

He II intensity responses in the photoelectron spectra. The  $\text{Cp}_3\text{CeOMe}$  electronic structure has been studied using the nonrelativistic  $X\alpha$ -DVM formalism, and the results are in good agreement with He I/He II photoelectron spectroscopic data. The calculations reveal some Ce-Cp f orbital bond covalency. Although it is well-known that nonrelativistic  $X\alpha$  calculations tend to overestimate f orbital contributions to metal-ligand bonding (and to underestimate d orbital contributions),<sup>29,30</sup> this effect should be relatively minor for lanthanides, in contrast to actin-

ides.<sup>29b,c</sup> In sum, the Ce(IV) ligation is rather different in these two organometallic compounds.

**Acknowledgment.** This research was supported by the National Science Foundation (Grant CHE8306255), the Consiglio Nazionale delle Ricerche, Rome, Italy, and the NATO Research Grants Program (Grant 068 184 to I.F. and T.J.M.). H.M. was a Rhône-Poulenc Fellow, and V.P.C. is an N.S.F. Predoctoral Fellow. We thank Dr. G. E. Kellogg for helpful comments.

**Registry No.**  $\text{Ce}(\text{O}-i\text{-Pr})_4$ , 63007-83-0;  $\text{Me}_3\text{SnCp}$ , 2726-34-3;  $\text{Cp}_3\text{Ce}(\text{O}-i\text{-Pr})$ , 39452-86-3;  $\text{Cp}_3\text{CeOMe}$ , 39452-83-0;  $\text{Bu}_3\text{SnCp}$ , 94930-04-8;  $\text{Me}_3\text{Sn}(\text{O}-i\text{-Pr})$ , 30955-89-6.

(30) Hohl, D.; Ellis, D. E.; Rösch, N. *Inorg. Chim. Acta* 1987, 127, 195-202.

## Effects of Mixed-Metal Composition upon the Kinetics and Thermodynamics of Cluster Reactions. Preparation of $\text{HRu}_{3-n}\text{Os}_n(\mu\text{-COMe})(\text{CO})_{10}$ and $\text{H}_3\text{Ru}_{3-n}\text{Os}_n(\mu_3\text{-COMe})(\text{CO})_9$ ( $n = 1$ or $2$ ) and Their Relative Reactivities toward Ligand Substitution and Reductive Elimination of Hydrogen

Jerome B. Keister\*<sup>1</sup> and Christian C. O. Onyeso

Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14214

Received April 28, 1988

The new clusters  $\text{HRu}_2\text{Os}(\mu\text{-COMe})(\text{CO})_{10}$ ,  $\text{H}_3\text{Ru}_2\text{Os}(\mu_3\text{-COMe})(\text{CO})_9$ ,  $\text{HRuOs}_2(\mu\text{-COMe})(\text{CO})_{10}$ , and  $\text{H}_3\text{RuOs}_2(\mu_3\text{-COMe})(\text{CO})_9$  have been synthesized and characterized by spectroscopic methods. Retention of the mixed-metal core during hydrogenation of  $\text{HM}_2\text{M}'(\mu\text{-COMe})(\text{CO})_{10}$  and carbonylation of  $\text{H}_3\text{M}_2\text{M}'(\mu_3\text{-COMe})(\text{CO})_9$  proves that cluster fragmentation does not occur during these reactions. Competition experiments were used to determine relative rates of hydrogenation of  $\text{HM}_3(\mu\text{-COMe})(\text{CO})_{10}$  to  $\text{H}_3\text{M}_3(\mu_3\text{-COMe})(\text{CO})_9$ , attributed to the relative rates of CO dissociation, as  $\text{M}_3 = \text{Ru}_3$  (4500) >  $\text{Ru}_2\text{Os}$  (1100) >  $\text{RuOs}_2$  (220) >>  $\text{Os}_3$  (1) at 343 K. Direct measurements of the rate constants for carbonylation of  $\text{H}_3\text{M}_3(\mu_3\text{-COMe})(\text{CO})_9$  to  $\text{HM}_3(\mu\text{-COMe})(\text{CO})_{10}$  give relative rates:  $\text{M}_3 = \text{Ru}_3$  (210) >  $\text{Ru}_2\text{Os}$  (72) >  $\text{RuOs}_2$  (38) >>  $\text{Os}_3$  (1) at 353 K. The similarity of the rates of carbonylation for all clusters having at least one Ru atom, but a greatly reduced rate for the  $\text{Os}_3$  cluster, suggests that reductive elimination of dihydrogen occurs from a single metal atom in the transition state, even though the hydride ligands bridge two metal atoms in the ground state. Equilibrium constants for hydrogenation and for isomerization of  $\text{HM}_2\text{M}'(\mu\text{-COMe})(\text{CO})_{10}$  were used to obtain estimates of the Ru-H-Ru (408 kJ/mol) and Os-H-Os (425 kJ/mol) bond energies and for the differences in bond energies  $\{E(\text{RuHOs}) - E(\text{RuOs})\}$  (299 kJ/mol),  $\{E(\text{Os}_2(\mu\text{-C})) - E(\text{Ru}_2(\mu\text{-C}))\}$  (42 kJ/mol), and  $\{E(\text{Os}_2(\mu\text{-C})) - E(\text{RuOs}(\mu\text{-C}))\}$  (24 kJ/mol), based upon the assumptions that  $\{E(\text{M}_2(\mu\text{-C})) - E(\text{M}_3(\mu_3\text{-C}))\} = 0$  ( $\text{M} = \text{Ru}$  or  $\text{Os}$ ),  $\{E(\text{Os}_3(\mu_3\text{-C})) - E(\text{RuOs}_2(\mu_3\text{-C}))\} = (1/3)\{E(\text{Os}_3(\mu_3\text{-C})) - E(\text{Ru}_3(\mu_3\text{-C}))\}$ , and  $\{E(\text{Os}_3(\mu_3\text{-C})) - E(\text{Ru}_2\text{Os}(\mu_3\text{-C}))\} = (2/3)\{E(\text{Os}_3(\mu_3\text{-C})) - E(\text{Ru}_3(\mu_3\text{-C}))\}$ .

The reactivity of mixed-metal clusters has been of interest for many years.<sup>2</sup> One goal of research in this area has been to combine, in one molecule, metals having very different chemical properties and thus to induce unique chemical transformations. Another valuable property of mixed-metal clusters is that their lower symmetry allows an additional probe for cluster reactivity.

We have investigated the mechanisms of a number of reactions of the alkylidyne cluster series  $\text{HM}_3(\mu\text{-CX})(\text{CO})_{10}$  ( $\text{M} = \text{Ru}$  or  $\text{Os}$ ;  $\text{X} = \text{OMe}$  or  $\text{NR}_2$ ) and  $\text{H}_3\text{M}_3(\mu_3\text{-CX})(\text{CO})_9$  ( $\text{X} = \text{OMe}$ ,  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{CO}_2\text{Me}$ ,  $\text{SEt}$ ,  $\text{Ph}$ ,  $\text{H}$ , or  $\text{alkyl}$ ), including ligand substitution,<sup>3</sup> oxidative addition and reductive

elimination of molecular hydrogen,<sup>4</sup> reductive elimination of C-H bonds,<sup>5</sup> hydrogen transfer to alkenes and alkynes,<sup>6</sup> and alkylidyne-alkyne coupling.<sup>7</sup> In several of these studies, important questions have remained, concerning the number of metal atoms involved in the mechanism, the site of reactivity, and the possible involvement of cluster fragmentation.

In an effort to answer these questions we have now prepared the mixed-metal alkylidynes  $\text{HRu}_2\text{Os}(\mu\text{-COMe})(\text{CO})_{10}$ ,  $\text{HRuOs}_2(\mu\text{-COMe})(\text{CO})_{10}$ ,  $\text{H}_3\text{Ru}_2\text{Os}(\mu_3\text{-COMe})(\text{CO})_9$ , and  $\text{H}_3\text{RuOs}_2(\mu_3\text{-COMe})(\text{CO})_9$ .

(4) (a) Bavaro, L. M.; Montangero, P.; Keister, J. B. *J. Am. Chem. Soc.*, 1983, 105, 4977. (b) Bavaro, L. M.; Keister, J. B. *J. Organomet. Chem.* 1985, 287, 357.

(5) (a) Duggan, T. P.; Barnett, D. J.; Muscatella, M. J.; Keister, J. B. *J. Am. Chem. Soc.* 1986, 108, 6076. (b) Churchill, M. R.; Janik, T. S.; Duggan, T. P.; Keister, J. B. *Organometallics* 1987, 6, 799. (c) Churchill, M. R.; Ziller, J. W.; Dalton, D. M.; Keister, J. B. *Organometallics* 1987, 6, 806.

(6) Churchill, M. R.; Beanan, L. R.; Wasserman, H. J.; Bueno, C.; Abdul, Rahman, Z.; Keister, J. B. *Organometallics* 1983, 2, 1179.

(7) Beanan, L. R.; Keister, J. B. *Organometallics* 1985, 4, 1713.

(1) Alfred P. Sloan Fellow, 1987-1989.

(2) (a) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* 1980, 18, 207. (b) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 6, Chapter 40. (c) Langenbach, H. J.; Vahrenkamp, H. *Chem. Ber.* 1979, 112, 3773.

(3) Dalton, D. M.; Barnett, D. J.; Duggan, T. P.; Keister, J. B.; Malik, P. T.; Modi, S. P.; Shaffer, M. R.; Smesko, S. A. *Organometallics* 1985, 4, 1854.

COMe)(CO)<sub>9</sub>, and H<sub>3</sub>RuOs<sub>2</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub>. With use of procedures developed in our laboratory, the methoxymethylidyne substituent may be modified to generate an extensive series of mixed Ru/Os alkylidyne clusters.<sup>8</sup> These mixed-metal clusters can provide important information concerning the number and location of the metal atoms involved in reaction mechanisms. It would be expected that the lability of Os atoms in these clusters would be considerably lower than that of the Ru atoms. Therefore, significant differences in cluster reactivity may occur when the number of Ru atoms in the cluster falls below the number of metal atoms involved in the transition state of a reaction.

We present here the first study of the influence of metal composition in a mixed-metal cluster upon the kinetics of reductive elimination of hydrogen. Relative reactivities of these mixed Ru/Os clusters toward CO substitution are also presented. Finally, the equilibrium constants for several reactions of these homo- and heterometallic, methoxymethylidyne-containing clusters are used to provide estimates of metal-hydrogen-metal and relative metal-alkylidyne bond strengths.

### Experimental Section

**General Data.** Infrared spectra were recorded on a Beckman 4250 spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a Varian EM-390 or a JEOL FX-90Q instrument. <sup>13</sup>C NMR spectra were recorded on a Varian Gemini 300-MHz spectrometer; Cr(acac)<sub>3</sub> was added as a relaxation agent. Mass spectra were obtained on a VG 70SE instrument; elemental composition was verified by comparison of experimental spectra with spectra calculated by using the program MSCALC, adapted by J. B. Keister from MASPAN<sup>9</sup> for use on IBM PC computers. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory.

**Starting Materials.** Ru<sub>3</sub>(CO)<sub>12</sub>,<sup>10</sup> Os<sub>3</sub>(CO)<sub>12</sub>,<sup>11</sup> and the mixtures Ru<sub>3-n</sub>Os<sub>n</sub>(CO)<sub>12</sub> (*n* = 0–3)<sup>12</sup> were prepared by using published procedures.

**Preparation of HRu<sub>3-n</sub>Os<sub>n</sub>(COMe)(CO)<sub>10</sub>.** A mixture of Ru<sub>3-n</sub>Os<sub>n</sub>(CO)<sub>12</sub> (*n* = 0–3) was prepared from equimolar quantities of Ru<sub>3</sub>(CO)<sub>12</sub> and Os<sub>3</sub>(CO)<sub>12</sub>. A portion of the mixture (946 mg) was dissolved in THF (100 mL) in 250-mL, three-necked, round-bottomed flask equipped with stir bar, reflux condenser, 50-mL pressure equalizing addition funnel, and nitrogen gas inlet. Then water (10 mL) and triethylamine (10 mL) were added from the addition funnel, and the solution was heated at 60–70 °C under nitrogen for 2 h; during this period the color of the solution changed from yellow-orange to red-purple. Next the solvent was removed by vacuum transfer, and the residue was dried under vacuum. To the dry residue was added a solution of methyl trifluoromethanesulfonate (500 μL) in dry dichloromethane (40 mL). The resulting solution was stirred under nitrogen for 24 h. Then the solvent and unreacted methyl trifluoromethanesulfonate were removed by vacuum transfer (a slurry of potassium carbonate and methanol was used to destroy the collected methyl trifluoromethanesulfonate). The residue was recrystallized from methanol to give 457 mg; additional product (158 mg) was obtained by using thin-layer chromatography on silica, eluting with hexane. Total yield: 615 mg. <sup>1</sup>H NMR analysis showed that the HRu<sub>3-n</sub>Os<sub>n</sub>(μ-COMe)(CO)<sub>10</sub> mixture contained the following: *n* = 0, 17%; *n* = 1, 37%; *n* = 2, 35%; and *n* = 3, 11%; also present were small amounts of unreacted Ru<sub>3-n</sub>Os<sub>n</sub>(CO)<sub>12</sub>.

**Preparation of H<sub>3</sub>Ru<sub>3-n</sub>Os<sub>n</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub> (*n* = 1 and 2).** A solution of HRu<sub>3-n</sub>Os<sub>n</sub>(μ-COMe)(CO)<sub>10</sub> (286 mg) in cyclohexane (90 mL) was placed in a 250-mL, three-necked, round-bottomed

flask equipped with stir bar, reflux condenser, and gas inlet tube. The solution was heated at 70 °C with hydrogen bubbling through the solution for 2.5 h. Then the solvent was removed by rotary evaporation, and the residue was separated by thin-layer chromatography on four silica plates (20 cm<sup>2</sup>, freshly activated), eluting with dry hexanes. Although H<sub>3</sub>Ru<sub>3-n</sub>Os<sub>n</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub> (*n* = 0 and 1), are slightly air-sensitive and partially decompose during chromatography, the separation required the use of the entire length of the plates, which is achieved by evaporation of solvent from the top edge of the plates; for this reason chromatography was not done under inert-atmosphere conditions. The products, in order of elution, were Ru<sub>3-n</sub>Os<sub>n</sub>(CO)<sub>12</sub>, HO<sub>3</sub>(μ-COMe)(CO)<sub>10</sub>, H<sub>3</sub>Ru<sub>3</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub>, H<sub>3</sub>Ru<sub>2</sub>Os(μ<sub>3</sub>-COMe)(CO)<sub>9</sub>, and H<sub>3</sub>RuOs<sub>2</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub>. An additional separation was performed for each of the three hydrogenated products. Yield: H<sub>3</sub>Ru<sub>2</sub>Os(μ<sub>3</sub>-COMe)(CO)<sub>9</sub>, 33 mg; H<sub>3</sub>RuOs<sub>2</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub>, 51 mg.

**H<sub>3</sub>Ru<sub>2</sub>Os(μ<sub>3</sub>-COMe)(CO)<sub>9</sub>:** IR (C<sub>6</sub>H<sub>12</sub>) 2108 vw, 2077 vs, 2032 s, 2022 w, 2012 s, 1996 vw cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) 3.85 (s, 3 H, Me), -16.92 (t, 1 H<sub>a</sub>, RuHRu), -18.22 (d, 2 H<sub>b</sub>, RuHOs) ppm, *J*<sub>ab</sub> = 2.3 Hz; FAB MS, *m/z* 692 (<sup>102</sup>Ru<sup>190</sup>Os). Anal. Calcd for C<sub>11</sub>H<sub>6</sub>O<sub>10</sub>OsRu<sub>2</sub>: C, 19.13; H, 0.88. Found: C, 19.00; H, 0.92.

**H<sub>3</sub>RuOs<sub>2</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub>:** IR (C<sub>6</sub>H<sub>12</sub>) 2106 w, 2076 vs, 2032 s, 2023 s, 2010 s, 1996 w, 1975 vw cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) 3.84 (s, 3 H), -17.66 (d, 2 H<sub>a</sub>), -19.22 (t, 1 H<sub>b</sub>) ppm, *J*<sub>ab</sub> = 2.1 Hz; EI MS, *m/z* 780 (<sup>102</sup>Ru<sup>190</sup>Os<sub>2</sub>). Anal. Calcd for C<sub>11</sub>H<sub>6</sub>O<sub>10</sub>RuOs<sub>2</sub>: C, 16.95; H, 0.78. Found: C, 16.87; H, 0.86.

**Carbonylation of H<sub>3</sub>Ru<sub>2</sub>Os(μ<sub>3</sub>-COMe)(CO)<sub>9</sub>.** A sample of H<sub>3</sub>Ru<sub>2</sub>Os(μ<sub>3</sub>-COMe)(CO)<sub>9</sub> (33 mg, 0.048 mmol), which had been verified to be pure by <sup>1</sup>H NMR spectroscopy, was dissolved in decane (20 mL), and the solution was placed in a 50-mL Schlenk flask under 1 atm of carbon monoxide. The flask was heated at 80 °C in an oil bath for 4 days. At that time the IR spectrum showed that almost complete reaction had occurred. The solution was evaporated to dryness, and the residue was purified by using thin-layer chromatography. The first band that was eluted appeared to be Ru<sub>2</sub>Os(CO)<sub>12</sub>. The middle of three bands, the major product, was extracted with dichloromethane to give 28 mg of a yellow crystalline solid, shown to be HRu<sub>2</sub>Os(μ-COMe)(CO)<sub>10</sub> (82%); the cluster was recrystallized from methanol for elemental analysis. The third band was unreacted H<sub>3</sub>Ru<sub>2</sub>Os(μ<sub>3</sub>-COMe)(CO)<sub>9</sub> (1.3 mg).

Hydrogenation of HRu<sub>2</sub>Os(μ-COMe)(CO)<sub>10</sub> at 60–70 °C for 3 h gave only H<sub>3</sub>Ru<sub>2</sub>Os(μ<sub>3</sub>-COMe)(CO)<sub>9</sub>, as analyzed by <sup>1</sup>H NMR spectroscopy.

**HRu<sub>2</sub>Os(μ-COMe)(CO)<sub>10</sub>:** IR (C<sub>6</sub>H<sub>12</sub>) 2105 w, 2064 vs, 2055 s, 2030 vs, 2018 sh, 2013 s, 2001 s, 1995 sh, 1984 w cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 22 °C) 4.60 (s, 0.24 H), 4.56 (s, 2.34 H), -14.21 (s, 0.08 H), -15.54 (s, 0.92 H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 22 °C), see Table I; EI MS, *m/z* 718 (<sup>102</sup>Ru<sup>190</sup>Os). Anal. Calcd for C<sub>12</sub>H<sub>4</sub>O<sub>11</sub>Ru<sub>2</sub>Os: C, 20.12; H, 0.56. Found: C, 20.25; H, 0.46.

**Carbonylation of H<sub>3</sub>RuOs<sub>2</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub>.** A solution of H<sub>3</sub>RuOs<sub>2</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub> (20 mg, 0.026 mmol), verified to be pure by <sup>1</sup>H NMR spectroscopy, in decane (20 mL) was placed in a Schlenk flask under a CO atmosphere. The sealed flask was heated at 80 °C for 200 h, at which time the IR spectrum indicated that complete reaction had occurred. The solvent was then removed by rotary evaporation. Thin-layer chromatography of the residue on silica, eluting with hexane, gave two closely spaced yellow bands. The first band yielded what appeared to be RuOs<sub>2</sub>(CO)<sub>12</sub> (<1 mg). The second was shown to be HRuOs<sub>2</sub>(μ-COMe)(CO)<sub>10</sub> (11 mg, 55%).

**HRuOs<sub>2</sub>(μ-COMe)(CO)<sub>10</sub>:** IR (C<sub>6</sub>H<sub>12</sub>) 2108 vw, 2064 vs, 2054 s, 2028 s, 2014 s, 2010 m, 1998 m, 1994 m sh, 1982 vw cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) 4.61 (s, 1.4 H), 4.56 (s, 1.6 H), -15.14 (s, 0.44 H), -16.56 (s, 0.56 H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 22 °C), see Table I; EI MS, *m/z* 810 (<sup>102</sup>Ru<sup>192</sup>Os<sub>2</sub>). Anal. Calcd for C<sub>12</sub>H<sub>4</sub>O<sub>11</sub>RuOs<sub>2</sub>: C, 17.89; H, 0.50. Found: C, 17.99; H, 0.47.

**Partial Hydrogenation of HRu<sub>3-n</sub>Os<sub>n</sub>(μ-COMe)(CO)<sub>10</sub> (*n* = 0–3).** Estimates of the relative rates for hydrogenation of HRu<sub>3-n</sub>Os<sub>n</sub>(μ-COMe)(CO)<sub>10</sub> were obtained from percent conversions for partial hydrogenations of mixtures at 70 °C. In a typical example, a cyclohexane solution containing a mixture of composition HRu<sub>3</sub>(μ-COMe)(CO)<sub>10</sub>, 25%, HRu<sub>2</sub>Os(μ-COMe)(CO)<sub>10</sub>, 41%, HRuOs<sub>2</sub>(μ-COMe)(CO)<sub>10</sub>, 27%, and HO<sub>3</sub>(μ-COMe)(CO)<sub>10</sub>, 7%, was heated at 70 °C with hydrogen bubbling through the

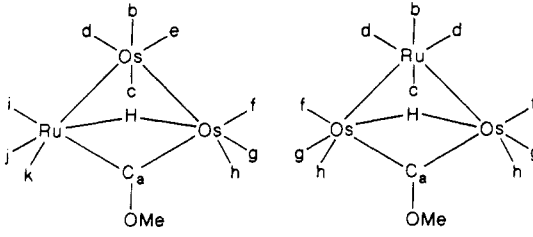
(8) Keister, J. B.; Horling, T. L. *Inorg. Chem.* 1980, 19, 2304.

(9) (a) Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* 1975, 97, 3942. (b) Andrews, M. A. Ph. D. Dissertation, University of California, Los Angeles, Los Angeles, California, 1977.

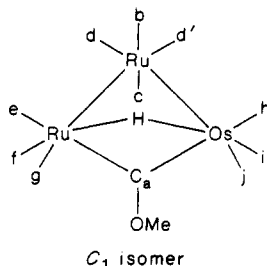
(10) Dawes, J. L.; Holmes, J. D. *Inorg. Nucl. Chem. Lett.* 1971, 7, 847.

(11) Bradford, C. W.; Nyholm, R. S. *J. Chem. Soc., Chem. Commun.* 1967, 384.

(12) Johnson, B. F. G.; Johnston, R. D.; Lewis, J.; Williams, I. G.; Kilty, P. A. *J. Chem. Soc., Chem. Commun.* 1968, 861.

**Table I.**  $^{13}\text{C}$  NMR Spectra for  $\text{HRu}_2\text{Os}(\mu\text{-COMe})(\text{CO})_{10}$  and Both Isomers of  $\text{HRuOs}_2(\mu\text{-COMe})(\text{CO})_{10}$ 


chem shift (ppm)	intensity	assignmt
363.90	26	1a
350.30	47	2a
200.61	13	2b (2c)
198.10	16	2c (2b)
196.45	43	1i
193.25	37	1j
192.37	28	2d
183.93	45	1k
181.64	21	1b (1c)
179.39	40	1f
179.01	should.	1c (1b)
178.97	121	2f
175.80	44	1g
174.52	25	1d (1e)
174.34	20	1e (1d)
173.66	110	2g
169.56	112	2h
169.05	48	1h



chem shift (ppm)	intensity	assignt
361.4	35	a
202.3	11 (br)	b (c)
200.3	12 (br)	c (b)
197.8	82	e
194.2	48	f
193.0	5 (v br)	d, d'
187.1	85	g
180.7	64	h
176.2	56	i
169.8	75	j

solution for 40 min. Then the solution was evaporated to dryness, and the products were analyzed by  $^1\text{H}$  NMR spectroscopy in deuteriochloroform solution. The composition was determined by integration of hydride resonances to be  $\text{HRu}_3(\mu\text{-COMe})(\text{CO})_{10}$ , 3%,  $\text{H}_3\text{Ru}_3(\mu_3\text{-COMe})(\text{CO})_9$ , 25%,  $\text{HRu}_2\text{Os}(\mu\text{-COMe})(\text{CO})_{10}$ , 22%,  $\text{H}_3\text{Ru}_2\text{Os}(\mu_3\text{-COMe})(\text{CO})_9$ , 18%,  $\text{HRuOs}_2(\mu\text{-COMe})(\text{CO})_{10}$ , 24%,  $\text{H}_3\text{RuOs}_2(\mu_3\text{-COMe})(\text{CO})_9$ , 2%,  $\text{H}_3\text{Os}_3(\mu_3\text{-COMe})(\text{CO})_9$ , 5%, and  $\text{H}_3\text{Os}_3(\mu_3\text{-COMe})(\text{CO})_9$ , 0%. Differences in mixed-metal composition between initial and final spectra were assumed to be due to experimental error of the NMR integrals since hydrogenations of homometallic  $\text{HM}_3(\mu\text{-COMe})(\text{CO})_{10}$  are essentially quantitative.

Assuming first-order kinetics, relative rates were taken from the values of  $\ln$  (total percent of  $\text{HRu}_{3-n}\text{Os}_n(\mu\text{-COMe})(\text{CO})_{10}$  +  $\text{H}_3\text{Ru}_{3-n}\text{Os}_n(\mu_3\text{-COMe})(\text{CO})_9$  / percent of  $\text{HRu}_{3-n}\text{Os}_n(\mu\text{-COMe})(\text{CO})_{10}$  unreacted) for  $n = 0-2$  for each experiment. Results from four such experiments using different times for hydrogenation gave average relative rates:  $\text{Ru}_3$  ( $20 \pm 5$ ) >  $\text{Ru}_2\text{Os}$  ( $5 \pm 1$ ) >  $\text{RuOs}_2$  (1) >>  $\text{Os}_3$  (not observed).

**Kinetics of Carbonylation of  $\text{H}_3\text{M}_2\text{M}'(\mu_3\text{-COMe})(\text{CO})_9$ .** For each run, 10 mL of a decane solution of the cluster (ca.  $10^{-3}$  M)

**Table II.** Rate Constants for Carbonylation of  $\text{H}_3\text{M}_2\text{M}'(\mu_3\text{-COMe})(\text{CO})_9$ 

compound	$T$ ( $^\circ\text{C}$ )	rate constant ( $\text{s}^{-1}$ )
$\text{H}_3\text{Ru}_3(\text{COMe})(\text{CO})_9^a$	80.2	$2.50 (\pm 0.10) \times 10^{-5}$
$\text{H}_3\text{Ru}_2\text{Os}(\text{COMe})(\text{CO})_9^b$	80.0	$8.6 (\pm 0.7) \times 10^{-6}$
$\text{H}_3\text{RuOs}_2(\text{COMe})(\text{CO})_9^b$	80.0	$4.5 (\pm 0.3) \times 10^{-6}$
$\text{H}_3\text{Os}_3(\text{COMe})(\text{CO})_9^c$	80	$1.2 \times 10^{-7}$

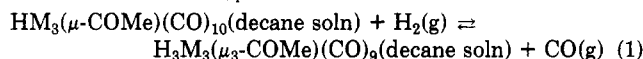
<sup>a</sup> Reference 4a.  $P_{\text{CO}} = 3.7$  atm. <sup>b</sup> In decane solution.  $P_{\text{CO}} = 1$  atm. <sup>c</sup> Extrapolated from 100  $^\circ\text{C}$ . Reference 4b.

was used. Two procedures were followed for determination of the kinetics; identical rate constants were obtained by either procedure.

For reactions at pressures of up to 4 atm the solution was placed in a 250-mL Parr pressure bottle, which was then flushed four times to 3.7 atm and then was pressurized to 3.7 atm with carbon monoxide. The pressure bottle was then immersed in a Lauda constant temperature bath ( $\pm 0.1$   $^\circ\text{C}$ ). Periodically the bottle was removed, was briefly allowed to cool, and then was dismantled for sampling. For reactions at 1 atm the solution was placed under 1 atm of CO in a 50-mL Schlenk flask, which was wrapped in aluminum foil and immersed in the constant temperature bath. The solution was periodically sampled under a CO flush.

The progress of each reaction was monitored by infrared spectroscopy using the 2077  $\text{cm}^{-1}$  absorption for  $\text{H}_3\text{Ru}_2\text{Os}(\mu_3\text{-COMe})(\text{CO})_9$  and the 2076  $\text{cm}^{-1}$  peak for  $\text{H}_3\text{RuOs}_2(\mu_3\text{-COMe})(\text{CO})_9$ . Linear plots of  $\ln$  (absorbance) vs time were obtained for greater than 3 half-lives. Rate constants (Table II) and error limits (95% confidence limits using Student's  $t$  values) were determined by using a linear least-squares program KINPLOT, written by Dr. Ronald J. Ruzszyk and locally modified for graphics output.

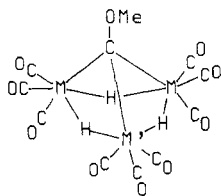
**Determination of Equilibrium Constants for Reactions of  $\text{HRu}_{3-n}\text{Os}_n(\mu\text{-COMe})(\text{CO})_{10}$  ( $n = 1$  or 2) with  $\text{CO}/\text{H}_2$ .** Solutions of  $\text{HRu}_{3-n}\text{Os}_n(\mu\text{-COMe})(\text{CO})_{10}$  (ca. 2 mM) in decane were placed in sealed, 50-mL Schlenk flasks under 1 atm of a  $\text{CO}/\text{H}_2$  gas mixture (50:50.0, Linde). The flasks were placed in a constant temperature bath ( $\pm 0.1$   $^\circ\text{C}$ ) at 80.0  $^\circ\text{C}$ . The progress of each reaction was monitored by IR spectroscopy until a constant value for the ratio of the absorbance due to  $\text{H}_3\text{Ru}_{3-n}\text{Os}_n(\mu_3\text{-COMe})(\text{CO})_9$  ( $n = 1$ , 2077  $\text{cm}^{-1}$ ;  $n = 2$ , 2076  $\text{cm}^{-1}$ ) to the absorbance due to  $\text{HRu}_{3-n}\text{Os}_n(\mu\text{-COMe})(\text{CO})_{10}$  ( $n = 1$ , 2055  $\text{cm}^{-1}$ ;  $n = 2$ , 2054  $\text{cm}^{-1}$ ) was obtained. Then the solution was evaporated to dryness, the residue was dissolved in deuteriochloroform, and the relative amount of each cluster was determined by integration of its  $^1\text{H}$  NMR resonances. Values obtained from the IR spectra of the decane solutions at equilibrium and from the NMR spectra of the product residues were in excellent agreement. For the  $\text{Ru}_2\text{Os}$  system,  $K_{\text{eq}}$  for eq 1 was determined to be  $0.93 \pm 0.20$ ; for the  $\text{RuOs}_2$  system,  $K_{\text{eq}}$  was  $0.27 \pm 0.04$ .



**Reaction of  $\text{H}_3\text{Ru}_{3-n}\text{Os}_n(\mu_3\text{-COMe})(\text{CO})_9$  ( $n = 0-2$ ) with  $\text{AsPh}_3$ .** A 0.364-g sample of composition  $\text{H}_3\text{Ru}_3(\mu_3\text{-COMe})(\text{CO})_9$ , 20%,  $\text{H}_3\text{Ru}_2\text{Os}(\mu_3\text{-COMe})(\text{CO})_9$ , 41%, and  $\text{H}_3\text{RuOs}_2(\mu_3\text{-COMe})(\text{CO})_9$ , 39%, was combined with excess  $\text{AsPh}_3$  (0.5 g, 1.6 mmol) in deuteriochloroform (3.0 mL) in an NMR tube. The reaction was monitored by  $^1\text{H}$  NMR spectroscopy over a period of 10 days. Sequential substitution produced  $\text{H}_3\text{Ru}_{3-n}\text{Os}_n(\mu_3\text{-COMe})(\text{CO})_9(\text{AsPh}_3)$  ( $n = 0-2$ ) and then  $\text{H}_3\text{Ru}_{3-n}\text{Os}_n(\mu_3\text{-COMe})(\text{CO})_7(\text{AsPh}_3)_2$  ( $n = 0, 1$ ). The final solution contained  $\text{H}_3\text{Ru}_3(\mu_3\text{-COMe})(\text{CO})_9(\text{AsPh}_3)_3$ ,  $\text{H}_3\text{Ru}_2\text{Os}(\mu_3\text{-COMe})(\text{CO})_7(\text{AsPh}_3)_2$ , and  $\text{H}_3\text{RuOs}_2(\mu_3\text{-COMe})(\text{CO})_8(\text{AsPh}_3)$ . The products were separated by thin-layer chromatography on silica eluting with 1:1 cyclohexane-dichloromethane. The products, in order of elution, were  $\text{H}_3\text{RuOs}_2(\mu_3\text{-COMe})(\text{CO})_8(\text{AsPh}_3)$  (60 mg, 0.057 mmol),  $\text{H}_3\text{Ru}_2\text{Os}(\mu_3\text{-COMe})(\text{CO})_7(\text{AsPh}_3)_2$  (70 mg, 0.056 mmol), and  $\text{H}_3\text{Ru}_3(\mu_3\text{-COMe})(\text{CO})_9(\text{AsPh}_3)_3$  (62 mg, 0.043 mmol).

**$\text{H}_3\text{Ru}_2\text{Os}(\mu_3\text{-COMe})(\text{CO})_7(\text{AsPh}_3)_2$ :** IR ( $\text{C}_6\text{H}_{12}$ ) 2081 m, 2075 w, 2029 s, 2022 vs, 1966 w  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ): 7.15 (m, 30 H), 3.95 (s, 3 H), -15.3 (t, 1  $\text{H}_a$ ), -17.3 (d, 2  $\text{H}_b$ ) ppm,  $J_{\text{ab}} = 2$  Hz. Anal. Calcd for  $\text{C}_{45}\text{H}_{36}\text{O}_8\text{As}_2\text{OsRu}_2$ : C, 43.35; H, 2.91; As, 12.02; Ru, 16.21. Found: C, 43.79; H, 3.05; As, 12.52; Ru, 15.40.

**$\text{H}_3\text{RuOs}_2(\mu_3\text{-COMe})(\text{CO})_8(\text{AsPh}_3)$ :** IR ( $\text{C}_6\text{H}_{12}$ ) 2094 s, 2080 w, 2070 s, 1984 s, 1916  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) 7.1 (m, 15



**Figure 1.** Structures of  $H_3M_2M'(\mu_3\text{-COMe})(CO)_9$  ( $M = Ru, M' = Os$ ;  $M = Os, M' = Ru$ ).

H), 4.1 (s, 3 H), -16.7 (d, 2  $H_a$ ), -18.3 (t, 1  $H_b$ ) ppm,  $J_{ab} = 2$  Hz.  $H_3Ru_2Os(\mu_3\text{-COMe})(CO)_8(\text{AsPh}_3)$  (in situ):  $^1H$  NMR ( $CD_3Cl_3$ ) hydride region only, -16.3 (dd, 1  $H_a$ ), -17.6 (dd, 1  $H_b$ ), -18.2 (dd, 1  $H_c$ ) ppm,  $J_{ab} = J_{ac} = J_{bc} = 2.5$  Hz.

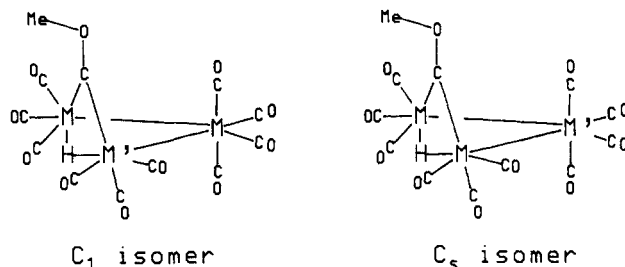
## Results

**Syntheses and Characterizations.** The preparation of the mixture of  $HRu_{3-n}Os_n(\mu\text{-COMe})(CO)_{10}$  ( $n = 0-3$ ) from the mixture of  $Ru_{3-n}Os_n(CO)_{12}$  is a straightforward extension of the procedure used to prepare homometallic clusters.<sup>13</sup> Repeated attempts to separate these products by using thin-layer chromatography were unsuccessful, although the  $^1H$  NMR spectrum of the mixture clearly indicated that the desired clusters had been formed. On the other hand, we knew that  $HM_3(\mu\text{-COMe})(CO)_{10}$  ( $M = Ru$  or  $Os$ ) clusters were easily separated from  $H_3M_3(\mu_3\text{-COMe})(CO)_9$  by using chromatography. Therefore, we sought to use the differing reactivities of Ru and Os clusters to chemically separate the mixed-metal products.

Hydrogenation of  $HRu_3(\mu\text{-COMe})(CO)_{10}$  to  $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$  occurs at a much greater rate than does hydrogenation of the Os analogue; in previous studies we have shown that the rate-limiting step in the cluster hydrogenation is CO dissociation.<sup>4</sup> Hydrogenation of the  $HRu_{3-n}Os_n(\mu\text{-COMe})(CO)_{10}$  ( $n = 0-3$ ) mixture under relatively mild conditions (40–60 °C, 1 atm) allowed selective conversion to  $H_3Ru_{3-n}Os_n(\mu_3\text{-COMe})(CO)_9$  ( $n = 0-2$ ), easily separated from unreacted  $HOs_3(\mu\text{-COMe})(CO)_{10}$ . However, the relative rates for CO dissociation of the various Ru-containing clusters (vide infra) were not sufficiently different to allow selective hydrogenation of each of these. Nonetheless, it proved possible to separate the mixture  $H_3Ru_{3-n}Os_n(\mu_3\text{-COMe})(CO)_9$  ( $n = 0-2$ ) by using thin-layer chromatography.

The characterizations of  $H_3Ru_2Os(\mu_3\text{-COMe})(CO)_9$  and  $H_3RuOs_2(\mu_3\text{-COMe})(CO)_9$  are straightforward by comparison of their spectroscopic data with data for the homometallic analogues.<sup>13</sup> Molecular ions having the expected isotope patterns are found in the mass spectra of both. Satisfactory elemental analyses have been obtained. IR spectra in the 2150–1900  $cm^{-1}$  region are very similar to those of  $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$  and  $H_3Os_3(\mu_3\text{-COMe})(CO)_9$ . The  $^1H$  NMR spectrum for each contains the expected singlet methyl resonance and 2:1 doublet/triplet hydride resonances; the observed coupling constants of ca. 2 Hz between the hydrides are typical of hydride ligands bridging adjacent edges of a metal triangle. The chemical shifts of M–H–M' hydrides move to higher field in the order: Ru–H–Ru < Ru–H–Os < Os–H–Os. Thus, spectroscopic data indicate that these mixed-metal clusters are isostructural with the homometallic analogues (Figure 1).

Although pure  $HRu_2Os(\mu\text{-COMe})(CO)_{10}$  and  $HRuOs_2(\mu\text{-COMe})(CO)_{10}$  could not be obtained by chromatographic separation of the mixture  $HRu_{3-n}Os_n(\mu\text{-COMe})(CO)_{10}$ , carbonylation of the pure, mixed-metal



**Figure 2.** Structures of  $C_1$  and  $C_s$  isomers of  $HM_2M'(\mu\text{-COMe})(CO)_{10}$  ( $M = Ru, M' = Os$ ;  $M = Os, M' = Ru$ ).

$H_3Ru_2Os(\mu_3\text{-COMe})(CO)_9$  and  $H_3RuOs_2(\mu_3\text{-COMe})(CO)_9$  did allow the preparation of  $HRu_2Os(\mu\text{-COMe})(CO)_{10}$  and  $HRuOs_2(\mu\text{-COMe})(CO)_{10}$ , respectively. The fact that the cluster framework is maintained during the carbonylation is excellent evidence that cluster fragmentation does not take place during reductive elimination of hydrogen from this cluster series.

Characterizations of  $HRu_2Os(\mu\text{-COMe})(CO)_{10}$  and  $HRuOs_2(\mu\text{-COMe})(CO)_{10}$  are easily made by comparisons of their spectroscopic data with data from the homometallic analogues, which have been structurally characterized by X-ray crystallography.<sup>6,14,15</sup> For each mixed-metal cluster there exist two isomers differing in the metal atoms bridged by the hydride and COMe ligands; these isomers will be designated as  $C_1$  and  $C_s$  (Figure 2), according to the symmetry of the  $HM_2M'(\mu\text{-C})$  core. The IR spectrum of each mixed-metal cluster is very similar to that of  $HRu_3(\mu\text{-COMe})(CO)_{10}$ . The EI mass spectrum of each contains the molecular ion, with the expected isotope multiplet, and ions resulting from the stepwise loss of 10 CO ligands and the COMe unit. The  $^1H$  NMR spectra indicate that each exists in solution as a mixture of the two possible isomers having bridging ligands along the different cluster edges; since at room temperature the rate of rotation about the C–OMe bond is fast on the NMR timescale,<sup>13-15</sup> isomers due to differing orientations of the methyl group are not observed. Thus, for  $HRu_2Os(\mu\text{-COMe})(CO)_{10}$  two sets of resonances, each consisting of singlets due to methyl and hydride ligands in a 3:1 ratio, are found, with the major isomer displaying a hydride resonance at -15.54 (92%) ppm and the minor isomer having the hydride resonance at -14.21 (8%) ppm; on the basis of the chemical shifts of the hydrides, the major isomer is presumed to contain bridging ligands along the Ru–Os edge ( $C_1$  isomer, Figure 2). Additional support for this assignment is provided by the  $^{13}C$  NMR spectrum (vide infra). For  $HRuOs_2(\mu\text{-COMe})(CO)_{10}$  the relative amounts of the two isomers are nearly identical; again, with the assumption that the trend in chemical shifts of the hydride resonances parallels that established for  $H_3Ru_{3-n}Os_n(\mu_3\text{-COMe})(CO)_9$ , the chemical shifts of the hydride resonances for the two isomers at -15.14 (44%) and -16.56 (56%) ppm indicate a slightly lower free energy for the isomer with bridging ligands along the Os–Os edge ( $C_s$  isomer).

The  $^{13}C$  NMR spectrum of  $HRu_2Os(\mu\text{-COMe})(CO)_{10}$  at 22 °C in deuteriochloroform consists of 10 resonances (Table I); the resonance of the methyl carbon is obscured by the solvent. The methylidyne carbon resonance has a chemical shift midway between the values found for the homometallic Ru (366.5 ppm)<sup>14</sup> and Os (352.2 ppm)<sup>15</sup> analogues; the chemical shift is thus consistent with the

(14) Johnson, B. F. G.; Lewis, J.; Orpen, A. G.; Raithby, P. R.; Suss, G. *J. Organomet. Chem.* 1979, 173, 187.

(15) Gavens, P. D.; Mays, M. J. *J. Organomet. Chem.* 1978, 162, 389.

(13) Keister, J. B.; Payne, M. W.; Muscatella, M. J. *Organometallics* 1983, 2, 219.

proposed structure in which the  $\mu$ -COMe ligand bridges Ru and Os. Resonances due to the four CO ligands on the  $\text{Ru}(\text{CO})_4$  fragment are broad at room temperature, presumably due to fluxional threefold exchange; fluxional broadening of the carbonyls on the  $\text{Ru}(\text{CO})_4$  unit of  $\text{HRu}_3(\mu\text{-COMe})(\text{CO})_{10}$  at 26 °C has previously been reported.<sup>14</sup> The resonances due to six inequivalent CO ligands on the  $\text{Ru}(\text{CO})_3$  and  $\text{Os}(\text{CO})_3$  units have chemical shifts very similar to the corresponding carbonyl resonances of the homometallic clusters.<sup>14,15</sup> Thus, the major isomer is the  $C_1$  isomer (Figure 2).

The <sup>13</sup>C NMR spectrum of  $\text{HRuOs}_2(\mu\text{-COMe})(\text{CO})_{10}$  shows the expected two sets of signals, one for each isomer. Assignments (Table I) are made by comparison of the chemical shifts with those of the homometallic analogues and of  $\text{HRu}_2\text{Os}(\mu\text{-COMe})(\text{CO})_{10}$ . Broadening of the carbonyl resonances on the  $\text{Ru}(\text{CO})_4$  fragment of the  $C_s$  isomer is attributed to a threefold exchange process, as is the case for  $\text{HRu}_3(\mu\text{-COMe})(\text{CO})_{10}$ .

A qualitative comparison of the degree of line broadening of carbonyl resonances of  $\text{Ru}(\text{CO})_4$  units for the various  $\text{HM}_3(\mu\text{-COMe})(\text{CO})_{10}$  clusters gives relative rates:  $\text{HRu}_3(\mu\text{-COMe})(\text{CO})_{10} > \text{HRu}_2\text{Os}(\mu\text{-COMe})(\text{CO})_{10}$  ( $C_1$  isomer)  $>$   $\text{HRuOs}_2(\mu\text{-COMe})(\text{CO})_{10}$  ( $C_s$  isomer). Exchange on  $\text{Ru}(\text{CO})_4$  units is much faster than on  $\text{Os}(\text{CO})_4$  units, for which no line broadening is seen at room temperature.

The rates of interconversion of the  $C_s$  and  $C_1$  isomers of  $\text{HRu}_{3-n}\text{Os}_n(\mu\text{-COMe})(\text{CO})_{10}$  ( $n = 1$  or  $2$ ) cannot be determined, but from previous study of the intramolecular isomerizations of  $\text{HRu}_3(\mu\text{-CNMe}_2)(\text{CO})_9\text{L}$  ( $\text{L} = \text{PR}_3, \text{AsPh}_3, \text{or SbPh}_3$ ) and  $\text{HOS}_3(\mu\text{-CNMe}_2)(\text{CO})_9(\text{AsPh}_3)$ ,<sup>16</sup> we believe that the rates of interconversion of these mixed-metal isomers should be fast on the chemical time scale. Corresponding rate constants for isomerization of  $\text{HM}_3(\mu\text{-CNMe}_2)(\text{CO})_9(\text{AsPh}_3)$  are  $6.8 \times 10^{-4} \text{ s}^{-1}$  at 292 K for  $\text{M} = \text{Ru}$  and  $5.1 \times 10^{-5} \text{ s}^{-1}$  for  $\text{M} = \text{Os}$ . We have previously argued that the greater migratory ability of the COMe ligand should give rise to a much faster rate for isomerization of related clusters  $\text{HM}_3(\mu\text{-COMe})(\text{CO})_9\text{L}$ . Thus, we expect that the isomer distributions are thermodynamically, rather than kinetically, determined. This is supported by the small, but detectable, changes in the equilibrium constants for isomerization which are obtained in different solvents.

The equilibrium constants for the  $C_s \rightarrow C_1$  isomerizations are relatively insensitive to solvent effects. For  $\text{HRu}_2\text{Os}(\mu\text{-COMe})(\text{CO})_{10}$ , values for the  $C_1/C_s$  isomer ratio range from 14 in toluene- $d_6$  to 11 in acetone- $d_6$ ; the value in chloroform- $d$  is  $13.1 \pm 0.5$  at 298 K. For  $\text{HRuOs}_2(\mu\text{-COMe})(\text{CO})_{10}$ , values for the  $C_1/C_s$  isomer ratio are 0.79 in toluene- $d_6$  and 0.88 in acetone- $d_6$ ; in chloroform- $d$  at 298 K the value is  $0.82 \pm 0.09$ . For both equilibria more polar solvents slightly favor the isomer for which a Ru atom is in the unique, nonbridged site.

For  $\text{HRuOs}_2(\mu\text{-COMe})(\text{CO})_{10}$ , the  $C_1/C_s$  isomer ratio in toluene is relatively insensitive to temperature, varying from 0.79 at 298 K to 0.90 at 342 K. A rough estimate of the value of  $\Delta H^\circ$ , calculated from the values of the equilibrium constant at these two temperatures, is +2.6 kJ/mol. If it is assumed that the only contribution to  $\Delta S^\circ$  is from the 2:1 statistical preference for the  $C_1$  isomer ( $\Delta S^\circ = +5.8 \text{ J}/(\text{K}\cdot\text{mol})$ ), then the value of  $\Delta G^\circ$  at 298 K, +0.58 kJ/mol, yields  $\Delta H^\circ = +2.3 \text{ kJ}/\text{mol}$ , essentially the same as the measured value.

**Ligand substitution on  $\text{H}_3\text{Ru}_{3-n}\text{Os}_n(\mu_3\text{-COMe})(\text{CO})_9$  ( $n = 0-2$ ).** A second approach to using the different la-

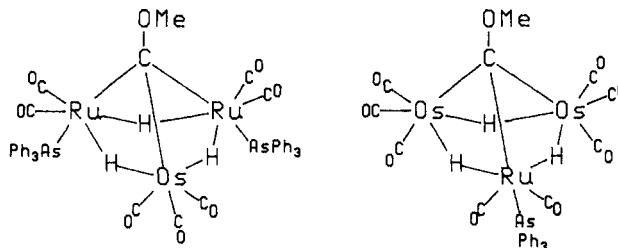


Figure 3. Structures of  $\text{H}_3\text{Ru}_{3-n}\text{Os}_n(\mu_3\text{-COMe})(\text{CO})_{9-n}(\text{AsPh}_3)_n$  ( $n = 1$  or  $2$ ).

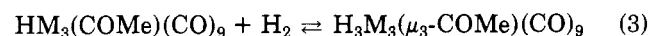
bilities of Ru and Os atoms to allow separation of the mixed-metal clusters was to substitute group 15 donor ligands for CO and then to separate the substituted products by using chromatography. Treatment of a mixture of  $\text{H}_3\text{Ru}_{3-n}\text{Os}_n(\mu_3\text{-COMe})(\text{CO})_9$  ( $n = 0-2$ ) with excess  $\text{AsPh}_3$  caused sequential substitution on Ru atoms only, forming ultimately  $\text{H}_3\text{Ru}_3(\mu_3\text{-COMe})(\text{CO})_6(\text{AsPh}_3)_3$ ,  $\text{H}_3\text{Ru}_2\text{Os}(\mu_3\text{-COMe})(\text{CO})_7(\text{AsPh}_3)_2$ , and  $\text{H}_3\text{RuOs}_2(\mu_3\text{-COMe})(\text{CO})_8(\text{AsPh}_3)$ . The mono-, di-, and trisubstituted clusters were easily separated by using chromatography, but this procedure did not prove to be a useful method for the preparation of the desired mixed-metal carbonyls, since the  $\text{AsPh}_3$  ligands could not be replaced by CO without decomposition.

The characterizations of the substituted clusters  $\text{H}_3\text{Ru}_n\text{Os}_{3-n}(\mu_3\text{-COMe})(\text{CO})_{9-n}(\text{AsPh}_3)_n$  are easily made by comparison of their spectroscopic data with corresponding data for  $\text{H}_3\text{Ru}_3(\mu_3\text{-COMe})(\text{CO})_{9-n}(\text{AsPh}_3)_n$ .<sup>17</sup> IR spectra are very similar for homometallic Ru and mixed-metal analogues. <sup>1</sup>H NMR spectra differ only in that the resonances due to hydrides bridging to Os are shifted upfield from those bridging to Ru. The spectral data are consistent with axially coordinated  $\text{AsPh}_3$  ligands, as is the case for the homometallic Ru analogs (Figure 3).

Our previous study of ligand substitution on  $\text{H}_3\text{Ru}_3(\mu_3\text{-CX})(\text{CO})_9$  ( $\text{X} = \text{OMe}, \text{Ph}, \text{Me}, \text{or Cl}$ ) found that the rate of CO dissociation from each metal atom is largely independent of the degree of substitution on other metals in the molecule.<sup>17</sup> In these mixed-metal Ru-Os clusters it appears that CO dissociation from the Ru atoms is much faster than from the Os atoms, as would be expected from the generally greater lability of Ru.

## Discussion

The purpose of this work was to use the variation in cluster reactivity as a function of mixed-metal content to probe for the number of metal centers involved in cluster hydrogenation and reductive elimination. Previous studies by our group of the homometallic cluster systems established that hydrogenation of  $\text{HM}_3(\mu\text{-COMe})(\text{CO})_{10}$  involves rate-determining CO dissociation, while carbonylation of  $\text{H}_3\text{M}_3(\mu_3\text{-COMe})(\text{CO})_9$  appears to occur by rate-determining reductive elimination of molecular hydrogen (eq 2 and 3).<sup>3,4</sup> However, the kinetics of the carbonylation are relatively uninformative concerning the nature of the transition state, in particular the number of metal atoms involved in bonding to hydrogens.



**CO Dissociation from  $\text{HRu}_{3-n}\text{Os}_n(\mu\text{-COMe})(\text{CO})_{10}$ .** Conversion of  $\text{HRu}_{3-n}\text{Os}_n(\mu\text{-COMe})(\text{CO})_{10}$  to  $\text{H}_3\text{Ru}_{3-n}\text{Os}_n(\mu_3\text{-COMe})(\text{CO})_9$  ( $n = 1$  or  $2$ ) is presumed to

(16) Shaffer, M. R.; Keister, J. B. *Organometallics* 1986, 5, 561.

(17) Abdul Rahman, Z.; Beanan, L. R.; Bavaro, L. M.; Modi, S. P.; Keister, J. B.; Churchill, M. R. *J. Organomet. Chem.* 1984, 263, 75.

occur via the same mechanism as that established for the Ru<sub>3</sub> and Os<sub>3</sub> analogues, namely rate-limiting CO dissociation.<sup>3,4</sup> The retention of the Ru<sub>2</sub>Os core during the hydrogenation of HRu<sub>2</sub>Os(μ-COMe)(CO)<sub>10</sub> indicates that cluster fragmentation does not occur during the replacement of CO by hydrogen. Although accurate measurements of the kinetics for hydrogenation of HRu<sub>3-n</sub>Os<sub>n</sub>(μ-COMe)(CO)<sub>10</sub> were not made, the percent conversions from partial hydrogenations of mixtures could be used to estimate the relative rates for CO dissociation from HRu<sub>3-n</sub>Os<sub>n</sub>(μ-COMe)(CO)<sub>10</sub> (*n* = 0–2); the rate constants for HM<sub>3</sub>(μ-COMe)(CO)<sub>10</sub> (*M* = Ru or Os) are available from our previous studies. On the basis of these data, relative rates for CO dissociation are as follows: HRu<sub>3</sub>(μ-COMe)(CO)<sub>10</sub> (4500) > HRu<sub>2</sub>Os(μ-COMe)(CO)<sub>10</sub> (1100) > HRuOs<sub>2</sub>(μ-COMe)(CO)<sub>10</sub> (220) >> HOs<sub>3</sub>(μ-COMe)(CO)<sub>10</sub> (1).

Only a few studies comparing the reactivity of isostructural homometallic and mixed-metal clusters have been previously reported.<sup>2,18</sup> The relative rate of 5700 for CO dissociation from Ru<sub>3</sub>(CO)<sub>12</sub>, compared with that for Os<sub>3</sub>(CO)<sub>12</sub> at 343 K,<sup>19</sup> is close to that found for HRu<sub>3</sub>(μ-COMe)(CO)<sub>10</sub>, compared with that for HOs<sub>3</sub>(μ-COMe)(CO)<sub>10</sub>, but no studies of the mixed Ru/Os dodecacarbonyls have been made. Relative rates for CO dissociation from mixed Fe/Ru and Fe/Os dodecacarbonyls have been determined,<sup>20</sup> but interpretation of these results is complicated by the differences in structure between the various mixed-metal clusters, some having both bridging and terminal carbonyls but others having only terminal carbonyls. Furthermore, substitution appears to occur only on the least labile metals,<sup>21</sup> suggesting perhaps that the products are thermodynamically rather than kinetically determined.

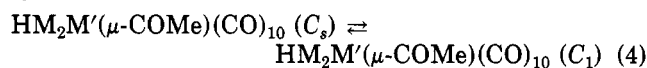
The conclusion of our previous studies of ligand substitution on HM<sub>3</sub>(μ-COMe)(CO)<sub>10</sub> (*M* = Ru or Os) was that CO dissociation occurs from the unique, nonbridged metal atom, perhaps assisted by a change in the coordination mode of the COMe ligand from a three-electron donor, μ-η<sup>1</sup>-ligand to a five-electron donor, μ<sub>3</sub>-η<sup>2</sup>-ligand.<sup>3</sup> Our data for the mixed-metal clusters are consistent with this mechanism, with CO dissociation occurring from the more labile Ru atom in the mixed-metal clusters. Both clusters exist in solution as equilibrium mixtures of the two isomers, with the more stable isomer of each containing a Ru atom in the nonbridged position. Previous studies of the homometallic clusters indicate that the rate of interconversion between the isomers should be fast compared with the rate of CO dissociation. Then the differences in rates for CO dissociation from these clusters probably reflect a small reduction in the rate of CO dissociation from the Ru(CO)<sub>4</sub> fragment when Os replaces Ru in an adjacent position. The only significant differences in reactivities are between the Ru containing clusters and HOs<sub>3</sub>(μ-COMe)(CO)<sub>10</sub>, the only cluster which must lose CO from an Os atom.

**Reductive Elimination of Hydrogen from H<sub>3</sub>Ru<sub>3-n</sub>Os<sub>n</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub>.** Retention of the mixed-

metal core upon carbonylation of H<sub>3</sub>Ru<sub>3-n</sub>Os<sub>n</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub> to HRu<sub>3-n</sub>Os<sub>n</sub>(μ-COMe)(CO)<sub>10</sub> (*n* = 1 or 2), indicates that cluster fragmentation does not occur during reductive elimination of hydrogen. The rate laws for reductive elimination of hydrogen from H<sub>3</sub>Ru<sub>3-n</sub>Os<sub>n</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub> (*n* = 1 or 2), are assumed to be the same as those established for the homometallic analogues, namely, first order in cluster concentration and zero order in CO concentration.<sup>4</sup> The relative rates (Table II) for hydrogen elimination fall in the series: H<sub>3</sub>Ru<sub>3</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub> (210) > H<sub>3</sub>Ru<sub>2</sub>Os(μ<sub>3</sub>-COMe)(CO)<sub>9</sub> (72) > H<sub>3</sub>RuOs<sub>2</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub> (38) >> H<sub>3</sub>Os<sub>3</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub> (1). Although the range of relative rates for the cluster series is not as large as that found for CO dissociation from HRu<sub>3-n</sub>Os<sub>n</sub>(μ-COMe)(CO)<sub>10</sub>, the same observation of similar rates for all Ru-containing clusters and a sharply lower rate for the Os<sub>3</sub> cluster is found. This suggests that, despite the fact that the hydride ligands bridge two metal centers in the ground states of these clusters, reductive elimination of hydrogen occurs from a single metal center, thus resulting in similar reactivities for all clusters containing at least one Ru atom.

Migration of two hydrides from bridging to terminal coordination sites prior to reductive elimination is a plausible mechanism. The rate for migration of hydride ligands from bridging to terminal coordination sites is expected to be fast, compared with the rate of reductive elimination. Although hydride fluxionality is not observed in H<sub>3</sub>Ru<sub>3-n</sub>Os<sub>n</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub>, free energies of activation for hydride exchange, presumably through bridge-terminal interconversion, in related clusters, for example, H<sub>2</sub>Ru<sub>3</sub>(μ-CHCO<sub>2</sub>Me)(CO)<sub>9</sub>,<sup>5b,22</sup> are 40–70 kJ. Furthermore, only small differences are found between the free energies of activation for hydride fluxionality on analogous Ru and Os clusters; for example, only 2 kJ separates the free energies of activation for bridge-terminal hydride exchange on H(μ-H)M<sub>3</sub>(CO)<sub>11</sub> (*M* = Ru, 52 kJ,<sup>22</sup> *M* = Os, 54 kJ<sup>23</sup>).

**Energetics.** The thermodynamics of metal cluster reactions are even more poorly defined than their kinetics. The equilibrium constants for eq 1 and 4, in conjunction with available thermodynamic data, can provide estimates of the metal-ligand bond energies in the HRu<sub>3-n</sub>Os<sub>n</sub>(μ-COMe)(CO)<sub>10</sub> and H<sub>3</sub>Ru<sub>3-n</sub>Os<sub>n</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub> cluster systems.



Fehlner et al.<sup>24</sup> have determined the energy of the Fe–H–Fe bond from the equilibrium constant for hydrogenation of HFe<sub>3</sub>(μ<sub>3</sub>-CMe)(CO)<sub>10</sub> to H<sub>3</sub>Fe<sub>3</sub>(μ<sub>3</sub>-CMe)(CO)<sub>9</sub>. By using literature data for Ru–Ru, Os–Os, Ru–CO, and Os–CO bond energies and the equilibrium constants for eq 1 (*M* = Ru or Os), we can, in the same manner, estimate the energies of the Ru–H–Ru and Os–H–Os bonds.

In addition to the M–CO and M–M bond energies, there are 11 bond energies associated with these clusters: *E*(RuOs), *E*(RuHRu), *E*(OsHOs), *E*(RuHOs), *E*(Ru<sub>2</sub>(μ-C)), *E*(Os<sub>2</sub>(μ-C)), *E*(RuOs(μ-C)), *E*(Ru<sub>3</sub>(μ<sub>3</sub>-C)), *E*(Os<sub>3</sub>(μ<sub>3</sub>-C)), *E*(Ru<sub>2</sub>Os(μ<sub>3</sub>-C)), and *E*(Ru<sub>2</sub>Os(μ<sub>3</sub>-C)). Furthermore, since *E*(RuOs) and *E*(RuHOs), as well as the methylidyne-metal bond energies, cannot be treated as independent variables in these equilibria, we can calculate {*E*(RuHOs) – *E*(RuOs)} and differences between the various methylidyne-metal bond energies, compared with *E*(Os<sub>3</sub>(μ<sub>3</sub>-C)) (arbitrarily chosen as the reference bond energy), but not their absolute values. This means that the number of independent

(18) (a) Fox, J. R.; Gladfelter, W. L.; Wood, T. G.; Smegal, J. A.; Foreman, T. K.; Geoffroy, G. L.; Tavanaiepour, I.; Day, V. W.; Day, C. S. *Inorg. Chem.* **1981**, *20*, 3214. (b) Gladfelter, W. L.; Fox, J. R.; Smegal, J. A.; Wood, T. G.; Geoffroy, G. L. *Inorg. Chem.* **1981**, *20*, 3223. (c) Sonnenberger, D.; Atwood, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 3484.

(19) (a) Shojaiie, A.; Atwood, J. D. *Organometallics* **1985**, *4*, 187. (b) Pöe, A.; Twigg, M. V. *J. Chem. Soc., Dalton Trans.* **1974**, 1860. (c) Candlin, J. P.; Shortland, A. C. *J. Organomet. Chem.* **1969**, *16*, 289.

(20) (a) Shojaiie, R.; Atwood, J. D. *Inorg. Chem.* **1987**, *26*, 2199. (b) Shojaiie, R.; Atwood, J. D. *Inorg. Chem.* **1988**, *27*, 2558.

(21) Venäläinen, T.; Pakkanen, T. *J. Organomet. Chem.* **1984**, *266*, 269.

(22) Nevinger, L. R.; Keister, J. B., unpublished results.

(23) Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3304.

(24) Vites, J.; Fehlner, T. P. *Organometallics* **1984**, *3*, 491.



unknowns is nine. Our results provide six equilibrium relationships involving the various bond energies, so three other independent relationships must be provided. We have chosen to postulate four relationships, one more than actually required, between various  $E(M_2(\mu-C))$  and  $E(M_2M'(\mu_3-C))$  values, primarily because direct measurements of these energies will be extremely difficult to obtain and because the wide variation in coordination geometry adopted by alkylidyne ligands, depending upon metal, alkylidyne substituent, and other ligands present on the cluster, seems to suggest relatively small energy differences between these bonding modes.<sup>6</sup> This small difference in energy between doubly and triply bridging alkylidynes minimizes the likelihood that large errors will be introduced into the calculated bond energies by making these assumptions.

Previously, measurements of the enthalpies of disruption,  $\Delta H_D$ , for  $M_3(CO)_{12}$  ( $M = Ru$  and  $Os$ ) have been used to estimate the average bond enthalpies for  $M-CO$  and  $M-M$  bonds. Two methods have been used to factor  $\Delta H_D$  into contributions from the  $M-M$  and  $M-CO$  bonds. One approach uses an empirical relationship between bond length and bond enthalpy.<sup>25</sup> The second assumes a two-center, two-electron metal-metal bond.<sup>26</sup> The latter approach gives substantially higher values for the metal-metal bond energies and correspondingly lower values for the metal-ligand bond energies. For example, the former approach gives the  $Ru-Ru$  bond energy,  $E(Ru-Ru)$ , as 78 kJ and the  $Ru-CO$  average bond dissociation energy,  $D(Ru-CO)$ , as 182 kJ, compared with 115 and 172 kJ, respectively, by the latter method. Because of the greater number of  $M-CO$  bonds, a small error in the assignment of the  $M-CO$  bond dissociation energy gives rise to a large error in the calculated  $M-M$  bond energy. For the following thermochemical calculations we will use values obtained by the two-center, two-electron bond method, since this model should be suitable for trimetallic clusters and since the values obtained seem more consistent with the reactivity of the  $M_3(CO)_{12}$  clusters, for which  $CO$  dissociation appears to be more facile than cluster fragmentation.<sup>27</sup> It should be emphasized that the absolute bond energies which are calculated below are critically dependent upon the choice of the  $M-CO$  bond energy, but to a large degree the differences between various bond energies are relatively insensitive to this choice.

We will use to following bond energy data, determined by Connor et al.<sup>26</sup> by using microcalorimetry and the two-center, two-electron bond model:

$$\begin{array}{ll} D(Ru-CO) = 172 \text{ kJ/mol} & D(Os-CO) = 192 \text{ kJ/mol} \\ E(Ru-Ru) = 115 \text{ kJ/mol} & E(Os-Os) = 128 \text{ kJ/mol} \end{array}$$

Our earlier studies of the homometallic cluster systems determined equilibrium constants for eq 1, where  $M = Ru$  ( $K_{eq} = 1.1$  in decane at 343 K) or  $Os$  ( $K_{eq} = 0.08$  in decane at 383 K).<sup>4</sup> Values for  $\Delta G^\circ$  for eq 1, calculated from these equilibrium constants, are  $-0.27$  kJ/mol for  $M = Ru$  at 343 K and  $+8.0$  kJ/mol for  $M = Os$  at 383 K. We will assume that (1) the entropies, (2) the heats of solution, and (3) heats of vaporization for  $HM_3(\mu-COMe)(CO)_{10}$  are identical with those for the corresponding  $H_3M_3(\mu_3-COMe)(CO)_9$ . Then  $\Delta S^\circ$  for eq 1 ( $M = Ru$  or  $Os$ ), is  $+67$  J/(K·mol), due

entirely to the difference in the entropies of  $CO$  and  $H_2$ .<sup>28</sup> From the free energies,  $\Delta H^\circ_1$  for eq 1 is  $+23$  kJ/mol for  $M = Ru$  and  $+34$  kJ/mol for  $M = Os$ . Equation 5 ex-

$$\Delta H^\circ_1 = D(M-CO) + E(HH) + 2E(MM) + E(M_2(\mu-C)) - 2E(MHM) - E(M_3(\mu_3-C)) \quad (5)$$

presses the enthalpy for the reaction in terms of the individual bond energies, where  $D(M-CO)$  is the average metal-carbonyl bond dissociation energy,  $E(HH)$  is the dihydrogen bond energy,<sup>29</sup>  $E(MM)$  is the metal-metal bond energy,  $E(M_2(\mu-C))$  is the energy required to remove the neutral  $\mu-COMe$  ligand from the trimetal framework, and  $E(M_3(\mu_3-C))$  is the energy required to remove the  $\mu_3-COMe$  neutral ligand from the trimetal framework.

We now make the additional assumption that  $E(M_2(\mu-C)) = E(M_3(\mu_3-C))$  for  $M = Ru$  or  $Os$ . This is reasonable because the energy difference between the two coordination modes of the alkylidyne must be small, small enough that changes in the metal, the alkylidyne substituent, or in the other ligands on the cluster can cause the ground-state structure to change from one coordination type to the other.<sup>30</sup> This assumption allows calculation of  $E(RuHRu) = 408$  kJ/mol and  $E(OsHOs) = 425$  kJ/mol.

The equilibrium constants for  $C_s \rightarrow C_1$  isomerizations (eq 4) of  $HRu_2Os(\mu-COMe)(CO)_{10}$  and  $HRuOs_2(\mu-COMe)(CO)_{10}$  provide additional bond energy estimates. The small temperature dependence of the equilibrium constant for the latter indicates that the entropy difference between the two isomers can be largely attributed to differences in symmetry. If  $\Delta S^\circ$  for the  $C_s \rightarrow C_1$  isomerization is taken as the statistical value,  $+5.8$  J/(K·mol), then values for  $\Delta H^\circ$  can be calculated from the equilibrium constants in deuteriochloroform as  $-4.7$  kJ/mol ( $\Delta H^\circ_6$ ) for the  $Ru_2Os$  system and  $+2.2$  kJ/mol ( $\Delta H^\circ_7$ ) for the  $RuOs_2$  system. The enthalpies for isomerization are broken down into the contributions from the bond enthalpies in eq 6 and 7.

$$\begin{aligned} \Delta H^\circ_6 = & E(Ru-Os) + D(Os-CO) + E(Ru_2(\mu-C)) + E(RuHRu) - \\ & E(RuRu) - D(Ru-CO) - E(RuHOs) - E(RuOs(\mu-C)) \end{aligned} \quad (6)$$

$$\begin{aligned} \Delta H^\circ_7 = & E(Ru-Os) + D(Ru-CO) + E(Os_2(\mu-C)) + E(OsHOs) - \\ & E(OsOs) - D(Os-CO) - E(RuHOs) - E(RuOs(\mu-C)) \end{aligned} \quad (7)$$

Subtraction of eq 6 from eq 7 and substitution of the values given above for  $D(M-CO)$ ,  $E(MM)$ , and  $E(MHM)$  lead to the difference in energies  $\{E(Os_2(\mu-C)) - E(Ru_2(\mu-C))\} = 42$  kJ/mol. Since we have already assumed that  $E(M_2(\mu-C)) = E(M_3(\mu_3-C))$ , this requires that  $\{E(Os_3(\mu_3-C)) - E(Ru_3(\mu_3-C))\} = 42$  kJ/mol.

To estimate a value for  $\{E(RuHOs) - E(RuOs)\}$ , we must make a further assumption concerning energies of  $M_2M'(\mu_3-C)$  bonds. We will assume that the  $M_3(\mu_3-C)$  system may be considered to consist of three, two-center, two-electron  $M-C$  bonds. This is nothing more than the assumption that the energy of each  $M-C$  bond is independent of the energies of the other two. By this assumption,  $\{E(Os_3(\mu_3-C)) - E(Ru_2Os(\mu_3-C))\} = (2/3)\{E(Os_3-$

(25) Housecroft, C. E.; O'Neill, M. E.; Wade, K.; Smith, B. C. *J. Organomet. Chem.* 1981, 213, 35.

(26) Connor, J. A. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: London, 1980; Chapter 5.

(27) In their calculation of the energy of the  $Fe-H-Fe$  bond, Fehlner et al. used values for  $D(Fe-CO)$  and  $E(Fe-Fe)$  calculated by the bond length-bond enthalpy relationship.<sup>24</sup>

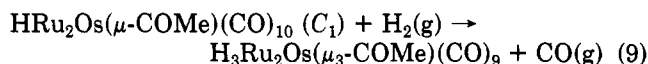
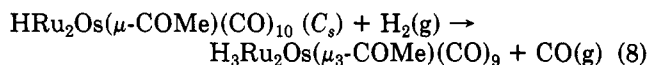
(28) Kerr, J. A.; Parsonage, M. J.; Trotman-Dickenson, A. F. In *CRC Handbook of Chemistry and Physics*, 54th ed.; Weast, R. C., Ed.; CRC: Cleveland, OH, 1973; p F200.

(29) The value for  $E(HH)$  is taken as 436 kJ/mol.<sup>28</sup>

(30) For example, replacement of two  $CO$  ligands on  $HRu_3(\mu-COMe)(CO)_{10}$  by cyclohexadiene changes the coordination mode of the  $COMe$  ligand from doubly bridging to triply bridging.<sup>6</sup>

$(\mu_3\text{-C}) - E(\text{Ru}_3(\mu_3\text{-C}))$ }, or 28 kJ/mol, and  $\{E(\text{Os}_3(\mu_3\text{-C})) - E(\text{RuOs}_2(\mu_3\text{-C}))\} = (1/3)[E(\text{Os}_3(\mu_3\text{-C})) - E(\text{Ru}_3(\mu_3\text{-C}))]$ , or 14 kJ/mol. Only one of these two assumptions (the former one will be used) is actually required to calculate the remaining bond energy differences, but since the choice is arbitrary and the reasoning must be equally valid for both bond energy differences, we chose to postulate average energies for both. Later, we will use the comparison of the calculated value of  $\{E(\text{Os}_3(\mu_3\text{-C})) - E(\text{RuOs}_2(\mu_3\text{-C}))\}$  with the postulated value of 14 kJ as an indicator of the internal consistency our calculations. Since we have already postulated the energy differences  $\{E(\text{Ru}_2(\mu\text{-C})) - E(\text{Ru}_3(\mu_3\text{-C}))\}$  and  $\{E(\text{Os}_2(\mu\text{-C})) - E(\text{Os}_3(\mu_3\text{-C}))\}$ , only the value of  $\{E(\text{Os}_3(\mu_3\text{-C})) - E(\text{RuOs}(\mu\text{-C}))\}$  remains to be calculated.

The equilibrium constants for eq 8 and 9 may be calculated from the  $C_3 \rightarrow C_1$  equilibrium constants (measured in  $\text{CDCl}_3$  at 298 K) and the equilibrium constants for the  $\text{H}_2/\text{CO}$  reactions (measured in decane at 353 K). These are 13.1 for eq 8 and 1.00 for eq 9. To evaluate  $\Delta H^\circ$ , we need to estimate  $\Delta S^\circ$  for each; we now assume that the entropy for the  $C_3$  isomer is in each case identical with the entropy of  $\text{H}_3\text{M}_2\text{M}'(\mu_3\text{-COMe})(\text{CO})_9$ , since both molecules have the same symmetry and since this assumption was made previously for the homometallic analogues. With use of these numbers,  $\Delta H^\circ$  for eq 8 and 9 are +16 ( $\Delta H^\circ_8$ ) and +26 kJ/mol ( $\Delta H^\circ_9$ ), respectively. Equations 10 and 11 express the enthalpies of eq 8 and 9, respectively, in terms of the component bond energies.



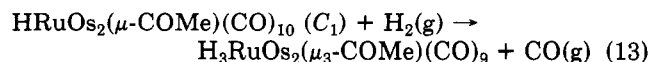
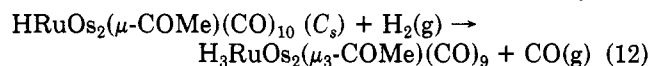
$$\Delta H^\circ = D(\text{Os-CO}) + 2\{E(\text{RuOs}) - E(\text{RuHOs})\} + \{E(\text{Ru}_2(\mu\text{-C})) - E(\text{Ru}_2\text{Os}(\mu_3\text{-C}))\} + E(\text{H-H}) \quad (10)$$

$$\Delta H^\circ = D(\text{Ru-CO}) + E(\text{RuRu}) + \{E(\text{RuOs}) - E(\text{RuHOs})\} + \{E(\text{RuOs}(\mu\text{-C})) - E(\text{Ru}_2\text{Os}(\mu_3\text{-C}))\} + E(\text{H-H}) - E(\text{RuHRu}) \quad (11)$$

Now eq 10 allows the calculation of  $\{E(\text{RuHOs}) - E(\text{RuOs})\} = 299$  kJ/mol. Since none of the equilibrium relationships contain independent relationships between  $E(\text{RuOs})$  and  $E(\text{RuHOs})$ , the absolute values are not presently accessible. Calorimetric measurements on  $\text{Ru}_2\text{Os}(\text{CO})_{12}$  and  $\text{RuOs}_2(\text{CO})_{12}$  would allow these to be determined.

Substitution of  $\{E(\text{RuHOs}) - E(\text{RuOs})\} = 299$  kJ/mol into eq 7 allows calculation of  $\{E(\text{Os}_2(\mu\text{-C})) - E(\text{RuOs}(\mu\text{-C}))\}$  as +24 kJ/mol. Thus, the assumption that  $\{E(\text{Os}_3(\mu_3\text{-C})) - E(\text{Ru}_2\text{Os}(\mu_3\text{-C}))\} = (2/3)\{E(\text{Os}_3(\mu_3\text{-C})) - E(\text{Ru}_3(\mu_3\text{-C}))\}$  leads to the conclusion that  $E(\text{RuOs}(\mu\text{-C}))$  is close to the average of  $E(\text{Ru}_2(\mu\text{-C}))$  and  $E(\text{Os}_2(\mu\text{-C}))$ .

The same treatment for the  $\text{RuOs}_2$  systems (eq 12 and 13) leads to  $\Delta H^\circ = +26$  ( $\Delta H^\circ_{14}$ ) and +24 kJ/mol ( $\Delta H^\circ_{15}$ ), respectively. Equations 14 and 15 express enthalpies of (12) and (13), respectively, in terms of bond energies.



$$\Delta H^\circ_{14} = E(\text{Ru-CO}) + \{E(\text{Os}_2(\mu\text{-C})) - E(\text{RuOs}_2(\mu_3\text{-C}))\} + E(\text{H-H}) + 2\{E(\text{RuOs}) - E(\text{RuHOs})\} \quad (14)$$

$$\Delta H^\circ_{15} = E(\text{Os-CO}) + \{E(\text{OsRu}(\mu\text{-C})) - E(\text{RuOs}_2(\mu_3\text{-C}))\} + E(\text{H-H}) + E(\text{OsOs}) + \{E(\text{RuOs}) - E(\text{RuHOs})\} - E(\text{OsHOs}) \quad (15)$$

Since the value for  $\{E(\text{Os}_3(\mu_3\text{-C})) - E(\text{RuOs}_2(\mu_3\text{-C}))\}$  was not used to calculate the above bond energies and bond energy differences, the comparison of its value of 15.5 kJ/mol (retaining extra significant figures) calculated from eq 14 with the postulated value of 14.1 kJ shows that these calculations are at least internally consistent.

Very few measurements of bond energies involving cluster-bound ligands have been performed previously. Vites and Fehlner have noted that the Fe-H-Fe bond energy is ca. 40 kJ/mol stronger than the energy associated with a terminal hydride and a Fe-Fe bond.<sup>24</sup> Our results show that  $\{E(\text{MHM}') - E(\text{MM}')\}$  is very similar for all the trimetallic clusters of iron triad metals: 274 (Fe),<sup>24</sup> 293 (Ru), 297 (Os), and 299 (RuOs) kJ/mol. Although there are no experimental determinations of terminal Ru-H bond energies, the estimate of ca. 250 kJ/mol<sup>31</sup> for the Ru-H bond energy would imply that  $\{E(\text{RuHRu}) - (E(\text{RuRu}) - E(\text{RuH}))\}$  is also ca. 40 kJ/mol. Estimates of the terminal Os-H bond energy are still more speculative. In general, bond energies involving third-row metals are greater than those involving second-row metals. An Ir-H bond energy of 310 kJ/mol has been measured,<sup>32</sup> and Calderazzo<sup>33</sup> has proposed that  $E(\text{Os-H})$  may be as high as 310 kJ. However, those Os-L bond energies that have been measured are only on the order of 10% larger than the analogous Ru-L bond energies. For this reason we would predict a terminal Os-H bond energy of ca. 280 kJ/mol.<sup>34</sup> Thus, it appears that the energetic preference for a bridging hydride ligand, versus a terminal hydride, is ca. 40 kJ/mol for all iron triad metals. It should also be noted that free energies of activation for migration of bridging hydride ligands on  $\text{Ru}_3$  and  $\text{Os}_3$  clusters are also of this magnitude. This observation is consistent with the notion that hydride migration occurs via migration of a single hydride ligand from a bridging position to a terminal coordination mode.

## Conclusion

In this work we have used the low symmetry and composition-dependent reactivity of mixed-metal clusters to study the mechanism of reductive elimination of hydrogen from trimetallic clusters. The mechanism appears to involve reductive elimination of hydrogen from a single metal atom, following hydride migration from bridging to terminal coordination sites. These results suggest that, for metal cluster reactions which occur at only one metal atom of the cluster, the rate will be largely determined by a single metal atom, the most labile one; further incorporation of atoms of a labile metal will result in only a modest increase in the rate.

**Acknowledgment.** The mass spectrometer (CHE-850962) and the Varian Gemini NMR spectrometer (CHE-8613066) used for this work was purchased with funds from the National Science Foundation. This work was supported by the National Science Foundation through Grant No. CHE-8520276. J.B.K. acknowledges the Alfred P. Sloan Foundation for support. Thanks to

(31) (a) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41. (b) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41. (c) Sternal, R. S.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7920.

(32) Nolan, S. P.; Hoff, C. D.; Stoutland, P. O.; Newman, L. J.; Buchanan, J. M.; Bergman, R. G.; Yang, G. K.; Peters, K. S. *J. Am. Chem. Soc.* **1987**, *109*, 3143.

(33) Calderazzo, F. *Ann. N. Y. Acad. Sci.* **1983**, *415*, 37.

(34) Our calculations indicate that, if the terminal Os-H bond energy were any greater than 297 kJ/mol, then hydride ligands on Os clusters should be terminally coordinated, contrary to what is found in almost all cases.



Professor J. D. Atwood for helpful discussions and Mr. Leigh Nevinger for the mass spectral determinations.

**Registry No.** HRu<sub>3</sub>(μ-COMe)(CO)<sub>10</sub>, 71737-42-3; HRu<sub>2</sub>Os(μ-COMe)(CO)<sub>10</sub>(C<sub>1</sub> isomer), 116079-24-4; HRuOS<sub>2</sub>(μ-COMe)(CO)<sub>10</sub>(C<sub>1</sub> isomer), 116079-25-5; HOs<sub>3</sub>(μ-COMe)(CO)<sub>10</sub>, 69048-01-7; H<sub>3</sub>Ru<sub>3</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub>, 71562-47-5; H<sub>3</sub>Ru<sub>2</sub>O<sub>5</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub>,

116079-26-6; H<sub>3</sub>RuOs<sub>2</sub>(μ<sub>3</sub>-COMe)(CO)<sub>9</sub>, 116079-27-7; H<sub>3</sub>Ru<sub>2</sub>Os(μ<sub>3</sub>-COMe)(CO)<sub>7</sub>(AsPh<sub>3</sub>)<sub>2</sub>, 116079-28-8; H<sub>3</sub>RuOs<sub>2</sub>(μ<sub>3</sub>-COMe)(CO)<sub>8</sub>(AsPh<sub>3</sub>), 116079-29-9; H<sub>3</sub>Ru<sub>2</sub>Os(μ<sub>3</sub>-COMe)(CO)<sub>8</sub>(AsPh<sub>3</sub>), 116079-30-2; Ru<sub>3</sub>(CO)<sub>12</sub>, 15243-33-1; Ru<sub>2</sub>Os(CO)<sub>12</sub>, 12389-47-8; RuOs<sub>2</sub>(CO)<sub>12</sub>, 12389-50-3; Os<sub>3</sub>(CO)<sub>12</sub>, 15696-40-9; Os, 7440-04-2; Ru, 7440-18-8; HRu<sub>2</sub>Os(μ-COMe)(CO)<sub>10</sub>(C<sub>5</sub> isomer), 116079-31-3; HRuOs<sub>2</sub>(μ-COMe)(CO)<sub>10</sub>(C<sub>5</sub> isomer), 116102-37-5.

## Twelve-Electron Organochromium Species: Synthesis and Characterization of High-Spin Square-Planar Chromium(II) Alkyls and Aryls

Ann R. Hermes, Robert J. Morris, and Gregory S. Girolami\*

School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

Received April 28, 1988

Alkylation of the chromium phosphine complex [CrCl<sub>2</sub>(dippe)]<sub>2</sub> (dippe = 1,2-bis(diisopropylphosphino)ethane) with Grignard or dialkylmagnesium reagents gives the unusual 12-electron chromium(II) alkyls *cis*-CrR<sub>2</sub>(dippe) (R = CH<sub>2</sub>CMe<sub>3</sub>, CH<sub>2</sub>SiMe<sub>3</sub>, C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>). The unidentate phosphine complex *trans*-Cr(C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> may be prepared similarly by treatment of CrCl<sub>2</sub>(THF) with dimesitylmagnesium in the presence of PMe<sub>3</sub>. All of these four-coordinate alkyls possess magnetic moments characteristic of high-spin species, μ = 4.9 μ<sub>B</sub>, and exhibit broadened <sup>1</sup>H NMR resonances consistent with the paramagnetism. X-ray crystal structures of Cr(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(dippe) and Cr(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(dippe) reveal tetrahedral distorted square-planar structures, where the dihedral angle between the C-Cr-C and P-Cr-P planes is larger in the neopentyl complex, 28.4° vs 15.8°, due to steric effects. For similar reasons, the Cr-C and Cr-P distances in the neopentyl compound of 2.149 (8) and 2.556 (2) Å are slightly longer than those of 2.128 (4) and 2.517 (1) Å in the (trimethylsilyl)methyl derivative, and the C-Cr-C angle is also larger in the neopentyl complex at 101.9 (3)° vs 95.7 (2)°. In contrast to these results, the mesityl complex Cr(C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> is essentially flat: the ipso carbon atoms and the phosphorus atoms are +0.9° and -0.9° out of the mean CrC<sub>2</sub>P<sub>2</sub> plane, respectively. The Cr-C and Cr-P distances in this molecule are 2.130 (6) and 2.462 (2) Å, while all the C-Cr-P angles fall between 89.3 (2)° and 90.8 (2)°. Crystal data: for Cr(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(dippe), space group C2/c, a = 15.867 (5) Å, b = 10.401 (4) Å, c = 18.154 (6) Å, β = 106.67 (3)°, V = 2870 (2) Å<sup>3</sup>, Z = 4, R<sub>F</sub> = 5.9%, R<sub>wF</sub> = 7.7% on 126 variables and 1205 data; for Cr(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(dippe), space group C2/c, a = 15.666 (4) Å, b = 10.983 (3) Å, c = 18.099 (6) Å, β = 102.43 (2)°, V = 3041 (1) Å<sup>3</sup>, Z = 4, R<sub>F</sub> = 4.1%, R<sub>wF</sub> = 4.6% on 128 variables and 1472 data; for Cr(C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>, space group P2<sub>1</sub>/n, a = 9.710 (2) Å, b = 14.121 (3) Å, c = 19.446 (3) Å, β = 98.36 (1)°, V = 2638.0 (9) Å<sup>3</sup>, Z = 4, R<sub>F</sub> = 5.1%, R<sub>wF</sub> = 6.1% on 260 variables and 2199 data. The chromium alkyls are able to polymerize ethylene slowly at 25 °C and 10 atm.

### Introduction

Square-planar d<sup>8</sup> complexes of the platinum metals constitute one of the largest and most useful classes of homogeneous catalysts.<sup>1-4</sup> Such species are active for the hydrogenation, hydroformylation, and hydrosilation of olefins and are consequently of great utility both in the laboratory and in industry. Even apart from their catalytic activity, square-planar d<sup>8</sup> complexes exhibit interesting stoichiometric reactivity; perhaps most notable is their ability to activate C-H bonds of saturated hydrocarbons under mild conditions.<sup>5-7</sup>

In part, the versatility of square-planar d<sup>8</sup> complexes as catalysts is due to the ease with which oxidative addition

processes can occur. The relatively low coordination number facilitates oxidative addition since open coordination sites are already available. Furthermore, the products of oxidative addition are electronically favorable octahedral d<sup>6</sup> species, which can readily undergo reductive elimination to regenerate a d<sup>8</sup> complex if the electronic properties of the attendant ligands are properly chosen.

Apart from d<sup>8</sup> electronic configurations, square-planar geometries can also be adopted by d<sup>7</sup> and d<sup>9</sup> species. Among the former is the cobalt(II) aryl Co(C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>)<sub>2</sub>(PEtPh<sub>2</sub>)<sub>2</sub>,<sup>8</sup> while the latter class is represented by numerous copper(II) complexes such as the dithiocarbamate Cu(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>.<sup>9</sup> In these cases, the electronic preference for a square-planar geometry is not as great as for d<sup>8</sup> species, and this is reflected by the fact that four-coordinate cobalt(II) and copper(II) complexes are more commonly tetrahedral.

Of other electronic configurations, high-spin d<sup>4</sup> metal centers are expected to exhibit a preference for square-

(1) Jardine, F. H. *Prog. Inorg. Chem.* 1981, 28, 63-202.

(2) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980.

(3) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; Chapter 30.

(4) Wilkinson, T.; Stone, F. G. A.; Abel, E. W. *Comprehensive Organometallic Chemistry*; Pergamon: New York, 1982; Vol. 8.

(5) Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* 1980, 102, 6713-6725.

(6) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* 1981, 103, 2448-2450.

(7) Crabtree, R. H.; Demov, P. C.; Eden, D.; Mihelcic, J. M.; Farnell, C. A.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* 1982, 104, 6994-7001.

(8) Falvello, L.; Gerloch, M. *Acta Crystallogr., Sect. B. Struct. Crystallogr. Cryst. Chem.* 1979, B35, 2547-2550.

(9) Bonamico, M.; Dessy, G.; Mugnoli, A.; Vacic, A.; Zambonelli, L. *Acta Crystallogr.* 1965, 19, 886-897.