters varied, converged to a value of R1 = 0.0300. Atomic coordinates and displacement parameters for the non-hydrogen core atoms are given in the Supporting Information, and selected bond lengths and angles are given in Tables 3 and 4, respectively.

(b) $[RhOs(C(CH_3){=}C(CH_3)_2)(CH_3)(CO)_3(dppm)_2][CF_3SO_3]\cdot 2CH_2Cl_2$ (8a,b). The structure of compound **8** was disordered due to the presence of two isomers in the crystal, resulting in the superposition of two differently oriented trimethylvinyl groups as shown (one ligand fragment consists of unprimed atoms while the other has primed atom labels; atoms C(6) and C(8) correspond to the superposition of methyl group positions from both isomers).

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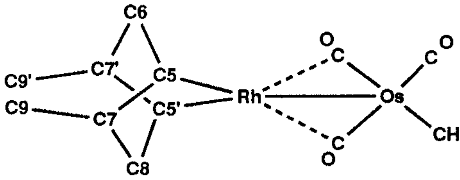
(11) Sheldrick, G. M. *SHELXL-93. Program for crystal structure determination*; University of Göttingen, Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of those having $F_o^2 > -3\sigma(F_o^2)$). Weighted *R* factors wR2 and all goodnesses of fit are based on F_o^2; conventional R factors R1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R1 and is not relevant to the choice of reflections for refinement. *R* factors based on F_o^2 are statistically about twice as large as those based on F_o, and *R* factors based on ALL data will be even larger.

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

Table 2. Crystallographic Experimental Details

	[RhOs(C(CH$_3$)=CH$_2$)(CO)$_3$(dppm)$_2$] (**3**)	[RhOs(C(CH$_3$)=C(CH$_3$)$_2$)(CO)$_3$-(CH$_3$)(dppm)$_2$][CF$_3$SO$_3$]·2CH$_2$Cl$_2$ (**8**)
	A. Crystal Data	
formula	$C_{56}H_{49}O_3OsP_4Rh$	$C_{62}H_{60}Cl_4F_3O_6OsP_4RhS$
fw	1186.94	1579.92
cryst dimens (mm)	0.66 × 0.55 × 0.35	0.39 × 0.20 × 0.10
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
unit cell parameters[a]		
a (Å)	11.247(2)	20.445(2)
b (Å)	11.737(2)	10.3890(12)
c (Å)	11.061(3)	29.300(3)
α (deg)	113.72(2)	90
β (deg)	93.24(2)	98.231(10)
γ (deg)	68.567(15)	90
V (Å^3)	1237.3(4)	6159.3(11)
Z	1	4
ρ_{calcd} (g cm^{-3})	1.593	1.704
μ (cm^{-1})	30.71	27.27
	B. Data Collection and Refinement Conditions	
diffractometer	Enraf-Nonius CAD4[b]	Enraf-Nonius CAD4[b]
radiation (λ[Å])	Mo Kα (0.710 73)	Mo Kα (0.710 73)
monochromator	incident-beam, graphite crystal	incident-beam, graphite crystal
temperature (°C)	22	−50
scan type	$\theta-2\theta$	$\theta-2\theta$
data collection, 2θ limit (deg)	56.0	50.0
total data collected	6248 ($-13 \leq h \leq 14$, $0 \leq k \leq 15$, $-14 \leq l \leq 13$)	10991 ($-24 \leq h \leq 24$, $0 \leq k \leq 12$, $0 \leq l \leq 34$)
no. of independent reflns	5959	10754
no. of observations (NO)	5367 ($F_o^2 \geq 2\sigma(F_o^2)$)	5757 ($F_o^2 \geq 2\sigma(F_o^2)$)
structure solution method	direct methods (*SHELXS-86*)[c]	direct methods (*SHELXS-86*)[c]
refinement method	full-matrix least-squares on F^2 (*SHELXL-93*)[c]	full-matrix least-squares on F^2 (*SHELXL-93*)[d]
abs corr method	*DIFABS*[e]	*DIFABS*[e]
range of abs corr factors	1.195−0.835	1.084−0.853
data/restraints/parameters	5959 ($F_o^2 \geq -3\sigma(F_o^2)$)/0/316	10738 ($F_o^2 \geq -3\sigma(F_o^2)$)/1[b]/753
goodness-of-fit (S)[g]	1.191 ($F_o^2 \geq -3\sigma(F_o^2)$)	1.006 ($F_o^2 \geq -3\sigma(F_o^2)$)
final R indices[h]		
$F_o^2 > 2\sigma(F_o^2)$	R1 = 0.0300, wR2 = 0.900	R1 = 0.0556, wR2 = 0.0.989
all data	R1 = 0.0409, wR2 = 0.1073	R1 = 0.1758, wR2 = 0.1321
largest diff peak and hole	1.281 and −2.043 e Å^{-3}	1.604 and −1.635 e Å^{-3}

[a] Obtained from least-squares refinement of 24 reflections, with $17.3° < 2\theta < 25.6°$ for **3** and 20 reflections with $20° < 2\theta < 25°$ for **8**. [b] Programs for diffractometer operation and data collection were those supplied by Enraf-Nonius. [c] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. [d] Reference 11. [e] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158. [f] d(Rh−C(5′)) was fixed at 2.05 Å. [g] $S = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (a_1P)^2 + a_2P]^{-1}$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$), $a_1 = 0.0675$ and $a_2 = 0.3857$ for **3** and $a_1 = 0.0314$ and $a_2 = 40.2796$ for **8**. [h] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; w$R_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$.



The positions of the Rh and Os atoms were obtained through use of the direct-methods program SHELXS-86.[10] The remaining non-hydrogen atoms of the major isomer were located using successive difference Fourier maps. However, unusually large thermal parameters and severe elongation of the thermal ellipsoids for atoms C(5), C(7), and C(9) suggested the possibility of a disordered position for the vinyl group. Atoms C(5′), C(7′), and C(9′) of the minor isomer were then located using electron density contour plots. The disorder between the C(5), C(7), C(9) and C(5′), C(7′), C(9′) sets of positions did not follow an even 50:50 distribution; the most satisfactory results were obtained when C(5), C(7), and C(9) were given occupancy factors of 0.7 and C(5′), C(7′) and C(9′) were given occupancy factors of 0.3. Furthermore, the Rh−C(5′) distance was fixed at 2.05 Å (as suggested by the Rh−C(5) distance) to allow C(5′) to refine satisfactorily. Elongation of the thermal ellipsoid of C(4) (the Os-bound methyl carbon) suggested the possibility of disorder involving the superposition of the this group and carbonyl C(1)O(1). In addition, O(1′) was located on the Fourier map and refined acceptably, with an occupancy of 0.2. Attempts were made to refine the two disorder modes (the Rh-bound isopropenyl group and the Os-bound CO and Me groups) with the same occupancy, but the results were unsatisfactory, indicating that the disorder modes are independent. The position of O(1′) could result from rotamers of either the major or the minor isomer. A view of the equatorial plane of the cation of **8**, showing the disorder of the trimethylvinyl ligand is given in Figure 2. Refinement was completed using the program SHELXL-93.[11] Hydrogen atom positions for the major isomer were calculated by assuming idealized

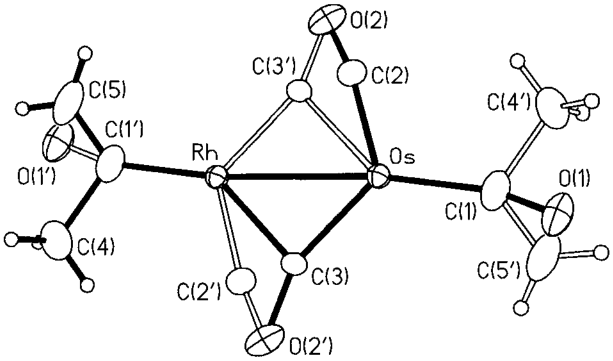


Figure 1. View of the equatorial plane of compound **3**, showing the positions of the disordered atoms. One disordered molecule is shown with dark bonds while the other has open bonds. The positions labeled Rh and Os actually contain a 50:50 occupancy of each.

Table 3. Selected Interatomic Distances (Å) for Compound 3

Os−Rh	2.8165(10)	P(1)−C(6)	1.827(4)
Os−P(1)	2.3235(11)	P(2)−C(6)	1.841(4)
Os−P(2′)	2.3173(11)	O(1)−C(1)	1.08(2)
Os−C(1)	1.955(5)	O(2)−C(2)	1.089(9)
Os−C(2)	1.874(9)	O(2′)−C(3)	1.341(8)
Os−C(3)	2.032(8)	C(1′)−C(4)	1.635(15)
Rh−C(1′)	1.955(5)	C(1′)−C(5)	1.33(2)
Rh−C(3)	2.075(8)		

Table 4. Selected Interatomic Angles (deg) in Compound 3

Rh−Os−P(1)	93.12(3)	Os−Rh−P(2)	91.98(3)
Rh−Os−P(2′)	91.98(3)	Os−Rh−C(3)	47.3(2)
Rh−Os−C(1)	172.8(2)	P(1′)−Rh−C(3)	97.8(2)
Rh−Os−C(2)	73.3(3)	P(2)−Rh−C(3)	90.3(2)
Rh−Os−C(3)	47.3(2)	C(1′)−Rh−C(3)	140.9(3)
P(1)−Os−P(2′)	171.91(3)	Os−P(1)−C(6)	113.78(13)
P(1)−Os−C(1)	87.5(2)	Rh−P(2)−C(6)	112.51(14)
P(1)−Os−C(2)	98.8(3)	Os−C(1)−O(1)	165.5(11)
P(1)−Os−C(3)	86.4(2)	Rh−C(1′)−C(4)	116.6(6)
P(2′)−Os−C(1)	86.6(2)	Rh−C(1′)−C(5)	132.8(13)
P(2′)−Os−C(2)	88.7(3)	C(4)−C(1′)−C(5)	109.9(14)
P(2′)−Os−C(3)	92.4(2)	Os−C(2)−O(2)	169.7(9)
C(1)−Os−C(2)	113.7(4)	Os−C(3)−Rh	86.6(3)
C(1)−Os−C(3)	125.7(3)	Os−C(3)−O(2′)	155.2(6)
C(2)−Os−C(3)	120.7(4)	Rh−C(3)−O(2′)	118.0(6)
Os−Rh−P(1)	93.12(3)	P(1)−C(6)−P(2)	111.6(2)

sp^2 or sp^3 geometries about their attached carbons, and the methyl groups were allowed to rotate freely. These hydrogens were given thermal parameters equal to 120% of the equivalent isotropic displacement parameters of their attached carbons. After all of the atoms had been located and the structure was refined to convergence, using isotropic displacement parameters, the data were corrected for absorption using the method of Walker and Stuart.[12] The structure was further refined with all non-hydrogen atoms of the major isomer having anisotropic thermal parameters. Atoms C(5′), C(7′), C(9′) and O(1′) were refined isotropically. The final model for complex **8**, with 753 parameters varied, converged to a value of R1 = 0.0556. Atomic coordinates and displacement parameters for the non-hydrogen core atoms are given in the Supporting Information, and selected bond lengths and angles are given in Tables 5 and 6, respectively.

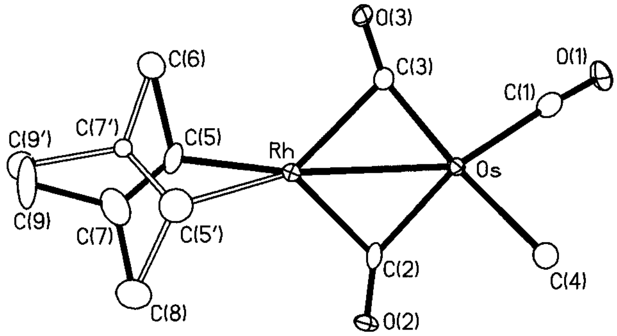


Figure 2. View of the equatorial plane of the cation of compound **8**, showing the positions of the disordered atoms of the trimethylvinyl group. The dark bonds show the predominant disordered group. The additional disorder involving the carbonyl C(1)O(1) and the methyl group carbon C(4) is not shown.

Table 5. Selected Interatomic Distances (Å) for Compound 8

Os−Rh	2.8505(9)	Rh−C(5′)	2.05
Os−P(1)	2.390(3)	O(1)−C(1)	1.089(13)
Os−P(3)	2.386(3)	O(2)−C(2)	1.167(13)
Os−C(1)	1.990(13)	C(5)−C(6)	1.65(2)
Os−C(2)	2.094(12)	C(5)−C(7)	1.27(3)
Os−C(3)	1.975(12)	C(7)−C(8)	1.52(3)
Os−C(4)	2.179(12)	C(7)−C(9)	1.53(3)
Rh−P(2)	2.359(3)	C(5′)−C(7′)	1.37(4)
Rh−P(4)	2.340(3)	C(5′)−C(8)	1.68(2)
Rh−C(2)	2.022(11)	C(6)−C(7′)	1.50(4)
Rh−C(3)	2.268(11)	C(7′)−C(9′)	1.73(5)
Rh−C(5)	2.04(2)		

Table 6. Selected Interatomic Angles (deg) for Compound 8

Rh−C(2)−Os	87.6(5)	C(2)−Rh−P(4)	88.9(3)
Os−C(3)−Rh	84.1(4)	C(5)−Rh−P(4)	84.4(5)
C(3)−Os−C(1)	96.8(5)	C(5′)−Rh−P(4)	91.70(7)
C(3)−Os−C(2)	97.5(4)	C(3)−Rh−P(4)	98.5(3)
C(1)−Os−C(2)	165.5(5)	P(4)−Rh−P(2)	170.96(10)
C(3)−Os−C(4)	173.3(5)	C(2)−Rh−Os	47.2(3)
C(1)−Os−C(4)	78.0(5)	C(5)−Rh−Os	170.8(6)
C(2)−Os−C(4)	88.0(4)	C(3)−Rh−Os	43.6(3)
C(3)−Os−P(1)	85.2(3)	C(5′)−Rh−Os	164.03(2)
C(1)−Os−P(1)	89.2(4)	P(2)−Rh−Os	93.56(7)
C(2)−Os−P(1)	94.9(3)	P(4)−Rh−Os	94.96(7)
C(4)−Os−P(1)	90.5(3)	O(1)−C(1)−Os	175.5(12)
P(3)−Os−P(1)	177.87(10)	O(2)−C(2)−Rh	128.7(8)
C(3)−Os−P(3)	94.2(3)	O(2)−C(2)−Os	143.5(9)
C(1)−Os−P(3)	88.9(4)	O(3)−C(3)−Os	159.5(10)
C(2)−Os−P(3)	87.2(3)	O(3)−C(3)−Rh	116.3(8)
C(4)−Os−P(3)	89.9(3)	C(7)−C(5)−Rh	132(2)
C(3)−Os−Rh	52.3(3)	C(6)−C(5)−Rh	110.2(11)
C(1)−Os−Rh	148.9(3)	C(7′)−C(5′)−Rh	114(2)
C(2)−Os−Rh	45.1(3)	C(8)−C(5′)−Rh	129.0(5)
C(4)−Os−Rh	133.1(3)	C(7)−C(5)−C(6)	117(2)
P(3)−Os−Rh	90.13(7)	C(5)−C(7)−C(8)	118(2)
P(1)−Os−Rh	91.12(7)	C(5)−C(7)−C(9)	116(3)
C(2)−Rh−C(5)	141.8(7)	C(5)−C(7)−C(9)	124(3)
C(2)−Rh−C(3)	90.8(4)	C(7′)−C(5′)−C(8)	109(2)
C(5)−Rh−C(3)	127.4(6)	C(5′)−C(7′)−C(6)	119(3)
C(2)−Rh−C(5′)	118.6(3)	C(5′)−C(7′)−C(9′)	122(3)
C(5′)−Rh−C(3)	149.1(3)	C(6)−C(7′)−C(9′)	118(3)
C(2)−Rh−P(2)	94.6(3)		
C(5)−Rh−P(2)	87.8(5)		
C(5)−Rh−P(2)	79.30(7)		
C(3)−Rh−P(2)	89.7(3)		

Results and Compound Characterization

(a) Preparation of Vinyl Complexes. A number of routes can be used to generate vinyl complexes, including reactions with vinyl Grignard reagents or with lithium vinyl compounds.[13] They can also be obtained via reaction of metal hydrides with alkynes and their tautomers, as previously demonstrated for this system in the reaction of $[RhOsH(CO)_3(dppm)_2]$ (**1**) with dimethyl acetylenedicarboxylate (DMAD).[5b] Attempts to obtain a species, $[RhOs(CH{=}CH_2)(CO)_3(dppm)_2]$ containing the unsubstituted vinyl group by reaction of **1** with acetylene failed, resulting in complex mixtures of products over a range of reaction conditions. However, the analogous isopropenyl species $[RhOs(C(CH_3){=}CH_2)(CO)_3(dppm)_2]$ (**3**), containing the monosubstituted vinyl group, is obtained in the reaction of **1** with propyne, as shown in Scheme 1. The species obtained is the product which results from hydrogen transfer to the terminal carbon of the alkyne, with the metal ending up in the 2-position. No evidence of the other isomer, the *n*-propenyl species, was observed.

The ^1H NMR spectrum of **3** shows a singlet for the methyl group and singlets for each of the olefinic hydrogens of the isopropenyl group. The methylene groups of the bridging dppm ligands appear as an AB

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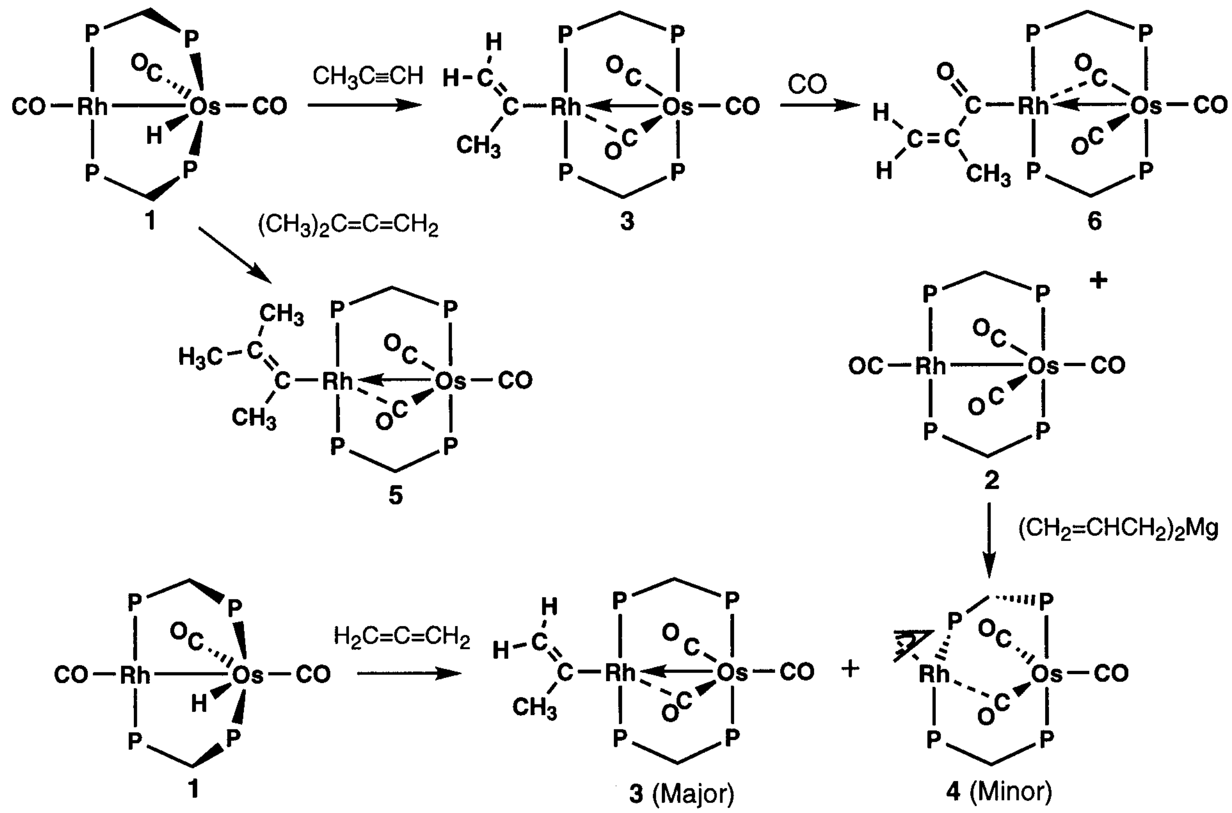
(13) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987, pp 101−104. (b) Elschenbroich, Ch.; Salzer, A. *Organometallics*; VCH Publishers: New York, NY, 1989; pp 206−207.

Scheme 1



quartet with additional ^{31}P coupling at temperatures below 0 °C, indicating asymmetry on either side of the RhOsP$_4$ plane in the molecule resulting from the orientation of the vinyl group. Above 0 °C, the peaks broaden and coalesce, becoming a sharp quintet at 75 °C, indicating an average front–back symmetry in the molecule, presumably resulting from rotation of vinyl group about the Rh–C bond. The ^{13}C{^{1}H} NMR spectrum at ambient temperature shows three unique carbonyl resonances at δ 195.46, 212.24, and 229.41, for which the high-field signal appears as a triplet, showing coupling of 14 Hz to the osmium-bound phosphines, while the other two resonances are broad, showing no resolvable coupling. The lack of any observed rhodium coupling rules out a terminal carbonyl on rhodium; however, the breadth of the two lower-field resonances (ca. 40 Hz line widths at half height) could mask substantial Rh coupling, so the possibility of semibridging interactions cannot be ruled out. In fact, the low-frequency IR stretch at 1725 cm^{-1}, as well as the low-field ^{13}C resonance, suggests the involvement of a bridging carbonyl. The α-carbon of the vinyl group appears in the ^{13}C NMR spectrum as a doublet of triplets at δ 181.37, showing coupling to Rh (29 Hz) and to the Rh-bound phosphines, clearly indicating that the vinyl group is bound to Rh. The chemical shift is as expected for Rh-bound vinyl groups.[14] The methyl carbon and vinyl β-carbon appear at 31.02 and δ 115.29, respectively; both signals are triplets, showing coupling to the Rh-bound phosphines. The broadness of the carbonyl resonances in **3** suggests an exchange process in which the two carbonyls on opposite faces of the molecule move back and forth from bridging to terminal positions. This behavior parallels that of the methyl analog [RhOs(CH$_3$)(CO)$_3$(dppm)$_2$], which has a semibridging carbonyl on one face and a terminal carbonyl on the opposite face in the solid state, but two equivalent carbonyls in solution.[5b] In the case of compound **3**, the carbonyls do not become equivalent at ambient temperature, owing to the orientation of the isopropenyl group having the methyl substituent on one side of the RhOsP$_4$ plane and the vinylic moiety on the other side, but the exchange causes broadening. At −80 °C, the carbonyl resonances sharpen significantly, but are still broad enough to mask any coupling. The presence of a semibridging carbonyl, which acts as a π-acceptor from the electron-rich rhodium center, is typical of these types of complexes[5b,9] and appears to be necessary because of the absence of another good π acceptor on rhodium.

The same isopropenyl complex **3** can also be obtained by the reaction of **1** with allene, as shown in Scheme 1. In this reaction, a small amount (approximately 10%, by ^{31}P NMR) of [RhOs(η^3-C$_3$H$_5$)(CO)$_3$(dppm)$_2$] (**4**) is also obtained. This η^3-allyl product has been independently synthesized by reaction of [RhOs(CO)$_4$(dppm)$_2$][BF$_4$] (**2**) with diallylmagnesium. At ambient temperature, the ^{31}P NMR spectrum of **4** consists of two resonances, a multiplet for the osmium-bound phosphines and a very broad resonance for the rhodium-bound phosphines. At −80 °C, the spectrum shows four unique phosphorus resonances. The coupling constant between the osmium-bound phosphines is 242 Hz, indicating a trans arrangement of the phosphines on this metal, whereas the P–P coupling at Rh is only 22 Hz, indicating that the phosphines are cis. At ambient temperature, the ^{1}H NMR shows only a broad singlet for the dppm methylene hydrogens. At −80 °C, the ^{1}H NMR spec-

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[14] Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, 1981; pp 88, 140.

trum displays nine unique resonances, four for the dppm methylene hydrogens and five for the allyl ligand. Unfortunately, all resonances are broad, even at −110 °C, so the coupling information could not be obtained. The chemical shifts of two of the allyl hydrogens are at unusually high field (δ 1.30 (syn), 0.22 (anti) compared with typical values of δ 2-5 for syn and δ 1−3 for anti[15]), suggesting that the allyl ligand is unsymmetrically bound, approaching a σ,π-coordination mode. The other allyl hydrogens appear in the normal region, δ 2.53 (syn) and 0.99 (anti). The possibility of an η^1-allyl is ruled out because all five allyl hydrogens show coupling to phosphorus (as shown by the substantial sharpening of all signals in the $^1H\{^{31}P\}$ spectrum), and the chemical shifts are not consistent with a free olefin moiety.[16] The η^1 mode is also inconsistent with the cis arrangement of the phosphines on Rh; an η^1-allyl compound would be expected to have a structure much like **3** (*vide infra*) and like all other [RhOs(R)(CO)$_3$(dppm)$_2$] compounds.[5b] Presumably, the η^3-allyl coordination requires the cis phosphine arrangement due to its increased steric requirements over the η^1 mode. The ^{13}C NMR spectrum at −80 °C shows three broad resonances at δ 188.3, 204.7, and 253.4. Again, the low-field resonance is consistent with a semibridging carbonyl, although no coupling to Rh is observed due to the broadness of this signal. Compounds **3** and **4** could not be interconverted by heating.

The reaction of 3-methyl-1,2-butadiene (dimethylallene) with **1** yields the trimethylvinyl analogue [RhOs(C(CH$_3$)=C(CH$_3$)$_2$)(CO)$_3$(dppm)$_2$] (**5**), the ^1H NMR spectrum of which shows three singlets for the methyl groups of the trimethylvinyl ligand. All other features of the NMR spectra for **5** are nearly identical to those of **3**. The IR spectrum of **5** shows carbonyl stretches at 1924, 1875, and 1707 cm^{-1}, with the latter suggesting a strong semibridging interaction.

The X-ray structure of **3**, showing only one of the disordered molecules, appears in Figure 3 and confirms the structure proposed for these vinyl compounds. Although the structure was inversion-disordered, giving rise to superposition of the vinyl ligand and the axial carbonyl, the disorder was resolved satisfactorily as explained earlier, allowing a meaningful discussion of the key structural features. Important bond lengths and angles are given in Tables 3 and 4. At osmium, the geometry is that of a coordinatively-saturated, trigonal-bipyramidal OsL$_2$(CO)$_3$ moiety, in which the phosphines are essentially trans (P(1)−Os−P(2′) = 171.91(3)°) and the angles between the equatorial carbonyl groups are all close to 120°. Ignoring the semibridging carbonyl, the geometry at rhodium is essentially square planar, consistent with a 16-electron configuration. To achieve a 16-electron count, a dative bond from Os to Rh is required, yielding a Rh−Os separation of 2.817(1) Å, which is normal for a single bond. As observed in a number of related species,[5b,9] the build up of electron density on rhodium (by virtue of two phosphines and an alkyl or alkenyl group) is alleviated by the semibridging interaction with C(3)−O(2′). The resulting Rh−C(3) distance, 2.075(8) Å, is consistent with a strong interaction with rhodium, however, this carbonyl is significantly more linear with respect to Os (Os−C(3)−O(2′) = 155.2(6)°, Rh−C(3)−O(2′) = 118.0(6)°). Whether the unusually short Rh−C(3) distance is chemically meaningful and, therefore, indicative of a strong semibridging interaction with Rh or whether it is merely an artifact of the disorder is not known.

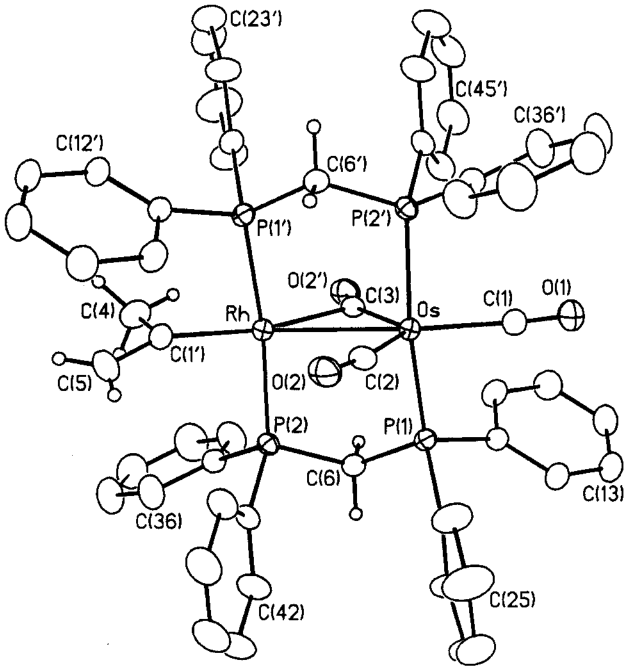

Figure 3. Perspective view of [RhOs(C(CH$_3$)=CH$_2$)(CO)$_3$(dppm)$_2$] (**3**), showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters for the isopropenyl and dppm methylene groups and are not shown for the dppm phenyl groups.

The vinyl group is bound in an η^1-fashion to rhodium. The Rh−C distance (1.955(5) Å) is shorter than expected, relative to other Rh−vinyl complexes (ca. 2.040 Å),[17] but this is likely a result of the disorder since the α-carbon is essentially superimposed on the inversion-disordered carbon of the carbonyl opposite the metal−metal bond. All other distances involving this group are as expected. In particular, the C(1′)−C(5) distance of 1.33(2) Å is consistent with a C=C double bond. The angles about C(1′) suggest that the vinyl group is bent slightly away from Rh, opening up the Rh−C(1′)−C(5) angle to 132.8(13)° and compressing the C(5)−C(1′)−C(4) angle to 109.9(14)°. This vinyl-group distortion may be a result of steric interactions with the dppm phenyl groups. Although the nonbonded distance between one of the methyl hydrogens (H(5a)) and one of the phenyl hydrogens (H(46)) (2.43 Å) is an acceptable van der Waals separation, any compression of the Rh−C(1′)−C(5) angle would lead to an unfavorable shortening of this distance.

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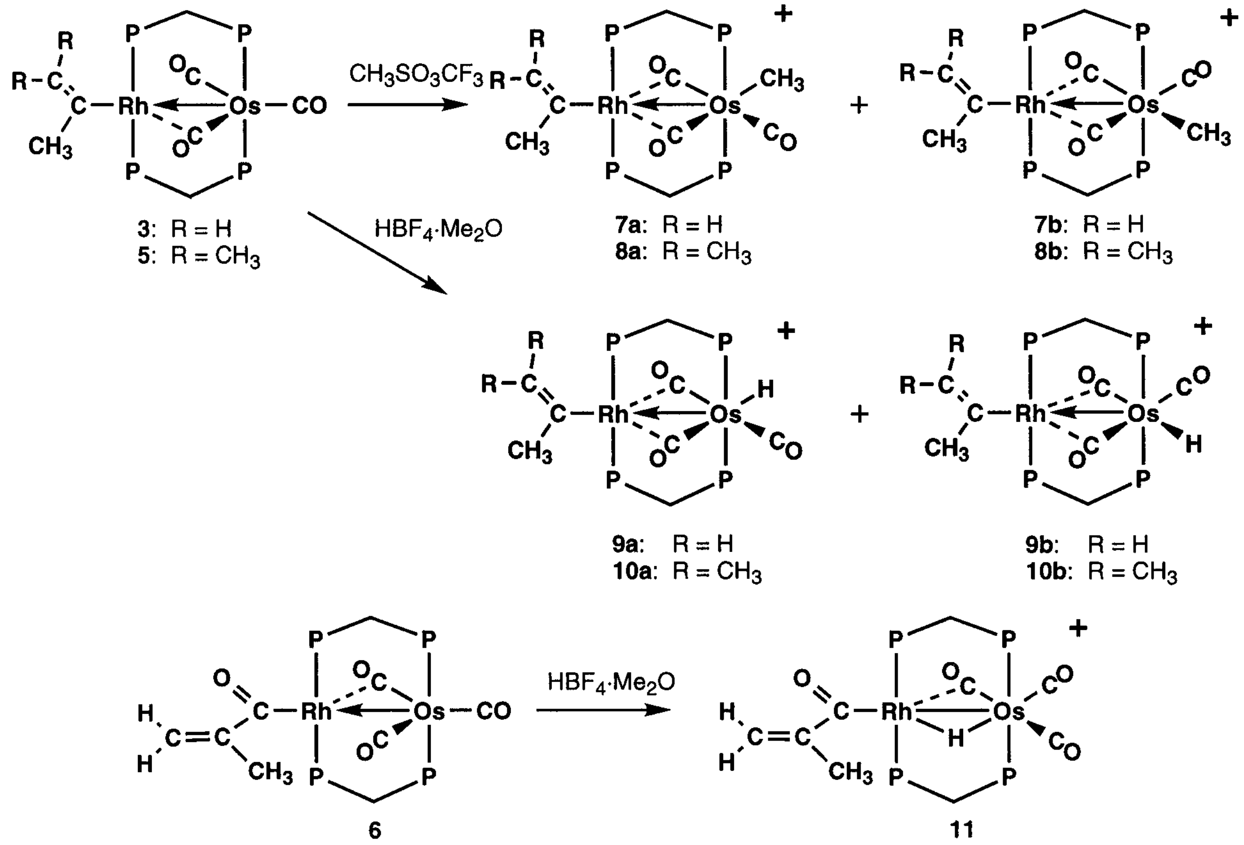
(15) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 176−177.

(16) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495. Numata, S.; Okawara, R.; Kurosawa, H. *Inorg. Chem.* **1977**, *16*, 1737. Deeming, A. J.; Shaw, B. L.; Stainbank, R. E. *J. Chem. Soc.* **1971**, 374.

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

Scheme 2



(b) Reactivity of Vinyl Complexes. (i) With CO. Compound **3** reacts with carbon monoxide to give the migratory-insertion product [RhOs(C(O)C(CH$_3$)=CH$_2$)(CO)$_3$(dppm)$_2$] (**6**) (see Scheme 1), the IR spectrum of which shows bands at 1934 and 1882 cm^{-1} for the metal-bound carbonyls and 1720 cm^{-1} for the acyl group. The C=C stretch is also observed at 1555 cm^{-1}. The ^{1}H NMR spectrum of **6** is similar to that of **3**, showing singlets at δ 6.07, 5.04, and 0.66 for the two olefinic protons and the methyl group, respectively. In the ^{13}CO-enriched complex, the olefinic protons are split into doublets, with the higher field signal being assigned as trans to the acyl carbonyl on the basis of the larger coupling to ^{13}C (15 vs 7 Hz). The ^{13}C{^{1}H} NMR spectrum of **6** shows three resonances at δ 194.10, 206.38, and 230.47 for the carbonyls on osmium, very similar to those seen for **3**. As in previous compounds, the high-field resonance shows coupling to the osmium-bound phosphines while the other two resonances are broad. An additional resonance occurs at δ 271.93 for the acyl carbonyl and appears as a doublet of triplets, with coupling of 31 Hz to rhodium and 5 Hz to the rhodium-bound phosphines. The insertion can be reversed by refluxing **6** in benzene. Whereas refluxing for 1 h in benzene resulted in decarbonylation of approximately half of the isopropenoyl complex, refluxing in the lower boiling solvent CH$_2$Cl$_2$ resulted in no reaction. The trimethylvinyl species **5** also reacts with CO, but more slowly than **3**, giving several sparingly soluble products that could not be characterized.

(ii) With Electrophiles. One of the goals of this research was to form complexes containing two organic groups or one organic group and a hydride on adjacent metals, with the goal of effecting reductive elimination. Reaction of neutral complexes of the type [RhOsR(CO)$_3$(dppm)$_2$] with electrophiles has previously been used to generate dialkyl, alkyl–hydride, and related complexes,[5b] suggesting a parallel route to species containing a vinyl group together with either alkyl or hydride ligands. At ambient temperature, reaction of [RhOs(C(CH$_3$)=CH$_2$)(CO)$_3$(dppm)$_2$] (**3**) with methyl triflate leads to a mixture of several products. However, at −40 °C, the reaction is clean, yielding two isomers of [RhOs(C(CH$_3$)=CH$_2$)(CH$_3$)(CO)$_3$(dppm)$_2$][CF$_3$SO$_3$] (**7a,b**) in a 1:1 ratio, as shown in Scheme 2. The ^{1}H NMR spectrum of the mixture of isomers shows two sets of resonances that are very similar to the resonances of the vinyl group in **3**. In addition, two triplets at δ −0.23 and −0.12 correspond to the osmium-bound methyl groups of the two isomers, as shown by ^{31}P-decoupling experiments. The position of the methyl group on osmium is consistent with previous results in which electrophilic attack was shown to occur at osmium.[5b] The ^{13}C{^{1}H} NMR spectrum shows three resonances due to osmium-bound carbonyls for each compound, and the IR spectrum of the mixture displays broad, unresolved peaks in the carbonyl region, but a strong peak at 1805 cm^{-1} suggests the presence of semibridging carbonyls. The spectroscopic parameters of the two isomers are nearly identical, suggesting minor differences between the two. On the basis of this information, we propose that these isomers result from the two possible arrangements of the methyl group, either syn or anti to the vinyl double bond, as shown in Scheme 2. Isomers in which the methyl group occupies a site on Os, directed toward rhodium (replacing a semibridging CO), are also possible but appear less likely given the strong tendency for the carbonyls to occupy semibridging positions in these complexes. Furthermore, the two isomers proposed are consistent with electrophilic attack at either of the two vacant sites on Os in the precursor **3**.

At elevated temperatures, the two isomers of **7** can interconvert, as shown by variable-temperature NMR studies. As the temperature is raised to 50 °C, the peaks in the ^{1}H NMR spectrum that correspond to the osmium-bound methyl groups of the two isomers broaden, and at 70 °C, the peaks coalesce into a single broad peak. The resonances for the methyl groups of the propenyl ligand show similar behavior, but do not quite coalesce at the highest temperature because of their larger chemical shift difference. The olefinic hydrogens are broad and not clearly resolved at the high temperatures. The coalescence appears to result from rotation of the vinyl group about the Rh−C bond, similar to that proposed for **3**.

An alternate route to compound **7** is the reaction of the unstable methyl−hydride complex, $[RhOs(CH_3)(\mu\text{-}H)(CO)_3(dppm)_2][CF_3SO_3]$,[5b] with allene at −40 °C to form the two isomers of **7** in the same ratio. Although this hydrido−methyl precursor is susceptible to methane loss at higher temperatures, the reaction with allene at −40 °C instead gives the migratory insertion product **7**.

Reaction of the trimethylvinyl compound $[RhOs(C(CH_3){=}C(CH_3)_2)(CO)_3(dppm)_2]$ (**5**) with methyl triflate at room temperature also yields two isomers of the corresponding trimethyl vinyl−methyl complex $[RhOs(C(CH_3){=}C(CH_3)_2)(CH_3)(CO)_3(dppm)_2][CF_3SO_3]$ (**8a,b**), in a ratio of 3.8:1.0. The ^{1}H NMR spectrum shows six singlets corresponding to the methyl groups of the vinyl ligand of both isomers and two triplets corresponding to their osmium-bound methyl groups. The ^{13}C NMR spectrum is similar to that of **7**; however, the IR spectrum is much more clearly resolved than that of **7** and shows three bands for each isomer. Although the middle frequency bands (1860, 1832 cm^{-1}) are in the same region as the terminal bands in the neutral complex (1875 cm^{-1} for **5**), they are assigned as bridging carbonyls because they are now on a cationic Os(II) center rather than a neutral Os(0) center. In moving from Os(0) to Os(II), a shift to higher frequency for ν(CO) is expected and is, indeed, observed for both the highest (1924 cm^{-1} in **5** vs 2041, 2032 cm^{-1} in **8a,8b**) and the lowest frequency bands (1707 cm^{-1} in **5** vs 1808, 1789 cm^{-1} in **8a,8b**). Since the middle bands shift to slightly *lower* frequency, rather than higher, they are assigned as bridging carbonyls; therefore, two of the carbonyls are involved in semibridging interactions in **8a** and **8b**, rather than just one as in the neutral complexes. It is not possible, on the basis of the spectroscopic data, to identify which structure (**8a** or **8b**) corresponds to the major species. However, on the basis of the X-ray structure determination, which was found to be disordered, containing both isomers superimposed, it has been established that **8a**, having the osmium-bound methyl group syn to the vinyl double bond, is the major isomer (*vide infra*). We assume that this is also the major isomer in solution.

The X-ray structure determination of **8**, shown in Figure 4, confirms the proposed structure, and although disordered, due to the presence of two isomers in the crystal, this disorder was resolved satisfactorily as described in the Experimental Section. Important bond lengths and angles are given in Tables 5 and 6. Although the parameters for both isomers are given in the tables, only those of the major isomer are discussed, since they are more reliable, having 70% rather than 30% occupancy. Ignoring the metal−metal interaction, the geometry at osmium is octahedral. The phosphines are essentially mutually trans (P(1)−Os−P(3) = 177.87(10)°) and the angles between all adjacent groups on Os are close to 90°, giving rise to an 18-electron configuration at the $Os(CH_3)(CO)_3L_2^+$ center. In this bonding model, the carbonyls C(2)O(2) and C(3)O(3) are considered as semibridging, donating their electron pairs to Os and functioning as π-acceptors from Rh. An extension of this model has Os donating a pair of electrons from its filled d_{xy} orbital to Rh giving it a favored 16-electron count and resulting in a Rh−Os bond length of 2.8505(9) Å, which is consistent with a single bond. The need for the two strong semibridging interactions arises from the absence of other π-acid ligands on Rh, coupled with the dative Os-Rh bond and the strong σ-donor trimethylvinyl group. Although both carbonyls are considered as semibridging, C(2)O(2) approaches a symmetrically bridged group. Whereas C(3)O(3) has a short, strong interaction with Os (1.975(12) Å), a weak interaction with Rh (2.268(11) Å), and is much more linear with respect to Os than Rh (Os−C(3)−O(3) = 159.5(10)°, Rh−C(3)−O(3) = 116.3(8)°), carbonyl group C(2)O(2) has comparable metal−carbon distances to Os and Rh (2.094(12) and 2.022(11) Å, respectively) and is much less linear with respect to Os (Os−C(2)−O(2) = 143.5(9)°, Rh−C(2)−O(2) = 128.7(8)°). The differing natures of the carbonyls can be rationalized on the basis of the ligands in the trans positions. C(3)O(3) is opposite the strong σ-donor methyl group, so is strongly bound to Os, whereas C(2)O(2) competes for π-electron density with C(1)O(1) opposite it and is less tightly bound to Os as a consequence. The osmium−methyl bond length (2.179(12) Å) is normal for a sp^3-hybridized carbon.

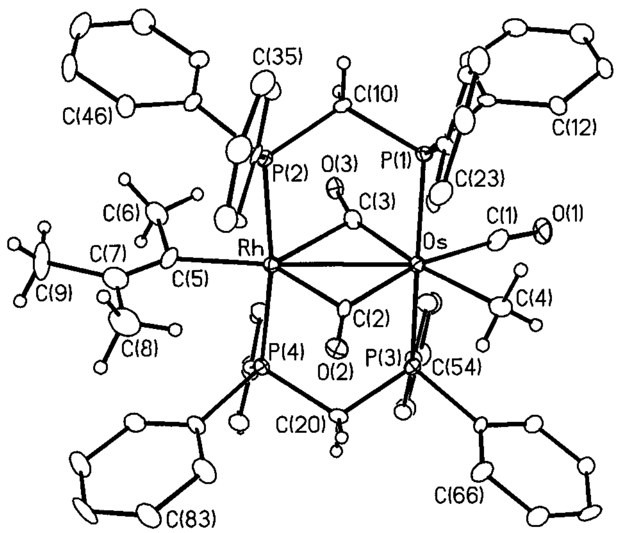


Figure 4. Perspective view of the $[RhOs(C(CH_3){=}C(CH_3)_2)(CO)_3(CH_3)(dppm)_2]^+$ cation, showing atoms of the major isomer only. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters for the trimethylvinyl, methyl, and dppm methylene groups and are not shown for the dppm phenyl groups.

Compound **8** differs significantly from all related RhOs structures which have a σ-bound organic group on only Rh and an adjacent $Os(CO)_3L_2$ moiety. Whereas the monoalkyl or monoalkenyl species generally have a single bridging carbonyl, compound **8** has both carbonyls adjacent to Rh in bridging interactions. This may reflect the increased steric crowding at Os, as a consequence of an increase in its coordination number from five to six upon alkylation. In support of this idea, the structurally related $[RhRe(CH_3)(CO)_4(dppm)_2]^+$ [9] has a similar octahedral geometry at Re and again has two semibridging carbonyl groups.

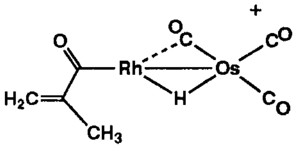
The trimethylvinyl group is bound to Rh in an η^1-fashion, resulting in a normal Rh−C(sp^2) distance of 2.04(2) Å. All other distances within the vinyl group are as expected, with the possible exception of C(5)−C(7) (1.27(3) Å), which is somewhat shorter than expected for a C−C double bond (1.345 Å);[18] this is likely a result of the disorder. The angles about C(5) reveal a similar distortion of the vinyl group to that seen in compound **3**, with an expanded Rh−C(5)−C(7) angle of 132(2)° and a compensating small Rh−C(5)−C(6) angle of 110.2(11)°. Again, the distortion is likely caused by steric interactions involving the phenyl groups, with the shortest nonbonded contact involving H(8b) and H(32) (1.88 Å).

We assume that the very different isomer ratio in **8**, in contrast to the 1:1 isomer ratio in **7**, is a consequence of the greater steric repulsions involving the two additional methyl substituents in the former. Although the trimethylvinyl and the methyl ligands are on different metals, a consideration of Figure 4 shows that a transmission of steric effects between the two groups can occur via the ortho hydrogens (H(32) and H(22)) and the semibridging carbonyl C(2)O(2).

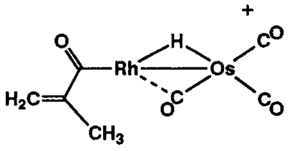
Protonation of the vinyl complexes leads to the formation of products that are structurally analogous to the vinyl−methyl complexes described. Compound **3** reacts with 1 equiv of $HBF_4{\cdot}Me_2O$ at −40 °C to form two isomers of $[RhOs(C(CH_3){=}CH_2)(H)(CO)_3(dppm)_2][BF_4]$ (**9a,b**), in a ratio of 1.5:1.0. The ^1H NMR spectrum of this mixture shows two sets of resonances for the isopropenyl groups, as well as hydride resonances at δ −6.80 and −6.70, appearing as triplets with coupling to the Os-bound phosphines.

Protonation of the trimethylvinyl complex **5** occurs cleanly at room temperature to form $[RhOs(C(CH_3){=}C(CH_3)_2)(H)(CO_3)(dppm)_2][BF_4]$ (**10a,b**), in a ratio of 1.6:1.0. The ^1H NMR spectrum shows two sets of three methyl groups as expected. In this case, however, one of the methyl groups in each isomer shows a small coupling to the rhodium-bound phosphines. This resonance is assigned to the methyl group on the α-carbon. The hydride resonances appear as triplets at δ −7.02 and −6.55 for the major and minor isomers, respectively, showing coupling to the osmium-bound phosphines and confirming that the hydrides are terminally bound to this metal. The $^{13}C\{^{31}P\}$ NMR spectrum shows rhodium couplings of 25 and 13 Hz in two of the carbonyls of **10a** and 29 and 8 Hz for **10b**, consistent with a strong and weak semibridging interaction, as confirmed in the structure of **8**.

In contrast to the vinyl complexes, protonation of the isopropenoyl species $[RhOs(C(O)C(CH_3){=}CH_2)(CO)_3(dppm)_2]$ (**6**) at −80 °C with 1 equiv of HBF_4 leads to a *hydride-bridged* complex $[RhOs(C(O)C(CH_3){=}CH_2)(\mu\text{-}H)(CO)_3(dppm)_2][BF_4]$ (**11**). No species containing a terminal hydride ligand was seen, even at −80 °C. Although two isomers (**a** or **b**) are again possible, as diagrammed below, only one is observed. Presumably, this results from unfavorable interactions between the semibridging carbonyl and the methyl substituent of the isopropenoyl group (isomer **11b**); we, therefore, assume that **11a** is the isomer observed.



11a



11b

The ^1H NMR spectrum of **11** shows singlets at δ 5.88, 4.95, and 0.52 for the isopropenoyl group and a broad multiplet at δ −8.82 for the bridging hydride. The ^{13}C NMR spectrum shows three carbonyls at δ 174.17, 179.97, and 234.26, with the low-field resonance showing rhodium coupling of 22 Hz, indicating a semibridging interaction. The acyl carbonyl appears as a doublet at δ 254.05, with rhodium coupling of 31 Hz.

(iii) Reductive Elimination. The cationic vinyl−methyl and vinyl−hydride complexes were reacted with CO in an attempt to induce migratory insertion of the CO and methyl or vinyl groups. We had assumed, for example, that compound **9** would yield **11** under CO. However, in no case was insertion to give acyl products seen, and in fact, the vinyl−methyl complexes were unreactive toward CO. The isopropenyl−hydride complex $[RhOs(C(CH_3){=}CH_2)(H)(CO)_3(dppm)_2][BF_4]$ (**9a,b**) reacts rapidly with CO, with isomerization to $[RhOs(C(CH_3){=}CH_2)(\mu\text{-}H)(CO)_3(dppm)_2][BF_4]$ (**12a,b**), in which the hydride has moved from a terminal position on Os to the bridging position (see Scheme 3), as confirmed by ^1H, ^{13}C, and ^{31}P NMR studies. The reaction rate increases as the CO pressure is increased. Like compounds **7**−**10**, compound **12** has two isomeric forms resulting from the position of the bridging hydride ligand relative to the vinyl group. These isomers could be distinguished spectroscopically but could not be unambiguously assigned to the structures shown. Although formation of the hydride-bridged complexes is complete within minutes, they react slowly with subsequent elimination of propene to form the known tetracarbonyl product $[RhOs(CO)_4(dppm)_2][BF_4]$ under CO.[5a] The rates of propene elimination from **12a** and **12b** are very different. One isomer disappears completely within 1 h while the other persists for ca. 20 h. If the CO atmosphere is removed under vacuum immediately after conversion to the hydride-bridged intermediate, reductive elimination leads to the previously characterized $[RhOs(CO)_3(\mu\text{-}H)(\mu^2\text{-}\eta^3\text{-}(o\text{-}C_6H_4)PhPCH_2PPh_2)(dppm)][BF_4]$,[5b] along with $[RhOs(CO)_4(dppm)_2][BF_4]$ and some unidentified decomposition products. The first product results from orthometalation of a dppm phenyl ring at Os, whereas the second product is presumably a result of CO scavenging from the decomposition products. The trimethylvinyl−hydride complex $[RhOs(C(CH_3){=}C(CH_3)_2)(H)(CO)_3(dppm)_2][BF_4]$ (**10a,b**) reacts in an analogous fashion under CO to form 2-methyl-2-butene and $[RhOs(CO)_4(dppm)_2][BF_4]$. In this case, formation of the intermediate, hydride-bridged

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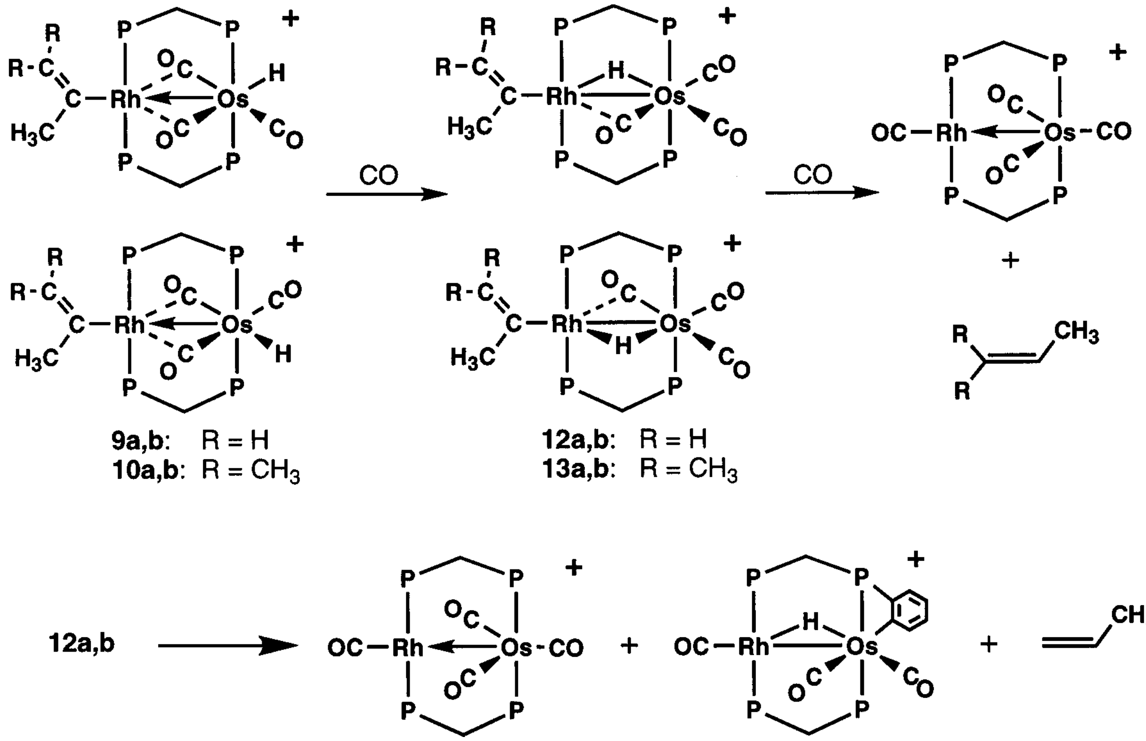
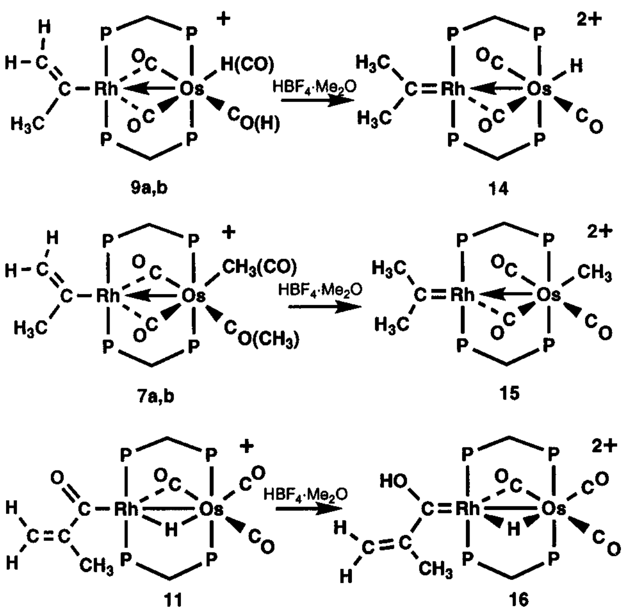
[18] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. II* **1987**, 51.

Scheme 3


9a,b: R = H
10a,b: R = CH3
12a,b: R = H
13a,b: R = CH3

Scheme 4



complexes is slower, requiring 2 h for complete reaction. The reductive elimination step is also slower, with one isomer disappearing in 2 h and the other persisting for days.

(c) Formation of Carbene Complexes. Reaction of **3** with 1 equiv of acid yields the vinyl−hydride complex described (**9**). Addition of a second equivalent of acid results in a subsequent protonation at the β-carbon of the vinyl group to yield the dicationic carbene complex [RhOs(=C(CH$_3$)$_2$)(H)(CO)$_3$(dppm)$_2$][BF$_4$]$_2$ (**14**), as shown in Scheme 4. Compound **14** is stable in solution only below 0 °C in the presence of excess acid; above 0 °C, deprotonation occurs, reforming **9a,b**, along with some decomposition products. Lowering the temperature results in reformation of **14**. Although two isomers of the monoprotonation product are formed, only one isomer can result from the second protonation since the carbene ligand is now symmetrical. The ^{1}H NMR spectrum of **14** shows singlets at δ 2.65 and 2.18 for the methyl groups of the carbene moiety and a triplet at δ −6.21 for the hydride, showing coupling of 13 Hz to the osmium-bound phosphines. The ^{13}C{^{1}H} NMR spectrum shows three carbonyl resonances at δ 172.8, 193.1, and 204.0, with the low-field resonance showing rhodium coupling of 10 Hz, indicating a semibridging interaction. The carbene carbon appears as a doublet of triplets at δ 377.9, with a rhodium coupling of 35 Hz and coupling to the rhodium-bound phosphines of 5 Hz. The rhodium coupling is consistent with that involving an sp^2 carbon,[14] and the low-field chemical shift is expected for a dicationic carbene complex.[19]

In a similar manner, protonation of [RhOs(C(CH$_3$)=CH$_2$)(CH$_3$)(CO)$_3$(dppm)$_2$][CF$_3$SO$_3$] (**7a,b**) with HBF$_4$·Me$_2$O at −40 °C leads to [RhOs(=C(CH$_3$)$_2$)(CH$_3$)(CO)$_3$(dppm)$_2$][BF$_4$][CF$_3$SO$_3$] (**15**). The spectroscopy of **15** is similar to that of **14**, except that instead of the hydride resonance a triplet is seen in the ^{1}H NMR spectrum for the osmium-bound methyl group at δ −0.10, showing an 8 Hz coupling to the osmium-bound phosphines.

Protonation of [RhOs(C(O)C(CH$_3$)=CH$_2$)(μ-H)(CO)$_3$(dppm)$_2$][BF$_4$] (**11**) occurs at the acyl oxygen, yielding the carbene [RhOs(=C(OH)C(CH$_3$)=CH$_2$)(μ-H)(CO)$_3$(dppm)$_2$][BF$_4$]$_2$ (**16**), which has a heteroatom in one of the β positions. The ^{1}H NMR spectrum of **16** shows the expected resonances for the propenyl group on the carbene ligand, as well as a broad multiplet at δ −9.85 for the hydride. In the reaction with HBF$_4$, the hydroxyl proton was obscured by the resonance for the excess HBF$_4$ at δ 9.95. However, if triflic acid is used, the hydroxyl hydrogen appears as a singlet at δ 9.56. The

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[19] Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121.

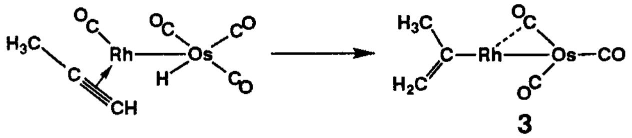
carbene resonance in the ^{13}C NMR spectrum again appears typically low-field at δ 301.2 as a doublet of triplets, showing rhodium coupling of 49 Hz. As expected, the heteroatom-stabilized carbene is more stable than the alkyl-substituted carbene complexes,[20] persisting to ambient temperature but decomposing upon workup.

Discussion

One reason for an interest in binuclear vinyl compounds relates to the proposed involvement of vinyl groups in Fischer-Tropsch chemistry.[6] Not only do these groups undergo migratory insertions with bridging methylene groups more readily than do saturated alkyl groups,[6d] but the intermediacy of the resulting allyl fragments allows an explanation of the small amounts of branched hydrocarbons that result.[6a] The isomerism of allyl to vinyl groups that has been proposed as a key step in alkyl chain growth has been observed in only a few homogeneous systems.[21,22]

We are also interested in the ability of vinyl groups to function as terminal ligands, bound to either Rh or Os, or as bridging ligands, being σ-bound to one metal while π-bonding to the other (μ_2-η^1,η^2-mode). The ability of the vinyl moiety to transform from the η^1- to the μ_2-η^1,η^2-bonding mode may have a number of effects; it may influence the reactivity of this group, owing to the additional π involvement, it may facilitate its transfer from one metal to another, or it may stabilize intermediates resulting from ligand loss, owing again to donation of the π electrons. In the chemistry described herein, we see no direct evidence of bridging vinyl coordination modes; all vinyl groups are terminally bound to Rh. It is assumed that the absence of bridging vinyl groups is a function of the steric crowding between the metals by virtue of the dppm phenyl groups.

Formation of a methylvinyl compound from the reaction of [RhOsH(CO)$_3$(dppm)$_2$] with propyne was predictable, although the isomer obtained, [RhOs(C(CH$_3$)=CH$_2$)-(CO)$_3$(dppm)$_2$] (**3**), containing the 1-methylvinyl (isopropenyl) group rather than the 2-methylvinyl product is of some surprise. The latter species, having the methyl substituent on the β-carbon should be sterically more favorable than the observed product in which the methyl group is closer to Os. Although we have no mechanistic details about how this migratory insertion occurs (at Rh or Os), it may be that upon alkyne coordination at Rh the bulkier methyl substituent is aimed away from the adjacent Os center, minimizing steric interactions, as diagrammed below (phosphines omitted). Hydrogen transfer to the terminal carbon of the alkyne (presumably via the Rh center) would then yield the observed isomer.



3

Even more surprising was the formation of the isopropenyl product from the reaction of allene with compound **1**. We had expected that the migratory insertion of allene would occur, with transfer of the hydride ligand to the central carbon, to give an allyl product, as more often occurs.[23] However, the present reaction does have precedent, as a number of examples of allene insertions into metal–hydride bonds to give substituted vinyl ligands have been reported.[24] It is probable that the more familiar tendency to yield allyl products results from the stabilizing influence of the η^3-binding mode of this group. We suggest that when only the η^1-binding mode of these groups is considered, the isopropenyl ligand is actually thermodynamically favored, owing to the stronger metal-carbon bond involving sp^2 rather than sp^3 hybridization of the α-carbon. Others have previously suggested a greater stability of the vinyl group.[21] Apparently, the η^3-allyl coordination mode is sterically unfavorable in these dppm-bridged complexes in which the phosphines have a trans arrangement at both metals, although when the diphosphines are bent back in a cis cis arrangement, η^3-allyl bonding has been proposed.[25] Consistent with these ideas, small amounts of an η^3-allyl product (**4**) were obtained as a minor product (ca. 10%), along with the isopropenyl species (**3**), in reactions of **1** with allene. This allyl product was also synthesized more directly from the reaction of [RhOs(CO)$_4$(dppm)$_2$][BF$_4$] with diallylmagnesium. Coordination of all three allyl carbons, it appears, can only occur with the phosphines on Rh bent back into a cis arrangement, presumably for the steric reasons alluded to above. Attempts to interconvert isomers **3** and **4** by heating resulted only in decomposition.

The allyl complex (**4**) exhibits some interesting features. At ambient temperature, it is highly fluxional, such that in the ^{1}H NMR spectrum the allyl hydrogens are not observed, while all of the dppm methylene hydrogens are equivalent. In addition, the ^{13}C{^{1}H} NMR spectrum indicates that the two carbonyls directed toward Rh are equivalent, while in the ^{31}P{^{1}H} NMR spectrum, the two Rh-bound phosphines also become equivalent, as do the two Os-bound phosphines. These observations can be explained by a process involving an η^1-allyl intermediate, which is structurally analogous to compounds **3** and **5**. In this intermediate, the two carbonyls can readily exchange, the opposite end of the allyl can recoordinate after rotation about the C–C σ-bond and either of the Rh-bound phosphines can bend back into the cis position. At −80 °C, the fluxional process is frozen out to give the more complex NMR spectra discussed earlier.

The allyl ligand in the static structure shows unusually high-field chemical shifts for one end of the allyl ligand (δ 1.30 (syn), 0.22 (anti)).[14] The chemical shifts are, in fact, consistent with the chemical shifts for σ-bound alkyl groups on Rh, suggesting that this end of the allyl ligand is essentially σ-bound while the other end coordinates as a π-bound olefin. Such unsym-

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(25) Fryzuk, M. D. *Inorg. Chim. Acta* **1981**, *54*, L265.

metrical allyl ligands have been described.[26] The reason for the asymmetry of the allyl ligand may be the position of either end of the ligand relative to the semibridging carbonyl. If one end of the allyl ligand is trans to the carbonyl, it will favor strong σ-donation while the end of the allyl ligand that is cis to the carbonyl will favor π-back-donation. However, without X-ray structural characterization, the exact geometry at Rh cannot be determined.

It is notable that in all compounds characterized herein, the vinyl groups are bound to Rh, although the hydride precursor **1** has the electronically similar hydrido group bound to Os. This parallels a number of studies on related mixed-metal "Rh/M" complexes (M = Ru,[27] Os,[5b] Mn,[22] Re,[28] Cr, Mo, W[29]) in which the σ-bound organic group is on Rh but is in contrast with a number of "Rh/Ir" analogues in which these groups are bound to Ir.[30] It is not clear what factors dictate the favored binding site of hydrido or σ-bound organic groups on one metal or the other in these systems.

One structural feature common to all $[RhOs(R)(CO)_3(dppm)_2]$ (R = alkyl, alkenyl) and related compounds is the presence of a semibridging carbonyl which is strongly σ-bound to the saturated metal while simultaneously functioning as a π-acceptor from Rh. This appears to arise due to the basicity of Rh, having σ-donor alkyl or alkenyl and phosphine groups attached but having no terminally bound π-acceptor ligands. The semibridging carbonyl functions to remove some of the excess electron density from Rh. This bonding is also consistent with the notion that Os functions as a σ-donor to Rh (vide supra), causing an additional electron-density buildup on this metal and further necessitating its removal. Semibridging carbonyls seem to commonly accompany M−M′ dative bonds.[31] Consistent with these arguments, the IR stretch of the semibridging carbonyl correlates well with the basicity of the organic group. Therefore, this stretch is lower for **5** ($R = C(CH_3){=}C(CH_3)_2$; $\nu(CO) = 1707\ cm^{-1}$), in which two hydrogens have been replaced by better donor methyl groups, than for **3** ($R = C(CH_3){=}CH_2$; $\nu(CO) = 1725\ cm^{-1}$). Furthermore, the compound $[RhOs(C(R){=}C(H)R)(CO)_3(dppm)_2]$ ($R = CO_2Me$), having strongly electron-withdrawing methoxy carbonyl groups, has its lowest metal-bound carbonyl stretch at $1895\ cm^{-1}$, suggesting the absence of any substantial bridging interaction.[5b]

The reaction of **3** with CO readily yields the isopropenoyl product $[RhOs(C(O)C(CH_3){=}CH_2)(CO)_3(dppm)_2]$ (**6**) via migratory insertion of the isopropenyl and carbonyl groups. There have been surprisingly few examples of carbonyl insertions into metal−alkenyl groups,[32] even though insertions involving other σ-bound organic groups are common.[33] Compound **5** also reacts slowly with CO, however, a number of products were obtained and these were not identified. Attempts to generate methyl methacrylate from **6** by reaction with a sodium methoxide/methanol mix, as previously reported in a related Pt(II) system, failed with no reaction being observed. The failure of **6** to react is not surprising if prior coordination of the alcohol or alkoxide to the metals is required since these low-valent, electron-rich metals are not expected to be electrophilic.

We were interested in the possible sites of electrophilic attack in the substituted vinyl and isopropenoyl compounds **3**, **5**, and **6**. In addition to attack at either metal or at the metal−metal bond, attack at the vinyl or the propenoyl group could generate carbene species, as previously observed.[34] In the two vinyl species **3** and **5**, the electrophiles (H^+ and CH_3^+) appear to attack at either of the two available sites on Os, remote from Rh, yielding two isomers. This has been supported by the X-ray structure determination of $[RhOs(C(CH_3){=}C(CH_3)_2)(CH_3)(CO)_3(dppm)_2][SO_3CF_3]$ (**8**). In contrast, protonation of the isopropenoyl species (**6**) yields a hydride-bridged complex $[RhOs(C(O)C(CH_3){=}CH_2)(\mu\text{-}H)(CO)_3(dppm)_2][BF_4]$ (**11**).

Rearrangement of the terminal-hydride species $[RhOsH(C(CH_3){=}CR_2)(CO)_3(dppm)_2][BF_4]$ (R = H (**9**), CH_3 (**10**)) to the thermodynamically favored hydride-bridged isomers $[RhOs(C(CH_3){=}CR_2)(CO)_3(\mu\text{-}H)(dppm)_2][BF_4]$ (**12**,**13**), analogous to the product obtained (**11**) upon protonation of the isopropenoyl compound (**6**), occurs upon reaction of these precursors with CO. It is not clear why the isomerization requires the addition of CO. In the analogous compounds in which the group on Rh is either CH_3 or $C(CO_2Me){=}C(H)(CO_2Me)$, the rearrangement occurs readily at low temperature without CO addition.[5b] As noted above, protonation of the isopropenoyl compound **6** appears to differ, yielding the hydride-bridged product instead of a terminal hydride species. If the protonation of **6** had occurred at Os, as was the case for **3**, **5**, and the methoxycarbonyl-substituted vinyl complex noted above, we would have expected to observe an intermediate having a terminal hydride ligand. The absence of such an intermediate, even at low temperature, suggests an alternate site of protonation. We suggest that this may occur at the acyl oxygen, with facile subsequent transfer of the proton to the Rh−Os bond. Although the proposed product (**11a**, shown earlier) is not the isomer expected based on a proton transfer from the acetyl group to the Rh−Os bond, which would have geometry **11b**, conversion of **11b** to **11a** would be facile by tunneling of the hydride between the metals. This rearrangement results in a more favorable arrangement of isopropenoyl and μ-CO groups in **11a**.

Rearrangement of the vinyl−hydride species **9** and **10** to the respective hydrido-bridged products **12** and **13** is slow in the case of the trimethylvinyl compound

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10 but occurs within minutes with the isopropenyl analogue **9**. It appears that the rate of rearrangement is inversely proportional to the steric bulk of the vinyl groups. Although these groups themselves are not migrating, we suggest that they can influence the migration of the hydride and carbonyl groups indirectly by interacting with the dppm−phenyl groups. Consistent with these size arguments, the related methyl complex $[RhOs(CH_3)(H)(CO)_3(dppm)_2]^+$ rearranges, even at −60 °C in the absence of CO.[5b]

In the related hydrido−methyl complex $[RhOs(CH_3)(H)(CO)_3(dppm)_2]^+$, rearrangement to a hydride-bridged species, still having the methyl group on Rh (not unlike compounds **12** and **13**), was followed by a transfer of the Rh-bound, terminal methyl group to Os immediately preceding methane elimination.[5b] It, therefore, appeared that reductive elimination occurred from Os. In the above hydrido-bridged vinyl species, reductive elimination again occurs, but at a much slower rate. On the basis of our data, we are not able to unequivocally determine whether elimination occurs from Rh or from Os, but the fact the reductive elimination in the absence of CO leads to orthometalation at Os suggests that the elimination is occurring from this center, as observed for the methyl analogue. The slow rates, compared to the methyl analogue, can be rationalized on the basis of the larger sizes of the vinyl groups which inhibit their migration from Rh to Os prior to elimination. Our failure to observe an intermediate in which the vinyl group is bound to Os immediately prior to reductive elimination indicates that reductive elimination is fast compared to the migration.

Attempts to alkylate the isopropenoyl compound $[RhOs(C(O)C(CH_3){=}CH_2)(CO)_3(dppm)_2]$ (**6**) to form a compound analogous to **7** and **8** resulted in a mixture of products. The ^{13}C NMR spectrum of the mixture suggested that one of the products resulted from alkylation of the acyl oxygen to form a Rh-bound carbene product, suggesting that conversion of both the isopropenyl (**3**) and the isopropenoyl (**6**) complexes to carbenes should be possible. As noted, protonation of **3** does not occur at the isopropenyl group but occurs at Os to give $[RhOs(C(CH_3){=}CH_2)(H)(CO)_3(dppm)_2]^+$ (**9**), and protonation of **6** yields the hydrido-bridged species $[RhOs(C(O)C(CH_3){=}CH_2)(\mu\text{-}H)(CO)_3(dppm)_2][BF_4]$ (**11**). However, reaction with an additional equivalent of acid in each case yields the dicationic carbene products $[RhOs({=}C(CH_3)_2)(H)(CO)_3(dppm)_2]^{2+}$ (**14**) and $[RhOs({=}C(OH)C(CH_3){=}CH_2)(\mu\text{-}H)(CO)_3(dppm)_2]^{2+}$ (**16**). In addition, the dimethylcarbene−methyl species $[RhOs({=}C(CH_3)_2)(CH_3)(CO)_3(dppm)_2]^{2+}$ (**15**) is obtained upon protonation of the isopropenyl group in the isopropenyl−methyl complex **7**. Although carbene complexes of Rh are well-known in which there are heteroatoms in the β-position,[35] complexes containing terminal carbene groups on Rh lacking heteroatoms, such as **14** and **15**, are quite rare.[36] In addition, terminal carbene species of Rh are far less common than those containing bridging carbene groups,[37] so it is possibly surprising that the carbene groups do not bridge the metals in compounds **14**−**16**. It may be that such a bridging mode is unfavorable, owing to the steric interactions involving the carbene substituents and the dppm groups. Compounds **14** and **15** are unstable at ambient temperature, being readily deprotonated. As expected, the Fischer carbene (**16**) has a greater stability, owing to delocalization involving the hydroxyl group.[20]

The carbene complexes **14** and **15** are expected to be very electrophilic in nature, owing to the dicationic charge of the complexes. We, therefore, refer to them as carbenes, as opposed to alkylidenes, for which nucleophilic character is implied.[38] As has been observed in other electrophilic carbenes,[39] the hydrogens α to the carbene carbons are acidic, as noted above. Similar nonheteroatom-stabilized, electrophilic carbene complexes of W, Fe, Mo, and Ni, some prepared by similar routes, have been shown to display unusual reactivity, including the cyclopropanation of olefin substrates[39] and insertion reactions of organosilanes.[40] The initial step in the cyclopropanation reactions is generally dissociation of a carbonyl or other ligand to allow coordination of the olefin. This step may not be necessary in complexes **14** and **15**, described herein, since the Rh center is already unsaturated. The potential of these carbene complexes to function as reagents for cyclopropanation and organosilane insertions is currently under study.

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Supporting Information Available: Tables of atomic coordinates, interatomic distances, interatomic angles, and calculated hydrogen parameters for compounds **3** and **8** (12 pages). Ordering information is given on any masthead page.

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