Synthesis, Reactivity, and Ligand Dynamics of $Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-alkyne})$ Compounds

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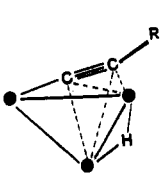
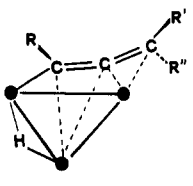
Acetylene, terminal HC_2R (R = COOH, CHO), and nonterminal RC_2R (R = Et, CH_2OH, Ph) alkynes react at room temperature with $Ru_3(CO)_{10}(MeCN)_2$ to give almost quantitatively $Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-alkyne})$ compounds, which are shown to be the precursors of the acetylides $Ru_3(CO)_9(\mu\text{-}H)(C_2R)$ in the case of acetylene and of terminal alkynes or of the allenic $Ru_3(CO)_9(\mu\text{-}H)(RC{=}C{=}CR'R'')$ complexes in the case of internal alkynes. $Ru_3(CO)_9(\mu\text{-}CO)(C_2H_2)$ at room temperature adds H_2 to give $Ru_3(CO)_9(\mu\text{-}H)_2(HC{=}CH)$, which is further hydrogenated at 3 atm to give $Ru_3(CO)_9(\mu\text{-}H)_3CCH_3$. $Ru_3(CO)_9(\mu\text{-}CO)(C_2H_2)$ is stereochemically nonrigid: a low-energy process averages, on the NMR time scale, the semibridging CO with two pairs of terminal carbonyls at the bridged Ru atoms, and it is coupled to an alternate lengthening of one of the Ru–C σ bonds at the same metal atoms. At high temperature, all the carbonyls are equivalent.

Introduction

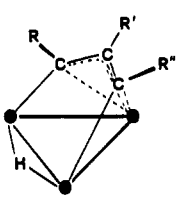
Quite a few organometal carbonyl clusters of ruthenium[1] and osmium[2] with simple ligands (e.g., acetylene, ethylene, and derivatives) have been synthesized, since these molecular compounds provide a very good model for such ligands at metal surfaces, and their transformations are models for reactions such as hydrogenation at surfaces. Several studies on the reactions of dodecacarbonyltriruthenium with alkynes have shown that trinuclear organoruthenium clusters are generally stable products and that normally in such compounds the alkyne may adopt a variety of bonding frameworks and retain an intact carbon skeleton. However, no report has so far appeared in the literature on the isolation of triruthenium clusters containing monomeric acetylene: cluster degradation or acetylene oligomerization is instead observed.[1] On the contrary, in the Os case, $Os_3(CO)_9(\mu\text{-}CO)(C_2H_2)$ has been isolated.[2] Also, the organoruthenium alkyne clusters obtained via cluster decarbonylation and oxidative addition of the alkyne ligand are nonacarbonyl species. The acetylide compound 1 is formed if the alkyne is terminal,



[1]



[2]

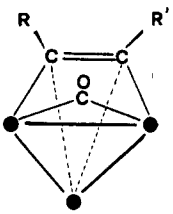


[3]

whereas the allenic compound 2 is obtained if the alkyne is nonterminal; upon heating, compound 2 isomerizes to the allylic compound 3 if R′ or R″ is hydrogen.[1] Earlier intermediates in the reaction have not been isolated. This contrasts with the reactivity, similar in many other ways, of osmium carbonyls with alkynes: in such cases, analogous "$Os_3(CO)_9$" species are obtained, but precursors are also isolated.[2] A good reason for these Ru vs Os differences might be the milder reaction conditions used in the Os case, that is, the preferential use of substituted osmium carbonyls more reactive than $Os_3(CO)_{12}$, such as $Os_3(\mu\text{-}H)_2(CO)_{10}$ or, better still, $Os_3(CO)_{10}(MeCN)_2$, or some similar species with easily displaced ligands.[2] To fill the Ru vs Os gaps, we have chosen as the ruthenium reagent $Ru_3(CO)_{10}(MeCN)_2$ (4), which has recently been shown to react under mild conditions with various ligands.[3] $Ru_3(CO)_9(\mu\text{-}CO)(C_2R_2)$ compounds have been readily obtained, including the so far elusive acetylene derivative. Recently, two papers have discussed the relationship between structure and ligand dynamics in a number of $Os_3(CO)_9(\mu\text{-}CO)(C_2R_2)$ derivatives.[4] We report here a solution NMR study of $Ru_3(CO)_9(\mu\text{-}CO)(C_2H_2)$.

Results and Discussion

Synthesis and Reactivity of $Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-alkyne})$. The reaction of 4[3b] with C_2H_2 in CH_2Cl_2 quantitatively yields in a few minutes an orange, air-stable compound, characterized as $Ru_3(CO)_9(\mu\text{-}CO)(HC{=}CH)$ (**5a**). We suggest that **5a** is isostructural with the analo-



5a, R = R′ = H
5b, R = H; R′ = COOH
5c, R = H; R′ = CHO
5d, R = R′ = Et
5e, R = R′ = CH_2OH
5f, R = R′ = Ph

[5]

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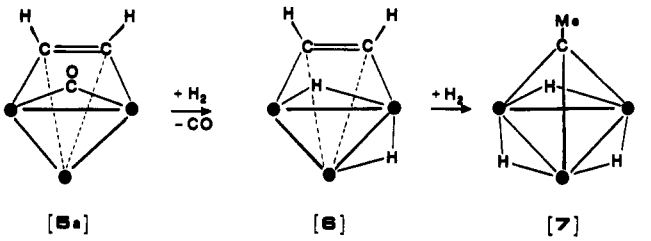
Scheme I



gous $Os_3(CO)_9(\mu\text{-}CO)(HC{=}CH)$.[5] That is, the organic moiety bonds to the $Ru_3(CO)_9$ core as a triply bridged four-electron donor. $Ru_3(CO)_9(\mu\text{-}CO)(HC{=}CR)$ complexes (R = COOH, **5b**; R = CHO, **5c**) are obtained from a similar reaction of **4** with terminal alkynes HC_2R in CH_2Cl_2, as recently reported by some of us for R = CH_2OMe.[3f] Compounds **5** are also formed from the reaction of **4** with nonterminal alkynes RC_2R (R = Et, **5d**; R = CH_2OH, **5e**; R = Ph, **5f**). It has been recently reported that the reaction of either $Ru_3(CO)_{11}(MeCN)$ or **4** with C_2Ph_2 at room temperature in CH_2Cl_2 yields $Ru_3(CO)_8(C_2Ph_2)_2$ almost quantitatively.[3b] The preparation of **5f** is not straightforward as in other cases: a slight excess of the ruthenium carbonyl is required to avoid ligand oligomerization, and more importantly, the purification of **5f** has been hindered by its extreme reactivity. For example, it is destroyed upon application to a chromatographic plate. $Ru_3(CO)_9(\mu\text{-}CO)(MeC{=}CMe)$ and **5f** have been recently synthesized by reacting a dichloromethane solution of the halide-activated cluster $(PPN)(Ru_3(CO)_9(\mu\text{-}Cl)(RC{=}CR))$ (R = Me, Ph) with CO, upon addition of methanol.[6] Compound **5a** is completely converted by refluxing in pentane for 1 h into a yellow compound, characterized as $Ru_3(CO)_9(\mu\text{-}H)(C_2H)$ (**1**, R = H). Compound **5d** is converted under similar conditions into a yellow compound readily recognized as $Ru_3(CO)_9(\mu\text{-}H)(EtC{=}C{=}C(H)Me)$ (**2**, R = Et, R′ = H, R″ = Me).[7] By bubbling hydrogen through an *n*-hexane solution of **5a** for 12 h at room temperature, a pale yellow compound was isolated in 70% yield. It has been characterized as $Ru_3(CO)_9(\mu\text{-}H)_2(HC{=}CH)$ (**6**) (Scheme I). Further treatment of an *n*-hexane solution of **6** with hydrogen at 3 atm for 2 days at room temperature yielded quantitatively a pale yellow compound, identified as $Ru_3(CO)_9(\mu\text{-}H)_3(CMe)$ (**7**).[8] For Ru, this chemistry has some precedent in the stoichiometric photohydrogenation of $Ru_3(CO)_9(\mu\text{-}H)(C_2Bu^t)$ to $Ru_3(CO)_9(\mu\text{-}H)_3(CCH_2Bu^t)$,[9] as well as for Os in the thermal hydrogenation of $Os_3(CO)_9(\mu\text{-}CO)(RC{=}CR')$ (R = R′ = Me; R = H, R′ = Me; R = H, R′ = OEt) to $Os_3(CO)_9(\mu\text{-}H)_2(RC{=}CR')$.[5-10] However, the photohydrogenation of $Ru_3(CO)_9(\mu\text{-}H)(C_2Bu^t)$ (**1**, R = Bu^t) gives an equimolar mixture of $Ru_3(CO)_9(\mu\text{-}H)_2(HC{=}CBu^t)$ and $Ru_3(CO)_9(\mu\text{-}H)_2(C{=}CHBu^t)$, which is further hydrogenated to the trihydrido derivative.

Stereochemical Nonrigidity of $Ru_3(CO)_9(\mu\text{-}CO)(C_2H_2)$. To elucidate ligand migrations in the novel

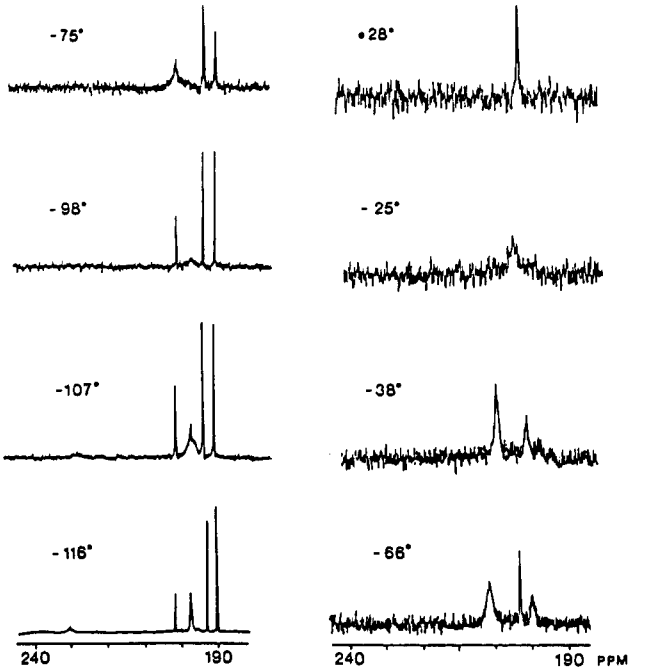
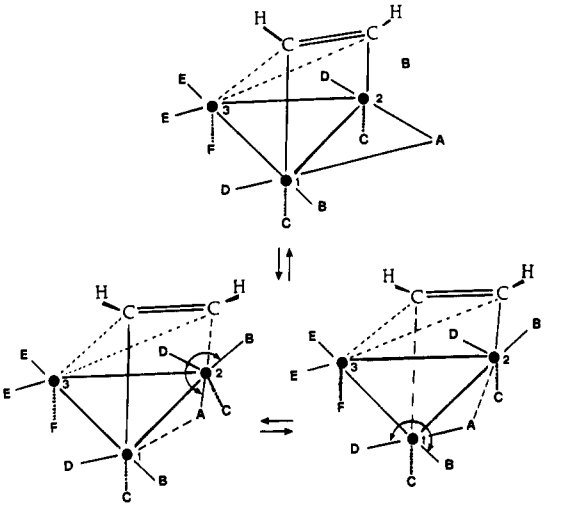


Figure 1. Variable-temperature ^{13}C NMR spectra of $Ru_3(CO)_9(\mu\text{-}CO)(C_2H_2)$, **5a**, in the carbonyl region (solvent: Freon $22/CD_2Cl_2$, 4/1, v/v).

Scheme II



$Ru_3(CO)_9(\mu\text{-}CO)(C_2H_2)$ complex, we obtained variable-temperature ^{13}C NMR spectra of a 20% ^{13}CO-enriched sample at 67.8 MHz (Figure 1). The −116 °C spectrum shows five resonances at ca. 228 (1), 201.8 (1), 197.5 (br, 4), 194.1 (2), and 190.8 (2) ppm. The low-field resonance is substantially upfield of the usual CO bridging region, suggesting semibridging character. Further evidence of the asymmetry of μ-CO is the 1885-cm^{-1} ν_{CO} band in the infrared region. The resonance at 223 ppm in the solid-state ^{13}C NMR spectrum[11] and its 227 ppm chemical shift anisotropy calculated from the analysis of the spinning side bands[12] is further evidence for the asymmetry. As the temperature in solution is increased, the resonances at 228 and 197.5 ppm average to a new 202.2 ppm resonance at −75 °C, overlapping the 201.8 ppm resonance of relative intensity 1. At this temperature, the resonance at 190.8

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ppm shows an incipient broadening, likely suggesting its averaging with the resonance at 201.8 ppm, which, however, is buried under the averaged 202.2 ppm resonance. At −38 °C, the 194.1 ppm resonance also broadens. Eventually, the weighted average peak of all resonances is observed in the room-temperature spectrum at 197.9 ppm (Scheme II). These observations point to a three-stage carbonyl-exchange process. The low-energy one consists of the exchange of μ-CO with $CO_{B,D}$ at Ru_1 and Ru_2, respectively, concerted with the oscillation of the acetylene ligand between the two unsymmetrical structures as shown in Scheme II. A similar oscillatory motion of an alkyne has been suggested to account for a subtle charge imbalance at the bridged metal centers in $M_3(CO)_9(\mu\text{-}H)_2$(alkyne) (M = Ru, Os) derivatives.[13] The carbonyl exchange at Ru_1 and Ru_2 may be envisaged as a trigonal twist exchange process at a pseudooctahedral $Ru(CO)_4$ center: this type of mechanism has been previously observed in trimetallic carbonyl clusters.[14] Local CO exchange at Ru_3 is observed in the second stage of the carbonyl migration process. All the carbonyls become equivalent in the final step as the alkyne is free to migrate about the metal core.[4] The ligand dynamics in **5a** partially differ from that reported for $Os_3(CO)_9(\mu\text{-}CO)$(alkyne).[4] In the Os case, the low-energy process is axial–radial carbonyl exchange at the bridging osmium atoms, which does not involve μ-CO. The stronger metal acetylenic carbon bonds in Os vs Ru require a higher energy for the alternate lengthening of one of the two Ru–C σ bonds, necessary to make room for μ-CO exchange.

Experimental Section

Materials. $Ru_3(CO)_{10}(MeCN0_2$ was prepared by a published method.[3b] The alkynes were purchased from Aldrich and used as received except for prop-2-ynal, which was synthesized according to the literature.[15] All solvents were degassed with N_2 and dried over molecular sieves before use.

Spectra. ^1H and ^{13}C NMR spectra (room temperature if not otherwise stated) were obtained on a Jeol GX 270/89 spectrometer. Infrared spectra were obtained on a Perkin-Elmer 580B spectrometer.

Reaction of $Ru_3(CO)_{10}(MeCN)_2$ (4) with C_2H_2. To an acetylene-saturated CH_2Cl_2 solution (10 mL) was added 100 mg of compound 4 (0.150 mmol), and acetylene was slowly bubbled for 5 min at room temperature. The orange solution was concentrated under reduced pressure and was chromatoghraphed by TLC on silica gel using 30–60 wt % petroleum ether as eluant. The orange band eluted was extracted with pentane to give 85.2 mg (93%) of $Ru_3(CO)_9(\mu\text{-}CO)(HC{=}CH)$ (**5a**). **5a**: Anal. Calcd for $C_{12}H_2O_{10}Ru_3$: C, 23.66; H, 0.331; Ru, 49.77. Found: C, 23.35; H, 0.342; Ru, 49.01. ^1H NMR (δ, ppm, $CDCl_3$): 8.59 (s, integration against added MeI shows the signal to be due to 2 H).[13] C NMR (δ, ppm, $CDCl_3$): 197.9 (s, CO's average), 147.1 (d, =CH, J_{HC} = 161.9 Hz). IR (ν_{CO}, cm^{-1}, cyclohexane): 2099 (m), 2061 (vs), 2055 (vs), 2031 (s), 2012 (m), 1988 (w), 1885 (m, br).

Reaction of 4 with HC_2COOH. In 10 mL of CH_2Cl_2, 100 mg (0.150 mmol) of 4 and 10 μL (0.162 mmol) of HC_2COOH were combined. The solution was stirred at room temperature under N_2 for 5 min. Workup as above gave 84.1 mg (86%) of $Ru_3(CO)_9(\mu\text{-}CO)(HC{=}CCOOH)$ (**5b**). **5b**: Anal. Calcd for $C_{13}H_2O_{12}Ru_3$: C, 23.90; H, 0.309; Ru, 46.42. Found: C, 23.47; H, 0.318; Ru, 47.10. ^1H NMR (δ, ppm, $CDCl_3$): COOH and CH, 9.46 (s), 9.72 (s). IR(ν_{CO}, cm^{-1}, cyclohexane): 2105 (m), 2071 (vs), 2056 (vs), 2038 (s), 2018 (s), 1993 (w), 1890 (m, br), 1751 (w).

Reaction of 4 with HC_2CHO. In 10 mL of CH_2Cl_2, 100 mg of 4 (0.150 mmol) and 8 μL (0.167 mmol) of HC_2CHO were combined. The solution was stirred at room temperature under N_2 for 5 min. Workup as above gave 78.6 mg (82%) of $Ru_3(CO)_9(\mu\text{-}CO)(HC{=}CHO)$ (**5c**). **5c**: Anal. Calcd for $C_{13}H_2O_{11}Ru_3$: C, 24.50; H, 0.316; Ru, 47.59. Found: C, 23.86; H, 0.324; Ru, 48.12. ^1H NMR (δ, ppm, $CDCl_3$): CHO and CH, 9.62 (s), 9.18 (s). IR (ν_{CO}, cm^{-1}, cyclohexane): 2107 (m), 2071 (vs), 2058 (vs), 2029 (s), 2013 (s), 1995 (w), 1898 (m, br), 1725 (w).

Reaction of 4 with C_2Et_2. In 10 mL of CH_2Cl_2, 100 mg of 4 (0.150 mmol) and 20 μL (0.174 mmol) of C_2Et_2 were combined. The solution was stirred at room temperature under N_2 for 5 min. Workup as above gave 80.6 mg (81%) of $Ru_3(CO)_9(\mu\text{-}CO)(EtC{=}CEt)$ (**5d**). **5d**: Anal. Calcd for $C_{16}H_{10}O_{10}Ru_3$: C, 28.89; H, 1.52; Ru, 45.58. Found: C, 28.25; H, 1.62; Ru, 46.08. ^1H NMR (δ, ppm, $CDCl_3$, −60 °C): 3.03 (dq, CH_2), 2.32 (dq, CH_2), 1.33 (t, CH_3). IR (ν_{CO}, cm^{-1}, cyclohexane): 2095 (m), 2060 (vs), 2050 (vs), 2027 (s), 2006 (m), 1974 (w), 1879 (m, br).

Reaction of 4 with $C_2(CH_2OH)_2$. In 10 mL of CH_2Cl_2, 100 mg of 4 (0.150 mmol) and 14.8 mg (0.172 mmol) of $C_2(CH_2OH)_2$ were combined. The solution was stirred at room temperature under N_2 for 10 min. Workup as above, but eluting with 4:1 (v:v) petroleum ether–diethyl ether, gave 72.6 mg (72%) of $Ru_3(CO)_9(\mu\text{-}CO)(HOCH_2C{=}CCH_2OH)$ (**5e**). **5e**: Anal. Calcd for $C_{14}H_6O_{12}Ru_3$: C, 25.13; H, 0.904; Ru, 45.31. Found: C, 24.66; H, 0.919; Ru, 45.00. ^1H NMR (δ, ppm, $CDCl_3$): 5.28 (s, OH), 4.22 (s, CH_2). IR (ν_{CO}, cm^{-1}, cyclohexane): 2097 (m), 2061 (vs), 2053 (vs), 2020 (s), 2007 (m), 1975 (w), 1877 (m, br).

Reaction of 4 with C_2Ph_2. In 50 mL of CH_2Cl_2, 100 mg of 4 (0.150 mmol) and 23 mg (0.129 mmol) of C_2Ph_2 were combined. The solution was stirred at room temperature under N_2 for 5 min. The red solution was concentrated under reduced pressure and was chromatographed on a SiO_2 column in the dark, using pentane as eluant. Two fractions were obtained; crystallization from hexane gave 34.4 mg (30%) of $Ru_3(CO)_9(\mu\text{-}CO)(PhC{=}CPh)$ (**5f**) and 29.4 mg (22%) of $Ru_3(CO)_8(C_2Ph_2)_2$.[16] **5f**: Anal. Calcd for $C_{24}H_{10}O_{10}Ru_3$: C, 37.86; H, 1.32; Ru, 39.82. Found: C, 37.43; H, 1.41; Ru, 40.47. ^1H NMR (δ, ppm, $CDCl_3$): 7.6–6.9 (m, Ph). IR (ν_{CO}, cm^{-1}, cyclohexane): 2097 (m), 2060 (vs), 2054 (vs), 2030 (s), 2009 (m), 1979 (w), 1886 (m, br).

Thermolysis of $Ru_3(CO)_9(\mu\text{-}CO)(HC{=}CH)$ (5a). A 25-mL pentane solution of 40 mg of **5a** was refluxed under nitrogen for 1 h. TLC on silica gel of the residue, 30–60 wt % petroleum ether as eluant, gave 34.6 mg (91%) of $Ru_3(CO)_9(\mu\text{-}H)(C_2H)$ (1, R = H). 1 (R = H): Anal. Calcd for $C_{11}H_2O_9Ru_3$: C, 22.72; H, 0.347; Ru, 52.16. Found: C, 22.38; H,0.352; Ru, 51.81. ^1H NMR (δ, ppm, $CDCl_3$): 10.64 (s, ≡CH), −19.48 (s, μ-H). IR (ν_{CO}, cm^{-1}, cyclohexane): 2095 (m), 2066 (vs), 2051 (vs), 2022 (vs), 2018 (s), 1990 (m).

Thermolysis of $Ru_3(CO)_9(\mu\text{-}CO)(EtC{=}CEt)$ (5d). Thirty milligrams of **5d** was treated as above. TLC separation gave 21.8 mg (76%) of $Ru_3(CO)_9(\mu\text{-}H)(EtC{=}C{=}C(H)Me)$ (2, R = Et, R′ = H, R″ = Me).[7]

Reaction of $Ru_3(CO)_9(\mu\text{-}CO)(HC{=}CH)$ (5a) with H_2. Hydrogen was slowly bubbled into a 100-mL hexane solution of 40 mg of **5a** for 12 h at room temperature. TLC separation gave 27.4 mg (72%) of $Ru_3(CO)_9(\mu\text{-}H)_2(HC{=}CH)$ (6). 6: Anal. Calcd for $C_{11}H_4O_9Ru_3$: C, 22.65; H, 0.691; Ru, 51.98. Found: C, 22.40, H, 0.699, Ru, 52.21. ^1H NMR (δ, ppm, $CDCl_3$): 8.53 (s, =CH), −15.58 (s, μ-H), −19.72 (s, μ-H). IR (ν_{CO}, cm^{-1}, cyclohexane): 2109 (w), 2080 (s), 2058 (vs), 2044 (s), 2033 (m), 2017 (s), 1994 (m).

Reaction of $Ru_3(CO)_9(\mu\text{-}H)_2(HC{=}CH)$ (6) with H_2. A hexane solution of 20 mg of 6 was introduced in a 125-mL steel autoclave. Hydrogen was added up to 3 atm. The autoclave was rocked at room temperature for 2 days. TLC separation gave 17.6 mg (88%) of $Ru_3(CO)_9(\mu\text{-}H)_3(CMe)$ (7).[8]

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