Methylidyne–Alkyne Coupling on Triruthenium Clusters and Hydrogenation of Cluster-Bound 1,3-Dimetalloallyl Units. A New Model for Fischer–Tropsch Chain Growth

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Alkylidyne–alkyne coupling occurs upon reaction of $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$ (X = OMe, Me, Ph, or $CH_2CH_2CMe_3$) at 25 °C or $HRu_3(\mu\text{-}CX)(CO)_{10}$ (X = OMe) at 60 °C with alkynes $R^1C_2R^2$, forming 1,3-dimetalloallyl clusters $HRu_3(\mu_3\text{-}\eta^3\text{-}XCCRCR)(CO)_9$ (X = OMe, (R^1, R^2) = (H, H), (Me, Me), (Ph, Ph), (H, Ph), (H, CMe_3), (H, *n*-Bu), (H, CO_2Me), (Ph, CO_2Me), (H, OEt); X = Ph, (R^1, R^2) = (Ph, Ph); X = Me, (R^1, R^2) = (Me, Me); X = $CH_2CH_2CMe_3$, (R^1, R^2) = (Ph, Ph)) in yields of 15–90%. In an analogous fashion, $HOs_3(\mu\text{-}COMe)(CO)_{10}$ and PhC_2Ph yield $HOs_3(\mu_3\text{-}\eta^3\text{-}MeOCCPhCPh)(CO)_9$. One equivalent of the appropriate *cis*-alkene is formed from reduction of alkyne by $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$. With unsymmetrical alkynes the relative amounts of the two possible regioisomers depend upon the alkyne substituents. Coupling from either $H_3R_3(\mu_3\text{-}COMe)(CO)_9$ or $HRu_3(\mu\text{-}COMe)(CO)_{10}$ forms $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCR^1CR^2)(CO)_9$ in the relative amounts (R^1, R^2) = (H, Ph)/(Ph, H), 3:1, (H, *n*-Bu)/(*n*-Bu, H), 2:1, (H, CMe_3)/(CMe_3, H), 20:1, (H, CO_2Me)/(CO_2Me, H), 2:1, (H, OEt)/(OEt, H), 1:0, (Me, C_7H_{15})/(C_7H_{15}, Me), 3:1, and (CO_2Me, Ph)/(Ph, CO_2Me), 2:1. Hydrogenation (90 °C, 1–4 atm) of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCR^1CR^2)(CO)_9$ ((R^1, R^2) = (H, H), (H, CMe_3), (Me, Me), (Ph, Ph), (H, OEt), (H, Ph), (H, *n*-Bu), (*n*-Bu, H), (H, CO_2Me)) produces in each case the corresponding $H_3Ru_3(\mu_3\text{-}CCHR^1CH_2R^2)(CO)_9$ in yields of 6–43%; also formed are substantial quantities of $H_4Ru_4(CO)_{12}$. Hydrogenation of $DRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCCMe_3)(CO)_9$ produces exclusively $H_3Ru_3(\mu_3\text{-}CCH_2CHDCMe_3)(CO)_9$. This alkylidyne–alkyne coupling and subsequent hydrogenation to form an alkylidyne of longer carbon chain length suggests a mechanism to account for 2-methylated hydrocarbon products in the Fischer–Tropsch reaction.

The structures, bonding, and chemical reactivity of metal clusters containing alkylidene (CR_2) or alkylidyne (CR) fragments have been of interest for many years.[1,2] This interest has intensified recently due to the implication of surface-bound C_1 and C_2 units in some heterogeneous, metal-catalyzed processes[3] including the Fischer–Tropsch reaction.[4]

We have undertaken a comprehensive investigation of the physical and chemical properties of substituted methylidyne clusters $HM_3(\mu\text{-}CX)(CO)_{10}$ (M = Fe, Ru, or Os; X = OR or NR_2)[5-10] and $H_3M_3(\mu_3\text{-}CX)(CO)_9$ (X = H, alkyl, aryl, halide, CO_2Me, OMe, or SR).[11-15] These clusters allow systematic studies of the variation in chemical reactivity with the identity of the metal, the methylidyne substituent, and other ligands. Reactions involving the hydride ligands—dihydrogen elimination,[16,17] CH_3X elimination,[7,18] hydrogen transfer to unsaturated hydrocarbons[19,20]—are of particular interest.

We have previously reported that alkenes are stoichiometrically hydrogenated by $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$ (X = OMe or Ph).[19] This hydrogen transfer generates an unsaturated cluster species which can bind additional substrates. For example, hydrogenation of 1,3-cyclohexadiene by $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$ gives cyclohexene and $HRu_3(\mu_3\text{-}CX)(CO)_8(1,3\text{-}C_6H_8)$ in high yield. These results led us to investigate the reactions of $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$ with alkynes, which are generally more reactive than alkenes and which have been shown in other cluster systems to form a wide variety of products.[21] We describe here a new route to 1,3-dimetalloallyl clusters $HRu_3(\mu_3\text{-}\eta^3\text{-}C_3R_3)(CO)_9$ via alkylidyne–alkyne coupling and hydrogenation of these products

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to form new clusters containing alkylidynes of longer chain length. These reactions suggest a new mechanism to account for some of the products of the Fischer–Tropsch reaction. A preliminary account of some of these results has appeared.[20]

Experimental Section

Chemicals. Starting materials $HRu_3(\mu\text{-COMe})(CO)_{10}$,[7] $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$,[7] $H_3Ru_3(\mu_3\text{-CPh})(CO)_9$,[15] $H_3Ru_3(\mu_3\text{-CMe})(CO)_9$,[12] $HRu_3(\mu\text{-CNMe}_2)(CO)_{10}$,[7] $HRu_3(\mu\text{-CNMe}_2)(CO)_9(py)$,[22] $HRu_3(\mu\text{-CNMe}(CH_2Ph))(CO)_{10}$,[7] $HRu_3(CNMe(CH_2Ph))(CO)_9(py)$,[22] $HFe_3(\mu\text{-COMe})(CO)_{10}$,[5] $HOs_3(\mu\text{-COMe})(CO)_{10}$,[7] $HRu_3(\mu_3\text{-}\eta^3\text{-Et}_2NCCHCMe)(CO)_9$,[23] $HRu_3(\mu_3\text{-}\eta^3\text{-MeCCHCH})(CO)_9$,[24] and $HOs_3(\mu_3\text{-}\eta^3\text{-HOCCHCH})(CO)_9$[25] were prepared using published procedures. All alkynes were obtained from commercial sources and were used as received.

Characterization of Compounds. Infrared spectra were recorded for cyclohexane solutions by using Perkin-Elmer 267, 467, or 457 spectrophotometers and were calibrated by using the 2138.5 cm^{-1} bond of cyclohexane or using polystyrene. ^1H NMR spectra were obtained on a Varian EM-390 or JEOL FX-90Q (90 MHz) spectrometer. ^{13}C NMR spectra were obtained on a JEOL FX-90Q instrument; solutions contained 0.02 M $Cr(acac)_3$. Mass spectra were provided by Dr. Robert Minard and Mr. Gregg Hancock of the Penn State University Mass Spectrometry Facility. Elemental analyses were provided by Schwarzkopf Laboratories.

$HRu_3(\mu\text{-}\eta^3\text{-MeOCCHCH})(CO)_9$. Method 1. Acetylene gas was bubbled through a solution of $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$ (152 mg, 0.253 mmol) in cyclohexane (15 mL). After 2 h the solution was filtered, and the solvent was removed on a rotary evaporator. Thin-layer chromatography on silica, eluting with cyclohexane, yielded the product as the third, orange band (32 mg), contaminated with $HRu_3(\mu\text{-COMe})(CO)_{10}$ (25% by NMR).

Method 2. Acetylene gas was bubbled through a cyclohexane solution of $HRu_3(\mu\text{-COMe})(CO)_{10}$ (100 mg, 0.16 mmol) in a 100-mL, three-necked, round-bottomed flask equipped with stir bar, gas inlet, and reflux condenser topped with a gas outlet to an oil bubbler. The solution was heated at 55–65 °C for 5 h. Then the solution was cooled, filtered, and evaporated to dryness on a rotary evaporator. The products were separated by thin-layer chromatography on silica, eluting with hexanes. The third, yellow band was extracted with dichloromethane, and evaporation yielded 55 mg of $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCHCH})(CO)_9$ (55%).

$HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCMeCMe})(CO)_9$. A solution of $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$ (200 mg, 0.33 mmol) and 2-butyne (100 μL, 1.5 mmol) in cyclohexane (20 mL) was stirred for 1.5 h. The solvent was removed on a rotary evaporator, and the residue was purified by thin-layer chromatography on silica, eluting with cyclohexane. The first yellow band was extracted with dichloromethane; evaporation yielded $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCMeCMe})(CO)_9$ (195 mg, 90%).

Anal. Calcd for $C_{15}H_{10}O_{10}Ru_3$: C, 27.57; H, 1.54. Found: C, 27.54; H, 1.78.

$HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCPhCPh})(CO)_9$. Method 1. A solution of $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$ (100 mg, 0.166 mmol) and diphenylacetylene (177 mg, 0.99 mmol) in cyclohexane (30 mL) was stirred at 25 °C for 2 h. Chromatography on silica, eluting with hexanes, yielded $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCPhCPh})(CO)_9$ (85 mg, 66%) as the second, yellow band.

Method 2. A solution of $HRu_3(\mu\text{-COMe})(CO)_{10}$ (148 mg, 0.236 mmol) and diphenylacetylene (123 mg, 0.691 mmol) in cyclohexane (50 mL) was heated under nitrogen at 55 °C for 56 h. After the solution was cooled, the solvent was removed on a rotary evaporator. Chromatography on silica, eluting with hexanes, yielded $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCPhCPh})(CO)_9$ (129 mg, 70%) as the fifth, yellow band. The compound was recrystallized from methanol.

Anal. Calcd for $C_{25}H_{14}O_{10}Ru_3$: C, 38.62; H, 1.81. Found: C, 38.34; H, 2.04.

$HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCHCPh})(CO)_9$ and $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCPhCH})(CO)_9$. Method 1. A solution of $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$ (100 mg, 0.166 mmol) and phenylacetylene (100 μL, 1 mmol) in cyclohexane (30 mL) was stirred under nitrogen for 2 h; then the solvent was removed on a rotary evaporator. Thin-layer chromatography on silica, eluting with cyclohexane, yielded the products as the third, yellow band; extraction with dichloromethane and evaporation left 48 mg of a yellow oil. Further chromatographic separations of the oil gave $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCHCPh})(CO)_9$ (17 mg, 14%) as the top portion of the band and $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCPhCH})(CO)_9$ (23 mg, 20%) as the lower part of the band. The ratio of these two products in the crude mixture, as determined by ^1H NMR spectroscopy, was 2:1, respectively.

Method 2. A solution of $HRu_3(\mu\text{-COMe})(CO)_{10}$ (71 mg, 0.11 mmol) and phenylacetylene (75 μL, 0.67 mmol) in cyclohexane (25 mL) was heated at 60 °C under nitrogen for 5 h. Evaporation of solvent and chromatography yielded 45 mg of the yellow oil. Further chromatography yielded the two products in the same ratio as found for method 1.

$HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCHCCMe}_3)(CO)_9$. Method 1. A solution of $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$ (45 mg, 0.075 mmol), 3,3-dimethyl-1-butyne (40 μL, 33 mmol), and deuteriochloroform (0.6 mL) was placed in an NMR tube. After 0.5 h no starting cluster was detected by NMR. New peaks in the hydride region were noted at −14.80 (s, attributed to $HRu_3(\mu\text{-COMe})(CO)_{10}$), −15.27 (s), −16.84 (s), −17.75 (s), and−19.49 (d, attributed to $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCHCCMe}_3)(CO)_9$) ppm. Also detected was 3,3-dimethyl-1-butene (δ 5.8 (m), 4.8 (m)). After 3 h the signals at −15.27 and −16.84 ppm had disappeared. Thin-layer chromatography of the product mixture on silica, eluting with cyclohexane, yielded $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCHCCMe}_3)(CO)_9$ (20 mg, 23%) as the fifth, yellow band.

Method 2. A solution of $HRu_3(\mu\text{-COMe})(CO)_{10}$ (100 mg, 0.16 mmol) and 3,3-dimethyl-1-butyne (120 μL, 0.98 mmol) in cyclohexane (30 mL) in a 100-mL Schlenk flask was degassed by using two freeze–thaw cycles. Then the flask was heated in an oil bath at 55–70 °C. After 15 h the solvent was removed on a rotary evaporator, and the product mixture was separated by thin-layer chromatography on silica, eluting with cyclohexane. Extraction of the fourth, yellow band with dichloromethane yielded $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCHCMe}_3)(CO)_9$ (40 mg, 43%). In addition, $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCC(CMe}_3)CH)(CO)_9$ (2 mg, 2%) was obtained by extraction of the first yellow band.

$HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCHCOEt})(CO)_9$. A solution of $HRu_3(\mu\text{-COMe})(CO)_{10}$ (204 mg, 0.325 mmol) and ethoxyacetylene (125 μL, 0.32 mmol, purified through alumina) in cyclohexane (30 mL) in a Schlenk flask was degassed by three freeze–pump–thaw cycles. The flask, under a static vacuum, was heated at 60 °C for 48 h. After evaporation of solvent, thin-layer chromatography on silica, eluting with cyclohexane, yielded the product (58 mg, 27%) as the first, yellow band.

$HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCHCCO}_2Me)(CO)_9$ and $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCC(CO}_2Me)CH)(CO)_9$. A solution of $HRu_3(\mu\text{-COMe})(CO)_{10}$ (121 mg, 0.19 mmol) and methyl propiolate (85 μL, 0.96 mmol) in cyclohexane (20 mL) was placed in a 50-mL Schlenk flask and was degassed by three freeze–pump–thaw cycles. The flask was then heated at 70 °C for 5 h. Thin-layer chromatography (silica, 10% dichloromethane in hexanes) gave one yellow band trailing a trace of unreacted $HRu_3(\mu\text{-COMe})(CO)_{10}$. Extraction of the yellow band with dichloromethane yielded 84 mg (65%) of a 2:1 mixture of $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCHCCO}_2Me)(CO)_9$ and $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCC(CO}_2Me)CH)(CO)_9$ (determined by ^1H NMR spectroscopy). Careful chromatography of this mixture allowed separation into two bands, the upper band (the former cluster) yielding orange crystals, 51 mg, and the lower (the latter cluster), bright yellow crystals, 23 mg.

$HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCHC-}n\text{-Bu})(CO)_9$ and $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCC(}n\text{-Bu)CH})(CO)_9$. A solution of $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$ (100 mg, 0.166 mmol) and 1-hexyne (60 μL, 0.52 mmol) in cyclohexane (25 mL) was stirred at 25 °C for 1.5 h. Thin-layer chromatography of the product mixture (silica, eluting with cyclohexane) yielded $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCC(}n\text{-Bu)CH})(CO)_9$ (16 mg, 14%) as the second, yellow band, immediately followed by

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$HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHC\text{-}n\text{-}Bu)(CO)_9$ (49 mg, 42%). Also isolated was $HRu_3(\mu\text{-}COMe)(CO)_{10}$ (7 mg, 7%, first band).

$HRu_3(\mu_3\text{-}\eta^3\text{-}MeOC(PhC_2CO_2Me))(CO)_9$. A solution of $HRu_3(\mu\text{-}COMe)(CO)_{10}$ (71 mg, 0.11 mmol) and methyl phenylpropiolate (100 μL) in cyclohexane (50 mL) was heated under nitrogen at 65 °C for 6 h. Thin-layer chromatographic separation (silica, 1:5 dichloromethane–cyclohexane) of the products yielded $HRu_3(\mu\text{-}COMe)(CO)_{10}$ (33 mg, 46%; first, yellow band) and two isomers $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOC(PhC_2CO_2Me))(CO)_9$, designated isomer A (10.5 mg, 12%; second, yellow band) and isomer B (16.5 mg, 19%; third, yellow band). NMR analysis of the crude reaction mixture indicated an A/B ratio of 1:2.

$HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCC(Me)CC_7H_{15})(CO)_9$ and $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCC(C_7H_{15})CMe)(CO)_9$. A solution of $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ (51 mg, 0.086 mmol) and 2-decyne (36 μL, 0.20 mmol) in deuteriochloroform containing chloroform as an internal standard was placed in an NMR tube, and the reaction was monitored by ^1H NMR spectroscopy. After 1 h, the NMR spectrum showed the following products (yields): *cis*-2-decene (59%), $HRu_3(\mu\text{-}COMe)(CO)_{10}$ (10%), $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCC(Me)CC_7H_{15})(CO)_9$ (58%), and $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCC(C_7H_{15})CMe)(CO)_9$ (19%). The solvent was removed by rotary evaporation, and the residue was separated by thin-layer chromatography on silica eluting with hexanes. The one large, yellow band was extracted with dichloromethane and evaporation yielded 59 mg of a yellow oil, which was shown by ^1H NMR spectroscopy to contain all three cluster products in the ratios show above.

$HRu_3(\mu_3\text{-}\eta^3\text{-}PhCCPhCPh)(CO)_9$. To a solution of $H_3Ru_3(\mu_3\text{-}CPh)(CO)_9$ (62 mg, 0.1 mmol) in cyclohexane (25 mL) was added diphenylacetylene (165 mg, 0.6 mmol). The mixture was stirred at 25 °C for 4 days. Then the solution was evaporated to dryness, and the products were separated by thin-layer chromatography (silica gel, dichloromethane–cyclohexane (1:5, v/v)). Extraction of the second yellow band and evaporation yielded $HRu_3(\mu_3\text{-}\eta^3\text{-}PhCCPhCPh)(CO)_9$ (33 mg, 41%). The product was recrystallized from methanol.

$HRu_3(\mu_3\text{-}\eta^3\text{-}MeCCMeCMe)(CO)_9$. A solution of $H_3Ru_3(\mu_3\text{-}CMe)(CO)_9$ (80 mg, 0.14 mmol) and 2-butyne (60 μL, 0.9 mmol) in cyclohexane (25 mL) was stirred at 25 °C for 24 h. The solvent was evaporated, and thin-layer chromatography of the product mixture on silica, eluting with cyclohexane, yielded $HRu_3(\mu_3\text{-}\eta^3\text{-}MeCCMeCMe)(CO)_9$ (35 mg, 40%) as the third, yellow band.

$HRu_3(\mu_3\text{-}\eta^3\text{-}C(CH_2CH_2CMe_3)CPhCPh)(CO)_9$. A solution of $H_3Ru_3(\mu_3\text{-}CCH_2CH_2CMe_3)(CO)_9$ (39 mg, 0.059 mmol) and diphenylacetylene (40 mg, 0.23 mmol) in deuteriochloroform (0.6 mL) was monitored by ^1H NMR for 4 days. Then the solvent was evaporated, and the residue was separated by thin-layer chromatography on silica, eluting with cyclohexane. The product (27 mg, 55%) was isolated by extraction of the first band.

$HOs_3(\mu_3\text{-}\eta^3\text{-}MeOCCPhCPh)(CO)_9$. Method 1. A solution of $HOs_3(\mu\text{-}COMe)(CO)_{10}$ (35 mg, 0.040 mmol) and diphenylacetylene (27 mg, 0.15 mmol) in toluene (0.6 mL) was placed in an NMR tube, which was then heated under nitrogen at 95 °C for 106 h. At that point the NMR spectrum included a hydride resonance at −18.4 ppm, in addition to that due to starting material (−16.5 ppm). Chromatography (silica gel, cyclohexane) yielded starting material (20 mg) and $HOs_3(\mu_3\text{-}\eta^3\text{-}MeOCCPhCPh)(CO)_9$ (25 mg, 80% pure).

Method 2. A solution of $HOs_3(\mu\text{-}COMe)(CO)_{10}$ (40 mg, 0.043 mmol) and diphenylacetylene (39 mg, 0.22 mmol) in toluene (30 mL) was refluxed under nitrogen for 15 h. Chromatography yielded $HOs_3(\mu_3\text{-}\eta^3\text{-}MeOCCPhCPh)(CO)_9$ (17 mg, 35%) as the third yellow band.

Mass spectrum (EI): m/z 1050 ($^{192}Os_3$). IR (C_6H_{12}): 2096 m, 2070 vs, 2045 vs, 2020 s, 2001 vs, 1984 s, 1968 m cm^{-1}. ^1H NMR ($CDCl_3$): 6.8 (m, 10 H), 3.67 (s, 3 H), −18.45 (s, 1 H) ppm.

Reaction of $HFe_3(\mu\text{-}COMe)(CO)_{10}$ with 2-Butyne. A solution of $HFe_3(\mu\text{-}COMe)(CO)_{10}$ (53 mg, 0.11 mmol) and 2-butyne (100 μL, 1.5 mmol) in cyclohexane was stirred for 5 days. Chromatography (silica gel, cyclohexane) yielded only $Fe_3(CO)_{12}$ (17 mg, 35%) and four other products in low yield. No hydride resonances were observed in the ^1H NMR spectrum.

Hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCH)(CO)_9$. A solution of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCH)(CO)_9$ (209 mg, 0.334 mmol) in decane (50 mL) was placed in a 250-mL Parr bottle with a stir bar. The bottle was flushed with hydrogen gas, pressurized to 3.8 atm, and then heated in an oil bath at 95–105 °C for 18 h. The resulting solution was evaporated to dryness with vacuum. The residue was separated by thin-layer chromatography on silica, eluting with cyclohexane, into four yellow bands, which were extracted with dichloromethane. Band 1 was $H_3Ru(\mu_3\text{-}CEt)(CO)_9$ (78 mg, 39%). Band 4 was unreacted $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCH)(CO)_9$ (16 mg, 8%). The other two bands (band 2, 5 mg, and band 3, 24 mg) were not characterized and were contaminated with $H_4Ru_4(CO)_{12}$. Also isolated as a sparingly soluble yellow powder was $H_4Ru_4(CO)_{12}$ (54 mg), identified by its infrared and ^1H NMR spectra.

$H_3Ru_3(\mu_3\text{-}CEt)(CO)_9$. Anal. Calcd for $C_{12}H_8O_9Ru_3$: C, 24.05; H, 1.35. Found: C, 24.11; H, 1.27.

Hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCCMe_3)(CO)_9$. Hydrogen gas was bubbled through a refluxing solution of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCCMe_3)(CO)_9$ (50 mg, 0.073 mmol) in cyclohexane for 10 h. The solution was cooled, filtered, and evaporated to dryness. Thin-layer chromatography of the residue on silica, eluting with cyclohexane, yielded $H_3Ru_3(\mu_3\text{-}CCH_2CH_2CMe_3)(CO)_9$ (13 mg, 28%) as the first, yellow band.

Hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCMeCMe)(CO)_9$. Method 1. A solution of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCMeCMe)(CO)_9$ (90 mg, 0.14 mmol) in cyclohexane (50 mL) was placed in a 250-mL Parr pressure bottle, which was flushed and filled to 2 atm with hydrogen. The bottle was heated at 95 °C for 36 h. After being cooled, the solution was filtered and evaporated to dryness. Thin-layer chromatography (silica, cyclohexane) yielded $H_3Ru_3(\mu_3\text{-}CCHMeCH_2Me)(CO)_9$ (38 mg, 43%) as the first, yellow band and $H_4Ru_4(CO)_{12}$ as the second, yellow band.

Method 2. A solution of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCMeCMe)(CO)_9$ (38 mg, 0.057 mmol) in acetonitrile (25 mL) was placed in a 250-mL, round-bottomed flask equipped with hydrogen gas inlet and a pressure equalizing dropping funnel containing trimethylamine *N*-oxide dihydrate (6.6 mg, 0.059 mmol) in acetonitrile (50 mL). After hydrogen was bubbled through the solution for 20 min, the solution in the dropping funnel was added dropwise to the rapidly stirred solution of the cluster. When addition was complete, the solvent was removed on the rotary evaporator and the residue was separated by thin-layer chromatography (silica gel, cyclohexane). Products isolated were, in order of elution, $H_3Ru_3(\mu_3\text{-}CCHMeCH_2Me)(CO)_9$ (8 mg, 22%), $H_4Ru_4(CO)_{12}$ (4 mg, 11%), and unreacted starting material (7 mg, 19%).

Hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCPhCPh)(CO)_9$. A solution of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCPhCPh)(CO)_9$ (71 mg, 0.091 mmol) in cyclohexane (50 mL) was placed in a 250-mL Parr pressure bottle, which was then pressurized to 2.4 atm of hydrogen and heated in an oil bath at 90 °C for 16 h. Thin-layer chromatography of the product mixture on silica, eluting with cyclohexane, yielded $H_3Ru_3(\mu_3\text{-}CCHPhCH_2Ph)(CO)_9$ (30 mg, 43%) as the second, yellow band.

Hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCOEt)(CO)_9$. A solution of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCOEt)(CO)_9$ (95 mg, 0.14 mmol) in toluene (6 mL) was placed in a glass tube, which was sealed under 1 atm of hydrogen. (Caution! Hydrogen is highly flammable and explosive and great care must be taken in sealing this tube.) The tube was heated at 100 °C for 24 h. Upon opening the tube, gas chromatographic analysis of the solution could detect neither methanol nor ethanol. Thin-layer chromatography (silica, eluting with cyclohexane) of the solid residue after evaporation of solvent yielded $H_4Ru_4(CO)_{12}$ (5 mg, 5%, second, yellow band), $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCOEt)(CO)_9$ (46 mg, 48%, third band), and $H_3Ru_3(\mu_3\text{-}CCH_2CH_2OEt)(CO)_9$ (6 mg, 6%, fourth band).

Hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHC\text{-}n\text{-}Bu)(CO)_9$. Hydrogen gas was bubbled through a solution of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHC\text{-}n\text{-}Bu)(CO)_9$ (58 mg, 0.0852 mmol) in cyclohexane (45 mL) in a three-necked, 100-mL, round-bottomed flask equipped with gas inlet tube, reflux condenser topped with a gas outlet to an oil bubbler, and a stir bar. The solution was refluxed for 30 h. Thin-layer chromatography (silica, eluting with cyclohexane) of the residue after evaporation of solvent yielded $H_3Ru_3(\mu_3\text{-}C(CH_2)_5CH_3)(CO)_9$ (7 mg, 13%).

Hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCC(n\text{-}Bu)CH)(CO)_9$. A solution of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCC(n\text{-}Bu)CH)(CO)_9$ (38 mg, 0.055 mmol) in cyclohexane (45 mL) was placed in a 250-mL Parr pressure bottle, which was flushed with hydrogen, pressurized to 2.4 atm, and then heated in an oil bath at 105 °C for 3 days.

Then the solution was cooled, filtered, and evaporated to dryness. Thin-layer chromatography (silica, eluting with cyclohexane) of the residue yielded $H_3Ru_3(\mu_3\text{-}CCH(n\text{-}Bu)CH_3)(CO)_9$ (4 mg, 10%, band 1) and $H_4Ru_4(CO)_{12}$ (10 mg, 24%, band 2).

Hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCPh)(CO)_9$. A solution of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCPh)(CO)_9$ (43 mg, 0.061 mmol) in cyclohexane (50 mL) in a three-necked, 100-mL, round-bottom flask, equipped with gas inlet, stir bar, and reflux condenser topped with a gass outlet to a bubbler, was refluxed with hydrogen gas bubbling through for 14 h. Removal of the solvent by rotary evaporation and thin-layer chromatography on silica, eluting with cyclohexane, yielded $H_4Ru_4(CO)_{12}$ (1.6 mg, 5%, first, yellow band), $H_3Ru_3(\mu_3\text{-}CCH_2CH_2Ph)(CO)_9$ (10 mg, 25%, second, yellow band), and unreacted starting material (5.4 mg, 13%, third, yellow band).

Hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCCO_2Me)(CO)_9$. A solution of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCCO_2Me)(CO)_9$ (51 mg) in decane (20 mL) was placed in a 250-mL Parr pressure bottle, which was then flushed with hydrogen, pressurized to 3.4 atm and heated to 90 °C. After 40 h the solvent was stripped off by rotary evaporation, and the residue was separated by thin layer chromatography (silica, 1:9 dichloromethane–hexanes) to yield $H_4Ru_4(CO)_{12}$ (first band) and $H_3Ru(\mu_3\text{-}CCH_2CH_2CO_2Me)(CO)_9$ (second band, 5.4 mg, 11%).

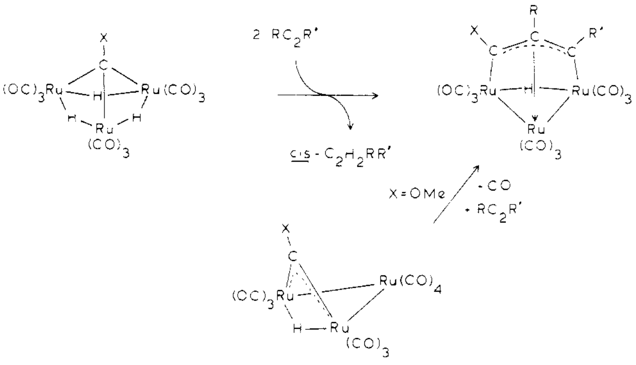
Hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}Et_2NCCHCMe)(CO)_9$. A solution of $HRu_3(\mu_3\text{-}\eta^3\text{-}Et_2NCCHCMe)(CO)_9$ (47 mg, 0.069 mmol) in cyclohexane (20 mL) in a 23 × 2 cm glass tube was degassed by using three freeze–pump–thaw cycles. Then the tube was filled with hydrogen gas (1 atm). After the system was closed off, the tube was cooled with liquid nitrogen and sealed off. Then the tube was placed in an oil bath at 100 °C. After 1 day the product mixture was characterized by IR and ^1H NMR spectroscopy. Only $H_4Ru_4(CO)_{12}$ was detected.

Hydrogenation of a Mixture of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCR)(CO)_9$ (R = CMe_3 and *n*-Bu). A solution containing $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCCMe_3)(CO)_9$ (47 mg, 0.068 mmol) and $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHC(n\text{-}Bu))(CO)_9$ (47 mg, 0.068 mmol) in cyclohexane (25 mL) was placed under hydrogen (2 atm) in a 250-mL Parr pressure bottle, and the bottle was then placed in an oil bath at 90 °C. After 24 h the solution was cooled, filtered, and evaporated to dryness. ^1H NMR analysis of the hydride region revealed $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHC\text{-}n\text{-}Bu)(CO)_9$, but no $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCCMe_3)(CO)_9$.

Solvent Effects on the Hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCCMe_3)(CO)_9$. Ethanol (25 mL) and cyclohexane (25 mL) solutions, each containing $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCCMe_3)(CO)_9$, were sealed under hydrogen (1 atm) in identical 25 × 2 cm glass tubes. Both were placed in an oil bath at 75 °C. After 24 h the tubes were opened, and the product mixture, after solvent evaporation, was analyzed by ^1H NMR spectroscopy. The hydride region of the sample from the cyclohexane solution contained peaks due to $H_3Ru_3(\mu_3\text{-}CCH_2CH_2CMe_3)(CO)_9$, $H_4Ru_4(CO)_{12}$, and unreacted starting material in a relative molar ratio of 10:1.2:1; the hydride region of the sample from ethanol solution consisted of peaks due to $H_3Ru_3(\mu_3\text{-}CCH_2CH_2CMe_3)(CO)_9$ and $H_4Ru_4(CO)_{12}$ in a ratio of 4.3:1. Thin-layer chromatography of the two product mixtures yielded the following results: $H_3Ru_3(\mu_3\text{-}CCH_2CH_2CMe_3)(CO)_9$ (ethanol, 12 mg; cyclohexane, 28 mg), $H_4Ru_4(CO)_{12}$ (ethanol, 4 mg; cyclohexane, 6 mg), $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCCMe_3)(CO)_9$ (ethanol, 2 mg; cyclohexane, 4 mg).

Hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}EtSCCMeCMe)(CO)_9$. A solution of $HRu_3(\mu_3\text{-}\eta^3\text{-}EtSCCMeCMe)(CO)_9$[26] (15 mg, 0.022 mmol) in cyclohexane (20 mL) was heated at 90 °C under hydrogen (2 atm) in a Parr pressure bottle for 22 h. After being cooled, the solution was evaporated to dryness. The ^1H NMR spectrum of the residue revealed hydride signals at −17.62 ppm ($H_3Ru_3(\mu_3\text{-}CCHMeCH_2Me)(CO)_9$), −17.75 ppm ($H_4Ru_4(CO)_{12}$), and −18.93 ppm. Thin-layer chromatography (silica, cyclohexane) yielded $H_3Ru_3(\mu_3\text{-}CCHMeCH_2Me)(CO)_9$ (3 mg, 18%), $H_4Ru_4(CO)_{12}$ (3 mg, 15%), and a third band (4 mg; IR (C_6H_{12}) 2119 m, 2085 s, 2062 s, 2049 s, 2029 m, 2019 s, 2011 s, 2001 m cm^{-1}; ^1H NMR ($CDCl_3$) −18.9 ppm, alkyl region masked by impurities). Products were identified by infrared and ^1H NMR spectroscopy. The quantity of material was too small to allow the detection of the organic product.

Scheme I. Methylidyne–Alkyne Coupling



Hydrogenation of $HOs_3(\mu_3\text{-}\eta^3\text{-}HOCCHCH)(CO)_9$. A solution of $HOs_3(\mu_3\text{-}\eta^3\text{-}HOCCHCH)(CO)_9$ (65 mg) in cyclohexane (80 mL) was placed in a 250-mL Parr pressure bottle, which was then flushed and filled to 2 atm with hydrogen. After 24 h at 80 °C, the infrared spectrum indicated no reaction. The solution was evaporated to dryness, and the residue was dissolved in octane (80 mL). After 6 days at 123 °C the only clusters which could be identified by infrared spectroscopy were the starting material and $H_4Os_4(CO)_{12}$. Thin-layer chromatography gave four products in low yield, all contaminated with $H_4Os_4(CO)_{12}$.

Results and Discussion

Methylidyne–Alkyne Coupling. Reactions of symmetrical alkynes C_2R_2 with $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$ produce the corresponding *cis*-alkenes (products identified by ^1H NMR spectroscopy) and the appropriate 1,3-dimetalloallyl clusters $HRu_3(\mu_3\text{-}\eta^3\text{-}XCCRCR)(CO)_9$ (Scheme I) (X = OMe, R = H (15%), Me (90%), Ph (66%); X = Me, R = Me (40%); X = Ph, R = Ph (41%)). Two regioisomers $HRu_3(\mu_3\text{-}\eta^3\text{-}XCCRCR')(CO)_9$ are formed from asymmetric alkynes (HC_2Ph (34%), HC_2CMe_3 (23%), HC_2Bu (56%), $MeC_2C_7H_{15}$ (77%)). In each case a large number of other metal-containing products in low yields and cyclotrimerized alkyne products are also formed. The coupling of methylidyne and alkyne units also occurs in reactions of $HRu_3(\mu\text{-}COMe)(CO)_{10}$ with alkynes (C_2H_2 (55%), C_2Ph_2 (70%), HC_2CMe_3 (45%), HC_2OEt (27%), HC_2CO_2Me (65%), PhC_2CO_2Me (31%)). Since $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ is prepared by hydrogenation of $HRu_3(\mu\text{-}COMe)(CO)_{10}$, the latter is usually the preferred starting material for alkyne coupling, but the former allows milder reaction temperatures. The analogous reaction of $HOs_3(\mu\text{-}COMe)(CO)_{10}$ with C_2Ph_2 yields $HOs_3(\mu_3\text{-}\eta^3\text{-}MeOCCPhCPh)(CO)_9$ (35%). All these cluster products are yellow or orange, air-stable, crystalline solids which are soluble in non-polar organic solvents.

Characterization of the new clusters was achieved by infrared and ^1H NMR spectroscopy, by mass spectrometry, and for selected examples by elemental analysis. The EI mass spectra (Table I) display molecular ions and ions resulting from the stepwise loss of CO ligands. The infrared (Table I) and ^1H NMR (Table II) spectra are very similar to those of analogous $HRu_3(\mu_3\text{-}\eta^3\text{-}R^1CCR^2CR^3)(CO)_9$ clusters prepared from reactions of mono- and dienes[24,27] or alkynes[23] with $Ru_3(CO)_{12}$, reactions which do not involve C–C bond formation. The structure of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeCCHCEt)(CO)_9$, formed from $Ru_3(CO)_{12}$ and 1,3-hexadiene, has been established by X-ray crystallography.[28]

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[26] This compound, prepared from $H_3Ru_3(\mu_3\text{-}CSEt)(CO)_9$ and 2-butyne, was supplied by D. M. Dalton. The preparation and characterization will be included in a later paper.

[27] (a) M. Castiglioni, L. Milone, D. Osella, G. A. Vaglio, and M. Valle, *Inorg. Chem.*, **15**, 394 (1976); (b) M. I. Bruce, M. A. Cairns, and M. Green, *J. Chem. Soc., Dalton Trans.*, 1293 (1972).

Table I. Infrared Spectra between 2150 and 1600 cm^{-1} for $HRu_3(\mu_3\text{-}\eta^3\text{-}XCCR^1CR^2)(CO)_9$ in Cyclohexane Solution and Molecular Ions from EI Mass Spectra

X	R^1	R^2	m/z ($^{102}Ru_3$)	ν, cm^{-1}
OMe	H	H	628	2099 w, 2074 s, 2043 vs, 2031 m, 2022 m, 2014 s, 2008 w, 1994 w, 1970 w
OMe	Me	Me	656	2092 w, 2064 s, 2040 vs, 2024 m, 2010 sh, 2005 s, 1990 w, 1972 w
OMe	Ph	Ph	780	2095 m, 2071 vs, 2045 sh, 2042 vs, 2028 m, 2013 s, 1992 w, 1965 w
OMe	H	Ph	704	2098, 2074 s, 2044 vs, 2033 m, 2023 m, 2015 m, 2004 m, 1994 w, 1971 w
OMe	Ph	H	704	2096 m, 2070 s, 2046 vs, 2028 m, 2017 m, 2009 m, 1993 w, 1980 w
OMe	H	CMe_3	684	2096 m, 2067 s, 2038 vs, 2029 m, 2017 m, 2005 m, 2002 sh, 1988 w, 1964 w
OMe	CMe_3	H	684	2093 m, 2065 s, 2040 vs, 2023 s, 2012 s, 2004 s, 1990 w, 1974 w
OMe	H	*n*-Bu	684	2099 m, 2070 s, 2041 vs, 2030 m, 2010 m, 2004 sh, 1992 w, 1972 w
OMe	*n*-Bu	H	684	2096 m, 2067 s, 2054 sh, 2043 vs, 2027 s, 2015 m, 2007 s, 1991 w, 1971 w
OMe	H	CO_2Me	686	2102 m, 2080 vs, 2050 vs, 2036 s, 2024 vs, 2001 m, 1966 w, 1711 w
OMe	CO_2Me	H	686	2098 m, 2071 vs, 2054 vs, 2028 s, 2020 m, 2011 s, 2000 w, 1980 w, 1742 w
OMe	Ph	CO_2Me	762	2100 m, 2073 vs, 2056 s, 2029 m, 2024 sh, 2016 m, 2010 w, 2002 w, 1970 w, 1729 w
OMe	CO_2Me	Ph	762	2097 m, 2070 s, 2050 vs, 2030 m, 2019 m, 2010 m, 2008 sh, 2001 w, 1974 w, 1746 w
OMe	H	OEt	672	2096 m, 2071 s, 2066 sh, 2044 w, 2036 vs, 2029 s, 2014 s, 2004 m, 1986 w, 1966 w
Ph	Ph	Ph	826	2096 vs, 2076 vs, 2043 s, 2036 m, 2027 m, 2022 w, 2009 m, 1993 m
Me	Me	Me	640	2093 w, 2066 s, 2039 vs, 2023 m, 2012 sh, 2007 s, 1992 w, 1963 w
$CH_2CH_2CMe_3$	Ph	Ph	834	2095 s, 2071 vs, 2045 sh, 2039 vs, 2028 s, 2016 sh, 2011 vs, 1990 vs, 1982 w

Confirmation of the μ_3-η^3-allyl structure for these products was obtained from the ^{13}C NMR spectrum (Table III) of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCH)(CO)_9$. In deuteriochloroform (22 °C, 0.02 M $Cr(acac)_3$) the spectrum consists of eight resonances: 59.0 (q, 1 C^a, $^1J(C\text{-}H) = 147$ Hz), 94.5 (dd, $1C^b$, $^1J(C\text{-}H^A) = 158.3$ Hz, $^3J(C\text{-}H^C) = 5.5$ Hz), 158.8 (d, 1 C^c, $^1J(C\text{-}H^B) = 148.0$ Hz), 189.7 (d, 2 C^d, $^2J(C\text{-}H^C) = 12.5$ Hz), 190.5 (d, 2 C^e, $^2J(C\text{-}H^C) = 4.4$ Hz), 196.9 (s, $3C^f$), 197.4 (d, $2C^g$, $^2J(C\text{-}H^C) = 4.4$ Hz), and 229.2 (d, $1C^h$, $^2J(C\text{-}H^C) = 13.2$ Hz) ppm. All coupling assignments were verified by selective decoupling of the proton resonances denoted in Table II. The resonances at 59.0, 94.5, 158.8, and 229.2 ppm are straightforwardly assigned to the methyl carbon, the methinyl carbon in the 2-position, the methinyl carbon in the 3-position, and the carbon in the 1-position of the MeOCCHCH unit, respectively, by virtue of the selective decoupling experiments. The carbonyl resonances are assigned as shown in Table III. The resonance (189.7 ppm) which displays the largest coupling constant to the hydride ligand is assigned to the two carbonyls trans to that ligand. The resonance at 197.4 ppm is assigned to the two axial carbonyls on the edge of the cluster bridged by the hydride; axial carbonyl ligands usually appear downfield from radial carbonyls. Thus, the other carbonyl resonance coupled to the hydride is assigned to the two radial carbonyls cis to the hydride. Finally the singlet of weight three is assigned to the three carbonyls on the Ru atom which is not bound to the hydride; these should be nonequivalent but may be coincidently isochronous or fluxionally averaged. These assignments may be compared with those for the spectrum of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeCCHCEt)(CO)_9$, for which the 2-carbon of the allyl fragment appears at 119.8 ppm (the other allylic carbon resonances were not observed) and the carbonyl ligands appear as five resonances: 192.1 (d, $J(CH) = 17.0$ Hz), 196.6 (d, $J(CH) = 8.5$ Hz), 198.5(s), 199.3 (d, $J(CH) = 4.0$ Hz), and 199.7 (d, $J(CH) = 4.0$ Hz) ppm.[28] Although both spectra should consist of nine carbonyl resonances, each of the spectra appears as if the allylic ligand were symmetrical.

The regiochemistry of each isomer produced from coupling of a terminal alkyne HC_2R with the methylidyne may be easily established from the ^1H NMR spectrum. The coupling constants between the hydride resonance and allylic hydrogens in the 2- and the 3-positions are 1–3 and 0 Hz, respectively. These values were previously established for $HRu_3(\mu_3\text{-}\eta^3\text{-}MeCCHCEt)(CO)_9$[24] and $HRu_3(\mu_3\text{-}\eta^3\text{-}MeCCMeCH)(CO)_9$.[24] Reactions of either $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ or $HRu_3(\mu\text{-}COMe)(CO)_{10}$ with HC_2R produce $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCR)(CO)_9$ (a) and $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCRCH)(CO)_9$ (b) with essentially the same a/b ratio from either methylidyne cluster but with notable variations depending upon the identity of R (R (a/b) = Ph (3:1), *n*-Bu (2 :1), CMe_3 (20:1), CO_2Me (2:1), OEt (1:0)). Both steric and electronic effects seem to influence the relative amounts of the two isomers. Coupling occurs preferentially to the least hindered alkyne carbon, and the a/b ratio increases as the size of R increases, but comparison of the a/b ratios for R = *n*-Bu and OEt, which are of similar size, indicates that electronic effects must also be important. The relative amounts of the two regioisomers appear to be kinetically determined since no $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHC\text{-}n\text{-}Bu)(CO)_9$ was formed from $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCC(n\text{-}Bu)CH)(CO)_9$ in refluxing cyclohexane (4.5 h).

Other unsymmetrical alkynes also produce mixtures of the two regioisomers, but the identities of the isomers are less well established. Products from 2-decyne and $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ are $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCMeCC_7H_{15})(CO)_9$ and $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCC(C_7H_{15})CMe)(CO)_9$ in a 3:1 ratio; identification of each is based upon the chemical shift of the methyl resonance (cf. $HRu_3(\mu_3\text{-}\eta^3\text{-}MeCCMeCMe)(CO)_9$, Table II). Two isomers of the formula $HRu_3(MeOCC_2Ph(CO_2Me))(CO)_9$ in a 2:1 ratio are formed from methyl phenylpropiolate and $HRu_3(\mu\text{-}COMe)(CO)_{10}$; on the basis of the comparison of the acyl stretching frequencies for the minor (1729 cm^{-1}) and major (1746 cm^{-1}) isomers with those of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCCO_2Me)(CO)_9$ (1711 cm^{-1}) and $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCC(CO_2Me)CH)(CO)_9$ (1742 cm^{-1}), the major isomer is proposed to be $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCC(CO_2Me)CPh)(CO)_9$.

The alkyne–methylidyne coupling reaction provides a method for the preparation of 1,3-dimetalloallyl cluster species not previously accessible, particularly those containing functional groups. Although considerable variations of the methylidyne substituent and alkyne substituents are possible, not all alkynes undergo coupling. Bis(trimethylsilyl)acetylene does not react with either $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ (25 °C, 3 weeks) or $HRu_3(\mu\text{-}COMe)(CO)_{10}$ (60 °C, 21 h). (Trimethylsilyl)acetylene does react with $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ but no coupling products can be isolated. Furthermore, a number of closely related methylidyne clusters do not yield observable quantities of coupled products—$H_3Ru_3(\mu_3\text{-}CCl)(CO)_9$ and diphenylacetylene, $HFe_3(\mu\text{-}COMe)(CO)_{10}$ and 2-butyne, $HRu_3(\mu\text{-}CNMe(CH_2Ph))(CO)_{10}$ and either 2-butyne or diphenyl-

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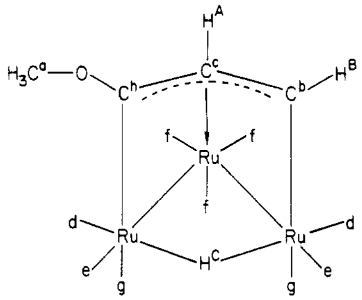
[28] M. Evans, M. Hursthouse, E. W. Randall, E. Rosenberg, L. Milone, and M. Valle, *J. Chem. Soc., Chem. Commun.*, 545 (1972).

Table II. ^{1}H NMR Spectra for $HRu_3(\mu_3\text{-}\eta^3\text{-}XCCR^1CR^2)(CO)_9$ in Deuteriochloroform

X	R^1	R^2	δ
OMe	H	H	8.43 (d, 1 H_A, R^2), 6.73 (dd, 1 H_B, R^1), 3.82 (s, 3 H, X), −19.97 (d, 1 H_c, RuH), J_{AB} = 8 Hz, J_{AC} = 2.4 Hz
OMe	Me	Me	3.99 (s, 3 H, X), 2.89 (s, 3 H, R^2), 2.08 (s, 3 H, R^1), −19.46 (s, 1 H, RuH)
OMe	Ph	Ph	6.8 (m, 10 H, R^1, R^2), 3.61 (s, 3 H, X), −19.58 (s, 1 H, RuH)
OMe	H	Ph	7.4 (m, 5 H, R^2), 6.87 (d, 1 H_A, R^1), 3.82 (s, 3 H, X), −19.77 (d, 1 H_B, RuH), J_{AB} = 2.4 Hz
OMe	Ph	H	8.41 (s, 1 H, R^2), 7.2 (m, 5 H, R^1), 3.82 (s, 3 H, X), −19.60 (s, 1 H, RuH)
OMe	H	CMe_3	6.90 (d, 1 H_A, R^1), 3.80 (s, 3 H, X), 1.45 (s, 9 H, R^2), −19.41 (d, 1 H_B, RuH), J_{AB} = 3.0 Hz
OMe	CMe_3	H	8.80 (s, 1 H, R^2), 3.95 (s, 3 H, X), 1.27 (s, 9 H, R^1), −19.62 (s, 1 H, RuH)
OMe	H	*n*-Bu	6.46 (d, 1 H_A, R^1), 3.79 (s, 3 H, X), 2.8 (m, 2 H), 1.4 (m, 4 H), 1.00 (t, 3 H, J = 6 Hz), −19.78 (d, 1 H_B, RuH), J_{AB} = 2.6 Hz
OMe	*n*-Bu	H	8.45 (s, 1 H, R^2), 3.94 (s, 3 H, X), 2.6 (m, 1 H), 2.0 (m, 1 H), 1.4 (m), 0.9 (m), −19.62 (s, 1 H, RuH)
OMe	H	CO_2Me	7.00 (d, 1 H_A, R^1), 3.76 (s, 6 H, R^2, X), −20.18 (d, 1 H_B, RuH), J_{AB} = 2.1 Hz
OMe	CO_2Me	H	8.48 (s, 1 H, R^2), 3.94 (s, 3 H), 3.73 (s, 3 H), −19.80 (s, 1 H, RuH)
OMe	Ph	CO_2Me	7.2 (m, 5 H, R^1), 3.75 (s, 3 H), 3.67 (s, 3 H), −19.53 (s, 1 H, RuH)
OMe	CO_2Me	Ph	7.2 (m, 5 H, R^2), 3.95 (s, 3 H), 3.67 (s, 3 H), −19.53 (s, 1 H, RuH)
OMe	H	OEt	6.51 (d, 1 H_A, R^1), 3.74 (s, 3 H, X), 3.80 (m, 2 H_B, R^2), 1.37 (t, 3 H_C, R^2), −19.19 (d, 1 H_D, RuH), J_{AD} = 2.5 Hz, J_{BC} = 8 Hz
Ph	Ph	Ph	7.0 (m, 15 H), −20.1 (s, 1 H, RuH)
Me	Me	Me	2.89 (s, 6 H, X = R^2), 2.13 (s, 3 H, R^1), −20.13 (s, 1 H, RuH)
$CH_2CH_2CMe_3$	Ph	Ph	6.8 (m, 10 H, R^1, R^2), 2.7 (m, 2 H, X), 1.3 (m, 2 H, X), 1.0 (m, 9 H, X), −20.18 (s, 1 H, RuH)
OMe	Me	C_7H_{15}	3.98 (s, X), 2.07 (s, 3 H, R^1), 1.4 (m), −19.53 (s, 1 H, RuH)
OMe	C_7H_{15}	Me	3.98 (s, X), 2.84 (s, 3 H, R^2), 1.4 (m), −19.54 (s, 1 H, Ru H)

acetylene (80°, 24 h), or $HRu_3(\mu\text{-}CNMe_2)(CO)_9(py)$ and dimethyl acetylenedicarboxylate. The examples involving the (dialkylamino)methylidyne ligand are particularly puzzling since $HRu_3(\mu_3\text{-}\eta^3\text{-}Me_2NCCHCMe)(CO)_9$, prepared from $Ru_3(CO)_{12}$ and 1-(dimethylamino)-2-butyne, is stable in refluxing hexane.[23]

Table III. ^{13}C NMR Spectrum of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCH)(CO)_9$ in Deuteriochloroform (25 °C, 0.02 M $Cr(acac)_3$)



resonance, ppm	coupling const, Hz	assignt
59.0 (q, 1 C)	^1J (C-H) = 147	a
94.5 (dd, 1 C)	$^1J(C\text{-}H^A)$ = 158.3, $^3J(C\text{–}H^C)$ = 5.5	b
158.8 (d, 1 C)	$^1J(C\text{–}H^B)$ = 148.0	c
189.7 (d, 2 C)	$^2J(C\text{–}H^C)$ = 12.5	d
190.5 (d, 2 C)	$^2J(C\text{–}H^C)$ = 4.4	e
196.9 (s, 3 C)		f
197.4 (d, 2 C)	$^2J(C\text{–}H^C)$ = 4.4	g
229.2 (d, 1 C)	$^2J(C\text{–}H^C)$ = 13.2	h

Coupling of methylidyne and alkyne ligands on these triruthenium clusters is proposed to occur from a precursor of the formula $HRu_3(CX)(CO)_9(C_2R_2)$. This intermediate may be formed by alkyne substitution for CO on $HRu_3(\mu\text{-}COMe)(CO)_{10}$, presumably by a CO dissociative process (the half-life for the reaction is similar to that for substitution on $HRu_3(\mu\text{-}COMe)(CO)_{10}$ by $AsPh_3$).[22] However, a number of steps are required to generate this intermediate from $H_3Ru_3(\mu\text{-}CX)(CO)_9$ – CO dissociation, alkyne coordination, alkyne hydrogenation, CO recombination, and coordination of the second alkyne molecule; it is most likely the necessity for CO to dissociate and then recombine with the cluster which gives rise to the lower yields of coupled products from these methylidyne clusters. That CO dissociation is the first step in the reactions of alkynes with $H_3Ru_3(\mu\text{-}CX)(CO)_9$ is indicated by the order of relative reactivities of these clusters for alkyne hydrogenation, X = OMe ≫ Me > Ph, which parallels the order of rates for ligand substitution by a CO dissociative path.[29] The lack of reaction between either $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ or $HRu_3(\mu\text{-}COMe)(CO)_{10}$ and bis(trimethylsilyl)acetylene may be due to instability of the intermediate alkyne complex because of the unfavorable steric interactions. On the other hand, the lack of alkyne–methylidyne coupling products from $HRu_3(\mu\text{-}CN(Me)CH_2Ph)(CO)_{10}$ or $HRu_3(\mu\text{-}CNMe_2)(CO)_{10}$ may be due to the structure of the intermediate $HRu_3(CNR_2)(CO)_9(alkyne)$. The alkyne and methylidyne most likely must be in adjacent coordination sites for coupling to occur, but we have shown that complexes $HRu_3(\mu\text{-}CNR_2)(CO)_9L$, where L is a group 15 donor ligand, exist in *three* isomeric forms, only one of which has cis-oriented methylidyne and L.[22,30] These three forms are in equilibrium with the equilibrium constant depending upon the steric properties of R and the electronic properties of L.[30] The requisite cis isomer may be much less favorable for $HRu_3(\mu\text{-}CNR_2)(CO)_9(alkyne)$ than for other $HRu_3(CX)(CO)_9(alkyne)$ intermediates.

The orientation of the alkyne and methylidyne prior to coupling will determine the regiochemistry. Steric interactions between the methylidyne and alkyne substituents should favor coupling to the least hindered alkyne carbon. The nature of the electronic effect is not yet understood.

Coupling reactions of alkylidyne or alkylidene fragments with alkynes have been reported for other cluster systems. Reactions of $CoW(\mu\text{-}CR)(CO)_3Cp_2$ or other dimetallic carbyne complexes with alkynes form $\mu\text{-}\eta^3$-1,3-dimetalloallyl species; in these systems the predominant regioisomer arises from coupling of the *most* sterically hindered alkyne

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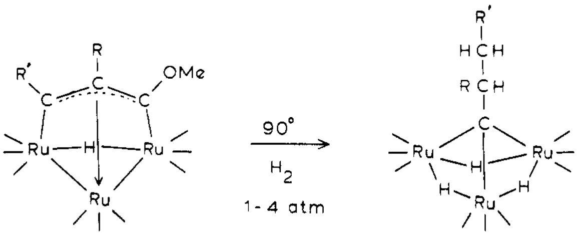
Table IV. Spectroscopic Data for $H_3Ru_3(\mu_3\text{-}CR)(CO)_9$

R	m/z ($^{102}Ru_3$)[a]	infrared spectra,[b] 2150–1700 cm^{-1}	^1H NMR spectra,[c] ppm
CH_2CH_3	602	2076 vs, 2070 sh, 2031 s, 2014 m	4.14 (q, 2 H, J = 7.3 Hz), 1.54 (t, 3 H), −17.56 (s, 3 H)
$CH_2CH_2CMe_3$	658	2105 w, 2077 vs, 2070 sh, 2057 w, 2032 s, 2015 m, 1992 w, 1979 w	4.1 (m, 2 H), 1.8 (m, 2 H), 1.06 (s, 9 H), −17.52 (s, 3 H)
$CHMeCH_2Me$	630	2092 w, 2077 vs, 2067 w, 2046 w, 2031 s, 2015 m	3.8 (m, 1 H), 2.2 (m, 2 H), 1.53 (d, 3 H, J = 6 Hz), 1.15 (m, 3 H), −17.61 (s, 3 H)
$CHPhCH_2Ph$	754	2106 w, 2079 vs, 2073 sh, 2033 s, 2018 m, 2007 w, 1992 w	7.1 (m, 10 H), 5.75 (dd, 1 H_A), 3.75 (dd, 1 H_B), 3.55 (dd, 1 H_C), −17.62 (s, 3 H), J_{AB} = 4 Hz, J_{AC} = 10 Hz, J_{BC} = 12 Hz
CH_2CH_2OEt	646	2092 w, 2077 vs, 2070 sh, 2042 w, 2031 s, 2014 m	4.4 (m, 2 H), 3.6 (m, 4 H), 1.4 (t, 3 H, J = 7 Hz), −17.59 (s, 3 H)
CH_2CH_2Ph	666	2106 w, 2091 w, 2077 vs, 2054 w, 2044 w, 2033 s, 2015 m, 2005 w	7.3 (m, 5 H), 4.30 (t, 2 H), 3.13 (t, 2 H), −17.51 (s, 3 H)
$(CH_2)_5Me$	658	2091 w, 2078 vs, 2046 w, 2034 s, 2017 m, 1992 w, 1979 w, 1971 w	4.10 (m, 2 H), 1.5 (m, 11 H), −17.52 (s, 3 H)
$CHMe(CH_2)_3Me$	658	2076 vs, 2068 sh, 2031 s, 2015 m	
$CH_2CH_2CO_2Me$	660[d]	2107 vw, 2078 vs, 2056 w, 2048 w, 2036 vs, 2017 s, 2005 w, 1993 w, 1743 w	4.25 (m, 2 H), 3.67 (s, 3 H), 2.79 (m, 2 H), −17.69 (s, 3 H)

[a] Electron-impact mass spectrum. [b] In cyclohexane. [c] In deuteriochloroform. [d] High-resolution mass spectrum: found, 653.7353 ($^{100}Ru_3$); calcd for $C_{14}H_{10}O_{11}Ru_3$, 653.7349.

Scheme II. Hydrogenation of 1-Methoxy-1,3-dimetalloallyl Moieties To Form μ_3-Alkylidynes



carbon with the alkylidyne.[31] Coupling of alkynes with CO, isoelectronic with $COMe^+$, also occurs on dimetallic systems.[32] Pyrolysis of $Os_3(CO)_9(C_2Ph_2)(CH_2)$ generates $HOs_3(\mu_3\text{-}\eta^3\text{-}HCCPhCPh)(CO)_9$.[33] Coupling of two methylidynes and an alkyne has been observed in reactions of $Fe_3(CO)_9(\mu_3\text{-}COEt)(\mu_3\text{-}CMe)$ with alkynes.[40] Other related reactions include alkylidene–alkyne and alkylidyne–vinyl coupling.[34] Many of these systems have previously been suggested as models for C–C bond forming steps on metal surfaces.

Hydrogenation of 1,3-Dimetalloallyl Clusters. Since $HRu_3(\mu_3\text{-}\eta^3\text{-}XCC_2R_2)(CO)_9$ might serve as models for surface-bound hydrogenation fragments, we were interested in reactions of these molecules with hydrogen, particularly reactions leading to partially reduced hydrocarbon units. Valle and co-workers had previously reported that hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeCCHCMe)(CO)_9$ produces $H_4Ru_4(CO)_{12}$ and metallic Ru; no other products were identified.[27a] We have also found that hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}HCCHCMe)(CO)_9$ (110 °C, 2 h, 1 atm hydrogen) produces only $H_4Ru_4(CO)_{12}$.

Very different results were found for $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCRCR')(CO)_9$. For each cluster, hydrogenation (1–4 atm) at 90 °C gives the appropriate methylidyne cluster $H_3Ru_3(\mu_3\text{-}CCHRCH_2R')(CO)_9$ (Scheme II, R,R′ = Me (43%), R,R′ = H (39%), R,R′ = Ph (43%), R,R′ = H, CMe_3 (28%), R,R′ = H, OEt (6%), R,R′ = H, n-Bu (13%), R,R′ = n-Bu, H (10%), R,R′ = H, Ph (25%) R,R′ = H, CO_2Me (11%)). These cluster products have been characterized by infrared and ^1H NMR spectroscopy and by mass spectrometry. Characterization of $H_3Ru_3(\mu_3\text{-}CEt)(CO)_9$ was also effected by ^{13}C NMR spectroscopy and elemental analysis. All spectral features (Table IV) are very similar to those of previously characterized alkylidyne clusters $H_3Ru_3(\mu_3\text{-}CR)(CO)_9$ (R = Me,[12] CH_2CMe_3[35]) and characterizations are quite straightforward. The molecular ions and ions resulting from CO loss from the molecular ion are observed in the EI mass spectra. The ^1H NMR spectra each consist of a singlet at ca. −18 ppm due to three equivalent hydride ligands and signals appropriate for the R group. The infrared spectra display only terminal CO stretching frequencies in a rather simple pattern which is characteristic of $H_3M_3(\mu_3\text{-}CX)(CO)_9$ clusters.[7,15,39] The organic product from the hydrogenation, presumably methanol, was not detected by gas chromatography, despite repeated attempts.

The characterization of $H_3Ru_3(\mu_3\text{-}CEt)(CO)_9$ was confirmed by comparison of its ^{13}C NMR spectrum with that reported for $H_3Ru_3(\mu_3\text{-}CMe)(CO)_9$.[39] In deuteriochloroform (25 °C, 0.02 M $Cr(acac)_3$) the spectrum of the former consists of five resonances at 232.6 (1C, methylidyne carbon), 190.6 (6 C, radial CO ligands), 189.8 (3 C, axial CO ligands), 53.6 (1 C, methylene carbon), and 24.4 (1 C, methyl carbon) ppm. This compares very closely to the spectrum reported for the methyl analogue: 219.3 (methylidyne carbon), 190.6 (radial CO ligands), 189.9 (axial CO ligands), and 47.9 (methyl carbon) ppm.

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The mechanism of this unprecedented hydrogenation reaction is obviously of interest. Kinetic studies are unlikely to provide useful information because of the low yields of the products. The hydrogenation reaction proceeds at a considerably slower rate than CO substitution, suggesting that CO dissociation may take place prior to hydrogen addition and C–OMe bond cleavage. Indeed, the hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCMeCMe)(CO)_9$ was possible at 25 °C with trimethylamine *N*-oxide to chemically remove CO.

The destination in the product of the hydride ligand present in the dimetalloallyl cluster was determined by a labeling experiment. The labeled cluster $DRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCCMe_3)(CO)_9$, prepared from $DRu_3(\mu\text{-}COMe)(CO)_{10}$ and 3,3-dimethyl-1-butyne, was heated at 90 °C under hydrogen for 10 h. After chromatographic separation of the methylidyne product, the ^1H NMR spectrum contained resonances at 1.8 (m, 1 H), 4.1 (m, 2 H), 1.1 (s, 9 H), and −17.52 (s, 3 H) ppm; the ^2H NMR spectrum consisted of a single resonance at 5.34 (br) ppm upfield from deuteriochloroform. This experiment showed conclusively that only $H_3Ru_3(\mu\text{-}CCH_2CHDCMe_3)(CO)_9$ was formed. Thus, hydride transfer to the 3-carbon of the allyl unit most likely occurs early in the reaction sequence.

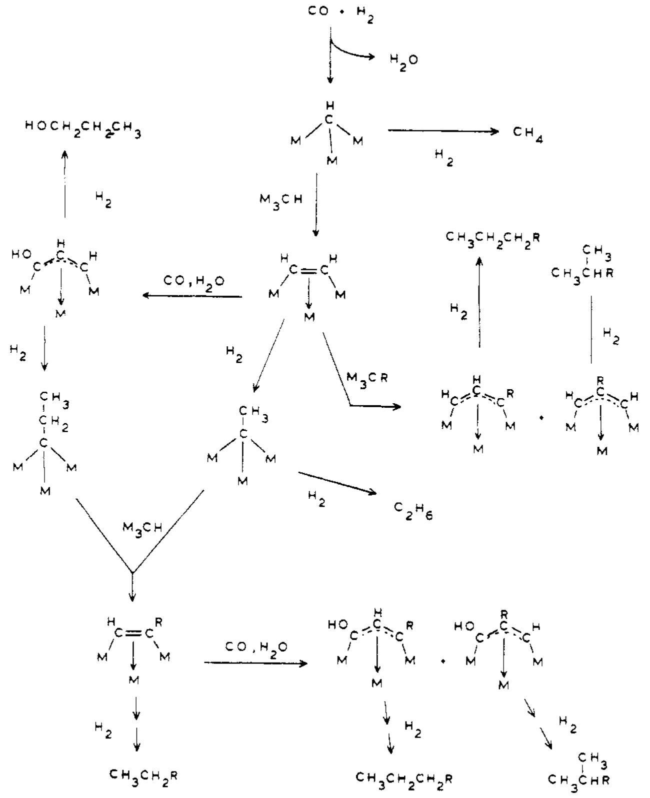
Competition experiments were conducted to determine the influence of the metalloallyl substituents upon the reaction. Hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCR)(CO)_9$ (R = *n*-Bu and CMe_3) under identical conditions demonstrated that the rate of disappearance of starting material was faster for R = CMe_3. Hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCOEt)(CO)_9$ gave $H_3Ru_3(\mu_3\text{-}CCH_2CH_2OR)(CO)_9$ with the major product having R = Et. These experiments suggest steric acceleration of Ru–CR bond cleavage and hydrogen transfer to that carbon.

The identity of the heteroatom is crucial to the reaction. No methylidyne products have been isolated from nonfunctionalized 1,3-dimetalloallyls. Hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}Et_2NCCHCMe)(CO)_9$ did not lead to observable quantities of $H_3Ru_3(\mu_3\text{-}CCH_2CH_2Me)(CO)_9$, only $H_4Ru_4(CO)_{12}$. On the other hand, in one experiment hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}EtSCCMeCMe)(CO)_9$ produced $H_3Ru_3(\mu_3\text{-}CCHMeCH_2Me)(CO)_9$; the quantity of material was too small to allow detection of the organic product. The lack of reactivity for the 1-(diethylamino))-1,3-dimetalloallyl cluster is presumed due to strong C–N bond,[23] this making cluster hydrogenation to $H_3Ru_3(CCH_2CH_2Me)(CO)_9$ a slower reaction than decomposition of the starting material or product to $H_4Ru_4(CO)_{12}$. Hydrogenation of $HOs_3(\mu_3\text{-}\eta^3\text{-}HOCCHCH)(CO)_9$[25] at 123 °C produced only $H_4Os_4(CO)_{12}$; however, the significance of this experiment is unclear since no characterizable quantities of $H_3Os_3(\mu_3\text{-}CCHPhCH_2Ph)(CO)_9$ have yet been obtained by hydrogenation of $HOs_3(\mu_3\text{-}\eta^3\text{-}MeOCCPhCPh)(CO)_9$, only $H_4Os_4(CO)_{12}$.

These new methylidyne clusters which are formed by hydrogenation of 1,3-dimetalloallyl clusters can react with alkyne to form 1,3-dimetalloallyl clusters containing longer carbon chains. This was demonstrated by hydrogenation of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCHCCMe_3)(CO)_9$ to $H_3Ru_3(\mu_3\text{-}CCH_2CH_2CMe_3)(CO)_9$ and then reaction of the product with diphenylacetylene to yield $HRu_3(\mu_3\text{-}\eta^3\text{-}PhCC(Ph)CH_2CH_2CMe_3)(CO)_9$.

Methylidyne–Alkyne Coupling and Hydrogenation as a Model for Fischer–Tropsch Chain Growth. Coupling of C_1 fragments has been proposed as a mechanism for hydrocarbon chain growth in the Fischer–Tropsch (F–T) process, which converts CO and hydrogen to predominantly linear alkanes and water. However, the mechanism remains controversial. Other proposed chain growth mechanisms include CO insertion into metal–alkyl bonds and coupling of hydroxymethylenes. The mechanism which is currently most popular invokes surface-bound methylene or methylidyne fragments. However, oxygenated products can be formed under some conditions.[4]

Scheme III. Fischer-Tropsch Carbon Chain Growth through Alkylidyne and 1,3-Dimetalloallyl Species



The unprecedented reaction sequence described here—coupling of methylidyne and alkyne to form a 1,3-dimetalloallyl and then hydrogenation of this species to form an alkylidyne of longer chain length—suggests a new mechanism for F–T chain growth through 1,3-dimetalloallyl intermediates (Scheme III). Reduction of CO by hydrogen on the catalyst surface has previously been proposed to yield water and surface-bound methylene or methylidyne units.[4] Cluster models[14,36] on which methyl, methylene, and methylidyne units can be interconverted suggest that all these species may be in equilibrium on the catalyst surface. Coupling of two methylidyne units would generate a surface-bound acetylene molecule; cluster models for this step are available.[37] Further reduction of the acetylene unit could generate an ethylidyne. Hydrogenation of any alkylidyne would yield alkane, but for C_2 and higher hydrocarbons, β-hydrogen elimination could also yield 1-alkenes. Cluster models for reductive cleavage of alkylidyne units to alkanes and alkenes are known.[7,35,38]

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Sequential methylidyne–alkylidyne coupling and hydrogenation provides one pathway for linear hydrocarbon formation. However, these intermediates may also combine to form 1,3-dimetalloallyl units. Two pathways for the generation of 1,3-dimetalloallyls may be envisioned. First, alkyne–methylidyne coupling, as demonstrated in this work, would generate a 1,3-dimetalloallyl having only alkyl or hydrogen substituents. Second, combination of CO, alkyne, and water could give rise to a 1-hydroxy-1,3-dimetalloallyl species; this pathway is suggested by the formation of $HOs_3(\mu_3\text{-}\eta^3\text{-HOCCHCH})(CO)_9$ from $Os_3(CO)_{10}(NCMe)_2$, acetylene, and water.[25]

The significance of these 1,3-dimetalloallyl species to the product distribution of the F–T reaction is with respect to the branched and oxygenated hydrocarbons, which are formed in small amounts. Some other mechanisms have invoked secondary reaction pathways involving alkene products to explain these minor products. The only significant branched hydrocarbon products are 2-methyl substituted. If the predominate alkylidyne on the surface is CH, the primary product from CO reduction, then the predominate alkyne on the surface will always be a terminal alkyne derived from alkylidyne–methylidyne coupling. Formation of a 1,3-dimetalloallyl species by either pathway can give rise to two regioisomers. By the first pathway these are HCCHCR and HCCRCH and by the second, HOCCHCR and HOCCRCH. Our work indicates that the *linear* carbon chain would be the preferred product; but *the minor product would yield a 2-methyl-substituted hydrocarbon upon hydrogenation.* As long as the principal alkylidyne species is methylidyne, the branched products must be methyl-substituted. Hydrogenation of the 1-hydroxy-1,3-dimetalloallyl species could yield an alkylidyne and water, as suggested by this work, and continue the chain growth. Alternatively, hydrogenolysis could yield an alcohol or aldehyde; such species are minor products of the F–T reaction under some conditions and the major oxygenated species are terminally substituted, as predicted by the above mechanism. Of course, methanol and ethanol would have to be formed by other mechanisms.

We should present a caveat here. As anyone who has followed the F–T literature is well aware, there is no lack of suggested mechanisms for the F–T reaction, rather there is a lack of evidence to substantiate any of these mechanisms on the actual catalyst. All of the mechanisms that have been proposed have been able to account more or less satisfactorily for the F–T products. Since a mechanism can be exluded but cannot be proven by experiment, model systems are useful in that they provide a basis for the design of experiments with actual catalysts which will disprove or which will be consistent with one or more suggested mechanisms. Comparisons of the spectroscopic features of these cluster models with similar studies of hydrocarbon fragments adsorbed on surfaces may provide some evidence for the existence of 1,3-dimetalloallyl units on surfaces, but it seems unlikely that any one mechanistic proposal can be proven to satisfy all of the experimental observations concerning the F–T reaction to the exclusion of all other mechanisms.

Regardless of the relevance of this alkylidyne cluster chemistry to surface chemistry, the rearrangements of hydrocarbon fragments on polymetallic arrays and hydrogen transfers to these fragments are intrinsically of interest. Relatively little is known about the differences, if any, between organometallic reaction mechanisms for mononuclear and for polynuclear complexes. Further experiments are in progress to delineate the mechanisms of methylidyne–alkyne coupling and of 1-alkoxy-1,3-dimetalloallyl reduction.

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Registry No. $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCHCH})(CO)_9$, 97633-55-1; $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCMeCMe})(CO)_9$, 97633-56-2; $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCPhCPh})(CO)_9$, 97633-57-3; $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCHCPh})(CO)_9$, 97633-58-4; $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCPhCH})(CO)_9$, 97633-59-5; $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCHCCMe}_3)(CO)_9$, 97633-60-8; $HRu_3(\mu_3\text{-}\eta^3\text{-MeOC(ClMe}_3\text{)CH})(CO)_9$, 97633-61-9; $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCHCOEt})(CO)_9$, 97633-62-0; $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCHCCO}_2\text{Me})(CO)_9$, 97633-63-1; $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCC(CO}_2\text{Me)CH})(CO)_9$, 97633-64-2; $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCC(}n\text{-Bu)CH})(CO)_9$, 86409-44-1; $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCHC-}n\text{-Bu})(CO)_9$, 97633-65-3; $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCC(CO}_2\text{Me)CPh})(CO)_9$, 97633-66-4; $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCC(Me)CC}_7\text{H}_{15})(CO)_9$, 97633-67-5; $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCC(C}_7\text{H}_{15}\text{)CMe})(CO)_9$, 97633-68-6; $HRu_3(\mu_3\text{-}\eta^3\text{-PhCCPhCPh})(CO)_9$, 86409-39-4; $HRu_3(\mu_3\text{-}\eta^3\text{-MeCCMeCMe})(CO)_9$, 86409-40-7; $HRu_3(\mu_3\text{-}\eta^3\text{-C(CH}_2\text{CH}_2\text{CMe}_3\text{)CPhCPh})(CO)_9$, 97633-69-7; $HRu_3(\mu_3\text{-}\eta^3\text{-Et}_2\text{NCCHCMe})(CO)_9$, 97633-75-5; $HRu_3(\mu_3\text{-}\eta^3\text{-EtSCCMeCMe})(CO)_9$, 97633-76-6; $HRu_3(\mu_3\text{-}\eta^3\text{-HCCHCMe})(CO)_9$, 52504-78-6; $DRu_3(\mu_3\text{-}\eta^3\text{-MeOCCHCCMe}_3)(CO)_9$, 97633-77-7; $HOs_3(\mu_3\text{-}\eta^3\text{-MeOCCPhCPh})(CO)_9$, 97689-39-9; $HOs_3(\mu_3\text{-}\eta^3\text{-HOCCHCH((CO)}_9$, 76287-22-4; $H_3Ru(\mu_3\text{-COMe})(CO)_9$, 71562-47-5; $H_3Ru(\mu_3\text{-CMe})(CO)_9$, 40810-15-9; $H_3Ru_3(\mu_3\text{-CPh})(CO)_9$, 73746-99-3; $H_3Ru_3(\mu_3\text{-CCH}_2\text{CH}_2\text{CMe}_3)(CO)_9$, 86409-46-3; $H_3Ru_3(\mu_3\text{-CEt})(CO)_9$, 73747-02-1; $H_3Ru_3(\mu_3\text{-CCHMeCH}_2\text{Me})(CO)_9$, 97633-70-0; $H_3Ru_3(\mu_3\text{-CCHPhCH}_2\text{Ph})(CO)_9$, 86409-47-4; $H_3Ru_3(\mu_3\text{-CCH}_2\text{CH}_2\text{OEt})(CO)_9$, 97633-71-1; $H_3Ru_3(\mu_3\text{-C(CH}_2\text{)}_5\text{CH}_3)(CO)_9$, 97633-72-2; $H_3Ru_3(\mu_3\text{-CCH(}n\text{-Bu)CH}_3)(CO)_9$, 97633-73-3; $H_3Ru_3(\mu_3\text{-CCH}_2\text{CH}_2\text{Ph})(CO)_9$, 86409-48-5; $H_3Ru_3(\mu_3\text{-CCH}_2\text{CH}_2\text{CO}_2\text{Me})(CO)_9$, 97633-74-4; $H_3Ru_3(\mu_3\text{-CCl})(CO)_9$, 73746-97-1; $D_3Ru_3(\mu\text{-COMe})(CO)_9$, 97633-78-8; $H_3Ru_3(\mu_3\text{-CCH}_2\text{CHDCMe}_3)(CO)_9$, 97633-79-9; $HRu_3(\mu\text{-COMe})(CO)_{10}$, 71737-42-3; $HOs_3(\mu\text{-COMe})(CO)_{10}$, 69048-01-7; $HFe_3(\mu\text{-COMe})(CO)_{10}$, 55992-19-3; $HRu_3(\mu\text{-CNMe(CH}_2\text{Ph)})(CO)_{10}$, 84027-58-7; $H_4Ru_4(CO)_{12}$, 34438-91-0; $H_4Os_4(CO)_{12}$, 12375-04-1; $Fe_3(CO)_{12}$, 17685-52-8; acetylene, 74-86-2; 2-butyne, 503-17-3; diphenylacetylene, 501-65-5; phenylacetylene, 536-74-3; 3,3-dimethyl-1-butyne, 917-92-0; ethoxyacetylene, 927-80-0; methyl propiolate, 922-67-8; 1-hexyne, 693-02-7; methyl phenylpropiolate, 4891-38-7; *cis*-2-decene, 20348-51-0; bis(trimethylsilyl)acetylene, 14630-40-1; (trimethylsilyl)acetylene, 1066-54-2; 2-decyne, 2384-70-5.

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