Reactions of electrophiles with ruthenium clusters (.mu.-H)Ru3(.mu.3-.eta.3-XCCRCR')(CO)9-n(PPh3)n: one-electron oxidation or adduct formation

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Reactions of Electrophiles with $(\mu\text{-H})Ru_3(\mu_3\text{-}\eta^3\text{-XCCRCR}')(CO)_{9-n}(PPh_3)_n$: One-Electron Oxidation or Adduct Formation

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Summary: Electrochemical or chemical oxidations of the clusters $HRu_3(\mu_3\text{-}\eta^3\text{-XCCRCR}')(CO)_{9-n}(PPh_3)_n$ *(X = OMe, R = R′ = Me, n = 1–3; X = OMe, R = H, R′ = OEt, n = 2, 3; X =* NEt_2*, R = H, R′ = Me, n = 1, 2) produce radical cations which are stabilized by π donation from the OR or* NEt_2 *groups into the cluster framework orbitals. Treatment of the neutral clusters with* E^+ *(E = H, Ag, Au(PPh*$_3$*)) forms the adducts* $[ERu_3H(\mu_3\text{-}\eta^3\text{-XCCRCR}')(CO)_{9-n}(PPh_3)_n]^+$ *with electrophilic addition either to a Ru–Ru edge or to the* Ru_3 *face.*

Since most compounds containing metal–metal bonds have a HOMO which is metal–metal bonding in character, reactions of metal clusters with electrophiles provide direct information concerning the chemistry of metal–metal linkages. We report here on the reactions of clusters containing a Ru_3C_3 skeletal framework with electrophilic reagents which proceed either by one-electron transfer or by Lewis acid–base adduct formation.

The structure of the metal-carbon cluster core of the 1,3-dimetalloallyl clusters $HRu_3(\mu_3\text{-}\eta^3\text{-XCCRCR}')(CO)_{9-n}(PPh_3)_n$ (see Figure 1: X = OMe, R = R′ = Me, n = 1 (**1a**, L = PPh_3; **1b**, L′ = PPh_3), 2 (**2**, L = L′ = PPh_3), 3 (**3**); X = OMe, R = H, R′ = OEt, n = 2 (**4**, L = L′ = PPh_3), 3 (**5**); X = NEt_2, R = H, R′ = Me, n = 1 (**6a**, L = PPh_3; **6b**, L′ = PPh_3), 2 (**7**, L = L′ = PPh_3)) is notably affected by the nature of the substituents on the allyl fragment but is insensitive to the degree of phosphine substitution.[3,6] The skeletal framework of clusters **1**-**3** may be described as a pentagonal pyramid with the apical Ru atom η^5-coordinated to the Ru_2C_3 five-membered ring.[3,6] However, increasing π-donor ability of the substituent X causes a distortion of the Ru_3C_3 cluster framework such that the structures of **6** and **7** are more properly viewed in terms of a Ru_3C_2 skeleton which adopts an arachno structure based upon a pentagonal bipyramid. However, the HOMO for all members of the series is primarily metal–metal bonding in nature.[4,5] We were therefore interested in the comparison of the reactivity of this cluster class toward oxidants/electrophiles with the reactivity previously established for $H_3Ru_3(\mu_3\text{-CX})(CO)_{9-n}(PPh_3)_n$,[2] for which the HOMO is metal–carbon bonding in character and for which both addition to the Ru–C bond and one-electron oxidations are found in the reactions with electrophiles.

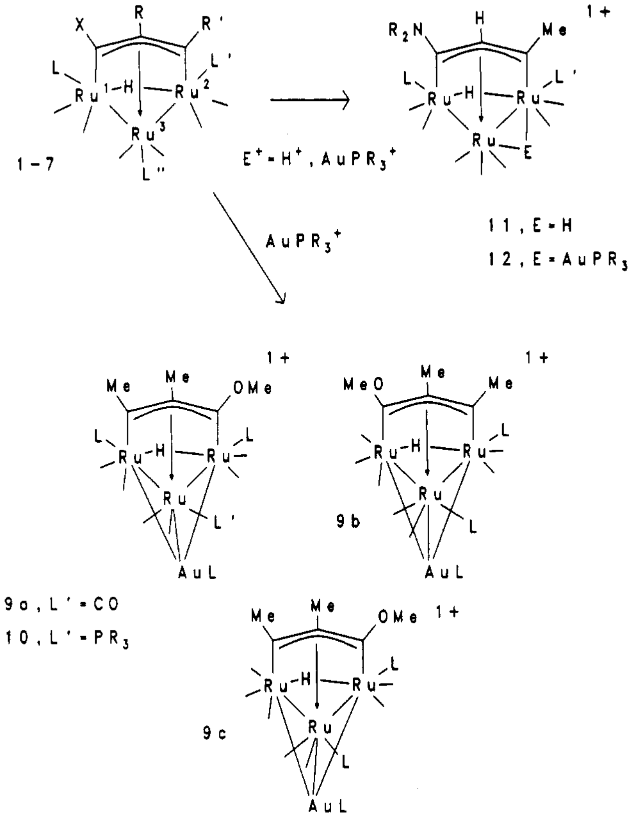

Figure 1. Structure for $HRu_3(\mu_3\text{-}\eta^3\text{-XCCRCR}')(CO)_{9-n}(PPh_3)_n$ and proposed stuctures for 9–12.

The electrochemical behavior of this cluster series[8] was investigated. A previous study of the electrochemistry of $HRu_3(\mu_3\text{-}\eta^3\text{-XCCHCMe})(CO)_9$ (X = Me, NMe_2) had found only irreversible oxidation processes but noted that the presence of the π-donor amino substituent reduced $E_{p,a}$ by 250 mV.[8] Cyclic voltammograms for **2**–**5** and **7** each display a reversible to quasi-reversible, one-electron oxidation, followed by a second, irreversible, one-electron oxidation at a considerably more positive potential.[9] Cyclic

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[1] Bower, D. K.; Keister, J. B. *Organometallics* **1990**, *9*, 2321.

[2] (a) Feighery, W. G.; Allendoerfer, R. D.; Keister, J. B. *Organometallics* **1990**, *9*, 2424. (b) Churchill, M. R.; Lake, C. H.; Feighery, W. G.; Keister, J. B. *Organometallics* **1991**, *10*, 2384.

[3] Churchill, M. R.; Buttrey, L. A.; Keister, J. B.; Ziller, J. W.; Janik, T. S.; Striejewske, W. S. *Organometallics* **1990**, *9*, 766.

[4] CNDO calculations have been performed for $HRu_3(MeCCHCMe)(CO)_9$. The results differ somewhat from the Fenske–Hall calculations reported here for $HRu_3(MeCCMeCMe)(CO)_9$ in that the HOMO/SHOMO gap is much smaller (1.09 (F–H) vs. 0.08 (CNDO) eV): Ganozzi, G.; Tondello, E.; Bertoncello, R.; Aime, S.; Osella, D. *Inorg. Chem.* **1985**, *24*, 570.

[5] Fenske–Hall calculations were performed for $HRu_3(\mu_3\text{-}\eta^3\text{-MeCCMeCMe})(CO)_9$, $HRu_3(\mu_3\text{-}\eta^3\text{-MeOCCMeCMe})(CO)_9$, and $HRu_3(\mu_3\text{-}\eta^3\text{-Me}_2\text{NCCHCMe})(CO)_9$ using version 5.1, kindly provided by Professor M. B. Hall.

[6] Churchill, M. R.; Lake, C. H.; Lashewycz-Rubycz, R. A.; Yao, H.; McCargar, R. D.; Keister, J. B. *J. Organomet. Chem.* **1993**, *452*, 151. $HRu_3(MeCCMeCH)(CO)_8(PPh_3)$, $HRu_3(MeCCHCH)(CO)_{9-n}(PPh_3)_n$ (n = 1, 2), and $HRu_3(Me_2NCCHCMe)(CO)_8(PR_3)$ were previously reported: (a) Jangala, C.; Rosenberg, E.; Skinner, D.; Aime, S.; Milone, L.; Sappa, E. *Inorg. Chem.* **1980**, *19*, 1571. (b) Aime, S.; Gobetto, R.; Osella, D.; Milone, L.; Rosenberg, E. *Organometallics* **1982**, 1, 640. (c) Aime, S.; Jannon, G.; Osella, D.; Deeming, A. J. *J. Organomet. Chem.* **1981**, *214*, C15. (d) Rao, K. M.; Angelici, R. J.; Young, V. G., Jr. *Inorg. Chim. Acta* **1992**, *198-200*, 211.

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voltammograms for **1a**,**b** and **6a**,**b** display irreversible oxidation waves.[9] The potential for the first oxidation process is lowered both by an increasing degree of PPh_3 substitution (e.g. **1a**, $E_{p,a}$ = 1.12 V; **1b**, $E_{p,a}$ = 0.93 V; **2**, $E_{1/2}$ = 0.80 V; **3**, $E_{1/2}$ = 0.52 V) and by an increasing π-donor capability of the allyl substituents (**2**, $E_{1/2}$ = 0.82 V; **7**, $E_{1/2}$ = 0.62 V). Radical cations $\mathbf{3}^+$, $\mathbf{4}^+$, $\mathbf{5}^+$, and $\mathbf{7}^+$ can be generated by oxidation with tris(4-bromophenyl)nitrogen(1+) hexachloroantimonate. These radical cations decompose within a few minutes at room temperature but are stable for long periods at temperatures below −40 °C. EPR spectra have been obtained for $\mathbf{3}^+$, $\mathbf{4}^+$, $\mathbf{5}^+$, and $\mathbf{7}^+$. The *g* values[10] are consistent with a metal-centered unpaired electron and are relatively insensitive to the nature of the carbon substituents. No phosphorus hyperfine coupling is observed.

In contrast, for electrophiles/oxidants H^+, Ag^+ and $Au(PPh_3)^+$, the initial reaction is addition of the electrophile to the Ru–Ru bonds. The reaction of $AgSO_3CF_3$ with **7** initially produces a red solution, presumed to contain a silver cluster complex, but the color of the solution changes to green with formation of a silver mirror within a few minutes, and no product could be identified from the green solution. The adducts $[ERu_3H(XCCRCR')(CO)_{9-n}(PPh_3)_n][A]$ (n = 2, X = OMe, R = R′ = Me, [E][A] = $[Ag][SO_3CF_3]$ (**8**), $[Au(PPh_3)][SO_3CF_3]$ (**9**); n = 3, X = OMe, R = R′ = Me, [E][A] = $[Au(PPh_3)][SO_3CF_3]$ (**10**); n = 2, X = NEt_2, R = H, R′ = Me, [E][A] = $[H][O_2CCF_3]$ (**11**), $[Au(PPh_3)][SO_3CF_3]$ (**12**)) have been characterized by IR and ^1H and ^{31}P NMR spectroscopies.[7] Protonation of **7** with trifluoroacetic acid generates **11**, for which the ^{31}P chemical shifts and ^1H–^{31}P coupling constants indicate that the protonation occurs at the Ru–Ru edge syn to the methyl substituent and trans to the PPh_3 ligand (Figure 1).[12] Similarly for **12**, the $Au(PPh_3)$ moiety appears to bridge the Ru–Ru bond which is syn to the methyl substituent, since only one of the Ru-bound ^{31}P nuclei (41.2 ppm, shown by selective $^1H\{^{31}P\}$ decoupling to be also coupled to the methyl protons) is coupled to the Au-bound ^{31}P nucleus (60.2 ppm, J_{PP} = 30 Hz). Different stuctures which contain μ_3-$AuPPh_3$ moieties seem to be adopted by adducts **9** and **10**. Adduct **10** displays coupling constants between the three Ru-bound ^{31}P nuclei (48.5 (m), 45.1 (ddd), and 38.9 (m) ppm) and the Au-bound nucleus (58.7 (ddd) ppm, J_{PP} = 26, 19, and 17 Hz) which are all very similar, indicating that the Ru_3 face is capped by the Au atom (Figure 1). For **9** the kinetic product **9a** rearranges to a 40:10:50 mixture of isomers **9a**–**c** within 24 h; proposed structures shown in Figure 1 are based upon the ^{31}P coupling constants associated with the hydride, alkyl, and ^{31}P resonances. The similarity of the three ^{31}P–^{31}P coupling constants for **9a** (30, 20, and 10 Hz) indicates that the $Au(PPh_3)$ moiety bridges the Ru_3 triangle rather than a single Ru–Ru bond.

Fenske–Hall MO calculations were performed on $HRu_3(\mu_3\text{-}\eta^3\text{-}MeCCMeCMe)(CO)_9$, $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCMeCMe)(CO)_9$, and $HRu_3(\mu_3\text{-}\eta^3\text{-}Me_2NCCHCMe)(CO)_9$, for which accurate structural data[3,11] are available.[5] The substituent dependence of the energy of the HOMO (−7.04, −6.90, and −6.63 eV, respectively) parallels the electrochemical data for the substituted analogs; increased π donation by the allyl substituents lowers the ionization energy of the cluster. The calculations also reveal that, while the total contributions of the basal Ru atoms to the HOMO remain relatively constant throughout the series, the contribution of the basal Ru adjacent to the heteroatom substituent increases with its π-donor character (contributions to the HOMO by orbitals of Ru(1), Ru(2), and Ru(3), respectively, in Figure 1: 14, 14, and 33% for $HRu_3(\mu_3\text{-}\eta^3\text{-}MeCCMeCMe)(CO)_9$; 16, 13, and 31% for $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCMeCMe)(CO)_9$; 21, 9, and 30% for $HRu_3(\mu_3\text{-}\eta^3\text{-}Me_2NCCHCMe)(CO)_9$). Thus, the contributions from the two basal Ru atoms to the HOMO are approximately equal for **2** but the basal Ru adjacent to the NEt_2 substituent makes a much larger contribution for **7**. These calculations indicate that the regiochemistry of Lewis acid addition is not determined by the nature of the HOMO of the reactant cluster. Face bridging might be expected to be more favorable for adducts of **2** than for adducts of

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(7) $[HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCMeCMe)(CO)_7(PPh_3)_2(AuPPh_3)][SO_3CF_3]$ (**9**). To a 100-mL Schlenk flask was added $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCMeCMe)(CO)_7(PPh_3)_2$ (61 mg, 0.054 mmol) and dichloromethane (15 mL) under nitrogen. In a separate 50-mL Schlenk flask was placed $Au(PPh_3)Cl$ (32 mg, 0.066 mmol) and $AgSO_3CF_3$ (17 mg, 0.065 mmol) in dichloromethane; the mixture was stirred for 10 min under nitrogen to allow complete precipitation of AgCl. The solution was then passed through a 60-mL coarse frit into the cluster solution. Over a period of 10 min the solution underwent a color change, from red-orange to deep purple. An IR spectrum was taken after 30 min, and it was observed that the starting material had completely disappeared. The NMR spectra initially showed only one isomer (**9a**); however, after 24 h a 40:10:50 mixture of isomers **9a**–**c** was noted. The reaction was stirred overnight to ensure complete reaction. The solvent was removed by rotavaporation, and the resulting solid was recrystallized from dichloromethane/cyclohexane (1:1) to give a dark purple powder (46.9 mg, 49.8%). IR (CH_2Cl_2): 2065 (s), 2022 (vs), 1983 (m, br) cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): **9a**, 7.2 (m, 45H), 3.03 (s, 3H), 2.28 (s, 3H), 2.10 (d, 3H, J_{PH} = 3.3 Hz) −18.96 (t, 1H, J_{PH} = 12.0 Hz) ppm; **9b**, 3.65 (s, 3H), 1.90 (s, 3H), 1.51 (d, 3H, J_{PH} = 5.0 Hz), −20.90 (d, 1H, J_{PH} = 14.0 Hz) ppm; **9c**, 2.92 (s, H), 2.00 (s, 3H), 1.60 (s, 3H), −21.00 (d, 1H, J_{PH} = 16.2 Hz). ^{31}P NMR ($CDCl_3$): **9a**, 62.3 (dd, $1P_A$), 47.7 (dd, $1P_B$), and 45.5 (dd, 1P) ppm, J_{AB} = 30 Hz, J_{AC} = 20 Hz, and J_{BC} = 10 Hz; **9b**, 61.9 (t) ppm, J_{PP} = 10 Hz (other resonances were likely obscured by those due to isomers **9a**,**b**); **9c**, 66.7 (t, $1P_A$), 47.3 (dd, $1P_B$), and 43.5 (dd, $1P_C$) ppm, J_{AB} = J_{AC} = 20 Hz, J_{BC} = 10 Hz. Anal. Calcd for $AuC_{68}H_{55}F_3O_{11}P_3Ru_3S$: C, 47.20; H, 3.20. Found: C, 46.45; H, 3.27. Experimental details of syntheses and characterizations of **8** and **10**–**12** are available as supplementary material. **8**: IR (CH_2Cl_2) 2065 (s), 2022 (vs), 1983 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 25 °C) 7.1 (m, 30 H), 2.98 (s, 3 H), 2.24 (s, 3 H), 2.03 (d, 3 H, J_{PH} = 2.4 Hz), −19.21 (t, 1 H, J_{PH} = 12.2 Hz) ppm; ^{31}P NMR ($CDCl_3$) 45.8 (s, 1 P), 42.2 (s, 1 P) ppm. **10**. IR (CH_2Cl_2) 2025 (vs), 2009 (vs), 1986 (s), 1966 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 25 °C) 7.3 (m, 60H), 3.12 (s, 3H), 1.87 (s, 3H), 1.27 (d, 3H, J_{PH} = 3.6 Hz), −18.98 (t, 1H, J_{PH} = 11.8 Hz) ppm; ^{31}P NMR ($CDCl_3$) 58.7 (ddd, $1P_a$, J_{ac} = 26 Hz, J_{PP} = 19, 17 Hz), 48.5 (m, $1P_b$), 45.1 (ddd, $1P_c$, J_{ac} = 26 Hz, J_{PP} = 14, 12 Hz), 38.9 (m, $1P_d$) ppm. **11**: IR (CH_2Cl_2) 2085 (vs), 2055 (m), 2040 (s), 2005 (sh), 1973 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 25 °C) 7.3 (m, 45H), 6.72 (s, 1H), 4.01 (dq, 1H, J_{HH} = 10, 7 Hz), 3.97 (dq, 1H, J_{HH} = 10, 7 Hz), 3.66 (dq, 1H, J_{HH} = 10, 7 Hz), 3.44 (dq, 1H, J_{HH} = 10, 7 Hz), 2.79 (d, 3H, J_{PH} = 2.4 Hz), 1.58 (t, 3H, J_{HH} = 7 Hz), 0.85 (t, 3H, J_{HH} = 7 Hz), −14.56 (dd, 1H, J_{PH} = 20.8 Hz, J_{HH} = 2 Hz), −16.73 (dt, 1H, J_{PH} = 12.2 Hz, J_{HH} = 2 Hz) ppm; ^{31}P NMR ($CDCl_3$) 34.8 (br, 1P), 33.6 (br, 1P) ppm. **12**: IR (CH_2Cl_2) 2049 (s), 2013 (vs), 1966 (m, br) cm^{-1}; ^1H NMR ($CDCl_3$, 25 °C) 7.3 (m, 45H), 6.82 (d, $1H_A$, J_{AB} = 2.5 Hz), 4.10 (dq, 1H, J_{HH} = 14, 7 Hz), 3.97 (dq, ^1H, J_{HH} = 14, 7 Hz), 3.61 (dq, 1H, J_{HH} = 14, 7 Hz), 3.34 (dq, 1H, J_{HH} = 14, 7 Hz), 2.51 (d, 3H, J_{PH} = 3.2 Hz), 1.64 (t, 3H, J_{HH} = 7 Hz), 0.84 (t, 3H, J_{HH} = 7 Hz), −16.85 (dt, $1H_B$, J_{PH} = 12.1, J_{AB} = 2.5 Hz) ppm; ^{31}P NMR ($CDCl_3$) 60.2 (d, $1P_A$), 41.2 (d, $1P_B$), 37.2 (s, 1P) ppm, J_{AB} = 30.0 Hz.

(8) Zanello, P.; Aime, S.; Osella, D. *Organometallics* 1984, *3*, 1374.

(9) In 0.1 M NBu_4BF_4 in dichloromethane, at 100 mV/s, referenced to ferrocene/ferrocenium at 0.53 V (ΔE_p = 72 mV). First oxidation: **1a**, $E_{p,a}$ = 1.12 V; **1b**, $E_{p,a}$ = 0.93 V; **2**, $E_{1/2}$ = 0.80 V, ΔE_p = 74 mV, $i_{p,c}/i_{p,a}$ 0.90; **3**, $E_{1/2}$ = 0.52 V, ΔE_p 70 mV, $i_{p,c}/i_{p,a}$ = 1.0; **4**, $E_{1/2}$ = 0.62 V, ΔE_p = 72 mV, $i_{p,c}/i_{p,a}$ = 0.89; **5**, $E_{1/2}$ = 0.33 V, ΔE_p = 68 mV, $i_{p,c}/i_{p,a}$ = 1.0; **6a**, $E_{p,a}$ = 0.97 V; **6b**, $E_{p,a}$ = 1.04 V; **7**, $E_{1/2}$ = 0.62 V, ΔE_p = 75 mV, $i_{p,c}/i_{p,a}$ = 0.88. Second oxidation: **2**, $E_{p,a}$ = 1.27 V; **3**, $E_{p,a}$ 0.98 V; **4**, $E_{p,a}$ = 1.01 V; **5**, $E_{p,a}$ = 0.78 V; **7**, $E_{p,a}$ = 1.02 V.

(10) ESR data for frozen methylene chloride solutions, g_1, g_2, g_3 (125 K): $\mathbf{7}^+$, 2.221, 2.098, and 2.048; $\mathbf{4}^+$, 2.208, 2.095, and 2.020; $\mathbf{5}^+$, 2.204, 2.088, and 2.040; $\mathbf{3}^+$, 2.208, 2.107, and 2.047.

(11) Aime, S.; Osella, D.; Deeming, A. J.; Arce, A. J.; Hursthouse, M. B.; Dawes, H. M. *J. Chem. Soc., Dalton Trans.* 1986, 1459.

(12) Protonation of the dimethylamino analog of **6b** occurs on the Ru–Ru bond trans to the PR_3 ligand.[6c] In this case it is impossible to determine whether the regiochemistry is controlled by the location of the PR_3 ligand or by the allyl substituents. Protonation of $HRu_3(\mu_3\text{-}\eta^3\text{-}MeCCHCMe)(CO)_8(PPh_3)$ also has been reported (Rosenberg, E.; Skinner, D. M.; Aime, S.; Gobetto, R.; Milone, L.; Osella, D. *Gazz. Chim. Ital.* 1991, *121*, 313).

7, but bridging the Ru–Ru bond adjacent to the NEt_2 unit of 7 would have been expected.

In summary, for these 1,3-dimetalloallyl clusters both σ-donor substituents on the metal skeletal atoms and π-donor substituents of the carbon skeletal atoms lower the oxidation potential of the skeletal framework orbitals and stabilize radical cation products. Electrophilic addition to the Ru_3C_3 skeleton is more complicated, and the regiochemistry of addition is not strictly determined by the nature of the HOMO of the reactant cluster. The factors which determine the thermodynamic stabilities of the isomeric Lewis acid adducts of organometallic clusters, the most important of which are cluster hydrides, remain to be elucidated.

Acknowledgment. We thank Dr. Sunil-Dutta Soni of Varian Associates for recording the $^{31}P\{^1H\}$ NMR spectra. This work was supported by Grants CHE 8900921 and CHE9213695 from the National Science Foundation.

Supplementary Material Available: Text giving syntheses and characterization data for 8–12 (3 pages). Ordering information is given on any current masthead page.

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