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Synthesis, Structures, and Transformations of Bridging and Terminally-Coordinated Trimethylammonioalkenyl Ligands in Zwitterionic Pentaruthenium Carbido Carbonyl Complexes

Richard D. Adams,* Humaiara Akter, Meenal Kaushal, Mark D. Smith, and Jonathan D. Tedder

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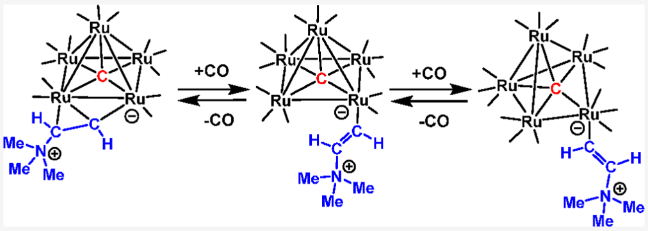


ABSTRACT: Reactions of the pentaruthenium cluster complexes $Ru_5(\mu_5\text{-}C)(CO)_{15}$ (**5**), $Ru_5(\mu_5\text{-}C)(CO)_{14}[\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)](\mu\text{-}H)$ (**6**), and $Ru_5(\mu_5\text{-}C)(CO)_{15}Cl(\mu\text{-}H)$ (**7**) with ethyne (C_2H_2) in the presence of Me_3NO yielded the zwitterionic complexes $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}CHCH(NMe_3)]$ (**8**), $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)](\eta^1\text{-}E\text{-}CH{=}CH(NMe_3)(\mu\text{-}H)$ (**9**), and $Ru_5(\mu_5\text{-}C)(CO)_{13}Cl[\eta^1\text{-}E\text{-}CH{=}CH(NMe_3)](\mu\text{-}H)$ (**11**). Each product contains a positively charged trimethylammonioethenyl ligand, $CH{=}CH(^+NMe_3)$, that is derived from a 2-trimethylammonioethenide, $^-CH{=}CH(^+NMe_3)$, zwitterion that formally has a positive charge on the nitrogen atom and a negative charge on the terminal enyl carbon atom. The trimethylammonioethenyl ligand, $CH{=}CH(^+NMe_3)$ in **8** is a η^2-ligand that bridges a Ru−Ru bond on a basal edge of the square-pyramidal Ru_5 cluster by a combination of $\sigma + \pi$ cooordination of the ethenyl group. Compounds **9** and **11** each contain a η^1-terminally coordinated $[\eta^1\text{-}E\text{-}CH{=}CH(^+NMe_3)]$ ligand with an *E* stereochemistry at the C═C double bond in open Ru_5 cluster complexes. Compound **9** was decarbonylated to yield the compound $Ru_5(\mu_5\text{-}C)(CO)_{12}[\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)][\mu\text{-}\eta^2\text{-}CH{=}CH(NMe_3)](\mu\text{-}H)$ (**10**) containing a η^2-bridging $CHCH(^+NMe_3)$ ligand. Compound **10** was converted back to **9** by the addition of CO. Two zwitterionic products, $Ru_5(\mu_5\text{-}C)(CO)_{14}[\eta^1\text{-}E\text{-}CH{=}CH(NMe_3)]$ (**12**) and $Ru_5(\mu_5\text{-}C)(CO)_{15}[\eta^1\text{-}E\text{-}CH{=}CH(NMe_3)]$ (**13**), were obtained by the addition of CO to **8**. Compound **12** is an intermediate en route to **13**. Compound **12** contains a terminally coordinated $\eta^1\text{-}E\text{-}CH{=}CH(^+NMe_3)$ ligand on one of the basal Ru atoms of a square-pyramidal Ru_5 cluster. Compound **13** also contains a terminally coordinated $\eta^1\text{-}E\text{-}CH{=}CH(^+NMe_3)$ ligand on the wing-tip bridging Ru atom of a butterfly Ru_4C cluster. Treatment of **6** with methyl propiolate ($HC{\equiv}CCO_2Me$) yielded the zwitterionic complex $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)][\eta^1\text{-}E\text{-}(MeO_2C)C{=}C(H)NMe_3](\mu\text{-}H)$ (**14**) that is structurally similar to **9** but contains a $\eta^1\text{-}E\text{-}(MeO_2C)C{=}C(H)(^+NMe_3)$ ligand. Compound **14** eliminated the NMe_3 group to yield the compounds $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)][\mu\text{-}\eta^2\text{-}(MeO_2C)HC{=}CH]$ (**15**) which contains a bridging methoxycarbonyl-substituted alkenyl ligand and the known compound $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)](HNMe_2)(\mu\text{-}H)$ (**16**).

■ INTRODUCTION

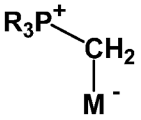
Hydrocarbyl onium zwitterions have been of great interest for many years. The best known examples of these are the phosphorus- and sulfur-ylides **A**[1] and **B**[2] that were first reported by Wittig in the 1950s.[1] These and other ylides are valuable reagents in organic syntheses.[2,3] These ylides are well known to coordinate to metal atoms by using the negatively charged carbon atom which formally transfers its negative charge to the metal atom upon coordination, see **C** and **D** below, and the complex becomes a zwitterion.[4,5]

$R_3P^+{-}^-CR'_2$

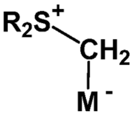
A

$R_2S^+{-}^-CR'_2$

B



C



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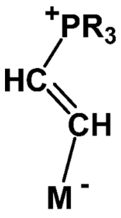

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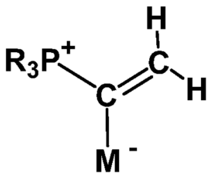

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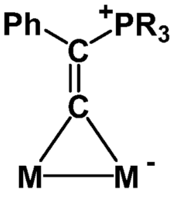

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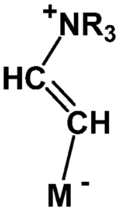

H

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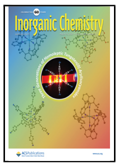

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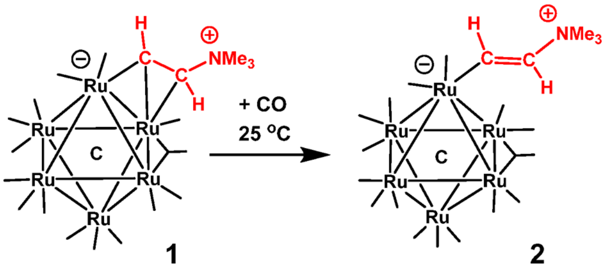
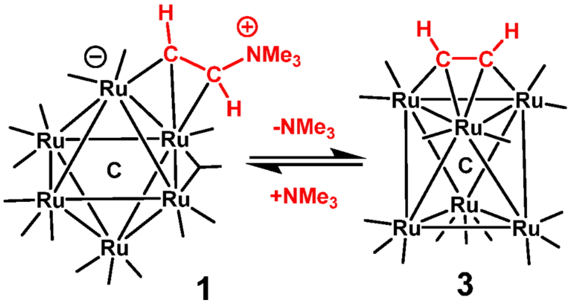
In recent years, new families of unsaturated hydrocarbyl onium ligands have been synthesized in metal complexes. Some examples of these are shown in the structures **E**−**G**.[6−8] They can be obtained by the addition of tertiary phosphines to certain alkyne or vinylidene ligands. There are only a few examples of complexes containing the ammonioethenyl ligand shown in structure **H**.[9,10]

In recent studies, we have synthesized the first example of a bridging η^2-trimethylammonioethenyl ligand in the zwitterionic hexaruthenium carbonyl complex $Ru_6(\mu_6\text{-}C)(CO)_{15}(\mu\text{-}\eta^2\text{-}CHCHNMe_3)$ (**1**) and have found that this bridging ligand can be readily converted to a terminally coordinated η^1-ligand in the complex $Ru_6(\mu_6\text{-}C)(CO)_{16}[\mu\text{-}\eta^2\text{-}CH{=}CH(NMe_3)]$ (**2**) by the addition of CO to **1**, as shown in eq 1.[10] Interestingly, the bridging η^2-trimethylammonioethenyl ligand, $(\mu\text{-}\eta^2\text{-}CHCH^+NMe_3)$, in **1** can also be converted to a simple alkyne ligand in the complex $Ru_6C(CO)_{15}(\mu_3\text{-}C_2H_2)$ (**3**) by the reversible elimination of NMe_3 from the bridging η^2-ligand in **1**, as shown in eq 2.



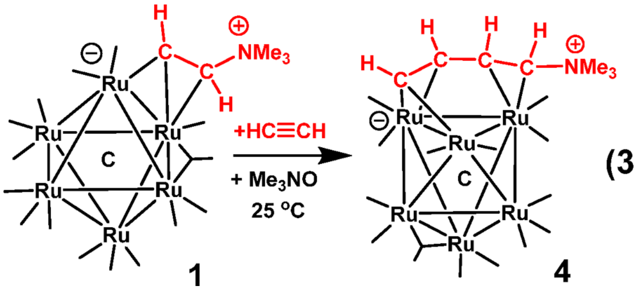
(1)

Even more interestingly, it was also found that ethyne (C_2H_2) can be added to the bridging η^2-$CHCH(^+NMe_3)$ ligand in **1** to form a triply bridging η^4-trimethylammoniobutadienyl, $(\mu_3\text{-}\eta^4\text{-}CHCHCHCH^+NMe_3)$, ligand in the zwitterionic complex $Ru_6(\mu_6\text{-}C)(CO)_{14}[\mu_3\text{-}\eta^4\text{-}C_4H_4(NMe_3)]$ (**4**) by a C—C bond forming coupling to the η^2-$CHCH^+NMe_3$ ligand, as shown in eq 3.



(2)

In hopes of finding new structures and reactivity of alkylammonioethenyl zwitterions for applications in organic synthesis, we have now investigated reactions of the pentaruthenium carbonyl complexes $Ru_5(\mu_5\text{-}C)(CO)_{15}$[11] (**5**), $Ru_5(\mu_5\text{-}C)(CO)_{14}[\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)](\mu\text{-}H)$[12] (**6**), and $Ru_5(\mu_5\text{-}C)(CO)_{15}Cl(\mu\text{-}H)$[11] (**7**) with ethyne (C_2H_2) and methyl propiolate ($HC{\equiv}CCO_2Me$) in the presence of Me_3NO. We have obtained a series of new pentaruthenium complexes containing terminally coordinated η^1-trimethylammonioethenyl ligands, two new complexes containing bridging η^2-trimethylammonioethenyl ligands, and one complex containing a terminally coordinated η^1-2-trimethylammonio(1-methoxycarbonyl)ethenyl ligand. The syntheses, structures, and chemistry of these new complexes are described in this report.



(3)

■ EXPERIMENTAL SECTION

General Data. All reactions were performed under nitrogen atmosphere. Reagent grade solvents were dried by standard procedures and were freshly distilled prior to use. $Ru_3(CO)_{12}$ was obtained from STREM and was used without further purification. *N*,*N*-Dimethylformamide (DMF, $Me_2NC({=}O)H$), hydrochloric acid (HCl, 37%), methyl propiolate ($HC{\equiv}C(CO_2Me)$, MP), trimethylamine-*N*-oxide (Me_3NO), and anhydrous trimethylamine gas (NMe_3) were purchased from Sigma-Aldrich and were used without further purification. Ethyne gas (HC_2H) (industrial grade) was purchased from Praxair and was used without further purification. Research grade carbon monoxide (CO) was purchased from Airgas Specialty Chemicals and was used without further purification. ***WARNING!*** Carbon monoxide is a hazardous gas that should be used only in a well-ventilated fume hood. $Ru_5(\mu_5\text{-}C)(CO)_{15}$,[11] **5**, $Ru_5(\mu_5\text{-}C)(CO)_{14}[\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)](\mu\text{-}H)$,[12] **6**, and $Ru_5(\mu_5\text{-}C)(CO)_{15}Cl(\mu\text{-}H)$,[11] **7**, were prepared according to previously reported procedures. Product separations were performed by TLC in the air on Analtech 0.25 mm and 0.50 mm silica gel 60 Å F254 glass plates. Column chromatography was performed by using silica gel 60, 0.606−0.2 mm (70−230 mesh).

Synthesis of $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}CHCH(NMe_3)]$ (8) from Reaction of 5 with NMe_3, Me_3NO, and C_2H_2 at −78 °C. First, 22.2 mg (0.0237 mmol) of **5** was added to a 100 mL three-neck flask and then was dissolved in 25 mL of degassed CH_2Cl_2. The solution was cooled to −78 °C using a dry ice/acetone bath. Then, 3 mL of NMe_3 (gas/1 atm) was added to the solution through the rubber septum by syringe. A solution of 4.7 mg (0.0626 mmol) of Me_3NO in CH_2Cl_2 was then added to the flask. A color change from red to dark red was observed. Then, 4 mL of C_2H_2(gas/1 atm) was added to the flask, and the reaction solution was allowed to stir for 30 min. The progress of the reaction was monitored by IR spectroscopy. The excess unreacted gases were then removed by flushing the solution with nitrogen. The reaction mixture warmed to room temperature, and the solvent was removed *in vacuo*. The product was then isolated by TLC on silica gel by using a solvent mixture of hexane/methylene chloride to yield 1.2 mg of red-orange $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}CHCH(NMe_3)]$, **8** (5.2% yield). Spectral data for **8**: IR, νCO (cm^{-1} in CH_2Cl_2): 2071(w), 2033(s), 2016(s), 2006(vs). ^1H NMR (in acetone-d_6 solvent, δ in ppm): 11.23 (C**H**CHN(CH$_3$)$_3$, d, $^3J_{H-H}$ = 10.0 Hz, 1H), 5.87 (CHC**H**N(CH$_3$)$_3$, m, $^3J_{H-H}$ = 10.0 Hz, 1H), 3.64 (CHCHN(C**H**$_3$)$_3$, s, 9H). ^{13}C NMR (in $(CD_3)_2CO$, 100.66 MHz, δ in ppm): 204.33 (CO), 202.85 (CO), 201.60 (CO), 199.83 (CO), 197.72 (CO), 192.73 (CO), 191.40 (CO), 170.41 (**C**HCHN(CH$_3$)$_3$), 94.80 (CH**C**HN(CH$_3$)$_3$), 54.65 (t, $^1J_{C-N}$ = 16 Hz, CHCHN(**C**H$_3$)$_3$). Elemental anal. calcd for $Ru_5NO_{13}C_{19}H_{11}$: C, 23.61%; H, 1.15%; N, 1.45%. Found: C, 23.74%; H, 0.96%; N, 1.39%.

Reaction of $Ru_5(\mu_5\text{-}C)(CO)_{14}[\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)](\mu\text{-}H)$ (6) with C_2H_2 and Me_3NO at 25 °C. First, 66.5 mg (0.0677 mmol) of **6** in 20 mL of degassed dichloromethane was added to a 100 mL three-neck flask. A slow purge of C_2H_2 (1 atm) was then passed through the solution. Then, 10.2 mg (0.136 mmol) of Me_3NO was added to the solution while the flask was kept under C_2H_2 (1 atm) at 25 °C. The solution was stirred for 15 min until an IR spectrum showed no **6** remained. The products were then isolated by TLC by using a hexane/methylene chloride solvent mixture to yield in order of elution: 34.2 mg (48% yield) of $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)](\eta^1\text{-}E\text{-}CH{=}CH(NMe_3))(\mu\text{-}H)$, **9**, and 4.4 mg (6.4%

yield) of $Ru_5(\mu_5\text{-}C)(CO)_{12}[\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)][\mu\text{-}\eta^2\text{-}CHCH(NMe_3)](\mu\text{-}H)$, **10**. Spectral data for **9**: IR νCO (cm^{-1} in CH_2Cl_2): 2076(m), 2038(vs), 2030(vs), 2016(s), 1999(sh), 1973(m), 1923(w). ^1H NMR (in CD_2Cl_2, δ in ppm): 8.25 ($\mathbf{CH}CHN(CH_3)_3$, d, $^3J_{H-H}$ = 14 Hz, 1H), 5.90 ($CH\mathbf{CH}N(CH_3)_3$, d, $^3J_{H-H}$ = 14 Hz, 1H), 3.25 ($N(CH_3)_2$, s, 3H), 3.22 ($CHCHN(\mathbf{CH}_3)_3$, s, 9H), 2.55 ($N(CH_3)_2$, s, 3H), −22.07 (μ-H, s, 1H). ^{13}C NMR ($(CD_3)_2CO$, 100.66 MHz, δ in ppm): 219.55 (d, $^2J_{C-H}$ = 1.6 Hz, $\mathbf{C}ON(CH_3)_2$), 206.11 (CO), 206.09 (CO), 205.77 (CO), 205.75 (CO), 202.30 (CO), 197.92 (CO), 141.95 ($\mathbf{C}HCHN(CH_3)_3$), 133.05 ($CH\mathbf{C}HN(CH_3)_3$), 53.88 ($CHCHN(\mathbf{C}H_3)_3$), 43.35 (1C, $CON(\mathbf{C}H_3)_2$), 34.38 (1C, $CON(\mathbf{C}H_3)_2$). ESI/MS: m/z = 1040 M^+ and 996 $[M - N(CH_3)_2]^+$. Elemental anal. calcd for $Ru_5N_2O_{14}C_{22}H_{18}$: C, 25.41%; H, 1.74%; N, 2.69%. Found: C, 25.79%; H, 1.64%; N, 2.50%. Spectral data for **10**: IR νCO (cm^{-1} in CH_2Cl_2): 2075(m), 2035(s), 2014(vs), 1987(w), 1971(m). ^1H NMR (in acetone-d_6 solvent, δ in ppm): 10.57 ($\mathbf{CH}CHN(CH_3)_3$, d, $^3J_{H-H}$ = 8.8 Hz, 1H), 4.46 ($CH\mathbf{CH}N(CH_3)_3$, m, $^3J_{H-H}$ = 8.8 Hz, 1H), 3.51 ($CHCHN(\mathbf{CH}_3)_3$, s, 9H), 3.15 ($N(CH_3)_2$, s, 3H), 2.39 ($N(CH_3)_2$, s, 3H), −21.44 (μ-H, s, 1H). Elemental anal. calcd for $Ru_5N_2O_{13}C_{21}H_{18}\cdot 0.79CH_2Cl_2$: C, 24.26%; H, 1.83%; N, 2.60%. Found: C, 24.10%; H, 1.22%; N, 2.52%.

Synthesis of 10 from Reaction of 9 with Me_3NO at 25 °C. First, 10.0 mg (0.00963 mmol) of **9** was taken in an NMR tube in d_6-acetone solvent. Then, 2.9 mg (0.0386 mmol) of Me_3NO was added to the solution and mixed thoroughly. The reaction mixture kept at 25 °C for 22 h. The reaction products were then separated by TLC by using a hexane/methylene chloride/acetone mixture to yield in order of elution 2.1 mg of starting material **9**, 1.3 mg of **8** (14% yield), and 4.0 mg of **10** (41% yield).

Conversion of 9 to 8 by the Elimination of DMF at 60 °C. First, 22.0 mg (0.0212 mmol) of **9** was dissolved in an NMR tube in d_6-acetone. The solution in the tube was then heated in a constant-temperature oil bath at 60 °C for 9.5 h. The reaction was monitored by ^1H NMR spectroscopy, and DMF was observed in the solution. The cluster complexes were then isolated by TLC by using a hexane/methylene chloride/acetone mixture to yield in order of elution 2.0 mg of unreacted **9** and 15.0 mg of **8** (73% yield).

Conversion of 10 to 8 at 50 °C. First, 5.5 mg (0.0054 mmol) of **10** was dissolved an NMR tube in d_6-acetone solvent. The NMR tube was sealed with a rubber septum and degassed under nitrogen. The tube was then heated in a constant-temperature oil bath at 50 °C for 13 h. The formation of dimethylformamide (DMF) was observed in a ^1H NMR spectrum of the reaction solution. Workup by TLC using methylene chloride solvent yielded 2.6 mg of **8** (50% yield) and 0.3 mg of unreacted **10**.

Addition of CO to 10. First, 4.6 mg (0.0045 mmol) of **10** was dissolved in d_6-acetone and then the mixture was transferred to an NMR tube. The NMR tube was sealed with a rubber septum and degassed under nitrogen three times. In a fume hood, CO gas at 1 atm was bubbled through the solution for 60 s. The sample was then heated at 35 °C. Reaction progress was monitored by ^1H NMR spectroscopy. After 24 h, compounds **9** (36% yield) and **13** (50% yield) were observed by ^1H NMR spectroscopy and resonance integrations. In addition, the resonances of DMF in approximately 34% yield were also observed.

Synthesis of $Ru_5(\mu_5\text{-}C)(CO)_{14}Cl[\eta^1\text{-}E\text{-}CH{=}CH(NMe_3)](\mu\text{-}H)$ (11) from 7 plus C_2H_2 and Me_3NO. Compound 7 was first prepared *in situ*. First, 37.4 mg (0.040 mmol) of **5** was placed in a 100 mL three-neck flask and then dissolved in 30 mL of freshly distilled dichloromethane. Twenty microliters of concentrated HCl (37%) was added to the solution, which was then stirred at room temperature for 12 h. The conversion of **5** to **7** was followed by IR spectroscopy and appeared to be complete. The solvent was removed *in vacuo*, and compound **7** was then redissolved in 30 mL of freshly distilled dichloromethane. A steady flow of $C_2H_2(g)$ was then passed through the solution at 1 atm for 5 min. After this time, 6.2 mg (0.0825 mmol) of Me_3NO was added to the solution, and the solution was stirred for 15 min under an atmosphere of C_2H_2 gas at 25 °C. The products were separated by TLC by using a solvent mixture of hexane/methylene chloride and finally with acetone to yield two bands in the elution order of 3.6 mg of orange **8** (9% yield) and 22.9 mg of $Ru_5(\mu_5\text{-}C)(CO)_{14}Cl[\eta^1\text{-}E\text{-}CH{=}CH(NMe_3)](\mu\text{-}H)$, **11** (56% yield). Spectral data for **11**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2091(w), 2060(s), 2051(vs), 2040(m), 2025(w), 2013(w), 1975(sh). ^1H NMR (in acetone-d_6 solvent, δ in ppm): 8.51 ($\mathbf{CH}CHN(CH_3)_3$, d, $^3J_{H-H}$ = 14.4 Hz, 1H), 6.17 ($CH\mathbf{CH}N(CH_3)_3$, d, $^3J_{H-H}$ = 14.4 Hz, 1H), 3.51 ($CHCHN(\mathbf{CH}_3)_3$, s, 9H) −22.53 (μ-H, s, 1H). ESI/MS: m/z 996 $[M - Cl]^+$.

Synthesis of 8 from 11 at 48 °C. First, 12.2 mg (0.012 mmol) of **11** was dissolved in d_6-acetone in an NMR tube. The NMR tube was sealed with a rubber septum and vacuum degassed under nitrogen three times. The sample was then heated at 48 °C in a constant-temperature oil bath. The reaction progress was monitored by ^1H NMR spectroscopy. After it was heated for 18 h, the product was then isolated by TLC using a hexane/methylene chloride solvent mixture to yield 3.6 mg of **8** (32% yield).

Syntheses of $Ru_5(\mu_5\text{-}C)(CO)_{14}[\eta^1\text{-}E\text{-}CH{=}CH(NMe_3)]$ (12) and $Ru_5(\mu_5\text{-}C)(CO)_{15}[\eta^1\text{-}E\text{-}CH{=}CH(NMe_3)]$ (13) by Addition of CO to 8. *Reaction 1.* First, 11.6 mg (0.0111 mmol) of **8** was dissolved in d_6-acetone and then transferred to an NMR tube. The NMR tube was sealed with a rubber septum and degassed under nitrogen three times. CO gas at 1 atm was bubbled through the solution for 30 s. After 22 h at 25 °C, the reaction mixture was passed through a paper filter into a vial and then the solvent was removed under a flow of nitrogen. The oily residue was redissolved in a mixture of CH_2Cl_2 and hexane, was filtered into a clean vial, and was allowed to evaporate in air in a fume hood overnight. A small number of red crystalline plates of $Ru_5(\mu_5\text{-}C)(CO)_{14}[\eta^1\text{-}E\text{-}CH{=}CH(NMe_3)]$, **12**, formed on the walls of the vial. One of these crystals was used for a single-crystal X-ray diffraction analysis (see below). Compound **8** was present on the bottom of the vial. Spectral data for **12**: ^1H NMR (in acetone-d_6 solvent, δ in ppm): 7.51 ($\mathbf{CH}CHN(CH_3)_3$, d, $^3J_{H-H}$ = 12.9 Hz, 1H), 5.47 ($CH\mathbf{CH}N(CH_3)_3$, d, $^3J_{H-H}$ = 12.9 Hz, 1H), 3.25 ($CHCHN(\mathbf{CH}_3)_3$, s, 9H).

Reaction 2. In a similar reaction, 12.8 mg (0.0132 mmol) of **8** was treated with CO and filtered into a clean vial; the vial was sealed with a rubber septum. In a fume hood, CO gas was then passed over the solution to remove the solvent by using two syringe needles (one input/one output) through the septum. Upon removal of the solvent (approximately 1 h), red crystals of **13** remained in the vial, i.e., 11.8 mg of $Ru_5(\mu_5\text{-}C)(CO)_{15}[\eta^1\text{-}E\text{-}CH{=}CH(NMe_3)]$, **13** (87% yield). One of these red crystals was used for a single-crystal X-ray diffraction analysis. Spectral data for **13**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2089(w), 2058(s), 2041(vs), 2022(s), 2014(m), 2003(s), 1986(w), 1971(w). ^1H NMR (in $(CD_3)_2CO$ solvent, δ in ppm): 6.01 ($\mathbf{CH}CHN(CH_3)_3$, d, $^3J_{H-H}$ = 15.2 Hz, 1H), 5.59 ($CH\mathbf{CH}N(CH_3)_3$, d, $^3J_{H-H}$ = 15.2 Hz, 1H), 3.16 ($CHCHN(\mathbf{CH}_3)_3$, s, 9H). Elemental anal. calcd for $Ru_5NO_{15}C_{21}H_{11}$: C, 24.66%; H, 1.08%; N, 1.37%. Found: C, 25.00%; H, 0.86%; N, 1.34%.

Decarbonylation of 13 to 12 and 8. First, 9.2 mg of (0.0090 mmol) of **13** was dissolved in acetone-d_6 and then was transferred to an NMR tube under nitrogen at 25 °C. The tube was closed. After 10 h, compound **13** was transformed to compounds **12** and **8** with 35% and 15% yield, respectively, as determined by ^1H NMR analysis. After 24 h, the conversion to compounds **12** and **8** was 40% and 29%, respectively, as determined by ^1H NMR analysis.

Synthesis of $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)][\eta^1\text{-}E\text{-}(MeO_2C)C{=}C(H)(NMe_3)](\mu\text{-}H)$ 14: Reaction of 6 with $HC{\equiv}C(CO_2CH_3)$ and Me_3NO at 25 °C. First, 28.5 mg (0.0290 mmol) of **6** was dissolved in CD_2Cl_2 solvent in an NMR tube. The sample was vacuum degassed and placed under nitrogen. Then, 8.0 μL (0.087 mmol) of methyl propiolate, $HC{\equiv}C(CO_2Me)$, was added to the solution via syringe and mixed thoroughly. Next, 4.3 mg (0.058 mmol) of Me_3NO was then added to the solution, and the tube was shaken. The color of the solution changed from yellow to brown. The reaction progress was monitored by ^1H NMR after each addition of reagents. The reaction began immediately after addition of Me_3NO as there was no sign of hydride resonances for the starting material after 4 h at 25 °C. The solvent was removed *in vacuo*, and the product was then isolated by TLC using a hexane/methylene chloride/acetone solvent mixture to yield 9.7 mg of $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}O{=}$

C(NMe$_2$)][η^1-*E*-(MeO$_2$C)C=C(H)(NMe$_3$)](μ-H), **14** (31% yield). Spectral data for **14**: IR νCO (cm^{-1} in CH$_2$Cl$_2$): 2079(m), 2040(vs), 2022(s), 2004(w), 1978(m), 1927(vw). ^{1}H NMR (CD$_2$Cl$_2$, δ in ppm): 5.61 (**H**C$_2$CO$_2$Me,s, 1H), 3.83 (HC$_2$CO$_2$**Me**, s, 3H), 3.26 (N**Me**, s, 3H), 3.23 (N**Me$_3$**, s, 9H), 2.53 (s, 3H, N**Me**), −22.07 (μ-H, s, 1H). Elemental anal. calcd for Ru$_5$N$_2$O$_{16}$C$_{24}$H$_{20}$: C, 26.26%; H, 1.84%; N, 2.55%. Found: C, 26.43%; H, 1.70%; N, 2.50%.

Synthesis of Ru$_5$(C)(CO)$_{13}$[μ-η^2-O=C(NMe$_2$)][μ-η^2-(MeO$_2$C)-HC=CH] (15) by Thermal Elimination of NMe$_3$ from 14. First, 12.0 mg (0.00091 mmol) of **14** was dissolved in benzene-d_6 in an NMR tube. The solution was then heated in a constant-temperature oil bath at 80 °C for 4 h. The reaction was monitored by ^{1}H NMR spectroscopy. The products were then isolated by TLC using a hexane/methylene chloride mixture to yield in order of elution 1.9 mg of unreacted **6**, 0.6 mg of the new compound Ru$_5$(μ_5-C)(CO)$_{13}$[μ-η^2-O=C(NMe$_2$)][μ-η^2-(MeO$_2$C)HC=CH], **15** (5% yield), and 0.9 mg of the known compound Ru$_5$(μ_5-C)(CO)$_{13}$[μ-η^2-O=C(NMe$_2$)]-(HNMe$_2$)(μ-H), **16** (8% yield).[12] Spectral data for **15**: IR νCO (cm^{-1} in hexane): 2091(m), 2077(w), 2058(w), 2048(vs), 2029(s), 2022(w), 2013(w), 2000(m), 1991(w). ^{1}H NMR (CD$_2$Cl$_2$, δ in ppm): 11.41 (μ-η^2-O=C(OCH$_3$)HC=C**H**, d, $^3J_{\text{H-H}}$ = 8.4 Hz, 1H), 6.37 (μ-η^2-O=C(OCH$_3$)**H**C=CH, d, $^3J_{\text{H-H}}$ = 8.7 Hz, 1H), 3.79 (μ-η^2-O=C(OC**H$_3$**)HC=CH, s, 3H), 3.11 (N(CH$_3$)$_2$, s, 3H), 2.40 (N(CH$_3$)$_2$, s, 3H). EI/MS: m/z = 1039 [M$^+$].

Crystallographic Analyses. Crystals of each compound suitable for single-crystal X-ray diffraction analyses were grown by slow evaporation of solvent from a solution of the pure compound in the open air, except for compound **13**. Single crystals of **13** (red) were obtained from a CH$_2$Cl$_2$/hexane solvent mixture by slow evaporation of solvent under a slow purge of CO at 25 °C. X-ray intensity data for all compounds were collected at 100(2) K by using a Bruker D8 QUEST diffractometer equipped with a PHOTON-100 CMOS area detector and an Incoatec microfocus source (Mo K$_\alpha$ radiation, λ = 0.71073 Å).[13] The raw area detector data frames were reduced, scaled, and corrected for absorption effects by using the SAINT and SADABS programs. All structures were solved and refined by using the programs SHELX[14] or OLEX.[15] For all structures, all non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrido ligands were located and refined with isotropic displacement parameters. Other hydrogen atoms were placed in geometrically idealized positions and were included as riding atoms with d(C−H) = 0.98 Å and Uiso(H) = 1.5Ueq(C). Full details for these analyses are available in the Supporting Information. Crystal data, data collection parameters, and results for each analysis are summarized in Table S1. See the Supporting Information for additional details. Cambridge Crystallographic Data Centre (CCDC) files 2043913 for **7**, 2043914 for **8**, 2043915 for **9**, 2043916 for **10**, 2043917 for **11**, 2043918 for **12**, 2043919 for **13**, for 2043920 **14**, and 2043921 for **15** contain the supplementary crystallographic data for the structural analyses in this paper.

■ RESULTS

The reaction of **5** with C$_2$H$_2$ in the presence of Me$_3$NO and Me$_3$N at −78 °C provided the new compound Ru$_5$(μ_5-C)(CO)$_{13}$[μ-η^2-CHCH(NMe$_3$)], **8**, in a low yield (5.2%). Compound **8** was characterized by IR, ^{1}H NMR, and ^{13}C NMR analyses, single-crystal X-ray diffraction analyses, and elemental analyses. An ORTEP diagram of the molecular structure of compound **8** is shown in Figure 1. Compound **8** contains a square-pyramidal shaped Ru$_5$ cluster of metal atoms with a carbido ligand in the center of the square base and 13 linear terminal carbonyl ligands distributed about the cluster as shown in Figure 1. The most interesting ligand in **8** is a 2-trimethylammonioethenyl ligand, CH=CH($^+$NMe$_3$), that bridges the Ru2−Ru3 edge of the cluster. The positively charged 2-trimethylammonioethenyl ligand, the CH=CH-($^+$NMe$_3$) ligand, is formally derived from a 2-trimethylammonioethenide, $^-$CH=CH($^+$NMe$_3$), zwitterion that has a positive charge on the nitrogen atom and a negative charge on the terminal enyl carbon atom. Upon coordination, the negative charge on the carbon atom is formally transferred to the coordinated metal atom, and the complex overall becomes a zwitterion with the negative charge on a metal atom (see below). The CH=CH($^+$NMe$_3$) ligand is similar to the one recently observed in the hexaruthenium compound **1**.[10] It is coordinated to two metal atoms in the bridging σ + π coordination fashion that is well established for bridging alkenyl ligands.[16] The C1−C2 double bond is π-bonded to Ru(2), with Ru2−C1 = 2.210(2) Å and Ru2−C2 = 2.243(2) Å, and σ-bonded to Ru(3), with Ru3−C1 = 2.031(2) Å. The C(1)−C(2) bond length, 1.388(3) Å, is similar in length to that of the CH=CH($^+$NMe$_3$) ligand found in **1** (1.427(19) Å). Compound **8** is formally a zwitterion with a positive charge located on the nitrogen atom. The negative charge would be formally located on Ru(3), but this negative charge will certainly be delocalized via molecular orbitals that spread across the entire Ru$_5$ cluster.[17]

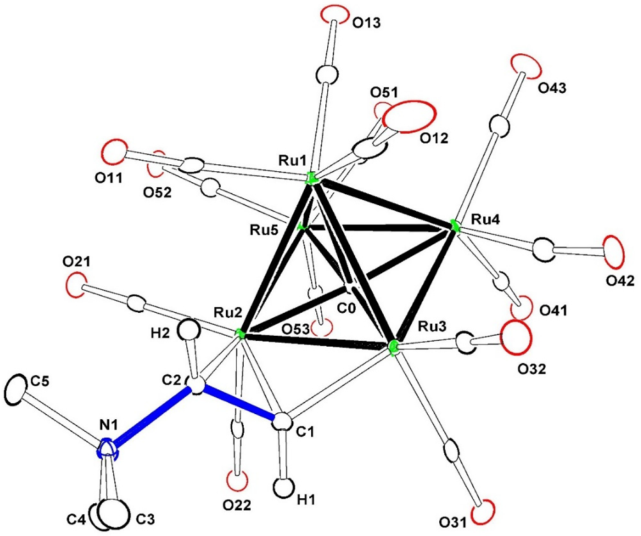


Figure 1. ORTEP diagram of the molecular structure of Ru$_5$(μ_5-C)(CO)$_{13}$[μ-η^2-CHCH(NMe$_3$)], **8**, showing 40% thermal ellipsoid probability. Hydrogen atoms on the methyl groups have been omitted for clarity. Selected interatomic bond distances (Å) are as follows: Ru1−Ru2 = 2.8338(3), Ru1−Ru3 = 2.8903(3), Ru1−Ru4 = 2.8026(3), Ru1−Ru5 = 2.7795(3), Ru2−Ru3 = 2.7047(3), Ru2−Ru5 = 2.8795(3), Ru3−Ru4 = 2.8690(3), Ru4−Ru5 = 2.8859(3), Ru1−C0 = 2.134(2), Ru2−C0 = 2.024(2), Ru3−C0 = 2.022(2), Ru4−C0 = 1.993(2), Ru5−C0 = 2.004(2), Ru2−C1 = 2.210(2), Ru2−C2 = 2.243(2), Ru3−C1 = 2.031(2), C1−C2 = 1.388(3), C2−N1 = 1.516(3).

The CH = CH($^+$NMe$_3$) ligand in **8** exhibits three proton resonances in the ^{1}H NMR spectrum: a pair of doublets at 11.23 and 5.87 ppm, ^{3}J$_{\text{H-H}}$ = 10.0 Hz, due to the protons on C(1) and C(2), respectively. The latter resonance shows some small unresolved coupling from the nitrogen atom N(1). The *N*-methyl resonance, a singlet at 3.64 ppm, is shifted downfield due to the positive charge on the nitrogen atom. The ^{13}C NMR spectrum of **8** exhibits three resonances for the CH=CH$^+$NMe$_3$ ligand, i.e., 170.41 ppm for C(1), 94.80 ppm for C(2), and 54.65 ppm for the methyl groups; the latter is a 1:1:1 triplet, $^1J_{\text{C-N}}$ = 16 Hz, due to coupling to the nitrogen atom. The bridging CH=CH$^+$NMe$_3$ ligand in **8** serves formally as a four-electron donor; thus, the complex overall achieves a total of 74 cluster valence electrons which is in accord with the observation of a square-pyramidal-shaped cluster of five metal atoms.[17]

In recent studies, we have synthesized the pentaruthenium complex **6** from the reaction of **5** with DMF.[12] Compound **6** contains an opened, wing-tip bridged, butterfly cluster of five ruthenium atoms with a dimethylformamido ligand bridging one of the nonbonded pairs of metal atoms. For comparisons with the reactivity of **5**, the reaction of **6** with C_2H_2 in the presence of Me_3NO at 25 °C was investigated. This reaction provided two new compounds $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)][\eta^1\text{-}E\text{-}CH{=}CH(NMe_3)](\mu\text{-}H)$, **9** (48% yield), and $Ru_5(\mu_5\text{-}C)(CO)_{12}[\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)][\mu\text{-}\eta^2\text{-}CHCH(NMe_3)](\mu\text{-}H)$, **10** (6.4% yield). Compound **9** was characterized by IR, ^1H NMR, and ^{13}C NMR analyses, single-crystal X-ray diffraction analyses, and elemental analyses. An ORTEP diagram of the molecular structure of compound **9** is shown in Figure 2. The metal cluster of compound **9** is structurally similar to that of its parent **6**, having an open, wing-tip bridged butterfly cluster of metal atoms with a carbido ligand in the center and a dimethylformamido ligand bridging one of the nonbonded pairs of metal atoms. Compound **9** contains 13 linear terminal carbonyl ligands distributed as shown in Figure 2, but the most interesting ligand in **9** is a 2-trimethylammonioethenyl ligand, $\eta^1\text{-}E\text{-}CH{=}CH(^+NMe_3)$, that is terminally coordinated to the wing-tip bridged Ru atom, Ru(4), in the equatorial coordination site that is *trans* to the metal atom Ru(3). NMe_3 was not added to this reaction, so the NMe_3 group that is present in the $CH{=}CH(^+NMe_3)$ ligand is believed to be derived solely from the Me_3NO after it reacted with a CO ligand in **6** to form CO_2 and NMe_3. The Ru4−C4 distance is 2.074(3) Å in length. There is *E*-stereochemistry at the C=C double bond, where C4−C5 = 1.286(5) Å, and both distances are slightly shorter than the corresponding distances, Ru−C = 2.097(2) Å and C1−C2 = 1.306(3) Å, in the terminally coordinated $E\text{-}CH{=}CH(^+NMe_3)$ ligand in compound **2**.[10] The ethenyl hydrogen atoms appear as two deshielded doublets at δ = 8.25 and 5.90 with a large coupling constant, $^3J_{H-H}$ = 14 Hz, that is consistent with the observed *E*-stereochemistry at the C=C double bond. There is a bridging hydrido ligand H1 on the Ru(1)−Ru(2) bond that exhibits the expected high-field resonance shift, δ = −22.07. The alkenyl carbon atoms, C4 and C5, exhibit significant shifts for their resonances in the ^{13}C NMR spectrum, δ = 141.95 and 133.05, respectively, relative to those observed for the carbon atoms of the bridging $CH{=}CH(^+NMe_3)$ ligand in **8**. The terminally coordinated $CH{=}CH(^+NMe_3)$ ligand in **9** serves as a 2-electron donor and the Ru_5 cluster achieves a 76-electron configuration as expected for the observed open-square pyramidal structure of metal atoms.[17] Compound **9** is formally a zwitterion with a positive charge on the nitrogen atom N(2) and a negative charge that is formally located on Ru(4).

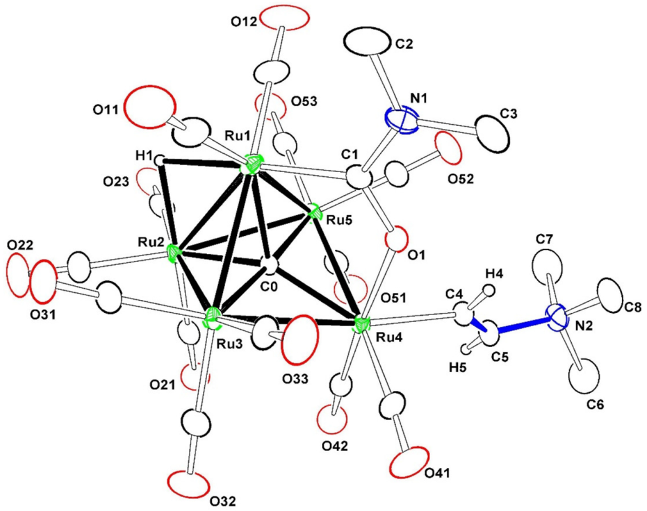


Figure 2. ORTEP diagram of the molecular structure of $Ru_5(\mu_5\text{-}C)(CO)_{13}(\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)[\eta^1\text{-}E\text{-}CH{=}CH(NMe_3)](\mu\text{-}H)$, **9**, showing 20% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follows: Ru1−Ru3 = 2.8176(4), Ru1−Ru5 = 2.8275(4), Ru1−Ru2 = 2.9580(4), Ru2−Ru5 = 2.8635(4), Ru2−Ru3 = 2.8479(4), Ru3−Ru4 = 2.9145(4), Ru4−Ru5 = 2.9087(4), Ru1−H1 = 2.07(4), Ru2−H1 = 2.01(4), Ru4−C4 = 2.074(3), Ru1−C1 = 2.089(4), Ru4−O1 = 2.114(2), C1−O1 = 1.276(4), C4−C5 = 1.286(5), C5−N2 = 1.503(5), Ru1−C0 = 2.071(3), Ru2−C0 = 2.101(3), Ru3−C0 = 1.982(3), Ru4−C0 = 2.068(3), Ru5−C0 = 1.979(3).

The coproduct **10** has been characterized by IR, ^1H NMR, single-crystal X-ray diffraction, and elemental analyses. An ORTEP diagram of the molecular structure of compound **10** is shown in Figure 3. The metal cluster of compound **10** is structurally similar to that of its parent **6** having an open, wing-tip bridged butterfly cluster of metal atoms with a carbido ligand in the center and a dimethylformamido ligand bridging one of the nonbonded pairs of metal atoms. Compound **10** contains only 12 CO ligands and one 2-trimethylammonioethenyl ligand, $CH{=}CH(^+NMe_3)$, that is a $\eta^2\text{-}\sigma + \pi$

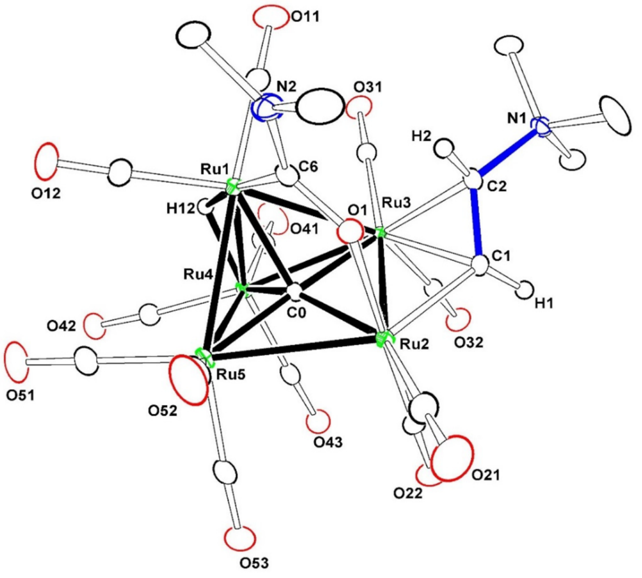


Figure 3. ORTEP diagram of the molecular structure of $Ru_5(\mu_5\text{-}C)(CO)_{12}[\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)][\mu\text{-}\eta^2\text{-}CH{=}CH(NMe_3)](\mu\text{-}H)$, **10**, showing 40% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follows: Ru1−Ru3 = 2.88374(18), Ru1−Ru4 = 2.86257(19), Ru1−Ru5 = 2.85533(18), Ru2−Ru3 = 2.74363(17), Ru2−Ru5 = 2.93192(19), Ru3−Ru4 = 2.84052(19), Ru4−Ru5 = 2.91228(19), Ru1−C0 = 2.0448(15), Ru2−C0 = 2.0675(15), Ru3−C0 = 1.9798(15), Ru4−C0 = 2.0898(15), Ru5−C0 = 1.9625(15), Ru1−C6 = 2.0661(17), O1−C6 = 1.2814(19), Ru2−O1 = 2.1135(11), Ru2−C1 = 2.0580(15), Ru3−C1 = 2.2176(15), Ru3−C2 = 2.2449(15), C1−C2 = 1.394(2), N1−C2 = 1.520(2).

coordinated, bridging ligand across the metal atoms Ru(2) and Ru(3). The Ru−C bond distances to the coordinated double bond C1 and C2, Ru2−C1 = 2.0580(15) Å, Ru3−C1 = 2.2176(15) Å, and Ru3−C2 = 2.2449(15) Å, are very similar to those in **8**. The coordinated double bond in **10**, C1−C2 = 1.394(2) Å, is significantly longer than the uncoordinated C=C double bond in **9**, of 1.280(5) Å, but it is very similar to the coordinated C=C double bond distance in **8**, of 1.388(3) Å. The ethenyl hydrogen atoms appear as two deshielded doublets at δ = 10.57 ($^3J_{H-H}$ = 8.8 Hz) and 4.46 ($^3J_{H-H}$ = 8.8 Hz). There is a formal positive charge on the nitrogen atom N(1), and the resonance of the *N*-methyl groups is appropriately deshielded, at δ = 3.51. There is a bridging hydrido ligand H(12) on the Ru(1)−Ru(4) bond that exhibits the usual high-field resonance shift of δ = −21.44.

Compound **10** is formally a zwitterion with a positive charge on the nitrogen atom N(1) and a negative charge that is formally on Ru(2), but this negative charge may delocalize between Ru(2) and Ru(3). The bridging CH=CH($^+$NMe$_3$) ligand in **10** serves as a 4-electron donor, and the cluster achieves a 76-electron configuration as expected for the observed open-square pyramidal structure of metal atoms.[17]

Compound **9** was converted to **8** (73% yield) by thermal elimination of the dimethylformamido ligand and the hydrido ligand as DMF when solutions of **9** were heated to 60 °C. Compound **9** can also be converted to **10** in a good yield (41%) by decarbonylation with Me$_3$NO at 25 °C. Small amounts of **8** (14%) were also formed in this reaction. Interestingly, **10** was easily converted to **8** in a good yield (50%) by very mild heating (50 °C/13 h) of solutions. It thus appears that **10** is an intermediate en route to **8** from **9**. Compound **10** was converted back to **9** (36% yield) by addition of CO at 35 °C, together with formation of the new compound Ru$_5$(μ_5-C)(CO)$_{15}$[η^1-*E*-CH=CH(NMe$_3$)], **13** (50% yield), which is a product of the addition of CO to **8** (see below).

Because of the interesting results obtained from the reactions of **6** with C$_2$H$_2$, we also investigated the reaction of compound **7** with C$_2$H$_2$ and Me$_3$NO. Compound **7** was first reported by Johnson and Lewis many years ago,[11] but it has not yet been structurally characterized. For the purpose of knowing its exact structure and for comparisons with the products that we have obtained from it (see below), we have performed a single-crystal X-ray diffraction analysis of **7**, which we have included in this report. An ORTEP diagram of the molecular structure of compound **7** is shown in Figure 4. The metal cluster of **7** is structurally similar to that of **6** and **9** having an open, wing-tip bridged butterfly cluster of metal atoms with a carbido ligand in the center. The hydrido ligand bridges the hinge bond of the Ru$_4$ butterfly, Ru(1)−Ru(2), and the chloro ligand Cl(1) is a terminally coordinated ligand in an axial position on the wing-tip bridging metal atom Ru(4), i.e., Ru(4)−Cl(1) = 2.4211(9) Å. Compound **7** contains 15 linear terminal carbonyl ligands distributed as shown in Figure 4.

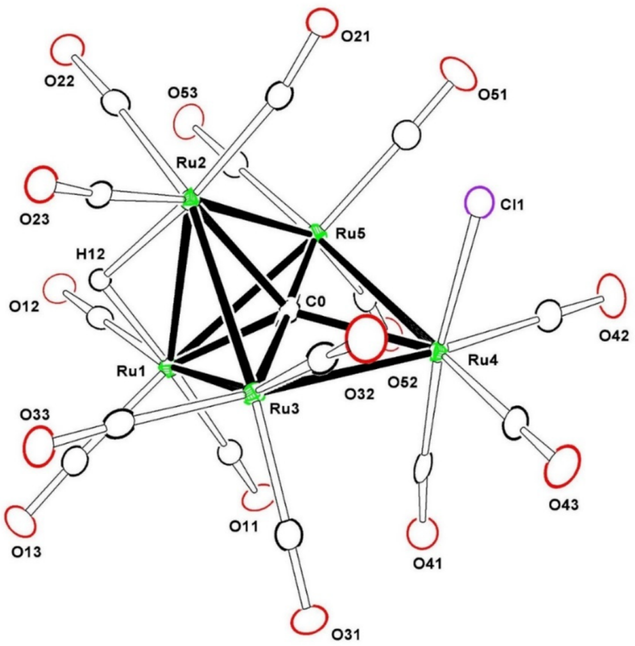


Figure 4. ORTEP diagram of the molecular structure of Ru$_5$(μ_5-C)(CO)$_{15}$Cl(μ-H), **7**, showing 40% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follows: Ru1−Ru2 = 2.8349(4), Ru1−Ru3 = 2.8757(4), Ru1−Ru5 = 2.8379(4), Ru2−Ru3 = 2.8601(4), Ru2−Ru5 = 2.8529(4), Ru3−Ru4 = 2.8909(4), Ru4−Ru5 = 2.9429(4), Ru1−C0 = 2.115(4), Ru2−C0 = 2.106(3), Ru3−C0 = 1.961(4), Ru4−C0 = 2.117(4), Ru5−C0 = 1.960(4), Ru4−Cl1 = 2.4211(9).

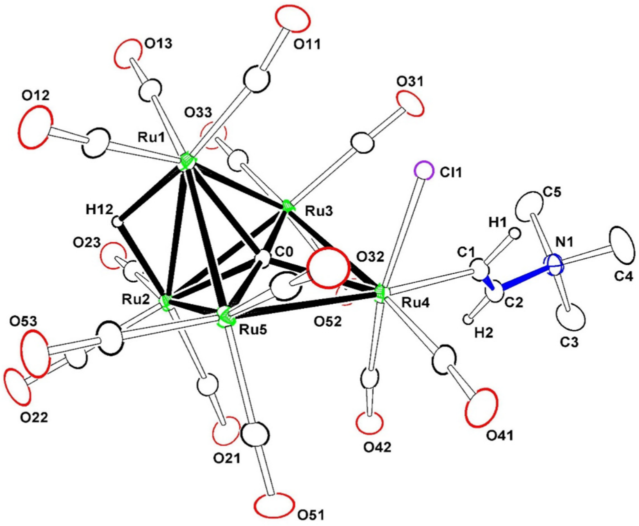


Figure 5. ORTEP diagram of the molecular structure of Ru$_5$(μ_5-C)(CO)$_{14}$[η^1-*E*-CH=CH(NMe$_3$)]Cl(μ-H), **11**, showing 15% thermal ellipsoid probability. Methyl hydrogen atoms have been omitted for clarity. Selected interatomic bond distances (Å) are as follows: Ru1−Ru2 = 2.8350(4), Ru1−Ru3 = 2.8413(4), Ru1−Ru5 = 2.8658(4), Ru2−Ru3 = 2.8447(3), Ru2−Ru5 = 2.8521(4), Ru3−Ru4 = 2.9626(3), Ru4−Ru5 = 2.9530(3), Ru1−C0 = 2.122(3), Ru2−C0 = 2.127(3), Ru3−C0 = 1.960(3), Ru4−C0 = 2.141(3), Ru5−C0 = 1.964(3), Ru1−H12 = 1.74(4), Ru2−H12 = 1.78(4), Ru4−Cl1 = 2.4612(10), Ru4−C1 = 2.091(3), C1−C2 = 1.292(5), C2−N1 = 1.514(4).

The reaction of **7** with C$_2$H$_2$ at 1 atm in the presence of Me$_3$NO for 15 min in CH$_2$Cl$_2$ solvent yielded two products, namely, compound **8** (9% yield) and the new compound Ru$_5$(μ_5-C)(CO)$_{14}$Cl[η^1-*E*-CH=CH(NMe$_3$)](μ-H), **11** (56% yield). Compound **11** was characterized by IR, ^{1}H NMR, single-crystal X-ray diffraction, and mass spectral analyses. An ORTEP diagram of the molecular structure of compound **11** is shown in Figure 5. The metal cluster of compound **11** is structurally similar to that of **6**, **9**, and **10**, having an open, wing-tip bridged butterfly cluster of metal atoms with a carbido ligand in the center. Compound **11** contains fourteen linear, terminal carbonyl ligands and one 2-trimethylammonioethenyl, CH═CH($^+$NMe$_3$), ligand that is terminally coordinated to the wing-tip bridging metal atom, Ru(4), with Ru4−C1 = 2.091(3) Å in an equatorial coordination site. The C═C double bond distance, C1−C2 = 1.292(5) Å, is very similar to that found for the terminally coordinated C(H)═C(H)$^+$NMe$_3$ ligand in **9**. The chloro ligand, Cl(1), is axially coordinated to Ru(4), with Ru(4)−Cl(1) = 2.4612(10) Å. The ^{1}H NMR spectrum of **11** exhibits two doublets for the ethenyl hydrogen atoms, i.e., δ = 8.51 and 6.17, with a large coupling constant, $^3J_{H-H}$ = 14.4 Hz, that is consistent with the structurally observed *E*-stereochemistry. The bridging hydrido ligand H(12) exhibits the usual high-field resonance shift of δ = −22.53.

Compound **11** is also a zwitterion with a positive charge on atom N(1) and a formal negative charge on atom Ru(4). The C(H)═C(H)$^+$NMe$_3$ ligand in **11** serves as a 2-electron donor and the cluster achieves a 76-electron configuration as expected for the observed open-square pyramidal structure of metal atoms.[17] When heated to 48 °C for 18 h, compound **11** was converted to compound **8** in 32% yield by elimination of CO, a reductive elimination of HCl, formation of a metal−metal bond between that atoms Ru(1) and Ru(4), and conversion of the CH═CH($^+$NMe$_3$) ligand into the $\sigma + \pi$ coordinated, bridging ligand.

Treatment of compound **8** with CO at 25 °C yielded two new products, namely, Ru$_5$(C)(CO)$_{14}$[η^1-*E*-CH═CH-(NMe$_3$)], **12**, and Ru$_5$(C)(CO)$_{15}$[η^1-*E*-CH═CH(NMe$_3$)], **13**, by the addition of one and two equivalents of CO. Compound **12** is an unstable intermediate en route to **13**. It can be isolated in very small amounts by allowing filtered solutions of the reaction mixture to evaporate in a vial in the open air in a fume hood. Small red plates of **12** will form on the walls of the vial. Solutions of **12** eventually convert back fully to **8** by loss of CO, but the crystals are more stable and can be analyzed by single-crystal X-ray diffraction analysis at low temperature (see below). Compound **12** adds CO to yield **13** at room temperature. Compound **13** is stable in solution only when maintained under an atmosphere of CO. Compound **13** can be obtained as pure red crystals in a good yield (87%) by filtering the reaction solutions and then carefully removing the reaction solvent under a flow of CO in a fume hood. Solutions of **13** slowly lose CO and convert back to **8** via **12** under an atmosphere of nitrogen. Red crystals of **13** were also suitable for single-crystal X-ray diffraction analysis.

ORTEP diagrams of the molecular structures of compounds **12** and **13** are shown in Figures 6 and 7, respectively. The metal cluster of compound **12** has the shape of a square pyramid like **8** with a carbido ligand in the center of the square base. There is a terminally coordinated C(H)═C(H)$^+$NMe$_3$ ligand in an axial position on the basal metal atom Ru(1), where Ru1−C1 = 2.041(11) Å. The C═C double bond is short, at C1−C2 = 1.290(15) Å, and has an *E*-conformation as observed for the terminal CH═CH($^+$NMe$_3$) ligands in **9** and **11**. Compound **12** contains 14 linear, terminal carbonyl ligands distributed about the cluster as shown in Figure 6. The apical−basal Ru−Ru bond, Ru1−Ru5 = 2.9034(13) Å, *trans* to the CH═CH($^+$NMe$_3$) ligand is significantly longer than the three other apical−basal Ru−Ru bonds, i.e., Ru2−Ru5 = 2.8487(13) Å, Ru3−Ru5 = 2.7771(13) Å, and Ru4−Ru5 = 2.8068(12) Å, which suggests that the CH═CH($^+$NMe$_3$) ligand has a stronger *trans* effect than a CO ligand.

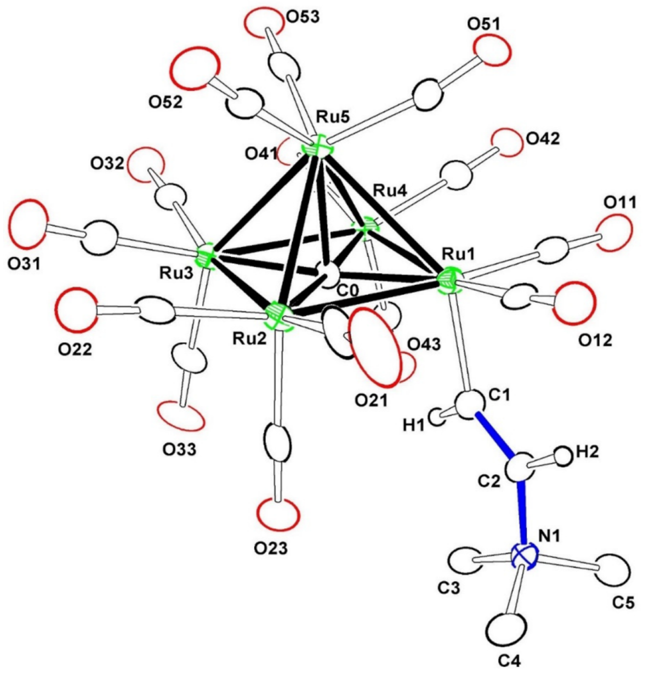


Figure 6. ORTEP diagram of the molecular structure of Ru$_5$(μ_5-C)(CO)$_{14}$[η^1-*E*-CH═CH(NMe$_3$)], **12**, showing 35% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follows: Ru1−Ru2 = 2.8548(14), Ru1−Ru4 = 2.8737(13), Ru1−Ru5 = 2.9034(13), Ru2−Ru3 = 2.8472(13), Ru2−Ru5 = 2.8487(13), Ru3−Ru4 = 2.8616(14), Ru3−Ru5 = 2.7771(13), Ru4−Ru5 = 2.8068(12), Ru1−C0 = 2.037(11), Ru2−C0 = 2.039(10), Ru3−C0 = 2.053(11), Ru4−C0 = 1.970(10), Ru5−C0 = 2.090(11), Ru1−C1 = 2.041(11), C1−C2 = 1.290(15), N1−C2 = 1.505(14).

The ^{1}H NMR spectrum of **12** exhibits two doublets for the ethenyl hydrogen atoms, δ = 7.51 and 5.47, with a large coupling constant, $^3J_{H-H}$ = 12.9 Hz, as expected for the *E*-stereochemistry observed in the solid-state structure. Compound **12** is also a zwitterion with a positive charge on the nitrogen atom N(1) and a negative charge formally located on Ru(1), but this negative charge should delocalize across the Ru$_5$ cluster. The metal cluster of compound **12** contains a total of 74 valence electrons which is consistent with its square-pyramidal structure.

The structure of **13** consists of an opened square-pyramidal cluster (a wing-tipped bridged butterfly cluster) of five Ru atoms similar to that observed for compounds **9**, **10**, and **11**. There is a terminally coordinated CH═CH($^+$NMe$_3$) ligand in an axial position on the wing-tip, bridging metal atom Ru(4), where Ru4−C1 = 2.1183(17) Å. This distance is slightly longer than the corresponding distances in **9**, **11**, and **12**. The C═C double bond length, C1−C2 = 1.315(2) Å, is similar to that observed for the terminal CH═CH($^+$NMe$_3$) ligands in compounds **9**, **11**, and **12**. There are a number of examples of nucleophile-induced openings of square-pyramidal Ru$_5$ cluster complexes by the addition of donor ligands to a basal-positioned metal atom.[11,18] The ethenyl hydrogen atoms on C(1) and C(2) in **13** appear as two mutually coupled, deshielded doublets at δ = 6.01 and 5.59 with a large coupling constant, $^3J_{H-H}$ = 15.2 Hz, that is consistent with the *E*-stereochemistry observed in the solid state. Compound **13** is a zwitterion with a positive charge on the nitrogen atom N(1) and a formal negative charge concentrated on the metal atom Ru(4). The metal cluster of compound **13** contains a total of

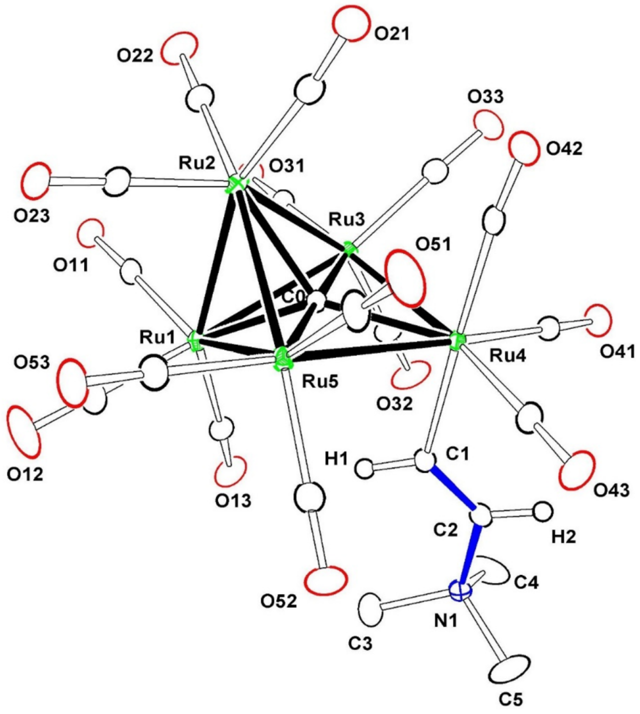


Figure 7. ORTEP diagram of the molecular structure of $Ru_5(\mu_5\text{-}C)(CO)_{15}[\eta^1\text{-}E\text{-}CH{=}CH(NMe_3)]$, **13**, showing 40% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follows: Ru1−Ru2 = 2.7060(2), Ru1−Ru3 = 2.8718(2), Ru1−Ru5 = 2.8928(2), Ru2−Ru3 = 2.8793(2), Ru2−Ru5 = 2.8716(2), Ru3−Ru4 = 2.8996(2), Ru4−Ru5 = 2.90372(19), Ru1−C0 = 2.0917(15), Ru2−C0 = 2.0959(15), Ru3−C0 = 1.9601(15), Ru4−C0 = 2.1580(15), Ru5−C0 = 1.9617(15), Ru4−C1 = 2.1183(17), C1−C2 = 1.315(2), N1−C2 = 1.504(2).

76 valence electrons which is consistent with its observed open structure.

The reaction of **6** with methyl propiolate, $HC{\equiv}C(CO_2Me)$, and Me_3NO in CH_2Cl_2 at 25 °C yielded the new compound $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)][\eta^1\text{-}E\text{-}(MeO_2C)C{=}CH(NMe_3)](\mu\text{-}H)$, **14**, in 31% yield. Compound **14** was characterized by IR and ^1H NMR spectroscopy and structurally by single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of compound **14** is shown in Figure 8. Compound **14** is very similar to that of **9** having a wing-tipped bridged butterfly Ru_5 cluster of metal atoms and a bridging dimethylformamido ligand, but it has a terminally coordinated, 1-methoxycarbonyl, 2-trimethylammonioethenyl ligand, $\eta^1\text{-}E\text{-}(1\text{-}MeO_2C)C{=}C(H)(2\text{-}^+NMe_3)$, in an equatorial coordination site on Ru(1) in the location of the 2-trimethylammonioethenyl ligand found in **9**. The Ru(1)−C(2) distance of 2.1401(18) Å is slightly longer than the corresponding Ru−C bond in **9** of 2.097(2) Å. The C=C double bond in the $(MeO_2C)C{=}C(H)^+NMe_3$ ligand has an *E*-conformation at the double bond, and its bond length, C1−C2 = 1.320(3) Å, is similar to that observed in compounds **9**, **11**, **12**, and **13**.

The resonances of the single ethenyl hydrogen atom on C(1) and the trimethylammonio methyl groups in **14** are deshielded at 5.61 and 3.23 ppm, respectively, in the ^1H NMR spectrum. A hydrido ligand bridges the Ru(2)−Ru(3) bond in **14** and exhibits the expected high-field resonance shift at −22.07 ppm. Compound **14** is a zwitterion with a positive charge on the nitrogen atom N2 and a formal negative charge on the metal atom Ru(1). The metal cluster of compound **14** contains a total of 76 valence electrons which is consistent with its observed open structure.

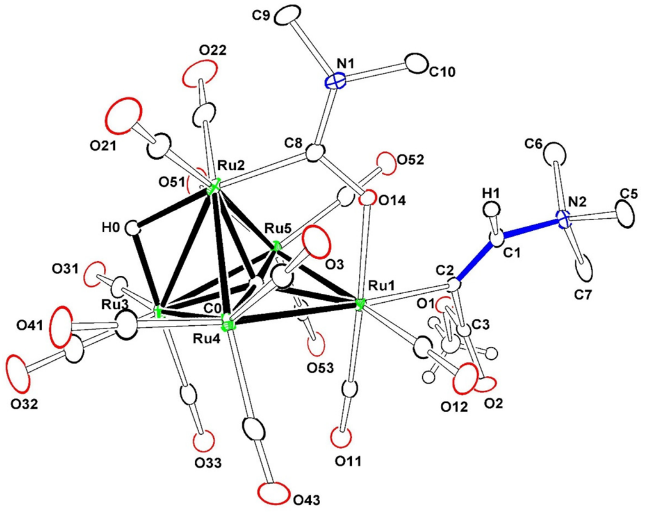


Figure 8. ORTEP diagram of the molecular structure of $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)][\eta^1\text{-}E\text{-}1\text{-}(MeO_2C)C{=}C(H)(2\text{-}NMe_3)](\mu\text{-}H)$, **14**, showing 40% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follows: Ru1−Ru4 = 2.8817(2), Ru1−Ru5 = 2.9036(2), Ru2−Ru3 = 2.8782(2), Ru2−Ru4 = 2.8157(2), Ru2−Ru5 = 2.8317(2), Ru3−Ru4 = 2.8734(2), Ru3−Ru5 = 2.8613(2), Ru1−C0 = 2.0622(18), Ru2−C0 = 2.0545(19), Ru3−C0 = 2.1076(18), Ru4−C0 = 1.9890(18), Ru5−C0 = 1.9705(18), Ru2−C8 = 2.0762(19), C8−N1 = 1.351(2), C8−O14 = 1.285(2), Ru1−O14 = 2.1214(13), Ru1−C2 = 2.1401(18), C1−C2 = 1.320(3), C1−N2 = 1.502(2), N2−C5 = 1.502(3), N2−C6 = 1.491(3), N2−C7 = 1.498(3), C2−C3 = 1.479(3).

When a solution of **14** dissolved in benzene-d_6 was heated to 80 °C for 4 h, two products were formed in low yields, namely, a new compound $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}O{=}C(NMe_2)][\mu\text{-}\eta^2\text{-}(MeO_2C)HC{=}CH]$, **15** (5% yield), and the known compound $Ru_5(\mu_5\text{-}C)(CO)_{13}[\mu\text{-}\eta^2\text{-}O{=}CNMe_2](HNMe_2)(\mu\text{-}H)$, **16** (8% yield).[12] An ORTEP diagram of the molecular structure of compound **15** is shown in Figure 9. Compound **15** was formed from **14** by elimination of the NMe_3 grouping from the $(MeO_2C)C{=}C(H)(^+NMe_3)$ ligand. The compound contains an open Ru_5 cluster with an approximately trigonal bipyramidal carbido ligand in the center. There is an η^2-bridging dimethylformamido ligand across the open Ru(1)−Ru(2) edge of the cluster, and there is a bridging η^2-$(CH_3O_2C)(H)C{=}C(H)$ ligand across the open Ru(1)−Ru(4) edge of the cluster. The carbonyl oxygen atom O(2) of the methoxycarbonyl group asymmetrically bridges the two metal atoms Ru(1) and Ru(4), where Ru1−O2 = 2.396(4) Å and Ru4−O2 = 2.199(4) Å. The carbonyl C—O bond is short, at C(6)−O2 = 1.245(8) Å, indicating that it still contains considerable double bond character. There is a hydrogen atom on C(5) that was presumably derived from the bridging hydrido ligand in **14** by a C−H bond-forming step. The C4−C5 bond is also short, at 1.364(10) Å, and is formally a C=C double bond. The hydrogen atoms on C(4) and C(5) are significantly deshielded in the ^1H NMR spectrum, where δ = 11.41 and 6.37 with a coupling constant, $^3J_{H-H}$ = 8.4 Hz, that is consistent with the observed *Z*-conformation at the double bond. Compound **15** contains a total of 78 cluster valence electrons which is in accord with an electron-precise metal cluster of five metal atoms (n) having six metal−metal bonds

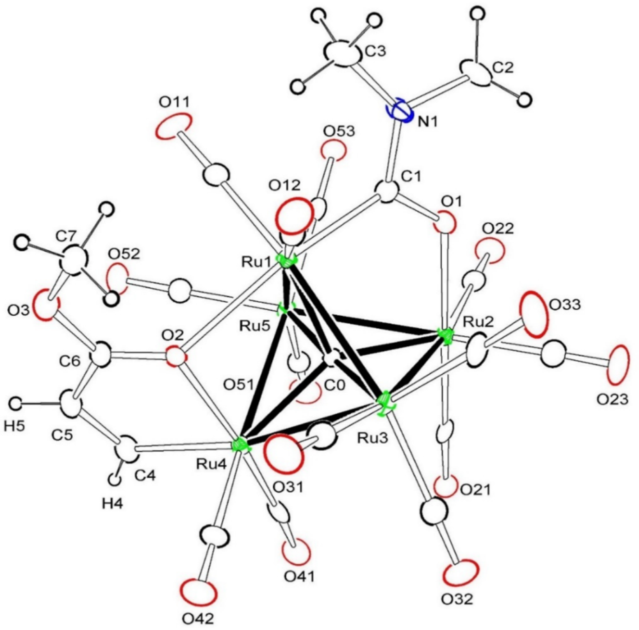


Figure 9. ORTEP diagram of the molecular structure of $Ru_5(C)(CO)_{13}(\mu\text{-}\eta^2\text{-}O{=}CNMe_2)[\mu\text{-}\eta^2\text{-}Z\text{-}(MeO_2C)(H)C{=}C(H)]$, **15**, showing 30% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follows: Ru1−Ru3 = 2.8591(7), Ru1−Ru5 = 2.8493(7), Ru2−Ru3 = 2.8453(7), Ru2−Ru5 = 2.8516(7), Ru3−Ru4 = 2.8959(7), Ru4−Ru5 = 2.9195(7), Ru1−C0 = 2.106(6), Ru2−C0 = 2.108(6), Ru3−C0 = 1.950(6), Ru4−C0 = 2.098(6), Ru5−C0 = 1.960(6), Ru1−C1 = 2.005(6), C1−O1 = 1.261(8), C1−N1 = 1.349(8), Ru2−O1 = 2.107(4), Ru1−O2 = 2.396(4), Ru4−O2 = 2.199(4), Ru4−C4 = 2.041(7), C4−C5 = 1.364(10), C5−C6 = 1.419(10), O2−C6 = 1.245(8), O3−C6 = 1.323(8), O3−C7 = 1.448(8).

(m), according to the formula $18n{-}6(2m)$. The side product **16** was obtained previously by the thermal decomposition of **6** which generates Me_2NH by decarbonylation of the dimethylformamido ligand.[12]

■ DISCUSSION

A summary of our studies of the reactions of **5**, **6**, and **7** with ethyne in the presence of Me_3NO is shown in Scheme 1.

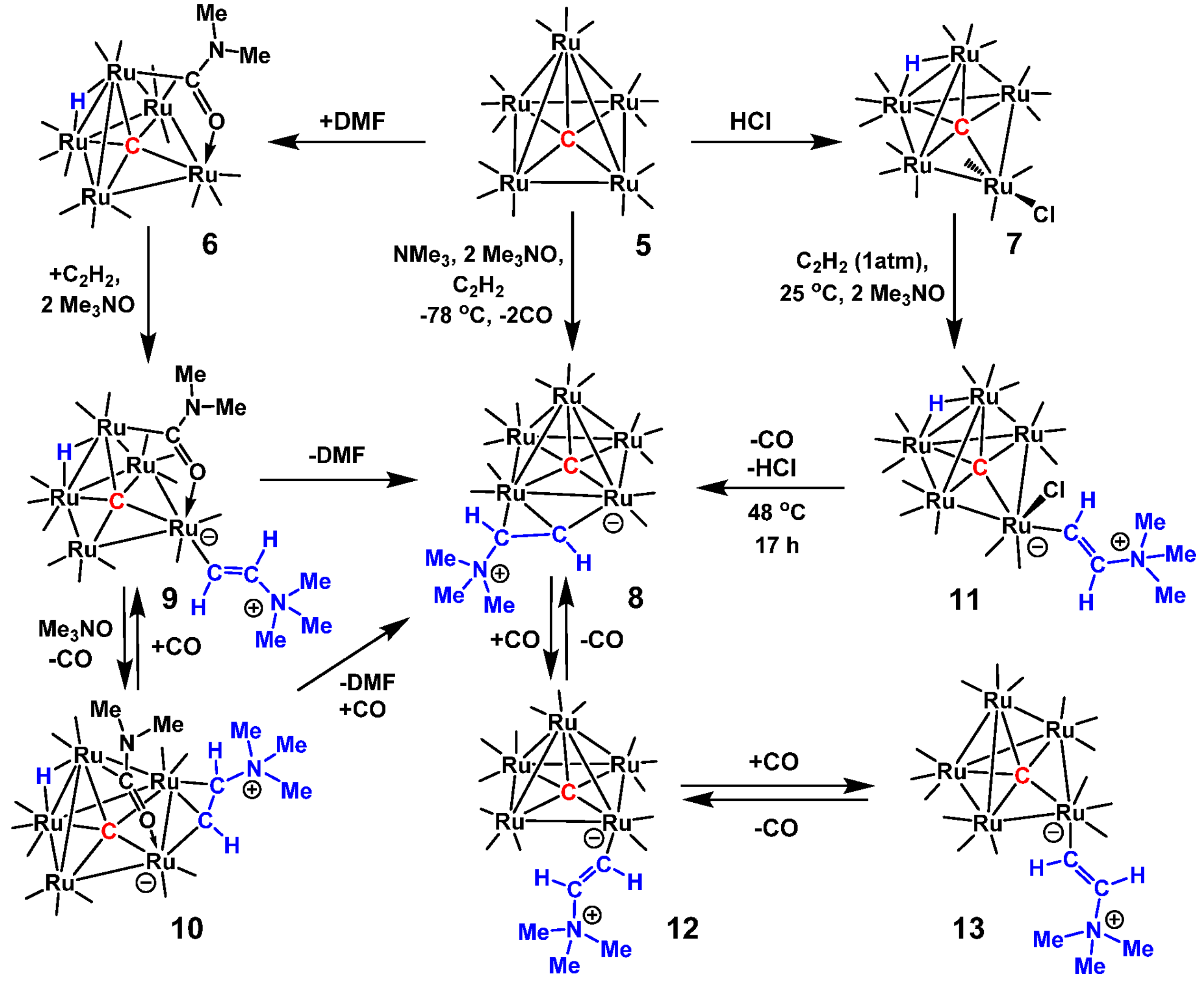
The reaction of the square-pyramidal Ru_5 cluster complex **5** with the decarbonylation agent Me_3NO in the presence C_2H_2 and NMe_3 provided a low yield of the square-pyramidal Ru_5 cluster complex **8** containing a 2-trimethylammonioethenyl ligand, $CH{=}CH^+NMe_3$, that bridges a basal edge of a square-pyramidal Ru_5 cluster. Further investigations showed that the open cluster complexes **6** and **7** provided good yields of open Ru_5 cluster complexes **9** and **11**, respectively, containing terminally coordinated, 2-trimethylammonioethenyl ligands having *E*-stereochemistry located on the wing-tip bridging ruthenium atom of the Ru_4C portion of clusters. Compounds **9** and **11** were both converted to **8** thermally in good yields by the elimination of DMF from **9** and CO and HCl from **11**. An important intermediate, **10**, was observed in the conversion of **9** to **8**. Compound **10** was formed from **9** by a Me_3NO-induced decarbonylation with a conversion of the terminally coordinated $\eta^1\text{-}CH{=}CH^+NMe_3$ ligand into a η^2-bridging ligand by coordination of its C=C double bond, a prerequisite to the formation of **8**. Compound **10** reacted with CO to regenerate **9** in 36% yield at 35 °C in 24 h by adding one CO ligand and by converting the $\eta^2\text{-}CH{=}CH^+NMe_3$ ligand back into a terminal-coordinated $\eta^1\text{-}CH{=}CH^+NMe_3$ ligand. Compound **13** was also formed in 50% yield in this reaction. Compound **13** was presumably formed by conversion of some of **9** to **8** by loss of DMF (also observed as a reaction product) and subsequent addition of CO to yield **13** via **12** (see below). It was observed previously that the bridging η^2-trimethylammonioethenyl ligand in **1** could be converted to a terminally coordinated η^2-trimethylammonioethenyl ligand in complex **2** by the addition of CO to **1** at 25 °C, as shown in eq 1.[10]

It was also observed in a separate reaction that the η^2-bridging $CH{=}CH^+NMe_3$ ligand in **8** was converted into a terminally coordinated, $\eta^1\text{-}CH{=}CH^+NMe_3$ ligand by CO addition; in fact, two CO addition products were obtained. The first product **12** was formed by the addition of only one equivalent of CO to **8**, and it consists of a square-pyramidal cluster of five ruthenium atoms with a terminally coordinated $\eta^1\text{-}CH{=}CH^+NMe_3$ ligand bonded to one of the Ru atoms in the base of the square pyramid. The second CO addition product **13** was formed by a cluster opening addition of CO to the first one, **12**, by cleavage of the axial−basal Ru−Ru bond to the $\eta^1\text{-}CH{=}CH^+NMe_3$-substituted Ru atom. Compounds **12** and **13** are both unstable in solution in the absence of a CO atmosphere, and they both revert back to **8** in high yield by loss of CO.

A summary of our reactions of **6** with methyl propiolate, $HC{\equiv}C(CO_2Me)$, is shown schematically in Scheme 2. The reaction of **6** with a combination of methyl propiolate and Me_3NO yielded the complex **14**, containing a terminally coordinated, 2-trimethylammonio(1-methyoxycarbonyl)-ethenyl, $\eta^1\text{-}E\text{-}1\text{-}(MeO_2C)C{=}C(H)(2\text{-}^+NMe_3)$, ligand. The $\eta^1\text{-}E\text{-}(1\text{-}CO_2Me)C{=}C(H)(2\text{-}^+NMe_3)$ ligand in **14** is structurally similar to the $\eta^2\text{-}E\text{-}1\text{-}(MeO_2C)C{=}C(H)(2\text{-}^+NMe_3)$ ligand found in the complex $Ru_6C(CO)_{16}[\eta^2\text{-}E\text{-}(1\text{-}(MeO_2C)C{=}C(H)(2\text{-}^+NMe_3)]$, **17**,[10] which contains an uncoordinated C=C double bond of similar length, of 1.304(7) Å. Note that the $(MeO_2C)C{=}C(H)(2\text{-}^+NMe_3)$ ligands in **14** and **17** were both formed by the addition of the NMe_3 molecule to the unsubstituted end of the methyl propiolate, presumably for steric reasons. The mechanism of this coupling has not yet been established.

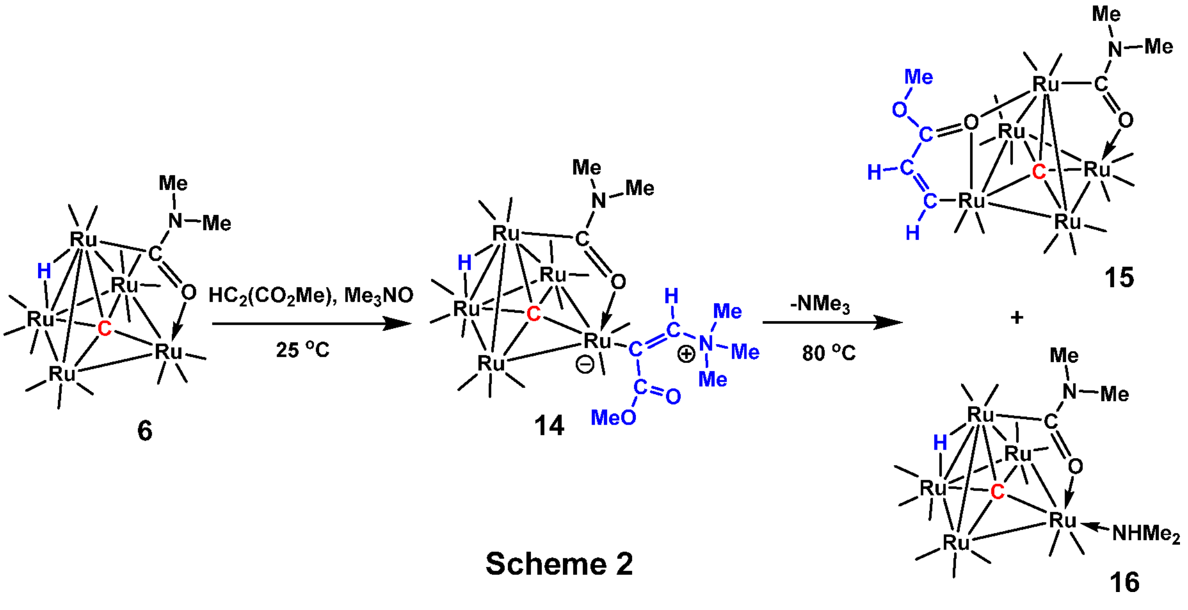
When a solution of **14** was heated to 80 °C, it eliminated the NMe_3 group from the $1\text{-}(MeO_2C)C{=}C(H)(2\text{-}^+NMe_3)$ ligand to yield compound **15**. This process presumably proceeded through an unobserved intermediate containing an alkyne ligand that promptly coupled with the hydrido ligand to yield the observed carboxylate-substituted alkenyl ligand, $\mu\text{-}\eta^2\text{-}HC{=}C(H)(CO_2Me)$, that subsequently inserted the oxygen of its carbonyl group into one of the Ru−Ru bonds to form the O-bridged carbonyl group, thus completing the formation of **15**. An $\eta^2\text{-}HC{=}C(H)(CO_2Me)$ ligand obtained by a β-CH activation on the vinyl group of methyl acrylate in a reaction with $Ru_5(\mu_5\text{-}C)(CO)_{15}$ was also observed in the Ru_5 complex $Ru_5(\mu_5\text{-}C)(CO)_{14}[\eta^2\text{-}O{=}C(OMe)CH{=}CH](\mu\text{-}H)$, but in this case, the ligand is coordinated as a chelate to only one ruthenium atom of the cluster.[19] π-Coordinated bridging η^3-$HC{=}C(H)(CO_2Me)$ ligands were found in the complexes $Ru_5(\mu_5\text{-}C)(CO)_{12}(C_2H_4)[\mu\text{-}\eta^3\text{-}O{=}C(OMe)CHCH](\mu\text{-}H)$[19] and $Ru_5(\mu_5\text{-}C)(CO)_{12}[H_2CC(H)CO_2Me][\mu\text{-}\eta^3\text{-}O{=}C\text{-}(OMe)CHCH](\mu\text{-}H)$[20] that were obtained from reactions of $Ru_5(\mu_5\text{-}C)(CO)_{14}[\eta^2\text{-}O{=}C(OMe)CH{=}CH](\mu\text{-}H)$ with Me_3NO and ethylene or $H_2C_2(H)CO_2Me$, respectively.

Scheme 1. Structures and Chemical Relationships of Compounds 5−13[a]



[a]These compounds were investigated in this study. CO ligands are represented only as lines from the Ru atoms.

Scheme 2. Structures and Relationships of Compounds 6 and 14−16[a]



[a]CO ligands are represented only as lines from the Ru atoms.

The side product, Ru$_5$(μ_5-C)(CO)$_{13}$[μ-η^2-O=C(NMe$_2$)](HNMe$_2$)(μ-H), **16**, was also formed in a low yield in the thermal transformation of **14**. We have shown previously that Me$_2$NH is formed by decarbonylation of the dimethylformamido ligand in **6**.[12] A similar formation of Me$_2$NH from a dimethylformamido ligand **14** accompanied by the complete elimination of the 1-(MeO$_2$C)C=C(H)(2-$^+$NMe$_3$) ligand in another molecule of **14** and an addition of Me$_2$NH could have yielded the small amounts of **16** observed in this reaction.

■ CONCLUSIONS

In this work the first procedures for the synthesis of zwitterionic pentaruthenium carbonyl complexes containing bridging and terminally coordinated 2-trimethylammonioethenyl ligands have been established. The bridging trimethylammonioethenyl ligands adopt a $\sigma + \pi$, η^2 coordination of the C=C double bond to two neighboring metal atoms. The bridging and terminally coordinated trimethylammonioethenyl ligands can be interconverted by the addition and elimination of CO ligands to and from the metal atoms. One zwitterionic pentaruthenium carbonyl complex containing a 1-methyoxycarbonyl-substituted, 2-trimethylammonioethenyl ligand, 1-(MeO$_2$C)C=C(H)(2-$^+$NMe$_3$), was obtained from the reaction of **6** with methyl propiolate. The C−N bond in the 1-(MeO$_2$C)C=C(H)(2-$^+$NMe$_3$) ligand was cleaved thermally and the NMe$_3$ group was eliminated from the complex to yield complex **15** containing a bridging [μ-η^2-HC=C(H)-(CO$_2$Me)] alkenyl ligand formed by transfer of the hydrido ligand in **14** to the resultant alkyne ligand.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03541.

Details of the syntheses and characterizations of the new compounds (PDF)

Accession Codes

CCDC 2043913−2043921 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Richard D. Adams − *Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States*; orcid.org/0000-0003-2596-5100; Email: Adamsrd@mailbox.sc.edu

Authors

Humaiara Akter − *Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States*

Meenal Kaushal − *Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States*

Mark D. Smith − *Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States*

Jonathan D. Tedder − *Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c03541

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Wittig, G.; Schöllkopf, U. Über Triphenyl-phosphinmethylene als olefinbildende Reagenzien I. *Chem. Ber.* **1954**, *87*, 1318−1330. (b) Wittig, G.; Haag, W. Über Triphenyl-phosphinmethylene als olefinbildende Reagenzien II. *Chem. Ber.* **1955**, *88*, 1654−1666. (c) Bart, J. C. J. Structure of the Non-stabilized Phosphonium Ylid Methylenetriphenylphosphorane. *J. Chem. Soc. B* **1969**, 350−365.

(2) (a) Trost, B. M.; Melvin, L. S. *Sulfur Ylides: Emerging Synthetic Intermediates*; Academic Press: New York, 1975. (b) Neuhaus, J. D.; Oost, R.; Merad, J.; Maulide, N. Sulfur-Based Ylides in Transition-Metal-Catalysed Processes. *Top. Curr. Chem.* **2018**, *376*, 15. (c) Lu, L.-Q.; Li, T.-R.; Wang, Q.; Xiao, W.-J. Beyond Sulfide-Centric Catalysis: Recent Advances in the Catalytic Cyclization Reactions of Sulfur Ylides. *Chem. Soc. Rev.* **2017**, *46*, 4135−4149. (d) Zhang, Y.; Wang, J. Catalytic [2,3]-Sigmatropic Rearrangement of Sulfur Ylide Derived from Metal Carbene. *Coord. Chem. Rev.* **2010**, *254*, 941−953. (e) Burtoloso, A. C. B.; Dias, R. M. P.; Leonarczyk, I. A. Sulfoxonium and Sulfonium Ylides as Diazocarbonyl Equivalents in Metal-Catalyzed Insertion Reactions. *Eur. J. Org. Chem.* **2013**, *2013*, 5005−5016. (f) Li, A.-H.; Dai, L.-X.; Aggarwal, V. K. Asymmetric Ylide Reactions: Epoxidation, Cyclopropanation, Aziridination, Olefination, and Rearrangement. *Chem. Rev.* **1997**, *97*, 2341−2372.

(3) (a) Maryanoff, B. E.; Reitz, A. B. The Wittig Olefination Reaction and Modifications Involving Phosphoryl-Stabilized Carbanions. Stereochemistry, Mechanism, and Selected Synthetic Aspects. *Chem. Rev.* **1989**, *89*, 863−927. (b) Johnson, A. W.; Kaska, W. C.; Starzewski, K. A. O.; Dixon, D. *Ylides and Imines of Phosphorus*; Wiley: New York, 1993. (c) Dequina, H. J.; Schomaker, J. M. Aziridinium Ylides: Underused Intermediates for Complex Amine Synthesis. *Trends in Chem.* **2020**, *2*, 874−887. (d) Li, A.-H.; Dai, L.-X.; Aggarwal, V. K. Asymmetric Ylide Reactions: Epoxidation, Cyclopropanation, Aziridination, Olefination, and Rearrangement. *Chem. Rev.* **1997**, *97*, 2341−2372. (e) Huang, Y.; Liao, J.; Wang, W.; Liu, H.; Guo, H. Synthesis of heterocyclic compounds through nucleophilc catalysis. *Chem. Commun.* **2020**, *56*, 15235−15281.

(4) Selected examples include: (a) Pattacini, R.; Jie, S.; Braunstein, P. Facile dichloromethane activation and phosphine methylation. Isolation of unprecedented zwitterionic organozinc and organocobalt Intermediates. *Chem. Commun.* **2009**, 890−892. (b) Engelter, C.; Moss, J. R.; Niven, M. L.; Nassimbeni, L. R.; Reid, G. A cationic ylide complex of platinum(II): its structure and formation from a chloromethyl-platinum complex. *J. Organomet. Chem.* **1982**, *232*, C78−C80. (c) Kermode, N. J.; Lappert, M. F.; Skelton, B. W.; White, A. H.; Holton, J. Synthesis of ylideplatinum(II) complexes via α-functionalised alkylplatinum(II) intermediates and some comparative data on palladium(II) complexes; X-ray structure of *trans*-[Pt(CH$_2$PEt$_3$)I(PEt$_3$)$_2$]I. *J. Organomet. Chem.* **1982**, *228*, C71−C75. (d) Azam, K. A.; Frew, A. A.; Lloyd, B. R.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. μ-Methylene)diplatinum complexes: their syntheses, structures, and properties. *Organometallics* **1985**, *4*, 1400−1406. (e) Churchill, M. R.; Wasserman, H. J. Crystal and molecular structure of [W(CH$_2$PMe$_3$)(CO)$_2$Cl(PMe$_3$)$_3$][CF$_3$SO$_3$], a seven-coordinate tungsten(II) complex produced by transfer of a

trimethylphosphine to the W:CH_2 system. *Inorg. Chem.* **1982**, *21*, 3913−3916. (f) Toupet, L.; Weinberger, B.; Des Abbayes, H.; Grosse, U. Structure du Complexe Tetracarbonyle(methylenetriphenylphosphorane-C)fer(II), $[Fe(C_{19}H_{17}P)(CO)_4]$. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *40*, 2056−2058. (g) Moss, J. R.; Niven, M. L.; Stretch, P. M. Haloalkyl complexes of the transition metals. Part 5. The synthesis and reactions of some new pentamethylcyclopentadienyl halomethyl and methoxymethyl complexes of molybdenum(II) and tungsten(II) and the X-ray crystal structure of the cationic ylide complex $[\eta\text{-}C_5Me_5W(CO)_3CH_2PPh_3]I$. *Inorg. Chim. Acta* **1986**, *119*, 177−186. (h) Porter, L. C.; Knachel, H.; Fackler Jnr, J. P. A Mononuelear Gold (l) Complex Containing a Covalently Bound Ylide Ligand. The Structure of Chloro[methyl(methylene)diphenylphosphoranyI-C]gold(I). *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *43*, 1833−1835. (i) Uson, R.; Laguna, A.; Uson, A.; Jones, P. G.; Meyer-Base, K. Synthesis of Pentafluorophenyl(ylide)silver (l) Complexes: X-Ray Structures of two Modifications of $[Ag(C_6F_5)(CH_2PPh_3)]$. *J. Chem. Soc., Dalton Trans.* **1988**, 341−345. (j) Usón, R.; Laguna, A.; Laguna, M.; Gimeno, M.C.; Pablo, A.; Jones, P. G.; Meyer-Bäse, K.; Erdbrügger, C.F. Synthesis and reactivity of neutral complexes of the types $[AuX_3(ylide)]$ and trans-$[Au(C_6F_5)X_2(ylide)]$ (X = halide or pseudohalide). X-ray structure of $[Au(SCN)_3(CH_2PPh_3)]$. *J. Organomet. Chem.* **1987**, *336*, 461−468. (k) Hoover, J. F.; Stryker, J. M. Synthesis of Platinum Bis(phosphonium ylide) Complexes from -Halomethyl Precursors. *Organometallics* **1988**, *7*, 2082−2084. (l) Cerrada, E.; Concepcion Gimeno, M.; Laguna, A.; Laguna, M.; Orera, V.; Jones, P. G. Charge-transfer salts with mononuclear and dinuclear ylide gold(I) complexes: x-ray structure of $[Au(CH_2PPh_3)_2](TCNQ)$, (TCNQ = 7,7′,8,8′-tetracyanoquinodimethane). *J. Organomet. Chem.* **1996**, *506*, 203−210.

(5) Selected examples include: (a) O'Connor, E. J.; Helquist, P. Stable precursors of transition-metal carbene complexes. Simplified preparation and crystal structure of η^5-cyclopentadienyl)-[(dimethylsulfonium)methyl]dicarbonyliron(II) fluorosulfonate. *J. Am. Chem. Soc.* **1982**, *104*, 1869−1874. (b) Hevia, E.; Perez, J.; Riera, V.; Miguel, D. Manganese(I) and Rhenium(I) Tricarbonyl-(Alkylthio)methyl and Alkylidenesulfonium Complexes. *Organometallics* **2002**, *21*, 5312−5319. (c) Leoni, P.; Marchetti, F.; Paoletti, M. Synthesis of Palladium Sulfonium Ylides and the Structures of *trans*-$[PdCl(CH_2SR_2)(PBu^t{}_2H)_2]X$ (X = CF_3SO_3, SR_2) Tetrahydrothiophene; X= PF_6, R = Et). *Organometallics* **1997**, *16*, 2146−2151. (d) Kilbourn, B. T.; Felix, D. The Crystal Structure of Methyldineopentylsulphonium Tri-iododineopentylsulphoniummethylzincate, $[(C_5H_{11})_2SMe]^+[(C_5H_{11})_2SCH_2ZnI_3]^-$. *J. Chem. Soc. A* **1969**, 163−168. (e) Fackler, J. P., Jr.; Paparizos, C. Trimethylgold(III) Complexes of Reactive Sulfoxonium and Sulfonium Ylides. *J. Am. Chem. Soc.* **1977**, *99*, 2363−2364. (f) Vicente, J.; Chicote, M.-T.; Abrisqueta, M. D.; Alvarez-Falcon, M. M.; Ramírez de Arellano, M. C.; Jones, P. G. New Carbenegold(I) Complexes Synthesized by the "Acac Method". *Organometallics* **2003**, *22*, 4327−4333.

(6) (a) Lappas, D.; Hoffman, D. M.; Folting, K.; Huffman, J. C. Synthesis and Structure of a Resonance Stabilized (Trimethylphosphonio)metallapropenide. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 587−589. (b) Hoffman, D. M.; Huffman, J. C.; Lappas, D.; Wierda, D. A. Alkyne Reactions with Rhenium(V) Oxo Alkyl Phosphine Complexes—Phosphine Displacement versus Apparent Re-P Insertion. *Organometallics* **1993**, *12*, 4312−4320. (c) Rogers, R. D.; Alt, H. G.; Maisel, H. E. Die Molekülstruktur des carbenartigen Ylidkomplexes $(C_5H_4Me)(CO)_2Mn[CHCH(PEt_3)]$. *J. Organomet. Chem.* **1990**, *381*, 233−238. (d) Chin, C. S.; Lee, S.; Oh, M.; Won, G.; Kim, M.; Park, Y. J. *cis*-Bis(alkenyl)iridium(III) Compounds by Apparent Insertion of Two Acetylenes into Two Ir-P Bonds: Crystal Structures of *cis, trans*-$[IrCl(\text{-}CH = CH^+PPh_3)_2(CO)(PPh_3)_2]^{2+}$ and $[Ir(OClO_3)(CH_3)(H_2O)(CO)(PPh_3)_2]^+$. *Organometallics* **2000**, *19*, 1572−1577. (e) Chin, C. S.; Park, Y.; Kim, J.; Lee, B. Facile Insertion of Alkynes into Ir-P (Phosphine) and Ir-As (Arsine) Bonds: Second and Third Alkyne Addition to Mononuclear Iridium Complexes. *J. Chem. Soc., Chem. Commun.* **1995**, 1495−1496. (f) Takats, J.; Washington, J.; Santarsiero, B. D. Condensation of $Os(CO)_4\eta^2\text{-}HCCH$) with $CpRh(CO)(PR_3)$. Unexpected Phosphine Dependence in the Formation of Dimetallacycles: Reverse Regiochemistry and a Zwitterionic Compound. *Organometallics* **1994**, *13*, 1078−1080. (g) Yang, K.; Bott, S. G.; Richmond, M. G. Regioselective phosphine attack on the coordinated alkyne in $Co_2\mu$-alkyne) complexes Reactivity studies and X-ray diffraction structures of $Co_2(CO)_4$(bma)-μ-HC≡C^{t}Bu) and the zwitterionic hydrocarbyl complexes $Co_2(CO)_4[\mu\text{-}^2\text{::}^2\text{::}^1\text{::}^1\text{:-}RC = C(R')PPh_2C = C(PPh_2)C(O)C(O)]$. *J. Organomet. Chem.* **1996**, *516*, 65−80. (h) Bott, S. G.; Shen, H.; Senter, R. A.; Richmond, M. G. Acetylide Participation in Ligand Substitution and P-C Bond Cleavage in the Reaction between $HRu_3(CO)_9([\mu\text{-}^2\text{::}^2\text{::}^1\text{-}C\equiv CPh)$ and 4,5-Bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd). Syntheses and X-ray Structures of $HRu_3(CO)_7[[\mu\text{-}^2\text{::}^2\text{::}^1\text{::}^1\text{::}^1\text{-}Ph_2PC = CC(O)CH_2C(O)PPh_2C = CPh]$ and $Ru_3(CO)_7\mu\text{-}^2\text{::}^1\text{:-}PhC = CHPh)[\mu\text{-}^2\text{::}^1\text{:-}PPhC = CC(O)CH_2C(O)PPh_2]$. *Organometallics* **2003**, *22*, 1953−1959.

(7) (a) Boland-Lussier, B. F.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L. Synthesis and characterization of cationic iron vinylidene compounds: formation of carbon-hydrogen, carbon-nitrogen and carbon-phosphorus bonds and the x-ray crystal structure of $[Fe((\text{-}C_5H_5)(CO)(PPh_3)\{C(PPh_3)=CH_2\}]^+BF_4^-$. *Organometallics* **1982**, *1*, 628−634. (b) Hogarth, G.; Knox, S. A. R.; Lloyd, B. R.; Macpherson, K. A.; Morton, D. A. V.; Orpen, A. G. Structural Observation of Bis(diphenyphosphino)methane Reactivity at a Di-iron Centre: Crystal Structures of Isomeric $[Fe_2(CO)_5((\text{-}CHCHCO)\{\{\text{-}P(Ph_2)CH_2PPh_2\}]$, $[Fe_2(CO)_6((\text{-}C(CH_2)P(Ph_2)CH_2PPh_2\}]$ and $[\ Fe_2(CO)_2\{\{\text{-}C(CH_2Ph)P(Ph_2)CH_2PPh\}]$. *J. Chem. Soc., Chem. Commun.* **1988**, 360−362. (c) Bamber, M.; Froom, S. F. T.; Green, M.; Schulz, M.; Werner, H. Nucleophilic attack by isocyanides, phosphines and cyclohexenesulphide on the -carbon of "side-on" bonded ^{2}-(4e)-vinylidenes; formation of thioketene and thioaldehyde dimolybdenum complexes. *J. Organomet. Chem.* **1992**, *434*, C19−C25.

(8) Henrick, K.; McPartlin, M.; Deeming, A. J.; Hasso, S.; Manning, P. Addition of dimethylphenylphosphine to μ- and μ_3-alkynyl and μ_3-allenyl ligands in triosmium clusters: *X*-ray crystal structures of three zwitterionic adducts. *J. Chem. Soc., Dalton Trans.* **1982**, 899−906.

(9) (a) Chin, C. S.; Lee, H.; Oh, M. Reactions of Iridium(III) Compounds with Alkynes in the Presence of Triethylamine: The First Example of M-CH = CH-$^+NR_3$. *Organometallics* **1997**, *16*, 816−818. (b) Chin, C. S.; Cho, H.; Won, G.; Oh, M.; Ok, K. M. Reaction of an (Alkyl)(alkenyl)(alkynyl)iridium(III) Complex with HCl: Intramolecular C-C Bond Formation from Alkyl, Alkenyl, and Alkynyl Groups Coordinated to "$Ir(CO)(PPh_3)_2$". H/D Exchange between CH3 and DCl. *Organometallics* **1999**, *18*, 4810−4816.

(10) Adams, R. D.; Smith, M. D.; Wakdikar, N. D. Zwitterionic Ammoniumalkenyl Ligands in Metal Cluster Complexes. Synthesis, Structures and Transformations of Zwitterionic Trimethylammoniumalkenyl Ligands in Hexaruthenium Carbido Carbonyl Complexes. *Inorg. Chem.* **2020**, *59*, 1513−1521.

(11) Johnson, B. F. G.; Lewis, J.; Nicholls, J. N.; Puga, J.; Raithby, P. R.; Rosales, M. J.; McPartlin, M.; Clegg, W. The Synthesis of $[Ru_5C(CO)_{15}]$ by the Carbonylation of $[Ru_6C(CO)_{17}]$ and the Reactions of the Pentanuclear Cluster with a Variety of Small Molecules: the X-Ray Structure Analyses of $[Ru_5C(CO)_{15}]$, $[Ru_5C(CO)_{15}(MeCN)]$, $[Ru_5C(CO)_{14}(PPh_3)]$, $[Ru_5C(CO)_{13}(PPh_3)_2]$ and $[Ru_5(\mu\text{-}H)_2(CO)_{12}(Ph_2PCH_2)_2Ph_2)]$. *J. Chem. Soc., Dalton Trans.* **1983**, 277−290.

(12) Adams, R. D.; Tedder, J. D. Formation of N,N-Dimethylacrylamide by a Multicenter Hydrocarbamoylation of C_2H_2 with N,N-Dimethylformamide Activated by $Ru_5(\mu_5\text{-}C)(CO)_{15}$. *Inorg. Chem.* **2018**, *57*, 5707−5710.

(13) APEX3, ver. 2016.5-0, and SAINT, ver. 8.37A. Bruker AXS, Inc.: Madison, WI, USA.

(14) Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *71*, 3−8.

(15) OLEX2: a complete structure solution, refinement, and analysis program. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339−341.

(16) (a) Orpen, A. G.; Pippard, D.; Sheldrick, G. M.; Rouse, K. D. Decacarbonyl-η-hydridoη-vinyl-triangulo-triosmium: A Combined X-ray and Neutron Diffraction Study. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 2466−2472. (b) Iggo, J. A.; Mays, M. J.; Raithby, P. R.; Hendrick, K. Substitution and Insertion Reactions of the Dinuclear Manganese μ-Hydride Complex [$M_2\mu$-H)μ-PPh_2)$(CO)_8$]; Crystal Structures of the Complexes [$Mn_2\mu$-:μ^2-CH = CH_2)μ-PPh_2)$(CO)_7$] and [$Mn_2\mu$-H)μ-PPh_2)$(CO)_6(CNBu^t)_2$]. *J. Chem. Soc., Dalton Trans.* **1983**, 205−215. (c) Dennett, J. N. L.; Knox, S. A. R.; Anderson, K. M.; Charmant, J. P. H.; Orpen, A. G. The synthesis of [FeRu$(CO)_2\mu$-CO$)_2\eta$-C_5H_5)η-C_5Me_5)] and convenient entries to its organometallic chemistry. *Dalton Trans.* **2005**, 63−73. (d) Adams, R. D.; Dhull, P.; Rassolov, V.; Wong, Y. O. Synthesis and Reactivity of the Electronically-Unsaturated Dirhenium Carbonyl Compounds containing bridging Gold-Carbene Groups. *Inorg. Chem.* **2016**, *55*, 10475−10483. (e) Adams, R. D.; Wong, Y. O. New rhenium carbonyl cluster complexes containing bridging hydrocarbyl and bridging mercury groups. *J. Organomet. Chem.* **2015**, *784*, 109−113. (f) Adams, R. D.; Dhull, P.; Kaushal, M.; Smith, M. D. The Activation and Transformations of Vinyl Acetate at a Dirhenium Carbonyl Center. *J. Organomet. Chem.* **2019**, *902*, 120969. (g) Zhao, X.; Yang, D.; Zhang, Y.; Wang, B.; Qu, J. Terminal alkyne insertion into a thiolate-bridged dirhodium hydride complex derived from heterolytic cleavage of H_2. *Chem. Commun.* **2018**, *54*, 11112−11115.

(17) (a) Mingos, D. M. P.; May, A. S. Chapter 2. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH Publishers: New York, 1990. (b) Mingos, D. M. P. Polyhedral Skeletal Electron Pair Approach. *Acc. Chem. Res.* **1984**, *17*, 311−319.

(18) (a) Farrar, D. H.; Poë, A. J.; Zheng, Y. Systematic Kinetics of High-Nuclearity Metal Carbonyl Clusters. Exceptional Behavior of $Ru_5C(CO)_{15}$ with P-Donor Nucleophiles. *J. Am. Chem. Soc.* **1994**, *116*, 6252−6261. (b) Freeman, G.; Ingham, S. L.; Johnson, B. F. G.; McPartlin, M.; Scowen, I. J. Reaction of [$Ru_5C(CO)_{15}$] and [$Ru_6C(CO)_{17}$] with 1,10-phenanthroline and 2,2-bipyridyl. *J. Chem. Soc., Dalton Trans.* **1997**, 2705−2711.

(19) Adams, R. D.; Smith, M. D.; Tedder, J. D.; Wakdikar, N. D. Selective Activation of CH Bonds in Polar Vinyl Olefins and Coupling of Ethylene to the Activated Carbon Atoms in Pentaruthenium Complexes. *Inorg. Chem.* **2019**, *58*, 8357−8368.

(20) Adams, R. D.; Prince, C.; Smith, M. D.; Tedder, J. D.; Wakdikar, N. D. C-C coupling of CH activated polar vinyl monomers by a pentaruthenium cluster complex. *J. Organomet. Chem.* **2019**, *901*, 120938.