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SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION AND CRYSTAL AND MOLECULAR STRUCTURE OF $HRu_3(OCN(CH_3)_2)(CO)_{10}$ *

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Summary

Dimethylamine reacts with $Ru_3(CO)_{12}$ to produce the η^2-hydrido-η^2-formamido cluster complex $HRu_3(OCN(CH_3)_2)(CO)_{10}$ (I). This formulation is consistent with spectroscopic features such as the absence of ν(NH) in the infrared, the presence in the Raman of ν(Ru—H—Ru) at 1400 cm^{-1} (ν(Ru—D—Ru) at 990 cm^{-1}) and indication in the ^1H NMR of diastereotopic methyl groups bonded to the nitrogen atom. Since these data could not lead to an unequivocal structure assignment a single crystal X-ray study at 115 K was undertaken. The complex crystallizes in the triclinic space group, $P\bar{1}$ with cell dimensions; a 7.299(33) Å, b 9.5037(40) Å, c 13.7454(57) Å, α 91.876(34)°, β 96.387(34)°, γ 95.341(34)° and $Z = 2$. The structure was solved by a combination of Patterson and Fourier techniques and refined by full matrix least squares to a final $R = 0.054$ and $R_w = 0.074$ for 3074 unique reflections. The three ruthenium atoms define a triangle of unequal sides with both the hydride and formamido groups bridging the longest edge; the formamido group is coordinated through the carbon and oxygen atoms. The edge of the ruthenium triangle bridged both by the hydrogen atom and the formamido group is 2.8755(15) Å; the other two edges of the ruthenium triangle are observed to be 2.8319(15) and 2.8577(14) Å, respectively. In the formamido group the distances C—O 1.287(9) Å and C—N 1.340(10) Å reflect partial double bond character in each bond consistent with observation of two chemically distinct methyl groups on the dinitrogen atom. The hydrogen atom bridging one edge of the ruthenium triangle is asymmetrically positioned at 1.73(9) Å from the ruthenium atom bonded to the oxygen atom and 1.91(9) Å from the ruthenium atom bonded to the carbon atom of the carboxamido group.

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* Dedicated to Professor Helmut Behrens on the occasion of his 65th birthday on May 30th, 1980.

Introduction

Earlier work in this laboratory has led to the isolation of a series of complexes illustrating the stepwise reduction of acetonitrile to a primary amine coordinated on the face of a triiron cluster [1a]. In attempts to extend this to the congeners of iron, we were prompted to explore the reaction of $Ru_3(CO)_{12}$ with various amines containing hydrogen atoms on the carbon, i.e. aliphatic primary or secondary amines [1b]. The reaction between $Ru_3(CO)_{12}$ and aniline had been studied in refluxing benzene [2]; two mol of CO are evolved with the formation of the amido-bridged complex, $HRu_3(NHPh)(CO)_{10}$. By contrast, in the reaction of $Ru_3(CO)_{12}$ with aliphatic primary or secondary amines with excess amine as its own solvent or in other polar solvents, we discovered an extremely facile reaction which takes place beginning around —30° C accompanied by the evolution of only one mol of CO. The isolation and characterization of the product in the reaction of dimethylamine and $Ru_3(CO)_{12}$ is the subject of this study.

Results

Synthesis

Dimethylamine and $Ru_3(CO)_{12}$ are combined at —78° C. Upon warming (—30 to 0° C) a blood red solution is produced accompanied by gas evolution. Volumetric analysis of the gas within the first 15 minutes reveals this to be one mol equivalent (within 15%) and the mass spectrometric analysis of this gas indicates CO exclusively. With passing time, the system slowly evolves more CO, an observation which we did not pursue further for the amine system *. After ten minutes the blood red color of the solution is transformed to orange and stirring is continued for ten minutes more. Excess amine is then evaporated by warming to room temperature. An alternative procedure is to bubble the amine through an ether solution of $Ru_3(CO)_{12}$ for several minutes until all the ruthenium carbonyl is dissolved. The solvent and excess amine is then removed. Chromatography of this residue results in three bands; the first is identified by its carbonyl IR as unreacted $Ru_3(CO)_{12}$ (about 10 to 20 percent of the starting material). The second band represents the principal product of this investigation. This was identified by spectroscopic and structural studies as $HRu_3(OCN(CH_3)_2)(CO)_{10}$ (I) and is obtained in about 65% yield. Spectroscopic data are summarized in Tables 1—3 and discussed in the next section. The crystallographic study is presented immediately after.

Recrystallization of I from hexane/dichloromethane affords moderately air stable red-orange crystals. Material in the third band elutes from the column with great difficulty. It was not identified due to its low volatility and solubility; a full-range IR spectrum was taken in KBr pellet; this spectrum is similar to that of I but with the bands of dimethylamine superimposed. We believe this to be a dimethylamine substituted derivative of I *.

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* From further studies of I with phosphine ligand [1b] we know an extremely facile substitution reaction can take place and the further evolution of CO from these complexes in neat amine most likely represents such a substitution.

TABLE 1

CARBONYL STRETCHING ABSORPTIONS FOR I AND RELATED COMPOUNDS

Complex	Frequencies (cm^{-1}) [a]	Reference
$HRu_3(OCN(CH_3)_2)(CO)_{10}$ (I)	2101m, 2064s, 2051s, 2023w, 2016s, 1999m, 1993vw, 1982w	This work
$Ru_3(CO)_{11}PPh_3$	2097m, 2046s, 2030(sh), 2023(sh), 2014s, 1996(sh), 1986m, 1972(sh), 1960(sh)	3
$HRu_3(N(H)Ph)(CO)_{10}$	2101m, 2064s, 2051s, 2026s, 2011s, 2003m, 1996vw, 1980w	2

[a] Cyclohexane solution.

TABLE 2

OTHER SPECTROSCOPIC DATA FOR $HRu_3(OCN(CH_3)_3)(CO)_{10}$

IR (cm^{-1}) [a] (for the O—CN$(CH_3)_2$ group)	1514s, 1460m, 1412m, 1391s(br), 1379(sh), 1357(sh), 1252m
RAMAN [b] (cm^{-1})	ν(Ru—H—Ru) 1400; ν(Ru—D—Ru) 990
^1H NMR [c] (δ, ppm)	2.52 (3H); 2.31 (3H); —13.78 (1H)
^{13}C NMR [d] (ppm rel. TMS)	206.6(0.6) a; 205.1(0.5) b; 203.3(0.8) c; 200.5(2) d; 195.9(1) ($J(^{13}C$—H)6.3 Hz) e; 194.3(1) ($J(^{13}C$—H)-8.4 Hz) f; 192.0(1.8) g; 189.7(1) h; 184.3(1) i

[a] KBr pellet. [b] Microcrystalline powder. [c] C_6D_6 solution (relative protons in parentheses). [d] $CDCl_3$ solution (relative intensity and coupling constant, if any, in parentheses) letter identifies resonance for discussion in text.

TABLE 3

OBSERVED AND CALCULATED SPECTRA FOR $HRu_3(OCN(CH_3)_2)(CO)_{10}$ (R = 6.8%)

Mass	Calculated	Observed [a]	Difference	Measured
641	0.01	0.0	—0.01	0
642	0.00	0.0	0.0	0
643	0.01	0.0	—0.01	0
644	0.10	0.0	—0.10	0
645	0.12	0.0	—0.12	0
646	0.22	0.0	—0.22	0
647	0.57	0.0	—0.57	0
648	0.63	0.0	—0.63	0
649	1.32	1.79	0.47	50
650	2.26	2.14	—0.11	60
651	2.79	3.22	0.43	90
652	4.39	4.47	0.08	125
653	6.10	5.93	—0.16	166
654	6.76	6.90	0.14	193
655	9.81	9.76	—0.06	273
656	10.40	10.54	0.14	295
657	10.98	11.26	0.28	315
658	11.83	11.69	—0.15	327
659	9.81	10.08	0.27	282
660	7.75	8.40	0.65	235
661	7.03	7.22	0.19	202
662	2.61	3.08	0.46	86
663	3.20	3.54	0.34	99
664	0.50	0.0	—0.50	0
665	0.74	0.0	—0.64	0
666	0.09	0.0	—0.09	0
667	0.02	0.0	—0.02	0

[a] Normalized to 100.0 total intensity.

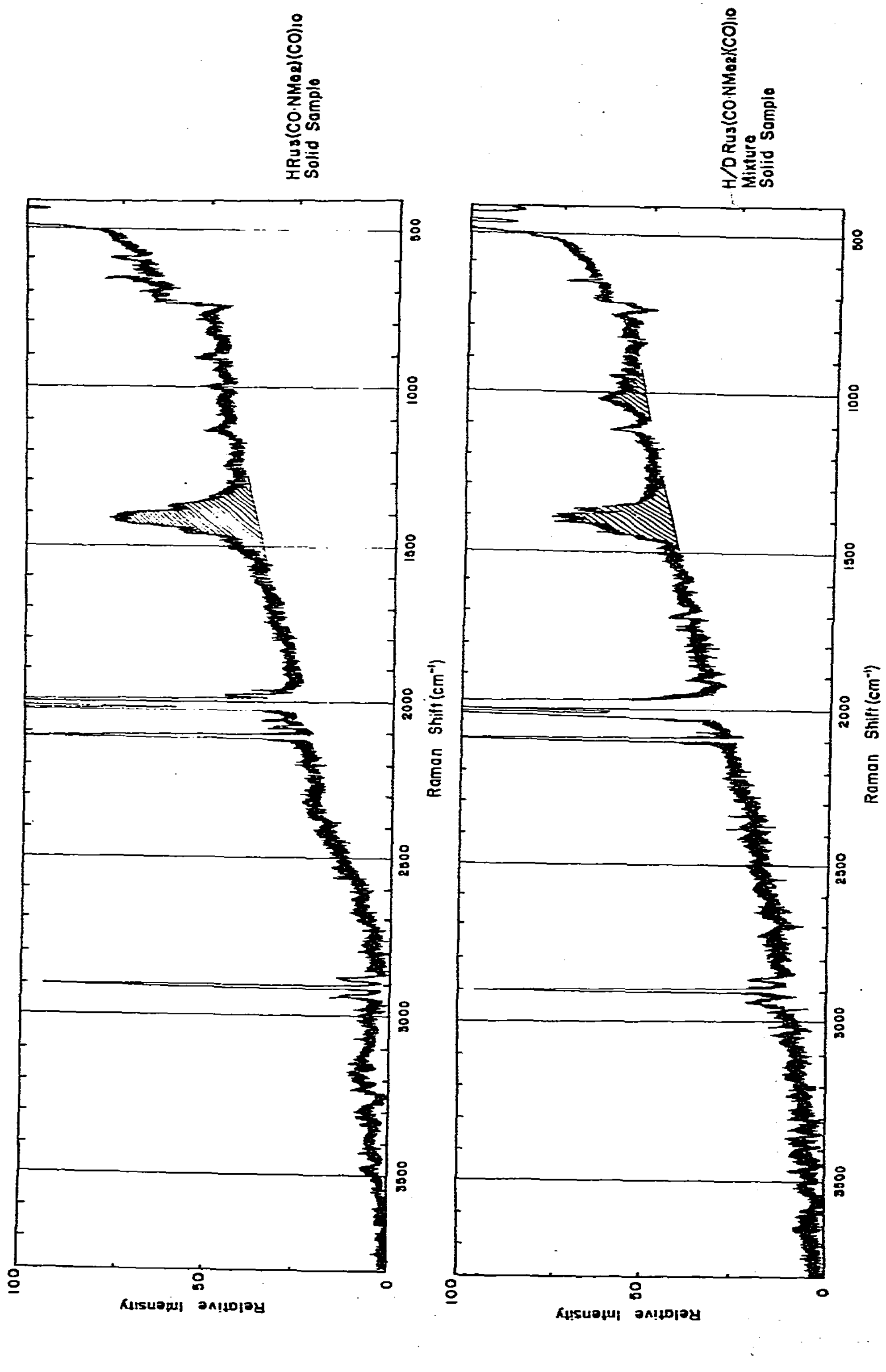


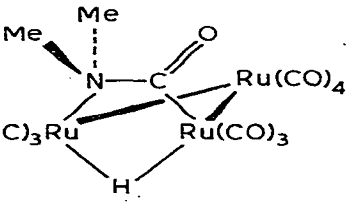
Fig. 1. Raman Spectra of $HRu_3(OCN(CH_3)_2)(CO)_{10}$ and $H/DRu_3(OCN(CH_3)_2)(CO)_{10}$, 4000 to 500 cm^{-1} region.

Spectroscopic characterization of I

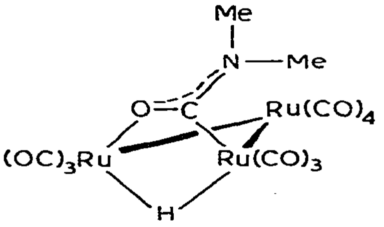
The mass spectrum of the product shows a parent multiplet centered around *m/e* 665. The calculated and observed intensities for the parent ion of I are listed in Table 3. These data are consistent with a trinuclear complex of overall formulation $Ru_3(CO)_{11}NH(CH_3)_2$. An infrared spectrum of the carbonyl stretching region is given in Table 1. This is not consistent with known examples of monosubstituted trimetal dodecacarbonyl complexes as may be compared with the carbonyl stretching frequencies in $Ru_3(CO)_{11}PPh_3$ [3] listed in Table 1. Greater similarity is seen between the spectrum of I and that of $HRu_3(NHPh)(CO)_{10}$, also listed in Table 1. The three bands at 2101, 2064, 2051 cm^{-1} are virtually identical in these compounds while the other five bands differ in frequency by a maximum of only 5 cm^{-1}. This data is consistent with formulation of the product as an edge bridged decacarbonyl complex suggesting that the amine and one carbonyl group had combined into a formamido group.

Precedent for the formation of formamido groups on metal complexes is obtained from the reactions of primary and secondary amines with mononuclear complexes [4—8]. This is supported by a very intense peak at *m/e* 73 in the lower mass range of the mass spectrum of I corresponding to the $HC(O)N(CH_3)_2^+$ fragment. The structure containing such a unit is confirmed by X-ray crystallographic means (see below).

The chemical shifts of the resonances in the ^1H NMR spectrum of I are given in Table 1. The presence of two nonequivalent methyl groups is indicated. This does not differentiate between two possible modes of bonding, A or B *. The nitrogen coordinated isomer B would give rise to two nonequivalent methyl groups due to different methyl environments on the chiral nitrogen atom. Isomer A would also exhibit two nonequivalent methyl resonances since partial double bond character in the C—N bond would lead to hindered rotation about that bond [9]. For the free ligand, *N,N*-dimethylformamide, two *N*-methyl peaks are observed up to 124°C [10].



(A)



(B)

Since the deuterated analog, $DRu_3(OCN(CH_3)_2)(CO)_{10}$ could easily be obtained by reaction of $Ru_3(CO)_{12}$ with $DN(CH_3)_2$, location and assignment of the hydride band in the Raman spectrum was undertaken. Due to the incomplete deuteration of the amine, a mixture containing both $DRu_3(OCN(CH_3)_2(CO)_{10}$ and $HRu_3(OCN(CH_3)_2)(CO)_{10}$ is obtained. Incorporation of deuterium is enough however, to observe the metal-deuterium frequency. The Raman spectra of I and the partially deuterated sample are shown in Fig. 1. The broad

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* The conventional vector between metal atoms of the doubly-bridged edge of the metal triangle has been omitted in these and subsequent structures in this work because we believe that this representation better reflects the octahedral coordination around the metal atoms in question.

band at 1400 cm^{-1} in the hydrido complex is found to shift to about 990 cm^{-1} upon deuteration in a ratio $\nu(H)/\nu(D)$ 1.414 close to that expected for the shift in frequency upon deuterium substitution. The position of the band falls within the broad range expected for a bridging hydride mode, 1600 to 900 cm^{-1} [11].

The infrared absorptions associated with the formamido group listed in Table 2 are not at all straightforward to assign. In the first place the C—O stretching mode has been shifted through coordination to the metal from 1850 cm^{-1} where it is observed in the free amides [12] directly into the region where the other amide frequencies (usually three in number) are expected [13]. Due to the rather complicated nature of this region, a separate study is underway to assist in the assignment of the bands [1b].

The ^{13}C NMR data for I are listed in Table 2. The room temperature spectrum indicates a relatively rigid structure for the molecule. The large number of ^{13}C signals in the carbonyl region of the spectrum is expected since the presence of the formamido group introduces an element of asymmetry into the molecule. Complete assignment of the individual peaks is not possible but some information can be obtained.

Fractional values for the relative intensities of several of the carbonyl carbons are indicative of the fact that the room temperature spectrum is not the limiting spectrum. A polytopal rearrangement of the carbonyl groups on the isolated $Ru(CO)_4$ unit may be anticipated at room temperature similar to what has been observed in the structurally related derivative $HRu_3(COCH_3)(CO)_{10}$ (II) [14]. The resonances with the fractional relative intensities in I, namely a, b, and g may thus be assigned to the $Ru(CO)_4$ unit with closely comparable chemical shifts: in II (ppm) 203.7, 202.8, 194.7, 193.9 (limiting low temperature spectrum); in I, (ppm) 205.1, 203.1, 192.0 (room temperature).

In the proton decoupled spectrum of I, $^1H—^{13}C$ splitting is observed in two of the signals, e and f. This parallels coupling observed in two of the signals of II, i.e. 195.9 ppm, $J(^1H—^{13}C)$ 5.2 Hz and 195.3 ppm, $J(^1H—^{13}C)$ 8.4 Hz [14]. Apparently the carbon atom of only one of the three carbonyls on each of the two $Ru(CO)_3$ groups adjacent to the hydrogen-bridged edge are sufficiently coupled to the hydrogen atom to show splitting. The similarity of this feature in I and II suggests similarity in the structural environment of the bridging hydrogen atom, as confirmed in the structure study below *.

Resonance c in I at 203.3 ppm appears somewhat broadened in the proton coupled spectrum and is thus tentatively assigned to the formamido group carbon atom; we anticipate some broadening due either to the quadrupole interaction with the nitrogen atom or to weak coupling to the hydrogen atoms of the methyl groups on nitrogen. Although resonance c falls within the range expected for carbenoid carbon atoms [15,16] structural data (discussed below) does not favor a significant participation of such a bonding representation in the C(formamido) to Ru bond.

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* The C(carbonyl)—Ru—H angles in II are observed as (deg): 85.3, 93.6 and 171.2 (on Ru(1)) and 87.2, 88.5 and 174.7 (on Ru(2)) [14]. In the present study we find the values (deg): 75.0, 99.0 and 168.2 (on Ru(1)) and 86.6, 90.4 and 173.1 (on Ru(2)), see Table 8, below. Due to the greater magnitude of coupling of substituents *trans* to hydrogen in hydrido complexes [11] it is generally accepted that the carbonyl group at the angle closest to 180° to the bridging hydrogen atom is the one responsible for the $^{13}C—H$ coupling observed.

Since none of the spectroscopic data could lead unequivocally to a structure assignment, an X-ray study of a single crystal of I was undertaken.

Experimental

Synthesis

Solvents and reagents were commercial reagent grade and were used without further purification unless otherwise noted. $Ru_3(CO)_{12}$ was purchased from Strem Chemical Co.. Reactions and handling of the compounds were all done under nitrogen using Schlenkware techniques though most of the compounds have since been determined to be reasonably stable to air. As solids they have been stored in air at room temperature for several months with only small amounts of decomposition observed. Chromatographic separation on Silica Gel 60 (70 to 230 mesh) 1 in. × 12 in. column was done in air.

Reaction of $Ru_3(CO)_{12}$ with $HN(CH_3)_2$

Method 1. Triruthenium dodecacarbonyl (0.120 g, 0.188 mol) was ground to a fine powder and placed in a Schlenk flask. After evacuation, an excess of $HN(CH_3)_2$ was condensed into the flask at −78°C. Upon warming (−30 to 0°C) the solution turned blood red in color with evolution of gas. After several minutes of vigorous stirring the red solution turned to a final orange color. Stirring was continued for 10 minutes. Evaporation of the amine led to a red-brown oil which was extracted several times with 10 ml aliquots of acetone. The acetone solutions were combined, concentrated and chromatographed to give three bands. The first was eluted with hexane and proved to be $Ru_3(CO)_{12}$. Band 2 was eluted with 10% dichloromethane in hexane and identified as the title compound, I; the third band eluted very slowly with 50% dichloromethane/acetone. The contents of this band were not characterized beyond full range IR due to low solubility and low volatility in the mass spectrometer. Yields of I by this method were variable and depended on the reaction time. Very long reaction time led to very low yields of both I and the materials in band 3 with an increase in the amount of decomposition product (i.e. a brown uncharacterizable tar). Recrystallization from hexane/dichloromethane produced dark red crystals; yield: 0.066 g. Mass spectrometric data and a crystallographic study (described below) indicated a formula of $HRu_3(OCN(CH_3)_2)(CO)_{10}$ for I, representing 0.096 mmol and a yield of 52% based on $Ru_3(CO)_{12}$.

Method 2. Triruthenium dodecacarbonyl (0.190 g, 0.298 mmol) was suspended in diethyl ether. Dimethylamine was bubbled through the solution until all the $Ru_3(CO)_{12}$ had dissolved. The resulting red solution was stirred under an atmosphere of amine for 10 minutes, whereupon the solvent and excess amine were then evaporated. The residue was chromatographed and the similar product distribution as in Method 1 was obtained. Less decomposition however was observed by this method and the yields were usually higher. I was recrystallized from hexane/dichloromethane and yielded 0.144 g of dark red crystals. Yield: 0.166 mmol, 56% based on $Ru_3(CO)_{12}$.

Preparation of $D/HRu_3(OCN(CH_3)_2)(CO)_{10}$

Triruthenium dodecacarbonyl (0.216 g, 0.339 mmol) was stirred in DN-

$(CH_3)_2$ (prepared by standard literature methods [17]). Chromatography and recrystallization afforded 0.104 g (0.152 mmol) of partially deuterated I. Yield 45%. Raman studies showed that complete deuteration of I was not obtained. The amount of deuterium incorporated was sufficient for the Raman studies.

Reaction of I with D_2O. An alternative route to the deuterated analog, $DRu_3(OCN(CH_3)_2)(CO)_{10}$ was attempted in order to increase the amount of deuterium incorporated into the cluster for the Raman studies. I was stirred in diethyl ether that had been saturated with D_2O and distilled. Several drops of D_2O were then added to the $Ru_3(CO)_{12}$/ether solution (0.119 g, 0.188 mmol) and the solution was stirred for 1 h at room temperature. A Raman spectrum of the resulting crystals showed no observable incorporation of the deuterium.

Preparation of ^{13}C enriched samples of I. 0.397 g (0.621 mmol) of $Ru_3(CO)_{12}$ were suspended in 10 ml of THF and sealed in a thick-walled glass tube under 500 mmHg ^{13}CO. The tube was then heated at 80°C for 10 days and the

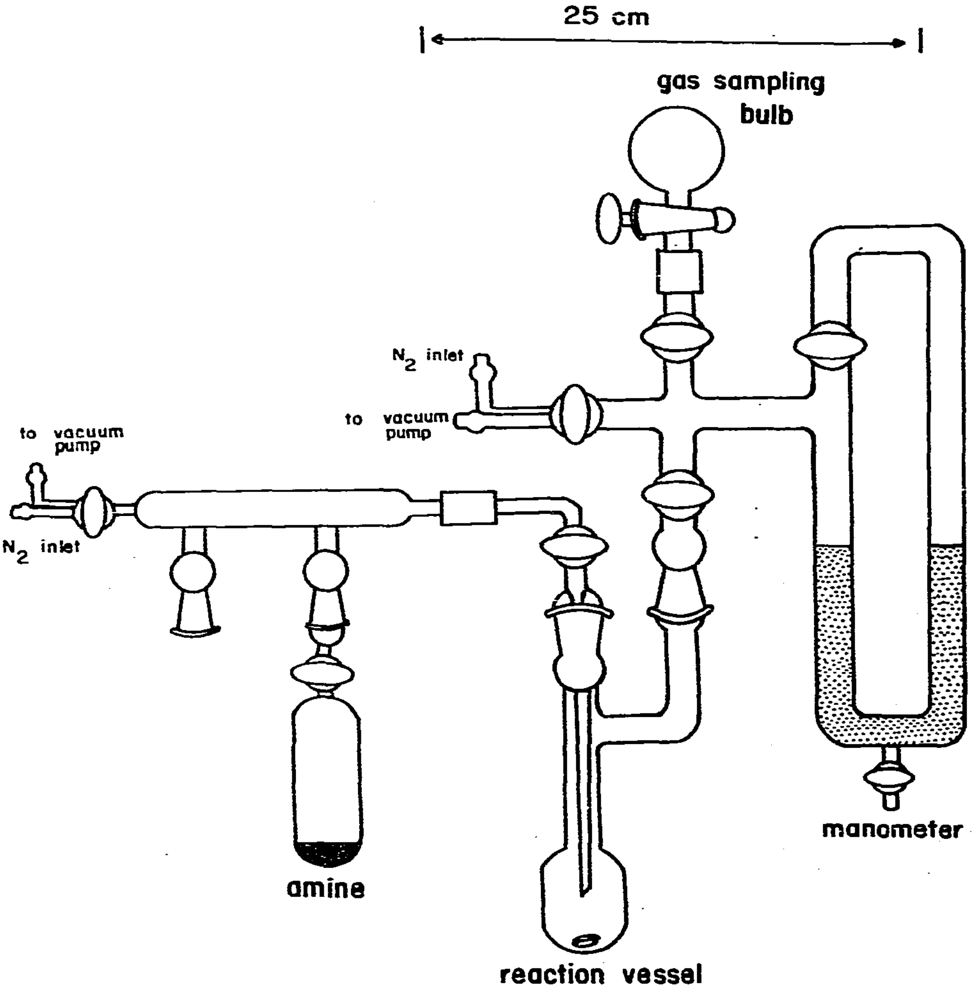

Fig. 2. Gas sampling apparatus.

resulting enriched sample of $Ru_3(CO)_{12}$ used to prepared 0.213 g I by method A. Yield: 0.310 mmol, 50% based on initial $Ru_3(CO)_{12}$ (20% enriched).

Gas collection and analysis

The apparatus used to collect samples of gas evolved from the reaction between $Ru_3(CO)_{12}$ and amine is shown in Fig. 2. $Ru_3(CO)_{12}$ was sublimed under high vacuum at 67° C for 36 h before using.

General procedure. About 100 mg of $Ru_3(CO)_{12}$ was placed in the bottom of the reaction vessel. 1.5 ml of amine (previously dried over sodium) was condensed into the flask. The reaction flask, sealed off from the rest of the vacuum line was warmed to room temperature with constant stirring. After 10 minutes the flask was cooled to —78° C and gas evolved from the reaction was collected. The procedure was repeated after 2 h and 20 h. The gas was analyzed by mass spectrometry and proved to be CO for each sample collected.

Spectroscopic studies

Vibrational spectroscopy

Carbonyl infrared spectra were recorded on a Beckman IR-4 spectrometer with LiF cells and were calibrated against a cyclohexane reference at 2138.5 cm^{-1}. Full range infrared spectra were recorded on Perkin—Elmer 521 spectrometer in C_2Cl_4 solution using 0.5 mm NaCl cells or as KBr pellets and calibrated against a polystyrene reference at 1028 cm^{-1}. CS_2 was found to be unacceptable as a solvent since the compounds began to decomposing within an hour after mixing even under N_2.

The Raman spectra were taken on a Cary Model 81 Raman Spectrometer equipped with a Spectra-Physics laser. Scan time was set at 20 cm^{-1} per minute. Slit width was set at 10 cm^{-1} and path length at 10 cm. Double beam optics were used and only solid samples were run. The 400 to 3000 cm^{-1} region of the spectrum was scanned. A sloping base line was a persistent problem partially solved by recrystallizing and regrinding the sample. Decomposition due to sample absorption was not observed.

NMR spectroscopy

^{13}C and ^{1}H NMR were recorded on a Bruker 200 MHz Fourier Transform Spectrometer at 298 K and calibrated against internal standards. ^{1}H chemical shifts were measured relative to TMS ($\delta = 0$). ^{13}C chemical shifts were measured relative to the $DCCl_3$ signal and related to the standard, TMS, by: $\delta = \delta(\text{obs}) + 76.9$.

Mass spectrometry

All mass spectra were obtained on an AE1-MS9 spectrometer using ionizing voltage of 70 eV and probe temperatures of 100 to 150° C, by Dr. K. Fang of this department. Calculated intensities for the mass spectra were obtained from the computer program MASPAN written by M.A. Andrews [18,19].

X-ray study

Collection and reduction of data. Red-orange crystals of $HRu_3(OCN(CH_3)_2)(CO)_{10}$ were grown from hexane/dichloromethane at 0° C over a period of

TABLE 4

CRYSTAL DATA FOR $HRu_3(OCN(CH_3)_2)(CO)_{10}$

Space group: $P\bar{1}$	
Temperature: 115 K	
Z 2	
a 7.2991(33) Å [a]	α 91.876(34)°
b 9.5037(40) Å	β 96.387(34)°
c 13.7454(57) Å	γ 95.341(34)°
V 942.6(7)	
Based on Mo-K_α 0.71069 Å	

[a] The numbers given in parenthesis here and in succeeding tables are the estimated standard deviations in the least significant digits.

several days. These were found to be both air and X-ray stable. A crystal of irregular dimensions determined suitable for intensity measurements was mounted on a Syntex P$\bar{1}$ automated diffractomator with scintillation counter and graphite monochrometer. Crystallographic data was obtained at 115 K using a device constructed by Dr. C.E. Strouse [20]. Fifteen high angle reflections were used as input to the automatic centering, auto-indexing and least-squares routines of the instrument and a set of lattice parameters obtained; the data are listed in Table 4.

Intensity data were collected using the $\theta/2\theta$ scan technique with a scan rate of 2° min^{-1}. The total background count time was equal to the scan time. Intensities for three standard reflections, (214), (30$\bar{4}$) and (2$\bar{1}$5) were monitored after every 97 reflections; no significant changes were observed. 3074 reflections were considered observed satisfying the requirement $I \geqslant 3\sigma(I)$; these were used in the structural refinement. 280 reflections were considered unobserved.

Solution and refinement of the structure

Programs used during the structural analysis includes the data reduction program PIBAR for the syntex diffractometer by Bell and Murphy; JBPATT, JBOUR and PKLIST, modified versions of Fourier Programs by Busing, Martin and Levy for full matrix least-squares and error analysis, ORTEP by Johnson for structural plots and PUBLIST by Hoel for structure factor table listing. All calculations were performed on the University of California (Los Angeles) Campus Computing Network's IBM 360/91. Atomic scattering factors for the non-hydrogen atoms were taken from the standard tables [21]. Hydrogen scattering factors were those of Stewart et al. [22].

The atomic coordinates for the three ruthenium atoms were obtained from a three dimensional Patterson map. A Fourier summation based on the three ruthenium atom positions revealed the positions of the remaining nonhydrogen atoms. Refinement was carried out by use of full matrix least-squares procedures. The quantity minimized was $\Sigma w(|F_0| - |F_c|)^2$ where $w = 1/\sigma(F_0)^2$ and $|F_0|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively. The agreement indices for the F_0 refinement are $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ and $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma wF_0]^{1/2}$ and the goodness of fit (GOF) was given by: GOF = $[\Sigma w(|F_0| - |F_c|)^2/(N_0 - N_v)]^{1/2}$ where N_0 is the number of observations and N_v is the number of variables. After several cycles of least squares refinement with all atoms assigned isotropic thermal parameters the discrepancy factors were $R_f = 0.088$ and $R_w = 0.144$. No anomalous dispersion correction was applied. All non-hydrogen atoms except for O(31) were refined with anisotropic thermal parameters; those for O(31) caused this atom to appear nonpositive definite and O(31) was therefore refined isotropically for the remaining least squares cycles. Careful examination of the difference map at that point revealed the positions of the methyl hydrogens and the hydride. On these maps several peaks were prominent but appeared close to the ruthenium atoms (0.6 to 0.8 Å) and were not chemically meaningful. The hydrogens were included in the least-squares refinement with isotropic temperature factors of 2.00. These were not refined. In the final least-squares cycle all atoms were refined with anisotropic temperature factors except the hydrogens and O(31). The final $R_f = 0.054$ and $R_w = 0.074$; GOF = 2.8 ($N_0 = 3074$, $N_v = 310$).

TABLE 5

ATOMIC COORDINATES FOR $HRu_3(OCN(CH_3)_2)(CO)_{10}$

Atom	x	y	z
Ru(1)	0.2848(1)	0.1545(1)	0.1605(0)
Ru(2)	0.3532(1)	0.4176(1)	0.2739(0)
Ru(3)	9.5003(1)	0.1675(1)	0.3456(0)
C	0.5197(10)	0.4056(8)	0.1595(6)
N	0.6549(9)	0.4980(7)	0.1345(5)
Me(1)	0.7189(13)	0.6311(9)	0.1886(8)
Me(2)	0.7606(13)	0.4662(10)	0.0531(7)
O	0.4817(7)	0.2937(5)	0.1028(4)
C(21)	0.2648(11)	0.5838(8)	0.2182(6)
C(22)	0.5397(11)	0.5079(8)	0.3682(6)
C(23)	0.1594(11)	0.4086(8)	0.3629(6)
C(31)	0.5419(12)	−0.0260(8)	0.3453(6)
C(32)	0.6998(11)	0.2133(8)	0.2666(6)
C(33)	0.2745(12)	0.1385(8)	0.4095(6)
C(34)	0.6496(12)	0.2340(8)	0.4674(6)
C(11)	0.1123(11)	0.0340(8)	0.2180(6)
C(12)	0.1163(12)	0.1645(8)	0.0414(6)
C(13)	0.4107(12)	−0.0023(9)	0.1221(7)
O(21)	0.2178(9)	0.6844(6)	0.1882(5)
O(22)	0.6473(8)	0.5633(6)	0.4266(5)
O(23)	0.0374(8)	0.4118(6)	0.4064(5)
O(31)	0.5696(9)	−0.1436(7)	0.3455(5)
O(32)	0.8221(8)	0.2349(7)	0.2239(5)
O(33)	0.1492(9)	0.1174(7)	0.4499(5)
O(34)	0.7415(9)	0.2670(6)	0.5375(5)
O(11)	0.0041(8)	−0.0418(6)	0.2485(5)
O(12)	0.0093(9)	0.1647(6)	−0.0226(5)
O(13)	0.4859(9)	−0.0939(6)	0.0965(5)
H(11)	0.6580(133)	0.6615(101)	0.2343(72)
H(12)	0.8332(142)	0.6406(101)	0.2169(71)
H(13)	0.7915(125)	0.7122(100)	0.1486(66)
H(21)	0.8946(127)	0.4542(96)	0.0922(66)
H(22)	0.7333(140)	0.4095(112)	0.0170(74)
H(23)	0.7601(127)	0.5301(107)	0.0085(72)
H	0.1867(122)	0.3123(94)	0.1741(64)

TABLE 6

THERMAL PARAMETERS FOR $HRu_3(OCN(CH_3)_2)(CO)_{10}$ [a]

Atom	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
Ru(1)	78(1)	16(1)	26(0)	4(1)	7(1)	−1(0)
Ru(2)	67(1)	15(1)	26(0)	8(1)	8(1)	0(0)
Ru(3)	82(1)	18(1)	27(0)	11(1)	6(1)	1(0)
C	69(14)	16(8)	20(4)	13(9)	3(6)	2(5)
Me(1)	88(18)	28(10)	43(6)	−9(10)	23(8)	−13(6)
Me(2)	107(19)	36(10)	32(5)	1(11)	24(8)	0(6)
C(21)	57(15)	19(9)	38(5)	12(9)	6(7)	−7(5)
C(22)	70(15)	14(8)	25(5)	8(9)	15(7)	2(5)
C(23)	76(16)	30(9)	20(4)	7(9)	3(7)	−4(5)
C(31)	123(18)	26(9)	14(4)	17(10)	8(7)	5(5)
C(32)	71(16)	11(8)	33(5)	11(9)	0(7)	1(5)
C(33)	101(17)	20(9)	27(5)	3(10)	3(7)	1(5)
C(34)	92(16)	21(9)	29(5)	14(10)	−2(8)	2(5)
C(11)	94(16)	13(8)	30(5)	14(10)	4(7)	−3(5)
C(12)	102(17)	12(8)	25(5)	−7(9)	5(8)	−1(5)
C(13)	90(17)	29(9)	36(5)	−4(10)	6(7)	0(6)
O	81(11)	18(6)	21(3)	3(6)	11(5)	−1(3)
O(21)	122(13)	30(7)	45(4)	25(8)	9(6)	9(4)
O(22)	112(13)	28(6)	31(4)	3(7)	0(6)	−1(4)
O(23)	84(12)	50(7)	35(4)	0(7)	15(6)	−8(4)
O(32)	81(12)	59(8)	37(4)	15(8)	16(6)	8(4)
O(33)	122(14)	68(8)	38(4)	0(9)	26(6)	4(5)
O(34)	130(14)	42(7)	33(4)	−3(8)	7(6)	−1(4)
O(11)	112(13)	35(7)	40(4)	−8(8)	21(6)	2(4)
O(12)	159(15)	30(7)	31(4)	−1(8)	−14(6)	4(4)
O(13)	165(15)	35(7)	41(4)	41(8)	25(6)	0(4)
N	76(13)	13(7)	26(4)	7(8)	8(6)	1(4)
O(31)	2.45 [b]					

[a] Anisotropic temperature factors are given for the form $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$ followed in parentheses by the estimated standard deviation. [b] Isotropic temperature factor B in $Å^2$.

The final atomic positional and thermal parameters are given in Tables 5 and 6. A table of F_0 and F_c [1b] is available upon request.

Description of the structure and discussion

The $HRu_3(OCN(CH_3)_2)(CO)_{10}$ molecule is shown in Fig. 3 indicating the numbering system used for labeling the atoms. Interatomic distances and angles along with their estimated standard deviations are listed in Tables 7 and 8. The molecule consists of a triangular array of ruthenium atoms with edges of unequal length, 2.8755(15), 2.8319(15), and 2.8577(14) Å, but are within the range of reported ruthenium—ruthenium distances [14,23—26]. The variations in length are similar to those found in $HOs_3[OCC(CHMe)CHCHCEt](CO)_8$ [27], which also contains oxygen and carbon atoms coordinated to two metal atoms. The inequality in length is presumed to arise from the difference in electronegativities of the coordinated carbon relative to the oxygen.

Both the fomamido group and the hydrogen atom bridge the longest edge. One may expect the hydrogen to be bridging along the longest edge except in cases where other bridging groups may exert a counteracting influence [28]. In

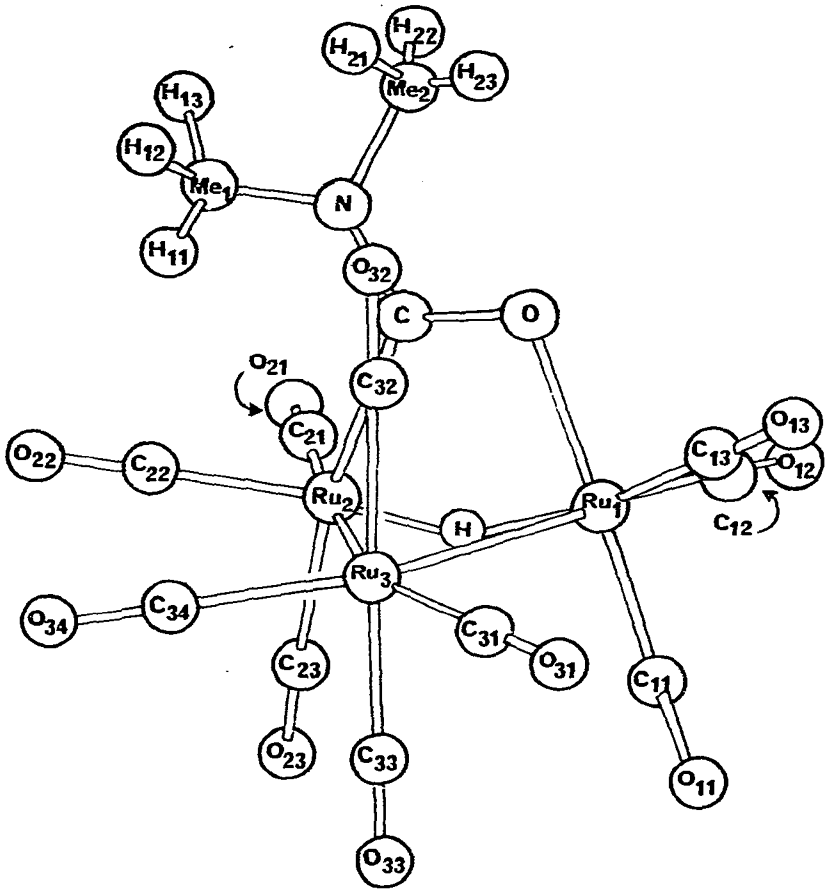

Fig. 3. Vertical projection of $HRu_3(OCN(CH_3)_2)(CO)_{10}$ showing the numbering scheme for the atoms *.

this case however it is obvious the formamido group is compatible with the longer metal—metal separation.

The unique ruthenium atom is linked to four terminal carbonyl ligands with OC—Ru—CO angles distorted somewhat from the octahedral orientation found in the $Ru(CO)_4$ units of $Ru_3(CO)_{12}$ [26]. The remaining two ruthenium atoms each contain three terminal carbonyls and are bridged by both the hydride and formamido group. These carbonyls is form a slightly distorted octahedron with the Ru(3), H and C atoms and the Ru(3), H and O atoms. The bridging hydrogen atom lies below the triruthenium plane, similar to other cluster complexes containing hydrogen atoms which bridge an edge also bridged by another group [25,27—29]. The Ru(1)—H distance (1.73(9) Å) is shorter than the Ru(2)—H distance (1.91(9) Å) which may reflect differences in charge on the two ruthenium atoms indicated in resonance structures C and D, which are discussed below. The Ru(1)—Ru(2)—C(21) and Ru(2)—Ru(1)—C(12) angles are opened up around the edge bridged by hydrogen (118.8(2) and 113.3(2)°) typical for this type of system and which may be used to indicate the presence of hydro-

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* See footnote on p. 247.

TABLE 7

INTERATOMIC DISTANCES (Å) FOR $HRu_3(OCN(CH_3)_2)(CO)_{10}$

Ru(1)—Ru(2)	2.8755 (15)	C(11)—O(11)	1.142(10)
Ru(1)—Ru(3)	2.8319 (15)	C(12)—O(12)	1.110(10)
Ru(2)—Ru(3)	2.8577 (14)	C(13)—O(13)	1.138(10)
Ru(1)—O	2.100(5)	C(21)—O(21)	1.121(10)
Ru(2)—O	2.098(8)	C(22)—O(22)	1.138(10)
Ru(1)—H	1.73(9)	C(23)—O(23)	1.129(10)
Ru(2)—H	1.91(9)	C(31)—O(31)	1.154(10)
Ru(1)—C(11)	1.881(9)	C(32)—O(32)	1.128(10)
Ru(1)—C(12)	1.945(9)	C(33)—O(33)	1.127(10)
Ru(1)—C(13)	1.912(9)	C(34)—O(34)	1.129(10)
Ru(3)—C(31)	1.892(8)	Me(2)—H(21)	1.08(9)
Ru(3)—C(32)	1.938(9)	Me(2)—H(22)	0.72(10)
Ru(3)—C(33)	1.954(9)	Me(2)—H(23)	0.88(10)
Ru(3)—C(34)	1.946(9)	Me(1)—H(12)	0.86(10)
Ru(2)—C(21)	1.913(8)	Me(1)—H(11)	0.87(10)
Ru(2)—C(22)	1.894(8)	Me(1)—H(13)	1.09(8)
Ru(2)—C(23)	1.968(8)	N—Me(1)	1.46(1)
C—O	1.287(9)	N—Me(2)	1.47(1)
C—N	1.340(10)		

gen bridging an edge when this atom can not be located directly [11].

The average Ru—C(carbonyl) distance is 1.924(9) Å and is similar to those found in $Ru_3(CO)_{12}$ (Ru—C(carbonyl)$_{av}$ = 1.932(4) Å) [26]. Ru—C(carbonyl) *trans* to the carbon of the formamido group is 0.044 Å longer than the average Ru—C(carbonyl) distance suggesting some *trans* influence [30] of the carbon atom of the formamido group. There is however no noticeable shortening of the C—O bond length in this carbonyl group (C(23)—O(23) 1.129(10) Å).

The Ru(2)—C distance at 2.098(8) Å is longer than what one would expect for an Ru—C(sp^2) single bond (2.06 Å) based on the covalent radii of Ru [31] and C(sp^2) [32]. It is also longer than the average Ru—C(carbonyl) distance in I and longer than the Ru—C(isocyanide) distance of 1.99(2) Å in the complex, $Ru_3(CO)_{11}$CN-t-Bu [33]. Although carbonyls function as good π acceptors, isocyanide ligands are generally regarded [34,35] as poor π acceptors. It therefore appears that there is little Ru—C(amide) multiple bonding in I.

The Ru(1)—O distance (2.100(5) Å) is slightly longer than the sum of the covalent radii (1.99 Å) [31,36] but is comparable with several Ru—O distances reported (range 1.96(2) to 2.103(7) Å) [37—39]. The formamido group is nearly perpendicular to the Ru_3 plane and shows no interaction with the Ru-$(CO)_4$ group.

Interatomic distances within the formamido group

Within the formamido group the CO and CN distances of 1.287(9) Å and 1.340(10) Å suggest delocalized bonding with bond lengths being intermediate between single and double bond values. This is best represented by resonance between the two canonical structures C and D *.

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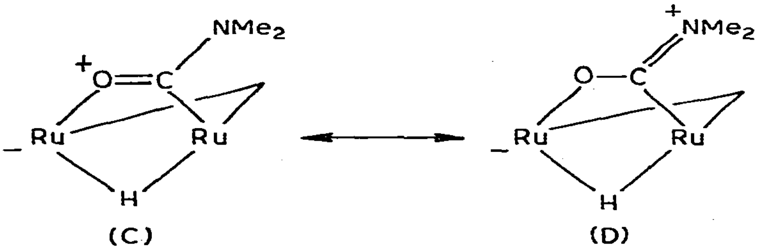
* See footnote on p. 247.

TABLE 8

INTERATOMIC ANGLES (deg)

Ru(1)—Ru(2)—Ru(3)	59.20(4)	Ru(3)—C(31)—O(31)	179.1(8)
Ru(1)—Ru(3)—Ru(2)	60.71(3)	Ru(3)—C(32)—O(32)	175.9(7)
Ru(2)—Ru(1)—Ru(3)	60.09(4)	Ru(3)—C(33)—O(33)	176.2(8)
Ru(1)—Ru(2)—C(21)	118.8(2)	Ru(3)—C(34)—O(34)	176.5(7)
Ru(1)—Ru(2)—C(22)	137.8(2)		
Ru(1)—Ru(2)—C(23)	104.4(2)	C(11)—Ru(1)—C(12)	92.5(3)
Ru(1)—Ru(2)—C	66.6(2)	C(11)—Ru(1)—C(13)	91.2(3)
Ru(1)—Ru(3)—C(31)	96.1(2)	C(12)—Ru(1)—C(13)	98.8(3)
Ru(1)—Ru(3)—C(32)	82.0(2)	C(21)—Ru(2)—C(22)	97.9(3)
Ru(1)—Ru(3)—C(33)	89.9(2)	C(21)—Ru(2)—C(23)	90.7(3)
Ru(1)—Ru(3)—C(34)	163.3(2)	C(22)—Ru(1)—C(23)	94.6(3)
Ru(2)—Ru(1)—C(11)	108.8(2)	C(22)—Ru(2)—C(21)	88.3(3)
Ru(2)—Ru(1)—C(12)	113.3(2)	C(22)—Ru(2)—C(22)	96.5(3)
Ru(2)—Ru(1)—C(13)	140.5(2)	C(22)—Ru(2)—C(23)	168.8(3)
Ru(2)—Ru(3)—C(31)	156.8(2)	C(31)—Ru(3)—C(32)	92.2(3)
Ru(2)—Ru(3)—C(32)	85.9(2)	C(31)—Ru(3)—C(33)	93.8(3)
Ru(2)—Ru(3)—C(33)	85.6(2)	C(31)—Ru(3)—C(34)	99.7(3)
Ru(2)—Ru(3)—C(34)	103.4(2)	C(32)—Ru(3)—C(33)	170.5(3)
Ru(3)—Ru(1)—C(11)	85.9(2)	C(32)—Ru(3)—C(34)	93.4(3)
Ru(3)—Ru(1)—C(12)	171.9(2)	C(33)—Ru(3)—C(34)	92.7(4)
Ru(3)—Ru(1)—C(13)	89.1(3)	Ru(2)—H—Ru(1)	103.8(43)
Ru(3)—Ru(2)—C(21)	175.9(2)	Ru(3)—Ru(2)—H	92.3(26)
Ru(3)—Ru(2)—C(22)	82.7(2)	Ru(3)—Ru(1)—H	97.4(3)
Ru(3)—Ru(2)—C(23)	93.1(2)	Ru(1)—Ru(2)—H	35.9(26)
Ru(3)—Ru(2)—C	87.7(2)	Ru(2)—Ru(1)—H	40.3(3)
Ru(1)—C(11)—O(11)	176.6(7)	C(11)—Ru(1)—H	99.0(29)
Ru(1)—C(12)—O(12)	174.3(7)	C(12)—Ru(1)—H	75.0(29)
Ru(1)—C(13)—O(13)	177.8(8)	C(13)—Ru(1)—H	168.2(29)
Ru(2)—C(21)—O(21)	177.3(7)	C(21)—Ru(2)—H	86.6(26)
Ru(2)—C(22)—O(22)	177.8(7)	C(22)—Ru(2)—H	173.1(26)
Ru(2)—C(23)—O(23)	172.3(7)	C(23)—Ru(2)—H	90.4(26)
Ru(2)—C—O	114.6(5)	Intraligand angles	
Ru(1)—O—N	109.6(5)	O—C—N	115.2(7)
Ru(2)—C—N	130.2(6)	C—N—Me(1)	124.1(7)
C—Ru(2)—C(21)	88.3(3)	C—N—Me(2)	121.4(7)
C—Ru(2)—C(22)	96.5(3)	Me(1)—C—Me(2)	114.2(7)
C—Ru(2)—C(23)	168.8(3)		
C(11)—Ru(1)—O	177.2(3)		
C(12)—Ru(1)—O	89.7(3)		
C(13)—Ru(1)—O	177.2(3)		

These account for the hindered rotation about the C—N bond as indicated by NMR non-equivalence of the two methyl groups bonded to the nitrogen atom



(C) (D)

and the planarity of the formamido group observed in the structure study.

The C—O distance in the coordinated formamido group is longer than the

TABLE 9

COMPARISON OF SELECTED BOND DISTANCES AND ANGLES

Free amide or complex	C—O (Å)	C—N (Å)	O—C—N (°)	C—N—R (°)	Reference
$HC(O)N(H)CH_3$ [a]	1.219(5)	1.306(8)	124.6	121.4(9)	40
$CH_3C(O)N(H)CH_3$ [a]	1.225(3)	1.386(4)	121.8(4)	119.7(8)	41
$NaI \cdot 3(CH_3)_2NC(H)O$ [b]	1.23(4)	1.34(4)	123.6(2)	120.9(2)	42
$Mn(CO)_4(NH_2CH_3)(CONHCH_3)$ [b,c]	1.251(10)	1.345(12)	117.4(8)	122.4(8)	43
η^5-$CpW(CO)_2(NH_2CH_3)(CONHCH_3)$ [b]	1.25(3)	1.41(3)	113(2)	125(2)	44
η^5-$CpMn(CO)(NO)(CONH_2)$ [b]	1.222(6)	1.346(6)	119.4(3)	119.9(7)	45
$[R_2NH_2][PtCl_2(CONR_2)(CO)]$ [b,d]	1.36(6)	1.30(3)	118(4)	125(4)	46
cis-$[PtCl_2(C(OEt)NHPh)PEt_3]$ [b]	1.33(2)	1.33(3)	110(2)	127(2)	49
$Fe_2(CO)_6[\mu\text{-}AsMe_2][\mu\text{-}CONMe_2]$ [b]	1.26(2)	1.35(2)	115.9(11)	119.6	47
$(\mu\text{-}p\text{-}MeC_6H_4NCHO)HOs_3(CO)_{10}$ [b]	1.27(1)	1.33(1)	124.8(8)	115.2(7)	48
$HRu_3(OCN(CH_3)(CO)_{10}$ [b]	1.287(9)	1.340(10)	115.2(7)	121.4(7)	*this work*
$[Ph_4P]_2[Mo(NO)(OCNMe_2)NCS)_4]$ [b]	1.322(7)	1.240(7)	123.96(60)	121.77(69)	50

[a] Gas electron diffraction. [b] X-ray diffraction. [c] Tetragonal form. [d] $R = i\text{-}C_3H_7$.

C—O distance found in the amides [40—42] and somewhat longer than the C—O distances observed for most of the carboxamidometal complexes [43—46]. It is consistent with the C—O distances found in the polynuclear metal complexes containing bridging formamido groups [47,48]. For comparison, bond distances and angles in free amides and in complexes containing the formamido group and an alkylated formamido group are listed in Table 9; parameters for an amide complex with an alkali metal ion are also included in this Table.

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References

1 (a) M.A. Andrews and H.D. Kaesz, J. Amer. Chem. Soc., 99 (1977) 6763; (b) the present work is taken in part from the Dissertation of R. Szostak, Univ. Calif. Los Angeles, 1980.
2 E. Sappa and L. Milone, J. Organometal. Chem., 61 (1973) 383.
3 S.K. Malik and A. Poë, Inorg. Chem., 17 (1978) 1484.
4 R.J. Angelici, Accounts Chem. Res., 5 (1972) 335.
5 W. Hieber, Advan. Organometal. Chem., 8 (1970) 1.
6 N. Kutepow and H. Kindler, Angew. Chem., 72 (1960) 802.
7 J. Wender, H.W. Sternberg and M. Orchin, J. Amer. Chem. Soc., 74 (1952) 1216.
8 H. Behrens, R.J. Lampe, P. Merbach and M. Moll, J. Organometal. Chem., 159 (1978) 201.
9 H. Kessler, Angew. Chem. Internat. Edit., 9 (1970) 219.
10 R.L. Jones, J. Mol. Spectrosc., 2 (1958) 581.
11 H.D. Kaesz and R.B. Saillant, Chem. Rev., 72 (1972) 231.
12 I. Suzuki, Bull. Chem. Soc. Japan, 35 (1962) 540.
13 Sr.M. Marinette, S. Mizushima and J.V. Quagliano, Spectrochim. Acta, 15 (1959) 77.
14 B.F.G. Johnson, J. Lewis, A.G. Orpen, P.R. Raithby and G. Suss, J. Organometal. Chem., 173 (1979) 187.
15 C.G. Kreiter and V. Formacek, Angew. Chem. Int. Ed., 11 (1972) 141.
16 (a) M.F. Lappert and P.L. Pye, J. Chem. Soc. Dalton, (1977) 2172; (b) B.V. Johnson, D.P. Sturtzel and J.E. Shade, J. Organometal. Chem., 154 (1978) 89.
17 E.R. Roberts, H.J. Emeleus and H.V.A. Briscoe, J. Chem. Soc., (1939) 41.
18 M.A. Andrews, Dissertation, Univ. Calif. Los Angeles, 1977.
19 S.A.R. Knox, J.W. Koepke, M.A. Andrews and H.D. Kaesz, J. Amer. Chem. Soc., 97 (1975) 3942.
20 C.E. Strouse, Rev. Sci. Inst., 47 (1976) 871.
21 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, England, 1975.
22 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
23 G.M. Sheldrick and J.P. Yesinowski, J. Chem. Soc. Dalton, (1975) B75.
24 F.A. Cotton, B.E. Hanson and J.D. Jamerson, J. Amer. Chem. Soc., 99 (1977) 6588.
25 J.Y. Jeannin and G. Lavigne, Inorg. Chem., 17 (1978) 2103.
26 M.R. Churchill, F.J. Hollander and J.P. Hutchinson, Inorg. Chem., 16 (1977) 2655.
27 M.R. Churchill and R.A. Lashewycz, Inorg. Chem., 17 (1978) 1291.
28 M.R. Churchill, B.G. DeBoer and F.J. Rotella, Inorg. Chem., 15 (1976) 1843.
29 M. Catti, G. Gervasio and S.A. Mason, J. Chem. Soc. Dalton, (1977) 2260.
30 (a) A. Pidcock, R.E. Richards and L.M. Venanzi, J. Chem. Soc. A, (1966) 1707; (b) L.J. Manojlovic-Muir and K.W. Muir, Inorg. Chim. Acta, 10 (1974) 47.
31 J.P. Jesson and E.L. Muetterties, Chemists Guide, Basic Chemical and Physical Data, Marcel Dekker, New York, N.Y., 1969, p. 2—3.
32 M.J.S. Dewar and H.N. Schneising, Tetrahedron, 5 (1959) 166.

33 M.I. Bruce, D. Schultz, R.C. Wallis and A.D. Redhouse, J. Organometal. Chem., 169 (1979) C15.
34 A.C. Sarapu and R.F. Fenske, Inorg. Chem., 11 (1972) 3021.
35 P.M. Treichel, Advan. Organometal. Chem., 11 (1973) 21.
36 L. Pauling, Nature of the Chemical Bond, 3rd ed. Cornell University Press, Ithaca, N.Y., 1960, p. 224.
37 A.J.P. Domingos, B.F.G. Johnson, J. Lewis and G.M. Sheldrick, J. Chem. Soc., Chem. Commun., (1973) 912.
38 M.J. Bennett, K.G. Caulton and F.A. Cotton, Inorg. Chem., 8 (1969) 1.
39 F.A. Cotton, J.G. Norman, A. Spencer and G. Wilkinson, J. Chem. Soc. Chem. Commun., (1971) 967.
40 M. Kitano and K. Kuchitsu, Bull. Chem. Soc. Japan, 47 (1974) 631.
41 M. Kitano and I. Fukuyama and K. Kuchitsu, Bull. Chem. Soc. Japan, 46 (1973) 384.
42 Y. Gobillon, P. Piret and M. VanMeerssche, Bull. Soc. Chim. France, (1963) 551.
43 D.M. Chipman and R.A. Jacobson, Inorg. Chim. Acta, (1967) 393.
44 R.D. Adams, D.F. Chodosh and N.M. Golembeski, Inorg. Chem., 17 (1978) 266.
45 D. Messer, G. Landgraf and H. Behrens, J. Organometal. Chem., 18 (1979) 1165.
46 D. Dell'Amico, F. Calderazzo and G. Pelizzi, Inorg. Chem., 18 (1979).
47 E. Keller, A. Trenkle and H. Vahrenkamp, Chem. Ber., 110 (1977) 441.
48 R.D. Adams and N.M. Golembeski, J. Organometal. Chem., 171 (1979) C21.
49 E.M. Badley, K.W. Muir and G.A. Sim, J. Chem. Soc. Dalton, (1976) 1930.
50 D. Messer, G. Landgraf and H. Behrens, J. Organometal. Chem., 172 (1979) 349.