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Preliminary communication

SYNTHESIS AND REACTIONS OF $H_3Ru_3(\mu_3\text{-CSEt})(CO)_9$. REDUCTIVE ELIMINATION OF C—H BONDS AND INSERTION OF ALKYNES INTO Ru—C AND Ru—H BONDS

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Summary

Synthesis of $H_3Ru_3(\mu_3\text{-CSEt})(CO)_9$ is accomplished by base-promoted attack of ethanethiol on $H_3Ru_3(\mu_3\text{-CBr})(CO)_9$. Thermolysis of this product under CO yields $HRu_3(CH_2SEt)(CO)_9$. Reactions of $H_3Ru_3(\mu_3\text{-CSEt})(CO)_9$ with alkynes C_2R_2 form $HRu_3(\mu_3\text{-}\eta^3\text{-EtSCCRCR})(CO)_9$ (R = Me or Ph) and Ru_3(*cis*-CR=CHR)(CSEt)$(CO)_9$ (R = Me). The chemistry of $H_3Ru_3(\mu_3\text{-CSEt})(CO)_9$ differs significantly from that of the analogous ether derivative $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$.

Previous studies in our laboratory of the chemical reactivity of methylidyne clusters $H_3Ru_3(\mu_3\text{-CX})(CO)_9$ have found that the properties of these molecules vary significantly with the identity of X. The rates of ligand substitution [1] and of hydrogen transfer to unsaturated hydrocarbons [2,3] and the relative rates for reductive elimination of H—H [4] or C—H [5] bonds depend upon the identity of X to the extent that different reaction pathways are followed for different methylidyne clusters under the same reaction conditions. For example, the reaction between CO and $H_3Ru_3(\mu_3\text{-CX})(CO)_9$ yields hydrogen and $HRu_3(\mu\text{-CX})(CO)_{10}$ when X = OMe, but when X = CO_2Me, Ph, or Cl, the products are $Ru_3(CO)_{12}$ and CH_3X. To further delineate the factors which determine the reactivity of these clusters, we have prepared the thioether substituted methylidyne cluster $H_3Ru_3(\mu_3\text{-CSEt})(CO)_9$ and have determined the products of its reactions with CO and with alkynes, products which are quite different from those from the analogous reactions of $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$.

Treatment of $H_3Ru_3(\mu_3\text{-CBr})(CO)_9$ [6] in dichloromethane with ethanethiol (10 equiv.) and triethylamine (3 equiv.) for 18 h forms ($H_3Ru_3(\mu_3\text{-CSEt})(CO)_9$ (structure I, Fig. 1), isolated after thin layer chromatography (silica gel,

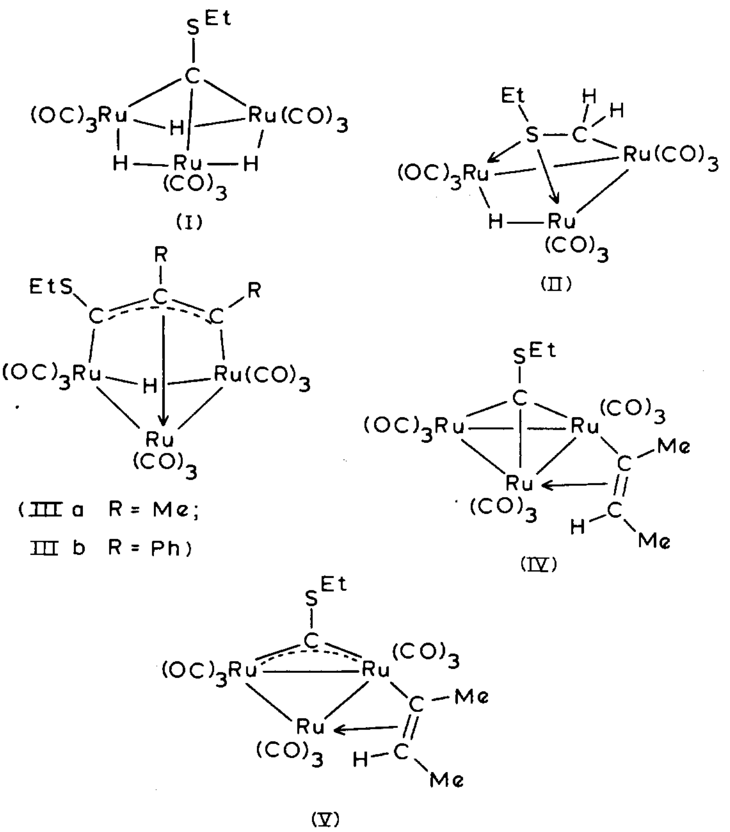

Fig. 1. Proposed structures for new clusters.

5% dichloromethane in cyclohexane) in 10—80% yield as orange crystals. The reason for the erratic yields has not yet been established. The product has been characterized by mass spectrometry and by infrared and ^1H NMR spectroscopy (Table 1). These data are very similar to characterizations of related methylidyne clusters [cf. $H_3Ru_3(\mu_3\text{-COEt})(CO)_9$ [6], IR (C_6H_{12}): 2107w, 2077vs, 2036vs, 2029m, 2014m, 2000w cm^{-1}, ^1H NMR ($CDCl_3$): 4.08 (q, 2H, *J* 6.9 Hz), 1.70 (t, 3H), —17.20 (s, 3H) ppm]. Displacement of halide from $Co_3(\mu_3\text{-CBr})(CO)_9$ by thiols in the presence of triethylamine previously has been used to prepare $Co_3(\mu_3\text{-CSR})(CO)_9$ derivatives [7].

Thermolysis of $H_3Ru_3(\mu_3\text{-CSEt})(CO)_9$ in cyclohexane solution in the presence or absence of CO (0—4 atm, 60°C, 12 h) yields a small amount of $Ru_3(CO)_{12}$ and the major product which has been characterized as $HRu_3(CH_2SEt)(CO)_9$ (thin layer chromatography on silica eluting with cyclohexane, second band, 50% yield). Although the mass spectrum (EI or FAB) of the latter is essentially identical to that of the starting material, the ^1H NMR spectrum is clearly indicative of the transfer of two hydrides to the methylidyne carbon. The proposed structure, II, (Fig. 1) is suggested by analogy to $H_2Os_3(NHC_6H_3F)(CO)_9$ [8] and to $HRu_3(C_2CMe_3)(CO)_9$ [9] and is consistent with the NMR spectrum. However, there is no conclusive evidence that the C—SEt bond is still present in this product. We propose that the stability of this product with respect to reductive elimination of CH_3SEt is due to the strong Ru—S bonds, which retard reductive elimination of a third C—H bond and which prevent CO from coordinating to the cluster after formation of the first and second C—H bonds. The existence of this product is significant in that it supports the stepwise and intramolecular nature of the reductive elimination of CH_3X from thee methylidyne clusters [5].

Reactions of $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$ (X = OMe, Me, or Ph) with alkynes C_2R_2 yield one equivalent of the appropriate *cis*-alkene and $HRu_3(\mu_3\text{-}\eta^3\text{-}XCCRCR)(CO)_9$ [3]. In the same manner, reactions of $H_3Ru_3(\mu_3\text{-}CSEt)(CO)_9$ with C_2R_2 (25°C, 19 h, 5/1 alkyne/cluster, work up by thin layer chromatography on silica using 10% dichloromethane in cyclohexane) yield $HRu_3(\mu_3\text{-}\eta^3\text{-}EtSCCRCR)(CO)_9$ (R = Me (27%) or Ph (12%)) (Structure III, Fig. 1). IR and ^1H NMR data (Table 1) for these products are very similar to data for related clusters previously reported (cf. $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCMeCMe)(CO)_9$ [3]; IR (C_6H_{12}): 2092w, 2064s, 2040vs, 2024m, 2010sh, 2005s, 1990w, 1972w cm^{-1}, ^1H NMR ($CDCl_3$): 3.99 (s, 3H), 2.89 (s, 3H), 2.08 (s, 3H), −19.46 (s, 1H) ppm); the EI mass spectra consist of the molecular ion and ions resulting

TABLE 1

SPECTROSCOPIC DATA FOR NEW COMPLEXES

Compound	ν(CO) (cm^{-1})[a]	^1H NMR (ppm)[b]	m/z ($^{102}Ru_3$)[c]
$H_3Ru_3(\mu_3\text{-}CSEt)(CO)_9$	2108 vw, 2080 s, 2037 s, 2029 m, 2021 m, 2008 w	3.18 (q, 2H, ^3J 7.2 Hz) 1.40 (t, 3H) −17.55 (s, 3H)	634
$HRu_3(CH_2SEt)(CO)_9$	2090 m, 2062 s, 2037 s, 2020 s, 2009 m, 2003 m, 1982 w, 1972 w	2.47 (q, $2H_A$) 1.37 (d, $2H_B$) 1.13 (t, $3H_C$) −16.58 (t, $1H_D$) $^3J_{AC}$ 7.3 Hz J_{BD} 1.5 Hz	634
$HRu_3(\mu_3\text{-}\eta^3\text{-}EtSCCPhCPh)(CO)_9$	2098 m, 2076 s, 2062 m, 2040 s, 2033 sh, 2009 m, 2001 m, 1990 m, 1982 m	7.1 (m, 10H) 2.25 (q, $1H_A$) 1.95 (q, $1H_{A'}$) 0.90 (t, $3H_B$) −19.93 (s, 1H) $^3J_{AB,A'B}$ 7.3Hz	810
$HRu_3(\mu_3\text{-}\eta^3\text{-}EtSCCMeCMe)(CO)_9$	2095 m, 2071 s, 2045 s, 2039 sh, 2027 m, 2021 m, 2011 s, 1997 w, 1978 w	2.87 (s, 3 H) 2.42 (s, 3 H) 2.30 (m, 1 H_A) 1.78 (m, $1H_B$) 1.38 (t, 3 H_C) −20.23 (s, 1 H) $J_{AC,BC}$ 7.3 Hz	686
$Ru_3(CSEt)(CMe{=}CHMe)(CO)_9$	2080 w, 2071 w, 2058 vs, 2041 s, 2009 vs, 2001 vs, 1994 vs, 1989 m, 1985 m	2.66 (m, $2H_{A,A'}$) 2.35 (s, 3H) 2.20 (q, $1H_B$) 1.78 (d, $3H_C$) 1.35 (t, 3 H_D) J_{AD} 7.3 Hz J_{BC} 5.3 Hz	686

[a] In cyclohexane solution. [b] In deuteriochloroform at 25°C. [c] Electron impact mass spectrum.

from the sequential loss of CO ligands. However, an additional product, of a type not previously isolated, is formed in the reaction with 2-butyne and has been characterized as $Ru_3(CSEt)(\textit{cis}\text{-}CMe{=}CHMe)(CO)_9$ (57%); structures IV or V (Fig. 1) are consistent with the spectroscopic data (Table 1), particularly the ^1H NMR resonances due to a *cis*-CMe=CHMe unit (^3J 5.3 Hz) and diasterotopic methylene protons of the SEt unit; the EI mass spectrum is not significantly different from that of $HRu_3(\mu_3\text{-}\eta^3\text{-}EtSCCMeCMe)(CO)_9$. The necessity for the CSEt and CMe=CHMe units to contribute six electrons to the $Ru_3(CO)_9$ fragment requires either that these units are not bonded together or that the sulfur is acting as a two electron donor. This product arises from insertion of 2-butyne into a Ru—H bond, rather than a Ru—CSEt bond as occurs during formation of $HRu_3(\mu_3\text{-}\eta^3\text{-}EtSCCMeCMe)(CO)_9$. By appropriate choice of methylidyne substituent it may be possible to control the direction of the insertion process. This divergence may be of significance to C—C and C—H bond forming processes occurring on metal surfaces [3].

The chemistry of $H_3Ru_3(\mu_3\text{-}CSEt)(CO)_9$ is significantly different from that of the closely related ether analogs, demonstrating the sensitivity of the reaction pathway to even minor changes in the electronic characteristics of these molecules. By appropriate "fine tuning" we should be able to use these reactivity differences to probe the mechanisms of cluster reactions.

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