Ligand Substitution on $HRu_3(\mu\text{-}CX)(CO)_{10}$ (X = OMe or NMe_2). Syntheses and Characterizations of Three Isomeric Forms $HRu_3(\mu\text{-}CX)(CO)_9L$ and Kinetics of Substitution. Implications for the Mechanism of Cluster Hydrogenation

Dennis M. Dalton, Daniel J. Barnett, Timothy P. Duggan, Jerome B. Keister,* Pauline T. Malik, Sandeep P. Modi, Mark R. Shaffer, and Sally Ann Smesko

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

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Ligand substitution by L = $AsPh_3$ or PPh_3 on $HRu_3(\mu\text{-}CX)(CO)_{10}$, X = OMe or NMe_2, sequentially forms $HRu_3(\mu\text{-}CX)(CO)_{10-n}L_n$, n = 1, 2, and 3, in which only one L is coordinated to each Ru atom. The "lightly stabilized" complexes $HRu_3(\mu\text{-}CX)(CO)_9L'$, X = NMe_2, $NMe(CH_2Ph)$, or $N(CH_2Ph)_2$ and L' = NCMe or py, can be prepared by the addition of a stoichiometric quantity of trimethylamine *N*-oxide to $HRu_3(\mu\text{-}CX)(CO)_{10}$ in the presence of an excess of L'. The py ligand of $HRu_3(\mu\text{-}CNMe_2)(CO)_9(py)$ is coordinated on a bridged Ru atom and in the axial position trans to the $CNMe_2$ ligand (b-a isomer). Upon mixing L = $SbPh_3$, $AsPh_3$, PPh_3, $P(c\text{-}C_6H_{11})_3$, or PBu_3 with $HRu_3(\mu\text{-}CX)(CO)_9L'$ immediate ligand exchange generates $HRu_3(\mu\text{-}CX)(CO)_9L$ in which the kinetic product contains an equatorially coordinated ligand on a nonbridged Ru atom (n-e isomer). This product then rearranges by an intramolecular process to give an equilibrium mixture, the same as that obtained by thermal substitution on $HRu_3(\mu\text{-}CX)(CO)_{10}$, containing a second isomer in which L is coordinated to a bridged Ru atom in an equatorial position (b-e isomer). The equilibrium constant depends upon the identity of both X and L. For $HRu_3(\mu\text{-}CX)(CO)_9(PPh_3)$ the n-e/b-e ratio decreases in the order: X = $N(CH_2Ph)_2$ (1:0) > NMe_2 (0.12:0.87) > OMe (0:1). For $HRu_3(\mu\text{-}CNMe_2)(CO)_9L$ the n-e/b-e ratio decreases in the order: L = $SbPh_3$ (2.7) > $AsPh_3$ (0.4) > PPh_3 (0.14) and PBu_3 (1.5) > $PPh_3 \approx P(c\text{-}C_6H_{11})_3$ (0.14). These products have been characterized by spectroscopic methods and in the cases of $HRu_3(CNMe_2)(CO)_9(py)$ and $HRu_3(CN(CH_2Ph)_2)(CO)_9(PPh_3)$ by X-ray crystallography. The kinetics of thermal substitution by $AsPh_3$ on $HRu_3(\mu\text{-}CNMe_2)(CO)_{10}$ and by $AsPh_3$, PPh_3, and $P(OMe)_3$ on $HRu_3(\mu\text{-}COMe)(CO)_{10}$ were determined. The rate laws and activation parameters are consistent with a mechanism which is primarily CO dissociative. The rate of $AsPh_3$ substitution on $HRu_3(\mu\text{-}CNMe_2)(CO)_{10}$ is slower than for substitution on the OMe analogue (X = OMe, $\Delta H^\ddagger$ = 26.6 kcal, $\Delta S^\ddagger$ = 8 eu; X = NMe_2, $\Delta H^\ddagger$ = 26.9 kcal, $\Delta S^\ddagger$ = 3 eu). Activation parameters for replacement of $AsPh_3$ from $HRu_3(\mu\text{-}CNMe_2)(CO)_9(AsPh_3)$ by CO were also determined ($\Delta H^\ddagger$ = 25.4 kcal, $\Delta S^\ddagger$ = 2 eu). A mechanism is proposed for ligand substitution on $HRu_3(\mu\text{-}CX)(CO)_{10}$ in which the CX ligand changes from a $\mu\text{-}\eta^1$ three-electron donor ligand to a $\mu_3\text{-}\eta^2$ five-electron donor in the transition state. These data in conjunction with results of a previous study suggest that the rate-determining step for dihydrogen elimination from $H_3Ru_3(COMe)(CO)_9$ to form $HRu_3(COMe)(CO)_{10}$ under CO involves intramolecular rearrangement of the hydride ligands from bridging to terminal coordination sites.

Our recent studies of the cluster series $HM_3(\mu\text{-}CX)(CO)_{10}$ (M = Fe, Ru, or Os; X = O^{1-}, OMe, or NR_2) have shown that the identities of M and X profoundly affect cluster reactivity.[1-5] For example, at 60 °C $HRu_3(\mu\text{-}COMe)(CO)_{10}$ yields $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ under a hydrogen atmosphere[1] or reacts with alkynes C_2R_2 to form the methylidyne–alkyne coupled products $HRu_3(\mu_3\text{-}\eta^3\text{-}MeOCCRCR)(CO)_9$,[2] but neither $HRu_3(\mu\text{-}CO)(CO)_{10}^{1-}$ nor $HRu_3(\mu\text{-}CNR_2)(CO)_{10}$ reacts in the same manner under similar conditions. The reasons for these differences in reactivity were unknown but were throught to reflect the decreasing degree of C–X multiple bonding along the series X = O^{1-} > NR_2 > OMe.

Further questions concern the mechanism or mechanisms of CO substitution for these clusters. We have proposed that CO dissociation is the initial step in hydrogenation of $HRu_3(\mu\text{-}COMe)(CO)_{10}$ and, based upon the relative rates of reaction of the intermediate $HRu_3(COMe)(CO)_9$ with hydrogen and with CO, have further proposed that two isomeric intermediates of that formulation which differ in the distribution of CO ligands between the three Ru atoms may be involved.[5]

We have examined the ligand substitution chemistry of $HRu_3(\mu\text{-}CX)(CO)_{10}$ (X = OMe, NMe_2, $NMe(CH_2Ph)$, and $N(CH_2Ph)_2$) with the goals of (1) determining the mechanism(s) of ligand substitution, (2) determining the coordination site(s) involved in the substitution, and (3) explaining the differing reactivities of $HRu_3(\mu\text{-}COMe)(CO)_{10}$ and $HRu_3(\mu\text{-}CNR_2)(CO)_{10}$. Our results demonstrate that the substitution chemistry is considerably more complex than we had expected, involving three isomeric forms of the monosubstituted products, which are intramolecularly interconvertible and of which the kinetic product from ligand substitution involves addition at the nonbridged Ru atom.

Experimental Section

Chemicals. Syntheses of $Ru_3(CO)_{12}$,[6] $HRu_3(COMe)(CO)_{10}$,[1] $HRu_3(CNHCH_2Ph)(CO)_{10}$,[1] $HRu_3(CNMe(CH_2Ph))(CO)_{10}$,[1] methyl isocyanide,[7] and benzyl isocyanide[8] were accomplished according to previously reported procedures. Solvents were obtained from commerical sources and were used without further purification.

(1) Keister, J. B.; Payne, M. W.; Muscatella, M. J. *Organometallics* **1983**, *2*, 219.
(2) Beanan, L. R.; Abdul Rahman, Z.; Keister, J. B. *Organometallics* **1983**, *2*, 1062.
(3) Churchill, M. R.; Beanan, L. R.; Wasserman, H. J.; Bueno, C.; Abdul Rahman, Z.; Keister, J. B. *Organometallics* **1983**, *2*, 1179.
(4) Abdul Rahman, Z.; Beanan, L. R.; Bavaro, L. M.; Modi, S. P.; Keister, J. B.; Churchill, M. R. *J. Organomet. Chem.* **1984**, *263*, 75.
(5) Bavaro, L. M.; Montangero, P.; Keister, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 4977.
(6) Mantovani, A.; Cenini, S. *Inorg. Synth.* **1975**, *16*, 47.
(7) Schuster, R. E.; Scott, J. E.; Casanova, J., Jr. "Organic Syntheses"; Wiley: New York, 1973; Coll. Vol. 5, p 772.
(8) Ugi, I.; Meyr, R.; Lipinski, M.; Bodesheim, F.; Rosendahl, F. "Organic Syntheses"; Wiley: New York, 1973; Coll. Vol. 5, p 300.

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Trimethyl phosphite was distilled before use; all other ligands were used as received.

Characterization of Products. Infrared spectra of all compounds in cyclohexane solution were recorded on a Perkin-Elmer 457 or 467 spectrophotometer and were calibrated with the 2138.5 cm^{-1} absorption of cyclohexane or with polystyrene. ^1H NMR spectra were obtained on a Varian EM-390 or JEOL FX-90Q 90-MHz instrument. ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer; all samples contained chromium(III) acetylacetonate (0.02 M) as a relaxation agent. Mass spectra were obtained from Dr. Robert Minard and Mr. Greg Hancock at the Penn State University Mass Spectrometry Facility. Elemental analyses were performed by Schwarzkopf Laboratories.

$HRu_3(COMe)(CO)_9(PPh_3)$. A solution of $HRu_3(COMe)(CO)_{10}$ (112 mg, 0.179 mmol) and PPh_3 (180 mg, 0.687 mmol) in cyclohexane (25 mL) was stirred under nitrogen and at 25 °C for 2 days. Then the solvent was removed on a rotary evaporator and the residue applied as a dichloromethane solution to a silica gel thin-layer chromatography plate. Elution with cyclohexane gave four bands. The third band was extracted with dichloromethane, and evaporation yielded the product (48 mg, 31%) as yellow crystals.

Mass spectrum (FAB): m/z 864 ($^{102}Ru_3$). Anal. Calcd for $C_{29}H_{19}O_{10}PRu_3$: C, 40.42; H, 2.22. Found: C, 40.44; H, 2.19.

$HRu_3(COMe)(CO)_9(AsPh_3)$. The procedure was the same as that used for the PPh_3 derivative. After chromatography the product (yellow crystals) was recrystallized from methanol.

Mass spectrum (FAB): m/z 908 ($^{102}Ru_3$). Anal. Calcd for $C_{29}H_{19}O_{10}AsRu_3$: C, 38.46; H, 2.11. Found: C, 38.29; H, 2.17.

$HRu_3(COMe)(CO)_7(AsPh_3)_3$. A solution of $HRu_3(COMe)(CO)_{10}$ (21 mg, 0.033 mmol) and triphenylarsine (382 mg, 1.2 mmol) in heptane (25 mL) was stirred under a nitrogen atmosphere for 5 days. The orange precipitate which formed was filtered off, washed with cyclohexane, and dried under vacuum.

Anal. Calcd for $C_{63}H_{49}O_8As_3Ru_3$: C, 51.76; H, 3.38. Found: C, 51.78; H, 3.48.

$HRu_3(CNMe_2)(CO)_{10}$. A solution of $Ru_3(CO)_{12}$ (408 mg, 0.638 mmol), water (10 mL), triethylamine (10 mL), and tetrahydrofuran (50 mL) was placed in a 100-mL Schlenk flask equipped with a reflux condenser topped with a nitrogen gas inlet. The solution was heated in an oil bath at 60–70 °C for 1 h. After being cooled, a solution of tetraethylammonium bromide (1.25 g) in water was added and then the volatile components were removed by vacuum transfer. When only water and a purple precipitate ($[NEt_4][HRu_3(CO)_{11}]$) remained, the water was pipeted off while a nitrogen atmosphere was maintained in the flask. The precipitate was washed with water (15 mL) and then was dried under vacuum. Next a solution of methyl iodide (400 μL) in dichloromethane (10 mL) was added to the flask under nitrogen. To the resulting purple solution was added methyl isocyanide (30 μL) in dichloromethane (20 mL) dropwise with stirring until the solution was yellow. Then the solution was evaporated to dryness and the residue applied as a dichloromethane solution to preparative thin-layer chromatography plates. Elution with cyclohexane gave one large, yellow band which after extraction with dichloromethane and evaporation yielded the product as a yellow solid (361 mg, 88%).

This product was previously prepared from $Ru_3(CO)_{12}$ and $Me_3Sn(CH_2NMe_2)$.[9] Characterization was effected by comparison of the spectroscopic data with literature values.

$HRu_3(CN(CH_2Ph)_2)(CO)_{10}$. To a slurry of $HRu_3(CNHCH_2Ph)(CO)_{10}$ (125 mg, 0.128 mmol) in ethanol (20 mL) in a Schlenk flask equipped with a stir bar and under a nitrogen atmosphere was added an excess of sodium metal (spatula tip). The solution turned bright red due to formation of $Na[HRu_3(CNCH_2Ph)(CO)_{10}]$. Then benzyl chloride (90 μL) was added, and the solution was stirred for 2–3 h. During this period a yellow precipitate formed. Next solid ammonium chloride was added to neutralize the solution, which immediately turned yellow in color. To this solution was added enough dichloromethane and water to form two layers. The dichloromethane layer was separated, the aqueous layer was washed with dichloromethane, and the organic layers were combined, dried over magnesium sulfate, and filtered. The residue from the organic layer was applied to a silica gel thin-layer chromatography plate, which was eluted with hexanes–dichloromethane (9:1, v/v) to give two yellow bands. The first of these was extracted with dichloromethane and evaporation yielded the product (61 mg, 43%). The second band was unreacted starting material.

Mass spectrum (EI): m/z 794 ($^{102}Ru_3$).

$HRu_3(CNMe_2)(CO)_9(py)$. To a stirred solution of $HRu_3(CNMe_2)(CO)_{10}$ (50 mg, 0.078 mmol) in acetonitrile (15 mL) under a nitrogen atmosphere was added dropwise from a pressure equalizing dropping funnel a solution of trimethylamine *N*-oxide dihydrate (9 mg, 0.081 mmol) in acetonitrile (25 mL). After the addition was complete, pyridine (5 mL) was added and the solvent was removed by vacuum transfer. The yellow solid residue was shown by ^1H NMR spectroscopy to contain only $HRu_3(CNMe_2)(CO)_9(py)$ and excess pyridine.

$HRu_3(CN(CH_2Ph)_2)(CO)_9(py)$ and $HRu_3(CNMe(CH_2Ph))(CO)_9(py)$ were prepared by using the same procedure.

$HRu_3(CNMe_2)(CO)_9(PPh_3)$. To a stirred solution of $HRu_3(CNMe_2)(CO)_{10}$ (193 mg, 0.302 mmol) in acetonitrile (15 mL) in a Schlenk flask containing a nitrogen atmosphere was added dropwise a solution of trimethylamine *N*-oxide dihydrate (37 mg, 0.33 mmol) in acetonitrile (20 mL). After the addition was complete, a solution of PPh_3 (80 mg, 0.305 mmol) in acetonitrile (20 mL) was added dropwise. Then the solvent was removed on a rotary evaporator, and the residue was recrystallized from acetone/methanol to yield orange crystals (170 mg, 61%). Additional product could be obtained by thin-layer chromatography of the residue from the mother liquor, eluting with 9:1 (v/v) dichloromethane–hexanes, but decomposition of the product on the plate resulted in material contaminated with excess PPh_3.

Anal. Calcd for $C_{30}H_{22}NO_9PRu_3$: C, 41.20; H, 2.54. Found: C, 41.04; H, 2.80.

$HRu_3(CNMe_2)(CO)_9(AsPh_3)$. The compound was prepared by using the procedure given for the PPh_3 derivative.

Mass spectrum (FAB): m/z 921 ($^{102}Ru_3$).

$HRu_3(CNR_2)(CO)_9L$. All other monosubstituted products were prepared by addition of a stoichiometric quantity of the ligand L to the appropriate $HRu_3(CNR_2)(CO)_9(py)$ complex and were characterized spectroscopically.

$HRu_3(CNMe(CH_2Ph))(CO)_8(PPh_3)_2$. A solution of $HRu_3(CNMe(CH_2Ph))(CO)_9(PPh_3)$ (303 mg, 0.32 mmol), trimethylamine *N*-oxide dihydrate (39 mg, 0.35 mmol) and PPh_3 (92 mg, 0.35 mmol) in acetonitrile (50 mL) was stirred under a nitrogen atmosphere for 1 h. Then the solvent was removed with vacuum, and the residue was recrystallized from acetone to give red crystals (110 mg, 29%).

Anal. Calcd for $C_{53}H_{41}NO_8P_2Ru_3$: C, 53.72; H, 3.48; Ru, 25.59; P, 5.23. Found: C, 50.88; H, 3.33; Ru, 22.25; P, 5.10.

$HRu_3(CNMe_2)(CO)_8(PPh_3)_2$. To a solution of $HRu_3(CNMe_2)(CO)_{10}$ (102 mg, 0.159 mmol) in acetonitrile (30 mL) was added dropwise with stirring a solution of trimethylamine *N*-oxide dihydrate (40 mg, 0.360 mmol) in acetonitrile (20 mL). The resulting solution was stirred under nitrogen for 1 h. Then a solution of PPh_3 (90 mg, 0.344 mmol) in acetonitrile (10 mL) was added dropwise. Finally, the solution was evaporated to dryness, and the residue was recrystallized from dichloromethane–2-propanol to give orange crystals (86 mg, 49%).

Anal. Calcd for $C_{47}H_{37}O_8NP_2Ru_3$: C, 50.91; H, 3.36; N, 1.26. Found: C, 50.96; H, 3.55; N, 1.30.

$HRu_3(CNMe_2)(CO)_7(PPh_3)_3$. To a stirred solution of $HRu_3(CNMe_2)(CO)_{10}$ (100 mg, 0.154 mmol) and PPh_3 (170 mg, 0.648 mmol) in acetonitrile (50 mL) was added dropwise a solution of trimethylamine *N*-oxide dihydrate (62 mg, 0.558 mmol) in acetonitrile (25 mL). The resulting mixture was stirred for 1 h, during which time a red-brown precipitate formed. The solvent was removed under vacuum, and the residue was recrystallized from dichloromethane–2-propanol to give maroon crystals (78 mg, 38%).

Anal. Calcd for $C_{64}H_{52}NP_3O_7Ru_3$: C, 57.21; H, 3.91. Found: C, 57.23; H, 4.39.

Kinetic Measurements. The progress of each substitution reaction, conducted in heptane solution, was monitored by infrared spectroscopy using a Beckman 4240 spectrophotometer in the 10% transmittance mode and using 0.5-mm KBr solution cells. Reactions were conducted in jacketed, glass vessels under nitrogen

(9) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J.; Abel, E. W.; Rowley, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 7158.

or CO atmospheres. Samples were withdrawn via syringes or pipet. The temperature was maintained to ±0.1 °C using a Neslab circulator bath.

The rate constant for each reaction was obtained by plotting the ln of the absorbance for the appropriate peak due to the starting material $HRu_3(COMe)(CO)_{10}$, 2106 cm^{-1}, $HRu_3(CNMe_2)(CO)_{10}$, 2098 cm^{-1}, $HRu_3(CNMe_2)(CO)_9(AsPh_3)$, 2081 cm^{-1}, $HRu_3(COMe)(CO)_9(AsPh_3)$, 2092 cm^{-1}, or $HRu_3(COMe)(CO)_9(PPh_3)$, 2087 cm^{-1}) vs. time. In all cases good linear plots were obtained for 2.5–3 half-lives. A computer-calculated least-squares procedure was used to determine the pseudo-first-order rate constant for each run. Two to five runs at each set of conditions were used and the best value taken as the average. Error limits are given as the computer calculated standard deviation. The number of degrees of freedom have not been considered.

Activation parameters were determined from plots of ln (k_{obsd}/T) vs. $1/T$ and values determined by a computer-calculated least-squares procedure. Error limits of one standard deviation were computer calculated. The number of degrees of freedom have not been considered.

The equilibrium constant for the reaction of $HRu_3(COMe)(CO)_{10}$ with $AsPh_3$ to form $HRu_3(COMe)(CO)_9(AsPh_3)$ and CO was determined by the following procedure. A heptane solution of either cluster and excess $AsPh_3$ in known concentrations was placed in a thermostated (35.7 °C) reaction vessel under CO (1 atm). The ratio $[HRu_3(COMe)(CO)_9(AsPh_3)]/[HRu_3(COMe)(CO)_{10}]$ was determined from the absorbances of the peaks at 2092 and 2106 cm^{-1}. At 35.7 °C the concentration of CO dissolved in heptane is 1.0×10^{-2} M.[10] Other experiments at 1–4 atm of CO pressure were conducted by using a Parr pressure bottle immersed in a constant temperature bath. No absorptions due to the disubstituted cluster were noted in the infrared spectrum during these measurements; the disubstituted product appears to be unstable under a CO atmosphere. Values determined from five experiments with varying CO pressure and $[AsPh_3]$ were averaged to give a value of 0.6 ± 0.2 for K_{eq} (standard states for all species, 1 M). The error limits are the 90% level of confidence calculated by using t values.

Results

In hydrocarbon solvents $HRu_3(CX)(CO)_{10}$ (X = OMe or NMe_2) reacts with L = $AsPh_3$ or PPh_3 to produce sequentially $HRu_3(CX)(CO)_{10-n}L_n$ (n = 1–3). The ^1H NMR spectra of the product mixtures in deuteriochloroform solution clearly show hydride resonances due to each of the three substitution products. The monosubstituted products $HRu_3(CX)(CO)_9L$ can be isolated by thin-layer chromatography of the product mixture, but decomposition on the silica surface prevents this from being an attractive synthetic route. The di- and trisubstituted clusters, which decompose during chromatography, precipitate from hydrocarbon solution during the thermal substitution reactions and cannot be obtained in a pure form by this method. Isolations of $HRu_3(COMe)(CO)_8L_2$ and $HRu_3(COMe)(CO)_7L_3$ in pure states are very difficult since these complexes slowly decompose in solution in the absence of excess L; in one instance, an analytically pure sample of $HRu_3(COMe)(CO)_7(AsPh_3)_3$ was isolated by precipitation from the reaction solution. However, the ^1H NMR spectral characterizations of mixtures of these polysubstituted products are clearly made by comparisons of the hydride resonances with those of $HRu_3(CNMe_2)(CO)_{10-n}(PPh_3)_n$ (n = 1, 2, or 3), which can be made in good yield by the addition of stoichiometric quantities of trimethylamine N-oxide dihydrate to acetonitrile solutions of $HRu_3(CNMe_2)(CO)_{10}$ containing stoichiometric quantities of triphenylphosphine.

The preferred route to $HRu_3(CNR_2)(CO)_9L$ or $HRu_3(CNR_2)(CO)_8L_2$ (R_2 = Me_2, $(CH_2Ph)_2$, or $Me(CH_2Ph)$), where L is a group 15[51] donor ligand, is through addition of a stoichiometric amount of L to the "lightly stabilized" clusters $HRu_3(CNR_2)(CO)_9(py)$ or $HRu_3(CNR_2)(CO)_8L(py)$. The pyridine complexes are prepared by treating an acetonitrile solution of $HRu_3(CNR_2)(CO)_{10}$ or $HRu_3(CNR_2)(CO)_9L$, respectively, with first trimethylamine N-oxide dihydrate and then pyridine. Vacuum removal of the solvent leaves the pyridine complex in almost quantitative yield. The intermediate acetonitrile complexes $HRu_3(CNMe_2)(CO)_9(NCMe)$ or $HRu_3(CNR_2)(CO)_8L(NCMe)$, which can be observed spectroscopically, may also be used for addition of L but are not sufficiently stable to allow their isolation. This method of substitution gives only poor yields of $HRu_3(COMe)(CO)_9L$ or $HRu_3(COMe)(CO)_8L_2$. In all cases examined, products from the thermal reaction and the trimethylamine N-oxide reactions are identical.

In polar solvents, such as dichloromethane, or with more nucleophilic phosphines a complicating side reaction during the thermal substitution on $HRu_3(COMe)(CO)_{10}$ is nucleophilic attack by PR_3 on the methyl group, forming $[MePR_3][HRu_3(CO)_{11}]$, which undergoes rapid substitution to $[MePR_3][HRu_3(CO)_{11-n}(PR_3)_n]$.[11] For example, when the reaction of $HRu_3(COMe)(CO)_{10}$ with 3 equiv of PPh_3 was conducted in dichloromethane, the ^1H NMR spectrum after 4 h indicated the following components: $HRu_3(COMe)(CO)_{10}$ (10%), $HRu_3(COMe)(CO)_9(PPh_3)$ (14%), $HRu_3(CO)_{10}(PPh_3)^{1-}$ (33%), $HRu_3(CO)_9(PPh_3)_2^{1-}$ (43%). Identification of the substituted cluster anions was accomplished by comparison of the chemical shifts of the hydride resonances with those of authentic samples prepared by substitution on $HRu_3(CO)_{11}^{1-}$.[11] Examination of the ^1H NMR spectra of dichloromethane solutions of product mixtures formed by thermal substitution in heptane found no observable quantities of $HRu_3(CO)_{11-n}(PPh_3)_n^{1-}$ species. The demethylation reaction presumably involves S_N2 displacement of $HRu_3(CO)_{11}^{1-}$, a relatively good leaving group, by PPh_3. S_N2 displacements are known to be favored by more polar solvents.[31] This pathway is not followed in hydrocarbon solvents.

Characterization of Monosubstituted Products. All monosubstituted clusters have been characterized by infrared (Table I) and ^1H NMR (Table II) spectroscopy. Representative compounds have also been characterized by ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis. In addition, the solid state structures of $HRu_3(CNMe_2)(CO)_9(py)$ and $HRu_3(CN(CH_2Ph)_2)(CO)_9(PPh_3)$ have been established by X-ray crystallography, the details of which are given in the following paper.[12]

To understand the mechanism of ligand substitution on $HRu_3(CX)(CO)_{10}$ and to explain the mechanism of hydrogenation of $HRu_3(COMe)(CO)_{10}$, it was essential that the metal site which was substituted and, if possible, the coordination site on the metal atom be known. The solid-state structures of $HRu_3(COMe)(CO)_{10}$[3,13] and $HRu_3(CNMe_2)(CO)_{10}$[14] have been established by X-ray crystallography. Each consists of a triangular array of Ru atoms, two of which are bridged by the hydride and CX ligand. To each of the two bridged Ru atoms are also coordinated three CO ligands; four CO ligands are coordinated to the unique, nonbridged Ru atom such that two

(10) Gjaldbaek, J. C. *Acta Chem. Scand.* **1952**, *6*, 623.

(11) Taube, D. J.; Ford, P. C. *Organometallics*, submitted for publication.

(12) Churchill, M. R.; Fettinger, J.; Keister, J. B. *Organometallics*, following paper in this issue.

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

(14) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843.

Table I. Infrared Spectra between 2150 and 1700 cm^{-1}

compound	ν_{CO}, cm^{-1}
$HRu_3(CN(CH_2Ph)_2)(CO)_{10}$[a]	2096 w, 2059 s, 2048 s, 2024 s, 2011 s, 2002 m, 1997 m, 1985 w
$HRu_3(COMe)(CO)_9(AsPh_3)$[a]	2088 m, 2048 vs, 2016 vs, 2005 s, 1994 m, 1990 sh, 1983 w, 1976 w, 1968 w, 1956 w
$HRu_3(COMe)(CO)_9(PPh_3)$[a]	2087 m, 2048 vs, 2016 vs, 2008 s, 1994 m, sh, 1992 m, sh, 1978 w, sh, 1972 w, sh, 1959 vw
$HRu_3(CNMe_2)(CO)_9(AsPh_3)$[a]	2081 m, 2076 w, sh, 2041 vs, 2015 vs, 2009 s, 2003 s, 1992 m, 1987 w, 1974 w, 1952 w
$HRu_3(CNMe_2)(CO)_9(PPh_3)$[a]	2086 s, 2042 vs, 2012 vs, 2004 s, 1997 s, 1986 s, 1981 m, 1968 m, 1949 m
$HRu_3(CNMe_2)(CO)_9(SbPh_3)$[a]	
n-e isomer	2076 m, 2047 s, 2036 m, 2015 s, 2008 vs, 2000 m, 1982 m, 1969 m
n-e/b-e mixture	2082 m, 2076 m, 2044 s, br, 2014 vs, 2008 vs, 2000 m, 1993 m, 1982 m, 1970 m, 1964 m, sh, 1951 m
$HRu_3(CNMe_2)(CO)_9(P(c\text{-}C_6H_{11})_3)$[a]	2095 w, 2083 vw, 2075 vw, 2062 s, 2050 s, 2027 s, 2013 vs, 2005 s, 1998 s, 1988m
$HRu_3(CNMe_2)(CO)_9(py)$[a]	2075 m, 2034 s, 2004 s, 1998 vs, 1980 m, 1973 m, 1968 m, 1936 m
$HRu_3(CNMe(CH_2Ph))(CO)_9(PPh_3)$[a]	2080 m, 2073 sh, 2040 s, 2036 sh, 2012 s, 2006 s, 1997 m, 1987 w, 1981 w
$HRu_3(CN(CH_2Ph)_2)(CO)_9(PPh_3)$[a]	2078 s, 2073 m, 2042 s, 2005 s, 1981 w, 1972 w
$HRu_3(CN(CH_2Ph)_2)(CO)_9(py)$[a]	2076 m, 2035 s, 2004 s, 1996 s, 1981 m, 1974 s, 1970 s, 1955 w, 1933 m
$HRu_3(CNMe_2)(CO)_8(PPh_3)_2$[b]	2056 m, 2012 s, 1982 s, 1950 s
$HRu_3(CNMe(CH_2Ph))(CO)_8(PPh_3)_2$[a]	2057 m, 2050 sh, 2017 vs, 1989 m, br
$HRu_3(CN(CH_2Ph)_2)(CO)_8(PPh_3)_2$[a]	2053 m, 2039 m, 2012 s, 1988 s, 1952 s
$HRu_3(CNMe_2)(CO)_7(PPh_3)_3$[b]	2013 w, 1978 vs, 1960 m, sh, 1937 s, 1912 w, sh

[a] In cyclohexane. [b] In dichloromethane.

Ru–CO vectors are perpendicular to the metal triangle (axial ligands) and two Ru–CO vectors are in the same plane as the metal triangle (equatorial ligands). Each of the bridged Ru atoms may be considered to be octahedrally coordinated by three facially oriented CO ligands and by facially oriented μ-$Ru(CO)_4$, μ-H, and μ-CX ligands. For both clusters the alkyl groups on N or on O are in the same plane as the $Ru_2(\mu\text{-}C)$ unit due to partial multiple bonding between the bridging carbon and the heteroatom. Thus, the symmetry of $HRu_3(CNMe_2)(CO)_{10}$ is C_s but that of $HRu_3(COMe)(CO)_{10}$ is only C_1. Assuming that no gross structural changes from the structures of the parent carbonys occur upon substitution of a CO ligand by a group 15 donor ligand, there are six possible geometric isomers for $HRu_3(CX)(CO)_9L$ when X = NMe_2 or $N(CH_2Ph)_2$ and ten possible geometric isomers when X = OMe or NMe(CH_2Ph).

For the clusters $HRu_3(CX)(CO)_9L$ (X = OMe, L = $AsPh_3$, PPh_3; X = NMe_2, L = py, $SbPh_3$, $AsPh_3$, PPh_3, $P(c\text{-}C_6H_{11})_3$, PBu_3; X = $N(CH_2Ph)_2$, L = py, $AsPh_3$, PPh_3; X = NMe(CH_2Ph), L = PPh_3) three substitutional isomers have been identified. The particular isomer or isomers

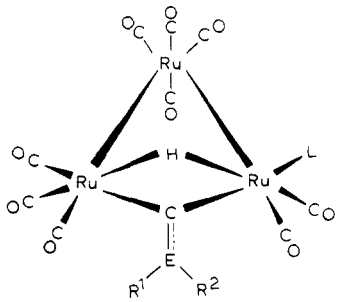


Figure 1. Structure of the bridged axially substituted (b-a) isomer of $HRu_3(\mu\text{-}CX)(CO)_9L$.

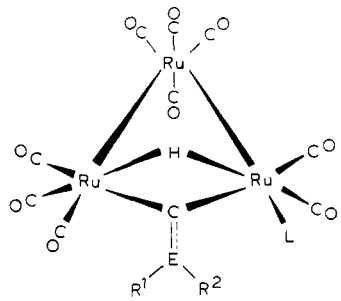


Figure 2. Structure of the bridged equatorially substituted (b-e) isomer of $HRu_3(\mu\text{-}CX)(CO)_9L$.

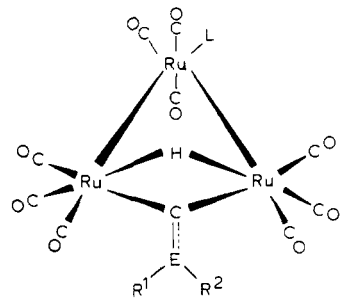


Figure 3. Structure of the nonbridged equatorially substituted (n-e) isomer of $HRu_3(\mu\text{-}CX)(CO)_9L$.

which are formed depend upon the identities of X and L. One isomer (Figure 1), found only for $HRu_3(CNR_2)(CO)_9(py)$, contains a py ligand which is coordinated to a bridged Ru atom and trans to the μ-CNR_2 ligand; this isomeric form will be called *bridged-axial* (b-a). The other two isomers have the ligand L coordinated in positions which are in the plane of the Ru_3 triangle, positions which are commonly termed equatorial or radial. One of these isomers is substituted on a bridged Ru atom (Figure 2) and will be termed *bridged-equatorial* (b-e); the other is substituted on the unique, nonbridged Ru atom (Figure 3) and will be termed *nonbridged-equatorial* (n-e). In general, the latter two isomers are in equilibrium with one another when L is a phosphine, arsine, or stibine ligand. For clusters having unsymmetrical X groups (OMe or NMe(CH_2Ph)) isomerism due to differing relative orientations of L and the alkyl substituents on X can also occur for all three isomeric forms.

Bridged Equatorially Substituted Isomers. The characterization of $HRu_3(CNMe_2)(CO)_9(PPh_3)$ is representative for the b-e isomers. This compound exists in solution as a 7:1 mixture of b-e and n-e isomers. The ^1H NMR spectrum contains signals due to both. The spectrum of the b-e isomer includes resonances at −14.25 (d, 1 H, J_{PH} = 8.2 Hz), 3.55 (d, 3 H, J_{PH} = 1.3 Hz), and 2.80 (s, 3 H) ppm which are assigned to the bridging hydride ligand and the nonequivalent *N*-methyl groups, respectively. Peaks due to the n-e isomer are −14.15 (d, 1 H, J_{PH} = 3 Hz) and 3.67 (s, 6 H) ppm. A coupling constant be-

Table II. ^{1}H NMR Spectra for $HRu_3(CX)(CO)_{10-n}L_n$ in Deuteriochloroform

compound	isomer, mol fractn	hydride resonance, δ	*O*- or *N*-alkyl resonances, δ	other, δ
$HRu_3(CN(CH_2Ph)_2)(CO)_{10}$		−14.64 (s, 1 H)	5.20 (s, 4 H)	7.3 (m, 10 H)
$HRu_3(COMe)(CO)_9(AsPh_3)$	b-e, 1	−14.43 (s, 1 H)	4.09 (s, 3 H)	7.5 (m, 15 H)
$HRu_3(COMe)(CO)_9(PPh_3)$	b-e, 1	−14.12 (d, 1 H, J_{PH} = 7.5 Hz)	4.00 (s, 3 H)	7.4 (m, 15 H)
$HRu_3(CNMe_2)(CO)_9(AsPh_3)$	b-e, 0.76	−14.28 (s, 1 H)	3.53 (s, 3 H), 2.91 (s, 3 H)	7.4 (m, 15 H)
	n-e, 0.23	−14.28	3.73 (s, 6 H)	
$HRu_3(CNMe_2)(CO)_9(PPh_3)$	b-e, 0.87	−14.25 (d, 1 H, J_{PH} = 8.2 Hz)	3.55 (d, 3 H, J_{PH} = 1.3 Hz), 2.80 (s, 3 H)	7.4 (m, 15 H)
	n-e, 0.12	−14.15 (d, 1 H, J_{PH} = 3 Hz)	3.67 (s, 6 H)	
$HRu_3(CNMe_2)(CO)_9(SbPh_3)$	b-e, 0.27	−14.62 (s, 1 H)	3.44 (s, 3 H), 3.01 (s, 3 H)	
	n-e,0.73	−14.47 (s, 1 H)	3.67 (s, 3 H), 3.72 (s, 3 H)	7.3 (m, 15 H)
$HRu_3(CNMe_2)(CO)_9(P(c\text{-}C_6H_{11})_3)$	b-e, 0.88	−14.66 (d, 1 H, J_{PH} = 7.7 Hz)	3.76 (s, 3 H), 3.73 (s, 3 H)	
	n-e, 0.12	−14.83 (s, 1 H)	3.81 (s, 6 H)	
$HRu_3(CNMe_2)(CO)_9(PBu_3)$	b-e, 0.39	−14.85 (d, 1 H, J_{PH} = 8.8 Hz)	3.7 (s, 6 H)	
	n-e, 0.61	−14.26 (d, 1 H, J_{PH} = 2.9 Hz)		
$HRu_3(CNMe_2)(CO)_9(py)$	b-a, 1	−12.15 (s, 1 H)	3.71 (s, 3 H), 3.73 (s, 3 H)	
$HRu_3(CNMe(CH_2Ph))(CO)_9(PPh_3)$	b-e, 0.5	−14.17 (d, 1 H, J_{PH} = 6 Hz)	2.83 (s, 3 H)	7.35 (m, 40 H), 5.35 (d, 1 H_A), 5.26 (d, 1 H_B), 4.95 (d, 1 H_C), 4.92 (d, 1 H_D), J_{AC} = 14.2 Hz, J_{BD} = 13.4 Hz
	n-e, 0.5	−14.08 (s, 1 H)	3.47 (s, 3 H)	
$HRu_3(CN(CH_2Ph)_2)(CO)_9(PPh_3)$	n-e, 1	−14.05 (d, 1 H, J_{PH} = 2.7 Hz)	5.15 (s, 4 H)	7.4 (m, 25 H)
$HRu_3(CN(CH_2Ph)_2)(CO)_9(py)$	b-a, 1	−12.10 (s, 1 H)	5.10 (m, 4 H)	8.8 (m, 5 H), 7.3 m, 10 H)
$HRu_3(COMe)(CO)_8(PPh_3)_2$[a]		−13.80 (dd, 1 H, J_{PH} = 1.9, 8.1 Hz)	3.91 (s, 3 H)	
$HRu_3(COMe)(CO)_8(AsPh_3)_2$[a]		−13.96 (s, 1 H)	3.95 (s, 3 H)	
$HRu_3(CNMe_2)(CO)_8(PPh_3)_2$		−13.74 (1:1:1 t, 1 H, J = 5 Hz)	3.49 (s, 3 H), 2.72 (s, 3 H)	
$HRu_3(CNMe(CH_2Ph))(CO)_8(PPh_3)_2$		−13.54 (br dd, 1 H, J_{PH} = 2.4, 8.0 Hz)	5.24 (d, 1 H_A), 4.87 (d, 1 H_B), 3.80 (s, 3 H), J_{AB} = 13.5 Hz	7.3 (m, 35 H)
$HRu_3(CN(CH_2Ph)_2)(CO)_8(PPh_3)_2$		−13.55 (dd, 1 H, J_{PH} = 2.4, 8.4 Hz)	5.32 (d, 1 H_A), 4.87 (d, 1 H_B), 4.79 (d, 1 H_C), 3.86 (d, 1 H_D), J_{AC} = 14.8 Hz, J_{BD} = 15.1 Hz	7.3 (m, 40 H)
$HRu_3(COMe)(CO)_7(PPh_3)_3$[a]		−13.24 (dt, 1 H, J_{PH} = 2.2, 8.4 Hz)	3.84 (s, 3 H)	
$HRu_3(COMe)(CO)_7(AsPh_3)_3$[a]		−13.22 (s, 1 H)	3.87 (s, 3 H)	
$HRu_3(CNMe_2)(CO)_7(PPh_3)_3$		−12.76 (dt, 1 H, J_{PH} = 3.0, 7.0 Hz)	3.46 (d, 3 H, J_{PH} = 1.3 Hz), 2.49 (s, 3 H)	7.3 (m, 45 H)

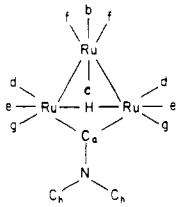
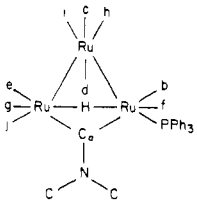
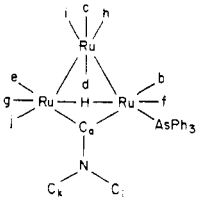
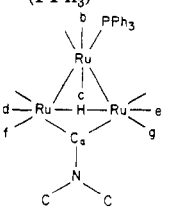
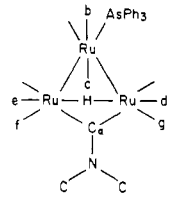
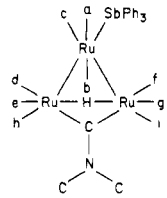
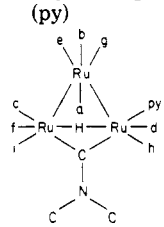
[a] Spectroscopic data obtained from mixtures of $HRu_3(COMe)(CO)_{10-n}L_n$, n = 2 and 3.

tween the hydride and ^{31}P of ca. 8 Hz is characteristic of all the b-e phosphine complexes. This value is close to the hydride–^{31}P coupling constant of 8.6 Hz reported for the closely related cluster $HOs_3(\mu\text{-}NCHCF_3)(CO)_9(PMe_2Ph)$, shown by X-ray crystallography to contain a b-e coordinated phosphine ligand.[15] An upfield shift of ca. 0.6 ppm for one of the *N*-methyl resonances is observed for b-e isomers of $HRu_3(CNMe_2)(CO)_9L$ when L = $AsPh_3$ or PPh_3 but only a small chemical shift difference between the *N*-methyl resonances is observed for the b-e isomer when L = $P(c\text{-}C_6H_{11})_3$; we attribute this to shielding by the phenyl ring current effect when the *N*-alkyl substituent is syn to PPh_3 or $AsPh_3$.

The ^{13}C NMR spectra of $HRu_3(CNMe_2)(CO)_9L$ (L = $AsPh_3$ or PPh_3) are indicative of b-e coordination by L (Table III). At 25 °C only one set of resonances due to CO ligands is apparent for either complex even though the ^{13}C resonance due to the *N*-methyl groups of the n-e isomer is clearly visible and the methylidyne resonance due to the n-e isomer of $HRu_3(CNMe_2)(CO)_9(AsPh_3)$ may also be

(15) (a) Adams, R. D.; Katahira, D. A.; Yang, L.-W. *J. Organomet. Chem.* **1981**, *219*, 85. (b) Adams, R. D.; Katahira, D. A.; Yang, L.-W. *J. Organomet. Chem.* **1981**, *219*, 241.

Table III. ^{13}C NMR Spectra in Deuteriochloroform Containing 0.02 M Chromium(III) Acetylacetonate

compound	chem shift, ppm	coupling const	assignt
$HRu_3(CNMe_2)(CO)_{10}$[a,b] 	312.6 (1 C)	unresolved J_{CH}	a
	205.8 (1 C)	J_{CC} = 38 Hz	b (c)
	204.5 (1 C)	J_{CC} = 38 Hz	c (b)
	207.7 (2 C)		d
	196.5 (2 C)	J_{CH} = 13 Hz	e
	194.0 (2 C)		f
	187.8 (2 C)		g
	54.1 (2 C)	J_{CH} = 141 Hz	h
$HRu_3(CNMe_2)(CO)_9(PPh_3)$[a,c] 	318.6 (1 C)	J_{CP} = 4 Hz, J_{CH} unresolved	a
	207.5 (1 C)	J_{CP} = 9 Hz	b
	206.8 (1 C)		c (d)
	206.2 (1 C)		d (c)
	201.7 (1 C)		e
	201.6 (1 C)	J_{CP} = 4 Hz, J_{CH} not determined	f
	197.9 (1 C)	J_{CH} = 14 Hz	g
	196.1 (1 C)		h
	195.2 (1 C)	J_{CP} = 7 Hz	i
	189.9 (1 C)		j
$HRu_3(CNMe_2)(CO)_9(AsPh_3)$[a,c] 	318.9 (1 C)	J_{CH} = 7 Hz	a
	207.4 (1 C)		b
	206.2 (1 C)		c (d)
	205.7 (1 C)		d (c)
	201.6 (1 C)		e
	200.7 (1 C)	J_{CH} = 10 Hz	f
	197.7 (1 C)	J_{CH} = 14.6 Hz	g
	195.1 (1 C)		h
	194.1 (1 C)		i
	189.6 (1 C)		j
	54.0 (1 C)		k (l)
	52.8 (1 C)		l (k)
$HRu_3(CN(CH_2Ph)_2)(CO)_9(PPh_3)$[c,d] 	318.8 (1 C)	J_{CH} unresolved	a
	211.8 (1 C)	J_{PH} = 10.7 Hz	b(c)
	210.4 (1 C)	J_{PH} = 10.7 Hz	c (b)
	204.8 (1 C)		
	201.9 (1 C)		
	200.9 (1 C)		
	199.3 (1 C)	J_{CH} = 11.7 Hz	d (e)
	198.0 (1 C)	J_{CH} = 14.7 Hz	e (d)
	188.0 (2 C)		f, g
$HRu_3(CN(CH_2Ph)_2)(CO)_9(AsPh_3)$[c,e] 	318.6 (1 C)	J_{CH} unresolved	a
	212.1 (1 C)		b (c)
	210.1 (1 C)		c (b)
	205.0 (1 C)		
	201.7 (2 C)		
	199.1 (1 C)		
	197.6 (1 C)	J_{CH} not determined	d (e)
	188.9 (1 C)		f (g)
	187.5 (1 C)		g (f)
$HRu_3(CNMe_2)(CO)_9(SbPh_3)$[b,f] n-e isomer 	211.3 (1 C)	J_{CC} = 32 Hz	a (b)
	208.8 (1 C)	J_{CC} = 32 Hz	b (a)
	203.9 (1 C)		c
	201.5 (1 C)		d
	200.5 (1 C)	J_{CH} = 13.6 Hz	e (g)
	199.5 (1 C)		f
	197.2 (1 C)	J_{CH} = 14.6 Hz	g (e)
	188.7 (1 C)		h (i)
	187.8 (1 C)		i (h)
$HRu_3(CNMe_2)(CO)_9(py)$ 	207.7 (br, 2 C)		a, b
	202.2 (1 C)		c
	201.5 (1 C)	J_{CH} = 13.2 Hz, J_{CC} = 4 Hz	d
	200.1 (br, 1 C)		e (g)
	198.0 (1 C)	J_{CH} = 14.6 Hz, J_{CC} = 4 Hz	f
	196.6 (br, 1 C)		g (e)
	192.6 (1 C)	J_{CC} = 4 Hz	h
	189.3 (1 C)	J_{CC} = 4 Hz	i

[a] At 25 °C. [b] Approximately 50% ^{13}C enriched. [c] Natural abundance ^{13}C content. [d] At −20 °C. [e] At −30 °C. [f] At 0 °C.

observed. The carbonyl resonances due to the n-e isomer may be exchange broadened at 25 °C, as is the case for $HRu_3(CN(CH_2Ph)_2)(CO)_9L$ (vide infra). The ^{13}C spectra for $HRu_3(CNMe_2)(CO)_9L$ are very similar to related $HRu_3(\mu\text{-}Y)(CO)_9(PPh_3)$ complexes, where Y = C(O)Me or Cl and PPh_3 is b-e coordinated and for which assignments have been clearly made by Kampe and Kaesz.[16]

For comparison we recorded the ^{13}C NMR spectrum of the parent molecule $HRu_3(CNMe_2)(CO)_{10}$ (Table III). The methylidyne carbon resonance is far downfield from the CO resonances, as is the case for other $HM_3(\mu\text{-}CX)(CO)_{10}$ compounds;[1,13,17-19] unresolved coupling to the hydride ligand is noted. Coupling to the hydride ligand (13 Hz) allows assignment of the resonance at 196.5 ppm to the CO ligands trans to the bridging hydride.[16,20] The two CO resonances of weight one, assigned to the trans-axial carbonyls on the $Ru(CO)_4$ fragment, display ^{13}C–^{13}C coupling of 38 Hz in ^{13}C enriched samples.[16,18,21] The resonance at 194.0 ppm shows a smaller NOE enhancement than the other three resonances of weight two and is assigned on this basis to the equatorial carbonyls on the $Ru(CO)_4$ fragment. Of the two remaining signals, the higher field one is assigned to the equatorial carbonyls on the bridged Ru atoms since equatorial carbonyls generally resonate at higher fields than axial ones.[16,22]

The ^{13}C NMR spectra of $HRu_3(CNMe_2)(CO)_9L$ (L = $AsPh_3$, PPh_3) are given in Table III. The spectra of the two compounds are very similar, except for the ^{13}C–^{31}P coupling. For each, the chemical shift of the methylidyne carbon is only slightly downfield from that of the parent carbonyl, indicating that the methylidyne remains dibridging; coupling of 4 Hz is observed between the ^{31}P nucleus and the methylidyne carbon. Assignments of the carbonyl resonances are based upon the following arguments. Resonances which are coupled to the hydride ligand are due to CO's trans to that ligand.[16,20] Resonances which are coupled to ^{31}P are due to CO ligands on the

(16) Kampe, C. E.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 4646.
(17) (a) Gavens, P. D.; Mays, M. J. *J. Organomet. Chem.* **1978**, *162*, 389. (b) Shriver, D. F.; Lehman, D.; Strope, D. *J. Am. Chem. Soc.* **1975**, *97*, 1594.
(18) Shapley, J. R.; Cree-Uchiyama, M. E.; St. George, G. M.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 140.
(19) Yeh, W.-Y.; Shapley, J. R.; Li, Y.; Churchill, M. R. *Organometallics* **1985**, *4*, 767.
(20) Bryan, E. G.; Forster, A.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *J. Chem. Soc., Dalton Trans.* **1978**, 196.
(21) Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3304.
(22) Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Schorpp, K. T. *J. Chem. Soc., Dalton Trans.* **1976**, 1403.

substituted metal center[22] *or* to the CO ligand on the $Ru(CO)_4$ fragment which is trans through the Ru–Ru bond to the PPh_3 ligand.[16,23] Carbonyls which are coordinated to the substituted metal atom will resonate ca. 4 ppm downfield from the chemical shift of the analogous CO on an unsubstituted metal atom.[16,22] Resonances in the ^1H decoupled spectra which show the smallest NOE enhancement are due to ligands on the $Ru(CO)_4$ unit. Using these arguments all CO resonances have been assigned as shown.

Nonbridged Equatorially Substituted Isomers. Although both n-e and b-e substituted isomers are observed in the ^1H NMR spectra of $HRu_3(CX)(CO)_9L$ when X = NMe_2 and L = $SbPh_3$, $AsPh_3$, PPh_3, or $P(c\text{-}C_6H_{11})_3$ and when X = $NMe(CH_2Ph)$ and L = PPh_3, the only complexes which exist in solution as exclusively the n-e isomers are $HRu_3(CN(CH_2Ph)_2)(CO)_9L$ (L = PPh_3 or $AsPh_3$). Spectroscopic methods were not sufficient to allow determination of the structures of these products. Therefore, the structure of $HRu_3(CN(CH_2Ph)_2)(CO)_9(PPh_3)$ was determined by X-ray crystallography. The details of the structural characterization are presented in the following paper.[12]

The spectroscopic properties of the n-e isomers $HRu_3(CX)(CO)_9L$ in solution are consistent with the solid-state structure established for $HRu_3(CN(CH_2Ph)_2)(CO)_9(PPh_3)$ (Figure 3). For phosphorus donor ligands the small ^{31}P–hydride coupling constant (2–3 Hz) is consistent with substitution on the Ru atom which is not bonded to the hydride; for comparison, a coupling constant of 2.4 Hz was reported for $HRu_3(\mu_3\text{-}C_2CMe_3)(CO)_8(PPh_3)$, in which the phosphine ligand is coordinated to the unique Ru atom which is not directly bonded to the bridging hydride.[24] Additionally, the ^1H and ^{13}C NMR resonances due to the two *N*-alkyl groups are coincidently isochronous for X = NMe_2 or $N(CH_2Ph)_2$; this is consistent with the very small influence upon the chemical shifts exerted by a phosphine ligand when it is far from the CX ligand. The infrared spectra for all complexes in cyclohexane contain only terminal carbonyl absorptions. For complexes which exist in solution as mixtures of n-e and b-e isomers, overlapping spectra due to each can be observed, with the highest frequency absorption for the n-e isomer slightly below that for the b-e one. For example, for $HRu_3(CNMe_2)(CO)_9(SbPh_3)$ (vide infra), these can be established as 2076 and 2081 cm^{-1}, respectively. The ^{13}C NMR spectra for $HRu_3(CN(CH_2Ph)_2)(CO)_9L$ (L = $AsPh_3$ or PPh_3), which exist in solution as only the n-e isomers, and for the n-e isomer of $HRu_3(CNMe_2)(CO)_9(SbPh_3)$, which undergoes rearrangement to the equilibrium mixture at a rate slow enough to allow determination of the spectrum, are very similar to one another and are fully consistent with the proposed structure.

The ^{13}C NMR spectrum of the n-e isomer of $HRu_3(CNMe_2)(CO)_9(SbPh_3)$ (ca. 50% ^{13}CO enriched) consists of nine resonances (25 °C) (Table III). Most spectra were recorded at −5 °C to slow down rearrangement to the equilibrium mixture. An unambiguous assignment for all resonances cannot be made, but the assignments are consistent with the proposed structure. The two resonances at lowest field are unambiguously assigned to the axial CO ligands on the nonbridged Ru atom by virtue of the large ^{13}C–^{13}C coupling constant between them (32 Hz); this feature is characteristic of *trans* axial CO ligands.[16,18,21] The resonances at 200.5 and 197.2 ppm are unambiguously assigned to CO ligands trans to the bridging hydride (J_{CH} = 13.6 and 14.6 Hz, respectively).[16,20] The resonances at 188.7 and 187.8 ppm are assigned to the bridged-equatorial CO pair by virtue of their upfield chemical shift. We assign the 203.4 ppm resonance to the nonbridged-equatorial CO ligand; this is shifted downfield by the $SbPh_3$ ligand.[16,22] The resonances at 201.5 and 199.5 ppm are then assigned to the bridged-axial CO ligands trans to the $CNMe_2$ ligand.

The ^{13}C NMR spectra for $HRu_3(CN(CH_2Ph)_2)(CO)_9L$ were obtained from unenriched samples. At 25 °C the spectra are exchange-broadened in the CO region. The spectrum of $HRu_3(CN(CH_2Ph)_2)(CO)_9(PPh_3)$ consists of four broad peaks centered at 210, 202, 198.5, and 188.5 ppm. At −30 °C the slow-exchange spectra may be obtained (Table III), and these appear to contain nine CO resonances, although some overlap occurs. Although complete assignments cannot be made, assignment of the lowest field CO resonances to the axial CO ligands on the nonbridged Ru atom is made by comparison to the spectrum of the n-e isomer of $HRu_3(CNMe_2)(CO)_9(SbPh_3)$. The observation of a ^{31}P–^{13}C coupling constant of 10.7 Hz to each of the two axial CO resonances for $HRu_3(CN(CH_2Ph)_2)(CO)_9(PPh_3)$ confirms the location of the PPh_3 ligand on the nonbridged Ru atom; coupling constants of 7 Hz between ^{31}P and the axial CO resonances were found in the spectrum of $\{Os(CO)_3(PEt_3)\}_3$, which contains equatorially coordinated phosphines.[22] No coupling between ^{31}P and the bridging methylidyne carbon resonance is observed, also consistent with phosphine coordination on the nonbridged Ru atom. Spectra for both $AsPh_3$ and PPh_3 derivatives were of poor quality, particularly the proton-coupled spectra, but the resonances which appear to be coupled to the hydride are assigned at 199.3 (J_{CH} = 11.7 Hz) and 198.0 (J_{CH} = 14.7 Hz) ppm for $HRu_3(CN(CH_2Ph)_2)(CO)_9(PPh_3)$; for $HRu_3(CN(CH_2Ph)_2)(CO)_9(AsPh_3)$ the only resonance which was clearly affected by proton coupling was at 197.6 ppm.

Bridged-Axial Isomers $HRu_3(CNR_2)(CO)_9(py)$. The solid-state structure (Figure 1) for $HRu_3(CNMe_2)(CO)_9(py)$ was established by X-ray crystallography, the details of which appear in the following paper. The spectroscopic properties of the py complexes in solution are consistent with the solid-state structure. Only terminal CO absorptions are found in the infrared spectra. The ^1H NMR spectrum of $HRu_3(CNMe_2)(CO)_9(py)$ consists of a single hydride resonance and two singlets of weight three due to the nonequivalent *N*-methyl groups, in addition to resonances due to the py ligand. The ^{13}C spectrum of $HRu_3(CNMe_2)(CO)_9(py)$ (ca. 50% ^{13}CO enriched) (Table III) is exchange broadened at 25 °C; the static spectrum (0 °C) consists of eight ^{13}C resonances in the carbonyl region. Peaks at 207.7 (2 C), 200.1 (1 C), and 196.6 (1 C) ppm are exchange broadened at 25 °C and remain broad even in the limiting slow-exchange spectrum; we assign these to the CO ligands on the $Ru(CO)_4$ unit, which can undergo facile exchange by a threefold exchange process[13,18] and which should show ^{13}C–^{13}C coupling to one another. Two resonances, 198.0 (1 C) and 201.5 (1 C) ppm, display coupling constants to the hydride ligand of 14.6 and 13.2 Hz, respectively; these are assigned to the CO ligands trans to the bridging hydride on the $Ru(CO)_3$ and $Ru(CO)_2(py)$ units, respectively. Cis ^{13}C–^{13}C couplings of ca. 4 Hz are observed for resonances at 198.0, 201.5, 192.6, and 189.3 ppm.[25] We assign the resonances at 192.6 and 189.3 ppm to bridged-equatorial CO ligands on the $Ru(CO)_2py$ and $Ru(CO)_3$ units, respectively, by virtue of their chemical

(23) Stuntz, G. F.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 607.
(24) (a) Barner-Thorsen, C.; Rosenburg, E.; Saatjian, G.; Aime, S.; Milone, L.; Osella, D. *Inorg. Chem.* **1981**, *20*, 1592. (b) Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J.; Sappa, E. *Inorg. Chem.* **1981**, *20*, 4437.
(25) Aime, S.; Osella, D. *J. Chem. Soc., Chem. Commun.* **1981**, 300.

shifts. Thus, the resonance at 202.2 ppm is assigned to the axial CO ligand which is trans to the $CNMe_2$ ligand and is coordinated on the $Ru(CO)_3$ fragment; this is consistent with its low field position.

Polysubstituted Clusters. The di- and trisubstituted clusters have not been characterized as thoroughly as the monosubstituted derivatives because of their low solubility, poor stability to chromatography, and, in the case of $HRu_3(COMe)(CO)_{10-n}L_n$ (n = 2, 3), ease of dissocation of L. However, the disubstituted derivatives $HRu_3(CNR_2)(CO)_8(PPh_3)_2$ and trisubstituted $HRu_3(CNMe_2)(CO)_7(PPh_3)_3$ have been prepared by the trimethylamine N-oxide route, and the polysubstituted complexes have been identified in the ^1H NMR spectra (Table II) of the product mixtures. Satisfactory elemental analyses were obtained for $HRu_3(COMe)(CO)_7(AsPh_3)_3$ and $HRu_3(CNMe_2)(CO)_{10-n}(PPh_3)_n$ (n = 2, 3). The infrared spectra (Table I) for these species display lower carbonyl stretching frequencies than those for the monosubstituted clusters.

The ^1H NMR spectra for $HRu_3(CX)(CO)_8(PPh_3)_2$ (X = OMe, NMe_2, $NMe(CH_2Ph)$ and $N(CH_2Ph)_2$) each indicate the existence of only one isomer in solution. The hydride resonances for $HRu_3(CX)(CO)_8(PPh_3)_2$ when X = OMe or $N(CH_2Ph)_2$ are clean doublets of doublets with one ^{31}P–^1H coupling constant of ca. 2.5 Hz and one of ca. 8 Hz, as would be expected for the presence of one nonbridged-equatorial and one bridged-equatorial phosphine ligand in each complex. The hydride resonances for $HRu_3(CX)(CO)_8(PPh_3)_2$, when X = NMe_2 or $NMe(CH_2Ph)$, are broad, and the patterns are not easily discernible. The hydride resonance for the $NMe(CH_2Ph)$ derivative appears to be a broad doublet of doublets with coupling constants of 2.4 and 8.0 Hz, but the hydride resonance for the NMe_2 derivative appears as a 1:1:1 triplet with separations of 5.1 Hz between the lines.

The spectra for $HRu_3(CX)(CO)_7(PPh_3)_3$ each show evidence for only one isomer which contains two b-e phosphine ligands and one n-e one. The hydride resonances are doublets of triplets with coupling constants of ca. 3 Hz to the n-e phosphine and ca. 7 Hz to the b-e phosphines.

Most $M_3(\mu\text{-}X)(\mu\text{-}Y)(CO)_8L_2$ species previously characterized have contained two b-e coordinated L.[26,27] We see no evidence for this isomer when Y = COMe, $CNMe_2$, $CNMe(CH_2Ph)$, or $CN(CH_2Ph)_2$. The crystal structure for $HRu_3(\mu\text{-}NO)(CO)_7(P(OMe)_3)_3$ contains two b-e phosphites and one n-e phosphite; ^{31}P–hydride coupling constants were not reported.[27]

Equilibrium between Nonbridged-Equatorial and Bridged-Equatorial Isomers of $HRu_3(CX)(CO)_9L$. In general, the monosubstituted products $HRu_3(CX)(CO)_9L$ exist as mixtures of n-e and b-e isomers in solution, with the n-e:b-e isomer ratio depending upon the identities of X and of L. For $HRu_3(CNMe_2)(CO)_9L$ in chloroform solution this ratio is 0.73:0.27 for $SbPh_3$, 0.23:0.76 for $AsPh_3$, 0.12:0.87 for PPh_3, 0.61:0.39 for PBu_3, and 0.12:0.87 for $P(c\text{-}C_6H_{11})_3$. For different X substituents on $HRu_3(CX)(CO)_9(PPh_3)$ the n-e:b-e ratios in chloroform solution are 0:1 for OMe, 0.12:0.87 for NMe_2, and 1:0 for $N(CH_2Ph)_2$. Only the py complexes exist as the b-a isomer.

The complexes having unsymmetrical methylidyne substituents X (OMe and $NMe(CH_2Ph)$) provide useful information about the influences of the alkyl substituents upon the structures of these monosubstituted clusters. Two isomers may be expected for each b-e or n-e substituted derivative because of differing relative orientations of the alkyl groups and L. Only the b-e isomer is found for $HRu_3(COMe)(CO)_9L$ where L = $AsPh_3$ or PPh_3, but only one hydride and one Me resonance are observed in the ^1H NMR spectrum at temperatures as low as −60 °C. Rapid interconversion of the syn and anti isomers by rotation or flipping of the Me group about the C–OMe bond is presumed to average the resonances in this instance. We have previously reported[28] that the syn and anti rotamers can be observed in the ^1H NMR spectrum of $HOs_3(COMe)(CO)_9(PPh_3)$ at −20 °C; in this case the less stable isomer appears to be the syn isomer, as might be expected on steric grounds. The free energy difference between syn-b-e and anti-b-e isomers of $HOs_3(COMe)(CO)_9(PPh_3)$ was found to be 0.4 kcal/mol, while the free energy of activation for conversion of the syn form to anti form is 16.1 kcal/mol at 35 °C.

Rotation about the C–NR_2 bond is much slower than about the C–OMe bond, and no rotation is observed on the NMR time scale at temperatures up to +50 °C for $HRu_3(CNMe(CH_2Ph))(CO)_{10}$. For $HRu_3(CNMe(CH_2Ph))(CO)_9(PPh_3)$ one might then expect four isomers, syn-n-e, anti-n-e, syn-b-e, and anti-b-e, where syn and anti refer to the orientation of the Me substituent with respect to the PPh_3 ligand. Only two isomers are observed in the ^1H NMR spectrum of $HRu_3(CNMe(CH_2Ph))(CO)_9(PPh_3)$ in deuteriochloroform solution. One isomer displays a doublet hydride resonance at −14.17 ppm with J_{PH} = 6 Hz and an N-methyl resonance at 2.83 ppm; the other displays a singlet hydride resonance at −14.08 ppm and an N-methyl resonance at 3.47 ppm. On the basis of the hydride–^{31}P coupling constants and the N-methyl chemical shifts we assign these isomers the syn-b-e and n-e structures, respectively. We are unable to distinguish between syn- and anti-n-e structures, and indeed these may be in equilibrium at a rate fast on the NMR time scale. However, this assignment implies that the syn substituent on N determines the coordination site of the ligand. When the methyl group is syn to PPh_3, the only isomer found is b-e, as is the most stable isomer of $HRu_3(CNMe_2)(CO)_9(PPh_3)$. The b-e isomer in which the benzyl group is syn to PPh_3 is not observed, as is the case for the b-e isomer of $HRu_3(CN(CH_2Ph)_2)(CO)_9(PPh_3)$.

On the basis of the examples presented above we propose that the influence of the methylidyne substituent upon the n-e:b-e isomer ratio is primarily steric in nature. The bulky substituents on N or O favor n-e coordination to minimize repulsions with L. This argument cannot be applied to the variation in the n-e:b-e ratio with different ligands L since for $HRu_3(CNMe_2)(CO)_9L$ there seems to be no correlation with the size of L. Both PPh_3 and $P(c\text{-}C_6H_{11})_3$ favor coordination to the bridged Ru atom, and PBu_3, of smaller size, coordinates preferentially to the nonbridged Ru atom, but the range of values for the equilibrium constants for the series $HRu_3(CNMe_2)(CO)_9(EPh_3)$, E = P, As, or Sb, in which steric factors should be minimal, is larger than the range of values for the phosphine complexes, regardless of size of the phosphine. The factors which determine the isomer ratio are currently under study and will be the subject of a later paper.[29]

Nonbridged to Bridged Isomerization. Ligand substitution by L = PPh_3 or $AsPh_3$ at 40–60 °C on $HRu_3(CNMe_2)(CO)_{10}$ produces an equilibrium mixture of n-e and b-e isomers $HRu_3(CNMe_2)(CO)_9L$. However, sub-

(26) (a) Deeming, A. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1970**, 897. (b) Collman, J. P.; Norton, J. R. *Inorg. Chem.* **1973**, *12*, 476.
(27) Johnson, B. F. G.; Raithby, P. R.; Zuccaro, C. *J. Chem. Soc., Dalton Trans.* **1980**, 99.
(28) Bavaro, L. M.; Keister, J. B. *J. Organomet. Chem.* **1985**, *287*, 357.
(29) Shaffer, M.; Keister, J. B. *Organometallics*, submitted for publication.

stitution of the b-a coordinated pyridine ligand of $HRu_3(CNMe_2)(CO)_9(py)$ occurs upon mixing with $AsPh_3$ in deuteriochloroform to give *exclusively the n-e isomer* of $HRu(CNMe_2)(CO)_9(AsPh_3)$. This isomer then rearranges to the equilibrium mixture of n-e and b-e isomers.

The n-e to b-e isomerization can be conveniently followed by ^1H NMR spectroscopy. To a sample of $HRu(CNMe_2)(CO)_9(py)$ in deuteriochloroform is added 1 equiv of $AsPh_3$, and the spectrum initially recorded shows only the n-e isomer of $HRu_3(CNMe_2)(CO)_9(AsPh_3)$. The rate of rearrangement to the equilibrium mixture can be measured by following the peak heights of the *N*-methyl resonances for each isomer. The mole fraction of the n-e isomer is measured as $m_n = h_n/(h_n + 2h_b)$, where h_n and h_b are the peak heights of the n-e and upfield b-e *N*-methyl resonances. (The factor of 2 arises from the relative weight of these signals for the n-e (six hydrogens) and b-e (three hydrogens) isomers.) Plots of ln $(m_n^t - m_n^\infty)$, where m_n^t and m_n^∞ are the mole fractions of the n-e isomer at time t and at $t = \infty$, vs. time were linear for greater than 3 half-lives. At 19 °C the first-order rate constant for conversion of the n-e isomer of $HRu_3(CNMe_2)(CO)_9(AsPh_3)$ to the equilibrium mixtuure is 6.5×10^{-4} s^{-1}. From the value of the equilibrium constant ($K_{eq} = 3.3$), the rate constants for the forward and reverse reactions are calculated to be 4.9×10^{-4} and 1.5×10^{-4} s^{-1}, respectively. The value of k_{obsd} is unaffected by the concentration of $AsPh_3$, and no exchange with added PPh_3 occurs during the rearrangement, suggesting an intramolecular process.

The reaction of $SbPh_3$ with $HRu_3(CNMe_2)(CO)_9(py)$ forms $HRu_3(CNMe_2)(CO)_9(SbPh_3)$ for which the kinetic product in either deuteriochloroform or cyclohexane is the n-e isomer. The rearrangement to the equilibrium mixture of b-e and n-e isomers has been monitored by ^1H and ^{13}C NMR spectroscopy in deuteriochloroform solution and by infrared spectroscopy in cyclohexane solution. Both ^1H and ^{13}C NMR spectra immediately after mixing show resonances for only the n-e isomer; rearrangement to the b-e:n-e equilibrium mixture occurs over the course of an hour. Resonances due to each isomer in both sets of spectra are readily assigned by comparison to the spectra of $HRu_3(CNMe_2)(CO)_9(PPh_3)$ (b-e) and $HRu_3(CN(CH_2Ph)_2)(CO)_9(PPh_3)$ (n-e). The infrared spectrum (Table I) immediately after mixing is very similar to that of $HRu_3(CN(CH_2Ph)_2)(CO)_9(PPh_3)$ (n-e), but gradually these absorptions decrease in intensity and a new set of absorptions grows in until the equilibrium mixture is obtained. The differences in wavenumbers between the two highest frequency bands for each set of absorptions are the same as the differences between the two highest frequency absorptions in the spectra of $HRu_3(CN(CH_2Ph)_2)(CO)_9(PPh_3)$ (n-e isomer) and $HRu_3(CNMe_2)(CO)_9(PPh_3)$ (most intense bands, b-e isomer), respectively. Thus, the identity of the kinetic product as the n-e isomer and the rearrangement to the equilibrium mixture are the same in either deuteriochloroform or cyclohexane solution. We see no evidence for a dependence upon solvent in this reaction sequence.

The mechanism of this n-e to b-e isomerization is presently unknown. The influences of the ligand and the metal upon the equilibrium constant and the rate of reaction are currently under investigation and will be the subject of a later paper.[29]

Kinetics of Ligand Substitution. In heptane solution $HRu_3(COMe)(CO)_{10}$ reacts with donor ligands L = $AsPh_3$, PPh_3, or $P(OMe)_3$ to form sequentially $HRu_3(COMe)(CO)_{10-n}L_n$, $n = 1$, 2, and 3. The rate of disappearance of the parent carbonyl was determined from the absorbance at 2101 cm^{-1} (Table IV). Under pseudo-first-order conditions, plots of ln (abs) vs. time were linear for 2.5–3 half-lives, indicating in each case a rate law which is first order in cluster concentration. The rate constant for the second substitution is similar in magnitude to that for the first; at $[PPh_3]$ of 16 mM and at 35.7 °C, k_{obsd} for substitution on $HRu_3(COMe)(CO)_9(PPh_3)$ is $(9.3 \pm 0.7) \times 10^{-5}$ s^{-1}, compared with 9.7×10^{-5} s^{-1} for substitution on $HRu_3(COMe)(CO)_{10}$ under the same conditions. For L = PPh_3 the observed rate constant for substitution is smaller ($(4.8 \pm 0.14) \times 10^{-5}$ s^{-1} at 35 °C with $[PPh_3] = 10.2$ mM and under 1 atm of CO) when the reaction is conducted under a CO atmosphere, even though the monosubstituted product does not react with CO under these conditions. At 35.7 °C the concentration of each ligand was varied over a fivefold range; only for PPh_3 was any difference in k_{obsd} noted, but even for this ligand the values at all concentrations are almost within experimental error (Table IV). Although there is only a small dependency of the rate constant upon the concentration of a given ligand, rate constants for different ligands are different by measurable amounts. At 35.7 °C and at ligand concentrations near 10 mM the rate constants increase in the order L = $AsPh_3$ (7.3×10^{-5} s^{-1}) < $P(OMe)_3$ (8.2×10^{-5} s^{-1}) < PPh_3 (9.4×10^{-5} s^{-1}); the order of increasing rate parallels the order of increasing ligand nucleophilicity. However, any contribution from a ligand dependent pathway is small, in most instances less than the experimental error of the measurement.

Table IV. Pseudo-First-Order Rate Constants for Reaction of $HRu_3(\mu\text{-}CX)(CO)_{10}$ (X = NMe_2, OMe)[a] with L (L = $AsPh_3$, PPh_3, $P(OMe)_3$)

X	L	[L], mM	T, °C	$10^5 k_{obsd}$, s^{-1}
NMe_2	$AsPh_3$	10.0	40.0	0.57 ± 0.04
		30.0	46.0	1.4 ± 0.1
		10.0	50.1	2.6 ± 0.2
		30.0	50.2	2.5 ± 0.2
		10.0	59.8	8.2 ± 0.8
		10.0	70.0	29 ± 2
OMe	$AsPh_3$	10.0	24.8	1.6 ± 0.2
		43.8	30.0	2.9 ± 0.3
		10.0	35.7	7.3 ± 0.4
		50.0	35.7	7.6 ± 0.4
		10.0	39.3	12.4 ± 0.2
		20.0	46.0	32 ± 3
	PPh_3	10	24.0	3.2 ± 0.2
		10	26.0	3.4 ± 0.2
		9.9	35.7	9.4 ± 0.6
		10.2	35.7	4.8 ± 0.2[b]
		39.5	35.7	9.7 ± 0.6
		50.0	35.7	10.7 ± 0.3
		29	46	56 ± 9
	$P(OMe)_3$	7.4	35.7	8.2 ± 0.8
		27.3	35.7	8.8 ± 0.8
		45.5	35.7	8.4 ± 0.8

[a] Initial concentration ca. 1 mM in heptane solution under a nitrogen atmosphere. [b] Under CO, 1 atm.

With the ligands used in this study and in the concentration ranges investigated, the mechanism for the first substitution can be adequately represented by eq 1 and eq 2. In the presence of a large excess of L the rate law for this mechanism is given by eq 3. In the absence of

$$HRu_3(CX)(CO)_{10} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HRu_3(CX)(CO)_9 + CO \quad (1)$$

$$HRu_3(CX)(CO)_9 + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HRu_3(CX)(CO)_9L \quad (2)$$

$$\text{rate} = [k_1k_2[L]/(k_{-1}[CO] + k_2[L])][HRu_3(CX)(CO)_{10}] \quad (3)$$

Table V. Rate Constants for Replacement of $AsPh_3$ from $HRu_3(CX)(CO)_9(AsPh_3)$ by CO (1 atm)

X	T, °C	$10^5 k_{obsd}$, s^{-1}
NMe_2	40.0	4.1 ± 0.4
	50.0	14 ± 1
	60.0	50 ± 3
OMe	35.7	12 ± 1

CO, $k_2[L] >> k_{-1}[CO]$ and the rate law becomes independent of ligand concentration with the first-order rate constant k_1 representing CO dissocation. For L = $AsPh_3$ the rate constant k_{-2} at 35.7 °C was determined to be 1.2×10^{-4} s^{-1} under 1 atm of CO. The PPh_3 analogue shows no reaction under comparable conditions.

An estimate of the value for $k_1k_2/k_{-1}k_{-2}$ was obtained by allowing the system to come to equilibrium in the presence of excess $AsPh_3$ and excess CO. Because of the lower stability of the polysubstituted products under CO, significant quantities of these species were not observed. Taking the solubility of CO at 1 atm in heptane at 35.7 °C to be 1.0×10^{-2} M,[10] measurements of the equilibrium ratio of $[HRu_3(COMe)(CO)_9(AsPh_3)]$ to $[HRu_3(COMe)(CO)_{10}]$ yielded a value of 0.6 ± 0.2 for $k_1k_2/k_{-1}k_{-2}$. From values of k_{-2} and k_1, measured in the presence of excess $AsPh_3$ and excess CO, respectively, the value for the competition ratio k_2/k_{-1} is 1, implying that the intermediate $HRu_3(COMe)(CO)_9$ is nondiscriminating. Similarly, from the value of k_{obsd} for PPh_3 substitution ($[PPh_3]$ = 10.2 mM) under CO (1 atm), an estimate of k_{-1}/k_2 for PPh_3 of 1 is also obtained. Thus, as was found for $Ru_3(CO)_{11}$,[30] the unsaturated cluster is nondiscriminating toward Lewis bases.

Activation parameters for substitution on $HRu_3(COMe)(CO)_{10}$ by $AsPh_3$ were determined from a plot of ln (k/T) vs. $1/T$. The enthalpy of activation was 26.6 ± 0.8 kcal/mol, while the entropy of activation was 8 ± 3 eu.

The kinetics of substitution on $HRu_3(CNMe_2)(CO)_{10}$ by $AsPh_3$ were also examined. The rate law was found to be first order in cluster concentration and zero order in ligand concentration over a three-fold change. The kinetic behavior is very similar to that found for the OMe analogue, but the rate constants are considerably smaller. At 46 °C the rate constant for substitution on $HRu_3(COMe)(CO)_{10}$ is 23 times that for the NMe_2 derivative. Activation parameters for substitution on $HRu_3(CNMe_2)(CO)_{10}$ were calculated to be 26.9 ± 0.5 kcal for $\Delta H^\ddagger$ and 3 ± 2 eu for $\Delta S^\ddagger$.

Rate constants for conversion of $HRu_3(CNMe_2)(CO)_9(AsPh_3)$ to $HRu_3(CNMe_2)(CO)_{10}$ under CO (1 atm) were also determined (Table V). The process is first order in cluster concentration; the order in CO concentration was not determined. Activation parameters for this process ($\Delta H^\ddagger$ = 25.4 ± 0.9 kcal/mol; $\Delta S^\ddagger$ = 2 ± 3 eu) are very similar to those for the substitution on $HRu_3(CNMe_2)(CO)_{10}$ by $AsPh_3$. The ratio of k_1/k_{-2} of 0.2 at 50 °C for the $HRu_3(CNMe_2)(CO)_{10}/HRu_3(CNMe_2)(CO)_9(AsPh_3)$ system compares closely with the ratio of 0.6 for the OMe system at 35.7 °C.

Discussion

The goals of this work were (1) to determine the mechanism of ligand substitution on $HRu_3(CX)(CO)_{10}$ (X = OMe and NMe_2) and the rate constants for CO dissociation, (2) to determine the site or sites of substitution, and (3) to account for the differing reactivities of $HRu_3(COMe)(CO)_{10}$ and $HRu_3(CNMe_2)(CO)_{10}$. These points are important for an understanding of the reactions of these clusters with hydrogen and with alkynes, reactions which appear to involve CO dissociation as the first step. Therefore, to minimize the magnitude of any associative pathway for ligand substitution, we chose to examine substitutions on $HRu_3(CX)(CO)_{10}$ by $AsPh_3$, which has been shown to be a poor nucleophile.

Thermally induced substitution on $HRu_3(CX)(CO)_{10}$ (X = OMe or NMe_2) by $AsPh_3$ in hydrocarbon solvents proceeds by a CO dissociative mechanism (eq 1 and 2). This is supported by the independence of the rate on $[AsPh_3]$ and by the activation parameters (relatively high $\Delta H^\ddagger$ and positive $\Delta S^\ddagger$), which are consistent with a dissociative but not an associative process. Substitutions on $HRu_3(COMe)(CO)_{10}$ by better nucleophiles $P(OMe)_3$ and PPh_3 also appear to proceed primarily, if not entirely, through CO dissociative mechanisms. There is only a small dependence of the rate constant for disappearance of $HRu_3(COMe)(CO)_{10}$ upon $[PPh_3]$, and the reaction is inhibited by CO.

Given that CO dissociation is the initial step for ligand substitution by poor nucleophiles such as $AsPh_3$, the limiting rate constants for reactions of $HRu_3(CX)(CO)_{10}$ with other substrates such as hydrogen or alkynes should be the same if CO dissocation is rate limiting. We have previously noted the similarity of the limiting rate for hydrogenation of $HRu_3(COMe)(CO)_{10}$ to that for ligand substitution,[5] and the kinetics of the reaction with alkynes is under investigation. As previously noted, $HRu_3(COMe)(CO)_{10}$ is much more reactive than $HRu_3(CNMe(CH_2Ph))(CO)_{10}$ toward these substrates. At 46 °C the rate constant for CO dissociation from the $HRu_3(COMe)(CO)_{10}$ is 23 times that for the NMe_2 analogue. Since the enthalpies of activation for these substitutions are almost identical, this relative reactivity should hold over a fairly large temperature range. This difference in the rate of CO dissocation may explain to some extent the differences in reactivities of these clusters toward hydrogen and toward alkynes, but it cannot be the sole explanation since no stable products from reactions of $HRu_3(CNR_2)(CO)_{10}$ are formed even at temperatures at which our results show that CO dissociation should readily occur. Furthermore, Ford and Taube have found $HRu_3(CO)_{11}^-$ much more labile than $HRu_3(COMe)(CO)_{10}$, even though the cluster anion does not react with hydrogen in the same manner.[11]

One important question addressed by our kinetic studies concerns the selectivity of the unsaturated intermediate $HRu_3(COMe)(CO)_9$. In our earlier study of hydrogenation of $HRu_3(COMe)(CO)_{10}$ and carbonylation of $H_3Ru_3(COMe)(CO)_9$, both of which proceed through an intermediate of the composition $HRu_3(COMe)(CO)_9$, we found an unusually high selectivity of the intermediate for CO over hydrogen. We suggested that the selectivity might arise from the existence of *two isomeric intermediates* differing in the distribution of CO ligands and that only one of these gave rise to the hydrogenated product $H_3Ru_3(COMe)(CO)_9$. If this postulate were true, we expected that the intermediate formed by CO dissocation would be unselective toward different Lewis bases, as are other unsaturated metal complexes.[32] From measurements of the equilibrium constant for $AsPh_3$ substitution and from the extent of CO inhibition of the rate of PPh_3 substitution, competition ratios for the rate constants of CO addition and of addition of L = $AsPh_3$ or PPh_3 at 35.7

(30) Poë, A.; Twigg, M. V. *J. Chem. Soc., Dalton Trans.* **1974**, 1860.
(31) Maccarone, E.; Perrini, G.; Torre, M. *Gazz. Chim. Ital.* **1982**, *112*, 25.
(32) Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557 and references therein.

°C were determined to be 1 in both cases, indicating that $HRu_3(COMe)(CO)_9$, formed by CO dissociation from $HRu_3(COMe)(CO)_{10}$, is indeed unselective toward the addition of Lewis bases. Thus, the high selectivity for CO addition to $HRu_3(COMe)(CO)_9$ relative to hydrogen addition must arise in the hydrogen addition step itself. For comparison, the values of k_{CO}/k_{PPh_3} and $k_{CO}/k_{P(OPh)_3}$ for addition of L to the unsaturated intermediate $Ru_3(CO)_{11}$ have been measured to be 5 and 2.9, respectively,[30] whereas the competition ratio k_{CO}/k_{H_2} for $HRu_3(COMe)(CO)_9$ was estimated to be 700.[5]

The second goal of this work was to determine the site of CO dissociation. This is a much more difficult problem. Three types of monosubstituted products $HRu_3(CX)(CO)_9L$ have been identified—b-a, b-e, and n-e—and the b-e and n-e isomers are in equilibrium with one another with the relative amounts of each depending upon X and L. The rates of interconversion between the isomers of $HRu_3(CNMe_2)(CO)_9(AsPh_3)$ are faster by 2 orders of magnitude than the rates of ligand dissociation. The stability of the b-a form for $HRu_3(CNMe_2)(CO)_9(py)$ is understandable since the best σ donor, py, is trans to the best π acceptor, $CNMe_2$, and for the small py ligand the steric crowding between py and the nonbridged-axial CO ligand is minimal. A similar situation is noted for $H_2Os_3(CO)_{10}L$, in which small ligands such as py and CNR occupy axial positions but phosphines and phosphites occupy equatorial ones.[21] The relative stabilities of the b-e and n-e isomers are harder to rationalize. The difference in free energy between these two isomers is small, less than 2 kcal in most cases, and the steric and electronic influences upon the equilibrium constant may be difficult to separate. Comparison of the n-e:b-e ratios for $HRu_3(CNMe_2)(CO)_9L$ suggest that the n-e isomer becomes more stable as the electron donor ability of L increases. The variation in the values of the equilibrium constant and the rate constant for intramolecular isomerization are currently under investigation and will be the subject of a later paper. In any case, since the equilibrium mixture of products $HRu_3(CX)(CO)_9L$ is obtained by thermally induced substitution on $HRu_3(CX)(CO)_{10}$ and since microscopic reversibility does not require that the incoming ligand L, other than CO, occupy the site vacated by CO, we cannot determine the site of CO dissociation from $HRu_3(CX)(CO)_{10}$ from the structures of the products. The fact that CO fluxionality is more rapid than CO substitution prevents ^{13}CO labeling from providing useful information. Although we *can* determine the kinetic product from substitution by L for py on $HRu_3(CNMe_2)(CO)_9(py)$, this is not necessarily the same as the kinetic product from substitution by L on $HRu_3(CNMe_2)(CO)_{10}$ because (1) microscopic reversibility does not require that L, other than py, occupy the site vacated by py and (2) the mechanism of py replacement is not known and may not involve rate-limiting py dissociation, although this certainly seems likely. If dissociation of py is the mechanism of substitution of $AsPh_3$ for py from $HRu_3(CNMe_2)(CO)_9(py)$, then the structure of the most stable form of the intermediate $HRu_3(CNMe_2)(CO)_9$ must have equivalent numbers of CO ligands on each Ru atom since the kinetic product of addition of L to the intermediate has three CO ligands on each Ru atom. Otherwise, there would be no reason why the b-a isomer $HRu_3(CNMe_2)(CO)_9(py)$ could not be converted directly into the b-e isomer $HRu_3(CNMe_2)(CO)_9L$, which is the thermodynamically most stable isomer when L = $AsPh_3$ or PPh_3.

We will make the assumption that substitutions by L on $HRu_3(CX)(CO)_{10}$ (X = OMe or NMe_2) and on $HRu_3(CNMe_2)(CO)_9(py)$ all proceed by dissociative mechanisms and that the same type of intermediate $HRu_3(CX)(CO)_9$ is formed in all these cases. This seems reasonable, since py is a weakly bound ligand and since the substitutional characteristics of $HRu_3(CX)(CO)_{10}$ (X = O^{1-}, NMe_2, or OMe) seem qualitatively much the same. If this assumption is true, then the characteristics of the intermediate $HRu_3(CX)(CO)_9$ are as follows. First, the intermediate is nondiscriminating toward donor ligands. Second, the kinetic product of ligand addition (including pyridine) is derived by addition at the Ru atom which is not bridged by the hydride; this suggests that the intermediate $HRu_3(CX)(CO)_9$ has three CO ligands on each Ru atom and contradicts our previous proposal[5] that the most stable isomeric form of $HRu_3(COMe)(CO)_9$ should have unequal numbers of CO ligands on each Ru atom—two, three, and four. Third, the intermediate $HRu_3(CX)(CO)_9$, although nondiscriminating toward Lewis bases, discriminates very strongly in favor of CO over hydrogen, even though the thermodynamic product from hydrogen addition may be thought to be derived from H_2 addition to the unique Ru atom of the proposed intermediate. Fourth, the relative rates of CO dissociation from $HRu_3(CX)(CO)_{10}$ are in the order X = O^{1-} >> OMe > NMe_2, even though a comparison of the ground-state structures suggest that the NMe_2 substituent should be placed between O^{1-} and OMe; this suggests that the order of rate constants for CO dissociation reflects the relative stabilities of the transition states.

The fourth point above bears some discussion. The strong trans influences of the μ-COMe and μ-$CNMe_2$ groups have been noted in the crystal structures of $HRu_3(COMe)(CO)_{10}$[3,13] and $HRu_3(CNMe_2)(CO)_{10}$.[14] In each structure the Ru–CO bond lengths trans to the μ-CX ligand are the longest in the molecule and the next longest RuCO bonds are the trans diaxial pair on the $Ru(CO)_4$ unit (X = OMe, trans to COMe, 1.984 Å, trans to H, 1.902 Å, trans to $Ru(CO)_4$, 1.907 Å, trans axial CO ligands on $Ru(CO)_4$, 1.944 Å; X = NMe_2, trans to $CNMe_2$, 1.967 Å, trans to H, 1.898 Å, trans to $Ru(CO)_4$, 1.899 Å, trans axial CO ligands on $Ru(CO)_4$, 1.921 Å). It should be noted that both of these structures are of high precision and that the average Ru–CO bond length trans to the μ-$CNMe_2$ ligand is 10σ longer than the average Ru–CO bond length for the axial CO ligands on the $Ru(CO)_4$ unit. The trans influence of the bridging CO ligand on $HRu_3(CO)_{11}^{1-}$ has been noted;[33] although the crystal structure was of lower precision than those of $HRu_3(CX)(CO)_{10}$, X = OMe or NMe_2, the same trends hold (X = O^{1-}, trans to μ-CO^{1-}, 1.962 Å, trans to H, 1.900 Å, trans to $Ru(CO)_4$, 1.88 Å, trans axial CO ligands on $Ru(CO)_4$, 1.93 Å). These data indicate that the order of increasing *trans* influence is μ-CO^{1-} < μ-$CNMe_2$ < μ-COMe. The rationalization for the order for the trans influence of the μ-CX moiety is that these ligands are good π acceptors, better than CO, and compete effectively for the d orbital electron density. By this argument the CO ligands trans to the μ-CX ligand should be most weakly bound and the unsaturated intermediate $HRu_3(CX)(CO)_9$ should contain a vacant site trans to the CX ligand. Clearly, the relative rates of CO dissociation do not parallel the order of increasing trans influence and the most stable form of the intermediate does not seeem to have a vacant site trans to the CX ligand.

An alternative which can account for the observations above is that the CX ligand in each of these intermediates is μ_3-η^2-coordinated (structure A) as a 5-electron donor. In this way the "unsaturated" intermediate would be stabi-

(33) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Suss, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1356.

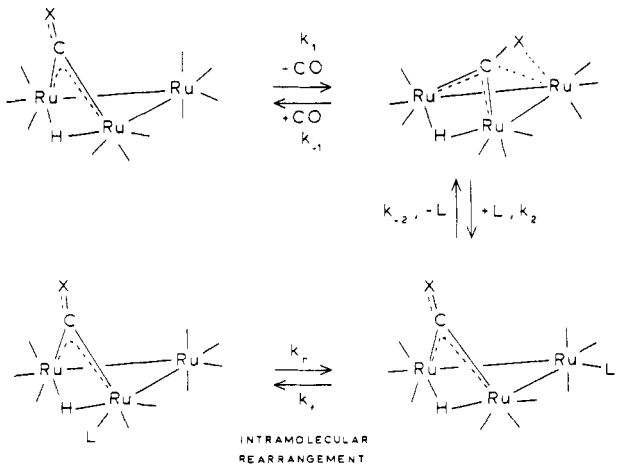
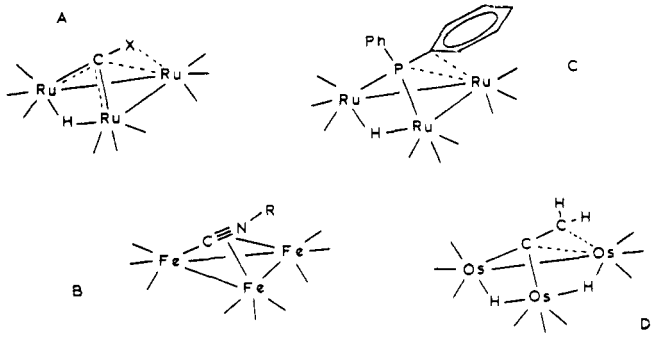


Figure 4. Proposed mechanism for ligand substitution on $HRu_3(\mu\text{-}CX)(CO)_{10}$.

lized by a weakly coordinating ligand. There are precedents for this proposal in other polymetallic systems. Pyrolysis of $Fe_3(CO)_{11}(CNCMe_3)$ generates $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNCMe_3)$ (structure B), a process in which the $CNCMe_3$ ligand is converted from a 2-electron donor to a 6-electron donor.[34] Recently, the "unsaturated" species $Mn_2(CO)_9$, prepared by photolytic CO ejection from $Mn_2(CO)_{10}$, was shown to contain a semibridging CO ligand, which was suggested to be a 4-electron donor.[35] The "unsaturated" cluster $HRu_3(\mu\text{-}PPh_2)(CO)_9$ (structure C) is stabilized by an interaction between a P–C(Ph) bond and the $Ru(CO)_3$ unit.[36] A similar donor interaction is found for $H_2Os_3(\mu_3\text{-}\eta^2\text{-}CCH_2)(CO)_9$ (structure D).[37] Conversion of a di-



bridging, 3-electron donor ligand to a tribridging, 5-electron donor ligand may be responsible for the high lability of $HRu_3(\mu\text{-}SR)(CO)_{10}$[38] and $HRu_3(\mu\text{-}X)(CO)_{10}$ (X = Cl, Br, I);[16] stable decarbonylated clusters $HOs_3(\mu_3\text{-}SEt)(CO)_9$[39] and $HRu_3(\mu_3\text{-}I)(CO)_9$[40] are known.

The mechanism shown in Figure 4 then completely accounts for the kinetics of ligand substitution on $HRu_3(CX)(CO)_{10}$ and substituted derivatives. Reversible dissociation of CO from the nonbridged Ru atom generates the intermediate $HRu_3(CX)(CO)_9$ in which X is weakly coordinated to the nonbridged Ru atom. This intermediate rapidly and reversibly adds donor ligands L to form the n-e isomer $HRu_3(CX)(CO)_9L$, which intramolecularly and reversbily rearranges to the n-e:b-e equilibrium mixture at a rate faster than the rate of dissociation of L. The reverse sequence would apply for replacement of L from $HRu_3(CX)(CO)_9L$ by L′ (including L′ = CO).

Coordination of the X substituent of the intermediate $HRu_3(CX)(CO)_9$ would explain the formation of the nonbridged-equatorial isomer as the kinetic product from addition of L to $HRu_3(CNMe_2)(CO)_9(py)$, since L will occupy the site to which X is coordinated. The activation parameters for ligand substitution imply that the mechansim is primarily CO dissociative and that the transition state must involve substantially more Ru–CO bond breaking than Ru–X bond making. If there is some small degree of bonding for both CO and X to the unique Ru atom in the transition state for CO dissociation from $HRu_3(CX)(CO)_{10}$ (a dissociative interchange type mechanism), then the relative rates of CO dissociation may be explained as due to the relative strengths of the Ru–X interactions on the transition states, $X = O^{1-} >> OMe > NMe_2$. Although NMe_2 should be a better donor than OMe, steric interactions may make this moiety a poorer ligand. We should point out that a number of $HM_3(\mu_3\text{-}CX)(CO)_{10}$ structures (M = Os, X = H[18] or Ph;[19] M = Fe, X = Me[41]) or substituted derivatives ($HRu_3(\mu_3\text{-}COMe)(CO)_8(1,3\text{-}C_6H_8)$[3]) containing $\mu_3\text{-}\eta^1\text{-}CX$ units have been reported; however, for these the CX ligand is acting as a 3-electron neutral donor.

Finally, the unusually large preference of the intermediate $HRu_3(COMe)(CO)_9$ for CO over hydrogen must be explained. As we have previously stated, it seems unlikely that a single, unsaturated intermediate, even if lightly stabilized, should be unselective toward Lewis bases but highly selective for CO over hydrogen. For monometallic species such a large selectivity most likely results from ground-state stabilities of the products rather than transition-state energies leading to those products.[42] A similar argument was originally proposed for this cluster system. If it is assumed that the intermediate has structure A, then there is no obvious reason why hydrogen addition should be slow. Two possibilities which can explain the large preference by $HRu_3(COMe)(CO)_9$ for CO over hydrogen may be presented. One, previously suggested,[5,28] is that there exist two isomeric intermediates $HRu_3(COMe)(CO)_9$, only one of which, the least abundant, adds hydrogen to yield the stable $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ product. Although this still remains a possibility, the results of ligand substitution studies presented here suggest that this explanation is unlikely. The second possibility is that there is only one unsaturated intermediate $HRu_3(COMe)(CO)_9$ but that hydrogen addition to this intermediate does not lead directly to the stable $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ product. If an intramolecular rearrangement is required to convert the kinetic product of hydrogen addition to the thermodynamic product and if hydrogen elimination from the kinetic product occurs at a rate faster than that for the rearrangement, then the unsaturated intermediate can appear to be highly selective for CO over hydrogen because addition of CO leads directly to a stable product.

The generalized mechanism for hydrogenation of $HRu_3(COMe)(CO)_{10}$ given by eq 4–6 will explain the ob-

(34) Bruce, M. I.; Hambley, T. W.; Nicholson, B. K. *J. Chem. Soc., Dalton Trans.* **1983**, 2385.
(35) Dunkin, I. R.; Harter, P.; Shields, C. J. *J. Am. Chem. Soc.* **1984**, *106*, 7248.
(36) MacLaughlin, S. A.; Carty, A. J.; Taylor, N. J. *Can. J. Chem.* **1982**, *60*, 87.
(37) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Chem. Commun.* **1973**, 277.
(38) Keister, J. B.; Baumann, B. E.; Kanter, J. A., unpublished results.
(39) Johnson, B. F. G.; Lewis, J.; Pippard, D.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1978**, 551.
(40) Kampe, C. E.; Boag, N. E.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 1390.
(41) Wong, K. S.; Fehlner, T. P. *J. Am. Chem. Soc.* **1981**, *103*, 966.
(42) Few examples have been established in which competition ratios have been measured between H_2 and CO for an unsaturated intermediate. For $Co(P(OMe)_3)_4^+$, $k_{H_2}/k_{P(OMe)_3}$ is 1.7.[43] On the other hand, $Fe(CO)_5$ does not lose CO below 90 °C,[44] while hydrogen elimination from $H_2Fe(CO)_4$ has a rate constant of 3×10^{-2} s^{-1} at 45°.[45]
(43) Muetterties, E. L.; Watson, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 6978.
(44) Siefert, E. E.; Angelici, R. J. *J. Organomet. Chem.* **1967**, *8*, 374.
(45) Pearson, R. G.; Mauerman, H. *J. Am. Chem. Soc.* **1982**, *104*, 500.

served kinetic behavior. In this mechanism $H_3Ru_3(COMe)(CO)_9$* is an activated isomeric intermediate of unspecified structure. The limiting rate constant for the hydrogenation is k_1, the rate constant for CO dissociation. The limiting rate constant for the reverse reaction, carbonylation of $H_3Ru_3(COMe)(CO)_9$, is given by $k_{-3}k_{-4}/(k_{-3} + k_4)$, assuming that hydrogen elimination is rate determining. Our previous treatments,[5] which assumed no intramolecular rearrangement of $H_3Ru_3(COMe)(CO)_9$ prior to hydrogen elimination, allowed for only one rate constant for hydrogen elimination, equivalent to k_{-3} here. There is no kinetic distinction between these two mechanisms. We previously calculated the competition ratio by multiplying the measured value for K_{eq} by the rate constant for carbonylation of $H_3Ru_3(COMe)(CO)_9$ and then dividing by the rate constant for ligand substitution, k_1. This calculation yields the value of k_3/k_{-1} if there is no rearrangement of $H_3Ru_3(COMe)(CO)_9$ prior to hydrogen loss. However, if the mechanism for hydrogenation is given by eq 4–6, then our calculation yields not the value of k_3/k_{-1} but rather the value of eq 7. If $k_4/(k_{-3} + k_4)$ is much less

$$HRu_3(COMe)(CO)_{10} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HRu_3(COMe)(CO)_9 + CO \quad (4)$$

$$HRu_3(COMe)(CO)_9 + H_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} H_3Ru_3(COMe)(CO)_9^* \quad (5)$$

$$H_3Ru_3(COMe)(CO)_9^* \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} H_3Ru_3(COMe)(CO)_9 \quad (6)$$

$$(K_{eq})(k_1^{-1})\frac{k_{-3}k_{-4}}{(k_{-3} + k_4)} = \frac{k_3k_4}{k_{-1}(k_{-3} + k_4)} \quad (7)$$

than 1, which is the case when hydrogen elimination from $H_3Ru_3(COMe)(CO)_9$* is much faster than the intramolecular rearrangement to the stable product, then the apparent value for the competition ratio between CO and hydrogen will be much greater than 1 even if the actual value of k_{-1}/k_3 is close to 1. This proposal implies that isomerization of $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ to $H_3Ru_3(COMe)(CO)_9$* is the rate-determining step for hydrogen elimination.

Three possibilities for the structure of $H_3Ru_3(COMe)(CO)_9$* can be proposed. First, this intermediate may have one or more terminal hydride ligands, rather than three bridging hydrides present in the ground state. Second, the intermediate may have a μ-COMe ligand, rather than the μ_3-form found in the ground state. Third, the intermediate may contain a seven-coordinate > $Ru(CO)_3H_2$ unit, i.e., two terminal hydrides and a μ-COMe ligand.[46] There is no information from the kinetics which would allow one to distinguish the structure of this intermediate. Because of the complex nature of the first-order rate constant for hydrogen loss, almost any value could be rationalized for the deuterium kinetic isotope effect (measured to be 1.4[5]) or the activation parameters ($\Delta H^{\ddagger}$ = 31.0 kcal; $\Delta S^{\ddagger}$ = +8 eu[5]). However, comparisons to other systems make either possibility seem reasonable. The propensity for hydrogen loss from $H_3Ru_3(CX)(CO)_9$ is found to fall in the order X = O^{1-} > NMe_2 > OMe;[1] this is also the order of decreasing tendency for the CX ligand to be dibridging and suggests that conversion from a μ_3-CX ligand to a μ_2-CX ligand may be important for hydrogen elimination.[1] Also, $H_3M_3(\mu_3\text{-}COMe)(CO)_9$ (M = Ru[5] or Os[28]), for which all hydride ligands are bridging, are very resistant to hydrogen loss, in contrast to $H_2M_3(CO)_{11}$ (M = Ru[47] or Os[21,48]), which each have one bridging and one terminal hydride ligand and which quite readily eliminate hydrogen. Recently Poë and Smith[48] have investigated the kinetics of reversible hydrogenation of $Os_3(CO)_{12}$ to $H_2Os_3(CO)_{11}$ and have found (1) that the unsaturated intermediate $Os_3(CO)_{11}$ is unselective and (2) that hydrogen elimination from $H_2Os_3(CO)_{11}$ occurs at a rate ca. 2000 times faster at 65 °C than CO loss from $Os_3(CO)_{12}$[49] at the same temperature. In contrast, the rate of hydrogen loss from $H_3Os_3(\mu_3\text{-}COMe)(CO)_9$ is slower than the rate of CO loss from $HOs_3(\mu\text{-}COMe)(CO)_{10}$ by a factor of ca. 0.04 and the competition ratio for k_{H_2}/k_{CO} is $<8 \times 10^{-3}$.[28] The value of $\Delta H^{\ddagger}$ for hydrogen loss from $H_3Os_3(\mu_3\text{-}COMe)(CO)_9$ is ca. 15 kcal greater than that for hydrogen loss from $H_2Os_3(CO)_{11}$.[28,48] Vites and Fehlner have estimated that the bridging Fe–H–Fe bond is more stable than a terminal Fe–Fe–H bond by 10–11 kcal/mol in the related $HFe_3(CMe)(CO)_{10}/H_3Fe_3(CMe)(CO)_9$ system.[50] This supports the proposal that conversion of the hydride ligands from bridging to terminal coordination is important for hydrogen elimination. Studies of hydrogen elimination from other related clusters will be required to make more definitive conclusions about the mechanism(s) or reductive elimination of hydrogen from multimetallic complexes.

The structures of the alkyne adducts $HRu_3(CX)(CO)_9$(alkyne) may account for the differing reactivities of these clusters for alkyne–methylidyne coupling.[2] The isomer initially formed by substitution of alkyne for CO on $HRu_3(CX)(CO)_{10}$ should be the nonbridged-equatorial one. However, for alkyne–methylidyne coupling to occur, these ligands must be oriented cis to one another. Since the equilibrium constant for the nonbridged-equatorial to bridged-equatorial interconversion is smaller when X = NMe_2 than for the OMe analogue, this may account for the reluctance of the former to undergo coupling reactions.

The facilitation of CO dissociation from one metal center by ligands of variable donicity on neighboring metal centers may be a quite general phenomenon. Such neighboring group effects will determine both the reactivity of the cluster and the structures of the kinetic products. Systematic investigations of relative rates of ligand dissociation from $HM_3(\mu\text{-}Y)(CO)_{10}$ as a function of the bridging group should provide information about the ability of Y to stabilize the transition state through bond formation to the labile metal center. Such studies are now in progress.

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(46) This was suggested by a reviewer.

(47) Keister, J. B. *J. Organomet. Chem.* **1980**, *190*, C36.
(48) Poë, A. J.; Smith, R., private communicaton.
(49) Shojaie, A.; Atwood, J. D. *Organometallics* **1985**, *4*, 187.
(50) Vites, J.; Fehlner, T. P. *Organometallics* **1984**, *3*, 491.
(51) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)