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Mixed-Metal Hydrocarbyl Complexes Involving the Rh/Mo and Rh/W Metal Combinations

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Reaction of [RhMo(H)(CO)$_4$(dppm)$_2$] (dppm = Ph$_2$PCH$_2$PPh$_2$) with a number of alkynes, RC≡CR′ (R = R′ = C(O)OCH$_3$, CF$_3$; R = H, R′ = C(O)CH$_3$, C(O)OCH$_3$) yields the alkenyl complexes [RhMo(C(R′)=C(H)R)(CO)$_4$(dppm)$_2$], which in all cases have an electron-withdrawing substituent on the α-carbon. A series of analogous complexes [RhMo(R)(CO)$_4$(dppm)$_2$] (R = CHCH$_2$, CH$_3$, CH$_2$CHCH$_2$, CH$_2$C$_6$H$_5$, C$_6$H$_5$) are prepared by the reaction of [RhMoCl(CO)$_4$(dppm)$_2$] and the appropriate Grignard reagent. The analogous Rh/W complex (R = CHCH$_2$) was prepared from [RhWCl(CO)$_4$(dppm)$_2$] and vinylmagnesium chloride. In all cases the hydrocarbyl fragment is η^1-bound to Rh, with the four carbonyl ligands primarily bound to the group 6 metal; two carbonyls assume a semibridging arrangement. The reaction of both vinyl complexes (Rh/Mo and Rh/W) with HBF$_4$ at −80 °C yields the respective ethylidene products [RhM(=C(H)CH$_3$)(CO)$_4$(dppm)$_2$][BF$_4$] by protonation at the β-carbon of the vinyl group. Upon warming, these carbenes transform to the ethylene adducts [RhM(C$_2$H$_4$)(CO)$_4$(dppm)$_2$][BF$_4$]. Owing to uncertainties concerning the structure of the halide precursor [RhMoCl(CO)$_4$(dppm)$_2$], its structure was determined by X-ray techniques and the chloro ligand was found to bridge the metals giving a square planar coordination at Rh and an octahedral coordination at Mo. One carbonyl on Mo assumes a weak semibridging interaction with Rh.

Introduction

Currently there is considerable industrial interest in the development of catalysts containing two or more different metals, applications for which can be found in a number of processes, including coal hydrodesulfurization, methanol carbonylation, naptha reforming, and olefin oxidation.[1] In addition, the use of Rh/Pt mixed-metal catalysts is widespread in the scrubbing of exhaust gases from automobile engines.[1] Most of the catalysts used are heterogeneous and are poorly characterized, so little is understood about the roles of the different metals in the catalytic transformations.

We have been attempting to determine the roles of adjacent metals in the transformations of organic substrates through studies of well-defined, mixed-metal complexes, which can serve as models for the heterogeneous systems. Until now we have investigated the Rh/Ir,[2] Rh/Os,[3] Rh/Ru,[4] Rh/Re,[5] Ir/Re,[5c] Rh/Mn,[5c,6] Ir/Os,[7] and Ir/Ru[8] combinations of metals. As a continuation of this work, we have initiated a study involving combinations of Rh with metals from group 6 (Mo, W), with a view toward establishing how these metal combinations can modify the reactivity of organic groups. The results of this study are presented herein.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified argon. Solvents were dried and distilled under nitrogen immediately before use. Sodium benzophenone was used as the drying agent except for CH$_2$Cl$_2$, which was distilled from P$_2$O$_5$. Hydrated rhodium trichloride was purchased from Johnston Matthey Ltd., whereas the group 6 metal hexacarbonyls were purchased from Aldrich and were used as received. Bis(diphenylphosphino)methane (dppm), HBF$_4$·(OMe$_2$)$_2$, all Grignard reagents, and alkynes were purchased from Aldrich and were used as received. The 99% ^{13}CO was purchased from Isotec Inc. The compounds [M(CO)$_3$(dppm-PP′)(dppm-P)][9] (M = Mo,[10a] W[10b]), [RhCl(CO)$_2$]$_2$,[11] [RhMo(H)-

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$(CO)_4(dppm)_2]$ (**1**),[12] $[RhMo(Cl)(CO)_4(dppm)_2]$ (**2**),[13a,b] and $[RhW(Cl)(CO)_4(dppm)_2]$ (**3**)[13a] were prepared according to published procedures.

All ^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. The internal deuterated solvent served as a lock for the spectrometer. Infrared spectra were run on a Nicolet 7199 FT interferometer as solids in Nujol or dichloromethane casts on KBr. Elemental analyses were performed by the microanalytical service within the department. Spectroscopic data for all compounds are given in Table 1.

Preparation of Compounds. (a) $[RhMo(MeO_2CC{=}C(H)CO_2Me)(CO)_4(dppm)_2]$ (4). A 20 μL (0.163 mmol) sample of $CH_3O_2CC{\equiv}CCO_2CH_3$ (DMAD) was added to 100 mg (0.0925 mmol) of compound **1** in 10 mL of THF. The mixture was stirred for 1 h and then 20 mL of *n*-pentane was added, resulting in the precipitation of an orange solid. The solvent was removed via cannula and the solid washed with 3 × 10 mL of *n*-pentane. Yield: 92 mg, 81%. Anal. Calcd for $C_{60}H_{51}P_4O_8RhMo$: C, 58.94; H, 4.20. Found: C, 59.01; H, 4.23.

(b) $[RhMo(C(CF_3){=}C(H)CF_3)(CO)_4(dppm)_2]$ (5). Hexafluoro-2-butyne (HFB) was bubbled slowly for 1 min through a solution of 54 mg (0.0500 mmol) of compound **1** in 10 mL of THF, resulting in a color change from dark red to light orange. The mixture was stirred for 20 min and then the solvent removed in vacuo. The yellow residue was recrystallized from CH_2Cl_2/Et_2O. Yield: 56 mg, 89%. Anal. Calcd for $C_{58}H_{45}F_6P_4O_8RhMo$: C, 56.06; H, 3.65. Found: C, 56.40; H, 3.63.

(c) $[RhMo(H_2C{=}CC(O)Me)(CO)_4(dppm)_2]$ (6). A 14 μL (0.179 mmol) sample of 3-butyn-2-one was added to a solution of 100 mg (0.0925 mmol) of compound **1** in 10 mL of THF. The solution was stirred for 18 h, and then the solvent was removed in vacuo. The residue was redissolved in 5 mL of benzene and filtered through Celite, and then 15 mL of a 2:1 mixture of Et_2O/*n*-pentane was added. After stirring for 1 h, the solvent was removed via cannula and the orange solid washed with 3 × 10 mL of the Et_2O/pentane mixture. Yield: 31 mg, 29%. Anal. Calcd for $C_{58}H_{49}P_4O_5RhMo$: C, 61.50; H, 4.36. Found: C, 61.41; H, 4.52.

(d) $[RhMo(H_2C{=}CCO_2Me)(CO)_4(dppm)_2]$ (7). A 40 μL (0.450 mmol) sample of methyl propiolate was added to a solution of 100 mg (0.0925 mmol) of compound **1** in 10 mL of THF. The solution was stirred for 18 h, and the solvent was removed in vacuo. The residue was redissolved in 10 mL of benzene and filtered through Celite. Slow addition of 15 mL of Et_2O resulted in the formation of an orange precipitate, which was then washed with 3 × 10 mL of Et_2O and dried in vacuo. Yield: 54 mg, 50%. Anal. Calcd for $C_{58}H_{49}P_4O_6RhMo$: C, 59.81; H, 4.24. Found: C, 59.24; H, 3.88. Analyses for C and H were always low, for which we have no explanation.

(e) $[RhMo(CH{=}CH_2)(CO)_4(dppm)_2]$ (8). A 1.5 mL sample of $CH_2{=}CHMgBr$ (1.0 M in THF, 1.5 mmol) was added to a suspension of 233 mg of compound **2** (0.209 mmol) in 100 mL of benzene and stirred for 1.5 h. The dark red-brown solution was washed with 5 × 10 mL of degassed water, followed by solvent removal in vacuo. The residue was extracted with 2 × 5 mL of CH_2Cl_2, and the extracts were filtered through Celite. Slow addition of 25 mL of a 1:1 mixture of Et_2O/*n*-pentane resulted in the formation of a yellow microcrystalline solid. The solvent was removed via cannula, and the solid was washed with 3 × 5 mL of a 1:1 Et_2O/*n*-pentane and then dried in vacuo. Yield: 153 mg, 66%. Anal. Calcd for $C_{56}H_{47}P_4O_4RhMo$: C, 60.78; H, 4.28. Found: C, 60.70; H, 4.04.

(f) $[RhW(CH{=}CH_2)(CO)_4(dppm)_2]$ (9). A 0.810 mL sample of $CH_2{=}CHMgBr$ (1.0 M in THF, 0.810 mmol) was added to 140 mg (0.116 mmol) of compound **3** in 45 mL of benzene and was then stirred for 1 h, during which time the solution turned from green to red. The solution was washed with 6 × 10 mL of degassed water, and then the solvent was removed in vacuo. The orange residue was dissolved in 10 mL of CH_2Cl_2 and filtered through Celite. An orange solid was precipitated by the addition of 25 mL of a 60:40 mixture of *n*-pentane/Et_2O. Yield: 110 mg, 79%. Anal. Calcd for $C_{56}H_{47}P_4O_4RhW$: C, 56.30; H, 4.00. Found: C, 55.93; H, 3.90.

(g) $[RhMo(CH_3)(CO)_4(dppm)_2]$ (10). A 225 μL sample of CH_3MgCl (3.0 M in THF, 0.825 mmol) was added to a suspension of 150 mg of compound **2** (0.135 mmol) in 15 mL of benzene. The mixture was stirred for 3 h, during which time the orange solid dissolved and a dark red-brown solution formed. The solution was washed with 5 × 10 mL of degassed water and then concentrated in vacuo to ca. 5 mL. Hexanes were added dropwise to precipitate a yellow solid, which was washed with 3 × 5 mL of hexanes and dried in vacuo. Yield: 90 mg, 61%. Anal. Calcd for $C_{55}H_{47}P_4O_4RhMo$: C, 60.34; H, 4.33. Found: C, 60.18; H, 4.26.

(h) $[RhMo(CH_2C_6H_5)(CO)_4(dppm)_2]$ (11) and $[RhMo(C(O)CH_2C_6H_5)(CO)_4(dppm)_2]$ (12). A 320 μL sample of 2.0 M benzylmagnesium chloride (0.640 mmol) was added to 100 mg (0.0897 mmol) of compound **2** in 100 mL of benzene under an atmosphere of CO. The solution was stirred under CO for 10 min and then for 50 min with a gentle argon purge. After washing the solution with 5 × 10 mL of water the solvent was removed in vacuo. The residue was redissolved in 5 mL of CH_2Cl_2 and filtered through Celite, and then an orange solid was precipitated by the addition of 10 mL of 1:1 *n*-pentane/Et_2O. The solid was washed with 3 × 5 mL of the pentane/Et_2O mixture and dried in vacuo. Yield: 67 mg. Extraction of this mixture with benzene/Et_2O (10:1) allowed the isolation of ca. 10 mg of compound **11**. Anal. Calcd for $C_{61}H_{51}P_4O_4RhMo$: C, 62.20; H, 4.30. Found, C, 62.20; H, 4.55.

(i) $[RhMoPh(CO)_4(dppm)_2]$ (13). A 1.6 mL sample of 2.0 M PhMgCl (3.2 mmol) was added to 134 mg of compound **2** (0.108 mmol) in 100 mL of benzene under an atmosphere of carbon monoxide, resulting in the immediate formation of a dark brown solution. The solution was stirred under an atmosphere of CO for 10 min and then with a gentle argon purge for 50 min. The solution was washed with 5 × 10 mL of degassed water followed by solvent removal in vacuo. After redissolving in 5 mL of CH_2Cl_2, the solution was filtered through Celite. An orange solid was precipitated by the addition of 30 mL of a 1:1 mixture of Et_2O/*n*-pentane and the solvent removed via cannula. The solid was washed with 3 × 5 mL of Et_2O/*n*-pentane and dried in vacuo. Yield: 55 mg, 40%. NMR spectra showed that the complex crystallized with 1/4 equiv of CH_2Cl_2. Anal. Calcd for $C_{60.25}H_{49.5}P_4O_4RhMo$: C, 61.43; H, 4.24; Cl, 2.08. Found: C, 61.68; H, 4.20; Cl, 1.51.

(j) $[RhMo(\eta^1\text{-}CH_2CH{=}CH_2)(CO)_4(dppm)_2]$ (14). A 1.3 mL sample of 2.0 M $CH_2{=}CHCH_2MgCl$ (2.6 mmol) was added to 85 mg (0.0762 mmol) of compound **2** in 5 mL of benzene and stirred for 30 min. A 95 mL sample of benzene was added, then the solution was washed with 5 × 10 mL of water, and the solvent was removed in vacuo. The residue was extracted with 2 × 5 mL of benzene, the extracts were filtered through Celite, and 15 mL of *n*-pentane was added slowly to precipitate an orange solid. Yield: 35 mg, 40%. Anal. Calcd for $C_{57}H_{49}P_4O_4RhMo$: C, 61.09; H, 4.41. Found: C, 61.28; H, 4.24.

(k) $[RhMo({=}CH(CH_3))(CO)_4(dppm)_2][BF_4]$ (15). This compound was characterized via low-temperature NMR spectroscopy. A 1.5 μL sample of $HBF_4{\cdot}(OMe_2)_2$ (0.014 mmol) was added to 15.4 mg (0.014 mmol) of compound **8** in 0.5 mL of CD_2Cl_2 in a septum-capped NMR tube at −80 °C, resulting in

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(9) The convention used is as follows: dppm-PP′ = chelating; dppm-P = pendant, monodentate; dppm with no designation in a binuclear complex indicates bridging.

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Table 1. Spectroscopic Data for Compounds[a]

		NMR[c]	
compound	IR (cm^{-1})[b]	δ(^{31}P{^{1}H}) (ppm)	δ(^{1}H) (ppm)[g]
RhMo(MeO$_2$CC=C(H)CO$_2$Me)(CO)$_4$(dppm)$_2$[e] (**4**)	1966(vs) 1911(s) 1771(vs) 1749(s) 1690(s)	23.9(dm, $^1J_{\mathrm{Rh-P}}$ = 136.1 Hz, Rh-*P*), 38.9(m, Mo-*P*)	2.87,2.97(m, 2H (each), Ph$_2$PCH_2PPh$_2$), 3.05(s, 6H, CO$_2$CH_3), 4.56(d, 1H, $^3J_{\mathrm{Rh-H}}$ = 2.5 Hz, MeO$_2$C(*H*)C=CCO$_2$Me(Rh))
RhMo(F$_3$CC=C(H)CF$_3$)(CO)$_4$(dppm)$_2$ (**5**)	1978(vs) 1923(vs) 1788(m)	22.0(dm, $^1J_{\mathrm{Rh-P}}$ = 132.8 Hz, Rh-*P*) 38.7(m, Mo-*P*)	2.95,3.04(m, 2H (each), Ph$_2$PCH_2PPh$_2$) 5.15(m, 1H, $^3J_{\mathrm{HF}}$ = 10.0 Hz, CF$_3$(*H*)C=CCF$_3$(Rh))
RhMo(H$_2$C=CCOMe)(CO)$_4$(dppm)$_2$[d] (**6**)	1965(vs) 1911(vs) 1776(s) 1739(s) 1646(m)	23.2(dm, $^1J_{\mathrm{Rh-P}}$ = 144.0 Hz, Rh-*P*) 41.0(m, Mo-*P*)	1.15(s, 3H, H$_2$C=CCO*Me*) 2.95,2.99(m, 2H (each), Ph$_2$PCH_2PPh$_2$) 5.36(bs, 1H, H_2C=CCOMe, cis to Rh) 5.59(d, 1H, $^3J_{\mathrm{Rh-H}}$ = 4.3 Hz, H_2C=CCOMe, trans to Rh)
RhMo(H$_2$C=CCO$_2$Me)(CO)$_4$(dppm)$_2$ (**7**)	1975(vs) 1921(vs) 1771(vs) 1738(s) 1698(m)	22.5(dm, $^1J_{\mathrm{Rh-P}}$ = 141.1 Hz, Rh-*P*) 40.9(m, Mo-*P*)	2.75(s, 3H, H$_2$C=CCO$_2$*Me*) 2.95(dm, 4H, Ph$_2$PCH_2PPh$_2$) 5.05(bs, 1H, H_2C=CCO$_2$Me, cis to Rh) 5.91(m, 1H, $^3J_{\mathrm{Rh-H}}$ = 4.0 Hz, $^1J_{\mathrm{HH}}$ = 1.8 Hz, H_2C=CCO$_2$Me, trans to Rh)
RhMo(CH=CH$_2$)(CO)$_4$(dppm)$_2$[d] (**8**)	1968(vs) 1919(m) 1776(s) 1760(s)	25.35(dm, $^1J_{\mathrm{Rh-P}}$ = 149.3 Hz, Rh-*P*) 43.20(m, Mo-*P*)	2.86(m, 4H, Ph$_2$PCH_2PPh$_2$) 4.27(dm, ^{1}H, $^3J_{\mathrm{HH}}$ = 18 Hz, CH=CH_2) 5.09(dm, 1H, $^3J_{\mathrm{HH}}$ = 11 Hz, CH=CH_2) 6.75(m, 1H, C*H*=CH$_2$)
RhW(CH=CH$_2$)(CO)$_4$(dppm)$_2$[d] (**9**)	1967(vs) 1903(m) 1771(s) 1749(s)	27.5(dm, $^1J_{\mathrm{Rh-P}}$ = 149.4 Hz, Rh-*P*) 18.3 (m, W-*P*)	2.95(m, 4H, Ph$_2$PCH_2PPh$_2$) 4.25(dm, ^{1}H, CH=CH_2) 5.15(dm, 1H, CH=CH_2) 6.78(m, 1H, C*H*=CH$_2$
RhMo(CH$_3$)(CO)$_4$(dppm)$_2$[d] (**10**)	1952(vs) 1900(vs) 1762(vs) 1744(vs)	31.72(dm, $^1J_{\mathrm{Rh-P}}$ = 147.7 Hz, Rh-*P*) 43.23(m, Mo-*P*)	0.15(dt, 3H, $^2J_{\mathrm{Rh-H}}$ = 2.3 Hz, $^3J_{\mathrm{H-P}}$ = 7.5 Hz, Rh−CH_3) 2.85(m, 4H, Ph$_2$PCH_2PPh$_2$)
RhMo(CH$_2$Ph)(CO)$_4$(dppm)$_2$[d] (**11**)	1954(vs) 1890(s) 1788(s)	26.12(dm, $^1J_{\mathrm{Rh-P}}$ = 151.4 Hz, Rh-*P*) 41.45(m, Mo-*P*)	2.66(dt, 2H, $^2J_{\mathrm{Rh-H}}$ = 3.6 Hz, $^3J_{\mathrm{P-H}}$ = 8.2 Hz, Rh−CH_2Ph) 2.93(m, 4H, Ph$_2$PCH_2PPh$_2$) 5.63(m, 2H C$_6H_5$CH$_2$) 6.35(m, 3H, C$_6H_5$CH$_2$)
RhMo(C(O)CH$_2$Ph)(CO)$_4$(dppm)$_2$[d,h] (**12**)	1600(m)	17.3(dm, $^1J_{\mathrm{Rh-P}}$ = 167.9 Hz, Rh-*P*) 40.9(m, Mo-*P*)	2.95(m, 4H, Ph$_2$PCH_2PPh$_2$) 3.15(s, 2H, RhC(O)CH_2Ph)
RhMo(Ph)(CO)$_4$(dppm)$_2$[d] (**13**)	1953(vs) 1907(s) 1763(vs)	23.65(dm, $^1J_{\mathrm{Rh-P}}$ = 148.7 Hz, Rh-*P*) 41.74(m, Mo-*P*)	2.96(m, 4H Ph$_2$PCH_2PPh$_2$) 5.97(m) 2H, C$_6H_5$[d]) 6.09(m, 1H, C$_6H_5$[d]) 6.50(m, 2H, C$_6H_5$[d])
RhMo(η^1-CH$_2$CH=CH$_2$)(CO)$_4$(dppm)$_2$[d,f] (**14**)	1963(vs) 1907 (s) 1760(s)	28.27(dm, $^1J_{\mathrm{Rh-P}}$ = 152.9 Hz, Rh-*P*) 41.89(m, Mo-*P*)	2.74(m, 2H, CH_2CH=CH$_2$) 2.85(m, 4H, Ph$_2$PCH_2PPh$_2$) 3.46(m, 1H, CH$_2$CH=CHH_{trans}) 4.10(dm, 1H, CH$_2$CH=CHH_{cis}) 5.87(m, 1H, CH$_2$C*H*=CH$_2$)
[RhMo(=CHCH$_3$)(CO)$_4$(dppm)$_2$][BF$_4$][i] (**15**)		11.7(dm, $^1J_{\mathrm{Rh-P}}$ = 146.1, Rh-*P*) 39.4(m, Mo-*P*)	1.73(d, 3H, $^3J_{\mathrm{HH}}$ = 7.3 Hz =CHCH_3) 3.01(m, 4H, Ph$_2$PCH_2PPh$_2$) 18.81(m, 1H, $^3J_{\mathrm{HH}}$ = 7.3 Hz, =C*H*CH$_3$)

Table 1 (Continued)

compound	IR (cm^{-1})^b	NMR^c	
		δ(^{31}P{^{1}H}) (ppm)	δ(^{1}H) (ppm)^g
[RhMo(η^2-$H_2C{=}CH_2$)(CO)$_4$(dppm)$_2$][BF$_4$] (**16**)	2010(vs) 1967(m) 1832(s) 1813(s)	29.9(dm, $^1J_{RhP}$ = 131.2 Hz, Rh-*P*) 37.3(m, Mo-*P*)	3.10(m, 4H $Ph_2PCH_2PPh_2$) 3.58(dt, 4H, $^2J_{RhH}$ = $^3J_{PH}$ = 2 Hz, C_2H_4)
[RhW(=CHCH$_3$)(CO)$_4$(dppm)$_2$][BF$_4$]^i (**17**)		26.9(dm, $^1J_{RhP}$ = 147.2 Hz, Rh-*P*) 17.0(m, Mo-*P*)	1.71(d, 3H, $^3J_{HH}$ = 7.5 Hz, =CHC*H*$_3$) 3.2(m, 4H, $Ph_2PCH_2PPh_2$) 18.79(m, 1H, $^3J_{HH}$ = 7.5 Hz, =C*H*CH$_3$)
[RhW(η^2-$H_2C{=}CH_2$)(CO)$_4$(dppm)$_2$][BF$_4$] (**18**)		31.7(dm, $^1J_{Rh-P}$ = 110 Hz, Rh-*P*) 13.1(m, Mo-*P*)	3.30(m, 4H, $Ph_2PCH_2PPh_2$) 3.59(br,s, 4H, C_2H_4)
[RhMo(PhC$_2$H)(CO)$_4$(dppm)$_2$][BF$_4$] (**19**)	2007(s) 1979(vs) 1843(m)	26.4(dm, $^1H_{Rh-P}$ = 103 Hz, Rh-*P*) 34.7(m, Mo-*P*)	2.59(m, 2H, $Ph_2PCH_2PPh_2$) 3.25(m, 2H, $Ph_2PCH_2PPh_2$) 6.58(m, 3H, *Ph*C$_2$H) 7.09(m, 2H, *Ph*C$_2$H)

[a] Abbreviations used: for IR spectra, (vs) very strong; (s) strong; (m) medium; for NMR (dt) doublet of triplets, (m) multiplet, (dm) doublet of multiplets, (br) broad. [b] IR spectra recorded as a Nujol mull unless otherwise stated. [c] NMR spectra recorded in CD_2Cl_2 unless otherwise stated. [d] IR spectra recorded as CH_2Cl_2 cast. [e] IR spectra recorded in CH_2Cl_2 solution. [f] NMR spectra recorded in C_6D_6. [g] dppm-bound phenyl groups omitted. [h] CO bands obscured by **12a**. [i] Characterized via low-temperature NMR.

the immediate formation of a purple solution. NMR spectra of the reaction mixture were obtained at temperatures starting from −80 °C to 25 °C by warming the probe to the desired temperature, with the sample in place, and allowing the sample to stand for 20 min before recording the spectra.

(l) [RhMo(η^2-$H_2C{=}CH_2$)(CO)$_4$(dppm)$_2$][BF$_4$] (16). A 3 μL (0.028 mmol) sample of HBF$_4$·(OMe$_2$)$_2$ was added to a solution of 25 mg (0.0226 mmol) of compound **8** in 5 mL of CH_2Cl_2 at −80 °C, resulting in the formation of a deep purple solution, which slowly turned brown upon warming to room temperature over a period of 1 h. A 7 mL sample of Et$_2$O was added, resulting in the formation of a brown solid. The solvent was removed via cannula, and the solid was washed with 3 × 10 mL of Et$_2$O and dried in vacuo. Yield: 19 mg, 70%. Elemental analyses were not obtained due to the unstable nature of the compound.

(m) [RhW(=CHCH$_3$)(CO)$_4$(dppm)$_2$][BF$_4$] (17). This compound was characterized via low-temperature NMR spectroscopy. A 1.6 μL sample of HBF$_4$·(OMe$_2$)$_2$ (0.0131 mmol) was added to 13.9 mg (0.0116 mmol) of compound **9** in 0.5 mL of CD_2Cl_2 in a septum-capped NMR tube at −80 °C, resulting in the immediate formation of a purple solution. NMR spectra of the reaction mixture were obtained at temperatures starting from −80 °C to 25 °C by warming the probe to the desired temperature, with the sample in place, and allowing the sample to stand for 20 min before recording the spectra.

(n) [RhW(η^2-$CH_2{=}CH_2$)(CO)$_4$(dppm)$_2$][BF$_4$] (18). A 4.1 μL sample of HBF$_4$·(OMe$_2$)$_2$ (0.0337 mmol) was added to 40 mg (0.0335 mmol) of compound **9** in 5 mL of CH_2Cl_2 at −80 °C. The solution was warmed to room temperature, during which time it turned brown. A 25 mL sample of Et$_2$O was added slowly, resulting in the formation of a brown precipitate. The solid was washed with 2 × 10 mL of Et$_2$O and dried briefly under vacuum. Yield: 30 mg, 70%. Elemental analyses were not obtained due to the unstable nature of the compound.

(o) [RhMo(PhC$_2$H)(CO)$_4$(dppm)$_2$][BF$_4$] (19). A 3 μL sample of HBF$_4$·(OMe$_2$)$_2$ (0.0246 mmol) was added to a solution of 25 mg (0.0226 mmol) of compound **8** in 5 mL of CH_2Cl_2 at −80 °C. The solution was warmed to −60 °C, and then 38 μL (0.346 mmol) of phenylacetylene was added. The solution was warmed to room temperature and stirred for 1 h, and then 15 mL of Et$_2$O was added, resulting in the formation of a green solid. The solvent was removed via cannula and the solid washed with 2 × 10 mL of Et$_2$O and dried in vacuo. Yield: 24 mg, 89%. Anal. Calcd for $C_{62}H_{50}BF_4P_4O_4RhMo \cdot 0.5CH_2Cl_2$: C, 57.26; H, 3.92. Found: C, 57.49; H, 3.72. The presence of half an equivalent of CH_2Cl_2 was confirmed by ^{1}H NMR.

X-ray Data Collection. Suitable crystals of compound **2** were grown by slow diffusion of Et$_2$O into a CH_2Cl_2 solution of **2** at ambient temperature. Data were collected to a maximum $2\theta = 50.0°$ 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 $21.2° < 2\theta < 23.8°$. The $2/m$ diffraction symmetry and the systematic absences established the space group as $P2_1/c$ (No. 14). Three reflections were chosen as intensity standards and were remeasured every 7200 s of X-ray exposure time, with no decay evident. Absorption corrections were applied to the data by the method of Walker and Stuart.[14] See Table 2 for a summary of crystal data and X-ray collection information.

The structure was solved by direct methods, using SHELX-86[15] to locate the Rh, Mo, P, and Cl atoms. All other atoms were located after subsequent least-squares cycles and difference Fourier syntheses. Refinement was completed using the program SHELXL-93.[16] All hydrogen atoms of the complex were included as fixed contributions; their idealized positions were generated from the geometries of the attached carbon atoms and their thermal parameters set at 20% greater than the isotropic thermal parameter of these carbons. The partial-occupancy CH_2Cl_2 solvent molecules were refined with fixed idealized geometries: d(Cl(91)−C(91)) = d(Cl(92)−C(91)) = d(Cl(93)−C(92)) = d(Cl(93)−C(92)) = 1.80 Å; d(Cl(91)°Cl(92)) = d(Cl(93)°Cl(94)) = 2.95 Å. The final model for the complex refined to values of $R_1(F) = 0.0369$ (for $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.1125$ (for all data with $F_o^2 \geq -3\sigma(F_o^2)$).

Results and Compound Characterization

Preparation of Alkyl and Alkenyl Complexes. Transition metal complexes containing σ-bound organic fragments occupy key positions as intermediates in many catalytic sequences.[17] These complexes may be prepared in a variety of ways, including reactions of metal−hydride complexes with unsaturated molecules such as alkynes and via halide displacement by organic nucleophiles. Our investigation into alkyl and alkenyl

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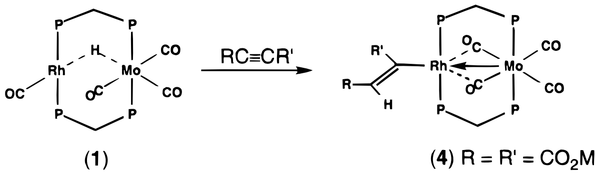
(14) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158−166.
(15) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.
(16) Sheldrick, G. M. *SHELXL-93*, Program for crystal structure determination; University of Göttingen: Germany, 1993.
(17) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 12.

Table 2. Crystallographic Experimental Details for Compound $2{\cdot}0.75CH_2Cl_2$

A. Crystal Data	
formula	$C_{54.75}H_{45.5}Cl_{2.5}MoO_4P_4Rh^a$
fw	1178.77
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell params	
a (Å)	12.940(3)
b (Å)	27.149(4)
c (Å)	15.3860(14)
β(deg)	95.955(13)
V (Å^3)	5376.3(16)
Z	4
ρ_{calcd} (g cm^{-3})	1.456
μ (mm^{-1})	0.827
B. Data Collection and Refinement Conditions	
diffractometer	Enraf-Nonius CAD4
radiation (λ [Å])	graphite-monochromated Mo Kα (0.710 73)
temperature (°C)	22
scan type	$\theta{-}2\theta$
data collec 2θ limit (deg)	50.0
total no. of data collc	9852 ($0 \le h \le 15, 0 \le k \le 32, -18 \le l \le 18$)
no. of independ refl	9408
no. of obs (NO)	6730 ($F_o^2 \ge 2\sigma(F_o^2)$)
structure solution method	direct methods (SHELXS-86)
refinement method	full-matrix least-squares on F^2 (SHELXL-93)
abs corr method	DIFABS
range of transm factors	1.090−0.815
no. of data/restraints/params	9402 [$F_o^2 \ge -3\sigma(F_o^2)$]/6/604
goodness-of-fit (S)^b	1.017 [$F_o^2 \ge -3\sigma(F_o^2)$]
final R indices^c	
$F_o^2 \ge 2\sigma(F_o^2)$	$R_1 = 0.0369$, $wR_2 = 0.0938$
all data	$R_1 = 0.0753$, $wR_2 = 0.1125$
largest diff peak and hole (e Å^{-3})	0.652 and −0.545

[a] For [RhMo(CO)$_4$(μ-Cl)(dppm)$_2$]·0.75 CH$_2$Cl$_2$. [b] $S = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0525P)^2 + 6.8113P]^{-1}$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$). [c] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$.

complexes of Rh and group 6 metals began with the preparation of a variety of vinyl species, through the reaction of the known hydride, [RhMo(H)(CO)$_4$(dppm)$_2$] (**1**),[12] with activated alkynes. Reaction of compound **1** with dimethyl acetylenedicarboxylate (DMAD) produces the targeted [RhMo(MeO$_2$CC=C(H)CO$_2$Me)(CO)$_4$(dppm)$_2$] (**4**) in high yield, as shown in eq 1. The ^{1}H NMR spectrum of **4** shows the DMAD methyl groups, apparently coincidentally degenerate, at δ 3.05, and the vinylic hydrogen resonating at δ 4.56 as a doublet with 2.5 Hz coupling to Rh, indicating that the alkenyl moiety is bound to this metal. The small rhodium−hydrogen coupling constant suggests that these two groups are in a mutually cis arrangement about the carbon−carbon double bond, as is often observed for alkyne insertions into metal−hydrogen bonds. Also in the ^{1}H NMR spectrum the dppm methylene hydrogens appear as two multiplets, indicating separate environments for these protons due to apparent front−back asymmetry in the planar RhMoP$_4$ framework. The source of the asymmetry is presumably the orientation of the vinyl group and suggests that rotation of the substituted vinyl group is hindered, presumably due to interactions of the vinyl substituents and the large phenyl groups on the dppm ligands. Hindered rotation of vinyl groups has previously been observed in a related Rh/Os system.[3b] The IR spectrum of **4** in the solid state shows terminal CO bands at 1966 and 1911 cm^{-1}, as well as bands at 1771 and 1749 cm^{-1}, suggesting the presence of bridging carbonyls, and DMAD carbonyl bands at 1690 cm^{-1}. In the ^{13}C{^{1}H} NMR spectrum of this compound, four carbonyl resonances appear at δ 208.3, 220.1, 235.1, and 247.5. All of these signals are broadened singlets (ca. 25 Hz half-width) except for the low-field resonance, which, although also broad, displays rhodium coupling of 24.5 Hz. The absence of resolvable ^{31}P coupling to the carbonyls seems typical of the alkyl and alkenyl Rh−Mo complexes prepared in this work and may be a consequence of the presence of quadrupolar isotopes of molybdenum (^{95}Mo and ^{97}Mo, $I = 5/2$ with ca. 16% and 10% natural abundance, respectively). The Rh−C coupling constant of the low-field ^{13}C NMR signal and the low CO stretching frequencies suggest a semibridging bonding mode for at least one of the carbonyls, in which this CO is bound more strongly to Mo. This can be compared to a symmetrically bridging arrangement, for which the Rh−C coupling generally exceeds 30 Hz.[18] The presence of two low-frequency CO bands in the IR spectrum, both in the solid and solution, suggests that two carbonyls on Mo are involved in semibridging interactions with rhodium. That only one CO resonance displays rhodium coupling in the ^{13}C{^{1}H} NMR spectrum suggests that one of these carbonyls may be engaged in a stronger semibridging interaction than the other. This could be a consequence of steric factors, in which the vinyl group forces the CO syn to this substituent away from the rhodium center, with the CO anti to the vinyl group compensating by accepting more electron density from rhodium. A similar "strong/weak" arrangement of semibridging carbonyls was observed in the X-ray structure of the isoelectronic vinyl complex [RhOs(C(CH$_3$)=C(CH$_3$)$_2$)(CH$_3$)(CO)(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$].[3b]



(1)

(**1**)

(**4**) R = R' = CO$_2$Me

(**5**) R = R' = CF$_3$

(**6**) R = H, R' = C(O)Me

(**7**) R = H, R' = CO$_2$ Me

The presence of semibridging carbonyls is typical of dppm-bridged binuclear complexes having an η^1-hydrocarbyl ligand bound to rhodium and is presumably necessary to alleviate the buildup of electron density on rhodium resulting from the presence of the two phosphines and the alkenyl group, since in this series of compounds rhodium has no strong π-acceptor ligands of its own. To give rhodium a favorable 16e configuration, a Mo→Rh dative bond is invoked in compound **4** and its analogues, all of which are proposed to have similar structures (vide infra). A similar arrangement, in which the η^1-hydrocarbyl group is bound to Rh, has been observed in the Rh/Os,[3a,b] Rh/Ru,[4] Rh/Mn,[6b,c] and Rh/Re[5d] complexes previously prepared in this group but is in contrast to a number of Rh/Ir complexes, in which the hydrocarbyl group is usually bound to iridium.[2b]

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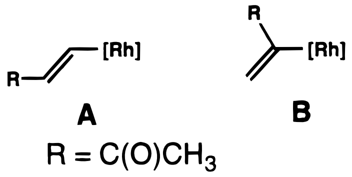
(18) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data For Organometallic Compounds*; Academic Press Inc.: New York, 1981.

Reaction of **1** with hexafluoro-2-butyne (HFB) produces $[RhMo(F_3CC{=}C(H)CF_3)(CO)_4(dppm)_2]$ (**5**), which is spectroscopically similar to **4**. The ^1H NMR spectrum shows the vinylic-hydrogen resonance at δ 5.15 as a slightly broadened quartet, in which the quartet structure is due to ^{19}F coupling (10 Hz) and the broadening is likely a result of unresolved Rh coupling; as was observed for **4**, the two dppm resonances indicate front–back asymmetry in the complex, as is also observed for compounds **6** and **7** (vide infra).

The reaction of 3-butyn-2-one with **1** yields the alkenyl-containing species $[RhMo(CH_3C(O)C{=}CH_2)(CO)_4(dppm)_2]$ (**6**), in which two regioisomers are possible, as shown in structures **A** and **B**. The ^1H NMR spectrum of this species shows the methyl singlet at δ 1.15 and the dppm methylene resonance centered at δ 2.97 as a broad AB quartet with additional phosphorus coupling. A slightly broadened singlet is observed at δ 5.36, and a doublet, with 4.3 Hz Rh coupling, at δ 5.59 is also apparent. If isomer **A** were formed, it is expected that the hydrogens on the α- and β-carbon of the vinyl group would show a large trans coupling of 15–18 Hz.[19] The observation of substantially lower coupling indicates that the less sterically favorable regioisomer, **B**, is formed. This presumably is due to the stronger metal–carbon bond in **B**, resulting from the presence of the electron-withdrawing $C(O)CH_3$ group on the α-carbon. Formation of the less sterically favored product has been observed previously when the resulting product has electron-withdrawing substituents on the α-carbon.[20] The vinyl-containing species $[RhMo((CH_3O_2C)C{=}CH_2)(CO)_4(dppm)_2]$ (**7**) is prepared similarly, via the reaction of compound **1** with methyl propiolate. Again, the electron-withdrawing substituent appears to be on the α-carbon.



Attempts to obtain an unsubstituted vinyl-containing species via the reaction of **1** with acetylene were unsuccessful. Although this reaction did result in the formation of some of the desired product, it was accompanied by a variety of uncharacterized impurities. We suggest that these additional products result from the tendency of acetylene to undergo a variety of competing reactions such as oligomerization and formation of vinylidenes.[21] In an earlier study the related hydride $[RhOsH(CO)_3(dppm)_2]$ also gave a mixture of products upon reaction with acetylene.[3b]

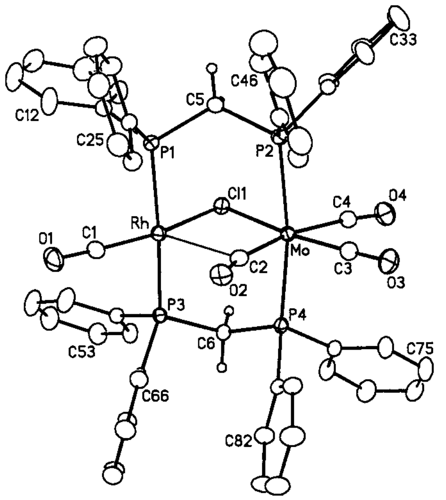


Figure 1. Perspective view of the $[RhMo(CO)_4(\mu\text{-}Cl)(dppm)_2]$ (**2**) molecule showing the atom-labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters for the dppm methylene groups and are not shown for the dppm phenyl groups.

Another common method for placing hydrocarbyl groups on transition metals involves the reaction of the appropriate metal–halide species with main-group organometallics such as alkyllithium or Grignard reagents. The known chloride species $[RhMo(Cl)(CO)_4(dppm)_2]$ (**2**) is a convenient precursor for this chemistry. However, we felt obliged to complete the characterization of this complex, since there was ambiguity in the literature about its structure.[13a,b] An X-ray structure of **2**, shown in Figure 1, confirms the normal “A-frame” geometry for the complex in which the chloro ligand bridges the two metals. In this arrangement the geometry at Rh is square planar, characteristic of Rh(+1), and at Mo is octahedral, characteristic of Mo(0). We view the chloro ligand as functioning as an anionic ligand to rhodium, while simultaneously donating a lone pair of electrons to molybdenum to complete the valence shell of this metal. The substantially shorter Rh–Cl (2.416(1) Å) compared to the Mo–Cl (2.651(1) Å) bond length is consistent with a Rh(+1)/Mo(0) formulation, on the basis of an expected smaller radius of Rh(+1) compared to Mo(0) (see Table 3 for selected bond lengths and angles). Consistent with this view, all bonds associated with Rh are shorter than the analogous bonds to Mo. For example, the average Rh–P distance (ca. 2.32 Å) is substantially shorter than the average Mo–P distance (ca. 2.48 Å), and the shortest metal–carbonyl distance is also that involving Rh. The carbonyl groups on Mo show the expected trends, with that opposite the donor chloride ligand having the shortest Mo–CO distance (1.919(5) Å), whereas the two mutually trans carbonyls have long Mo–CO distances (2.024(5) and 2.021(5) Å) due to decreased π back-donation resulting from competition for π-electron density. The carbonyl (C(2)O(2)) in the vicinity of rhodium appears to be involved in a weak semibridging interaction with this metal, as seen from the nonlinearity of this group (Mo–C(2)–O(2) = 165.2(4)°) and by the large asymmetry in its distances to the two metals (Mo–C(2) = 2.021(5) Å; Rh–C(2) = 2.720(5) Å). However, the rather long distance to rhodium, and the carbonyl bending, which is about 10° less than in other semibridging carbonyls, indicates a very

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(19) Lambert, J. B.; Shurvell, H. F.; Lightner, D.; Cooks, R. G. *Introduction to Organic Spectroscopy*; Macmillan Publishing Co.: New York, Chapter 4.

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

(21) 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.

Table 3. Selected Interatomic Distances and Angles for [RhMo(CO)$_4$(μ-Cl)(dppm)$_2$] (2)

(a) Distances (Å)

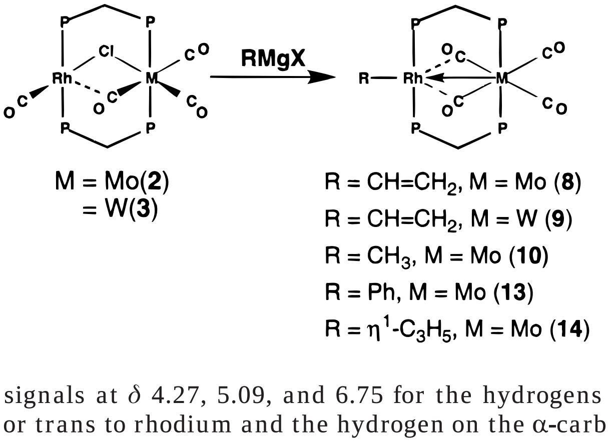
Rh−Cl(1)	2.4163(12)	Mo−C(4)	2.024(5)
Rh−P(1)	2.3127(12)	P(1)−C(5)	1.836(4)
Rh−P(3)	2.3212(11)	P(2)−C(5)	1.854(4)
Rh−C(1)	1.807(5)	P(3)−C(6)	1.833(4)
Mo−Cl(1)	2.6511(12)	P(4)−C(6)	1.847(4)
Mo−P(2)	2.4786(12)	O(1)−C(1)	1.141(5)
Mo−P(4)	2.4758(12)	O(2)−C(2)	1.155(5)
Mo−C(2)	2.021(5)	O(3)−C(3)	1.170(6)
Mo−C(3)	1.919(5)	O(4)−C(4)	1.140(6)

(b) Angles (deg)

Cl(1)−Rh−P(1)	88.95(4)	P(4)−Mo−C(3)	93.94(14)
Cl(1)−Rh−P(3)	86.97(4)	P(4)−Mo−C(4)	89.59(14)
Cl(1)−Rh−C(1)	165.5(2)	C(2)−Mo−C(3)	83.8(2)
P(1)−Rh−P(3)	170.64(4)	C(2)−Mo−C(4)	165.1(2)
P(1)−Rh−C(1)	89.56(15)	C(3)−Mo−C(4)	81.6(2)
P(3)−Rh−C(1)	92.28(15)	Rh−Cl(1)−Mo	77.74(3)
Cl(1)−Mo−P(2)	85.75(4)	Rh−P(1)−C(5)	112.90(15)
Cl(1)−Mo−P(4)	87.40(4)	Mo−P(2)−C(5)	112.97(15)
Cl(1)−Mo−C(2)	105.78(13)	Rh−P(3)−C(6)	114.24(14)
Cl(1)−Mo−C(3)	170.38(15)	Mo−P(4)−C(6)	112.21(14)
Cl(1)−Mo−C(4)	88.92(15)	Rh−C(1)−O(1)	177.0(5)
P(2)−Mo−P(4)	171.39(4)	Mo−C(2)−O(2)	165.2(4)
P(2)−Mo−C(2)	88.08(13)	Mo−C(3)−O(3)	179.1(5)
P(2)−Mo−C(3)	93.68(14)	Mo−C(4)−O(4)	171.7(5)
P(2)−Mo−C(4)	95.49(14)	P(1)−C(5)−P(2)	115.0(2)
P(4)−Mo−C(2)	88.77(13)	P(3)−C(6)−P(4)	114.1(2)

weak interaction with Rh in the present case. By comparison, in the compounds [RhMn(CO)$_4$(μ-S)(dppm)$_2$][6a] and [RhOs(C(CH$_3$)═CH$_2$)(CO)$_3$(dppm)$_2$],[3b] the Rh−CO interaction of the semibridging CO is 2.214(5) Å and the Mn−C−O angle is 149.9(4)° in the former, with the corresponding values in the Rh/Os complex being 2.075(8) Å and 155.2(6)°. The Rh−Mo separation in **2** (3.1852(7) Å) indicates that no metal−metal bond is present and consequently is longer than the P−P separations (3.113(2), 3.089(2) Å) within the diphosphine ligands.

Although the previous reaction of **1** with acetylene failed to generate the targeted species containing an unsubstituted vinyl ligand as the major product, the reaction of **2** with vinylmagnesium chloride produces the desired [RhMo(CH═CH$_2$)(CO)$_4$(dppm)$_2$] (**8**), in high yield, as outlined in eq 2. This vinyl ligand has ^{1}H NMR signals at δ 4.27, 5.09, and 6.75 for the hydrogens cis or trans to rhodium and the hydrogen on the α-carbon, respectively, having the expected cis and trans hydrogen−hydrogen couplings of 11 and 18 Hz. The dppm methylene region of the ^{1}H NMR spectrum differs from the previously mentioned substituted vinyl species in that only one signal (a pseudoquintet) is observed, suggesting that equilibration of the axial and equatorial hydrogens is occurring through rapid rotation of the vinyl group about the vinyl−rhodium bond, presumably reflecting the lower steric demands of the unsubstituted vinyl group. The IR spectrum of **8** shows carbonyl bands at 1968, 1919, 1776, and 1760 cm^{-1}, with the lower frequency bands indicative of bridging interactions. These CO bands are shifted to lower energy than those of the previously mentioned substituted vinyl species, presumably due to the electron-withdrawing groups in the former, which make them poorer σ-donors.



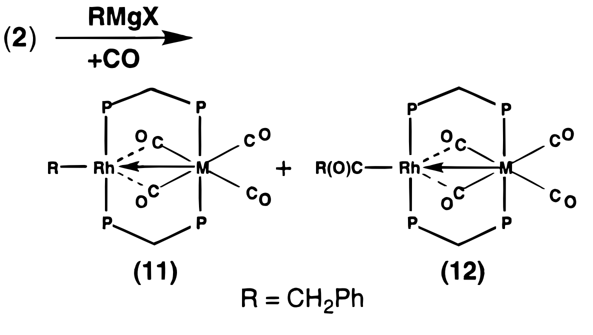
R = CH=CH$_2$, M = Mo (**8**)
R = CH=CH$_2$, M = W (**9**)
R = CH$_3$, M = Mo (**10**)
R = Ph, M = Mo (**13**)
R = η^1-C$_3$H$_5$, M = Mo (**14**)

(2)

The tungsten-containing analogue, [RhW(CH═CH$_2$)(CO)$_4$(dppm)$_2$] (**9**), is prepared in a similar manner and has spectroscopic properties comparable to compound **8**, indicating it has a similar structure.

The methyl-containing species, [RhMo(CH$_3$)(CO)$_4$(dppm)$_2$] (**10**), is prepared via the reaction of compound **2** with methylmagnesium chloride. As with the alkenyl products, the hydrocarbyl group is terminally bound to rhodium, as indicated by the ^{1}H NMR spectrum, which shows a triplet of doublets at δ 0.15 for the methyl resonance. The coupling constants for this signal ($^2J_{\mathrm{RhH}}$ = 2.3 Hz and $^3J_{\mathrm{PH}}$ = 7.5 Hz for the rhodium-bound phosphines) are quite similar to those of an isoelectronic complex [RhRe(CH$_3$)(CO)$_4$(dppm)$_2$][SO$_3$CF$_3$], the X-ray structure of which confirmed that the methyl group was terminally bound to rhodium.[5c] As with all previous products, the IR spectrum of **10** indicates that the complex has both terminal and bridging carbonyls, although the ^{13}C{^{1}H} NMR spectrum of this species is subtly different, having only two resonances, at δ 216.4 and 247.8, for the terminal and bridging groups, respectively. As has been observed in many of the above-mentioned Rh/Mo hydrocarbyl species, there is no observable coupling of either of these carbonyls with rhodium, but the large half-width (ca. 45 Hz) of the low-field resonance could easily mask a rhodium−carbon coupling that is characteristic of a semibridging carbonyl. In **10** the more symmetric environment (compared to the vinyl species) at Rh results in both semibridging carbonyls being equivalent, as are both terminal carbonyls.

Preparation of the benzyl analogue of **10** was of interest to us in view of previous reports of successful removal of a hydrogen from a terminal benzyl ligand to form an alkylidene.[22] When a large excess of benzylmagnesium chloride was added to **2**, no alkylation products were obtained. However, if the reaction is performed with 7 equiv of the Grignard reagent under an atmosphere of carbon monoxide, two compounds are obtained in a 1.8:1 ratio, as shown in eq 3. The major species is identified as the targeted benzyl compound,



(3)

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[22] Keil, W. A.; Lin, G. Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.

$[RhMo(CH_2Ph)(CO)_4(dppm)_2]$ (**11**), while the minor compound is the acyl product, $[RhMo(C(O)CH_2Ph)(CO)_4(dppm)_2]$ (**12**). As can be seen in Table 1, the ^{31}P NMR chemical shifts for the Mo-bound phosphorus nuclei are rather similar in both species, while there is a substantial difference in the Rh-bound signals, suggesting that the two have different chemical environments at the rhodium centers. An inspection of the ^1H NMR spectrum of **11** reveals the benzyl methylene hydrogen resonance at δ 2.66 as a doublet of triplets. The rhodium coupling of 3.6 Hz and the 8.2 Hz coupling to the rhodium-bound phosphines indicate that the benzyl ligand is σ-bound to the rhodium center. In contrast, the resonance for the benzyl hydrogens in **12** appears as a singlet at δ 3.15, with no coupling to either rhodium or phosphorus, suggesting the presence of a phenylacetyl group bound to rhodium, resulting from attack of the Grignard reagent on a coordinated carbonyl. Further evidence of this structure is obtained from the IR spectrum of **12**, which shows an acyl CO band at 1600 cm^{-1}. This compound was always obtained as a minor species, so the metal-bound carbonyl bands in the IR spectrum were always obscured by those of **11**.

An analogous aryl complex can be prepared by the reaction of $[RhMo(CO)_4(\mu\text{-}Cl)(dppm)_2]$ (**2**) with phenylmagnesium chloride under a carbon monoxide atmosphere, yielding $[RhMo(Ph)(CO)_4(dppm)_2]$ (**13**). Unlike the reaction involving the benzyl Grignard, the reaction of **2** with phenylmagnesium chloride gives only the product resulting from apparent attack at rhodium, although attack at coordinated CO, followed by subsequent CO loss, cannot be ruled out. Generally, the spectroscopy of this compound is similar to that of the compounds discussed above. Notable features are that no rhodium coupling of the β-hydrogens of the metal-bound phenyl group is observed, and the metal-bound phenyl hydrogens are shifted upfield from the phenyl–hydrogen resonances of the dppm-bound phenyl groups, presumably due to the proximity of this group to the rhodium center.

Addition of excess allylmagnesium chloride to **2** results in the formation of the η^1-allyl product, $[RhMo(\eta^1\text{-}C_3H_5)(CO)_4(dppm)_2]$ (**14**), the ^1H NMR spectrum of which shows the α-hydrogens of the allyl group resonating at δ 2.74. This signal is a multiplet, with unresolved rhodium, ^{31}P, and β-hydrogen coupling. The β-hydrogen signal is a multiplet at δ 5.87 with typical cis and trans couplings of 9 and 17 Hz to the other olefinic hydrogens, which appear as doublets at δ 4.10 and 3.46. An η^3-coordination mode for the allyl group can be ruled out since the observed ^1H chemical shifts for the allyl hydrogens are substantially different than for η^3-allyl groups, which generally appear in the range δ 1–3 for H_{anti}, δ 2–5 for H_{syn}, and δ 4–6.5 for $H_{central}$ with coupling between H_c and H_s or H_a of 7–11 Hz. Furthermore, the observation of rhodium and ^{31}P coupling to only the α-hydrogens supports only the η^1 formulation. All other spectral parameters for **14** suggest a structure much like those discussed previously for the other η^1-hydrocarbyl products.

Reactivity of Hydrocarbyl Complexes. One of our goals was to prepare dialkyl or alkyl–hydrido complexes via the reaction of neutral hydrocarbyl species with electrophiles and to investigate the effects of an adjacent metal on a variety of reaction types, including reductive eliminations. These neutral alkyl complexes were found, for the most part, to be quite unreactive toward a variety of reagents. As an example, the reaction of $[RhMo(CH_3)(CO)_4(dppm)_2]$ (**10**) with HBF_4 was followed by variable-temperature NMR spectroscopy, and no reaction was observed until the reaction mixture was warmed to 10 °C, at which point the known compound $[RhMo(CO)_5(dppm)_2][BF_4]$ was formed along with various decomposition products. Similar results were obtained upon protonation of the phenyl and benzyl compounds. In contrast to the inertness of the methyl compound **10** to acid at low temperature, protonation of $[RhMo(CH{=}CH_2)(CO)_4(dppm)_2]$ (**8**) with HBF_4 at −80 °C results in an immediate color change from yellow to purple, and NMR spectroscopy shows the presence of $[RhMo({=}CH(CH_3))(CO)_4(dppm)_2][BF_4]$ (**15**). The ^1H NMR spectrum of this compound shows no hydride signal, indicating that the proton is not attached to either metal. However, a multiplet is observed at δ 18.81 (1H) and a doublet observed at δ 1.73 (3H). The low-field resonance is typical of an alkylidene hydrogen[23a,b] and displays 7.3 Hz coupling to the methyl group at δ 1.73, as well as coupling to Rh and the Rh-bound phosphines; the methyl signal couples only to the alkylidene hydrogen. Decoupling the rhodium-bound phosphines significantly sharpens the low-field signal, whereas decoupling the molybdenum-bound phosphines has no effect on this signal, suggesting that the alkylidene functionality is bound to rhodium. These data suggest, as is observed in the reactions of many vinyl species with protic acids,[23c] that electrophilic attack has occurred on the β-carbon of the vinyl group of **8**, to form an ethylidene group on rhodium, as outlined in Scheme 1. The $^{13}C\{^1H\}$ NMR spectrum of **15** displays two carbonyl singlets at δ 231.7 and 206.7, attributed to two bridging and two terminal carbonyls, respectively. The broad low-field carbonyl signal again shows no rhodium coupling. All attempts to locate the ethylidene α-carbon in the $^{13}C\{^1H\}$ NMR spectrum were unsuccessful due to low signal intensity, and attempts to obtain an IR spectrum of **15** were unsuccessful due to its facile conversion to a new species, compound **16**. Upon warming to −10 °C, the conversion of **15** to the ethylene adduct, $[RhMo(\eta^2\text{-}C_2H_4)(CO)_4(dppm)_2][BF_4]$ (**16**), is complete. The dppm–methylene resonance for **16** appears as a pseudoquintet at δ 3.10 in the ^1H NMR spectrum, indicating that the complex has apparent front–back symmetry. This spectrum also displays the ethylene signal at δ 3.58, appearing as a doublet of triplets in which the coupling to Rh and the two adjacent phosphorus nuclei is approximately the same (~2 Hz). The IR spectrum of this compound again shows bands consistent with terminal and bridging carbonyls, and $^{13}C\{^1H\}$ NMR spectroscopy on this compound displays two resonances in the carbonyl region at δ 227.3 and 207.3. The low-field signal is somewhat broad (ca. 30 Hz), again presumably masking the small rhodium coupling of a semibridging carbonyl. Compound **16** was synthesized independently by the reaction of $[RhMo(CO)_5(dppm)_2][PF_6]$ with ethylene in the presence of trimethylamine

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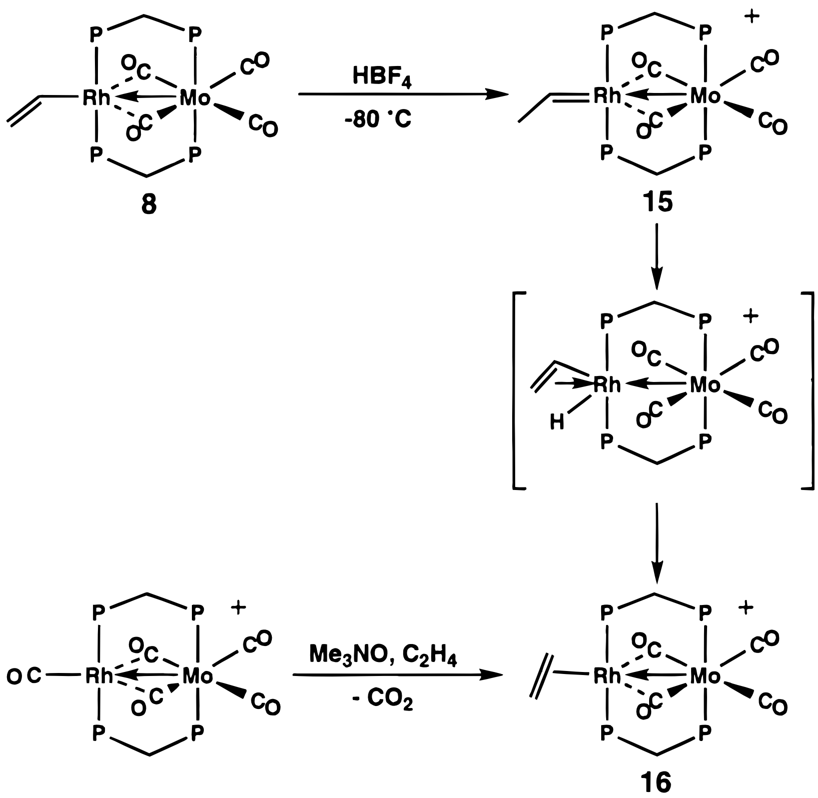
[23] (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258. (b) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S. Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958. (c) Hatton, W. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6157.

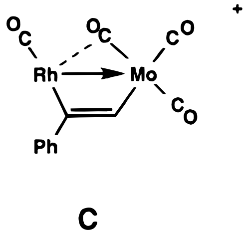
Scheme 1



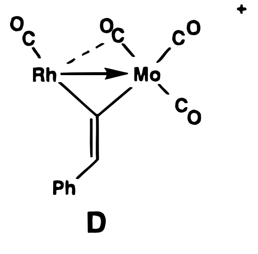
N-oxide, although the preparation by this route is dominated by various decomposition products. Similar alkylidene-to-olefin rearrangements have been observed previously upon hydride abstraction from [CpRe(NO)(PPh$_3$)(CH$_2$CH$_2$R)]^{23b} and upon protonation of the vinyl-containing species [CpRe(NO)(PPh$_3$)(CH=CH(CH$_3$)].^{23c}

In an attempt to determine the effect of an adjacent third-row metal on the stability of the alkylidene fragment, protonation of the analogous Rh/W vinyl species, [RhW(CH=CH$_2$)(CO)$_4$(dppm)$_2$] (**9**), was carried out. This resulted in the formation of spectroscopically similar ethylidene [RhW(=CH(CH$_3$))(CO)$_4$(dppm)$_2$][BF$_4$] (**17**) being formed at −80 °C. This product also rearranged to the analogous ethylene-containing species [RhW(η^2-C$_2$H$_4$)(CO)$_4$(dppm)$_2$][BF$_4$] (**18**), but not until warmed to approximately 0 °C. The higher temperature required for the ethylidene-to-ethylene transformation indicates that replacement of molybdenum for tungsten has resulted in a slightly more stable alkylidene species, showing a subtle effect due to the presence of an adjacent metal.

Since carbene species are known to undergo coupling reactions with unsaturated substrates,[21] the reactivity of **15** with such species was investigated. It was found, however, that the carbene moiety in compound **15** did not react with these substrates. Instead, their addition resulted in displacement of coordinated ethylene from the rearranged isomer. For example, the reaction of **8** with HBF$_4$·(OMe$_2$)$_2$ in the presence of phenylacetylene produces a green phenylacetylene-containing compound, [RhMo(C$_6$H$_5$C$_2$H)(CO)$_4$(dppm)$_2$][BF$_4$] (**19**). The ^{1}H NMR spectrum shows that no coupling of the carbene fragment and phenylacetylene has occurred, in that the only observable hydrogen resonances other than those from the dppm ligands are those due to the phenyl protons of the phenylacetylene moiety, which are shifted upfield slightly from the dppm−phenyl groups due to their presumed proximity to a metal center. The acetylenic hydrogen resonance was not located, presumably being obscured by the dppm−phenyl resonances. An attempt to locate the deuterium resonance derived from mono-deuterophenylacetylene in the ^{2}H NMR also failed, presumably due to H−D exchange between the deuterated compound and the protio solvent. The ^{13}C{^{1}H} NMR spectrum displays three singlets due to carbonyls bound to molybdenum and a doublet of triplets with Rh coupling of 75.4 Hz and ^{31}P coupling of 17.8 Hz, corresponding to a terminally bound carbonyl on Rh. The IR spectrum shows three CO bands at 2007, 1979, and 1843 cm^{-1} with the low-frequency band suggesting a bridging interaction. Again, the rhodium coupling to the presumed bridging carbonyl is likely obscured by the width of the peak (ca. 30 Hz). These spectroscopic data do not distinguish between a bridging phenylacetylene (**C**) or a phenylvinylidene ligand (**D**), and location of the phenylacetylene-derived carbons in the ^{13}C{^{1}H} NMR spectrum in order to differentiate between the two bonding modes was unsuccessful. Coordination of terminal alkynes in a bridging mode or in a rearranged vinylidene mode is common in binuclear complexes.[6b,22,24,25]



C



D

In both structures **C** and **D**, the phenyl group derived from phenylacetylene is shown to be directed away from the molybdenum center in order to minimize steric interactions with the molybdenum-bound ligands. The possibility of having the alkyne η^2-bound to molybdenum is ruled out, based on the already crowded environment at this metal. Further attempts to identify the fate of the phenylacetylene group were not made, since neither product is novel in binuclear chemistry.

Discussion

The two classes of compounds used as precursors in this study, namely, $[RhMoH(CO)_4(dppm)_2]$ (**1**) and $[RhMCl(CO)_4(dppm)_2]$ (M = Mo(**2**), W(**3**)), have previously been reported,[12,13] although our structural formulations for these species differ slightly from those given in the original reports. Two structures were independently proposed for **2**, having a terminal chloro ligand in each case, and both structures appeared to be consistent with the spectral data that were available.[13] The X-ray structure determination of **2** conclusively establishes that the structure is neither of those proposed, but instead has the chloro ligand in a bridging position. One of the previous formulations[13] was proposed on the basis of the single ^1H NMR resonance observed for the dppm−methylene protons, since the chloro-bridged structure, now established by us, should give rise to two closely spaced resonances. However, in **2** the methylene protons have accidentally equivalent chemical shifts, as is occasionally observed in A-frame compounds,[26] leading to the incorrect formulation. Although we have no X-ray data for **1**, we assume that it has an analogous structure having a bridging hydride ligand; similar structures have previously been observed for the halide- and hydride-bridged A-frame complexes, $[M_2(CO)_2(\mu\text{-}X)(\mu\text{-}CO)(dppm)_2]^+$ (M = Rh, Ir; X = Cl, H).[27]

The hydride- and halide-bridged structures for **1** and **2** suggested that the hydrocarbyl analogues, $[RhMo(R)(CO)_4(dppm)_2]$, may also have the hydrocarbyl group bridging the metals. With unsaturated ligands such as vinyl or allyl groups, a bridging mode in which these groups were σ-bound to Rh, while functioning as donor groups to Mo via their occupied π orbitals, seemed possible, and a number of such compounds have been reported.[28] In the case of saturated groups such as methyl ligands, a bridged geometry is also well documented.[29]

Several alkyl and alkenyl species of the form $[RhMoR(CO)_4(dppm)_2]$ have been prepared (M = Mo, R = $C(CF_3){=}CHCF_3$, $C(CO_2Me){=}CHCO_2Me$, $CH{=}CH_2$, CH_3, $\eta^1\text{-}C_3H_5$, CH_2Ph, $C(O)CH_2Ph$, and C_6H_5; M = W, R = $CH{=}CH_2$), and in all cases the hydrocarbyl fragment is σ-bound to rhodium in a terminal position opposite the metal−metal bond. Even when tungsten is substituted for molybdenum, the hydrocarbyl fragment remains σ-bound to rhodium despite the stronger W−C versus Mo−C bond expected.[30] Presumably, the structure having the organic group η^1-bound to rhodium is favored by the Rh(I)/M(0) configuration (M = group 6 metal) that results, whereas having this group η^1-bound to the group 6 metal would result in a more unusual Rh(0)/M(I) configuration. Interestingly, these hydrocarbyl-containing species have structures analogous to one of the incorrect proposals for the chloro species **2**.[13b] It is not clear why a hydrocarbyl-bridged structure is not observed in this series, although for larger hydrocarbyl groups unfavorable steric interactions between it and the dppm−phenyl groups and with the carbonyls on the crowded group 6 metal would tend to favor the terminal binding mode. For compound **10**, in which the hydrocarbyl group is a methyl ligand, it seems unlikely that steric factors are dominant in determining the methyl binding mode. However, the propensity of halides to bridge metals, compared with the relative paucity of methyl-bridged complexes, is consistent with the geometry of **10** in which the methyl group is terminally bound.

It was anticipated that these neutral alkyl and alkenyl complexes would provide access to complexes containing two hydrocarbyl or a hydrido and a hydrocarbyl ligand in which the influence of a second metal on the migratory insertion and reductive coupling of the organic fragments could be studied. It has been found however that these alkyl and alkenyl complexes are quite unreactive toward a variety of reagents, including CO, CH_2N_2, activated alkynes, and the powerful electrophile methyl triflate. Their failure to react with electrophiles is in sharp contrast to the reactivity displayed by a variety of isoelectronic alkyl and alkenyl complexes containing Rh and group 8 metals prepared previously in our group. For example, $[RhOs(CH_3)(CO)_3(dppm)_2]$ readily reacts with electrophiles such as protic acids and methyl triflate.[3a]

The unreactive nature of the above Rh/Mo alkyl complexes is likely a consequence of several factors. The d^6 octahedral molybdenum is inert to both associative and dissociative reactions, and nucleophilic attack on the molybdenum-bound carbonyls by reagents such as trimethylamine-*N*-oxide is also disfavored due to the presence of the two good donor phosphine groups of dppm. Consequently attempts to generate vacant coordination sites on molybdenum through the use of Me_3NO were not successful. Electrophilic attack at the molybdenum center is also inhibited by the steric hindrance caused by the presence of the two phosphines and the four carbonyls on this metal. The influence of

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(25) (a) George, D. S. A.; McDonald, R.; Cowie, M. *Organometallics* **1998**, *12*, 2553. (b) George, D. S. A.; McDonald, R.; Cowie, M. *Can. J. Chem.* **1996**, *74*, 2289.

(26) See, for example: ref 2d.

(27) (a) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1982**, *21*, 2119. (b) Cowie, M. *Inorg. Chem.* **1979**, *18*, 1286. (c) Sutherland, B. R.; Cowie, M. *Can. J. Chem.* **1986**, *64*, 464.

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(29) See for example: (a) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135. (b) Hursthouse, M. B.; Jones, R. A.; Malik, K. M. A.; Wilkinson, G. *J. Am. Chem. Soc.* **1979**, *101*, 4128. (c) Schwartz, D. J.; Ball, G. E.; Andersen, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 6027. (d) Schmidt, G. F.; Muetterties, E. L.; Beno, M. A.; Williams, J. M. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1318. (e) Reinking, M. K.; Fanwick, P. E.; Kubiak, C. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1377. (f) Dawkins, G. J.; Green, M.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 41. (g) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726. (h) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(30) (a) Ziegler, T.; Tschinke, V. *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; American Chemical Society: Washington, DC, 1990; Chapter 19. (b) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629.

the geometry at the saturated metal is particularly evident when comparing the reactions of [RhOs(CH_3)($CO)_3$(dppm$)_2$][3a] and [RhMo(CH_3)($CO)_4$(dppm$)_2$] (**10**) with HBF_4. Addition of HBF_4 to the five-coordinate osmium center in the Rh/Os methyl complex at −80 °C results in an immediate reaction, with the formation of the hydrido−alkyl species [RhOs(H)(CH_3)($CO)_3$(dppm$)_2$][BF_4], which subsequently eliminates methane upon warming. However, addition of HBF_4 to the analogous Rh/Mo methyl complex **10** at low temperature gives no reaction until the solution is warmed to 10 °C, at which point reductive elimination of methane occurs. No Rh/Mo hydrido−alkyl species is observed, possibly due to steric congestion causing a fast reductive elimination reaction of methane from a presumed hydrido−methyl intermediate. When the converse reaction is attempted (i.e., the addition of methyl triflate to [RhMo(CO$)_4$(μ-H)(dppm$)_2$] (**2**)), the results were much the same, with no immediate reaction observed.

Although a coordinatively unsaturated metal center adjacent to a saturated metal can increase reactivity at the saturated metal by providing a site for the added ligand to bind to the complex, this appears not be the case with the Rh/Mo system. It appears that the semibridging carbonyls not only serve to reduce the nucleophilicity of rhodium, due to their electron-withdrawing nature, but also result in increased steric congestion at rhodium.

Reaction of [RhMo(CO$)_4$(μ-Cl)(dppm$)_2$] (**2**) with allylmagnesium chloride forms [RhMo(η^1-$CH_2CH{=}CH_2$)(CO$)_4$(dppm$)_2$] (**14**), having the allyl group σ-bound to rhodium. The η^1-allyl structure is in contrast to the analogous compound, [RhOs(η^3-C_3H_5)(CO$)_3$(dppm$)_2$], having an η^3-allyl group.[3b] In this latter compound the η^3-coordination mode was facilitated by a cis orientation of the rhodium-bound phosphines, which are bent away from the η^3-allyl group. In the Rh/Mo case, a cis-phosphine arrangement is unfavorable owing to interactions with the four carbonyls on molybdenum; consequently the η^3-allyl binding is also unfavorable. The effect of increased crowding at the adjacent metal was demonstrated upon addition of methyl triflate to [RhOs(η^3-C_3H_5)(CO$)_3$(dppm$)_2$], yielding [RhOs(η^1-C_3H_5)(CH_3)(CO$)_3$(dppm$)_2$][OTf], which is isoelectronic with **14**. In this reaction the increased crowding at Os that resulted upon coordination of CH_3^+ resulted in a change in the allyl coordination mode at the other metal, presumably because the increased coordination number at osmium forced the phosphines into a trans arrangement at rhodium.

Our failure to obtain the benzyl analogue [RhMo(CH_2Ph)(CO$)_4$(dppm$)_2$] (**11**) in the reaction of **2** with benzylmagnesium chloride, together with its successful generation, together with the acyl byproduct [RhMo(C(O)CH_2Ph)(CO$)_4$(dppm$)_2$] (**12**), under an atmosphere of CO suggests that the reactive species is the cationic [RhMo(CO$)_5$(dppm$)_2$][Cl], generated from **2**. It has previously been shown by Shaw that the addition of NH_4PF_6 to a solution of [RhMo(Cl)(CO$)_4$(dppm$)_2$] under an atmosphere of carbon monoxide results in the rapid formation of the isolable pentacarbonyl species [RhMo(CO$)_5$(dppm$)_2$][PF_6].[13a] We propose that the increase in positive charge on the cationic pentacarbonyl species and the presence of an extra π-acidic carbonyl ligand increase the electrophilic nature of the rhodium center relative to **2**, resulting in rapid formation of the alkylation products. The two products obtained result from competitive attack either at a coordinated carbonyl ligand, to give the acyl compound, or at the rhodium center to give the benzyl species. Attempts to interconvert these two products either under reflux or under CO failed, supporting the idea that they arise by two independent pathways.

The other successful route used for the formation of alkenyl species was the reaction of [RhMo(CO$)_4$(μ-H)(dppm$)_2$] (**1**) with activated alkynes. Although, here again, the ligand being replaced (H by alkenyl) is in a bridging site, the resulting alkenyl groups are terminally bound to Rh. When the unsymmetrical alkynes 3-butyn-2-one and methyl propiolate were used, only the sterically *less-favored* isomers, having the electron-withdrawing substituent on the α-carbon, were obtained. Strengthening of a metal−carbon σ-bond by the incorporation of electron-withdrawing groups on the α-carbon is well documented and finds one explanation in Bent's rule,[31] with increased carbon s-orbital participation in the Rh−C bond.

Several methods are known for the preparation of carbene species, including hydride abstraction from alkyl species,[22,23b] protonation of vinyl complexes,[23c] and via the reaction of transition metal complexes with alkylidene sources such as diazoalkanes.[32−34] Attempts to generate a carbene by hydride removal from [RhMo(CH_2Ph)(CO$)_4$(dppm$)_2$] with the triphenylmethyl (trityl) cation[22,23b] failed, instead removing the benzyl group, forming [RhMo(CO$)_5$(dppm$)_2$][BF_4] along with various decomposition products. This is in contrast with the results obtained for the CpRe(PPh_3)(NO)(CH_2Ph) complex, in which reaction with trityl cation forms the phenyl-substituted carbene cation.[22] Attempts to obtain a carbene species via reaction with diazomethane also failed. The reaction of [RhMo(CO$)_5$(dppm$)_2$][PF_6] with a large excess of diazomethane produced polymethylene together with a very small amount of a new compound (<5% by ^{31}P NMR). However only the starting material could be isolated. In the presence of trimethylamine *N*-oxide, in the hope that CO removal would allow the isolation of a complex containing a methylene unit or coupled methylene fragments, the ^{31}P NMR spectrum again showed mostly the starting material and a small amount of a different new compound, which has not been identified owing to its low concentration.

A carbene species could be obtained via protonation of the vinyl complex [RhMo($CH{=}CH_2$)(CO$)_4$(dppm$)_2$] (**8**) at −80 °C, yielding the ethylidene product [RhMo(${=}CHCH_3$)(CO$)_4$(dppm$)_2$][BF_4] (**15**). The facile conversion of **15** to the ethylene adduct [RhMo(η^2-C_2H_4)(CO$)_4$(dppm$)_2$][BF_4] (**16**) may occur through β-hydrogen transfer from the alkylidene methyl to rhodium, forming an η^2-vinyl-containing species, followed by reductive elimination of the ethylene moiety to form **16**, as shown previously in Scheme 1. η^2-Vinyl species are not com-

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(34) (a) Puddephatt, R. J. *Polyhedron* **1988**, *7*, 767. (b) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

mon, but they have been previously observed and characterized.[35] Although rhodium–alkylidene complexes containing heteroatoms in the β-position are well-known, those without heteroatoms are quite rare. Of these alkylidene complexes of rhodium, very few have the alkylidene ligand in a terminal position, but are more often found bridging two metals. In the Rh/Mo case it may be that the alkylidene fragment cannot easily move into a bridging position due to unfavorable steric interactions with the dppm phenyl groups; certainly much of the low reactivity of these Rh/Mo species can be attributed to crowding. Similar results have been obtained previously, in which the carbene product $[RhOs(=C(CH_3)_2)(H)(CO)_3(dppm)_2][BF_4]_2$ was formed by protonation of the η^1-isopropenyl precursor. This complex again contains a carbene unit terminally bound to rhodium.[3b] Attempts to couple the alkylidene unit of compound **15** with unsaturated organic substrates were unsuccessful. Apparently the alkylidene complex is less reactive than its ethylene isomer (**16**), which reacts by simple ethylene substitution by the added substrate.

Conclusions

The hydrocarbyl complexes $[RhMo(R)(CO)_4(dppm)_2]$ are readily formed from either the reactions of the chloro precursor with the appropriate Grignard reagent (R = CH_3, CH_2Ph, Ph, $CH{=}CH_2$, $CH_2CH{=}CH_2$) or the reactions of the analogous hydride precursor with activated alkynes (R = $MeO_2CC{=}C(H)CO_2Me$, $CF_3C{=}C(H)CF_3$, $MeOCC{=}CH_2$, $MeO_2CC{=}CH_2$). In all cases the hydrocarbyl fragment is η^1-bound to Rh with two of the four carbonyls on Mo involved in semibridging interactions with Rh. These compounds are generally unreactive, with the exception of the vinyl species (R = $CHCH_2$), which is readily protonated at −80 °C to give the ethylidene product $[RhMo(=C(H)CH_3)(CO)_4(dppm)_2]^+$, in which the ethylidene moiety is again terminally bound to Rh. Upon warming, this ethylidene species rearranges to the ethylene adduct, in which the ethylene group is also Rh-bound. The analogous Rh/W ethylidene species behaves similarly except that rearrangement to the ethylene adduct occurs less readily. With all transformations of the hydrocarbyl fragments occurring at Rh, the change in rate of transformation of ethylidene to ethylene upon substituting Mo by W shows a subtle yet interesting adjacent-metal effect.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and the University of Alberta for financial support of this research.

Supporting Information Available: Tables of X-ray experimental details, atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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