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Bridging Vinylidene Complexes of RhMn and Evidence for Migratory Insertions To Give Terminal Vinyl Groups

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The reaction of the heterobinuclear complex [RhMn(CO)$_4$(dppm)$_2$] (**1**) (dppm = Ph$_2$PCH$_2$PPh$_2$) with 3-butyn-2-one at −40 °C yields the alkyne-bridged product [RhMn(CO)$_4$(μ-HC$_2$C(O)Me)(dppm)$_2$] (**3**), which undergoes a 1,2-hydrogen shift, yielding two isomers of the vinylidene-bridged species [RhMn(CO)$_4$(μ-CC(H)C(O)Me)(dppm)$_2$] (**4**) as the temperature is raised. Compound **4** undergoes facile CO loss to give [RhMn(CO)$_3$(μ-η^1:η^2-CC(H)C(O)Me)(dppm)$_2$] (**5**) in which the ketonic moiety of the bridging vinylidene group coordinates to Mn, filling the open coordination site left vacant by the departing CO. Protonation of the alkyne- or vinylidene-bridged species **3**−**5** yields a series of vinyl complexes. Addition of methyl triflate to **4** and **5** yields the respective methyl-substituted vinyl complexes, analogous to the protonation products. In the alkylation of **5** at low temperature an intermediate, [RhMn(CH$_3$)(CO)$_3$(μ-η^1:η^2-CC(H)C(O)Me)(dppm)$_2$][SO$_3$CF$_3$] (**12**), having a vinylidene bridge and a methyl group terminally bound to Rh, is obtained. The rearrangement of **12** to a vinyl complex upon warming presents evidence for a migratory insertion involving these groups. The structure of **5** was determined by X-ray crystallography. This compound crystallizes in the monoclinic space group $P2_1/n$ (nonstandard setting of $P2_1/c$ [No. 14]) with a = 14.489(1) Å, b = 15.754(2) Å, c = 24.104(2) Å, β = 91.41(1) Å, V = 5500(1) Å^3, and Z = 4. On the basis of 3980 observations the structure has refined to R = 0.058 and R_w = 0.063.

Introduction

The coordination and activation of alkynes at two metal centers and subsequent transformations involving these substrates have attracted considerable attention.[1] Our recent interest in such chemistry has been aimed at transformations in which vinyl[2−5] and vinylidene ligands[6−8] are generated. Vinyl complexes can be prepared from the insertion of alkynes into metal−hydrogen bonds, a fundamental process in organometallic chemistry,[9] or they can be generated from the related vinylidene complexes (vide infra).[10] Recent interest in vinyl complexes stems from a proposal suggesting the intermediacy of surface-vinyl species in Fischer−Tropsch chemistry.[11] Vinylidene complexes can be prepared from 1-alkynes via a 1,2-hydrogen shift occurring at the metals.[10,12] It has been suggested that, like vinyl groups, the vinylidene units may also play a key role in Fischer−Tropsch chemistry,[13] as well as in alkyne polymerization[14] and in C−C bond formation in the condensation of alkynes with a number of substrates.[15−23]

The similarity of the vinylidene unit to the isoelectronic carbonyl ligand has been noted,[12] and evidence suggests that a vinylidene group can be an even better π acceptor than CO.[15] Like the CO ligand, the vinylidene group can function as a terminal group bound to one metal or can bridge two or more metals.[10] Furthermore, like CO, the vinylidene bridge can be symmetric[10] or side-on-bound,[24,25] in which case it is σ-bound to one metal and π-bound to another.

In spite of the carbonyl−vinylidene analogy and the suggested role of vinylidene units in C−C bond-forming

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reactions, the migratory insertion of a hydrocarbyl ligand and vinylidene unit had until recently[26,27] *not* been clearly demonstrated, although evidence for these insertions had been obtained.[28-30] In fact, it has been noted[26] that complexes containing both a hydrocarbyl and a vinylidene unit are conspicuously lacking. This is surprising when it is recalled that migratory insertions involving CO and other unsaturated substrates are well documented and occupy a position of fundamental importance in the formation of C−C bonds.[31] Although little is known about the migratory-insertion reactions involving terminal vinylidenes, even less is known about the less studied bridging vinylidene unit.

Among the reactions typical of vinylidenes are nucleophilic attack at the α-carbon or electrophilic attack at the β-carbon.[32] While protonation usually occurs at the β-carbon, generating a carbyne moiety,[10] metal basicity can dominate in square-planar iridium(I) complexes to give hydrido−vinylidene complexes via protonation at the metal.[29,33] On the assumption that binuclear complexes containing a bridging vinylidene adjacent to a Rh(I) center could also have Rh as the most basic site, we have investigated the protonation and alkylation (using CH_3^+) reactions of such species in hopes of obtaining hydrido−vinylidene and alkyl−vinylidene complexes, which could be induced to undergo migratory insertions yielding vinyl complexes. The results of this study are reported herein.

Experimental Section

General Procedures. Purified argon and carbon monoxide were obtained from Linde. The 99% carbon-13-enriched carbon monoxide was purchased from Isotec Inc. All gases were used as received. Diethyl ether, hexane, and tetrahydrofuran were dried over Na/benzophenone ketyl, and methylene chloride was dried over P_2O_5. All solvents were distilled under argon before use. The perdeuterated methylene chloride was dried over molecular sieves and deoxygenated by repeated freeze−pump−thaw cycles. The compounds tetrafluoroboric acid−diethyl etherate, triflic acid, trifluoroacetic acid, 3-butyn-2-one, and methyl triflate were used as received from Aldrich. Hydrated rhodium trichloride was received from Johnson Matthey, and $Mn_2(CO)_{10}$ from Strem Chemicals Inc. Compounds $[RhMn(CO)_4(dppm)_2]$ (**1**)[34] and $[RhMn(CO)_4(\mu\text{-}H)(dppm)_2][BF_4]$ (**2**)[35] (dppm = $Ph_2PCH_2PPh_2$) were prepared by the reported procedures. Reactions were routinely carried out under Schlenk conditions.

All routine NMR experiments were conducted on a Bruker AM-400 spectrometer, whereas the $^{13}C\{^{31}P\}$ NMR experiments were run on a Bruker AM-200 spectrometer. For all NMR experiments CD_2Cl_2 (except ^2H experiments for which CH_2Cl_2 was used) was used as solvent. IR spectra were recorded on either a Nicolet 7199 Fourier transform interferometer or a Perkin-Elmer 883 spectrophotometer as solids (Nujol mull or CH_2Cl_2 cast) or CH_2Cl_2 solutions. Elemental analyses were performed by the microanalytical service within the department. The spectral data for all compounds are given in Tables 1 and 2. All compounds were moderately air sensitive in solution and so were routinely handled under dinitrogen or argon.

Preparation of Compounds. (a) $[RhMn(CO)_4(\mu\text{-}HC{=}CC(O)Me)(dppm)_2]$ (3). At −78 °C 10 μL of 3-butyn-2-one (128 μmol) was added to a CD_2Cl_2 solution of $[RhMn(CO)_4(dppm)_2]$ (**1**) (10 mg, 10 μmol in 0.5 mL) in an NMR tube. The compound was characterized by NMR experiments at −40 °C.

(b) $[RhMn(CO)_3(\mu\text{-}C{=}CHC(O)Me)(\mu\text{-}CO)(dppm)_2]$ (4a and 4b). To a CH_2Cl_2 solution of compound **1** (50 mg, 48 μmol in 5 mL) was added 8 μL of 3-butyn-2-one (102 μmol). The solution was stirred under CO for 1 h, causing the color to change from light yellow to red. The solvent was reduced under a rapid flow of CO. The residue was recrystallized from CH_2Cl_2/Et_2O under a CO atmosphere and washed with 5 mL of Et_2O, yielding a red solid (86%). Anal. Calcd for $RhMnP_4C_{58}O_5H_{48}$: C, 62.93; H, 4.34. Found: C, 62.02; H, 4.61.

(c) $[RhMn(CO)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}C{=}CHC(O)Me)(dppm)_2]$ (5). To a suspension of compound **1** (50 mg, 48 μmol in 5 mL of THF) was added 8 μL of 3-butyn-2-one (102 μmol), and the mixture was refluxed for 1 h. Removal of the solvent in vacuo and recrystallization from THF/hexane gave a red-brown crystalline solid (yield 90%). Anal. Calcd for $RhMnP_4C_{57}O_4H_{48}$: C, 63.45; H, 4.45. Found: C, 63.46; H, 4.64.

(d) $[RhMn(\textit{trans}\text{-}CH{=}CHC(O)Me)(CO)_2(\mu\text{-}CO)_2(dppm)_2][SO_3CF_3]$ (6a). To a CH_2Cl_2 solution of isomers **4a** and **4b** (50 mg, 45 μmol in 5 mL under CO) was added 4.0 μL of CF_3SO_3H (1 equiv) followed by stirring for 0.5 h. The color changed from red to light yellow. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a yellow solid (70%). Satisfactory elemental analyses could not be obtained owing to sample decomposition.

(e) $[RhMn(\textit{trans}\text{-}CH{=}CHC(O)Me)(CO)_2(\mu\text{-}CO)_2(dppm)_2][BF_4]$ (6b). To a CH_2Cl_2 solution of isomers **4a** and **4b** (50 mg, 45 μmol in 5 mL under CO) was added 7.8 μL of $HBF_4{\cdot}Et_2O$ (85%, 1 equiv). The color changed from red to light yellow immediately. The solution was stirred for 0.5 h, followed by removal of the solvent and recrystallization from CH_2Cl_2/Et_2O to give a yellow solid (74%).

(f) $[RhMn(CO)_3(\mu\text{-}CCH{=}C(OH)Me)(\mu\text{-}CO)(dppm)_2][BF_4]$ (7). To a CD_2Cl_2 solution of compound **1** (15 mg, 15 μmol in 0.5 mL in an NMR tube) under CO (10 psi) was added 3 μL of 3-butyn-2-one (38 μmol). The color changed from light yellow to red. The NMR tube was left for 3 h; then to this solution was added 3 μL of $HBF_4{\cdot}Me_2O$ (25 μmol) at −78 °C. The compound was characterized by variable-temperature NMR experiments.

(g) $[RhMn(\textit{cis}\text{-}CH{=}CHC(O)Me)(CO)_2(\mu\text{-}CO)_2(dppm)_2][SO_3CF_3]$ (8a). A 50 mg amount of $[RhMn(\eta^2\text{-}CHCHC(O)Me)(CO)_2(\mu\text{-}CO)(dppm)_2][SO_3CF_3]$ (**9a**) (41 μmol) was dissolved in 5 mL of CH_2Cl_2 and stirred overnight under CO (10 psi). Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave an orange solid (86%). Satisfactory elemental analyses could not be obtained owing to sample decomposition.

(h) $[RhMn(\textit{cis}\text{-}CD{=}CHC(O)Me)(CO)_2(\mu\text{-}CO)_2(dppm)_2][CO_2CF_3]$ (8b). To a CD_2Cl_2 solution of compound **5** (10 mg, 9 μmol in 0.5 mL) in an NMR tube was added 4 μL of CF_3CO_2D (52 μmol). The color changed from deep red-orange to orange immediately. The solution was put under CO (10 psi) for 12 h, followed by characterization by NMR.

(i) $[RhMn(\textit{cis}\text{-}CH{=}CDC(O)Me)(CO)_2(\mu\text{-}CO)_2(dppm)_2][CO_2CF_3]$ (8c). To a CD_2Cl_2 solution of compound **1** (15 mg, 15 μmol in 0.5 mL) in an NMR tube was added 50 μL of 3-butyn-2-one (639 μmol, excess) at −78 °C. After 1 h, a yellow suspension appeared. The ^{31}P NMR spectrum was run at −40 °C and showed the presence of only compound **3**. A 15 μL

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Table 1. Spectroscopic Data for the Compounds

compd	IR, cm^{-1} [a]	NMR[a]		
		δ (^{31}P{^{1}H})	δ (^{1}H)	δ (^{13}C)
RhMn(CO)$_4$(μ-HC≡CC(O)Me)(dppm)$_2$ (**3**)		56.7 (m),[e] 15.7 (dm, $^1J_{\mathrm{RhP}}$ = 157 Hz)	9.99 (b, 1H, HC≡C),[e] 3.87 (b, 2H, PCH$_2$P), 2.85 (b, 2H, PCH$_2$P), 0.59 (s, 3H, CH$_3$)	228.3 (b, 1CO),[e] 221.3 (b, 1CO), 220.5 (b, 1CO), 195.6 (dt, $^1J_{\mathrm{RhC}}$ = 58 Hz, $^2J_{\mathrm{P(Rh)C}}$ = 12 Hz, 1CO)
RhMn(CO)$_3$(μ-CCHC(O)Me)(μ-CO)(dppm)$_2$ (**4a**)		67.7 (m),[e] 35.2 (dm, $^1J_{\mathrm{RhP}}$ = 170 Hz)	6.59 (t, 1H$_\beta$, $^4J_{\mathrm{P(Rh)CCH}}$ = 12 Hz),[e] 2.98 (m, 2H, PCH$_2$P), 2.19 (m, 2H, PCH$_2$P), 1.55 (s, 3H, CH$_3$)	244.9 (dt, $^1J_{\mathrm{RhC}}$ = 15 Hz, $^2J_{\mathrm{P(Mn)C}}$ = 21 Hz, 1CO),[e] 229.5 (t, $^2J_{\mathrm{P(Mn)C}}$ = 13 Hz, 1CO), 223.4 (t, $^2J_{\mathrm{P(Mn)C}}$ = 18 Hz, 1CO), 206.2 (dt, $^1J_{\mathrm{RhC}}$ = 59 Hz, $^2J_{\mathrm{P(Mn)C}}$ = 20 Hz, 1CO)
RhMn(CO)$_3$(μ-CCHC(O)Me)(μ-CO)(dppm)$_2$ (**4b**)	1964 (w),[d] 1907 (st), 1857 (vs), 1788 (m), 1597 (st); 2002 (sh),[c] 1946 (vs), 1887 (st), 1801 (m), 1600 (w)	64.1 (m),[d] 23.1 (dm, $^1J_{\mathrm{RhP}}$ = 163 Hz)	8.09 (t, 1H$_\beta$, $^4J_{\mathrm{P(Rh)CCH}}$ = 7 Hz),[d] 3.28 (m, 2H, PCH$_2$P), 2.46 (m, 2H, PCH$_2$P), 0.62 (s, 3H, CH$_3$)	242.0 (dt, $^1J_{\mathrm{RhC}}$ = 10 Hz, $^2J_{\mathrm{P(Mn)C}}$ = 18 Hz, 1CO),[d] 226.6 (t, $^2J_{\mathrm{P(Mn)C}}$ = 17 Hz, 1CO), 223.8 (t, $^2J_{\mathrm{P(Mn)C}}$ = 20 Hz, 1CO), 207.6 (dt, $^1J_{\mathrm{RhC}}$ = 56 Hz, $^2J_{\mathrm{P(Rh)C}}$ = 20 Hz, 1CO), 193.8 (s, 1C, *C*(O)CH$_3$), 146.8 (s, 1C$_\beta$), 137.4 (dtt, $^1J_{\mathrm{RhC}}$ = 4 Hz, $^2J_{\mathrm{P(M)C}}$ = 19 Hz, $^2J_{\mathrm{P(M')C}}$ = 4 Hz, 1C$_\alpha$), 22.0 (s, 1C, CH$_3$)
RhMn(CO)$_3$(μ-η^1:η^2-CCHC(O)Me)(dppm)$_2$ (**5**)	1937 (st),[b] 1876 (vs), 1790 (m); 1942 (st),[c] 1893 (vs), 1808 (m)	73.1 (m),[d] 29.6 (dm, $^1J_{\mathrm{RhP}}$ = 175 Hz)	3.08 (m, 2H, PCH$_2$P),[d] 2.68 (m, 2H, PCH$_2$P), 0.99 (t, 3H, CH$_3$, $^5J_{\mathrm{P(Mn)OCCH}}$ = 2 Hz)	230.1 (*t*, $^2J_{\mathrm{P(Mn)C}}$ = 14 Hz, 1CO),[d] 228.7 (t, $^2J_{\mathrm{P(Mn)C}}$ = 20 Hz, 1CO), 206.2 (dt, $^1J_{\mathrm{RhC}}$ = 57 Hz, $^2J_{\mathrm{P(Rh)C}}$ = 15 Hz, 1CO), 190.8 (s, 1C, *C*(O)CH$_3$), 140.1 (s, 1C$_\beta$), 138.3 (tt, $^2J_{\mathrm{P(Mn)C}}$ = 14.4 Hz, $^2J_{\mathrm{P(Rh)C}}$ = 4 Hz, 1C$_\alpha$), 23.8 (s, 1C, CH$_3$)
[RhMn(*trans*-CH=CHC(O)Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (**6a**)	2036 (st),[b] 1974 (vs), 1845 (w), 1815 (st), 1654 (m); 2026 (vs),[c] 1984 (st), 1838 (sh), 1809 (st), 1654 (m)	58.8 (m),[d] 24.3 (dm, $^1J_{\mathrm{RhP}}$ = 134 Hz)	7.99 (dt, 1H$_\alpha$, $^3J_{\mathrm{HCCH}}$ = 17 Hz, $^3J_{\mathrm{P(Rh)CH}}$ = 7 Hz),[d] 5.32 (d, 1H$_\beta$, $^3J_{\mathrm{HCCH}}$ = 17 Hz), 3.16 (m, 4H, PCH$_2$P), 1.05 (s, 3H, CH$_3$)	244.1 (dt, $^1J_{\mathrm{RhC}}$ = 22 Hz, $^2J_{\mathrm{P(Mn)C}}$ = 11 Hz, 2CO),[d] 217.4 (t, $^2J_{\mathrm{P(Mn)C}}$ = 17 Hz, 2CO)
[RhMn(*trans*-CH=CHC(O)Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][BF$_4$] (**6b**)	2026 (vs),[c] 1982 (st), 1830 (sh), 1807 (st) 1652 (m)	58.8 (m),[d] 24.3 (dm, $^1J_{\mathrm{RhP}}$ = 134 Hz)	8.00 (dt, 1H$_\alpha$, $^3J_{\mathrm{HCCH}}$ = 17 Hz, $^3J_{\mathrm{P(Rh)CH}}$ = 7 Hz),[d] 5.32 (d, 1H$_\beta$, $^3J_{\mathrm{HCCH}}$ = 17 Hz), 3.16 (m, 4H, PCH$_2$P), 1.04 (s, 3H, CH$_3$)	244.1 (dt, $^1J_{\mathrm{RhP}}$ = 21 Hz, $^2J_{\mathrm{P(Mn)C}}$ = 12 Hz, 2CO),[d] 217.4 (t, $^2J_{\mathrm{P(Mn)C}}$ = 16 Hz, 2CO)
[RhMn(CO)$_3$(μ-CCHC(OH)Me)(μ-CO)(dppm)$_2$][BF$_4$] (**7**)		61.3 (m),[h] 23.6 (m)	9.30 (b, 1H, OH),[f] 2.62 (b, 2H, PCH$_2$P), 0.81 (s, 3H, Me)	236.0 (dt, $^1J_{\mathrm{RhC}}$ = 20 Hz, $^2J_{\mathrm{P(Mn)C}}$ = 16 Hz, 1CO),[h] 227.4 (t, $^2J_{\mathrm{P(Mn)C}}$ = 18 Hz, 1CO) 220.9 (t, $^2J_{\mathrm{P(Mn)C}}$ = 20 Hz, 1CO), 206.8 (dt, $^1J_{\mathrm{RhC}}$ = 56 Hz, $^2J_{\mathrm{P(Mn)C}}$ = 19 Hz, 1CO)
[RhMn(*cis*-CH=CHC(O)Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (**8a**)	2015 (st),[b] 1972 (st), 1857 (m), 1751 (m), 1617 (w); 2014 (vs),[c] 1966 (st), 1859 (st), 1736 (st), 1613 (w)	58.0 (m),[d] 25.3 (dm, $^1J_{\mathrm{RhP}}$ = 124 Hz)	9.20 (ddt, 1H$_\alpha$, $^3J_{\mathrm{HCCH}}$ = 7.5 Hz, $^2J_{\mathrm{RhCH}}$ = 5 Hz, $^3J_{\mathrm{P(Rh)CH}}$ = 6 Hz),[d] 6.42 (dd, 1H$_\beta$, $^3J_{\mathrm{HCCH}}$ = 7.5 Hz, $^3J_{\mathrm{RhCCC}}$ = 2.5 Hz), 3.34 (m, 2H, PCH$_2$P), 3.15 (m, 2H, PCH$_2$P), 1.03 (s, 3H, Me)	259.8 (dqui, $^1J_{\mathrm{RhC}}$ = 41 Hz, $^2J_{\mathrm{P(Rh)C}}$ = $^2J_{\mathrm{P(Mn)C}}$ = 9 Hz, 1CO),[d] 231.9 (dt, $^1J_{\mathrm{RhC}}$ = 12 Hz, $^2J_{\mathrm{P(Mn)C}}$ = 13 Hz, 1CO), 219.7 (t, $^2J_{\mathrm{P(Mn)C}}$ = 22 Hz, 1CO), 218.0 (t, $^2J_{\mathrm{P(Mn)C}}$ = 15 Hz, 1CO)
[RhMn(*cis*-CD=CHC(O)Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][CO$_2$CF$_3$] (**8b**)		57.6 (m),[d] 25.1 (dm, $^1J_{\mathrm{RhP}}$ = 126 Hz)	6.42 (d, 1H$_\beta$, $^3J_{\mathrm{RhCCH}}$ = 2.5 Hz),[d] 3.35 (m, 2H, PCH$_2$P), 3.13 (m, 2H, PCH$_2$P), 1.03 (s, 3H, CH$_3$)	
[RhMn(*cis*-CH=CDC(O)Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][CO$_2$CF$_3$] (**8c**)		57.8 (m),[d] 25.2 (dm, $^1J_{\mathrm{RhP}}$ = 126 Hz)	9.20 (m, 1H$_\alpha$),[d] 3.35 (m, 2H, PCH$_2$P), 3.13 (m, 2H, PCH$_2$P), 1.04 (s, 3H, CH$_3$)	
[RhMn(η^2-CH=CHC(O)Me)(CO)$_3$·(dppm)$_2$][SO$_3$CF$_3$] (**9a**)	1981 (vs),[b] 1934 (st), 1820 (st); 1987 (st),[c] 1939 (st), 1818 (m)	67.1 (m),[d] 25.7 (dm, $^1J_{\mathrm{RhP}}$ = 107 Hz)	8.04 (dt, $^3J_{\mathrm{HCCH}}$ = 10 Hz, $^3J_{\mathrm{P(Mn)CH}}$ = 2.5 Hz, 1H$_\beta$),[d] 3.24 (m, 2H, PCH$_2$P), 2.94 (m, 2H, PCH$_2$P), 0.98 (t, 3H, CH$_3$, $^5J_{\mathrm{P(Mn)OCCH}}$ = 3 Hz)	228.8 (t, $^2J_{\mathrm{P(Mn)C}}$ = 23 Hz, 1CO),[d] 225.0 (t, $^2J_{\mathrm{P(Mn)C}}$ = 17 Hz, 1CO), 186.7 (dt, $^1J_{\mathrm{RhC}}$ = 80 Hz, $^2J_{\mathrm{P(Rh)C}}$ = 18 Hz, 1CO)

Table 1 (Continued)

compd	IR, cm^{-1} ^{a}	NMR^a		
		δ (^{31}P{^{1}H})	δ (^{1}H)	δ (^{13}C) *
[RhMn(η^2-CD=CHC(O)Me)(CO)$_3$(dppm)$_2$][CO$_2$CF$_3$] (**9b**)		67.0 (m,),^{d} 25.6 (dm, $^1J_{RhP}$ = 107 Hz)	7.91 (t, $^3J_{P(Mn)CH}$ = 2.5 Hz, 1H$_\beta$),^{d} 3.24 (m, 2H, PCH$_2$P), 2.83 (m, 2H, PCH$_2$P), 0.92 (t, $^5J_{P(Mn)OCCH}$ = 3 Hz, 3H, CH$_3$)	
[RhMn(CH$_2$=CC(O)Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (**10**)		57.7 (m),^{d} 22.4 (dm, $^1J_{RhP}$ = 134 Hz)	5.89 (dt, $^3J_{RhCCH}$ = 3 Hz, $^4J_{PRhCCH}$ = 2 Hz, 1H, CH$_2$=C),^{d} 5.42 (t, $^4J_{PRhCCH}$ = 2 Hz, 1H, CH$_2$=C), 3.22 (m, 2H, PCH$_2$P), 3.10 (m, 2H, PCH$_2$P), 1.20 (s, 3H, CH$_3$)	249.7 (dm, $^1J_{RhC}$ = 32 Hz, 1CO),^{d} 237.8 (dt, $^1J_{RhC}$ = 13 Hz, $^2J_{P(Mn)C}$ = 15 Hz, 1CO), 218.5 (t, $^2J_{P(Mn)C}$ = 19 Hz, 1CO), 217.4 (t, $^2J_{P(Mn)C}$ = 18 Hz, 1CO)
[RhMn(Z-C(Me)=CHC(O)Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (**11**)	2006 (st),^{b} 1953 (st), 1864 (m), 1728 (m), 1605 (w); 2016 (st),^{c} 1957 (st), 1869 (st), 1723 (m), 1603 (w)	58.1 (m),^{d} 20.0 (dm, $^1J_{RhP}$ = 125 Hz)	6.30 (s, 1H, H$_\beta$),^{d} 3.30 (m, 2H, PCH$_2$P), 3.15 (m, 2H, PCH$_2$P), 1.57 (s, 3H, CH$_3$), 1.41 (s, 3H, CH$_3$)	260.7 (dtt, $^1J_{RhC}$ = 45 Hz, $^2J_{P(Rh)C}$ = $^2J_{P(Mn)C}$ = 8 Hz, 1CO),^{d} 230.1 (dt, $^1J_{RhC}$ = 5 Hz, $^2J_{P(Mn)C}$ = 15 Hz, 1CO), 220.0 (t, $^2J_{P(Mn)C}$ = 17 Hz, 1CO), 218.9 (t, $^2J_{P(Mn)C}$ = 20 Hz, 1CO)
[RhMn(Me)(CO)$_3$(μ-η^1:η^2-C=CHC(O)Me)(dppm)$_2$][SO$_3$CF$_3$] (**12**)		62.9 (m),^{e} 26.0 (dm, $^1J_{RhP}$ = 101 Hz)	3.40 (b, 2H, PCH$_2$P),^{e} 2.89 (b, 2H, PCH$_2$P), 1.43 (b, 3H, CH$_3$), 0.04 (b, 3H, CH$_3$)	227.6 (t, $^2J_{P(Mn)C}$ = 17 Hz, 1CO),^{e} 225.8 (t, $^2J_{P(Mn)C}$ = 13 Hz, 1CO), 193.2 (dt, $^1J_{RhC}$ = 47 Hz, $^2J_{P(Rh)C}$ = 16 Hz, 1CO); 26.0 (s, 1C, CH$_3$),^{i} 20.4 (m, 2C, PCH$_2$P), 9.0 (db, $^1J_{RhC}$ = 27 Hz, 1C, CH$_3$)
[RhMn(η^2-MeC=CHC(O)Me)(CO)$_3$(dppm)$_2$][SO$_3$CF$_3$] (**13**)		57.7 (m),^{i} 29.1 (dm, $^1J_{RhP}$ = 127 Hz)	6.04 (b, 1H$_\beta$),^{i} 3.70 (b, 2H, PCH$_2$P), 3.44 (b, 2H, PCH$_2$P), 1.44 (b, 3H, CH$_3$), 0.72 (b, 3H, CH$_3$)	231.0 (t, $^2J_{P(Mn)C}$ = 27 Hz, 1CO),^{i} 229.7 (t, $^2J_{P(Mn)C}$ = 15 Hz, 1CO), 192.4 (dt, $^1J_{RhC}$ = 49 Hz, $^2J_{P(Rh)C}$ = 14 Hz, 1CO); 29.6 (s, 1C, CH$_3$),^{f} 29.1 (s, 1C, CH$_3$), 28.5 (m, 2C, PCH$_2$P)
[RhMn(CO)$_3$(μ-η^1:η^1-MeC=CHC(O)Me)(dppm)$_2$][SO$_3$CF$_3$] (**14**)	1993 (st),^{b} 1979 (st), 1910 (st), 1846 (st); 1992 (st),^{c} 1926 (st), 1862 (vs)	58.2 (m),^{d} 24.2 (dm, $^1J_{RhP}$ = 128 Hz)	6.77 (s, 1H$_\beta$),^{d} 3.17 (m, 2H, PCH$_2$P), 2.43 (m, 2H, PCH$_2$P), 1.97 (t, 3H, CH$_3$, $^5J_{P(Mn)OCCH}$ = 3 Hz), 1.27 (s, 3H, CH$_3$)	231.3 (t, $^2J_{P(Mn)C}$ = 20 Hz, 1CO),^{d} 222.2 (t, $^2J_{P(Mn)C}$ = 19 Hz, 1CO), 190.4 (dt, $^1J_{RhC}$ = 77 Hz, $^2J_{P(Rh)C}$ = 15 Hz, 1CO), 202.1 (s, 1C, *C*(O)CH$_3$), 138.7 (m, 1C$_\alpha$), 36.0 (s, 1C, CH$_3$), 25.7 (s, 1C, CH$_3$)

[a] Abbreviations used: IR, w − weak, m = medium, st = strong, vs = very strong; NMR, s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet, b = broad, or any combination. [b] Nujol mull. [c] CH$_2$Cl$_2$ solution. [d] 22 °C. [e] −40 °C. [f] −60 °C. [g] −70 °C. [h] −80 °C. [i] −20 °C. [j] 0 °C.

amount of CF$_3$CO$_2$D (195 μmol, excess) was added, causing the solution to turn clear yellow. The NMR spectroscopic characterization was carried out at both −40 °C and room temperature. For the ^{2}H NMR spectrum 0.5 mL of CH$_2$Cl$_2$ was used as solvent instead of CD$_2$Cl$_2$.

(j) [RhMn(η^2-CH=CHC(O)Me)(CO)$_2$(μ-CO)(dppm)$_2$][SO$_3$CF$_3$] (9a). To a CH$_2$Cl$_2$ solution of compound **5** (50 mg, 46 μmol in 5 mL) was added 4.1 μL of CF$_3$SO$_3$H (1 equiv). The color changed to orange from deep red-orange immediately. Removal of the solvent and recrystallization from CH$_2$Cl$_2$/Et$_2$O gave an orange compound (96%). Anal. Calcd for RhMnSP$_4$F$_3$O$_7$C$_{58}$H$_{49}$: C, 56.68; H, 3.99. Found: C, 56.34; H, 3.85.

(k) [RhMn(η^2-CD=CHC(O)Me)(CO)$_2$(μ-CO)(dppm)$_2$][CO$_2$CF$_3$] (9b). To a CD$_2$Cl$_2$ solution of compound **5** (10 mg, 9 μmol in 0.5 mL) in an NMR tube was added 4 μL of CF$_3$CO$_2$D (52 μmol). The color changed from deep red-orange to orange immediately. Characterization was by NMR. To obtain the ^{2}H NMR spectrum 0.5 mL of CH$_2$Cl$_2$ was used as solvent instead of CD$_2$Cl$_2$.

(l) [RhMn(C(C(O)Me)=CH$_2$)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (10). To a CH$_2$Cl$_2$ solution of [RhMn(μ-H)(CO)$_4$(dppm)$_2$][SO$_3$CF$_3$] (**2**) (50 mg, 42 μmol in 5 mL) was added 100 μL of 3-butyn-2-one (1279 μmol), and the solution was stirred for 5 days. Recrystallization from CH$_2$Cl$_2$/Et$_2$O gave a yellow mixture (86%) which contained [RhMn(*trans*-CH=CHC(O)Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (**6a**) and [RhMn(C(C(O)Me)=CH$_2$)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (**10**) in a 1:1 ratio, as characterized by NMR experiments.

(m)[RhMn(Z-C(Me)=CHC(O)Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (11). To a CH$_2$Cl$_2$ solution of isomers **4a** and **4b** (50 mg, 45 μmol in 5 mL under CO) was added 5.0 μL of CF$_3$SO$_3$CH$_3$ (1 equiv) followed by stirring for 1 h. Removal of the solvent in vacuo and recrystallization from CH$_2$Cl$_2$/Et$_2$O gave a yellow solid (72%). Anal. Calcd for RhMnP$_4$SF$_3$C$_{60}$H$_{51}$O$_8$: C, 56.69; H, 4.02. Found: C, 56.66; H, 3.82.

(n) [RhMn(CH$_3$)(CO)$_3$(μ-η^1:η^2-CCHC(O)Me)(dppm)$_2$][SO$_3$CF$_3$] (12). To a CD$_2$Cl$_2$ solution of [RhMn(CO)$_3$(μ-η^1:η^2-CCHC(O)Me)(dppm)$_2$] (**5**) (10 mg, 9 μmol in 0.5 mL) in an NMR tube was added 2 μL of CF$_3$SO$_3$CH$_3$ (17 μmol) at −78 °C, causing the solution to turn from maroon to red. The compound was characterized by NMR experiments at −40 °C.

(o) [RhMn(CO)$_3$(η^2-MeC=CHC(O)Me)(dppm)$_2$][SO$_3$CF$_3$] (13). To a CD$_2$Cl$_2$ solution of [RhMn(CO)$_3$(μ-η^1:η^2-CCHC(O)Me)(dppm)$_2$] (**5**) (10 mg, 9 μmol in 0.5 mL) in an NMR tube was added 2 μL of CF$_3$SO$_3$CH$_3$ (17 μmol) at −78 °C. The solution turned black after the solution was warmed up to −20 °C. The compound was characterized by NMR experiments at −20 °C.

(p) [RhMn(CO)$_3$(μ-η^1:η^1-MeC=CHC(O)Me)(dppm)$_2$][SO$_3$CF$_3$] (14). To a CH$_2$Cl$_2$ solution of compound **5** (50 mg, 46 μmol in 5 mL) was added 5.2 μL of CF$_3$SO$_3$CH$_3$ (1 equiv) followed by stirring for 1 h. Removal of the solvent in vacuo and recrystallization from CH$_2$Cl$_2$/Et$_2$O gave a red crystalline

Table 2. Crystallographic Data for Compound 5

formula	$C_{60}H_{54}MnO_5P_4Rh$
formula wt	1136.84
space group	$P2_1/n$ (a non standard setting of $P2_1/c$ [No. 14])
unit cell params	
a (Å)	14.489(1)
b (Å)	15.754(2)
c (Å)	24.104(2)
β (deg)	91.41(1)
V (Å^3)	5500(1)
Z	4
D_{calcd} (g cm^{-3})	1.373
μ (cm^{-1})	6.756
diffractometer	Enraf-Nonius CAD4
temp (°C)	23
radiation (λ (Å))	graphite-monochromated Mo Kα (0.710 69)
cryst−detector distance (mm)	173
scan type	$\theta/2\theta$
scan rate (deg min^{-1})	1.73−6.71
scan width (deg)	$0.80 + 0.344 \tan\theta$
max 2θ (deg)	50.0
total unique rflns	9709 ($\pm h+k+l$)
total obs (NO)	3980 ($F_o^2 \geq 3.0\sigma(F_o^2)$)
range of abs cor factors	0.7792−1.1061
final no. of param varied (NV)	404
R^a	0.058
$R_w{}^b$	0.063
error in obs of unit wt (GOF)^c	1.615

$^a R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b R_w = [\Sigma w(|F_o - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. ^{c} GOF $= [\Sigma w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$.

solid (84%). Anal. Calcd for $RhMnSP_4F_3O_7C_{59}H_{51}$: C, 57.00; H, 4.11. Found: C, 56.82; H, 4.25.

Reactions. (a) Reaction of Compound 12 with CO. A 50 mg amount of compound **5** (46 μmol) was dissolved in 10 mL of CH_2Cl_2 at −78 °C to which 10 μL of $CF_3SO_3CH_3$ (85 μmol) was added, followed by stirring at −78 °C for 1 h. The color changed to red from maroon. The solution was partially evacuated and put under CO (10 psi). The sample was left in the acetone−dry ice bath overnight and allowed to slowly warm to room temperature. A yellow powder was obtained after recrystallization from Et_2O/CH_2Cl_2 (80% yield). It was shown to be compound **11** by ^{31}P and ^1H NMR spectra.

(b) Reaction of Compound 13 with CO. To a CD_2Cl_2 solution of compound **5** (10 mg, 9 μmol in 0.5 mL) in an NMR tube was added 2 μL of $CF_3SO_3CH_3$ (17 μmol) at −78 °C. The ^{31}P and ^1H NMR spectra showed the formation of compound **13** at −20 °C (black solution). To the solution was added 1 mL of CO by syringe. The sample was left in the acetone−dry ice bath overnight and allowed to slowly warm to room temperature. The ^{31}P and ^1H NMR spectra showed the presence of only compound **11**.

X-ray Data Collection. Red crystals of $[RhMn(CO)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}C{=}C(H)C(O)CH_3)(dppm)_2]\cdot(CH_3)_2CO$ (**5**·$(CH_3)_2CO$) were grown by diffusion of Et_2O into an acetone solution of the complex. Several of these were mounted and flame sealed in glass capillaries under an atmosphere of the solvent vapor to minimize solvent loss. Data were collected on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $20.0° < 2\theta < 23.8°$. The monoclinic diffraction symmetry and the systematic absences ($h0l$, $h + l \neq 2n$; $0k0$, $k \neq 2n$) defined the space group as $P2_1/n$ (a nonstandard setting of $P2_1/c$ [No. 14]).

Intensity data were collected at 22 °C by using the $\theta/2\theta$ scan technique, covering reflections having indices of the form $\pm h,+k,+l$ to a maximum of $2\theta = 50°$. Of the 10 259 data collected, 9709 were unique, and of these, 3980 were observed ($I \geq 3\sigma(I)$). Backgrounds were scanned for 25% of the scan width on either side of the scan. Three reflections were chosen as intensity standards and were remeasured after every 120 min of X-ray exposure. The intensities of these standards dropped by *ca* 7.5% over the duration of data collection, so a linear correction was applied to the data. The data were processed in the usual way, with a value of 0.04 for p employed to downweight intense reflections.[36,37] Absorption corrections were applied to the data according to the method of Walker and Stuart.[38] See Table 2 for crystal data and additional information on X-ray data collection.

Structure Solution and Refinement. The structure of $RhMn(CO)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}C{=}C(H)C(O)CH_3)(dppm)_2]\cdot(CH_3)_2CO$ was solved in space group $P2_1/n$ using standard Patterson and Fourier techniques. Full-matrix, least-squares refinements minimized the function $\Sigma w(|F_o| - |F_c|)^2$, where the weighting factor $w = 4F_o^2/\sigma^2(F_o)^2$. Atomic scattering factors[39] and anomalous dispersion terms[40] were taken from the usual tabulations. All hydrogen atoms were observed but were generated at idealized calculated positions by assuming a C−H bond length of 0.95 Å and the appropriate sp^2 or sp^3 geometry, except for the acetone hydrogens, which were not included. All hydrogens within the complex molecule were included in calculations with fixed, isotropic thermal parameters 20% greater than those of the attached atoms. Their positions were recalculated after every few cycles of refinement. In the final cycles of refinement the vinylidene hydrogen atom was allowed to refine and was shown to be well-behaved. There was no evidence of secondary extinction; therefore no correction was applied.

The final model with 404 parameters varied converged to $R = 0.058$ and $R_w = 0.063$. In the final difference Fourier map the highest residuals (0.47−0.65 e/Å^3) were found in the vicinities of Rh and the phenyl groups. The atomic coordinates and thermal parameters for selected atoms of compound **5** are given in Table 3, and selected bond lengths and angles are given in Table 4.

Results and Discussion

(a) Vinylidene Complexes. As a continuation of our studies into the reactivities of alkynes at two metal centers we have investigated reactions of $[RhMn(CO)_4(dppm)_2]$ (**1**) with terminal alkynes, with the goal of inducing alkyne-to-vinylidene transformations. Those alkynes not having strongly electron-withdrawing substituents, such as acetylene, phenylacetylene, and propyne, do not react with **1**, even when present in a large excess for extended periods of time. However, 3-butyn-2-one, having an electron-withdrawing C(O)Me substituent, reacts readily with **1**, even at −40 °C. The first species observed at this temperature is the alkyne-bridged product, $[RhMn(CO)_4(\mu\text{-}HC{\equiv}CC(O)Me)(dppm)_2]$ (**3**). All the NMR spectroscopic data (^1H, ^{13}C, ^{31}P) are very similar to those of $[RhMn(CO)_4(\mu\text{-}RC_2R)(dppm)_2]$ (R = CO_2Me, CF_3), which have recently been characterized;[5] therefore **3** is assigned an analogous structure, having a conventional alkyne bridge as shown in Scheme 1. The $^{13}C\{^1H\}$ NMR spectrum of **3** shows three terminal carbonyls on Mn (δ 220−228) and one on Rh (δ 195.6), with only the last one showing Rh-coupling

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Table 3. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for the Core Atoms of 5[a]

atom[a]	x	y	z	B, Å^2 [b]
Rh	0.12279(5)	0.22450(5)	−0.08839(3)	2.89(2)*
Mn	0.1503(1)	0.34558(9)	−0.18423(6)	2.63(4)*
P(1)	0.2693(2)	0.1729(2)	−0.0932(1)	2.86(7)*
P(2)	0.3022(2)	0.3075(2)	−0.1827(1)	2.87(7)*
P(3)	−0.0338(2)	0.2241(2)	−0.1021(1)	3.17(7)*
P(4)	−0.0064(2)	0.3598(2)	−0.1923(1)	3.15(7)*
O(1)	0.1179(5)	0.2338(5)	0.0366(3)	5.9(2)*
O(2)	0.1604(5)	0.4233(4)	−0.0739(3)	4.3(2)*
O(3)	0.1902(5)	0.5187(4)	−0.2235(3)	5.4(2)*
O(4)	0.1438(4)	0.2967(4)	−0.2637(2)	3.5(2)*
C(1)	0.1205(7)	0.2327(6)	−0.0105(4)	3.6(3)*
C(2)	0.1547(6)	0.3825(6)	−0.1156(4)	3.5(3)*
C(3)	0.1741(7)	0.4495(6)	−0.2095(4)	3.5(3)*
C(4)	0.1251(6)	0.2231(6)	−0.1701(3)	2.6(2)*
C(5)	0.1166(7)	0.1732(6)	−0.2162(4)	3.8(3)*
C(6)	0.1272(6)	0.2185(7)	−0.2660(4)	3.8(3)*
C(7)	0.1203(8)	0.1777(8)	−0.3230(4)	5.7(4)*
C(8)	0.3251(6)	0.1983(6)	−0.1590(4)	2.7(3)*
C(9)	−0.0728(7)	0.2671(6)	−0.1701(4)	3.7(3)*
H(5)	0.098(6)	0.110(6)	−0.207(4)	2.8(24)

[a] Phenyl carbons and solvent atoms are given in the supplementary material. [b] Anisotropically refined atoms are marked with an asterisk (*). Displacement parameters for the anisotropically refined atoms are given in the form of the equivalent isotropic Gaussian displacement parameter, B_{eq}, defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

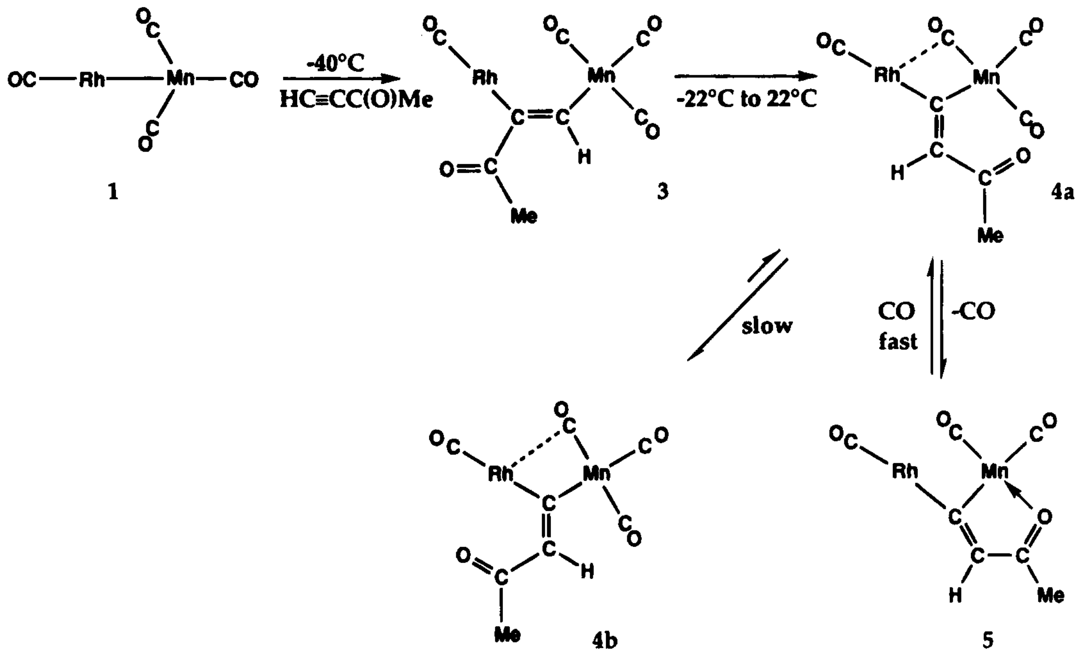
Table 4. Selected Bond Lengths (Å) and Angles (deg) for 5

	Distances		
Rh−P(1)	2.278(2)	Mn−C(4)	1.995(8)
Rh−P(3)	2.285(2)	O(1)−C(1)	1.138(8)
Rh−C(1)	1.883(9)	O(2)−C(2)	1.196(9)
Rh−C(4)	1.971(7)	O(3)−C(3)	1.167(9)
Mn−P(2)	2.282(2)	O(4)−C(6)	1.26(1)
Mn−P(4)	2.284(3)	C(4)−C(5)	1.36(1)
Mn−O(4)	2.065(5)	C(5)−C(6)	1.41(1)
Mn−C(2)	1.752(9)	C(5)−H(5)	1.05(8)
Mn−C(3)	1.783(9)	C(6)−C(7)	1.52(1)
	Angles		
P(1)−Rh−P(3)	156.17(9)	O(4)−Mn−C(4)	78.1(3)
P(1)−Rh−C(1)	96.6(3)	C(2)−Mn−C(3)	90.9(4)
P(1)−Rh−C(4)	84.7(2)	C(2)−Mn−C(4)	99.4(3)
P(3)−Rh−C(1)	95.9(3)	C(3)−Mn−C(4)	169.8(4)
P(3)−Rh−C(4)	84.0(2)	Mn−O(4)−C(6)	114.3(6)
C(1)−Rh−C(4)	176.7(4)	Rh−C(1)−O(1)	176.8(9)
P(2)−Mn−P(4)	169.6(1)	Mn−C(2)−O(2)	166.6(7)
P(2)−Mn−O(4)	86.5(2)	Mn−C(3)−O(3)	176.9(8)
P(2)−Mn−C(2)	93.4(3)	Rh−C(4)−Mn	99.6(4)
P(2)−Mn−C(3)	93.0(3)	Rh−C(4)−C(5)	144.8(7)
P(2)−Mn−C(4)	85.6(2)	Mn−C(4)−C(5)	115.6(6)
P(4)−Mn−O(4)	86.3(2)	C(4)−C(5)−C(6)	113.1(8)
P(4)−Mn−C(2)	93.5(3)	C(4)−C(5)−H(5)	113(4)
P(4)−Mn−C(3)	94.7(3)	C(6)−C(5)−H(5)	134(4)
P(4)−Mn−C(4)	85.6(2)	O(4)−C(6)−C(5)	118.9(8)
O(4)−Mn−C(2)	177.4(3)	O(4)−C(6)−C(7)	117.7(9)
O(4)−Mn−C(3)	91.7(3)	C(5)−C(6)−C(7)	123.4(9)

(58 Hz). In the ^{1}H NMR spectrum the acetylenic hydrogen appears at δ 9.99, but shows no coupling to either Rh or the phosphorus nuclei. The absence of coupling involving this hydrogen makes it impossible to unambiguously determine whether the alkyne unit is bound as shown in Scheme 1, or whether it has the opposite orientation in which the C(O)Me moiety is adjacent to Mn. The orientation shown should be sterically favored, having the less encumbered end of the alkyne adjacent to the more crowded $Mn(CO)_3P_2$ end of the complex, but would be less favorable for the subsequent oxidative addition into the alkyne C−H bond, a presumed step in the conversion to vinylidene-bridged species.[12,29] Upon warming solutions of **3**, two new compounds, **4a**and **5**, start to appear at *ca.* −20 °C, while warming to *ca.* 0 °C results in the appearance of a third species, **4b**. When ambient temperature is reached, compounds **4b** and **5** are the major species, with **4a** being present at only *ca.* 10% of the amount of **4b**. Compounds **4a** and **4b** are isomers of the vinylidene-bridged species $[RhMn(CO)_4(\mu\text{-}CC(H)C(O)Me)(dppm)_2]$, differing only in the orientations of the substituents on the vinylidene β-carbon. The major isomer (**4b**) shows four carbonyl resonances in the $^{13}C\{^1H\}$ NMR; the high-field signal corresponds to a carbonyl which is terminally bound to Rh ($^1J_{Rh-C}$ = 56 Hz), the intermediate two are terminally bound to Mn, and the low-field carbonyl is bound primarily to Mn with a semibridging interaction with Rh ($^1J_{Rh-C}$ = 10 Hz). For this isomer the ^{13}C resonances for the carbons within the vinylidene unit could be obtained using unenriched alkyne. The α-carbon appears at δ 137.4 and displays coupling to Rh (4 Hz) and to all phosphorus nuclei (one pair with 19 Hz coupling and one pair with 4 Hz coupling). Since overnight data acquisition on a 400 MHz instrument (for which we do not have appropriate heteronuclear decoupling capabilities) was necessary to observe these signals, no ^{31}P-decoupling experiments could be carried out, so we do not know whether the larger coupling is to the Rh- or the Mn-bound phosphorus nuclei. However, the surprisingly small coupling to Rh suggests that the Rh−C_α interaction may be weak, leading us to propose that coupling to the Rh-bound phosphines will also be weak. The chemical shift for C_α in our RhMn compounds appears to be anomalous compared to other bridging vinylidenes,[10] in which these carbons typically resonate *downfield* from δ 230. Even the complex $[Cp(P^iPr_3)Rh(\mu\text{-}CO)(\mu\text{-}CCH_2)Mn(CO)Cp]$,[41] having the same metal combination as our compounds, has the C_α resonance at δ 279, in the typical region. However, in related vinylidene-bridged complexes of Rh and Ir, we routinely observe chemical shifts for C_α *upfield* of δ 150,[5,7] with some even as high-field as δ 100. In addition compound **5**, which also has a high-field shift for C_α, has been structurally characterized, confirming the vinylidene formulation (vide infra). The ^{13}C signals for C_β, the ketonic carbonyl, and the methyl group appear at δ 146.8, 193.8, and 22.0, respectively, and ^{13}C APT experiments support these assignments. The ^{1}H resonance for the methyl group of **4b** appears as a singlet at δ 0.62, and the vinylidene hydrogen appears as a triplet at δ 8.09, displaying coupling to the Rh-bound phosphorus nuclei of 7 Hz, as shown by the appropriate heteronuclear decoupling experiments. The minor isomer (**4a**) has very similar spectroscopic properties to **4b**, with the major difference being in the ^{1}H NMR resonance for the vinylidene hydrogen which appears at δ 6.59, again showing coupling (12 Hz) to the Rh-bound phosphorus nuclei. It appears that **4b** is the thermodynamically favored isomer owing to steric considerations, with the more bulky C(O)Me substituent being directed away from the more crowded Mn center. In the IR spectrum the ketonic carbonyl stretch is observed at 1600 cm^{-1}.

The third species present (**5**) is shown (vide infra) to be a tricarbonyl species resulting from carbonyl loss from **4**. With this is mind, an equilibrium mixture of only **4a** and **4b** (in *ca.* 10:90 molar ratio) can be prepared by allowing **3** to warm up in the presence of CO, and

Scheme 1



conversely **5** results as the sole species by refluxing **4a** and **4b** in THF under an N_2 flush. Rearrangement of **4a** to **4b** is shown to be slow compared to CO attack on **5**, the former appearing as the only species at −40 °C under CO with slow equilibration to the 10:90 mix of isomers as the temperature is raised to 20 °C. On the basis of the structure established for **5** (vide infra), the structure of isomer **4a**, which is formed rapidly upon reaction of **5** with CO, can be assigned as shown, with rearrangement by rotation about the vinylidene unit, to give the thermodynamic product, being slow. Although rotation about the C=C bond in terminal vinylidenes is apparently facile,[12] a similar rotation in vinylidene-bridged complexed appears less common, but has been observed.[7,42]

The $^{13}C\{^1H\}$ NMR spectrum of **5** confirms the tricarbonyl formulation, displaying three equal intensity carbonyl resonances, with one bound terminally to Rh and two bound terminally to Mn. The C_α resonance of the bridging vinylidene unit appears at δ 138.3 and is coupled to all four phosphorus nuclei. Surprisingly no coupling to Rh is observed (although it should be recalled that this coupling in **4b** was only 4 Hz). Resonances for C_β, the ketonic carbon, and the methyl carbon appear as singlets at δ 140.1, 190.8, ad 23.8, respectively. Again, ^{13}C APT experiments support these assignments. The ^1H NMR spectrum is unexceptional, apart from the methyl resonance which shows 2 Hz coupling to the Mn-bound phosphorus nuclei; the vinylidene-proton resonance was not observed and is presumably obscured by phenyl resonances. It is also significant that no stretch for the ketone carbonyl was observed in the IR spectrum. This fact and the ^{31}P-coupling to the methyl protons in the ^1H NMR suggests that coordination of the ketonic oxygen to Mn occurs to occupy the coordination site vacated by CO in the transformation from **4a**. This coordination mode has previously been noted in related vinylidene-bridged compounds of manganese,[43-45] and has been confirmed in the present study by the X-ray structure determination of **5**, as shown in Figure 1.

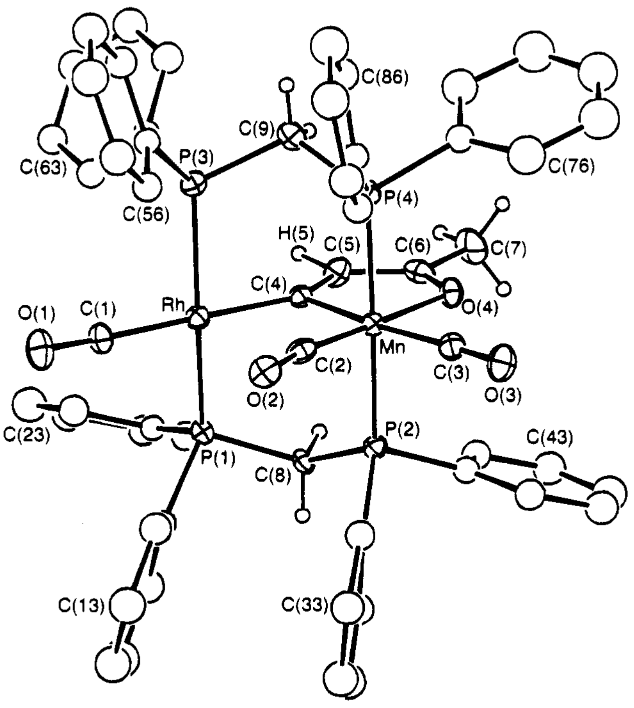


Figure 1. A perspective view of [RhMn(CO)$_3$(μ-η^1:η^2-CC(H)C(O)Me)(dppm)$_2$] (**5**) showing the numbering scheme. Thermal ellipsoids are shown at the 20% level except for hydrogens, which are shown artificially small or are omitted for phenyl groups. The numbering of the phenyl carbons starts at the ipso carbon and works sequentially around the ring.

Compound **5** crystallizes with 1 equiv of acetone, which has the expected geometry and displays no unusual contacts with the complex molecule. The bridging diphosphines have the common trans geometry at both

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(42) Afzol, D.; Lukehart, C. M. *Organometallics* **1987**, *6*, 546.

metal centers, and all parameters within these units are normal. At rhodium the geometry is square planar, having the vinylidene bridge opposite a carbonyl, whereas at Mn the geometry is distorted octahedral, having the carbonyls opposite the vinylidene unit and the dative bond from the ketonic carbonyl group. The major distortions from an idealized octahedral geometry result from the bite of the bidentate ligand, which gives rise to a C(4)−Mn−O(4) angle of 78.1(3)° within the five-membered metallacycle. Within this metallacycle the bond lengths suggest delocalized bonding. Although no single parameter is substantially different from that expected for a localized bonding model, all differ in the direction expected for delocalization. Therefore, the C(4)−C(5) distance (1.36(1) Å) is slightly longer than that expected (1.34 Å) when conjugated with a ketone group, the C(5)−C(6) distance (1.41(1) Å) is shorter than expected (1.464 Å) for a single bond between conjugated olefin and ketone moieties, and the C(6)−O(4) distance (1.26(1) Å) is also longer than expected for a C=O bond in this environment (1.22 Å).[46] By contrast the C(6)−C(7) distance is exactly as expected for a C(sp^2)−C(sp^3) bond in a ketone.[46] In addition all angles within the metallacycle are consistent with sp^2 hybridization of the carbon and oxygen atoms, keeping in mind the slight strain within the ring. The Mn−C(4) and Mn−O(4) distances are essentially as expected.[41,43−45]

Although the lack of coupling of the vinylidene C_α nucleus to Rh, together with the smaller coupling of C_α to the Rh-bound phosphorus nuclei than to those on Mn, suggests a weaker interaction of the vinylidene unit with Rh, this does not manifest itself in the structural parameters. Therefore the Rh−C(4) distance is actually shorter than Mn−C(4) (1.971(7) *vs* 1.995(8) Å), in spite of an opposite prediction based on the covalent radii of the metals. The Rh−Mn separation (3.030(1) Å) is significantly longer than the single bond (2.667(1) Å) in [Cp(P^{i}Pr$_3$)Rh(μ-CO)(μ-CCH$_2$)Mn(CO)Cp],[41] consistent with the absence of a metal−metal bond. However, the Rh−C(4)−Mn angle of 99.6(4)° is more acute than expected, and there seems to be no reason that the Rh−Mn distance could not expand to allow an undistorted sp^2 geometry at C(4). This suggests that the two metals are drawn together. Such a compression of the nominally nonbonded metal−metal separation has been noted in a related system, induced by a weak semibridging carbonyl interaction.[35] The carbonyl group C(2)O(2) in **5** is bent away from Rh slightly, consistent with a semibridging interaction, giving a Mn−C(2)−O(2) angle of 166.6(7)°, but the long Rh−C(2) contact (2.618(8) Å) suggests a weak interaction at best.

The vinylidene unit is not perpendicular to the Rh−Mn vector but is tilted substantially toward Mn, as shown by the Rh−C(4)−C(5) and Mn−C(4)−C(5) angles of 144.8(7)° and 115.6(6)°, respectively. Presumably this tilting occurs to accommodate coordination of the ketonic oxygen at the sixth site, giving Mn the octahedral geometry. This offers further support that Rh is being drawn in the direction of C(2) since movement in the opposite direction would give less distortion at C(4). A similar tilting of a bridging vinylidene unit has been observed in related complexes in which the vinylidene forms part of a five-membered metallacycle ring.[41,43−45]

In an attempt to detect the interconversion of compounds **4a** and **4b**, spin-saturation transfer experiments were attempted by irradiating the ^{31}P resonance corresponding to the Mn-bound phosphines in **4b**. No change in the resonances of **4a** was noted, presumably because exchange is too slow. However, when this experiment was carried out by irradiating the corresponding resonance (δ 73.1) of compound **5**, a decrease in intensity of 80% was noted in the appropriate resonance (δ 67.7) of **4a**. This indicates that reversible CO loss from **4a** and concomitant coordination of the ketonic carbonyl is occurring readily in solution.

(b) Vinylidene Reactivity. (i) Protonation. Having isolated and characterized the vinylidene-bridged complexes **4** and **5**, it was of interest to investigate their reactivities. In particular we were interested in the transformation of the vinylidene bridges to substituted vinyl moieties, either by protonation or alkylation. It was felt that the square planar Rh(I) center could be basic enough to react with electrophiles such as H^+ and CH_3^+, and that the resulting rhodium−hydride and rhodium−alkyl moieties might undergo migratory insertion with the bridging vinylidene units. Protonation of a mixture of **4a** and **4b** gives only one species at ambient temperature, the vinyl complex [RhMn(*trans*-CH=C(H)C(O)Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (**6a**), as shown in Scheme 2. This product is analogous to the vinyl compounds [RhMn(CR=C(H)R)(CO)$_2$(μ-CO)$_2$(dppm)$_2$]$^+$ (R = CO$_2$Me, CF$_3$) described earlier,[5] in which the vinyl groups were terminally bound to Rh. The trans geometry for **6a** (in which the C(O)Me group is opposite Rh) is as expected if the initial protonation were to occur at the vacant site on Rh, adjacent to the vinylidene unit in isomer **4b**. Significantly no species corresponding to a cis arrangement of vinyl hydrogens is observed, even though both isomers **4a** and **4b** were initially present.

At temperatures between −80 and −40 °C protonation of **4** yields an intermediate **7** in between 5% and 20% yield, transforming to **6**, even at these low temperatures. Owing to the presence of **4a**, **4b**, and **6**, together with impurities (ether, excess acid, etc.), not all the proton resonances of **7** could be identified. In the ^{1}H NMR spectrum, a low-field signal at δ 9.30, one of the dppm-methylene resonances at δ 2.62, and the methyl resonance at δ 0.81 were observed. The vinyl-hydrogen resonance and the second dppm-methylene resonance were not identified. Significantly, no evidence of a hydride resonance was observed. Compound **7** is assigned as the enol intermediate [RhMn(CO)$_3$(μ-CC(H)=C(OH)Me)(μ-CO)(dppm)$_2$][BF$_4$] on the basis of the broad low-field ^{1}H signal which appears to be typical for an enol proton.[47] Keto−enol tautomerism generally occurs via deprotonation and reprotonation at an alternative site.[48] Whether the Rh center or the anion of the acid functions as the base is not known, although

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[43] García Alonso, F. J.; Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Tiripicchio Camellini, M. *Organometallics* **1992**, *11*, 370.

[44] Adams, R. D.; Chen, G.; Chen, L.; Yin, J. *Organometallics* **1993**, *12*, 2644.

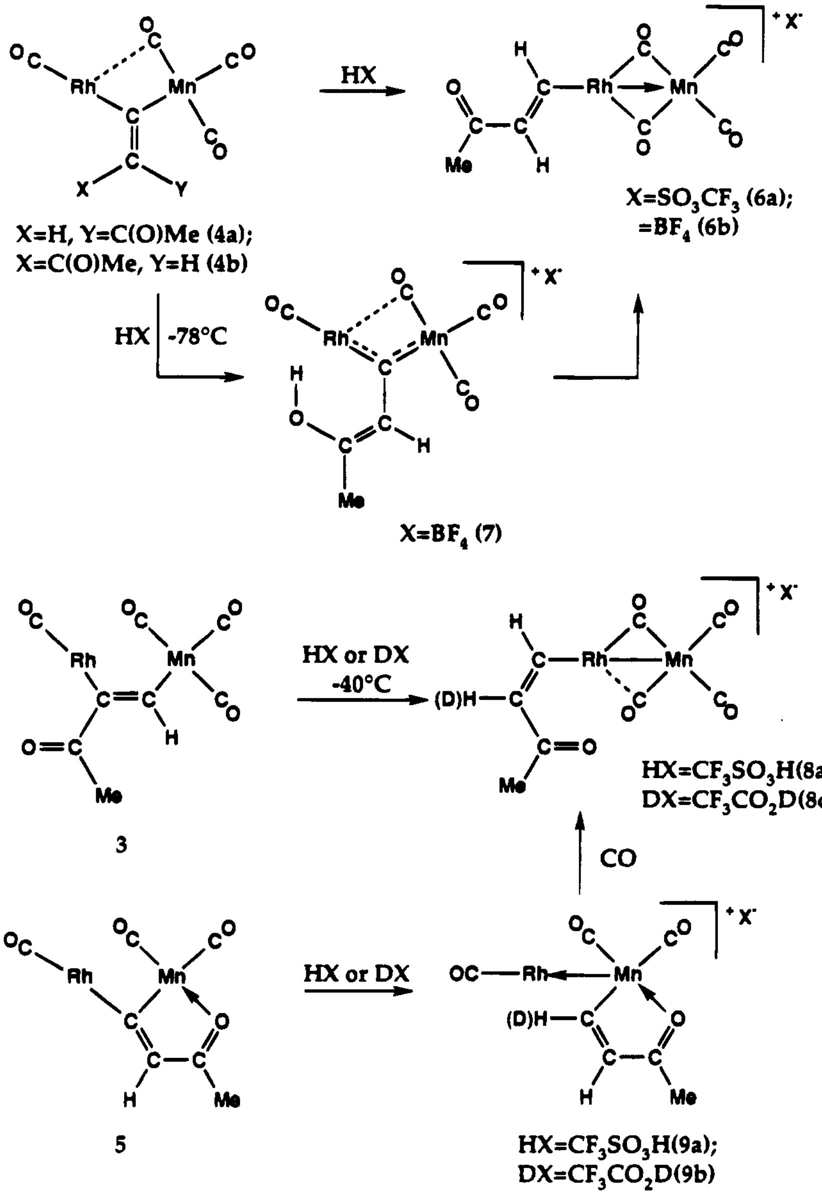
[45] Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Batsanov, A. S.; Struchkov, Yu. T. *J. Organomet. Chem.* **1985**, *279*, 419.

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

[47] (a) Silverstein, R. M.; Bassler, G. C. *Spectrometric Identification of Organic Compounds*, 2nd ed.; John Wiley and Sons: New York, NY, 1981; Ch. 4. (b) Bergens, S. H.; Bosnich, B. *J. Am. Chem. Soc.* **1991**, *113*, 958.

[48] Marsh, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley and Sons: New York, NY, 1992; p 585.

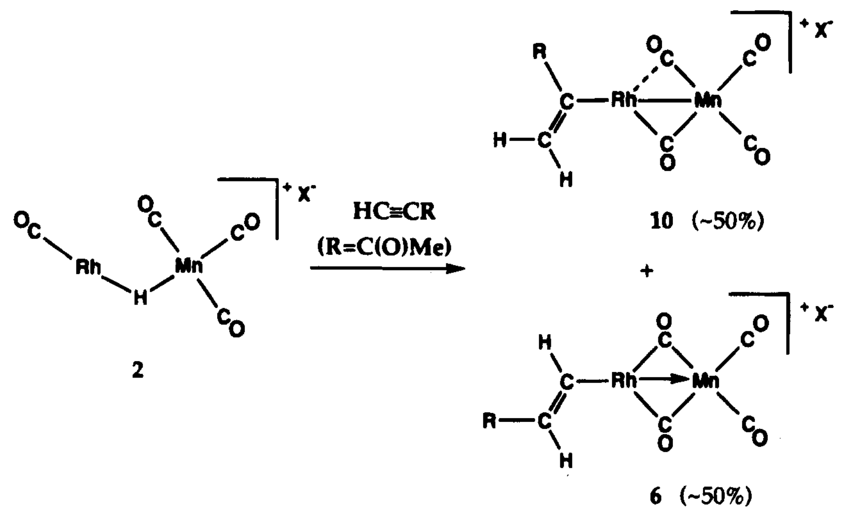
Scheme 2



as noted, no high-field ^{1}H signals, which would indicate proton transfer to the metal, was observed. If we assume the involvement of a rhodium−hydride intermediate in the protonation of **4a** and **4b**, the observation of only one isomer of **6** can be rationalized by the transfer of the enol proton to Rh, followed by rapid migratory insertion of the resulting hydride and vinylidene groups; only the orientation in which the enol oxygen is adjacent to Rh will favor proton transfer to this metal. We suggest that both isomers **4a** and **4b** are protonated to yield the respective enols but that their interconversion is facile by rotation about C_α−C_β single bond, yielding **7** which can then yield the vinyl product **6**.

Protonation of the alkyne-bridged precursor (**3**) yields the vinyl species **8**, in which the major difference to **6** is a cis arrangement of vinyl hydrogens in the new product. The ^{1}H NMR spectrum of **8** shows the vinyl protons at δ 9.20 (H_α) and 6.42 (H_β) with mutual coupling of 7.5 Hz, consistent with the cis arrangement shown in Scheme 2. Additional coupling of H_α to Rh ($^2J_{Rh-H}$ = 5 Hz) and to the Rh-bound phosphorus nuclei of 6 Hz is also observed. In addition, the β-hydrogen also shows coupling to Rh of 2.5 Hz. Subtle differences in the $^{13}C\{^1H\}$ NMR spectrum, compared to **6**, show a carbonyl resonance at δ 259.8 with relatively strong coupling to Rh (41 Hz) as well as equal coupling to all four phosphorus nuclei, indicating a conventionally bridged CO, another at δ 231.9 coupling weakly to Rh (12 Hz), and two other higher field resonances for the terminal carbonyls on Mn. The difference in the two bridged carbonyls of **8** may result from steric interactions, in which the mutually cis arrangement of the C(O)Me group and Rh forces one of the bridged carbonyls away from Rh. A similar affect was noted in related vinyl compounds of RhMn.[5] Confirmation of the vinyl hydrogen assignments comes from reaction of **3** with CF_3CO_2D to give [RhMn(*cis*-CH=C(D)C(O)Me)-$(CO)_2(\mu$-$CO)_2(dppm)_2][CF_3CO_2]$; as expected the signal for the β-hydrogen is absent in the ^{1}H NMR spectrum, but appears in the ^{2}H NMR. Similarly species **8** having deuterium incorporated into the α position can be prepared (vide infra) giving the expected NMR results. The generation of a *cis*-vinyl species **8** from the *cis*-

Scheme 3



dimetalated olefinic precursor **3** is unexpected since rotation about the C=C bond has apparently occurred, such that the originally cis H_α and C(O)Me groups are now in a mutually trans arrangement. It is not clear how this occurs.

Protonation of the vinylidene species **5** yields the vinyl product [RhMn(η^2-CH=C(H)C(O)Me)(CO)$_3$(dppm)$_2$][SO$_3$CF$_3$] (**9**), in which the vinyl group chelates the Mn atom, binding through C_α and the ketone oxygen. Although no metal–hydride species was observed, **9** is the anticipated product of protonation of **5** at Rh followed by hydrogen transfer to C_α accompanied by cleavage of the Rh–C_α bond. As was observed in **5**, which also has a five-membered metallacycle involving Mn, the methyl resonance in the ^{1}H NMR spectrum of **9** displays coupling to the Mn-bound ^{31}P nuclei ($^5J_{P-H}$ = 3 Hz). The resonance for H_α is not observed, being obscured by phenyl resonances; however, H_β appears at δ 8.04, showing 10 Hz coupling to H_α and 2.5 Hz coupling to the phosphorus nuclei on Mn. The magnitude of $H_\alpha H_\beta$ coupling is in line with a cis arrangement, which is also required by the chelated structure. If the protonation is carried out using CF$_3$CO$_2$D, the product having deuterium in the α position is obtained, and this signal is observed in the ^{2}H NMR spectrum at δ 7.66 (confirming the proposal that this resonance in the ^{1}H NMR spectrum is obscured by phenyl protons). As expected, no deuterium–hydrogen coupling is observed between the vinylic H and D atoms; H_β displays coupling (2.5 Hz) to only the ^{31}P nuclei on Mn. Unlike all species in which the ketonic carbonyl is not coordinated, but like the precursor (**5**), the IR spectrum of **9** shows no ketonic carbonyl stretch. Compound **9** can be transformed to **8** under CO, so replacing the donor bond from the ketone oxygen by a carbonyl group is also accompanied by migration of the vinyl group from Mn to Rh with concomitant transfer of the CO from Rh to Mn. This was the route used to generate **8** having deuterium incorporation at the α position (vide supra).

It is significant that protonation of the vinylidene-bridged species **4** and **5** has *not* yielded carbyne-bridged products as frequently occurs by attack of electrophiles at the β-carbon.[10] Instead the products obtained are consistent with the intervention of a Rh-hydride intermediate (although no such intermediate was observed). The formation of vinyl products via protonation of vinylidene complexes parallels an earlier study by Werner,[49] in which no metal–hydride species were detected, and is an interesting contrast to other work by the Werner group in which metal–hydride species rearranged by 1,3-hydride transfer to give carbynes.[29,33] Even though no metal–hydride species were observed in this part of our study, the formation of vinyl rather than carbyne products leads us to propose that they result from migratory insertion involving the vinylidene and hydride groups.

Vinyl species can also be generated by the insertion of alkynes into the metal–hydride bonds of [RhMn(CO)$_4$(μ-H)(dppm)$_2$][SO$_3$CF$_3$] (**2**).[5] Therefore **2** reacts with 3-butyn-2-one to give two isomers of the vinyl compound [RhMn(C$_2$H$_2$C(O)Me)(CO)$_4$(dppm)$_2$][SO$_3$CF$_3$] (**6** and **10**) in approximately equal proportions, as shown in Scheme 3. These isomers differ mainly in the stereochemistry of the vinyl C=C bond, depending on whether alkyne insertion yields the products having a geminal (**10**) or trans arrangement (**6**) of vinyl hydrogens. In isomer **6** the trans vinyl hydrogens resonate at δ 7.99 and 5.32 for H_α and H_β, respectively, in the ^{1}H NMR spectrum. The 17 Hz coupling between these protons is consistent with a trans arrangement, and in addition H_α shows additional coupling ($^3J_{P(Rh)-H}$ = 7 Hz) to the two Rh-bound phosphorus nuclei. The ^{13}C{^{1}H} NMR spectrum for this isomer shows two carbonyl resonances, one corresponding to two bridging groups (δ 244.1, $^1J_{Rh-C}$ = 22 Hz) and the other corresponding to two terminal groups (δ 217.4) bound to Mn. The slightly smaller Rh–C coupling observed for the bridging carbonyls (compared to that for the symmetrically bridged CO in **10**) suggests asymmetric bridges for these groups, with stronger binding to Mn. In addition to the four carbonyl stretches (two terminal, two bridging) in the IR spectrum, the ketonic stretch is observed at 1654 cm^{-1}. For the other isomer (**10**) the geminal protons on the β-carbon of the vinyl group appear at δ 5.89 and 5.42 in the ^{1}H NMR spectrum. Both protons show coupling of 2 Hz to the Rh-bound phosphorus nuclei, and the lower-field signal also displays 3 Hz coupling to Rh. No coupling between the geminal protons is observed. Isomer **10** differs subtly from **6** in the natures of the carbonyl groups, displaying four carbonyl resonances in

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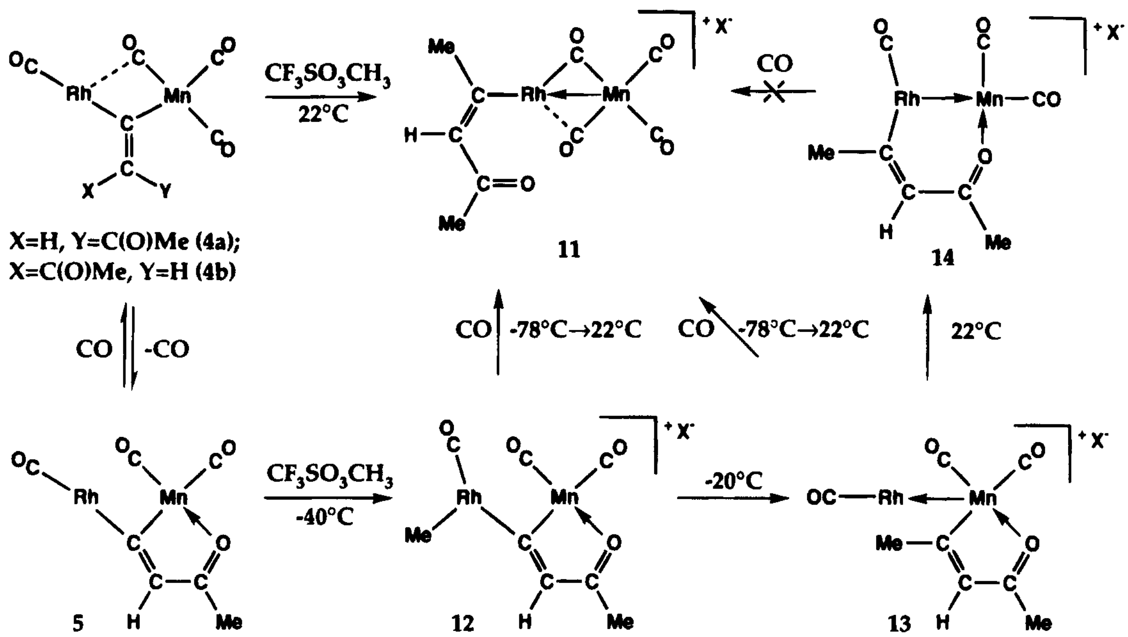
(49) Wolf, J.; Werner, H. *J. Organomet. Chem.* **1987**, 413.

Scheme 4



the $^{13}C\{^1H\}$ NMR spectrum. The lowest-field signal (δ 249.7) shows coupling of 32 Hz with Rh, suggesting a conventional, bridged geometry, whereas the signal at δ 237.8 displays coupling to Rh of only 13 Hz, indicating that it is semibridging. Again we suggest that this difference is steric in origin, in which the bulkier C(O)-Me group on the α-carbon forces the adjacent carbonyl away from Rh, weakening the Rh−CO interaction. This is compensated for by a stronger interaction between Rh and the other carbonyl, as reflected in the larger $^1J_{Rh-C}$ value for this carbonyl.

These subtle structural differences between **10** and **6** demonstrate how adjacent metal centers can "tune" the electron distributions within the complex to changes in ligand binding modes. In **10** one carbonyl is semibridging while the other is symmetrically bridging, having weak and strong interactions with Rh, respectively. In **6** the strengthening of the semibridging interaction with Rh is compensated for by a weakening of the other Rh−CO interaction such that both bridging carbonyls are asymmetrically bound. These changes in carbonyl binding modes, with each carbonyl being a one-electron donor to each metal for the symmetrically or asymmetrically bridged CO's or a two-electron donor to Mn in the semibridging CO,[50] are accompanied by a change in the nature of the Rh−Mn bond as shown in Scheme 3. Although such bonding descriptions are formalisms, they do demonstrate how the polarity of a metal−metal bond can change to compensate for changes in ligand binding.

(ii) Alkylation. Reaction of the vinylidene-bridged isomers **4a** and **4b** with methyl triflate yields [RhMn(MeC=C(H)C(O)Me)(CO)$_2$(μ-CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (**11**) as the sole observed product over the temperature range from −80 to 22 °C. Unlike protonation, which yields a vinyl group in which the proton ends up on the α-carbon *cis* to the C(O)Me group, the methyl carbocation ends up trans to C(O)Me to give a product that is analogous to **8** rather than **6** (see Scheme 4). This analogy to **8** carries through to the binding of the bridging CO's, in which one is semibridging while the other is conventionally bridging, presumably for the reasons discussed earlier. The ^{1}H NMR spectrum of **11** shows the methyl signals as singlets at δ 1.57 and 1.41 and the vinyl hydrogen at δ 6.30. The arrangement shown about the vinyl C=C bond is supported by proton NOE experiments which indicate that the vinyl proton has a positive NOE effect with both sets of methyl protons, whereas the two methyl groups show no NOE effect with each other. If **11** results from an undetected Rh−methyl intermediate followed by migratory insertion with the vinylidene group, it would appear that isomer **4a** is the favored target, since this isomer would yield the appropriate stereochemistry at the double bond. Attack at Rh in this isomer, as opposed to the more predominant **4b**, would appear to be steric in origin with the larger C(O)Me substituent blocking attack at Rh in the latter.

The tricarbonyl, vinylidene-bridged **5** also reacts with methyl triflate, but in this case a couple of key intermediates can be detected at low temperature. At −40 °C the first intermediate observed, [RhMnCH$_3$(CO)$_3$(μ-CC(H)C(O)Me)(dppm)$_2$][SO$_3$CF$_3$] (**12**), is a metal−alkyl species having the methyl group bound to Rh as shown in Scheme 4. This is the first complex in this study in which an alkyl unit is adjacent to a vinylidene unit, and as suggested earlier,[26] such species are unusual. In the ^{1}H NMR spectrum of **12** the resonance for the Rh-bound methyl group is broad, obscuring the expected 2−3 Hz coupling to Rh. However, the $^{13}C\{^1H\}$ NMR study shows the broad methyl resonance at δ 9.0 with coupling of 27 Hz to Rh, clearly indicating a direct bond between the two. In addition, the ^{13}C chemical shift for this methyl group is at higher field than the alkyne-bound methyl group, falling in the range observed for other Rh−methyl complexes.[51] The methyl group of the C(O)-Me moiety appears as a broad singlet at δ 26.0 in the $^{13}C\{^1H\}$ NMR spectrum with no obvious coupling to the Mn-bound phosphines, as was noted in the related

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(50) Colton, R.; McCormick, M. J. *Coord. Chem. Rev.* **1980**, *31*, 1.

(51) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, 1981; p 44.

metallacycles (**5**, **9**). It is noteworthy that upon reaction with CH_3^+ the value of $^1J_{Rh-P}$ drops from 175 Hz in **5** to 101 Hz in **12**, consistent with an increase in oxidation state from +1 to +3.[52] An analogous drop (from 155 to 104 Hz) was previously observed upon protonation of $[RhMn(CO)_4(\mu\text{-}RC_2R)(dppm)_2]$ to give $[RhMnH(CO)_4(\mu\text{-}RC_2R)(dppm)_2]^+$,[5] a product that is rather similar in formulation to **12**, except having a bridging alkyne (R = CO_2Me, CF_3) rather than vinylidene unit.

Upon warming a solution of **12** to −20 °C, a transformation to $[RhMn(CO)_3(\eta^2\text{-}MeC{=}C(H)C(O)Me)(dppm)_2][SO_3CF_3]$ (**13**) occurs in which migration of the methyl group from Rh to the vinylidene ligand occurs, apparently yielding the chelated vinyl complex. The $^{13}C\{^1H\}$ NMR spectrum shows two Mn-bound (δ 231.0, 229.7) and one Rh-bound (δ 192.4, $^1J_{Rh-C}$ = 49 Hz) carbonyls, in addition to singlets for the methyl groups at δ 29.6 and 29.1. The lack of coupling of these methyl groups to phosphorus or Rh and the downfield shift from that observed for the $Rh-CH_3$ group in **12** suggests that the methyl group now resides on the transformed vinyl moiety. Unfortunately, attempts to verify the geometry of the vinyl group in **13** by NOE experiments failed. The migratory insertion of the bridged vinylidene and methyl groups in **12** to give the vinyl moiety in **13** is unprecedented. This transformation can be regarded as reductive elimination from the Rh^{3+} center in **12** to give Rh^+ in **13**, and is supported by the increase in the value of $^1J_{Rh-P}$ that is observed (to 127 Hz in **13**). In the ^1H NMR spectrum, the methyl resonances appear as singlets at δ 1.44 and 0.72 and the vinyl proton appears at δ 6.04.

Under a CO atmosphere both **12** and **13** transform to **11**. This product was well characterized and offers support for the formulation of **13**. Furthermore, the transformation of **12** to **11** offers an additional example of migratory insertion of the bridging vinylidene group and the methyl group to give a substituted vinyl species. It may be that alkylation of **4** proceeds via intermediate **12**, since compounds **4a** and **5** were shown earlier to be in equilibrium. Alkylation to yield **12** would then be followed by attack of the CO initially lost from **4a**.

At ambient temperature compound **13** is unstable, even in the absence of CO, and gives a new species, $[RhMn(CO)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}MeC{=}C(H)C(O)Me)(dppm)_2][SO_3CF_3]$ (**14**) in which the chelated vinyl moiety appears to adopt a bridging arrangement. In the $^{13}C\{^1H\}$ NMR spectrum the three carbonyl resonances are not unlike those of **13**, apart from the larger $^1J_{Rh-C}$ value (77 Hz) for **14**. The ketonic carbon is observed at δ 202.1, the vinyl C_α carbon is a complex multiplet at δ 138.7, and the methyl singlets appear at δ 36.0 and 25.7. Since the alkyne used was not isotopically enriched, overnight data acquisition was required, ruling out heteronuclear decoupling experiments. For this reason we were unable to resolve coupling of C_α to Rh. In the ^1H NMR spectrum one methyl group (δ 1.97) displays 3 Hz coupling to the Mn-bound phosphines, reminiscent of the coupling observed in **5** and **9** in which the ketone oxygen is coordinated to Mn. Although compound **13**, containing the chelating vinyl ketone group, reacts with CO to displace the ketone oxygen and cause migration of the vinyl group to Rh, compound **14** is inert to CO. Presumably in **13** the ketone oxygen is labile owing to the strain within the five-membered metallacycle. Migration of the vinylic carbon to Rh in **14** generates a six-membered metallacycle in which the intraligand strain is much less, resulting in decreased lability of the ketone oxygen.

Summary and Conclusions

When reaction of $[RhMn(CO)_4(dppm)_2]$ (**1**) with the terminal alkyne 3-butyn-2-one is monitored at low temperature, the expected product having the alkyne coordinated in a bridging position, parallel to the metals, is observed. However, upon warming to ambient temperature this species undergoes a 1,2-hydrogen shift to give a vinylidene-bridged product, $[RhMn(CO)_4(\mu\text{-}CC(H)C(O)Me)(dppm)_2]$ (**4**). Compound **4** is observed as two isomers which are related by apparent rotation about the C=C bond of the bridging vinylidene unit. Transformation of one isomer to the other occurs readily at ambient temperature, requiring less than 1/2 h to reach an equilibrium mixture. Loss of one carbonyl from the Mn center is facile, assisted by the formation of a donor bond from the ketone oxygen of the vinylidene group to yield $[RhMn(CO)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}CC(H)C(O)Me)(dppm)_2]$ (**5**).

Although protonation of a vinylidene ligand generally occurs at the β-carbon, the C(O)Me substituent on this carbon appears to lower its nucleophilicity so bridging alkylidyne species are not obtained. In compound **4** the initial site of protonation appears to be at the ketone oxygen of the bridging vinylidene group, with subsequent proton transfer to the α-carbon. No metal−hydride species was observed, so it is not clear whether such an intermediate was present. Protonation of the tricarbonyl species **5** again yields a vinyl product in which the vinyl group is chelating Mn, bound through the α-carbon and the ketone oxygen, and reaction of this product with CO results in replacement of the ketone-to-Mn dative interaction by a carbonyl group and also in migration of the vinyl group from Mn to Rh. The isomer observed has the two vinyl hydrogens in a mutually cis arrangement, in contrast to the protonation product of **4**, in which the vinylic hydrogens are trans. These vinyl products are consistent with protonation at Rh at some stage in the reaction, followed by a migratory insertion of the vinylidene group.

The reaction of the vinylidene-bridged species **4** and **5** with methyl triflate yields the corresponding vinyl products in which the carbocation has again ended up on the α-carbon, again suggesting primary attack at Rh, followed by migration to the vinylidene groups. In the case of the tricarbonyl species **5**, the unusual vinylidene-bridged methyl complex $[RhMn(CH_3)(CO)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}CC(H)C(O)Me)(dppm)_2][SO_3CF_3]$ is observed at −40 °C and is shown to have the methyl group coordinated to Rh. Upon warming, this species undergoes a migratory insertion of the methyl and vinylidene ligands to give a tricarbonyl vinyl species in the absence of CO or a tetracarbonyl vinyl species in the presence of CO. These appear to be the only clearly defined examples involving the migratory insertion of a bridged vinylidene group; even examples involving terminal vinylidenes are not common.

It is significant that attack by the electrophiles H^+ and CH_3^+ on an equilibrium mixture of **4a** and **4b** yields

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[52] Nixon, J. F.; Pidcock, A. *Annu. Rev. NMR Spectrosc.* **1969**, *2*, 345.

only one product in each case, and it is even more significant that these products differ in their geometries about the vinyl C=C bond. In both cases the observations can be rationalized by the intervention of a rhodium–hydride or a rhodium–alkyl intermediate with subsequent migratory insertion involving the vinylidene group. Protonation appears to occur initially at the ketonic oxygen to give an enol product for which only one isomer can give facile proton transfer to Rh giving the vinyl product observed. Alkylation of a **4a**/**4b** mixture apparently occurs directly at Rh, with attack being favored in isomer **4a**, in which there is better access to Rh. Again, subsequent migratory insertion of this product would yield the observed product.

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Supplementary Material Available: Tables of positional and thermal parameters for the phenyl carbons and solvent atoms, anisotropic thermal parameters, idealized hydrogen parameters, and bond distances and angles for the dppm ligands and solvent molecule (6 pages). Ordering information is given on any current masthead page.

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