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Zwitterionic Ammoniumalkenyl Ligands in Metal Cluster Complexes. Synthesis, Structures, and Transformations of Zwitterionic Trimethylammoniumalkenyl Ligands in Hexaruthenium Carbido Carbonyl Complexes

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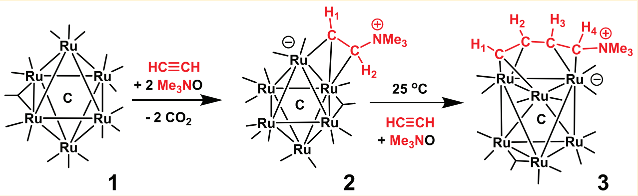
Supporting Information



ABSTRACT: $Ru_6(\mu_6\text{-}C)(CO)_{17}$, **1**, has been shown to react with C_2H_2 when activated by Me_3NO to yield the complexes $Ru_6C(CO)_{15}(\mu\text{−}\eta^2\text{-}C_2H_2NMe_3)$, **2**, and $Ru_6C(CO)_{14}(\mu_3\text{−}\eta^4\text{-}C_4H_4NMe_3)$, **3**, containing a bridging 2-trimethylammoniumethenyl ($C_2H_2NMe_3$) ligand and a triply bridging 4-trimethylammoniumbutadienyl ($C_4H_4NMe_3$) ligand, respectively. Complexes **2** and **3** are formally zwitterionic by virtue of the positive charge on the nitrogen atom and a negative charge that must be assigned formally to the Ru_6 cluster. Compound **2** added CO at room temperature to yield the compound $Ru_6C(CO)_{16}(\eta^1\text{−}E\text{-}C_2H_2NMe_3)$, **4**, that contains a terminally coordinated zwitterionic 2-trimethylammoniumethenyl ligand. Compounds **2** and **3** eliminated the NMe_3 grouping, reversibly, when heated to yield the ethyne cluster complex $Ru_6C(CO)_{15}(\mu_3\text{-}C_2H_2)$, **5**, and the butadiendiyl cluster complex $Ru_6C(CO)_{14}(\mu_3\text{−}\eta^4\text{-}C_4H_4)$, **6**, respectively. Compound **3** was obtained from **2** by addition of C_2H_2 in the presence of Me_3NO. Reaction of **1** with methyl propiolate, HC_2CO_2Me, yielded the CO_2CH_3 substituted zwitterionic complex $Ru_6C(CO)_{16}[\eta^1\text{−}E\text{-}(C(CO_2Me){=}C(H)NMe_3]$, **7**, which contains the terminally coordinated zwitterionic ligand, $C(CO_2Me){=}C(H)NMe_3$. Compound **7** eliminated NMe_3 and CO when heated to 83 °C to yield the methoxycarbonyl alkyne complex $Ru_6C(CO)_{15}[\mu_3\text{-}HC_2(CO_2Me)]$, **8**. All new products, **2**−**8**, were characterized structurally by single-crystal X-ray diffraction analyses.

INTRODUCTION

Hydrocarbylonium zwitterions have been of great interest ever since the first reports of the phosphorus ylides by Wittig in the 1950s.[1] Zwitterions are neutral molecules that formally have positively and negatively charged groups within the same molecule.[2] Phosphorus ylides **A** and their sulfur analogs **B** are an important family of zwitterions that are valuable reagents in organic synthesis.[3,4]

There are a number of examples in which these zwitterions are complexed to metal atoms, e.g., **C** and **D**. Almost all are coordinated exclusively through the carbon atom, and the negative charge is formally transferred to the metal atom.[5,6] There are also a variety of more extended zwitterionic hydrocarbylonium species. Most examples of these species contain the phosphonium grouping. Some examples of these are **E**, **F**, and **G**, and all of these have been isolated only as ligands in complexes containing one or more metal atoms.[7−9] Complexes containing the zwitterionic phosphoniumalkenyl ligands **E** are the most abundant.[7] Metal complexes containing zwitterionic ammoniumalkenyl ligands, such as **H**, are quite rare.[10]

In recent studies, we have been investigating the reactions of organic ligands with ethyne,[11] alkenes,[12] aldehydes,[13] and gold-phenyl compounds[14] with ruthenium carbonyl cluster complexes. We have now discovered some interesting new polynuclear ruthenium carbonyl complexes containing ammoniumethenyl ligands formed by the combination of ethyne and methyl propiolate with NMe_3 in reactions with the Ru_6 carbido carbonyl cluster complex $Ru_6(\mu_6\text{-}C)(CO)_{17}$, **1**, in the presence of Me_3NO. These results are reported herein.

RESULTS

Two products, $Ru_6(\mu_6\text{-}C)(CO)_{15}(\mu\text{−}\eta^2\text{-}CHCHNMe_3)$, **2** (39% yield), and $Ru_6(\mu_6\text{-}C)(CO)_{14}(\mu_3\text{−}\eta^4\text{-}C_4H_4NMe_3)$, **3** (17% yield), were obtained from the reaction of compound **1** with C_2H_2 in the presence of Me_3NO at room temperature for 20 min. Both products were characterized by IR, NMR, and by single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of compound **2** is shown in Figure 1. Compound **2** contains an octahedral-shaped Ru_6 cluster with 15 carbonyl ligands. The most interesting ligand in **2** is a 2-trimethylammoniumethenyl ligand, $CH{=}CHNMe_3$, that bridges the Ru1−Ru2 edge of the cluster. The $CH{=}CHNMe_3$ ligand is coordinated in the σ+π fashion that is well established for bridging alkenyl ligands.[15] The two CH groups exhibit a 50/50 disorder in the crystal as shown in the figure. The disordered ethenyl carbon atoms C1/C3 are σ-

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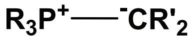
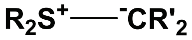


A



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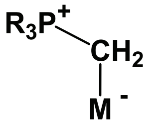

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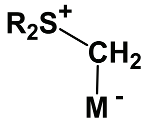

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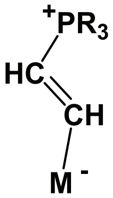

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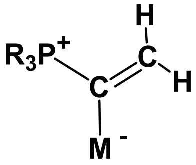

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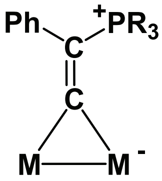
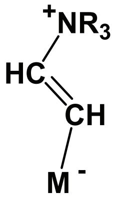


G



H

bonded to Ru1, Ru1−C1 = 2.057(14) Å, Ru1−C3 = 2.112(12) Å while atoms C(1) and C(2)/C(3 and C(4) are both bonded to Ru2, Ru2−C1 = 2.084(12) Å, Ru2−C2 = 2.155(12) Å and Ru2−C3 = 2.269(12) Å, Ru2−C4 = 2.253(13) Å. The C−C distance is short, C1−C2 = 1.427(19) Å and C3−C4 = 1.419(18) Å, and indicative of a π-coordinated C−C double bond. Takats et al. reported the synthesis of the complex $Os(CO)_3RhCp(\mu-\eta^2\text{-}CHCHPMe_3)(\mu\text{-}CO)$ a number of years ago which contains a similarly coordinated $\sigma+\pi$ ethenyl(trimethylphosphonium) ligand bridging two metal atoms.[7e] There is a NMe_3 group in **2** (not disordered) that is bonded to the disordered carbon atoms C2/C4 at a normal C−N single bond length, N1−C2 = 1.565(11) Å/N1−C4 = 1.553(11) Å. There is a single hydrogen atom (not shown) attached to each ethenyl carbon atom. They are observed at δ = 8.85 (d, $^3J_{H-H}$ = 7.5 Hz) and 4.29 (d, $^3J_{H-H}$ = 7.5 Hz) in the H NMR spectrum, and there is a singlet at 3.19 ppm for the NMe_3 group. Formally, there is a positive charge on the nitrogen atom N1. A negative charge could be formally assigned to the metal atom Ru1, but this charge is certainly distributed through the delocalized bonding molecular orbitals of the entire Ru_6 cluster. The bridging $CH{=}CHNMe_3$ ligand in **2** serves formally as a four electron donor, thus the complex overall obtains a total of 86 cluster valence electrons which is in complete accord with the observation of an octahedral cluster for six metal atoms.[16]

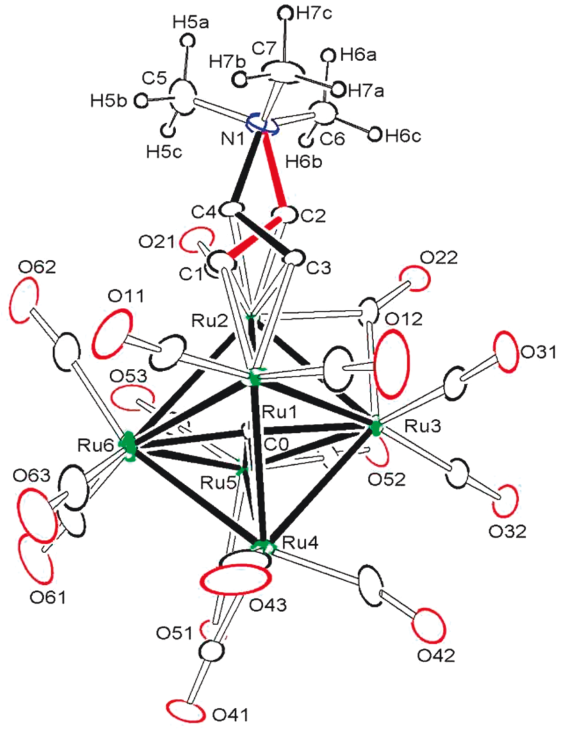


Figure 1. An ORTEP diagram of the molecular structure of the compound $Ru_6(\mu_6\text{-}C)(CO)_{15}(\mu-\eta^2\text{-}CHCHNMe_3)$, **2**, showing the disorder in the $CH{=}CHNMe_3$ ligand. Thermal ellipsoidal probabilities are shown at 25%. Selected interatomic distances (Å) are as follows: Ru1−C1 = 2.057(14), Ru1−C3 = 2.112(12), Ru2−C1 = 2.084(12), Ru2−C2 = 2.155(12), Ru2−C3 = 2.269(12), Ru2−C4 = 2.253(13), C1−C2 = 1.427(19), C3−C4 = 1.419(18), N1−C2 = 1.565(11), N1−C4 = 1.553(11), N1−C5 = 1.475(10), N1−C6 = 1.481(11), N1−C7 = 1.516(9).

An ORTEP diagram of the molecular structure of compound **3** is shown in Figure 2. Compound **3** contains an octahedral-shaped Ru_6 cluster with 14 carbonyl ligands. The most interesting ligand in **3** is a monometalated-η^4-4-trimethylammoniumbutadienyl ligand, $Me_3N^+CHCHCHCH$, that bridges the Ru1−Ru2−Ru3 face of the cluster. This novel ligand was formed by the coupling of two equivalents of HC_2H and addition of one molecule of NMe_3 to one of the terminal carbon atoms of the C_4-chain. Carbon atoms C1 and C2 are π-bonded to Ru2, Ru2−C1 = 2.108(8) Å, Ru2−C2 = 2.288(8) Å. Carbon atoms C3 and C4 are π-bonded to Ru1, Ru1−C3 = 2.227(8) Å, Ru1−C4 = 2.194(7) Å and C4 is also σ-bonded to Ru3, Ru3−C4 = 2.063(8) Å. The π-coordinated C−C double bonds are significantly shorter, C1−C2 = 1.437(11) Å and C3−C4 = 1.401(11) Å, than the C2−C3 bond which is formally a C−C single bond, C2−C3 = 1.462(12) Å. The C1−N1 bond is also a single bond, N1−C1 = 1.540(10) Å. Formally, there is a positive charge on the nitrogen atom N1 and a negative charge on the Ru_6 cluster. Each carbon atom in the C_4-chain contains one hydrogen atom. Accordingly, there are four proton resonances with appropriate H−H couplings in the ^1H NMR spectrum, δ = 9.53 (d, **CH**, $^3J_{H-H}$ = 6.0 Hz), 6.40 (dd, **CH**, $^3J_{H-H}$ = 6.0 Hz, $^3J_{H-H}$ = 6.3 Hz), 4.21 (d, **CH**, $^3J_{H-H}$ = 7.5 Hz), 2.44 (dd, **CH**, J = 7.5 Hz, $^3J_{H-H}$ = 6.3 Hz) and a singlet at δ = 3.38 for the NMe_3 protons. Compound **3** contains one less CO ligand than **2**. Formally, the $Me_3N^+CHCHCHCH$ ligand serves as a six electron donor to the cluster. Thus, the six ruthenium atoms contain a total of 86 electrons which is in accord with the observed octahedral-shaped Ru_6 cluster.[16] It was possible to obtain compound **3** from **2** in a low yield (10%) from the reaction of **2** with an

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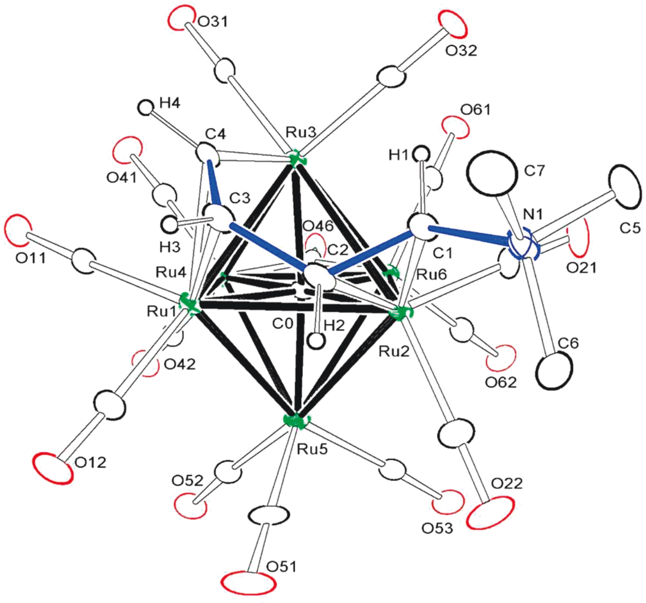


Figure 2. An ORTEP diagram of the molecular structure of the compound $Ru_6(\mu_6\text{-}C)(CO)_{14}(\mu_3\text{–}\eta^4\text{-}C_4H_4NMe_3)$, **3**, showing the 20% thermal ellipsoidal probability. Selected interatomic distances (Å) are as follows: Ru1−C3 = 2.227(8), Ru1−C4 = 2.194(7), Ru2−C1 = 2.108(8), Ru2−C2 = 2.288(8), Ru3−C4 = 2.063(8), N1−C1 = 1.540(10), C1−C2 = 1.437(11), C2−C3 = 1.462(12), C3−C4 = 1.401(11), N1−C1 = 1.540(10), N1−C5 = 1.484(11), N1−C6 = 1.480(11), N1−C7 = 1.518(11).

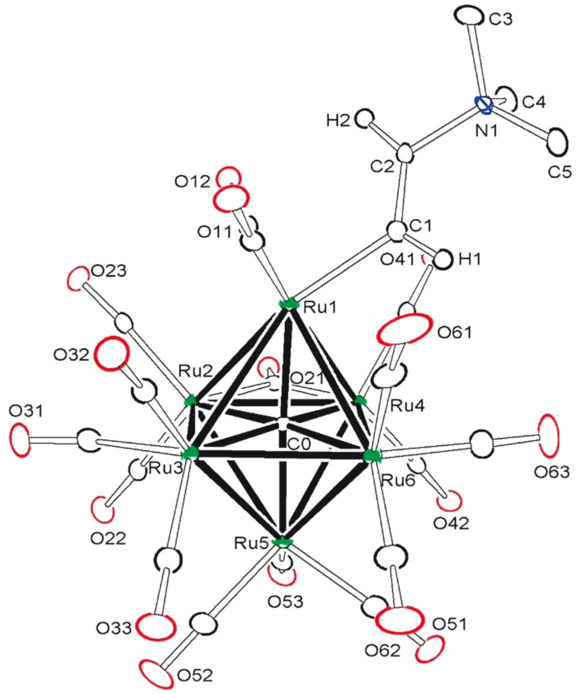


Figure 3. An ORTEP diagram of the molecular structure of the compound $Ru_6C(CO)_{16}(\eta^1\text{–}E\text{-}C_2H_2NMe_3)$, **4**, showing the 40% thermal ellipsoidal probability. Selected interatomic distances (Å) are as follows: Ru1−C1 = 2.097(2), C1−C2 = 1.306(3), C1−H1 = 0.90(4), C2−H2 = 0.93(3), N1−C2 = 1.508(3), N1−C5 = 1.494(3), N1−C3 = 1.499(3), N1−C4 = 1.502(3).

additional quantity of C_2H_2 in the presence of Me_3NO which was used to aid in the removal of a CO ligand.

When compound **2** was placed under an atmosphere of CO (1 atm) at 25 °C for 24 h, the new compound $Ru_6C(CO)_{16}(\eta^1\text{–}E\text{-}C_2H_2NMe_3)$, **4**, was obtained in 40% yield. An ORTEP diagram of the molecular structure of compound **4** is shown in Figure 3. Compound **4** contains an octahedral-shaped Ru_6 cluster with 16 carbonyl ligands. The most interesting ligand is a 2-trimethylammoniumethenyl, $HC{=}CH(NMe_3)$, ligand that is terminally coordinated to the metal atom Ru1 by the carbon atom C1, Ru1−C1 = 2.097(2) Å. There is a C−C double bond between the atoms C1 and C2, C1−C2 = 1.306(3) Å and a NMe_3 group bonded to atom C2, N1−C2 = 1.508(3) Å. The CH groups exhibit an *E*-stereochemistry, and this is confirmed by the large coupling, $^3J_{H-H}$ = 14.4 Hz, between the two CH resonances, δ = 7.58 and 5.83, observed in the ^1H NMR spectrum. The methyl resonance of the NMe_3 group occurs at 3.13 ppm. Compound **4** was formed by the addition of one CO ligand to the Ru_6 cluster. This addition induces the conversion of the $C_2H_2NMe_3$ ligand from a bridging four electron donating ligand to a terminally coordinated two electron donating ligand by release of the coordinated C−C double bond. The terminally coordinated $C_2H_2NMe_3$ ligand is a two electron donor, and compound **4** thus contains a total of 86 cluster valence electrons which is in accord with the observation of an octahedral cluster of six metal atoms.[16] Similar terminally coordinated $C(H){=}CH(NEt_3)$ ligands were found in the complexes, $[Ir(H)(-C{\equiv}CPh)(-CH{=}CHNEt_3)L_3]^+$ and $[Ir\text{-}CH{=}CHCH{=}CH)(-CH{=}CH-NEt_3)L_3]^+$.[10]

When a solution of **2** was heated to reflux in 1,2-dichloroethane solvent (83 °C) for 20 min, the NMe_3 group was eliminated from the molecule to yield the ethyne complex $Ru_6C(CO)_{15}(\mu_3\text{-}C_2H_2)$, **5**, in 55% yield. Similarly, when a solution of **4** in 1,2-dichloroethane was heated to reflux (83 °C) for 3 h, compound **5** was obtained in 86% yield by loss of one CO ligand and the NMe_3 group. Compound **5** was characterized structurally by a single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of **5** is shown in Figure 4. Compound **5** contains two independent molecules in the asymmetric crystal unit. One of the two molecules exhibits a 3-fold disorder of the C_2H_2 ligand in the solid state. An ORTEP diagram of the structure of the undisordered molecule of **5** is shown in Figure 4. Compound **5** contains 15 linear terminal carbonyl ligands on an octahedral Ru_6C cluster of metal atoms with a triply bridging ethyne ligand on one of the Ru_3 faces (Ru1−Ru2−Ru3) of the cluster. The C1−C2 distance of 1.352(9) Å is consistent with that of a coordinated triple bond. The structure of **5** is similar to the structures of $Ru_6C(CO)_{15}(\mu_3\text{-}HC_2Ph)$ and $Ru_6C(CO)_{15}(\mu_3\text{-}PhC_2Me)$ both of which contain triply bridging alkyne ligands on Ru_6 cluster complexes.[17] Compound **5** was first obtained a number of years ago by a reaction of the anion $[Ru_6C(CO)_{16}]^{2-}$ with ethyne and treatment by $[FeCp_2][BF_4]$, but it was not structurally characterized.[17]

Interestingly, the NMe_3 elimination from **2** is reversible. When NMe_3 gas was passed through a solution of **5** in an NMR tube in CD_2Cl_2 solvent, the immediate formation of compound **2** was observed at room temperature. It was subsequently isolated in 30% yield.

When a solution of **3** was heated to reflux in 1,2-dichloroethane solvent (83 °C) for 20 min, the NMe_3 group was eliminated from the molecule to yield the dimetalated butadiendiyl complex $Ru_6C(CO)_{14}(\mu_3\text{–}\eta^4\text{-}C_4H_4)$, **6**, in 64% yield. Compound **6** was also characterized structurally by

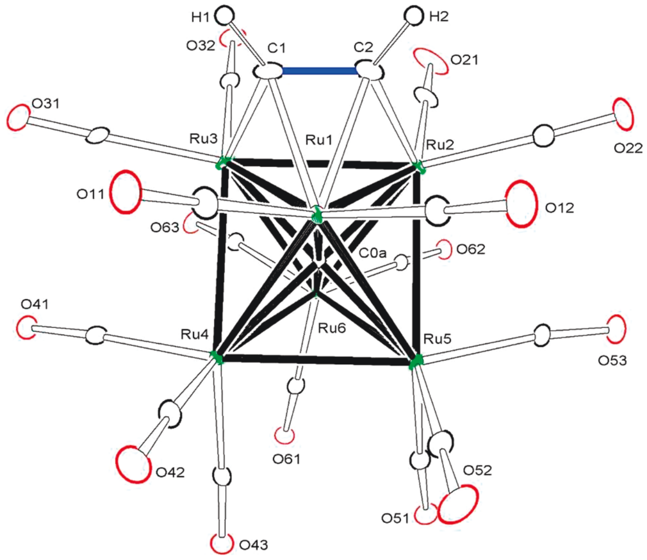


Figure 4. An ORTEP diagram of the molecular structure of the compound $Ru_6C(CO)_{15}(\mu_3\text{-}C_2H_2)$, **5**, showing the 25% thermal ellipsoidal probability. Selected interatomic distances (Å) are as follows: Ru1−C1 = 2.172(6), Ru1−C2 = 2.215(6), Ru2−C2 = 2.052(6), Ru3−C1 = 2.055(6), C1−C2 = 1.352(9).

single-crystal X-ray diffraction analysis. Compound **6** exhibits a 2-fold disorder in a 80/20 ratio in the solid state. An ORTEP diagram of its molecular structure of the major component from the disorder model is shown in Figure 5. Compound **6** contains 14 carbonyl ligands on an octahedral Ru_6C cluster. There is a η^4-triply bridging C_4H_4 butadiendiyl ligand on the Ru1−Ru2−Ru3 triangular face of the cluster. The coordinated C1a−C2a = 1.418(11) Å and C3a−C4a = 1.421(11) Å distances which are formally double bonds are slightly shorter than the C2a−C3a distance, 1.442(11) Å, which is formally a single bond. Two resonances with appropriate couplings were observed for the CH protons in the ^1H NMR spectrum: δ = 10.31 (dd, $^3J_{H-H}$ = 3.3 Hz, $^4J_{H-H}$ = 3.3 Hz) and 5.27 (dd, $^3J_{H-H}$ = 3.3 Hz, $^4J_{H-H}$ = 3.3 Hz). The bridging η^4-C_4H_4 ligand in **6** serves formally as a six electron donor, thus compound **6** contains a total of 86 cluster valence electrons which is in accord with the observation of an octahedral cluster of six metal atoms.[16] Compound **6** is structurally similar to the diphenyl-substituted dimetallabutadiendiyl compound $[Ru_6C(CO)_{14}\{(\mu_5\text{-}\eta^4\text{-}1,4\text{-}C(Ph)CHCHC(Ph)\}]$.[18]

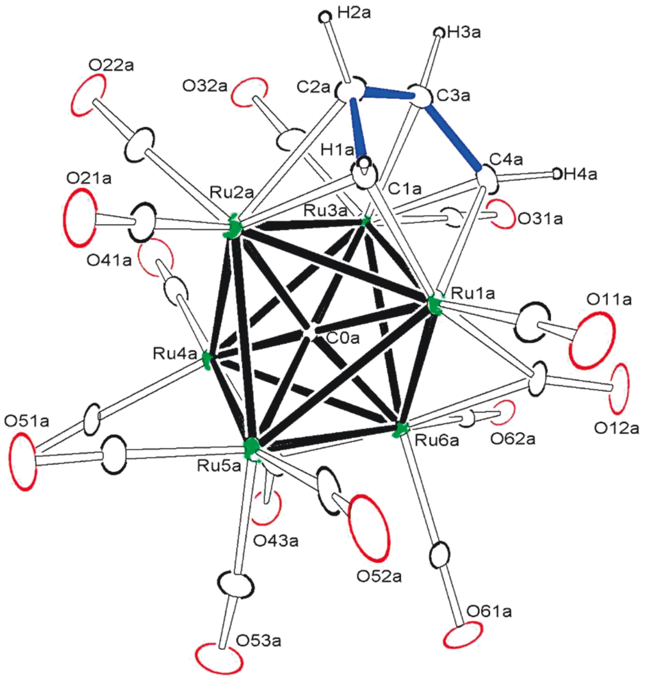


Figure 5. An ORTEP diagram of the molecular structure of compound $Ru_6C(CO)_{14}(\mu_3\text{-}\eta^4\text{-}C_4H_4)$, **6**, showing the 20% thermal ellipsoidal probability. Selected interatomic distances (Å) for the major disorder component are as follows: Ru1a−C1a = 2.108(8), Ru1a−C4a = 2.048(8), Ru2a−C1a = 2.106(8), Ru2a−C2a = 2.301(8), Ru3a−C3a = 2.253(7), Ru3a−C4a = 2.161(7), C1a−C2a = 1.418(11), C2a−C3a = 1.442(11), C3a−C4a = 1.421(11).

Interestingly, the elimination of NMe_3 from **3** is reversible, and when a solution of **6** in CD_2Cl_2 was treated with NMe_3 gas at 25 °C, compound **3** was regenerated and subsequently isolated in 18% yield.

In order to investigate the scope of the alkyne-tertiary amine zwitterion formation reaction further, we performed the reaction of **1** with methyl propiolate, $HC{\equiv}C(CO_2Me)$, and Me_3NO in CH_2Cl_2 at room temperature. After 15 min, the compound $Ru_6C(CO)_{16}[\eta^1\text{-}E\text{-}C(CO_2Me){=}C(H)NMe_3]$, **7**, was formed and subsequently isolated in 10% yield. Compound **7** was characterized structurally by single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of compound **7** is shown in Figure 6. Compound **7** contains an octahedral-shaped Ru_6 cluster with 16 carbonyl

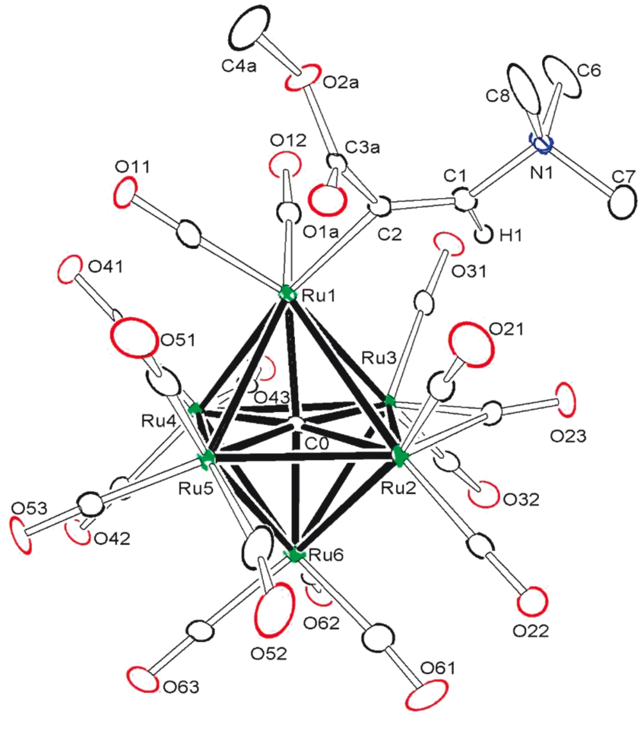


Figure 6. An ORTEP diagram of the molecular structure of the compound $Ru_6C(CO)_{16}[\eta^4\text{-}E\text{-}C(CO_2Me){=}C(H)NMe_3]$, **7**, showing the 30% thermal ellipsoidal probability. Selected interatomic distances (Å) are as follows: Ru1−C2 = 2.120(5), C1−C2 = 1.304(7), N1−C1 = 1.477(7), N1−C6 = 1.450(7), N1−C8 = 1.459(7), N1−C7 = 1.462(7), C2−C3a = 1.522(9), C3a−O1a = 1.182(10), C3a−O2a = 1.325(9), C4a−O2a = 1.440(9).

ligands similar to that of **4**. There is a 2-trimethylammonium-1-(methoxycarbonyl)ethenyl ligand, *E*-$C(CO_2M){=}C(H)NMe_3$, having an *E*-conformation at the C1 and C2 double bond that is terminally coordinated to the metal atom Ru1 at the carbon atom C2, Ru1−C2 = 2.120(5) Å. The C−C double bond distance, C1−C2 = 1.304(3) Å, is virtually the same as that found in **4**. The C−N bond distance to the NMe_3 group N1−C1 is 1.477(7) Å. There is a formal positive charge on the nitrogen atom N1 and a negative charge on the Ru_6 cluster. It is believed that the bulky NMe_3 group is bonded to the carbon atom C1 that contains the hydrogen atom for steric reasons. The single ethenyl CH resonance was observed at $\delta = 5.21$ (t, $^2J_{N-H} = 4.8$ Hz) in the ^1H NMR spectrum. The methyl resonance of the NMe_3 group occurs at $\delta = 3.13$. The $C(CO_2Me){=}C(H)NMe_3$ ligand serves as a two electron donor to the Ru_6 cluster which thus achieves a total cluster valence electron count of 86 electrons that is in accord with the observation of an octahedral-shaped cluster.[16]

When a solution of **7** in 1,2-dichloroethane solvent was heated to reflux (83 °C) for 30 min, it was transformed into the new compound $Ru_6C(CO)_{15}[\mu_3\text{-}HC_2(CO_2Me)]$, **8**, in 66% yield by loss of two CO ligands and the NMe_3 group on the $C(CO_2CH_3){=}C(H)NMe_3$ ligand. Compound **8** was characterized structurally by single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of compound **8** is shown in Figure 7. Compound **8** is a homologue of **5**. It contains an octahedral-shaped Ru_6 cluster with 15 linear terminal carbonyl ligands and a triply bridging methyl propiolate ligand. The alkyne C−C bond distance, C1−C2 = 1.392(5) Å, is slightly longer than that in **5**. The alkyne CH resonance occurs at $\delta = 10.50$ and the methoxy methyl resonance occurs at $\delta = 3.89$, as expected. Compound **8** contains a total of 86 cluster valence electrons which is in accord with the observation of an octahedral-shaped cluster.[16]

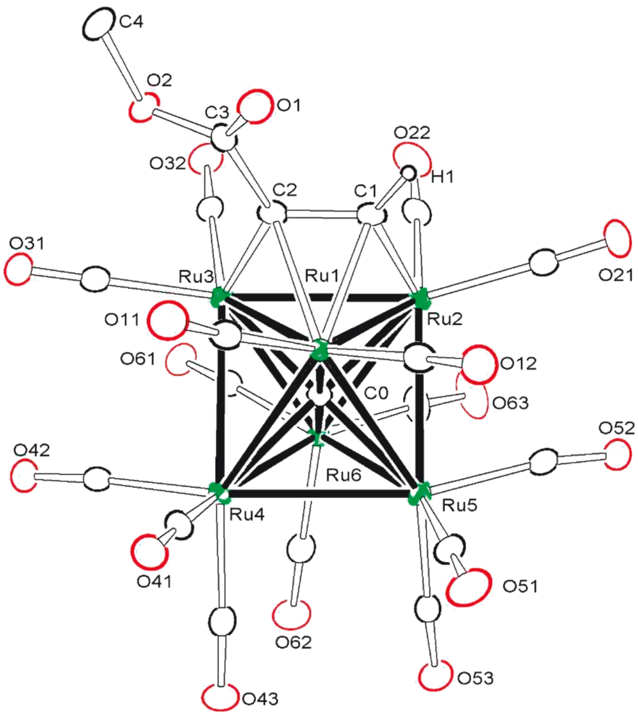


Figure 7. An ORTEP diagram of the molecular structure of the compound $Ru_6C(CO)_{15}[\mu_3{-}HC_2(CO_2CH_3)]$, **8**, showing the 30% thermal ellipsoidal probability. Selected interatomic distances (Å) are as follows: Ru1−C1 = 2.186(3), Ru1−C2 = 2.184(3), Ru2−C1 = 2.034(3), Ru3−C2 = 2.049(3), C1−C2 = 1.392(5), C2−C3 = 1.504(5), C3−O1 = 1.206(4), C3−O2 = 1.331(4), C4−O2 = 1.446(4).

DISCUSSION

A number of years ago, Johnson and Lewis et al. reported the synthesis of the complex $Ru_6C(CO)_{15}(\mu_3\text{-}HC_2Ph)$, **9**, from the reaction of **1** with HC_2Ph in the presence of Me_3NO.[18] The Me_3NO was added to assist in the removal of CO ligands by transferring its O atom to a CO ligand to form CO_2 which was then eliminated from the complex. The HC_2Ph molecule was then added to the Ru_6 cluster to become a bridging ligand similar to that found in compound **5**. Compound **9** was found to react with an additional quantity of HC_2Ph in the presence of Me_3NO to yield the complex $Ru_6C(CO)_{14}(\mu_3{-}\eta^4\text{-}C_4H_2Ph_2)$, **10**, that exists as two isomers formed by the head-to-tail and head-to-head coupling of the two molecules of HC_2Ph to form disubstituted, bridging dimetalated butadiendiyl ligands that are coordinated to the cluster in a fashion similar to that observed in compound **6**. No evidence for the formation of products containing NMe_3 groups was provided in this report.

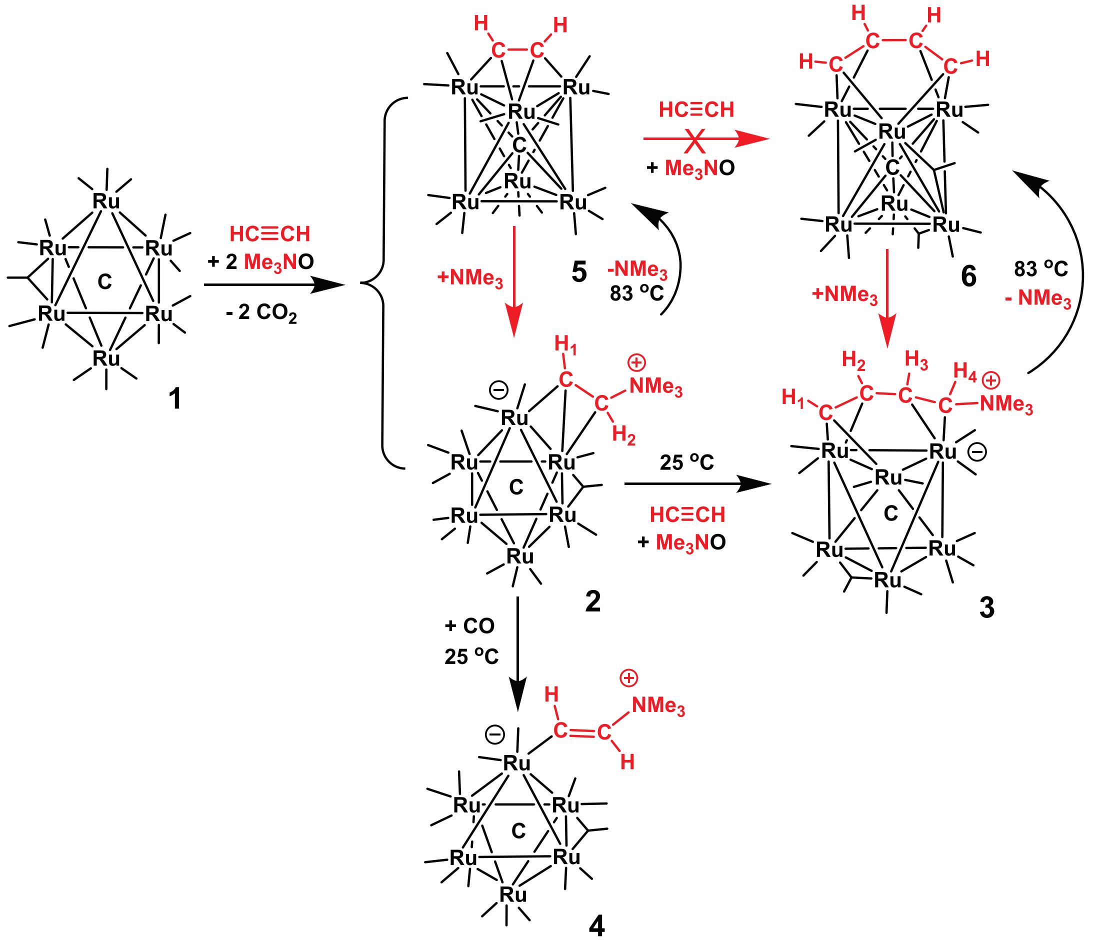
A summary of our studies of the reactions of **1** with ethyne in the presence of Me_3NO is shown in Scheme 1. Compounds **2** and **3** were the only products isolated from the original reaction mixture. Two additional new products, **5** and **6**, were formed by elimination of the NMe_3 group when solutions of **2** and **3** were heated to 83 °C, respectively. Most interestingly, it was found that when the reaction of **1** with HC_2H and Me_3NO was examined at room temperature, in situ, by following by ^1H NMR spectroscopy, the formation of compound **5** was observed as the major product in solution within the first 5 min. Compound **5** subsequently disappeared with the formation of compound **2**, presumably via the direct addition of NMe_3 to **5** as we later confirmed independently. It was also found that compound **3** can be obtained from **2** by reaction with additional quantities of HC_2H and Me_3NO, but no **6** was observed in this reaction. Compound **6** was obtained by heating solutions of **3** at 83 °C, but it could not be obtained from **5** with the use of additional HC_2H and Me_3NO at room temperature. We have been able to obtain **6** only through the **2** → **3** → **6** sequence. It thus appears that the low temperature C−C coupling that leads to the formation of C_4H_4 groupings in both **3** and **6** proceeds via **2** as an intermediate and not from **5**. This in turn suggests that the NMe_3 group may be serving as an "activator" for the HC_2H ligand in **5** for the $HC_2H{-}HC_2H$ coupling process. A number of years ago, Chin et al. demonstrated an example of C−C bond formation between a triethylammoniumethenyl ligand and an alkenyl ligand in an iridium complex by what appears to be a C−C reductive elimination process.[19]

Compound **4** containing the terminally coordinated $C(H){=}CH(NMe_3)$ ligand was obtained by the addition of CO to **2**. Compound **7** containing the terminally coordinated $C(CO_2Me){=}CH(NMe_3)$ ligand was obtained directly by the reaction of **1** with $HC{\equiv}C(CO_2Me)$ in the presence of Me_3NO, see Scheme 2.

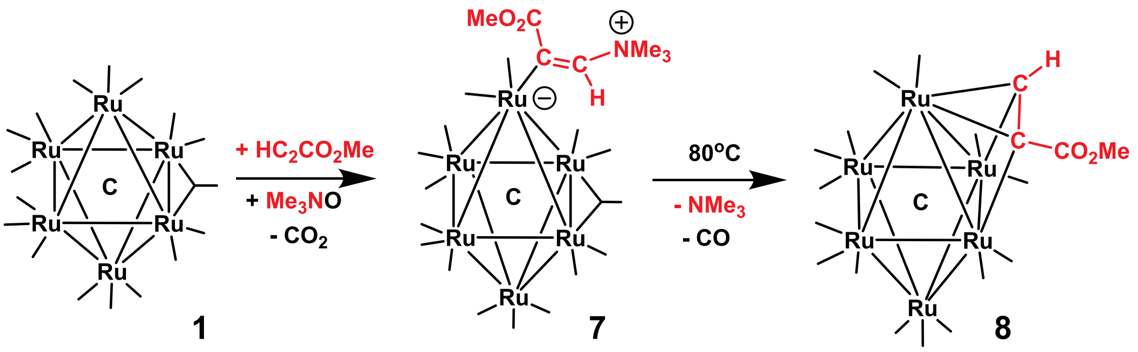
CONCLUSIONS

In this work it has been shown that zwitterionic complexes containing novel bridging trimethylammoniumethenyl ligands

Scheme 1. Schematic of the Structures and Chemical Relationships of Compounds 1−6



Scheme 2. Schematic of the Structures and Relationships of Compounds 1, 7, and 8



can be formed in Ru_6 cluster complexes by reactions of ethyne and NMe_3 generated *in situ* from reactions of Me_3NO with the CO ligands of **1** or by direct NMe_3 addition to the bridging ethyne ligand in complex **5** and the bridging butadiendiyl ligand in **6** to yield the complexes **2** and **3**, respectively, by formation of a C−N bond. The C−N bond formation steps can be reversed by mild heating. Compound **3** was also obtained by the addition of ethyne to compound **2** in the presence of Me_3NO by loss of CO and a C−C coupling to the trimethylammoniumethenyl ligand. It is worth noting that we were not able to obtain any substituted ammoniumethenyl zwitterionic ligands from disubstituted alkynes. This may be due to destabilizations caused by the increased steric interactions that would occur as a consequence of having the bulky NMe_3 group and a substituent located on the same carbon atom of such disubstituted ammoniumethenyl ligands.

■ EXPERIMENTAL SECTION

General Data. All reactions were performed under an atmosphere of nitrogen. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Thermo Scientific Nicolet IS10. ^1H NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1 MHz. Mass spectrometric (MS) measurements were performed by a direct-exposure probe by using electron impact (EI) ionization. $Ru_3(CO)_{12}$ was obtained from STREM and was used without further purification. $Ru_6(\mu_6\text{-}C)(CO)_{17}$, **1**, was prepared from $Ru_3(CO)_{12}$ according to a previously reported procedure.[20] Ethyne gas (HC_2H) (industrial grade) was obtained from National Welders and was used without further purification. Ethyne and carbon monoxide are hazardous gases and should be used only in a well-ventilated fume hood. Methyl propiolate and trimethylamine-*N*-oxide (Me_3NO) were obtained from Sigma-Aldrich and were used without further purification. Product separations were performed by TLC in the open air on Analtech 0.25 mm and 0.50 mm silica gel 60 Å F254 or alumina on glass plates.

Reaction of 1 with C_2H_2 and Me_3NO. A 37.0 mg (0.034 mmol) amount of **1** was added to a 50 mL three-neck flask in 15 mL of degassed dichloromethane. A slow purge of C_2H_2 was then allowed to pass through the solution for 30 min at room temperature. This was followed by addition of 7.0 mg (0.093 mmol) of Me_3NO. After stirring for 20 min, solvent was removed *in vacuo*. The products were then separated by TLC by using a solvent mixture of hexane/methylene chloride/acetone to yield two bands in the order of elution: 15.0 mg (39% yield) of dark red $Ru_6C(CO)_{15}(\mu-\eta^4\text{-}C_2H_2NMe_3)$, **2**, and 6.3 mg (17% yield) of brown $Ru_6C(CO)_{14}(\mu_3-\eta^4\text{-}C_4H_4NMe_3)$, **3**. Spectral data for **2**: IR, ν_{CO} (cm^{-1} in CH_2Cl_2): 2073.0 (m), 2025.9 (s), 1964.3 (w). ^1H NMR (in CD_2Cl_2, δ in ppm): 8.85 (d, C**H**, $^3J_{H-H}$ = 7.5 Hz), 4.28 (d, C**H**,$^3J_{H-H}$ = 7.5 Hz), 3.19 (s, $N(C\mathbf{H}_3)_3$). Elemental analysis: Calculated for $Ru_6NO_{15}C_{21}H_{11}$: C, 22.45%; H, 0.99%; N, 1.25%. Found: C, 21.80%; H, 0.97%; N, 1.13%. Spectral data for **3**: IR, ν_{CO} (cm^{-1} in CH_2Cl_2): 2065.2 (m), 2022.7 (vs), 2016.7 (s), 1995.1 (sh), 1964.0 (w), 1804.5 (w, br). ^1H NMR (in CD_2Cl_2, δ in ppm): 9.53 (d, C**H**, $^3J_{H-H}$ = 6.0 Hz), 6.40 (dd, C**H**, $^3J_{H-H}$ = 6.0 Hz, $^3J_{H-H}$ = 6.3 Hz), 4.21 (d, C**H**, $^3J_{H-H}$ = 7.5 Hz), 2.44 (dd, C**H**, J = 7.5 Hz, $^3J_{H-H}$ = 6.3 Hz), 3.38 (s, $N(C\mathbf{H}_3)_3$). Elemental analysis: Calculated for $Ru_6NO_{14}C_{22}H_{13}$: C, 23.56%; H, 1.17%; N, 1.25%. Found: C, 24.55%; H, 1.46%; N, 1.39%.

Reaction of 2 with Me_3NO and C_2H_2. A 10.0 mg (0.009 mmol) amount of **2** was added to 10 mL of CH_2Cl_2 in a 50 mL three-neck flask. A slow purge of C_2H_2 was then passed through the solution for 15 min at room temperature. This was followed by addition of 1.5 mg of Me_3NO with stirring for 30 min. The solvent was removed *in vacuo*. The product was then separated by TLC by using hexane/methylene chloride solvent mixtures to yield the following in the order of elution: 0.7 mg of unreacted **2** and 1.0 mg of compound **3** (10% yield).

Reaction of 2 with CO. A 4.2 mg (0.003 mmol) amount of **2** was dissolved in 2.5 mL of d_2-dichloromethane in an NMR tube. CO gas was allowed to purge through this solution for 1 min, and the NMR tube was then closed. The solution was then allowed to stand at room temperature for 24 h. After this period, CO was again purged through the solution for 1 min. The NMR tube was closed and was stored at room temperature for another 24 h. After this period, the resonances for a new product were observed by ^1H NMR spectroscopy. Workup of the reaction mixture by TLC by using a hexane/methylene chloride solvent mixture yielded the following products in the order of elution: 1.7 mg of $Ru_3(CO)_{12}$ and 1.7 mg (40% yield) of bright orange compound $Ru_6C(CO)_{16}(\eta^4-E\text{-}C_2H_2NMe_3)$, **4**. Spectral data of **4**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2074.9 (w), 2023.3 (s), 1967.4 (m). ^1H NMR (in CD_2Cl_2, δ in ppm): 7.58 (d, C**H**,$^3J_{H-H}$ = 14.4 Hz), 5.83 (d, C**H**, $^3J_{H-H}$ = 14.4 Hz), 3.13 (s, NMe_3). Mass Spectrum (ES^+): M^+ = 1148.0, $M^+ - C_2H_2NMe_3$ = 1066.0.

Thermal Transformation of 2. A 19.0 mg (0.017 mmol) amount of **2** was dissolved in 10 mL of 1,2-dichloroethane in a 50 mL three-neck flask. This reaction mixture was then heated to reflux (83 °C) for 20 min. The solvent was removed *in vacuo*. The product $Ru_6C(CO)_{15}(\mu_3\text{-}C_2H_2)$, **5**, was isolated by TLC to yield 10.0 mg (55% yield). Spectral data of **5**: IR, ν_{CO} (cm^{-1} in CH_2Cl_2): 2091.1 (w), 2044.7 (s), 2024.2 (m), 2016.3 (m). ^1H NMR (CD_2Cl_2, δ in ppm): 10.39 (s, C**H**). Mass Spectrum (ES^+): M^+ = 1065.0. The isotope distribution pattern is consistent with the presence of six ruthenium atoms.

Thermal Decarbonylation of 4. A 8.0 mg (0.0070 mmol) amount of **4** was dissolved in 10 mL of 1,2-dichloroethane in a 50 mL three-neck flask. This reaction mixture was then heated to reflux for 3 h. The solvent was removed *in vacuo*. Workup by using TLC yielded 6.4 mg (86% yield) of compound **5**.

Thermal Transformation of 3. 6.7 mg (0.006 mmol) of **3** was dissolved in 10 mL of 1,2-dichloroethane in a 50 mL three-neck flask. This reaction mixture was then heated to reflux for 20 min. The solvent was removed *in vacuo*. Workup by using TLC yielded 4.0 mg (64% yield) of compound $Ru_6C(CO)_{14}$ $(\mu_3-\eta^4\text{-}C_4H_4)$, **6**. Spectral data of **6**: IR, ν_{CO} (cm^{-1} in CH_2Cl_2): 2083.6 (m), 2045.9 (s), 2034.8 (vs), 1983.6 (w), 1852 (w, br). ^1H NMR (in CD_2Cl_2, δ in ppm): 10.31 (dd, C**H**, $^3J_{H-H}$ = 3.3 Hz, $^4J_{H-H}$ = 3.3 Hz), 5.27 (dd, C**H**, $^3J_{H-H}$ = 3.3 Hz, $^4J_{H-H}$ = 3.3 Hz). Mass Spectrum (ES^+): M^+ = 1063.0. The isotope distribution pattern is consistent with the presence of six ruthenium atoms.

Addition of NMe_3 to 5. A 10.0 mg (0.009 mmol) amount of **5** was dissolved in 2.5 mL of d_2-CH_2Cl_2 in an NMR tube. NMe_3 gas was then purged slowly through this solution for 1 min at room temperature. The formation of compound **2** was observed by ^1H NMR spectroscopy. Workup of the reaction mixture after 15 min by TLC yielded 3.0 mg of compound **2** (30% yield).

Addition of NMe_3 to 6. A 5.0 mg (0.005 mmol) amount of **6** was dissolved in 2.5 mL of d_2-CH_2Cl_2 in an NMR tube. NMe_3 gas was purged through this solution for 1 min at room temperature, and the NMR tube was then sealed. The formation of compound **3** was observed by ^1H NMR spectroscopy. Workup of the reaction mixture after 15 min by using TLC yielded 1.0 mg of compound **3** (18% yield).

Synthesis of $Ru_6C(CO)_{16}[\eta^1\text{-}E\text{-}(CO_2Me){=}C(H)NMe_3]$, 7. A 45.0 mg (0.041 mmol) amount of **1** was added to 50 mL three-neck flask in 15 mL of degassed dichloromethane. To this solution was added 40 μL of methyl propiolate followed by addition of 8.0 mg of Me_3NO. After stirring for 15 min, the solvent was removed *in vacuo*. The products were then separated by TLC by using a solvent mixture of hexane/methylene chloride to yield the band of 5.0 mg (10% yield) of orange $Ru_6C(CO)_{16}[\eta^1\text{-}E\text{-}C(CO_2Me){=}C(H)NMe_3]$, **7**. Spectral data of **7**: IR spectra, ν_{CO} (cm^{-1} in CH_2Cl_2): 2077.1 (m), 2026.3 (s). ^1H NMR (in CD_2Cl_2, δ in ppm): 5.21 (t, CH, $^2J_{N-H}$ = 4.8 Hz), 3.72 (s, $OC\mathbf{H}_3$), 3.13 (s, $N(C\mathbf{H}_3)_3$). Mass Spectrum (ES^+): M^+ = 1211.0. The isotope distribution pattern is consistent with the presence of six ruthenium atoms.

Synthesis of $Ru_6C(CO)_{15}[\mu_3\text{-}HC_2(CO_2Me)]$, 8. 20.0 mg (0.017 mmol) of **7** was dissolved in 10 mL of 1,2-dichloroethane in a 50 mL three-neck flask. This reaction mixture was then heated to reflux (83 °C) for 30 min. The solvent was removed *in vacuo*. Workup by using TLC provided 12.5 mg (66% yield) of compound $Ru_6C(CO)_{15}[\mu_3\text{-}HC_2(CO_2Me)]$, **8** (66% yield), and 1.8 mg of unreacted **7**. Spectral data of **8**: IR, ν_{CO} (cm^{-1} in CH_2Cl_2): 2093.6 (m), 2048.4 (vs), 2022.8 (s), 1996.4 (w). ^1H NMR (in CD_2Cl_2, δ in ppm): 10.50 (s, C**H**), 3.89 (s, $OC\mathbf{H}_3$). Mass Spectrum (EI^+): M^+ = 1124.0. The isotope distribution pattern is consistent with the presence of six ruthenium atoms.

Crystallographic Analyses. Single crystals of compounds **2**−**8** suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from solutions of the pure compounds at room temperature. X-ray intensity data were measured by using a Bruker D8 QUEST diffractometer equipped with a PHOTON-100 CMOS area detector and an Incoatec microfocus source (Mo K_α radiation, λ = 0.71073 Å).[21] The structures were solved with SHELXT.[22] Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed by using SHELXL-2018[22] or by using OLEX2.[23] 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 Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03349.

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

Accession Codes

CCDC 1963238−1963244 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.

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Notes

The authors declare no competing financial interest.

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