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Crystal Structure and Molecular Geometry of HRu$_3$(CO)$_{10}$(C═NMe$_2$), Including the Direct Location of the μ$_2$-Bridging Hydride Ligand

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The trinuclear complex HRu$_3$(CO)$_{10}$(C═NMe$_2$), previously prepared from the reaction of Ru$_3$(CO)$_{12}$ and (Me$_2$NCH$_2$)SnMe$_3$, has been characterized both by mass spectrometry and by a complete three-dimensional x-ray diffraction study. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with $a = 9.3171$ (9) Å, $b = 35.8137$ (35) Å, $c = 11.9616$ (10) Å, $\beta = 97.06$ (1)°, $V = 3961.1$ (6) Å^3, and ρ(calcd) = 2.147 g cm^{-3} for mol wt 640.41 and $Z = 8$. Diffraction data were collected with a Picker FACS-1 diffractometer, using Mo Kα radiation. The structure was solved by symbolic addition and was refined by difference-Fourier and least-squares refinement techniques. All atoms, including all hydrogen atoms, have been located, the final discrepancy indices being $R_F = 2.41\%$ and $R_{wF} = 3.45\%$ for the 3702 reliable independent reflections with $2\theta < 40°$. There are two crystallographically independent molecules within the asymmetric unit; a comparison of bond distances and angles within these two molecules shows excellent agreement, average disagreements between "equivalent" values being 0.004 Å for Ru–Ru, 0.011 Å for Ru–CO, 0.012 Å for Ru–CNMe$_2$, 0.009 Å for C–O, and 0.007 Å for N–C distances. Each molecule has approximate C_s symmetry and contains a triangular arrangement of ruthenium atoms, one of which is linked to four terminal carbonyl ligands and two of which are linked to three terminal carbonyl ligands. The two Ru(CO)$_3$ groups are linked by a bridging hydride and a bridging Me$_2$N$^+$═C$^-$ ligand and are associated with Ru–Ru distances of 2.7997 (5) Å [molecule 1] and 2.8016 (6) Å [molecule 2] as compared to nonbridged (OC)$_4$Ru–Ru(CO)$_3$ bonds of length 2.8216 (6)–2.8336 (6) Å. Ruthenium–hydrogen bond distances are Ru(11)–H(1) = 1.93 (5) Å and Ru(12)–H(1) = 1.85 (5) Å (in molecule 1) and Ru(21)–H(2) = 1.80 (3) Å and Ru(22)–H(2) = 1.82 (3) Å (in molecule 2); Ru–H–Ru angles are 95 (2) and 101 (2)°, respectively. The results of this structural study, taken in conjunction with available crystallographic information on other systems containing bridging hydride ligands, are used in assessing the effects of bridging hydride ligands on metal–metal distances.

Introduction

The fission reactions of organotin amines,[3] sulfides,[4] and allyls[5] with transition metal halides have led to a number of unusual transition metal complexes. Recently, Abel and co-workers have examined the reaction of metal carbonyl halides with (dialkylaminomethyl)trialkyltin [R$_2$NCH$_2$SnMe$_3$] complexes and have demonstrated[6,7] that species containing η^2-bonded dialkylaminomethylene ligands are produced; a crystal structure determination[6] of (aziridinylmethylene)-tetracarbonylmanganese (I) has confirmed this unequivocally.

I
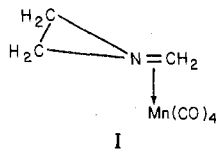
Abel and Rowley recently found[8] that (dimethylaminomethyl)trimethyltin reacts with triruthenium dodecacarbonyl to yield the known species (Me$_3$Sn)$_2$Ru(CO)$_4$ and a new triruthenium cluster complex for which no unique formulation was, at the time, possible. We have undertaken a single-crystal x-ray diffraction study of this latter species and found it to be HRu$_3$(CO)$_{10}$(C═NMe$_2$) (vide infra). A preliminary account of this work appeared earlier.[9]

Experimental Section

(A) Collection of the X-Ray Diffraction Data. A crystalline sample of the complex was provided by Professor E. W. Abel of the University of Exeter, Exeter, England. The crystals form characteristic orange hexagonal plates and decompose upon exposure to air for prolonged periods. The crystal selected for the diffraction experiment was a hexagonal plate between {010} faces 0.15 mm apart, bounded by {101}, {2$\bar{1}$0}, and {03$\bar{2}$}; the plate face was of maximum dimensions 0.55 mm × 0.40 mm. The crystal was mounted along its extended a direction by glueing it with General Electric "Glyptal" to the tip of a thin glass fiber which was fixed into a brass pin using beeswax and mounted on a eucentric goniometer head. The crystal was subsequently protected from air by coating it with a thin film of shellac.

Preliminary Weissenberg, rotation, precession, and cone-axis photographs yielded approximate cell dimensions, indicated C_{2h} (2/m) Laue symmetry, and revealed the systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/n$ is thus indicated. [$P2_1/n$ is a nonstandard setting of space group $P2_1/c$ (C_{2h}^5; No. 14) having the equipoints ±(x, y, z) and ±($^1/_2 + x$, $^1/_2 - y$, $^1/_2 + z$).]

The crystal was transferred to a Picker FACS-1 automated diffractometer, was accurately centered, and was oriented in a random orientation with a^* offset by 2.17° from the instrumental ϕ axis. Unit cell measurement and data collection were carried out as described

Table I. Experimental Data for the X-Ray Diffraction Study on $HRu_3(CO)_{10}(C=NMe_2)$

(A) Crystal Parameters (at 22.0 ± 0.5 °C)[a]

$a = 9.3171$ (9) A	Space group $P2_1/n$
$b = 35.8137$ (35) A	$Z = 8$
$c = 11.9616$ (10) A	Mol wt 640.41
$\cos\beta = -0.122\ 84$ (15)	ρ(calcd) = 2.147 g/cm^3
$\beta = 97.06$ (1)°	ρ(obsd) > 2.0 g/cm^3 (see text)
$V = 3961.1$ (6) A^3	

(B) Measurement of Intensity Data

Radiation: Mo Kα

Filter(s): Nb foil at counter aperture (~47% transmission of Mo Kα)

Attenuators: Cu foil, used if intensity exceeded 10^4 counts/s

Takeoff angle: 3.0°

Detector aperture: 6.3 × 6.3 mm

Crystal-detector distance: 330 mm

Crystal orientation: ϕ axis offset from [100] by 2.17°

Reflections measured: $+h, +k, \pm l$

Maximum 2θ: 40°

Scan type: coupled θ(crystal)–2θ(counter)

Scan speed: 1.0°/min

Scan length: $\Delta(2\theta) = (1.0 + 0.692 \tan\theta)°$, starting 0.5° below the Mo Kα_1 peak.

Background measurement: stationary-crystal, stationary-counter, 20 s each at beginning and end of 2θ scan

Standard reflections: three remeasured after every 50 reflections; rms deviations (after application of an anisotropic linear decay correction) were 0.61% for 0,20,0, 0.93% for 015, and 1.60% for 600[c,d]

Reflections collected: 3707 independent measurements, 2 duplicate or equivalent measurements (averaged into primary data set), and 97 systematic absences

(C) Treatment of Intensity Data[c]

Conversion to $|F_o|$ and $\sigma(|F_o|)$: as in ref 10, using "ignorance factor" of $p = 0.040$

Absorption coefficient: $\mu = 22.63$ cm^{-1}; data corrected for absorption;[e] maximum and minimum transmission factors 0.750 and 0.443, respectively

[a] Unit cell parameters are from a least-squares fit to the setting angles of the resolved Mo Kα_1 peaks (λ 0.709 300 A)[b] of 12 reflections ($2\theta = 46$–52°). Maximum and root-mean-square disagreements were 0.020 and 0.010°, respectively. [b] J. A. Bearden, *Rev. Mod. Phys.*, **39**, 78 (1967); see also "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, pp 5–19. [c] Data reduction and analysis, including an anisotropic decay correction, were carried out using the Fortran IV program RDUS2, by B. G. DeBoer. [d] The intensity of the check reflections decreased steadily during the course of data collection by a total of 9–10%. Rms deviations *before* application of the decay correction were as follows: 4.82% for 0,20,0, 5.23% for 015, and 5.53% for 600. Decay is not grossly anisotropic. [e] Absorption corrections were made using the Fortran IV program DRABZ, by B. G. DeBoer.

previously;[10] details of the present analysis are compiled in Table I.

With the completion of data collection, the crystal was reoriented such that a^* was precisely coincident with the ϕ axis and the intensity of the 200 reflection was measured via θ–2θ scans at 10° interval from $\phi = 0°$ to $\phi = 360°$. The intensity was found to vary by 48% [variation (%) = 100(max − min)/av] indicating that an absorption correction was required. These "ϕ-scan" data were corrected for absorption along with the 3707 symmetry-independent "intensity data". Their variation was reduced to 5.2% thereby confirming the validity of the applied correction. [Note that the ϕ dependence is not expected to decrease to zero except in the total absence of secondary extinction.[11]].

An attempt was made to measure the density of the crystals; the complex was found to be soluble in the usual high-density polyhalogenated organic solvents and crystals were found to sink in saturated aqueous BaI_2 ($\rho \approx 2.0$ g cm^{-3}) which was the most dense aqueous solution available to us at the time.

(B) Solution and Refinement of the Structure. Programs used during the course of the structural determination were FAME (Wilson plot and generation of $|E|$ values, by R. B. K. Dewar and A. L. Stone), MAGIC (phase generation from $|E|$ values via symbolic addition, for centric crystals, by Dewar and Stone), LSHF (full-matrix least-squares

Table II. Statistics for Intensity Distribution in $HRu_3(CO)_{10}(C=NMe_2)$

		Theoret[a]	
Quantity	Obsd	Centrosym	Non-centrosym
$\langle|E|\rangle$	0.803	0.798	0.886
$\langle|E|^2\rangle$	1.000[b]	1.000	1.000
$\langle|E^2 - 1|\rangle$	0.965	0.968	0.736
$|E| > 1$, %	32.05	32.0	37.0
$|E| > 2$, %	4.37	5.0	1.8
$|E| > 3$, %	0.30	0.3	0.01

[a] I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Crystallogr.*, **19**, 713 (1965). [b] Fixed by an adjustable scale factor.

refinement and structure factor calculations, by B. G. DeBoer), FORDAP (Fourier synthesis, by A. Zalkin), STAN1 (calculation of distances and angles, with esd's, by DeBoer), PLOD (least-squares planes and lines, by DeBoer), and ORTEP (thermal ellipsoid plotting program, by C. K. Johnson). All calculations were performed on an IBM 370/158 computer.

Scattering factors for neutral ruthenium, oxygen, nitrogen, and carbon were taken from the compilation of Cromer and Mann;[12] the "best floated spherical H atom" values of Stewart et al.[13] were converted into analytical form.[14] Both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included for all nonhydrogen atoms, using the values of Cromer and Liberman.[15]

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = \{\sigma(|F_o|)\}^{-2}$. Discrepancy indices used below are defined as

$$R_F = \left[\frac{\sum\||F_o| - |F_c|\|}{\sum|F_o|}\right] \times 100\ (\%)$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}\right]^{1/2} \times 100\ (\%)$$

Normalized structure factor amplitudes, $|E(hkl)|$, were generated from $|F_o(hkl)|$ values using eq 1 (where the sum $j = 1 \rightarrow N$ is over

$$|E(hkl)| = |F_o(hkl)|\left[\epsilon \sum_{j=1}^{j=N} f^2\ [j,\theta(hkl)]\right]^{-1/2} \tag{1}$$

all atoms in the unit cell, $\langle E^2(hkl)\rangle$ is normalized by adjustment of a scale factor, $f\ [j,\theta(hkl)]$ is the scattering factor for the jth atom at the Bragg angle $\theta(hkl)$, and ϵ is a coefficient which corrects for the effects of space group symmetry)[16] and were tested for large Σ_2 interactions by FAME. The statistical distribution of $|E|$ values was essentially identical with that expected for a centrosymmetric crystal (see Table II).

The origin of the unit cell was defined by assigning positive phases to three strong ($|E| > 3.3$) reflections of appropriate parity (oeo, eoo, eeo). An additional three reflections (parity ooo, eee, and oee, each with $|E| > 2.65$ and many Σ_2 interactions) were assigned symbols. Application of the symbolic addition procedure by MAGIC generated symbolic signs (in terms of those of the initial six reflections) to all 510 reflections having $|E| > 1.5$, with no sign indication of less than 99.9% probability being accepted. One assignment of real (i.e., + or −) signs to symbols had a much lower "contradiction index" than the other seven solutions. The 510 signed E values resulting from this assignment were used as coefficients for a Fourier synthesis. This "E map" quickly and unambiguously led to the location of the six ruthenium atoms in the asymmetric unit. Three cycles of full-matrix least-squares refinement of the scale factor and positional and isotropic thermal parameters for the six atoms (25 parameters in all) using, now, all 3707 reflections, led to convergence with $R_F = 30.2\%$ and $R_{wF} = 40.2\%$. A series of difference-Fourier syntheses each being phased by an increasing number of atoms led to the location of ten carbonyl groups and a four-atom "Y-shaped" bridging ligand on each Ru_3 cluster molecule. Since the nature of this "Y-shaped" ligand was not (at the time) known, we assumed (as a working hypothesis) that it was II with A = B = N. Three cycles of full-matrix least-squares refinement of all nonhydrogen atoms, using anisotropic thermal parameters for the metal atoms and isotropic thermal parameters for

$$\begin{array}{c}(Ru)\\ |\\ (Ru)\end{array}\Big\rangle A=B\Big\langle\begin{array}{c}CH_3\\ \\ CH_3\end{array}$$

II
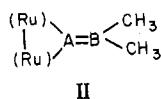
all other nonhydrogen atoms (247 parameters varied), resulted in R_F = 6.47% and R_{wF} = 10.72%. All atoms were now allowed anisotropic thermal parameters; five "cycles" of refinement [in which each "cycle" consisted of full-matrix refinement of the scale and all thermal parameters (325 variables) followed by full-matrix refinement of the scale and all positional parameters and anisotropic thermal parameters for the ruthenium atoms (199 variables)] led to R_F = 2.99% and R_{wF} = 4.73% for those 3694 reflections with $|\Delta F|/\sigma(F) < 10.0$ and R_F = 3.10% and R_{wF} = 5.74% for all 3707 data.

At this point it was clearly necessary to establish the true nature of the "Y-shaped" ligand and to determine unambiguously the correct stoichiometry of the decacarbonyltriruthenium derivative. These objectives were accomplished as follows.

The mass spectrum of the complex was measured on an AEI MS30 double-beam mass spectrometer using perfluorokerosene as a reference material. The mass spectrum showed well-separated multiplets of peaks corresponding to HRu₃[CN(CH₃)₂](CO)$_n^+$, n = 10 → 0 [most intense for n = 5], whose intensity distributions were in accord with those calculated from tabulated isotopic abundances of Ru and C. The positions of each of these multiplets on the m/e scale could be clearly ascertained both from the most intense peak and from the characteristic "reversal" on the high-mass side of each multiplet [i.e., $I(^{104}Ru_2{}^{102}Ru) > I(^{104}Ru_2{}^{101}Ru)$]. Other peaks in the mass spectrum defined multiplets corresponding to Ru₃(CNCH₃)⁺, Ru₃CN⁺, Ru₃C⁺, and Ru₃⁺ each of which, unfortunately, had an ambiguity of ±1 amu (i.e., ambiguous as to the presence or absence of the hydride ligand) due to overlaps between neighboring multiplets. Also present were multiplets of peaks at half-integral intervals, corresponding to the doubly-charged species {HRu₃[CN(CH₃)₂](CO)$_n$}²⁺, n = 3 → 0. Clearly the "Y-shaped" ligand was either CN(CH₃)₂ or NC(CH₃)₂. Examination of the thermal parameters of the central A and B atoms (see II), which had each been given the scattering factor of nitrogen, showed that those for the μ_2-bridging atom A were substantially higher than those for atom B. This, coupled with the mode of synthesis and bond lengths in the complex, leads to the "Y-shaped" ligand's identity being revealed as >C=NMe₂.

We now further investigated the hydride ligand. A ¹H NMR spectrum, taken with a Varian T-60 spectrometer, revealed two singlets (relative intensity 6:1) at τ 6.1 and 24.9 ppm. (The complex was dissolved in CCl₄ which had been deoxygenated by bubbling N₂ through it.)

We returned to the x-ray structural analysis, knowing now that the complex was HRu₃(CO)₁₀(CNMe₂). [Note also that a hydride ligand is required to satisfy the EAN (18 electron) rule for this diamagnetic complex.]

Following the observations that the nine most intense reflections showed $|F_c|$ systematically greater than $|F_o|$, a secondary extinction parameter was included in the refinement. With all nonhydrogen atoms now correctly identified, three "cycles" of refinement of the positional and anisotropic thermal parameters (each "cycle" consisting of refinement of half of the parameters, followed by refinement of the other half (488 parameters in all)) led to R_F = 2.78% and R_{wF} = 4.17% for those 3693 independent data with $|\Delta F|/\sigma(F) < 10$ and R_F = 2.90% and R_{wF} = 5.35% for all data.

We now undertook a search for all hydrogen atoms. A difference-Fourier map using the entire data set led to location of the bridging hydride ligands (one per molecule), but no unambiguous positions could be found for the methyl hydrogens. We now cut down our data set[17-21] to those 900 reflections for which (sin θ)/λ < 0.3 and obtained another difference-Fourier synthesis on which the hydride peaks were much enhanced and the positions of the 12 methyl hydrogens could clearly be seen. Continued refinement, now including positional and isotropic thermal parameters for all 14 hydrogen atoms (544 parameters in all), led to final convergence (maximum suggested parameter shifts from the last cycle of refinement were 0.012σ for Ru, 0.063σ for C or O, and 0.105σ for H) with R_F = 2.41% and R_{wF} = 3.45% for those 3702 reflections with $|\Delta F|/\sigma(F) < 10$ and R_F = 2.48% and R_{wF} = 4.15% for all 3707 data. [Note the sharp decrease in the number of data exhibiting large disagreements (i.e., $|\Delta F|/\sigma(F) \geq 10$) resulting from the inclusion of hydrogen atom contributions to the calculated structure factors. We have noted this same effect in a number of previous structural determinations—even in cases where
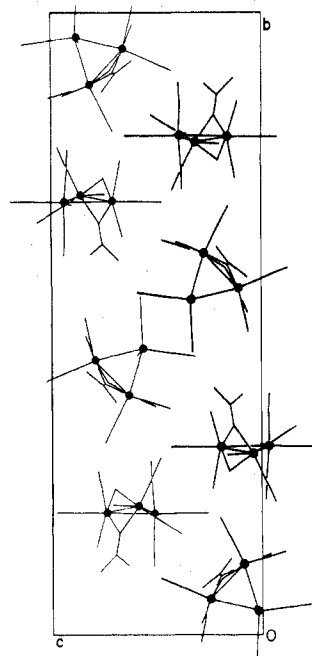

Figure 1. Packing of HRu₃(CO)₁₀(C=NMe₂) molecules within the unit cell, projected onto (100).

hydrogen atom positions could only be inferred, rather than located directly from the diffraction data (i.e., via a difference-Fourier synthesis).]

A final difference-Fourier map showed a number of features of height 0.61 → 0.35 e Å⁻³, all of which were either "on bonds" or very close to the heavy atoms. (For comparison, the two hydride ligands had peak heights ≥0.67 e Å⁻³.)

The final value for c, the secondary extinction parameter, was 1.28 (11) × 10⁻⁶ mm⁻¹ e⁻², where the corrected structure factor ($F_{c,cor}$) is given by[22-24]

$$F_{c,cor} = F_{c,uncor}(1 + c\beta F^2{}_{c,uncor})^{-1/4}$$

and

$$\beta = \left(\frac{1 + \cos^4 2\theta}{(\sin 2\theta)(1 + \cos^2 2\theta)}\right)\left(\frac{-d \ln T}{d\mu}\right)$$

The "goodness of fit", given by $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ had a value of 1.33 where m, the number of observations, was 3702 and n, the number of variables, was 544, yielding a data-to-parameter ratio of 6.80:1. The function $\sum w(|F_o| - |F_c|)^2$ showed no appreciable dependence either upon (sin θ)/λ or upon $|F_o|$; the weighting scheme is thus acceptable. A table of observed and calculated structure factor amplitudes is available.[25] Final positional and isotropic thermal parameters are collected in Table III; anisotropic thermal parameters are listed in Table IV.

Results and Discussion

Interatomic distances and their estimated standard deviations (esd's) are shown in Table V; intramolecular angles and their associated esd's are given in Table VI. Least-squares planes are collected in Table VII.

The crystal consists of discrete molecular units of HRu₃(CO)₁₀(C=NMe₂) which are mutually separated by normal van der Waals distances. The packing of molecules within the unit cell is illustrated in Figure 1. The crystallographic asymmetric unit consists of two independent molecules which we term "molecule 1" and "molecule 2". The scheme used in numbering atoms is such that the first digit designates the molecule to which that atom belongs. The numbering schemes
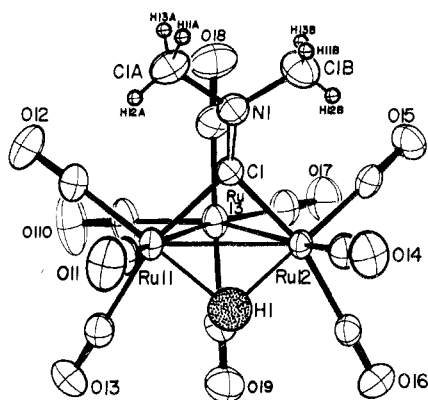
Figure 2. Molecular geometry and labeling for "molecule 1" in the $HRu_3(CO)_{10}(C=NMe_2)$ crystal (ORTEP diagram; 50% probability contours for all atoms except methyl hydrogens).
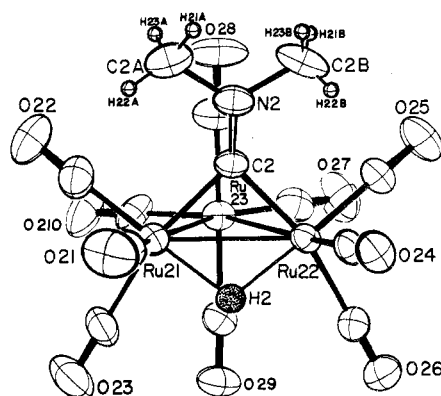

Figure 3. Geometry and labeling for $HRu_3(CO)_{10}(C=NMe_2)$ "molecule 2". Conditions are as for Figure 2.

and thermal vibration ellipsoids for the two molecules are shown in Figures 2 and 3.

The two crystallographically independent $HRu_3(CO)_{10}$-$(C=NMe_2)$ molecules have approximate $C_s(m)$ symmetry and appear to be equivalent. (Average disagreements between "equivalent" bond lengths are 0.004 Å for Ru–Ru, 0.011 Å for Ru–CO, 0.012 Å for Ru–(CNMe$_2$), 0.009 Å for C–O, and 0.007 Å for N–C distances.)

The $HRu_3(CO)_{10}(C=NMe_2)$ molecule contains a triangular array of ruthenium atoms, one of which [Ru(13) in molecule 1, Ru(23) in molecule 2] is linked to four terminal carbonyl ligands and two of which [Ru(11) and Ru(12) in molecule 1, Ru(21) and Ru(22) in molecule 2] are each linked to three terminal carbonyl ligands and are mutually bridged both by a hydride and by a $C=NMe_2$ ligand.

The triruthenium clusters each define *isosceles* triangles in which the doubly bridged ruthenium–ruthenium vectors [Ru(11)–Ru(12) = 2.7997 (5) Å in molecule 1 and Ru(21)–Ru(22) = 2.8016 (6) Å in molecule 2] are slightly, but significantly, *shorter* than the corresponding nonbridged vectors [Ru(11)–Ru(13) = 2.8288 (6) Å and Ru(12)–Ru(13) = 2.8279 (5) Å in molecule 1; Ru(21)–Ru(23) = 2.8336 (6) Å and Ru(22)–Ru(23) = 2.8216 (6) Å in molecule 2].

There are five symmetry-independent types of carbonyl ligand within the structure, and there are four independent measurements of each type. Statistics on these ruthenium–carbonyl bond lengths are collected in Table VIII. The results are somewhat surprising. Thus, on Ru(13) and Ru(23) the equatorial Ru–CO linkages (which are trans to other ruthenium atoms) average 1.913 Å ($\sigma(av) = 0.005$ Å) in length—a value which is only 0.008 (7) Å shorter than the average axial Ru–CO bond length of 1.921 Å ($\sigma(av) = 0.005$

Table III. Final Positional and Isotropic Thermal Parameters, with Esd's,[a] for $HRu_3(CO)_{10}(C=NMe_2)$

Atom	x	y	z	B,[b] Å^2
		(A) Molecule 1		
Ru(11)	0.708 98 (4)	0.303 10 (1)	0.263 34 (3)	3.44
Ru(12)	0.932 63 (4)	0.293 27 (1)	0.129 72 (3)	3.06
Ru(13)	0.646 47 (4)	0.304 39 (1)	0.025 89 (3)	3.79
C(11)	0.783 7 (5)	0.303 1 (1)	0.418 5 (4)	4.71
O(11)	0.825 5 (4)	0.303 1 (1)	0.511 4 (3)	7.64
C(12)	0.560 4 (5)	0.338 7 (2)	0.278 5 (4)	4.85
O(12)	0.471 2 (4)	0.359 3 (1)	0.287 9 (3)	7.40
C(13)	0.578 0 (5)	0.260 0 (1)	0.274 1 (4)	4.52
O(13)	0.503 1 (4)	0.236 1 (1)	0.280 5 (3)	6.97
C(14)	1.114 1 (5)	0.291 7 (1)	0.223 3 (4)	4.28
O(14)	1.220 1 (4)	0.291 1 (1)	0.278 0 (3)	6.67
C(15)	0.994 7 (5)	0.320 0 (1)	0.007 9 (4)	4.02
O(15)	1.029 5 (4)	0.336 7 (1)	−0.065 9 (3)	5.61
C(16)	0.955 8 (5)	0.244 1 (1)	0.061 7 (4)	4.06
O(16)	0.972 8 (4)	0.215 5 (1)	0.025 6 (3)	6.29
C(17)	0.667 7 (5)	0.303 5 (1)	−0.131 4 (4)	4.89
O(17)	0.675 3 (4)	0.303 5 (1)	−0.225 8 (3)	7.06
C(18)	0.675 7 (5)	0.357 6 (2)	0.032 4 (4)	5.10
O(18)	0.688 6 (5)	0.389 2 (1)	0.028 9 (4)	7.52
C(19)	0.644 6 (5)	0.250 9 (2)	0.038 8 (4)	4.94
O(19)	0.639 1 (4)	0.219 0 (1)	0.041 1 (3)	6.37
C(110)	0.442 8 (6)	0.307 4 (2)	0.029 5 (4)	6.04
O(110)	0.323 3 (4)	0.308 3 (2)	0.033 4 (4)	10.19
C(1)	0.864 9 (4)	0.337 3 (1)	0.214 6 (3)	3.25
N(1)	0.908 3 (4)	0.370 8 (1)	0.234 9 (3)	4.20
C(1A)	0.835 3 (8)	0.397 5 (2)	0.303 8 (6)	6.27
C(1B)	1.028 9 (7)	0.387 6 (2)	0.186 9 (6)	5.97
H(11A)	0.919 (7)	0.415 (2)	0.355 (5)	9.5 (17)
H(12A)	0.803 (6)	0.385 (2)	0.365 (5)	8.2 (18)
H(13A)	0.782 (6)	0.415 (2)	0.249 (5)	8.7 (17)
H(11B)	1.088 (5)	0.399 (1)	0.231 (4)	5.9 (14)
H(12B)	1.072 (9)	0.372 (2)	0.160 (7)	14.5 (29)
H(13B)	0.973 (6)	0.400 (2)	0.115 (5)	8.0 (15)
H(1)	0.847 (6)	0.265 (1)	0.234 (4)	8.2 (14)
		(B) Molecule 2		
Ru(21)	0.827 20 (4)	0.058 26 (1)	0.326 85 (3)	4.21
Ru(22)	0.822 25 (4)	0.114 91 (1)	0.164 92 (3)	3.76
Ru(23)	0.817 86 (4)	0.039 54 (1)	0.095 90 (3)	4.18
C(21)	0.818 0 (6)	0.079 4 (2)	0.471 1 (4)	5.91
O(21)	0.811 1 (5)	0.091 8 (2)	0.558 0 (4)	9.60
C(22)	0.716 2 (7)	0.015 0 (2)	0.347 0 (5)	6.80
O(22)	0.648 8 (6)	−0.010 9 (1)	0.357 0 (5)	9.75
C(23)	1.011 6 (6)	0.033 2 (2)	0.370 8 (5)	6.22
O(23)	1.117 3 (5)	0.018 9 (2)	0.398 7 (4)	9.68
C(24)	0.810 9 (5)	0.162 0 (1)	0.233 7 (4)	4.40
O(24)	0.802 4 (4)	0.190 4 (1)	0.275 4 (3)	6.11
C(25)	0.707 1 (6)	0.127 9 (1)	0.028 5 (4)	5.29
O(25)	0.638 4 (5)	0.135 8 (1)	−0.052 5 (3)	8.03
C(26)	1.001 8 (6)	0.125 6 (1)	0.099 6 (4)	5.20
O(26)	1.102 8 (4)	0.131 9 (1)	0.060 7 (4)	6.84
C(27)	0.814 0 (6)	0.047 1 (2)	−0.063 7 (5)	5.65
O(27)	0.808 9 (5)	0.050 9 (1)	−0.158 0 (3)	9.05
C(28)	0.609 5 (6)	0.039 4 (2)	0.085 9 (5)	6.21
O(28)	0.486 5 (4)	0.038 1 (1)	0.072 7 (4)	8.92
C(29)	1.022 1 (6)	0.045 6 (1)	0.129 1 (4)	4.86
O(29)	1.145 4 (4)	0.047 6 (1)	0.147 2 (3)	6.62
C(210)	0.833 5 (6)	−0.013 4 (2)	0.106 5 (5)	5.86
O(210)	0.845 3 (5)	−0.044 6 (1)	0.110 9 (4)	9.24
C(2)	0.668 3 (5)	0.091 8 (1)	0.250 4 (4)	3.92
N(2)	0.534 7 (4)	0.098 0 (1)	0.258 8 (3)	4.91
C(2A)	0.451 4 (7)	0.076 3 (2)	0.332 7 (6)	7.12
C(2B)	0.450 4 (7)	0.125 9 (2)	0.189 3 (7)	7.20
H(21A)	0.382 (7)	0.093 (2)	0.330 (5)	9.4 (19)
H(22A)	0.504 (8)	0.067 (2)	0.400 (6)	11.3 (24)
H(23A)	0.414 (6)	0.055 (2)	0.283 (5)	9.4 (18)
H(21B)	0.406 (8)	0.116 (2)	0.130 (6)	10.1 (20)
H(22B)	0.503 (9)	0.142 (2)	0.184 (6)	12.5 (24)
H(23B)	0.383 (7)	0.134 (2)	0.217 (5)	9.4 (19)
H(2)	0.937 (4)	0.096 (1)	0.286 (3)	3.3 (8)

[a] Esd's shown in parentheses, are right-adjusted to the last digit of the preceding number. [b] For anisotropic parameters, see Table IV.

Table IV. Anisotropic Thermal Parameters^{a,b} and Esd's for HRu$_3$(CO)$_{10}$(C=NMe$_2$)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	U^c
				Molecule 1			
Ru(11)	2.791 (22)	4.388 (24)	3.244 (22)	0.438 (14)	0.756 (15)	0.152 (14)	0.177, 0.205, 0.240
Ru(12)	2.421 (21)	3.597 (22)	3.222 (20)	0.372 (14)	0.586 (14)	0.237 (14)	0.169, 0.198, 0.220
Ru(13)	2.582 (22)	5.394 (26)	3.337 (22)	0.310 (15)	0.158 (15)	0.342 (15)	0.178, 0.207, 0.263
C(11)	3.75 (26)	6.29 (32)	4.14 (27)	0.92 (21)	0.69 (21)	0.46 (22)	0.21, 0.23, 0.29
O(11)	6.63 (24)	12.16 (35)	3.92 (19)	1.81 (21)	−0.24 (18)	−0.30 (19)	0.22, 0.28, 0.40
C(12)	4.36 (27)	6.04 (32)	4.24 (25)	0.60 (24)	0.91 (20)	−0.37 (22)	0.21, 0.24, 0.28
O(12)	5.46 (22)	8.28 (28)	8.50 (26)	3.14 (19)	1.03 (18)	−0.75 (21)	0.20, 0.32, 0.37
C(13)	3.83 (26)	5.23 (30)	4.59 (26)	0.45 (22)	0.86 (20)	0.20 (22)	0.21, 0.24, 0.26
O(13)	6.06 (23)	6.20 (24)	9.08 (26)	−1.67 (18)	2.68 (19)	0.89 (19)	0.21, 0.31, 0.35
C(14)	3.83 (25)	5.18 (28)	3.85 (24)	0.64 (22)	0.57 (19)	0.64 (21)	0.21, 0.22, 0.27
O(14)	4.00 (19)	9.45 (28)	6.15 (22)	0.50 (19)	−1.05 (16)	0.82 (19)	0.20, 0.30, 0.35
C(15)	2.98 (22)	4.76 (28)	4.29 (25)	1.25 (19)	0.32 (18)	−0.12 (21)	0.17, 0.23, 0.26
O(15)	6.26 (21)	6.32 (22)	4.44 (18)	−0.00 (17)	1.42 (15)	1.93 (16)	0.19, 0.28, 0.31
C(16)	3.18 (22)	4.61 (28)	4.53 (25)	0.23 (20)	0.99 (18)	0.24 (21)	0.19, 0.24, 0.25
O(16)	7.20 (23)	4.68 (21)	7.22 (23)	1.08 (18)	1.81 (18)	−0.77 (17)	0.22, 0.30, 0.32
C(17)	3.58 (25)	6.44 (33)	4.58 (27)	0.35 (21)	0.28 (22)	0.24 (23)	0.21, 0.24, 0.29
O(17)	7.26 (24)	10.01 (30)	4.06 (19)	0.30 (20)	1.27 (17)	0.29 (18)	0.22, 0.30, 0.36
C(18)	4.76 (28)	5.40 (30)	4.95 (27)	1.43 (24)	−0.18 (21)	0.77 (24)	0.20, 0.27, 0.29
O(18)	8.16 (27)	5.69 (23)	8.20 (26)	1.43 (20)	−1.05 (20)	1.16 (20)	0.23, 0.31, 0.36
C(19)	4.55 (27)	6.33 (33)	3.85 (25)	−0.42 (25)	0.15 (20)	−0.19 (23)	0.22, 0.24, 0.28
O(19)	6.46 (22)	5.59 (22)	6.99 (22)	−1.12 (18)	0.57 (17)	−0.61 (18)	0.24, 0.30, 0.30
C(110)	3.20 (26)	10.88 (46)	4.02 (27)	0.47 (27)	0.34 (21)	1.41 (25)	0.20, 0.22, 0.38
O(110)	3.61 (21)	20.06 (53)	6.99 (26)	0.91 (25)	1.01 (19)	2.47 (27)	0.21, 0.29, 0.51
C(1)	2.68 (20)	3.59 (24)	3.38 (21)	0.19 (18)	0.02 (16)	0.31 (18)	0.18, 0.21, 0.22
N(1)	4.54 (22)	4.04 (21)	4.04 (19)	−0.18 (18)	0.64 (16)	−0.50 (16)	0.21, 0.23, 0.24
C(1A)	7.58 (37)	4.40 (30)	6.98 (35)	0.33 (28)	1.48 (30)	−1.47 (29)	0.21, 0.30, 0.32
C(1B)	6.12 (34)	5.72 (33)	6.06 (33)	−1.83 (28)	0.65 (30)	−0.60 (28)	0.22, 0.28, 0.31
				Molecule 2			
Ru(21)	4.248 (24)	4.259 (25)	4.116 (23)	0.091 (16)	0.447 (17)	0.079 (15)	0.226, 0.232, 0.235
Ru(22)	3.675 (23)	3.618 (23)	3.826 (22)	0.168 (15)	−0.187 (16)	−0.250 (15)	0.200, 0.211, 0.241
Ru(23)	3.911 (24)	3.988 (25)	4.658 (24)	0.060 (16)	0.532 (17)	−0.838 (16)	0.207, 0.223, 0.258
C(21)	5.36 (30)	7.34 (37)	5.02 (29)	0.24 (26)	0.57 (24)	0.25 (26)	0.25, 0.26, 0.31
O(21)	9.61 (30)	13.87 (42)	5.45 (22)	0.86 (28)	1.41 (21)	−2.66 (24)	0.24, 0.35, 0.43
C(22)	7.64 (40)	5.58 (36)	7.31 (37)	0.04 (29)	1.44 (30)	0.86 (29)	0.26, 0.30, 0.32
O(22)	11.26 (36)	6.30 (27)	12.04 (35)	−3.11 (24)	2.78 (27)	0.92 (24)	0.25, 0.38, 0.41
C(23)	6.17 (34)	6.78 (36)	5.66 (30)	1.78 (27)	0.51 (25)	1.98 (26)	0.22, 0.28, 0.33
O(23)	7.66 (29)	12.20 (39)	8.88 (29)	3.94 (27)	−0.19 (23)	2.95 (26)	0.23, 0.35, 0.44
C(24)	5.07 (27)	3.08 (24)	4.73 (26)	0.26 (21)	−0.63 (20)	−0.22 (20)	0.20, 0.22, 0.28
O(24)	7.45 (24)	4.66 (20)	5.91 (21)	0.29 (17)	−0.46 (17)	−0.94 (16)	0.23, 0.27, 0.33
C(25)	5.66 (30)	5.20 (30)	4.76 (28)	0.90 (24)	−0.42 (22)	−0.09 (23)	0.23, 0.25, 0.30
O(25)	9.08 (29)	8.88 (30)	5.33 (21)	1.77 (23)	−2.34 (20)	−0.12 (19)	0.22, 0.32, 0.39
C(26)	5.24 (31)	4.60 (29)	5.67 (29)	−0.17 (34)	0.30 (24)	0.55 (22)	0.24, 0.25, 0.28
O(26)	5.37 (22)	6.95 (24)	8.39 (25)	−0.22 (18)	1.62 (18)	1.23 (19)	0.25, 0.29, 0.34
C(27)	5.22 (30)	5.38 (34)	6.31 (31)	0.88 (24)	0.53 (25)	−0.79 (26)	0.23, 0.27, 0.30
O(27)	11.44 (34)	11.22 (35)	4.45 (20)	2.39 (26)	0.80 (22)	0.82 (21)	0.24, 0.34, 0.42
C(28)	4.90 (30)	6.64 (35)	6.99 (33)	−0.16 (26)	0.30 (25)	−3.91 (27)	0.19, 0.25, 0.37
O(28)	3.99 (21)	11.05 (35)	11.46 (31)	−0.67 (21)	−0.10 (21)	−6.38 (26)	0.21, 0.26, 0.47
C(29)	5.07 (29)	4.36 (27)	5.08 (26)	0.56 (24)	0.35 (22)	−0.60 (21)	0.22, 0.25, 0.27
O(29)	3.83 (18)	7.50 (25)	8.42 (24)	0.73 (18)	0.27 (17)	−0.72 (18)	0.22, 0.30, 0.34
C(210)	5.80 (31)	5.14 (32)	7.28 (34)	−0.99 (26)	3.34 (26)	−0.36 (26)	0.20, 0.26, 0.34
O(210)	10.54 (33)	4.14 (22)	14.21 (38)	0.19 (22)	6.20 (28)	1.05 (23)	0.22, 0.29, 0.46
C(2)	3.53 (24)	4.09 (25)	4.02 (23)	−0.21 (20)	0.05 (19)	−0.89 (19)	0.19, 0.22, 0.25
N(2)	3.94 (21)	5.92 (25)	4.78 (22)	−0.05 (20)	0.16 (18)	−1.61 (18)	0.21, 0.23, 0.30
C(2A)	5.23 (33)	8.52 (43)	7.91 (41)	−1.12 (34)	2.02 (31)	−1.58 (34)	0.24, 0.29, 0.36
C(2B)	4.60 (31)	9.37 (45)	7.07 (38)	2.65 (35)	−1.51 (28)	−2.89 (33)	0.20, 0.26, 0.41

^{a} These anisotropic thermal parameters are analogous to the usual form of the isotropic thermal parameter and have units of A^2. They enter the expression for the structure factor in the form exp$[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. ^{b} See footnote a to Table III. ^{c} These values correspond to the root-mean-square amplitudes of vibration (in A) of the atom along the three principal axes (minor, median, major, respectively) of its vibration ellipsoid. For relative orientations, see the figures.

Å). The axial Ru–CO linkages are, of course, each trans to another carbonyl ligand and would normally be expected to have considerably more competition for π-electron density in their ruthenium–carbon bonds.

Ruthenium–carbonyl bond lengths involving the remaining ruthenium atoms show one significant feature—those trans to the C=NMe₂ ligand have an average value of 1.967 Å (σ(av) = 0.006 Å) and are significantly longer than those trans to Ru(13) or Ru(23) [by 0.069 (8) Å or ca. 8.5σ] and those trans to the hydride [by 0.069 (7) or ca. 10σ]. This result would tend to suggest that the C=NMe₂ ligand is an extraordinarily good π acceptor and/or that it exerts a strong

trans-lengthening influence (structural trans effect).

The bridging hydride and C=NMe₂ ligands take up orientations such that the Ru–H–Ru planes make angles of 117.10 and 116.62°, respectively, with the appropriate Ru₃ plane and the Ru–C(1 or 2)–Ru planes make angles of 100.38 and 100.10° with the Ru₃ planes. Angles between the bridging ligands are as follows: [Ru(11)–H(1)–Ru(12)]–[Ru(11)–C(1)–Ru(12)] = 142.51° and [Ru(21)–H(2)–Ru(22)]–[Ru(21)–C(2)–Ru(22)] = 143.28°.

The Ru(11)–C(1)–Ru(12) system is parallel to but is not coplanar with the plane defined by the C(1A)–N(1)–C(1B) system. The two planes are, however, separated by only 0.07

Table V. Interatomic Bond Distances (A) and Esd's[a] for $HRu_3(CO)_{10}(C=NMe_2)$

|	Molecule 1		Molecule 2
A. Ruthenium–Ruthenium and Ruthenium–Hydride Distances			
Ru(11)–Ru(12)	2.7997 (5)	Ru(21)–Ru(22)	2.8016 (6)
Ru(11)–Ru(13)	2.8288 (6)	Ru(21)–Ru(23)	2.8336 (6)
Ru(12)–Ru(13)	2.8279 (5)	Ru(22)–Ru(23)	2.8216 (6)
Ru(11)–H(1)	1.93 (5)	Ru(21)–H(2)	1.80 (3)
Ru(12)–H(1)	1.85 (5)	Ru(22)–H(2)	1.82 (3)
B. Ruthenium–Carbonyl Distances			
Ru(11)–C(11)	1.901 (5)	Ru(21)–C(21)	1.896 (6)
Ru(11)–C(12)	1.907 (5)	Ru(21)–C(22)	1.895 (6)
Ru(11)–C(13)	1.983 (5)	Ru(21)–C(23)	1.953 (6)
Ru(12)–C(14)	1.911 (5)	Ru(22)–C(24)	1.886 (6)
Ru(12)–C(15)	1.892 (5)	Ru(22)–C(25)	1.897 (5)
Ru(12)–C(16)	1.962 (5)	Ru(22)–C(26)	1.969 (6)
Ru(13)–C(17)	1.917 (5)	Ru(23)–C(27)	1.924 (6)
Ru(13)–C(18)	1.924 (6)	Ru(23)–C(28)	1.930 (6)
Ru(13)–C(19)	1.921 (6)	Ru(23)–C(29)	1.908 (5)
Ru(13)–C(110)	1.906 (5)	Ru(23)–C(210)	1.903 (6)
C. Ruthenium–Carbon Distances			
Ru(11)–C(1)	2.039 (4)	Ru(21)–C(2)	2.034 (5)
Ru(12)–C(1)	2.018 (4)	Ru(22)–C(2)	2.037 (5)
D. Carbon–Oxygen Distances			
C(11)–O(11)	1.131 (5)	C(21)–O(21)	1.140 (6)
C(12)–O(12)	1.127 (5)	C(22)–O(22)	1.133 (7)
C(13)–O(13)	1.110 (5)	C(23)–O(23)	1.122 (6)
C(14)–O(14)	1.115 (5)	C(24)–O(24)	1.138 (5)
C(15)–O(15)	1.146 (5)	C(25)–O(25)	1.130 (5)
C(16)–O(16)	1.131 (5)	C(26)–O(26)	1.124 (6)
C(17)–O(17)	1.139 (6)	C(27)–O(27)	1.131 (6)
C(18)–O(18)	1.142 (6)	C(28)–O(28)	1.139 (6)
C(19)–O(19)	1.143 (6)	C(29)–O(29)	1.145 (6)
C(110)–O(110)	1.121 (6)	C(210)–O(210)	1.126 (6)
E. Carbon–Nitrogen Distances			
C(1)–N(1)	1.279 (5)	C(2)–N(2)	1.280 (6)
C(1A)–N(1)	1.481 (7)	C(2A)–N(2)	1.469 (8)
C(1B)–N(1)	1.455 (7)	C(2B)–N(2)	1.465 (8)
F. Carbon–Methyl Hydrogen Distances			
C(1A)–H(11A)	1.12 (6)	C(2A)–H(21A)	0.87 (6)
C(1A)–H(12A)	0.94 (6)	C(2A)–H(22A)	0.95 (7)
C(1A)–H(13A)	1.00 (6)	C(2A)–H(23A)	1.01 (6)
C(1B)–H(11B)	0.81 (5)	C(2B)–H(21B)	0.86 (7)
C(1B)–H(12B)	0.78 (8)	C(2B)–H(22B)	0.78 (8)
C(1B)–H(13B)	1.04 (6)	C(2B)–H(23B)	0.80 (6)

[a] Esd's, shown in parentheses, are right-adjusted to the last digit of the preceding number. These calculations, via the Fortran IV program STAN1, include the effects of the full positional covariance matrix and the uncertainties in the unit cell parameters. No corrections were applied for the possible effects of thermal motion.

Å. A similar feature is observed for the Ru(21)–C(2)–Ru(22) and C(2A)–N(2)–C(2B) moieties. (See Table VII.) The $Ru_2C=NMe_2$ systems thus have a slightly "stepped" configuration.

Ruthenium–carbon bond lengths to the $C=NMe_2$ ligand are both symmetric and equivalent. Individual values are Ru(11)–C(1) = 2.039 (4) Å, Ru(12)–C(1) = 2.018 (4) Å, Ru(21)–C(2) = 2.034 (5) Å, and Ru(22)–C(2) = 2.037 (5) Å. The average value is 2.032 Å [σ(ext) = 0.010 Å, σ(av) = 0.005 Å].[26]

Distances within the $C=NMe_2$ ligands [C(1)–N(1) = 1.279 (5) Å, C(2)–N(2) = 1.280 (6) Å; C(1A)–N(1) = 1.481 (7) Å, C(1B)–N(1) = 1.455 (7) Å, C(2A)–N(2) = 1.469 (8) Å, C(2B)–N(2) = 1.465 (8) Å] are consistent with there being a C=N linkage. For comparison we may note that the two C=N linkages in $[(CF_3)_2C=N]_2Mn_2(CO)_7$, III,[27] are 1.258 (9) and 1.259 (9) Å.

Based upon the structural data, the $C=NMe_2$ ligand is correctly written in the 1,2-dipolar "ylide" form, IV, and is,

III

IV
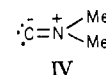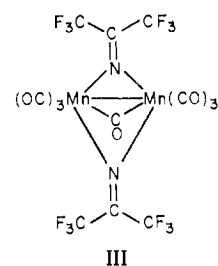
formally, a three-electron donor. As such, it is expected to show certain electronic and structural similarities to such other three-electron donors as nitric oxide (NO), aryldiazo (RN=N–) ligands, and alkylidenimino ($R_2C=N$–) ligands.

The Bridging Hydride Ligands in $HRu_3(CO)_{10}(C=NMe_2)$. Each of the μ_2-bridging hydride ligands has been located with reasonable precision (σ = 0.03–0.05 Å). The resulting ruthenium–hydrogen bond lengths are as follows: Ru(11)–H(1) = 1.93 (5) Å and Ru(12)–H(1) = 1.85 (5) Å in molecule 1; Ru(21)–H(2) = 1.80 (3) Å and Ru(22)–H(2) = 1.82 (3) Å in molecule 2. The average value is 1.85 Å (σ(ext) = 0.06 Å, σ(av) = 0.03 Å). Ruthenium–hydrogen–ruthenium angles are Ru(11)–H(1)–Ru(12) = 95.4 (24)° and Ru(21)–H(2)–Ru(22) = 101.3 (17)°; the average value is 98.4° (σ(ext) = 4.2°, σ(av) = 3.0°).

We have noted previously that a single, unsupported bridging hydride ligand normally causes a lengthening of a metal–metal bond (see below). In the present molecule the hydrido-bridged Ru–Ru bonds are *shorter* than the nonbridged Ru–Ru bonds by 0.0273 (26) Å [average bridged Ru–Ru distance is 2.8007 Å (σ(ext) = 0.0013 Å, σ(av) = 0.0010 Å); average nonbridged Ru–Ru distance is 2.8280 Å (σ(ext) = 0.0049 Å, σ(av) = 0.0025 Å)]. The explanation of this is, of course, that the (M–M) bond-lengthening influence of the μ_2-hydride ligand is more than counterbalanced by the (M–M) bond-shortening effect of the μ_2-$C^-=N^+Me_2$ ligand.

Bridging Hydride Ligands and Their Effect on the Associated Metal–Metal Distance(s)—a Coherent View. The effect of bridging hydride ligands on the associated metal–metal distance (or distances) has recently been subject to considerable obfuscation. It seems appropriate, therefore, to review the various types of hydrido-bridged metal–metal vectors which have been revealed by crystallographic scrutiny and to outline any generalizations pertinent to the assembled data.

(1) Species with a Single Unsupported μ_2-Hydride Ligand between Two Metal Atoms. At first glance it would seem appropriate to subdivide this category into "linear" and "bent" systems. Further considerations suggest that the borderline between these two possible classes is indistinct and could, in fact, be drawn at a number of different points (see below). For this reason these species are dealt with as a single group and we consider representative members in order of decreasing M–H–M angle.

It has been observed that species with a linear or "close-to-linear" unsupported M–H–M system (i) have an unusual *eclipsed* rotomeric conformation of ligands relative to the metal–metal vector and (ii) have long M⋯M distances. Even though such systems are conventionally represented as in V, it is believed that there is still direct overlap of metal

M- - -H- - -M

V
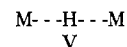
orbitals in the three-center M–H–M bond. Thus, Dahl and co-workers (ref 28, footnote 85) stated, ". . .calculations clearly demonstrated the dominance of the metal–metal interaction

Table VI. Intramolecular Angles (deg) and Esd's[a] for HRu₃(CO)₁₀(C=NMe₂)

Molecule 1		Molecule 2		Molecule 1		Molecule 2	
A. Ruthenium–Ruthenium–Ruthenium Angles				**F. Carbon–Ruthenium–Carbon Angles**			
Ru(13)–Ru(11)–Ru(12)	60.32 (1)	Ru(23)–Ru(21)–Ru(12)	60.09 (2)	C(11)–Ru(11)–C(1)	95.19 (19)	C(21)–Ru(21)–C(2)	93.56 (20)
Ru(11)–Ru(12)–Ru(13)	60.35 (1)	Ru(21)–Ru(22)–Ru(23)	60.52 (2)	C(12)–Ru(11)–C(1)	100.18 (20)	C(22)–Ru(21)–C(2)	99.27 (23)
Ru(12)–Ru(13)–Ru(11)	59.33 (1)	Ru(22)–Ru(23)–Ru(21)	59.39 (1)	C(13)–Ru(11)–C(1)	162.24 (18)	C(23)–Ru(21)–C(2)	163.82 (21)
				C(11)–Ru(11)–C(12)	95.14 (20)	C(21)–Ru(21)–C(22)	97.13 (26)
B. Ruthenium–Hydride–Ruthenium and Ruthenium–Carbon–Ruthenium Angles				C(11)–Ru(11)–C(13)	95.27 (20)	C(21)–Ru(21)–C(23)	94.33 (23)
Ru(11)–H(1)–Ru(12)	95.4 (24)	Ru(21)–H(2)–Ru(22)	101.3 (17)	C(12)–Ru(11)–C(13)	93.13 (21)	C(22)–Ru(21)–C(23)	93.74 (26)
Ru(11)–C(1)–Ru(12)	87.27 (17)	Ru(21)–C(2)–Ru(22)	87.98 (17)	C(14)–Ru(12)–C(1)	92.14 (18)	C(24)–Ru(22)–C(2)	93.70 (20)
				C(15)–Ru(12)–C(1)	97.85 (18)	C(25)–Ru(22)–C(2)	99.93 (21)
C. Ruthenium–Ruthenium–Hydride and Ruthenium–Ruthenium–Carbon Angles				C(16)–Ru(12)–C(1)	165.15 (17)	C(26)–Ru(22)–C(2)	164.38 (20)
Ru(12)–Ru(11)–H(1)	41.3 (16)	Ru(22)–Ru(21)–H(2)	39.6 (11)	C(14)–Ru(12)–C(15)	97.70 (19)	C(24)–Ru(22)–C(25)	95.77 (21)
Ru(11)–Ru(12)–H(1)	43.4 (17)	Ru(21)–Ru(22)–H(2)	39.1 (11)	C(14)–Ru(12)–C(16)	94.71 (20)	C(24)–Ru(22)–C(26)	95.48 (22)
Ru(13)–Ru(11)–H(1)	83.6 (15)	Ru(23)–Ru(21)–H(2)	82.1 (11)	C(15)–Ru(12)–C(16)	94.27 (19)	C(25)–Ru(22)–C(26)	91.70 (23)
Ru(13)–Ru(12)–H(1)	85.0 (16)	Ru(23)–Ru(22)–H(2)	82.2 (11)	C(17)–Ru(13)–C(18)	91.47 (22)	C(27)–Ru(23)–C(28)	92.46 (23)
Ru(12)–Ru(11)–C(1)	46.06 (12)	Ru(22)–Ru(21)–C(2)	46.57 (13)	C(17)–Ru(13)–C(19)	93.72 (21)	C(27)–Ru(23)–C(29)	95.00 (22)
Ru(11)–Ru(12)–C(1)	46.67 (12)	Ru(21)–Ru(22)–C(2)	46.46 (13)	C(17)–Ru(13)–C(110)	104.28 (21)	C(27)–Ru(23)–C(210)	101.40 (23)
Ru(13)–Ru(11)–C(1)	76.65 (12)	Ru(23)–Ru(21)–C(2)	76.56 (12)	C(18)–Ru(13)–C(19)	170.35 (21)	C(28)–Ru(23)–C(29)	169.41 (21)
Ru(13)–Ru(12)–C(1)	76.97 (12)	Ru(23)–Ru(22)–C(2)	76.80 (12)	C(18)–Ru(13)–C(110)	94.51 (24)	C(28)–Ru(23)–C(210)	93.93 (24)
				C(19)–Ru(13)–C(110)	92.09 (24)	C(29)–Ru(23)–C(210)	91.95 (22)
D. Ruthenium–Ruthenium–Carbonyl Angles				**G. Ruthenium–Carbon–Oxygen Angles**			
Ru(12)–Ru(11)–C(11)	110.41 (14)	Ru(22)–Ru(21)–C(21)	109.97 (18)	Ru(11)–C(11)–O(11)	178.7 (6)	Ru(21)–C(21)–O(21)	179.2 (4)
Ru(12)–Ru(11)–C(12)	137.59 (15)	Ru(22)–Ru(21)–C(22)	135.84 (19)	Ru(11)–C(12)–O(12)	178.9 (8)	Ru(21)–C(22)–O(22)	178.7 (9)
Ru(12)–Ru(11)–C(13)	116.51 (14)	Ru(22)–Ru(21)–C(23)	117.30 (17)	Ru(11)–C(13)–O(13)	179.0 (7)	Ru(21)–C(23)–O(23)	178.3 (7)
Ru(13)–Ru(11)–C(11)	170.43 (15)	Ru(23)–Ru(21)–C(21)	169.24 (18)	Ru(12)–C(14)–O(14)	179.4 (4)	Ru(22)–C(24)–O(24)	179.2 (4)
Ru(13)–Ru(11)–C(12)	91.27 (15)	Ru(23)–Ru(21)–C(22)	88.78 (18)	Ru(12)–C(15)–O(15)	178.4 (5)	Ru(22)–C(25)–O(25)	179.6 (3)
Ru(13)–Ru(11)–C(13)	91.46 (14)	Ru(23)–Ru(21)–C(23)	94.25 (17)	Ru(12)–C(16)–O(16)	177.5 (5)	Ru(22)–C(26)–O(26)	178.8 (6)
Ru(11)–Ru(12)–C(14)	109.66 (14)	Ru(21)–Ru(22)–C(24)	110.07 (15)	Ru(13)–C(17)–O(17)	177.4 (5)	Ru(23)–C(27)–O(27)	178.2 (8)
Ru(11)–Ru(12)–C(15)	134.05 (13)	Ru(21)–Ru(22)–C(25)	137.00 (17)	Ru(13)–C(18)–O(18)	175.3 (5)	Ru(23)–C(28)–O(28)	175.1 (5)
Ru(11)–Ru(12)–C(16)	118.49 (13)	Ru(21)–Ru(22)–C(26)	118.18 (15)	Ru(13)–C(19)–O(19)	176.4 (5)	Ru(23)–C(29)–O(29)	176.7 (5)
Ru(13)–Ru(12)–C(14)	168.62 (14)	Ru(23)–Ru(22)–C(24)	169.73 (16)	Ru(13)–C(110)–O(110)	178.0 (7)	Ru(23)–C(210)–O(210)	178.2 (6)
Ru(13)–Ru(12)–C(15)	87.20 (13)	Ru(23)–Ru(22)–C(25)	89.77 (16)				
Ru(13)–Ru(12)–C(16)	95.16 (13)	Ru(23)–Ru(22)–C(26)	92.98 (16)	**H. Ruthenium–Carbon–Nitrogen Angles**			
Ru(11)–Ru(13)–C(17)	162.20 (15)	Ru(21)–Ru(23)–C(27)	158.23 (17)	Ru(11)–C(1)–N(1)	136.8 (3)	Ru(21)–C(2)–N(2)	136.8 (4)
Ru(11)–Ru(13)–C(18)	87.98 (15)	Ru(21)–Ru(23)–C(28)	88.35 (16)	Ru(12)–C(1)–N(1)	135.8 (3)	Ru(22)–C(2)–N(2)	136.0 (4)
Ru(11)–Ru(13)–C(19)	84.60 (14)	Ru(21)–Ru(23)–C(29)	81.93 (15)	**I. Carbon–Nitrogen–Carbon Angles**			
Ru(11)–Ru(13)–C(110)	93.49 (15)	Ru(21)–Ru(23)–C(210)	100.25 (17)	C(1)–N(1)–C(1A)	123.7 (4)	C(2)–N(2)–C(2A)	123.0 (5)
Ru(12)–Ru(13)–C(17)	102.90 (14)	Ru(22)–Ru(23)–C(27)	98.84 (17)	C(1)–N(1)–C(1B)	123.7 (4)	C(2)–N(2)–C(2B)	122.2 (5)
Ru(12)–Ru(13)–C(18)	90.03 (14)	Ru(22)–Ru(23)–C(28)	89.99 (16)	C(1A)–N(1)–C(1B)	112.4 (4)	C(2A)–N(2)–C(2B)	114.6 (5)
Ru(12)–Ru(13)–C(19)	80.89 (15)	Ru(22)–Ru(23)–C(29)	81.45 (15)	**J. Methyl Hydrogen–Carbon–Hydrogen Angles**			
Ru(12)–Ru(13)–C(110)	152.30 (15)	Ru(22)–Ru(23)–C(210)	159.18 (17)	H(11A)–C(1A)–H(12A)	96 (4)	H(21A)–C(2A)–H(22A)	124 (6)
E. Hydride–Ruthenium–Carbon Angles				H(11A)–C(1A)–H(13A)	105 (4)	H(21A)–C(2A)–H(23A)	107 (5)
H(1)–Ru(11)–C(11)	90.3 (15)	H(2)–Ru(21)–C(21)	92.2 (11)	H(12A)–C(1A)–H(13A)	129 (5)	H(22A)–C(2A)–H(23A)	110 (5)
H(1)–Ru(11)–C(12)	174.0 (18)	H(2)–Ru(21)–C(22)	170.6 (12)	H(11B)–C(1B)–H(12B)	106 (7)	H(21B)–C(2B)–H(22B)	120 (8)
H(1)–Ru(11)–C(13)	84.0 (16)	H(2)–Ru(21)–C(23)	84.8 (11)	H(11B)–C(1B)–H(13B)	124 (5)	H(21B)–C(2B)–H(23B)	100 (6)
H(1)–Ru(11)–C(1)	81.7 (16)	H(2)–Ru(21)–C(2)	80.8 (11)	H(12B)–C(1B)–H(13B)	100 (6)	H(22B)–C(2B)–H(23B)	107 (7)
H(1)–Ru(12)–C(14)	90.7 (16)	H(2)–Ru(22)–C(24)	92.5 (13)				
H(1)–Ru(12)–C(15)	171.3 (18)	H(2)–Ru(22)–C(25)	171.7 (12)				
H(1)–Ru(12)–C(16)	82.7 (16)	H(2)–Ru(22)–C(26)	86.7 (11)				
H(1)–Ru(12)–C(1)	84.1 (16)	H(2)–Ru(22)–C(2)	80.3 (11)				

[a] See footnote to Table V.

Table VII. Least-Squares Planes, Deviations Therefrom,[a] and Angles between Planes, for $HRu_3(CO)_{10}(C=NMe_2)$

Atom	Dev, A	Atom	Dev, A

Molecule 1

Plane 1: $0.1549X + 0.9879Y + 0.0034Z = 11.698$

Atom	Dev, A	Atom	Dev, A
Ru(11)*	0.000	O(14)	0.311
Ru(12)*	0.000	C(17)	0.028
Ru(13)*	0.000	C(17)	0.057
C(11)	0.080	C(110)	−0.187
O(11)	0.123	O(110)	−0.330
C(14)	0.189		

Plane 2: $0.5684X + 0.3695Y + 0.7351Z = 9.844$

Ru(11)*	0.000	H(1)*	0.000
Ru(12)*	0.000		

Plane 3: $0.5222X - 0.2671Y + 0.8099Z = 2.880$

Ru(11)*	0.000	N(1)	0.072
Ru(12)*	0.000	C(1A)	0.070
C(1)*	0.000	C(1B)	0.072

Plane 4: $0.5217X - 0.2664Y + 0.8105Z = 2.957$

N(1)*	0.000	Ru(11)	−0.072
C(1A)*	0.000	Ru(12)	−0.074
C(1B)*	0.000	C(1)	−0.072

Molecule 2

Plane 5: $0.9956X - 0.0059Y + 0.0931Z = 7.544$

Ru(21)*	0.000	O(24)	−0.240
Ru(22)*	0.000	C(27)	0.019
Ru(23)*	0.000	O(27)	0.005
C(21)	−0.142	C(210)	0.152
O(21)	−0.239	O(210)	0.267
C(24)	−0.140		

Plane 6: $-0.5028X + 0.6191Y + 0.6033Z = -0.001$

Ru(21)*	0.000	H(2)*	0.000
Ru(22)*	0.000		

Plane 7: $0.1122X + 0.6778Y + 0.7266Z = 5.044$

Ru(21)*	0.000	N(2)	0.083
Ru(22)*	0.000	C(2A)	0.094
C(2)*	0.000	C(2B)	0.084

Plane 8: $0.1196X + 0.6797Y + 0.7236Z = 5.159$

N(2)*	0.000	Ru(21)	−0.069
C(2A)*	0.000	Ru(22)	−0.058
C(2B)*	0.000	C(2)	−0.074

Angles between the Planes

Angle	Value, deg
Plane 1–plane 2	62.90
Plane 1–plane 3	100.38
Plane 1–plane 4	100.35
Plane 2–plane 3	142.51
Plane 2–plane 4	142.55
Plane 3–plane 4	179.91
Plane 5–plane 6	63.38
Plane 5–plane 7	100.10
Plane 5–plane 8	100.51
Plane 6–plane 7	143.28
Plane 6–plane 8	142.87
Plane 7–plane 8	179.53
Plane 1–plane 5	98.55
Plane 2–plane 6	112.73
Plane 3–plane 7	117.78
Plane 4–plane 8	117.89

[a] Equations of planes are expressed in the orthonormal (A) coordinate system given by $X = xa + zc \cos \beta$, $Y = yb$, and $Z = zc \sin \beta$. Atoms marked by an asterisk were assigned unit weight; all others were given zero weight.

from orbital overlap considerations in the three center Cr–H–Cr bond [of $HCr_2(CO)_{10}^-$] at the observed Cr–Cr internuclear distance." Thus, rather surprisingly, even the linear M–H–M system is best described as a "closed" rather than "open" two-electron, three-center bond.

Table VIII. Statistics on Ruthenium–Carbonyl Linkages in $HRu_3(CO)_{10}(C=NMe_2)$

Location of carbonyl ligand	Linkages involved	Av bond length, A	σ(ext),[a] A	σ(av),[b] A
(a) "Axial" on Ru(13) and Ru(23)–trans to CO	Ru(13)–C(18) Ru(13)–C(19) Ru(23)–C(28) Ru(23)–C(29)	1.921	0.009	0.005
(b) "Equatorial" on Ru(13) and Ru(23)–trans to Ru	Ru(13)–C(17) Ru(13)–C(110) Ru(23)–C(27) Ru(23)–C(210)	1.913	0.010	0.005
(c) Trans to Ru(13) or Ru(23)	Ru(11)–C(11) Ru(12)–C(14) Ru(21)–C(21) Ru(22)–C(24)	1.898	0.010	0.005
(d) Trans to hydride	Ru(11)–C(12) Ru(12)–C(15) Ru(21)–C(22) Ru(22)–C(25)	1.898	0.007	0.003
(e) Trans to (C=NMe$_2$)	Ru(11)–C(13) Ru(12)–C(16) Ru(21)–C(23) Ru(22)–C(26)	1.967	0.013	0.006

[a] σ(ext), an *external* estimate of the esd on an individual measurement, is defined by $\sigma(ext) = [\Sigma(x_i - \bar{x})^2/(N - 1)]^{1/2}$ where x_i is the ith of N "equivalent" measurements and $\bar{x}$ is the average of these N measurements. [b] σ(av), the external estimate of the esd associated with the averaged value, is defined by $\sigma(av) = [\Sigma(x_i - \bar{x})^2/N(N - 1)]^{1/2}$.

The question of "open" vs. "closed" two-electron, three-center bonds in species with a bent M–H–M system has been considered by (among others) Churchill and Ni,[29] who depicted them as VI and VII, and by Olsen et al.,[30] who sug-

VI VII

VIII IX
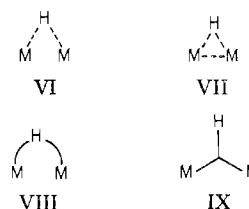
gested adopting the formalism of boron hydride chemistry, i.e., VIII and IX. Clearly, as emphasized by Churchill and Chang,[31] the *symmetry* of a system with M–H–M bridges is such that direct metal–metal interaction is always possible (since the hydrogen atom can use only its spherically symmetric 1s orbital for forming molecular orbitals). The problem, then, is in determining the magnitude of overlap between orbitals on the two metal atoms. All qualitative indications are, however, that direct metal–metal interaction is of considerable importance.[32,33]

In few cases have μ_2-hydride ligands been located directly; often their location is inferred indirectly by assuming them to be directly trans to another ligand in an otherwise symmetrical array about a metal atom (see footnote 84 of ref 28). Angles determined by this method are identified by "estd" in the following discussion.

The $HCr_2(CO)_{10}^-$ ion has a precisely linear[34] Cr–H–Cr system (i.e., Cr–H–Cr = 180° (estd)), the two $Cr(CO)_5$ moieties are in an eclipsed arrangement, and the chromium–chromium distance of 3.406 (9) A is ca. 0.44 A longer than that of 2.97 (1) A occurring in the conjugate base, $Cr_2(CO)_{10}^{2-}$.[28] The $HReCr(CO)_{10}$ molecule is, unfortunately, partly disordered in the crystalline state,[35] but the Re–H–Cr system in this molecule is close to linear (177.5° (estd)), the $M(CO)_5$ residues are eclipsed, and the rhenium–chromium distance of 3.435 (1) A is, again, ca. 0.44 A longer than that

estimated for a rhenium–chromium single bond (2.995 Å based on $r(Cr) = 1.485$ Å in $Cr_2(CO)_{10}^{2-}$ and $r(Re) = 1.51$ Å in $Re_2(CO)_{10}$).

The Re–H–Re bond in $HRe_2Mn(CO)_{14}$[36] is apparently somewhat perturbed from linearity (Re–H–Re = 164° (estd)), but the coordination spheres about the two rhenium atoms are still eclipsed and the rhenium⋯rhenium distance of 3.392 (2) Å is still ca. 0.37 Å longer than the accepted Re–Re single-bond length of 3.02 Å.

In contrast to these results, $HRe_3(CO)_{14}$[37] (which is iso-connective with $HRe_2Mn(CO)_{14}$) has an Re–H–Re angle of 159° (estd), has a *staggered* arrangement of ligands on the two hydride-bridged rhenium atoms, and has a rhenium⋯rhenium distance of 3.295 (2) Å (i.e., now 0.28 Å longer than an Re–Re single bond). It is thus clear that the M–H–M system can easily be deformed by nonbonded intramolecular or intermolecular repulsions.

We note here that the $HW_2(CO)_9(NO)$ molecule, which has a tungsten–tungsten distance of 3.3292 (12) Å and an overall staggered conformation, has a true W–H–W angle of only 125.5° (by neutron diffraction)[30] whereas the estimated W–H–W angle, based on the angle of intersection of the axial carbonyl groups, is 159°. This result both strengthens the case for "closed" three-center M–H–M bonds and weakens the case for using the axial O–C–M vectors in estimating hydride ligand positions!

A number of structural studies of polynuclear species with bent, unsupported M–H–M systems have been carried out. Of particular significance in this regard are studies on the conjugate acid–base pair $H_2Re_3(CO)_{12}^-$[38] (X) and HRe_3-

X   XI
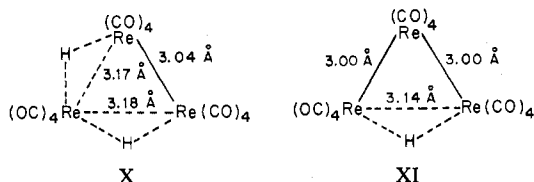
$(CO)_{12}^{2-}$[39] (XI) in which the effect of the hydride ligands on the metal–metal distances is unambiguously revealed. [Hydride ligands have actually been located in the related species $H_3Mn_3(CO)_{12}$; the hydride-bridged Mn–Mn distances average 3.112 (2) Å and the mean Mn–H–Mn angle is 131 (7)°.[21]]

In every known example, a single unsupported μ_2-hydride ligand causes its bridged metal–metal distance to be increased from its normal (M–M single-bond) value. The degree of expansion appears to be a function of the M–H–M angle and increases as the M–H–M angle increases, reaching a maximum for an angular value of 180°. It appears, also, that a reasonable estimate of an M–H–M angle may be made by assuming that each M–H distance is at (or just slightly longer than) the value expected for the analogous *terminal* M–H bond.

(2) Species with Two Unsupported μ_2-Hydrido Ligands Bridging a Pair of Metal Atoms. Few examples have been subjected to full crystallographic analysis. However, in $H_2Re_2(CO)_8$[40] the rhenium–rhenium distance is 2.896 (3) Å, in $H_2W_2(CO)_8^{2-}$[31] the tungsten–tungsten distance is 3.0162 (11) Å, and in $H_2Os_3(CO)_{10}$[32] the dihydro-bridged osmium–osmium distance is 2.670 Å. Each of these metal–metal distances is significantly *contracted* from the appropriate metal–metal single-bond length. However, a moment's reflection quickly reveals that comparing the metal–metal distance in a $M(\mu-H)_2M$ system with a metal–metal single bond is not a useful exercise. A mono(μ_2-hydrido)-bridged species may be regarded (crudely) as having a protonated metal–metal single bond (cf. $HCr_2(CO)_{10}^-$ and $Cr_2(CO)_{10}^{2-}$ above); a bis(μ_2-hydrido)-bridged species should corre-

spondingly be regarded as a doubly protonated double bond, and, as such, the resulting metal–metal distances should be compared with the lengths of metal–metal double bonds (most of which, regrettably, are unavailable). The three known $M(\mu-H)_2M$ species should therefore be depicted as in XII–XIV.

XII


XIII   XIV
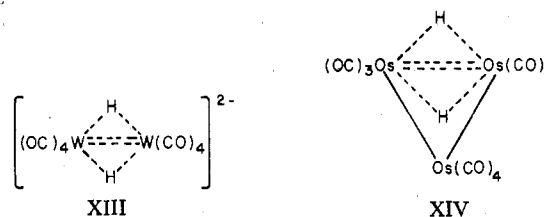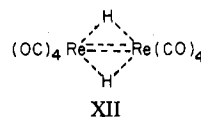
(3) Species with Three Unsupported μ_2-Hydrido Ligands between a Pair of Metal Atoms. To our knowledge, the only species of this nature investigated via x-ray crystallography are $H_3Fe_2(p_3)_2^+$[41] (p_3 = $CH_3C(CH_2PPh_2)_3$) and H_3Co_2-$(as_3)_2^+$[41] (as_3 = $CH_3C(CH_2AsPh_2)_3$). They have structures XV and XVI. The average Fe–H–Fe and Co–H–Co angles


XV   XVI
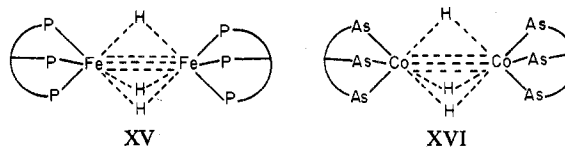
are 79.3 and 88.7°, respectively. Furthermore, the Fe–Fe distance of 2.332 (3) Å and the Co–Co distance of 2.377 (8) Å are each significantly shorter than the appropriate non-bridged metal–metal single bonds and (in keeping with our arguments in section (2), above) may be regarded as triply protonated triple bonds; the effect of the hydride ligands on the metal–metal linkage is then only properly assessed by comparing the observed values with those for the appropriate metal–metal triple bonds. [Triple-bond lengths in metal carbonyl species have been measured for very few species; one such measurement is for $[C_5Me_5Cr(CO)_2]_2$ in which d-$(Cr\equiv Cr) = 2.280$ (2) Å.[42]]

(4) Species with a Single Unsupported μ_3-Hydrido Ligand Spanning Three Metal Atoms. Only one molecule with this structural feature has been examined. In the octahedral metal cluster complex $H_2Ru_6(CO)_{18}$, two triply bridging hydride ligands span the mutually trans faces of the octahedron[43] (see XVII). The six hydrido-bridged ruthenium–ruthenium vectors

XVII
(all CO's omitted)
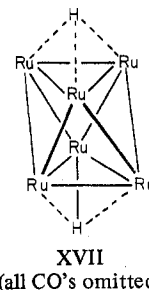
average 2.954 (3) Å and are 0.087 Å longer than the six nonbridged Ru–Ru bonds in the framework (average bond length 2.867 (5) Å).

(5) Species with More Than One μ_3-Hydrido Ligand Associated with a Metal–Metal Vector. The four Re–Re vectors in the tetrahedral cluster complex $H_4Re_4(CO)_{12}$ (XVIII) average 2.913 (8) Å[44]—i.e., are some 0.1 Å *shorter* than the recognized Re–Re single-bond distance of 3.02 Å. In
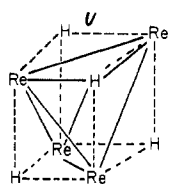
XVIII
(all CO's omitted)

$H_4Re_4(CO)_{12}$ each Re⋯Re vector is involved with *two* two-electron, four-center bonds. Detailed comparison of the Re–H–Re distances in this species can properly be made only with the deprotonated species $H_{4-n}Re_4(CO)_{12}{}^{n-}$, $4 \geq n > 0$.

(6) Species with μ_n-Bridging Ligands ($n > 3$). The only known species remaining in this category is HNb_6I_{11}; a neutron diffraction study on powdered samples of HNb_6I_{11} and DNb_6H_{11} has been interpreted[45] in terms of there being a μ_6-hydrido ligand in the center of an octahedral niobium cluster.

The claim that $HFeCo_3(CO)_{12}$ has a central μ_4-hydrido ligand[46,47] has been discredited by a structural study on $HFeCo_3(CO)_9[P(OMe)_3]_3$, which Kaesz et al.[48] have shown to possess a μ_3-hydride ligand (see XIX).
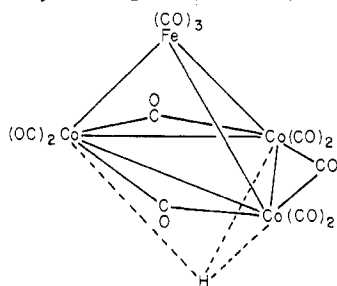
XIX

(7) M–H–M Bridges Supported by Other Bridging Ligands. This group of structures contains most of the species for which other authors have claimed that there is a lack of correlation of M–M distance with M–H–M bonding. The problem here can be outlined by considering the generalized bridging system $M(\mu\text{-H})(\mu\text{-A})M'$, XX. Clearly, the M⋯M' distance can be
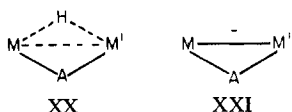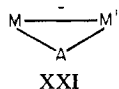
XX   **XXI**

used as a criterion for the presence or absence of the μ_2-hydrido ligand only if (i) A exerts no steric influence on the M⋯M distance or (ii) the magnitude of the steric influence of A can be estimated or measured and can thence be corrected for. (Probably, the best test that could be run is a structural study of XX in conjunction with one on its conjugate base $M(\mu\text{-A})M'^-$, XXI.)

Studies on the species $H_2Re_3(CO)_{12}{}^-$ and $HRe_3(CO)_{12}{}^{2-}$ (vide supra; X and XI) indicated that a triangulated metal cluster has a molecular architecture such that an unsupported μ_2-hydrido bridge causes the bridged metal–metal distance(s) to be expanded by ca. 0.1–0.2 Å relative to an analogous nonbridged metal–metal single bond. However, several trinuclear species are known in which the metal–metal distance for the $M(\mu\text{-H})(\mu\text{-A})M$ bridge is not appreciably greater (and, in some cases, is even shorter) than the nonbridged M–M distances within the same molecule. Despite some protestations to the contrary,[49] this phenomenon is not new. Thus, the nonbridged iron–iron distances in $HFe_3(CO)_{11}{}^-$ [50] (XXII) are 2.685 (3) Å while the iron–iron distance within the Fe(μ-H)(μ-CO)Fe system is 2.577 (3) Å—i.e., some 0.108 Å shorter! However, data on $Fe_3(CO)_{12}{}^{51}$ (XXIII) show that the bis(μ_2-carbonyl)-bridged iron–iron distance is 2.558 (1)
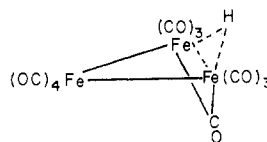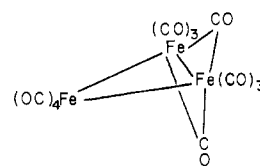
**XXII**   **XXIII**

Å; thus, clearly, the contraction of the hydrido-bridged Fe–Fe bond in $HFe_3(CO)_{12}{}^-$ is due to the bond-shortening influence of the μ_2-carbonyl ligand.
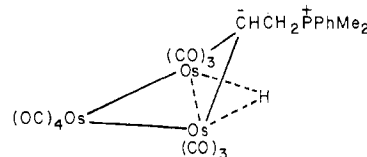
Similar arguments explain the very small differences between μ_2-hydrido-bridged metal–metal distances and nonbridged metal–metal distances in such molecules as HRu_3-$(CO)_{10}C{=}NMe_2$ (considered within this article), HFe_3-$(CO)_9(\mu_3\text{-}S(i\text{-}C_3H_7))$[49] (XXIV; Fe–Fe = 2.640 (2)–2.653 (2)
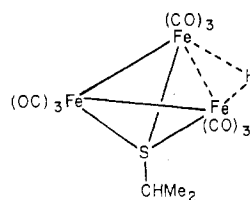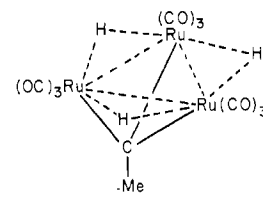
XXIV   **XXV**

XXVI

Å, Fe(H)Fe = 2.678 (2) Å), $H_3Ru_3(CO)_9(\mu_3\text{-CMe})$[52] (XXV; Ru(H)Ru = 2.842 Å as compared to Ru–Ru = 2.85 Å in $Ru_3(CO)_{12}$[53]), and $HOs_3(CO)_{10}(\mu_2\text{-C}^-HCH_2P^+PhMe_2)$[54] (XXVI; Os–Os = 2.8688 (6)–2.8729 (10) Å, Os(H)Os = 2.8002 (6) Å).

Registry No. $HRu_3(CO)_{10}(C{=}NMe_2)$, 59532-85-3.

Supplementary Material Available: Listing of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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Transition Metal Ions in High Formal Oxidation States. Structural Characterization of the Nickel and Copper Complexes of the 1,1-Dicarboethoxy-2,2-ethylenedithiolate Ligand

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Bis(trimethylphenylammonium) bis(1,1-dicarboethoxy-2,2-ethylenedithiolato)nickelate(II), $((CH_3)_3(C_6H_5)N)_2Ni(S_2C=C(COOC_2H_5)_2)_2$ (A), crystallizes in the triclinic space group $P\bar{1}$ with one molecule per unit cell. The cell dimensions are $a = 9.032$ (3) Å, $b = 8.716$ (4) Å, $c = 15.532$ (6) Å, $\alpha = 82.04$ (2)°, $\beta = 114.73$ (2)°, and $\gamma = 114.48$ (2) Å. Potassium bis(1,1-dicarboethoxy-2,2-ethylenedithiolato)cuprate(III) etherate, $KCu(S_2C=C(COOC_2H_5)_2)_2 \cdot O(C_2H_5)_2$ (B), crystallizes in the monoclinic space group $C2/c$ with four molecules per unit cell. The cell dimensions are $a = 13.781$ (3) Å, $b = 17.527$ (3) Å, $c = 12.903$ (2) Å, and $\beta = 107.21$ (1)°. Intensity data for both A and B were collected with a four-circle computer-controlled diffractometer using the θ–2θ scan technique. All 25 nonhydrogen atoms in A were refined anisotropically and the 24 hydrogen atoms were included as fixed atoms. In B one of the ligand ethyl groups and the unique ether ethyl group were constrained to refine as groups of fixed geometry. Of the remaining nonhydrogen atoms only the copper, sulfurs, and the carbonyl oxygen atoms were refined anisotropically. Refinement by full-matrix least squares on 451 data for A and 1571 data for B gave final R values of 0.038 for A and 0.060 for B. The geometry of the MS_4 moiety in both structures is square. Average values of selected bond distances and bond angles are as follows: for A, Ni–S = 2.195 (2) Å, S–S(intraligand) = 2.789 (2) Å, S–S(interligand) = 3.389 (2) Å, S–Ni–S(intraligand) = 78.90 (6)°, S–Ni–S(interligand) = 101.10 (6)°; for B, Cu–S = 2.195 (5) Å, S–S(intraligand) = 2.766 (6) Å, S–S(interligand) = 3.407 (8) Å, S–Cu–S(intraligand) = 78.14 (24)°, S–Cu–S(interligand) = 101.87 (23)°. A plot of normalized differences between corresponding structural parameters of the ligands in the two structures vs. the expected values of a normal distribution of random errors indicates systematic differences in the ligand structural parameters and a higher localization of charge on the sulfurs in B. These data and the identical M–S bond lengths in both structures suggest that in B the oxidation is centered in the Cu–S chromophore.

Introduction

One of the most interesting characteristics of coordination compounds with sulfur-containing ligands is the diversity of their redox properties. Detailed studies by various investigators[1] have indicated that the reversible oxidations observed with a variety of 1,2-dithiolate complexes[2] involve molecular orbitals whose metal and ligand characters vary with the type of ligand. With certain 1,1-dithiolates[3] irreversible oxidations give rise to sulfur-rich species[4] in which sulfur insertion results in an expansion of the metal–ligand four-membered ring.[5]

Recent electrochemical studies have shown that the dithiocarbamate complexes undergo reversible oxidation state changes.[6] Synthetic and x-ray studies indicate that the