

# Synthesis and Crystallographic Characterization of

## $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOMe})$

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Hydrogenation of the 1,3-dimetalloallyl cluster  $(\mu\text{-H})\text{Ru}_3(\mu_3\text{-}\eta^3\text{-HCCHCOMe})(\text{CO})_9$  forms the  $\mu_3$ -alkyne cluster  $(\mu\text{-H})_2\text{Ru}_3(\mu_3\text{-}\eta^2\text{-MeCCOMe})(\text{CO})_9$  in 11% yield, in addition to the major product  $(\mu\text{-H})_3\text{Ru}_3(\mu_3\text{-}\eta^2\text{-CET})(\text{CO})_9$  (previously reported, 39%). The former product has been characterized by spectroscopic methods and by a single-crystal X-ray diffraction study.  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOMe})$  crystallizes in the centrosymmetric triclinic space group  $P\bar{1}$  with  $a = 9.6879$  (30) Å,  $b = 9.7830$  (17) Å,  $c = 10.3423$  (17) Å,  $\alpha = 101.897$  (14)°,  $\beta = 91.014$  (20)°,  $\gamma = 96.835$  (20)°,  $V = 951.4$  (3) Å<sup>3</sup>, and  $Z = 2$ . Diffraction data (Mo  $K\alpha$ ,  $2\theta = 4.5\text{--}45.0^\circ$ ) were collected on a Syntex P2<sub>1</sub> diffractometer, and the structure was refined to  $R_F = 3.6\%$  and  $R_{wF} = 3.2\%$  for all 2790 data. All atoms, including all hydrogen atoms, were located and refined to convergence. The molecule contains a triangular array of ruthenium atoms, each of which is linked to three terminal carbonyl ligands. The intermetallic distances are Ru(1)–Ru(2) = 2.979 (1) Å, Ru(1)–Ru(3) = 2.743 (1) Å, and Ru(2)–Ru(3) = 2.827 (1) Å. Hydride ligands bridge the Ru(1)–Ru(2) vector (Ru(1)–H(12) = 1.69 (5) Å; Ru(2)–H(12) = 1.77 (5) Å) and the Ru(2)–Ru(3) vector (Ru(2)–H(23) = 1.73 (6) Å; Ru(3)–H(23) = 1.60 (6) Å). The MeCCOMe fragment behaves as a  $\mu_3\text{-}\eta^2$ -alkyne ligand with  $\sigma$ -bonds to Ru(1) and Ru(2) (Ru(1)–C(4) = 2.082 (15) Å; Ru(2)–C(5) = 2.134 (5) Å) and a  $\pi$ -linkage to Ru(3) (Ru(3)–C(4) = 2.391 (5) Å; Ru(3)–C(5) = 2.221 (5) Å). This is the first accurate structure determination of a member of the class  $(\mu\text{-H})_2\text{M}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-RCCR}')$  including location of the hydride ligands.

### Introduction

Reactions of unsaturated hydrocarbons with tri-ruthenium and triosmium clusters have been of interest for many years.<sup>1</sup> The most extensive area of research has concerned products derived from alkynes.<sup>2</sup> We have recently reported the coupling reaction of alkynes with  $(\mu\text{-H})_3\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-COMe})$  to form  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-RCCR'COMe})$  and the hydrogenation of these products to  $(\mu_3\text{-H})_3\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-CCHR'CH}_2\text{R})$ .<sup>3</sup> This is an example of the extensive rearrangements of hydrocarbon fragments which occur on trinuclear clusters, rearrangements which may mimic some processes occurring on metal surfaces during catalytic processes.<sup>4</sup>

We have now identified the new compound  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOMe})$  as an additional product from the hydrogenation of  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-HCCHCOMe})$  to  $(\mu\text{-H})_3\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-CET})$ . This molecule is isostructural with products from reactions of  $\text{Ru}_3(\text{CO})_{12}$  with alkynes or alkenes,<sup>5–10</sup> and although compounds of the formation  $(\mu\text{-H})_2\text{M}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-RCCR}')$ <sup>5–15</sup> have been known for many years, there have been no full reports concerning their structures<sup>16</sup> and the locations of the hydride ligands

Table I. Experimental Data for the X-ray Diffraction Study of  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOMe})$

(A) Unit Cell Data	
$a = 9.6879$ (30) Å	cryst stem: triclinic
$b = 9.7830$ (17) Å	space group: $P\bar{1}$ ( $C_i^1$ ; no. 2)
$c = 10.3423$ (17) Å	$Z = 2$
$\alpha = 101.897$ (14)°	formula = $\text{C}_{13}\text{H}_8\text{O}_{10}\text{Ru}_3$
$\beta = 91.014$ (20)°	mol wt = 627.4
$\gamma = 96.835$ (20)°	$D(\text{calcd}) = 2.19$ g cm <sup>-3</sup>
$V = 951.4$ (3) Å <sup>3</sup>	$T = 24$ °C (297 K)
(B) Collection of X-ray Diffraction Data	
diffractn: Syntex P2 <sub>1</sub>	
radiatn: Mo $K\alpha$ ( $\lambda = 0.710730$ Å)	
monochromator: highly oriented (pyrolytic) graphite; equatorial mode with $2\theta(m) = 12.160^\circ$ ; assumed to be 50% perfect/50% ideally mosaic for polarization correction	
reflectns measd: $+h, \pm k, \pm l$ for $2\theta = 4.5\text{--}45.0^\circ$ ; yielding 2790 symmetry-independent data (file name RUME-202)	
scan type: coupled $\theta(\text{crystal})\text{--}2\theta(\text{counter})$	
scan width: $[2\theta(K\alpha_1) - 1.0]^\circ \rightarrow [2\theta(K\alpha_2) + 1.0]^\circ$	
scan speed: 2.0 deg/min (in $2\theta$ )	
backgrounds: stationary-crystal, stationary-counter at the two extremes of the $2\theta$ scan; each for one-half of total scan time	
std reflectns: 3 collected after each batch of 97 reflectns; no significant fluctuations obsd	
absorptn correctn: $\mu(\text{Mo } K\alpha) = 23.4$ cm <sup>-1</sup> ; corrected empirically by interpolation (in $2\theta$ and $\phi$ ) between $\psi$ -scans of close-to-axial reflectns	

have been determined only on the basis of spectroscopic methods. We report here the crystal structure determination for  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOMe})$ , including the

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location of the bridging hydride ligands.

### Experimental Section

**Spectroscopic Characterization.** The infrared spectrum was recorded by using a Beckman 4250 spectrophotometer and was calibrated with the  $2138.5\text{ cm}^{-1}$  absorption of cyclohexane. The  $^1\text{H}$  NMR spectra were obtained on a JEOL FX-90Q instrument. The mass spectrum (EI) was provided by Dr. Robert Minard and Mr. Greg Hancock of the Penn State University Mass Spectrometry Facility.

**$\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeC}_2\text{OMe})$ .** A solution of  $\text{HRu}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-CHCHCOMe})^8$  (209 mg, 0.334 mmol) in decane (50 mL) was placed in a 250-mL Parr bottle with a magnetic stir bar. The bottle was flushed with hydrogen gas, pressurized to 3.8 atm, and then heated in an oil bath at  $95\text{--}105\text{ }^\circ\text{C}$  for 18 h. The product solution was evaporated to dryness with vacuum. The residue was separated by thin-layer chromatography (silica gel, cyclohexane) into four yellow bands which were extracted with dichloromethane. Band 1 was  $\text{H}_3\text{Ru}_3(\text{CO})_9(\mu_3\text{-CEt})$  (78 mg, 39%). Band 4 was unreacted starting material (16 mg, 8%). Band 3 was characterized as  $\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeC}_2\text{OMe})$  (24 mg, 11%). Also isolated as a sparingly soluble yellow solid was  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  (54 mg, 29%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $-65\text{ }^\circ\text{C}$ ): 3.70 (s, 3 H, OMe), 2.26 (s, 3 H, Me),  $-15.46$  (d, 1  $\text{H}_A$ , RuH),  $-19.94$  (d, 1  $\text{H}_B$ , RuH) ppm,  $J_{AB} = 3.0\text{ Hz}$ . IR ( $\text{C}_6\text{H}_{12}$ ): 2105 m, 2076 s, 2054 vs, 2038 s, 2030 m, 2012 s, 2004 s, 1998 w, 1988 w  $\text{cm}^{-1}$ . MS (EI):  $m/e$  630 ( $^{102}\text{Ru}_3$ ).

**Collection of the X-ray Diffraction Data.** A clear yellow parallelepiped of approximate dimensions  $0.28 \times 0.13 \times 0.10\text{ mm}^3$  was sealed in a thin-walled glass capillary and mounted on a Syntex P<sub>2</sub> automated diffractometer with its extended direction coincident with the  $\phi$ -axis. All operations were carried out as described previously;<sup>17</sup> details of data collection appear in Table I. There were no systematic absences and the only diffraction symmetry was the Friedel condition. The crystal therefore belongs to the triclinic class. Possible space groups are  $P1$  ( $C_1$ ; No. 1) or  $P\bar{1}$  ( $C_1$ ; No. 2). (The latter centrosymmetric case was confirmed by the successful solution of the structure in that higher space group.)

All data were converted to unscaled  $|F_o|$  values following corrections for absorption and for Lorentz and polarization factors. Any datum with  $I(\text{net}) < 0$  was assigned the value  $|F_o| = 0$ ; no data were rejected.

**Solution and Refinement of the Structure.** All calculations were performed with the SUNY—Buffalo modified version of the Syntex XTL crystallographic program package.<sup>19</sup> The  $F_c$  values are based upon the analytical form of the neutral atom scattering factors;<sup>20a</sup> both the real ( $\Delta f'$ ) and imaginary ( $i\Delta f''$ ) components of anomalous dispersion were included for all atoms.<sup>20b</sup> The function  $\sum w(|F_o| - |F_c|)^2$  was minimized; here,  $w = [(\sigma(|F_o|))^2 + \{0.015|F_o|\}^2]^{-1}$ .

The positions of the three ruthenium atoms were determined from a Patterson map. All other atoms (including all hydrogen atoms) were located from subsequent difference Fourier maps. All atomic positional parameters (including those of the hydrogen atoms) were refined; anisotropic thermal parameters were used for all non-hydrogen atoms. Convergence was reached with  $R_F = 3.6\%$ ,  $R_{wF} = 3.2\%$ , and  $\text{GOF} = 1.24$  for 267 variables refined against 2790 data. [ $R_F = 2.9\%$  and  $R_{wF} = 3.1\%$  for those 2456 data with  $|F_o| > 3\sigma(|F_o|)$ ;  $R_F = 2.4\%$  and  $R_{wF} = 2.9\%$  for those 2248 data with  $|F_o| > 6\sigma(|F_o|)$ .]

A final difference Fourier map was devoid of significant features; the structure is thus both correct and complete. Atomic

**Table II. Final Positional Parameters for  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOMe})$**

atom	x	y	z	B(iso), Å <sup>2</sup>
Ru(1)	0.36937 (5)	0.36347 (5)	0.16288 (4)	
Ru(2)	0.28786 (5)	0.07830 (5)	0.21774 (5)	
Ru(3)	0.10434 (5)	0.28456 (5)	0.23226 (5)	
O(4)	0.33218 (43)	0.48059 (38)	0.46598 (35)	
O(11)	0.34328 (65)	0.24832 (57)	-0.13917 (49)	
O(12)	0.30676 (53)	0.65365 (48)	0.13784 (47)	
O(13)	0.68504 (51)	0.43984 (50)	0.20358 (48)	
O(21)	0.31999 (56)	-0.11458 (50)	-0.05555 (49)	
O(22)	0.09345 (64)	-0.13290 (54)	0.32885 (57)	
O(23)	0.54294 (60)	0.01290 (61)	0.35906 (55)	
O(31)	-0.14312 (60)	0.12935 (70)	0.34329 (63)	
O(32)	-0.01395 (65)	0.30820 (71)	-0.03688 (59)	
O(33)	0.02255 (58)	0.56781 (53)	0.36504 (59)	
C(4)	0.31699 (56)	0.37339 (54)	0.35868 (51)	
C(5)	0.25473 (56)	0.24348 (56)	0.37996 (50)	
C(6)	0.22407 (83)	0.22053 (83)	0.51665 (65)	
C(7)	0.3767 (10)	0.61993 (73)	0.44956 (83)	
C(11)	0.35337 (73)	0.29454 (67)	-0.03076 (71)	
C(12)	0.32988 (66)	0.54374 (66)	0.14922 (58)	
C(13)	0.56912 (69)	0.41068 (61)	0.18741 (57)	
C(21)	0.30569 (71)	-0.04883 (62)	0.04495 (68)	
C(22)	0.16593 (77)	-0.05692 (69)	0.28579 (67)	
C(23)	0.44798 (75)	0.03545 (64)	0.30629 (65)	
C(31)	-0.05274 (76)	0.18740 (79)	0.30080 (74)	
C(32)	0.03003 (75)	0.29889 (77)	0.06251 (71)	
C(33)	0.05274 (64)	0.46328 (77)	0.31485 (67)	
H(12)	0.4110 (54)	0.2015 (50)	0.1652 (47)	3.8 (12)
H(23)	0.1515 (66)	0.1424 (63)	0.1493 (59)	6.7 (17)
H(61)	0.3147 (73)	0.2130 (65)	0.5700 (62)	5.7 (17)
H(62)	0.1505 (60)	0.1406 (59)	0.5089 (50)	3.6 (13)
H(63)	0.1943 (82)	0.2988 (84)	0.5643 (76)	8.1 (23)
H(71)	0.3014 (57)	0.6652 (53)	0.4181 (50)	3.1 (12)
H(72)	0.4731 (91)	0.6243 (85)	0.3827 (82)	10.0 (25)
H(73)	0.4005 (52)	0.6610 (51)	0.5155 (47)	1.3 (12)

coordinates are collected in Table II.

### Results and Discussion

**Hydrogenation of  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-HCCHCOMe})$  to  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOMe})$ .** As previously reported,<sup>3</sup> the major product of the hydrogenation of  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-HCCHCOMe})$  is  $(\mu\text{-H})_3\text{Ru}_3(\text{CO})_9(\mu_3\text{-CEt})$  (38%); a minor product (11%) is here characterized as  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOMe})$ . The latter product is structurally analogous to other  $(\mu\text{-H})_2\text{M}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-RCCR})$  species previously prepared by other routes.<sup>5-15</sup>

Characterization of  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOMe})$  has been achieved by IR and  $^1\text{H}$  NMR spectroscopy, by mass spectrometry, and, definitively, by X-ray crystallography. The IR spectrum between  $2150$  and  $1650\text{ cm}^{-1}$  displays only terminal CO stretching frequencies. The  $^1\text{H}$  NMR spectrum at room temperature consists of only two methyl resonances, but at  $-65\text{ }^\circ\text{C}$  (deuteriochloroform) the fluxionality of the hydride ligands can be frozen out to allow observation of two doublets, each of relative intensity one, at  $-15.46$  and  $-19.94$  ppm. At  $70\text{ }^\circ\text{C}$  (toluene- $d_6$ ) the coalesced resonance appears as a broad ( $\Delta\nu_{1/2} = 7\text{ Hz}$ ) signal of relative intensity two at  $-17.77$  ppm. The mass spectrum (EI) displays the molecular ion and stepwise loss of ligands down to the bare  $\text{Ru}_3\text{C}_2^+$  ion. All these data are similar to those for related clusters, such as  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOMe})^{10}$  and  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_2\text{H}_5)^{5,16}$

Previously reported routes to  $(\mu\text{-H})_2\text{M}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-RCCR})$  type clusters (eq 1-8) have involved reactions of alkenes or alkynes with  $\text{M}_3(\text{CO})_{12}$  or hydrogenated derivatives. The diversity of the reactions which form these species suggests that the  $(\mu\text{-H})_2\text{M}_3(\mu_3\text{-}\eta^2\text{-C}_2)$  unit is a very stable one and that this may be involved in a number of

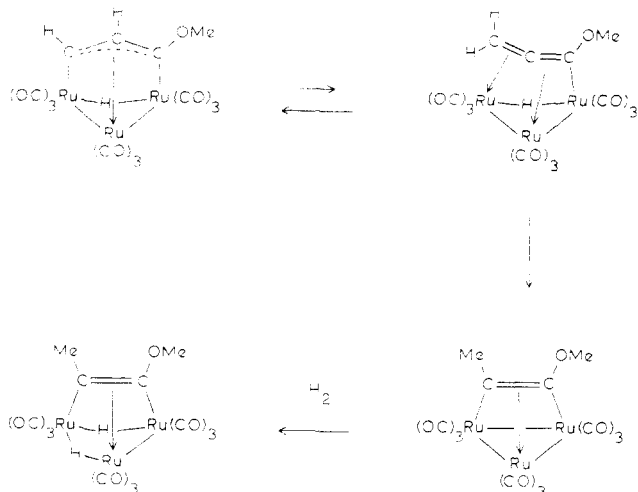
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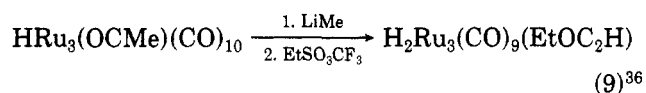
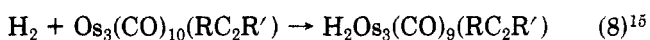
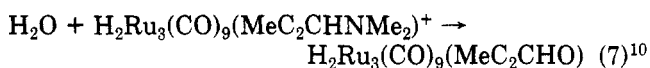
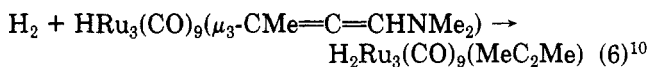
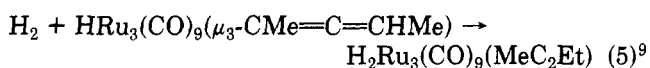
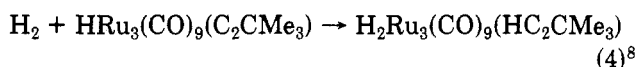
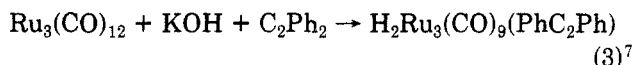
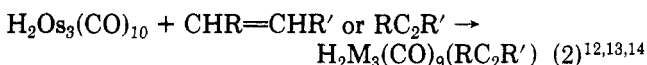
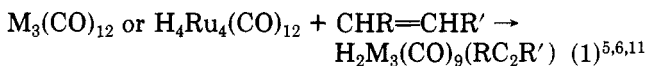
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(21)  $R_F = 100\sum|F_o| - |F_c|/|\sum|F_o||$ ;  $R_{wF} = 100[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ ;  $\text{GOF} = [\sum w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV})]^{1/2}$ , where NO = number of observations and NV = number of variables.

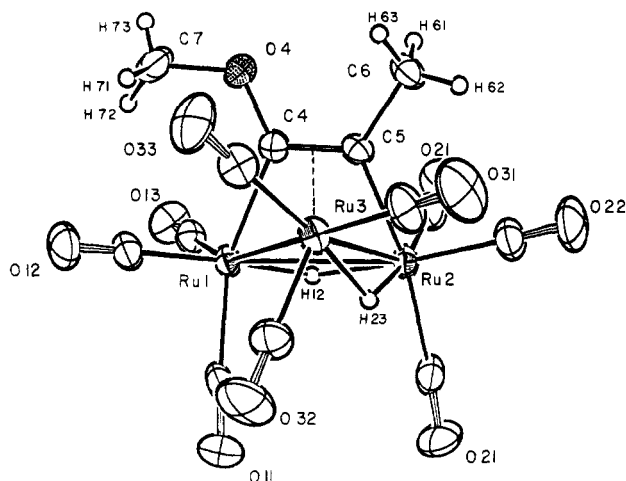


**Figure 1.** Proposed mechanism for conversion of  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-HCCHCOME})$  to  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOME})$ .

hydrocarbon transformations occurring on clusters or surfaces.



The formation of  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOME})$  is the first example of conversion of a 1,3-dimetalloally unit to an alkyne-type cluster. We can propose a mechanism (Figure 1) for this transformation which is based upon the precedent of eq 5 and upon the well-known conversion of  $\mu_3$ -allenyl clusters  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-CR}=\text{C}=\text{CHR}')$  to 1,3-dimetalloally clusters  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-RCCHCR}')$ . In general, reactions of dienes or alkynes with  $\text{Ru}_3(\text{CO})_{12}$  form both  $\mu_3$ -allenyl clusters  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-CR}=\text{C}=\text{CHR}')$  and 1,3-dimetalloally clusters  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-RCCHCR}')$ , and in these instances the former can easily be converted to the latter, which is thermodynamically more stable, by thermal or base-catalyzed isomerization.<sup>9,10,22,23</sup> However, there is no evidence to suggest that this transformation is reversible. If the 1,2-hydrogen migration is indeed reversible, then  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-HCCHCOME})$  may be converted to  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOME})$ . Then hydride migration to the  $\text{CH}_2$



**Figure 2.** Labeling of atoms in the  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOME})$  molecule (ORTEP-II; hydrogens reduced).

**Table III.** Interatomic Distances (in Å) within the  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOME})$

(A) Ru-Ru and Ru-H Distances			
Ru(1)-Ru(2)	2.979 (1)	Ru(1)-H(12)	1.69 (5)
Ru(1)-Ru(3)	2.743 (1)	Ru(2)-H(23)	1.77 (5)
Ru(2)-Ru(3)	2.827 (1)	Ru(2)-H(23)	1.73 (6)
		Ru(3)-H(23)	1.60 (6)
(B) Distances Involving $\mu_3\text{-}\eta^2\text{-MeCCOME}$ Ligand			
Ru(1)-C(4)	2.082 (5)	C(4)-C(5)	1.402 (8)
Ru(2)-C(5)	2.134 (5)	C(4)-O(4)	1.353 (6)
Ru(3)-C(4)	2.391 (5)	O(4)-C(7)	1.425 (8)
Ru(3)-C(5)	2.221 (5)	C(5)-C(6)	1.506 (9)
C(6)-H(61)	1.05 (7)	C(7)-H(71)	0.98 (6)
C(6)-H(62)	0.98 (6)	C(7)-H(72)	1.17 (9)
C(6)-H(63)	0.90 (8)	C(7)-H(73)	0.73 (5)
(C) Distances within Ru-C-O Systems			
Ru(1)-C(11)	1.974 (7)	C(11)-O(11)	1.117 (9)
Ru(1)-C(12)	1.881 (7)	C(12)-O(12)	1.153 (8)
Ru(1)-C(13)	1.935 (7)	C(13)-O(13)	1.126 (8)
Ru(2)-C(21)	1.979 (7)	C(21)-O(21)	1.124 (8)
Ru(2)-C(22)	1.919 (7)	C(22)-O(22)	1.126 (9)
Ru(2)-C(23)	1.919 (7)	C(23)-O(23)	1.128 (9)
Ru(3)-C(31)	1.922 (8)	C(31)-O(31)	1.132 (10)
Ru(3)-C(32)	1.924 (7)	C(32)-O(32)	1.131 (9)
Ru(3)-C(33)	1.909 (7)	C(33)-O(33)	1.122 (9)

moiety would generate the unsaturated "alkyne" adduct  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOME})$ , which could oxidatively add hydrogen to yield  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOME})$ . Unfortunately, the low yield of the reaction makes mechanistic studies impractical.

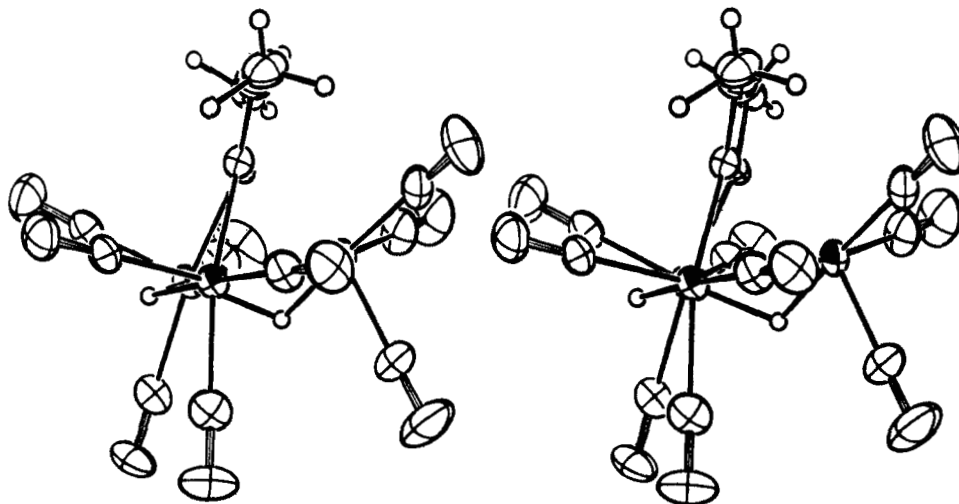
We attempted to carry out the analogous hydrogenation of  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^3\text{-MeCCHCNEt}_2)^{23}$  which we had previously<sup>9</sup> found to be unreactive for C-N bond cleavage to  $(\mu\text{-H})_3\text{Ru}_3(\text{CO})_9(\mu_3\text{-CET})$  and which might therefore be more susceptible to conversion to  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-EtCCNEt}_2)$ . However, hydrogenation of this cluster at 95–100 °C and 3 atm for 19 h yielded only  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ , unreacted starting material, and brown, insoluble solids.

**Structure of  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOME})$ .** Although clusters of the formulation  $(\mu\text{-H})_2\text{M}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-RCCR}')$  have been known for over 10 years, there have been no complete<sup>16</sup> reports of X-ray crystallographic studies of such molecules. Since these clusters are important products in a number of transformations of alkenes and alkynes on triruthenium and triosmium units, we have made an accurate X-ray structure determination for  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOME})$ .

The triclinic crystal contains an ordered array of discrete  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOME})$  molecules, which are

(22) Gambino, O.; Valle, M.; Aime, S.; Vaglio, G. A. *Inorg. Chim. Acta* **1974**, *8*, 71.

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**Figure 3.** Stereoscopic view of the  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOMe})$  molecule. The  $\pi$ -bond to Ru(3) (at right of diagram) is omitted for clarity. Note the torsion in the Ru(1)-C-C-Ru(2) system.

separated by normal van der Waals' distances; there are no abnormally short intermolecular contacts. No crystallographic symmetry is imposed upon the molecule. Each molecule is chiral, but the crystal contains an ordered racemic mixture of the two enantiomers by virtue of the crystallographic inversion centers present in space group  $P\bar{1}$ . The atomic labeling scheme is depicted in Figure 2. A stereoview is provided in Figure 3. Interatomic distances and angles and their estimated standard deviations (esd's) are collected in Tables III and IV, respectively.

The triangular  $\text{Ru}_3$  cluster is associated with the expected total of 48 outer valence electrons. [If we use the neutral metal-neutral ligand electron-counting formalism, we have three  $d^8$  Ru(O) atoms, eighteen electrons from the nine CO ligands, four electrons from the alkyne ligand, and two electrons from the two hydride ligands.] Electron counts at the individual metal atoms are uneven, with (formally)  $17\frac{1}{2}$  electrons at Ru(1), 18 at Ru(2), and  $18\frac{1}{2}$  electrons at Ru(3). The Ru-Ru distances show a wide variation. The Ru(1)-Ru(3) bond length of 2.743 (1) Å is the shortest of the three; this may be compared to Ru-Ru(av) = 2.854 Å in the parent trinuclear carbonyl  $\text{Ru}_3(\text{CO})_{12}$ .<sup>24</sup> The other two Ru-Ru distances (Ru(1)-Ru(2) = 2.979 (1) Å and Ru(2)-Ru(3) = 2.827 (1) Å) are for hydrido-bridged Ru-Ru bonds and are, as expected,<sup>25-27</sup> each longer than the non-hydrido-bridged Ru(1)-Ru(3) bond.

The two hydride ligands occupy bridging sites. The first, H(12), bridges Ru(1) and Ru(2) with Ru(1)-H(12) = 1.69 (5) Å, Ru(2)-H(12) = 1.77 (5) Å, and  $\angle\text{Ru(1)-H(12)-Ru(2)} = 119 (3)^\circ$ . The second, H(23), bridges Ru(2) and Ru(3) with Ru(2)-H(23) = 1.73 (6) Å, Ru(3)-H(23) = 1.60 (6) Å, and  $\angle\text{Ru(2)-H(23)-Ru(3)} = 116 (4)^\circ$ . The H(12)-Ru(2)-H(23) angle is  $92 (3)^\circ$ .

If we ignore direct Ru-Ru interactions in the hydrido-bridged Ru(1)-Ru(2) and Ru(2)-Ru(3) systems, then each ruthenium atom has a slightly distorted octahedral coordination environment. Thus, Ru(1) is coordinated to three carbonyl ligands, one hydride ligand, and Ru(3) and is  $\sigma$ -bonded to C(4) of the  $\mu_3\text{-}\eta^3$ -alkyne ligand; appropriate trans angles are C(12)-Ru(1)-H(12) =  $175.9 (17)^\circ$ , C-

**Table IV.** Selected Interatomic Angles (in deg) for  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-MeCCOMe})$

(A) Ru-Ru-Ru, Ru-H-Ru, H-Ru-H, and Ru-Ru-H Angles			
Ru(3)-Ru(1)-Ru(2)	59.05 (2)	Ru(3)-Ru(1)-H(12)	90.1 (17)
Ru(1)-Ru(2)-Ru(3)	56.32 (2)	Ru(1)-Ru(2)-H(12)	29.6 (16)
Ru(2)-Ru(3)-Ru(1)	64.63 (2)	Ru(1)-Ru(2)-H(23)	67.6 (21)
Ru(1)-H(12)-Ru(2)	119 (3)	Ru(3)-Ru(2)-H(12)	85.8 (16)
Ru(2)-H(23)-Ru(3)	116 (4)	Ru(3)-Ru(2)-H(23)	30.4 (21)
H(12)-Ru(2)-H(23)	92 (3)	Ru(1)-Ru(3)-H(23)	75.8 (22)
Ru(2)-Ru(1)-H(12)	31.2 (17)	Ru(2)-Ru(3)-H(23)	33.2 (22)
(B) Ru-Ru-CO Angles			
Ru(2)-Ru(1)-C(11)	93.4 (2)	Ru(1)-Ru(2)-C(21)	103.3 (2)
Ru(2)-Ru(1)-C(12)	152.0 (2)	Ru(1)-Ru(2)-C(22)	152.9 (2)
Ru(2)-Ru(1)-C(13)	109.4 (2)	Ru(1)-Ru(2)-C(23)	105.3 (2)
Ru(3)-Ru(1)-C(11)	101.2 (2)	Ru(3)-Ru(2)-C(21)	118.4 (2)
Ru(3)-Ru(1)-C(12)	92.9 (2)	Ru(3)-Ru(2)-C(22)	97.3 (2)
Ru(3)-Ru(1)-C(13)	156.4 (2)	Ru(3)-Ru(2)-C(23)	141.9 (2)
Ru(1)-Ru(3)-C(31)	162.4 (2)	Ru(2)-Ru(3)-C(31)	98.7 (2)
Ru(1)-Ru(3)-C(32)	90.9 (2)	Ru(2)-Ru(3)-C(32)	113.6 (2)
Ru(1)-Ru(3)-C(33)	100.5 (2)	Ru(2)-Ru(3)-C(33)	149.6 (2)
(C) OC-Ru-CO and Ru-C-O Angles			
C(11)-Ru(1)-C(12)	92.3 (3)	Ru(1)-C(11)-O(11)	176.2 (6)
C(11)-Ru(1)-C(13)	100.0 (3)	Ru(1)-C(12)-O(12)	178.4 (6)
C(12)-Ru(1)-C(13)	96.6 (3)	Ru(1)-C(13)-O(13)	178.8 (6)
C(21)-Ru(2)-C(22)	94.7 (3)	Ru(2)-C(21)-O(21)	176.0 (6)
C(21)-Ru(2)-C(23)	97.3 (3)	Ru(2)-C(22)-O(22)	177.8 (6)
C(22)-Ru(2)-C(23)	92.1 (3)	Ru(2)-C(23)-O(23)	178.7 (6)
C(31)-Ru(3)-C(32)	101.6 (3)	Ru(3)-C(31)-O(31)	178.3 (7)
C(31)-Ru(3)-C(33)	91.5 (3)	Ru(3)-C(32)-O(32)	179.5 (7)
C(32)-Ru(3)-C(33)	92.1 (3)	Ru(3)-C(33)-O(33)	179.0 (6)
(D) OC-Ru-H Angles			
C(11)-Ru(1)-H(12)	84.4 (17)	C(21)-Ru(2)-H(23)	89.0 (21)
C(12)-Ru(1)-H(12)	175.9 (17)	C(22)-Ru(2)-H(23)	92.9 (21)
C(13)-Ru(1)-H(12)	81.6 (17)	C(23)-Ru(2)-H(23)	171.6 (21)
C(21)-Ru(2)-H(12)	87.1 (16)	C(31)-Ru(3)-H(23)	93.3 (23)
C(22)-Ru(2)-H(12)	175.1 (16)	C(32)-Ru(3)-H(23)	82.9 (23)
C(23)-Ru(2)-H(12)	83.1 (16)	C(33)-Ru(3)-H(23)	173.7 (23)
(E) Angles Involving the MeCCOMe Ligand			
C(7)-O(4)-C(4)	119.3 (5)	Ru(2)-C(5)-Ru(3)	80.9 (2)
O(4)-C(4)-C(5)	115.8 (5)	Ru(2)-C(5)-C(4)	110.3 (4)
C(4)-C(5)-C(6)	121.8 (5)	Ru(2)-C(5)-C(6)	123.6 (4)
Ru(1)-C(4)-Ru(3)	75.3 (2)	Ru(3)-C(5)-C(4)	79.1 (3)
Ru(1)-C(4)-O(4)	131.9 (4)	Ru(3)-C(5)-C(6)	126.8 (4)
Ru(1)-C(4)-C(5)	112.3 (4)	C(4)-Ru(1)-C(11)	156.6 (30)
Ru(3)-C(4)-O(4)	125.3 (4)	C(5)-Ru(2)-C(21)	168.2 (2)
Ru(3)-C(4)-C(5)	65.8 (3)		

(11)-Ru(1)-C(4) =  $156.6 (3)^\circ$ , and Ru(3)-Ru(1)-C(13) =  $156.4 (2)^\circ$ . Atom Ru(2) is coordinated to three carbonyl ligands, two hydride ligands, and atom C(5) of the  $\mu_3\text{-}\eta^3$ -alkyne ligand, with C(22)-Ru(2)-H(12) =  $175.1 (16)^\circ$ ,

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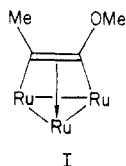
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C(23)–Ru(2)–H(23) = 171.6 (21)°, and C(21)–Ru(2)–C(5) = 168.2 (2)°. Atom Ru(3) is coordinated to three carbonyl ligands, one hydride ligand, and atom Ru(1) and is  $\pi$ -bonded to the  $\mu_3$ - $\eta^2$ -alkyne ligand; trans angles of note are Ru(1)–Ru(3)–C(31) = 162.4 (2)° and C(33)–Ru(3)–H(23) = 173.7 (23)°.

The nine carbonyl ligands are all in terminal positions, with three being attached to each ruthenium atom. Each Ru–C–O system is close to linear (176.0 (6)°  $\rightarrow$  179.5 (7)°; average = 178.1 [12]°) with internally consistent C–O distances (1.117 (9)–1.153 (8) Å; average = 1.129 [10] Å). The Ru–CO distances appear to break into sets consistent with their chemical sites. The two longest Ru–CO bonds are those trans to the  $\sigma$ -linkages from the  $\mu_3$ - $\eta^2$ -alkyne ligand, viz., Ru(1)–C(11) = 1.974 (7) Å and Ru(2)–C(21) = 1.979 (7) Å. The four shortest Ru–CO bonds are those trans to the  $\mu$ -hydride ligands (i.e., Ru(1)–C(12) = 1.881 (7) Å, Ru(2)–C(22) = 1.919 (7) Å, Ru(2)–C(23) = 1.919 (7) Å, Ru(3)–C(33) = 1.909 (7) Å). The Ru–CO bonds trans to Ru (Ru(1)–C(13) = 1.935 (7) Å and Ru(3)–C(31) = 1.922 (8) Å) and that trans to the alkyne  $\pi$ -system (Ru(3)–C(32) = 1.924 (7) Å) have intermediate values. These differences appear to result from  $\sigma$ -donor effects rather than from competition for  $\pi$ -electron density since most of the ligands (other than, possibly the  $\pi$ -alkyne system) are associated with little or no  $\pi$ -electron density.

**The  $\mu_3$ - $\eta^2$ -Alkyne Ligand.** The MeCCOMe ligand lies over the face of the triangular Ru<sub>3</sub> cluster. It is formally  $\sigma$ -bonded to Ru(1) and Ru(2) with rather inequivalent distances of Ru(1)–C(4) = 2.082 (5) Å and Ru(2)–C(5) = 2.134 (5) Å. Atoms C(4) and C(5) are linked via a  $\pi$ -bond (or  $\eta^2$ -linkage) to Ru(3), with Ru(3)–C(4) = 2.391 (5) Å and Ru(3)–C(5) = 2.221 (5) Å. The MeCCOMe ligand behaves as a  $2\sigma$ ,  $\pi$  donor as shown in I. The C(4)–C(5) bond length



is 1.402 (8) Å—substantially greater than for an uncoordinated alkyne (C $\equiv$ C  $\approx$  1.20 Å) or alkene (C=C  $\approx$  1.34 Å) and in the range usually associated with  $\eta^2$ -alkenes in monomolecular complexes.<sup>28</sup> Bond lengths to the substituents are normal (C(4)–O(4) = 1.353 (6) Å and C(5)–C(6) = 1.506 (9) Å), and the distortions from linearity are substantial, with  $\angle$ C(5)–C(4)–O(4) = 115.8 (5)° and  $\angle$ C(4)–C(5)–C(6) = 121.8 (5)°.

The ( $\mu$ -H)<sub>2</sub>Ru<sub>3</sub>( $\mu_3$ - $\eta^2$ -C<sub>2</sub>) framework is significantly distorted when compared with M<sub>3</sub>( $\mu_3$ - $\eta^2$ -C<sub>2</sub>) units not containing bridging hydrides. The Ru–Ru vectors bridged by the hydrides are, as expected, significantly longer than the

unbridged Ru–Ru vector, but the Ru–C bond lengths are also affected. Thus, the Ru(2)–C(5) bond distance is 0.05 Å longer than the Ru(1)–C(4) bond distance, and the Ru(3)–C(5) distance is 0.17 Å longer than the Ru(3)–C(4) distance. These variations are not due to the fact that the alkyne unit is unsymmetrical, since similar distortions, although not as accurately determined, have been noted for ( $\mu$ -H)<sub>2</sub>Ru<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ - $\eta^2$ -C<sub>8</sub>H<sub>8</sub>)<sup>16</sup> and ( $\mu$ -H)<sub>2</sub>Os<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ - $\eta^2$ -C<sub>6</sub>H<sub>4</sub>)<sup>29</sup> compounds having symmetrical hydrocarbon fragments. Although the hydride ligands were not located in the other structures, these results suggest that the alkyne fragment is placed in such a way that the differences in the formal electron counts for the three Ru atoms can be relieved. The Ru(1)–C(4) bond is shortened and the Ru(3)–C(4) bond lengthened to transfer electron density from the electron-rich Ru(3) (18<sup>1/2</sup> electrons) to the electron-poor Ru(1) (17<sup>1/2</sup> electrons).

A series of structural studies of  $\mu_3$ - $\eta^2$ -alkynes have appeared recently. Examples include Cp<sub>2</sub>W<sub>2</sub>Os(CO)<sub>7</sub>( $\mu_3$ - $\eta^2$ -MeC<sub>6</sub>H<sub>4</sub>CCC<sub>6</sub>H<sub>4</sub>Me),<sup>30</sup> CpW<sub>2</sub>Os<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ - $\eta^2$ -MeC<sub>6</sub>H<sub>4</sub>CCC<sub>6</sub>H<sub>4</sub>Me)H,<sup>31</sup> CpW<sub>2</sub>Os<sub>3</sub>(CO)<sub>8</sub>( $\mu$ -O)( $\mu_3$ - $\eta^2$ -C<sub>2</sub>H<sub>2</sub>)( $\mu$ -H),<sup>32</sup> Os<sub>3</sub>(CO)<sub>10</sub>( $\mu_3$ - $\eta^2$ -PhCCPh),<sup>33</sup> Os<sub>3</sub>(CO)<sub>9</sub>( $\mu$ -CH<sub>2</sub>)( $\mu_3$ - $\eta^2$ -PhCCPh),<sup>34</sup> FeCo<sub>2</sub>(CO)<sub>9</sub>( $\mu_3$ - $\eta^2$ -EtCCEt),<sup>35</sup> and Cp<sub>2</sub>Ni<sub>2</sub>Ru(CO)<sub>9</sub>( $\mu_3$ - $\eta^2$ -PhCCPh).<sup>36</sup> For other examples, see a review by Sappa, Tiripicchio, and Braunstein.<sup>2</sup> Such species are of substantial interest because they represent a situation where a C $\equiv$ C has been activated and may represent an intermediate in the cleavage of such a linkage. Indeed, thermolysis of the alkyne complex CpW<sub>2</sub>Os<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ - $\eta^2$ -MeC<sub>6</sub>H<sub>4</sub>CCC<sub>6</sub>H<sub>4</sub>Me)H does lead to the bis(alkylidyne) complex CpW<sub>2</sub>Os<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ -CC<sub>6</sub>H<sub>4</sub>Me)<sub>2</sub>H.<sup>31</sup>

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**Registry No.** HRu<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ - $\eta^3$ -CHCHCOMe), 86409-37-2; H<sub>3</sub>Ru<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ -CEt), 98799-10-1; H<sub>2</sub>Ru<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ - $\eta^2$ -MeC<sub>2</sub>OMe), 98799-11-2; H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub>, 34438-91-0; ( $\mu$ -H)Ru<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ - $\eta^3$ -MeC-CHCNEt<sub>2</sub>), 97633-75-5; Ru, 7440-18-8.

**Supplementary Material Available:** A listing of anisotropic thermal parameters and a table of observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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(28) Manojlovic-Muir, L.; Muir, K. W.; Ibers, J. A. *Discuss. Faraday Soc.* **1969**, *47*, 84 (see, especially, Table 3 on pp 88–89).