obtained.[10,11] These can be considered to be derivatives of the perrhenate ion, ReO_4^-. The reaction of perrhenic acid in concentrated hydrochloric acid produces a yellow solution from which the hydrolytically unstable *fac*-$Cs_2ReO_3Cl_3$ was isolated.[10] The cold concentrated hydrohalic acids HCl and HBr react with TcO_4^- to produce the Tc(V) species, $TcOX_4^-$ that have been conveniently isolated as tetrabutylammonium salts in high yield.[6,7] In some preparations of the chloro complex, a transient yellow species was observed that rapidly reacts to give the green $TcOCl_4^-$. The yellow species is thought to be $TcO_3Cl_3^{2-}$ by analogy to the known rhenium chemistry.

In an attempt to characterize such a species, the reaction of TcO_4^- with cold, ethanolic hydrohalic acids in the presence of bpy and phen was undertaken. This led to the formation of the technetium(VII) complexes, TcO_3XL. These complexes were readily isolated due to their insolubility in the reaction medium. They are hydrolytically unstable, giving TcO_4^- upon reaction with H_2O, and are sparingly soluble in polar organic solvents. Their formulation is based on elemental analyses and vibrational spectroscopy.

Heating the reaction mixture causes reduction to the technetium(V) species, $TcOX_3L$. Alternatively, when L = bpy, these complexes can be prepared from *n*-Bu_4NTcOX_4 and ethanolic HX containing excess bpy. It is important that HCl is present in this preparation of $TcOCl_3$(bpy), otherwise the unstable ethoxy compound $TcOCl_2$(OEt)(bpy) is produced. The latter can be converted to $TcOCl_3$(bpy) by treatment with acetone/HCl.

The oxo-technetium(V) complexes are nonelectrolytes in CH_3CN and show a single strong Tc=O stretch in their infrared spectra. The band assigned to the Tc=O stretch in $TcOCl_3$(bpy) occurs at lower energy (ca. 10 cm^{-1}) than that found in the analogous rhenium complex.[9] This difference can be explained by the greater orbital overlap of 5d orbitals (Re) with the 2p orbitals of oxygen contrasted with that of 4d orbitals (Tc).[5] The 575-cm^{-1} band in $TcOCl_2$(OEt)(bpy) is in the range of metal-alkoxide stretches.[12]

The geometry of the MO_3XL species is likely to be a facial arrangement in keeping with the known tendency of d^0 metals to have mutually cis oxo ligands.[11,13] This is supported by the fact that the TcO_3X(bpy) complexes show two bands in the Tc=O region of the Raman spectra which is consistent with an idealized C_{3v} symmetry of the oxo ligands.

The isolation of these technetium(VII) complexes with poorly reducing ligands shows that such complexes are capable of existence, and, therefore, there may be similar heptavalent intermediates in the reactions of MO_4^- (M = Re, Tc) under acidic conditions that lead to the preparation of complexes in lower oxidation states with other ligands.

Acknowledgment. We thank the Department of Energy and the National Institutes of Health for research grants. We also thank Kevin Penfield and the MIT Spectroscopy Laboratory for their help in obtaining Raman spectra on the complexes.

Registry No. Trioxochloro(2,2′-bipyridine)technetium(VII), 78939-76-1; trioxochloro(1,10-phenanthroline)technetium(VII), 78939-77-2; trioxobromo(2,2′-bipyridine)technetium(VII), 78939-78-3; trioxochloro(2,2′-bipyridine)rhenium(VII), 57526-16-6; oxotrichloro(2,2′-bipyridine)technetium(V), 78939-79-4; oxotribromo-(2,2′-bipyridine)technetium(V), 78939-80-7; oxotrichloro(1,10-phenanthroline)technetium(V), 78939-81-8; oxodichloroethoxy-(2,2′-bipyridine)technetium(V), 78939-82-9.

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Infrared Spectroscopic Characterization of Metal Cluster Complexes. Hydrohalogenation Products of $Ru_5C(CO)_{15}$

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The hydrohalogenation products of the semiinterstitial carbido metal clusters $Ru_5C(CO)_{15}$, $HRu_5C(CO)_{15}Cl$, and $HRu_5C(CO)_{15}Br$ have been examined by infrared spectroscopy in the solid state. The presence of μ-bridging hydride and terminal halide was inferred. The infrared absorptions due to the carbido ligands in the spectra of the two halide complexes differ considerably from those observed in the spectrum of $Ru_5C(CO)_{15}$. A structural rearrangement of the Ru_5C skeleton on hydrohalogenation, to a bridged butterfly configuration, similar to that found in an analogous osmium cluster, is postulated.

Introduction

This paper deals with the infrared spectroscopic characterization of the metal cluster species which were recently reported to result from the hydrohalogenation of the semiinterstitial carbido cluster $Ru_5C(CO)_{15}$.[1] Considerable interest is attached to the reactions of carbido species of this type in view of their potential catalytic value (see, for example, ref 2). The carbido complexes $M_5C(CO)_{15}$, M = Fe, Ru, and Os, are isostructural, each such cluster unit being composed of a square pyramid of metal atoms with the carbido atom located slightly (ca. 0.1 Å) below the basal plane.[3-5] Despite the presence of the four *axial* carbonyl groups which are disposed around it, the carbido atom is thus somewhat exposed.

Scheme I

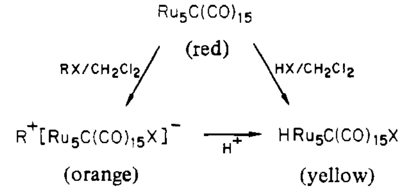

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Table I. Vibrational Frequencies (cm^{-1}) of the Cluster Complexes $Ru_5C(CO)_{15}$, $HRu_5C(CO)_{15}Cl$, and $HRu_5C(CO)_{15}Br^a$

	$Ru_5C(CO)_{15}$		$HRu_5C(CO)_{15}Cl$		$HRu_5C(CO)_{15}Br$	
mode	298 K	90 K	298 K	90 K	298 K	90 K
ν_{asym}(RuH)			1322 (br)	1323 (w)	1325 (br)	1325 (w)
ν_{sym}(RuH)			1260 (br)	1250 (br)	1267 (br)	1263 (br)
ν(RuC)		772 (sh)		830 (s)		829 (s)
		769 (s)	823 (vs)	825 (s)	823 (vs)	825 (s)
	757 (s)	752 (s)	685 (vs)	689 (vs)	687 (vs)	685 (vs)
	738 (s)	745 (s)				
	730 (vs)	735 (vs)				
ν(RuX)			313 (m)	*b*	256 (m)	*b*
ν(RuRu)	*c*		232 (vw)	*b*	234 (vw)	*b*
					225 (w)	
			207 (vw)		205 (vw)	
			190 (w)		190 (w)	
			180 (w)		182 (w)	
					175 (w)	

[a] Frequencies due to carbonyl modes are not tabulated. [b] Not investigated. [c] Volatility of the $Ru_5C(CO)_{15}$ has thus far precluded measurement of the far-infrared spectrum.

It has been shown recently that the metal–carbon stretching modes of metal clusters containing interstitial carbido atoms give rise to infrared absorptions of unexpectedly high intensity, which reflect simply the symmetry of the carbido environment.[6,7] In the present work it was hoped that this sensitivity could be utilized in a diagnostic manner in elucidating the structures of the carbido cluster species investigated. If reaction were to involve the semiinterstitial carbido atoms, a further possibility was the correlation of the vibrational spectra of these halogenated derivatives with those, described earlier[8,9] and reanalyzed recently in some detail,[10] of the μ_3-bridging halomethylidyne ligand in the complexes $(\mu_3\text{-YC})Co_3(CO)_9$, Y = F, Cl, and Br.

The reaction products which we are concerned with here may be produced via two different routes, as shown in Scheme I.[1] Here, R = Me_4N, $(Ph_3P)_2N$, etc., and X = Cl, Br, and I. Analogous reactions have been described for $Os_5C(CO)_{15}$;[4] structural analysis of $[(Ph_3P)_2N][Os_5C(CO)_{15}I]$ revealed that the anion adopts an *arachno*-pentagonal-bipyramidal configuration.

The hydrohalogenation products of $Ru_5C(CO)_{15}$, in contrast to the osmium analogue, have been found to crystallize in a form such that their crystals are unsuitable for crystallographic structure determinations. A principal aim of this study was therefore to use an alternative approach, that of infrared spectroscopy, to determine the structures of these complexes, and we will show that the most likely structure is one similar to that of the osmium anion.[4]

Experimental Section

Complexes. The preparation of $Ru_5C(CO)_{15}$ has been described briefly elsewhere.[1] $Ru_6C(CO)_{17}$ (250 mg) was placed in a German, Roth magnetically stirred autoclave (120-cm^3 volume) with heptane (50 mL). The autoclave was pressurized twice to 30 atm of carbon monoxide and vented to atmospheric pressure and then pressurized to 80 atm of carbon monoxide and heated to 80 °C for 3 h. The autoclave was then cooled, the pressure was released, and the red solution was evaporated to dryness. The resulting red solid was extracted into boiling hexane and filtered; slow evaporation gave red crystals of $Ru_5C(CO)_{15}$ (208 mg; 97.2%).

The adducts $HRh_5C(CO)_{15}X$, X = Cl, Br, were prepared directly by reaction with the appropriate hydrogen halide (see above). In the case of the former, for example, a steady stream of HCl gas was bubbled through a stirred solution of $Ru_5C(CO)_{15}$ (20 mg) in dichloromethane (20 mL) for 30 s. The yellow solution was then evaporated to dryness, giving a yellow solid (20.5 mg; 98%).

Anal. Calcd for $Ru_5C_{16}HO_{15}Cl$: C, 19.72; H, 0.1; Cl, 3.64. Found: C, 20.9; H, 0.97; Cl, 3.83. Calcd for $Ru_5C_{16}HO_{15}Br$: C, 18.86; H, 0.1. Found: C, 18.23; H, 0.43. IR (ν(CO)): $Ru_5C(CO)_{15}$ (hexane solution), 2067 (vs), 2034 (s), 2015 (w) cm^{-1}; $HRu_5C(CO)_{15}X$ (X = Cl or Br; dichloromethane solution), 2087 (s), 2072 (sh), 2069 (s), 2059 (s), 2028 (m, br). ^1H NMR: $HRu_5C(CO)_{15}Cl$ (CD_2Cl_2 solution) δ −22.2 (s); $HRu_5C(CO)_{15}Br$ (CD_2Cl_2 solution) δ −22.2 (s).

Infrared Spectra. Infrared spectra of the complexes were measured with Digilab FTS-14 (4000–400 cm^{-1}; KBr disks) and Beckman-R.I.I.C. IR-720M (400–100 cm^{-1}; Nujol mulls) spectrophotometers. A conventional liquid-nitrogen cell was used to obtain spectra at ca. 90 K.

Results and Discussion

The "noncarbonyl" vibrational frequencies of $Ru_5C(CO)_{15}$, $HRu_5C(CO)_{15}Cl$, and $HRu_5C(CO)_{15}Br$, at 298 K and 90 K, are given in Table I.

The Metal–Carbido Stretching Modes. Previous work has identified ν(MC) for interstitial, and semiinterstitial, metal carbido cluster complexes as occurring in the 820–550-cm^{-1} region.[3,6,7] Of particular relevance to the present work is the observation of two bands in the infrared spectrum of $Fe_5C(CO)_{15}$, at 790 and 770 cm^{-1}, which seem likely to arise from the two metal–carbido stretching modes expected for this square-pyramidal structure.[3] The isostructural cluster complex $Ru_5C(CO)_{15}$ gives rise to a slightly different spectrum at room temperature, in this region, in that the more intense absorption is split into two components, as seen in Figure 1; the three bands occur at 757, 738, and 730 cm^{-1}. When $Ru_5C(CO)_{15}$ is cooled to liquid-nitrogen temperature, a surprisingly complex spectrum is observed with four bands being clearly resolved and a fifth evident as a shoulder on the highest frequency of the resolved bands. There are three possible reasons for this complex spectrum: (i) the two types of cluster molecule present in the crystal[5] are sufficiently different that a "multiple-site" splitting is observed, (ii) the high absorptivity associated with these modes results in intermolecular vibrational coupling,[12] and (iii) the ν(RuC) modes are involved in

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(5) Although all three cluster species are *isostructural*, the Ru and Os complexes are not *isomorphous* with the Fe complex. Crystals of the former two clusters contain two sets of crystallographically nonequivalent molecules.[4]

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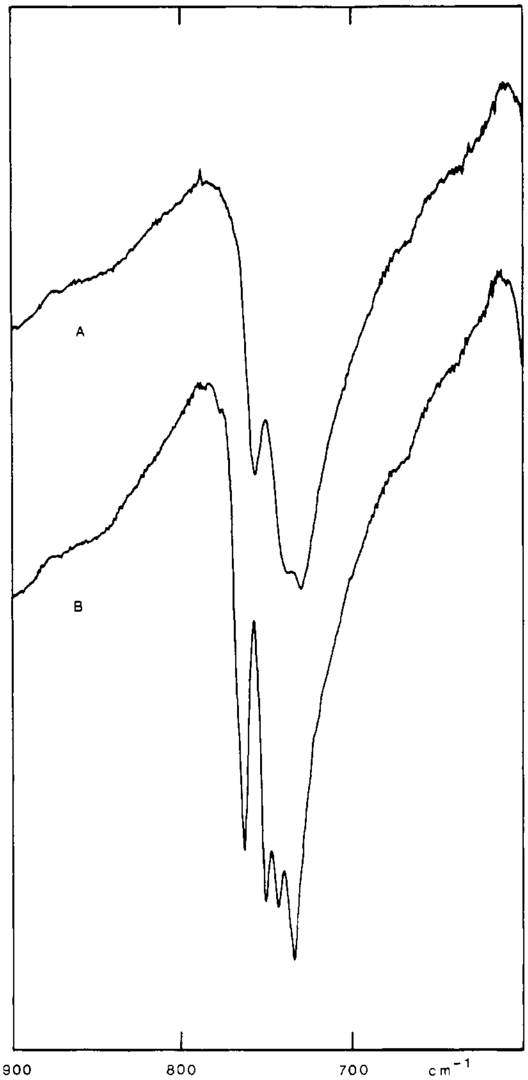

Figure 1. The 900–600-cm^{-1} region of the infrared spectrum of $Ru_5C(CO)_{15}$ at 298 (A) and 90 K (B).

Fermi resonance with overtone or combination modes originating in the δ(RuCO) and ν(RuC(O)) fundamentals (600–350 cm^{-1}). We will assume for the moment that the first explanation is correct; clearly, a low-temperature, infrared spectroscopic study of $Fe_5C(CO)_{15}$ would be desirable to resolve this ambiguity.

Absorptions quite different from those displayed by $Ru_5C(CO)_{15}$ are found in the infrared spectra of $HRu_5C(CO)_{15}Cl$ and $HRu_5C(CO)_{15}Br$, as seen in Figure 2 for the latter at ambient and liquid-nitrogen temperatures. Intense bands are observed at ca. 820 and 690 cm^{-1} in the room-temperature spectra; cooling to 90 K results in a small splitting (ca. 4 cm^{-1}) of the higher frequency of these bands.[13] The close similarity between the frequencies of the metal–carbido stretching modes in the chloro and bromo complexes rules out the possibility that these complexes contain μ-bridging halomethylidyne ligands. The large frequency difference, in each case, between the components of ν(RuC) points to a structural rearrangement of the metal cluster framework from the square-pyramidal $Ru_5C(CO)_{15}$ structure to one in which two ν(RuC) modes are of almost equal frequency and the third is considerably different. Although the spectra are suggestive of the splitting of a degenerate mode on cooling, this does not appear to be the case; further discussion of the nature of this rearrangement will be made below.

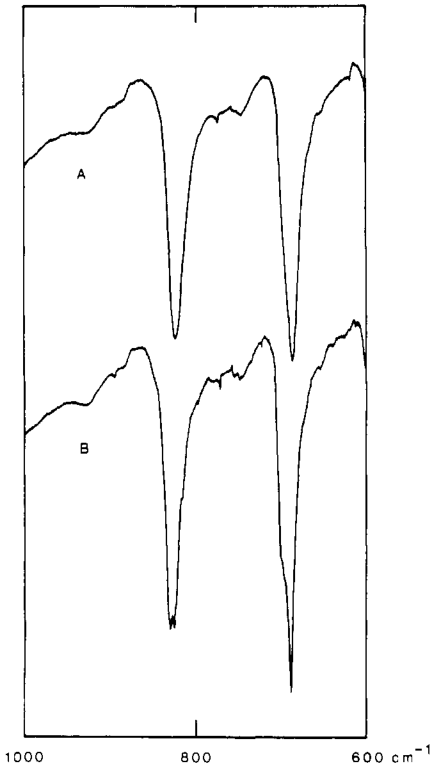

Figure 2. The 1000–600-cm^{-1} region of the infrared spectrum of $HRu_5C(CO)_{15}Cl$ at 298 (A) and 90 K (B).

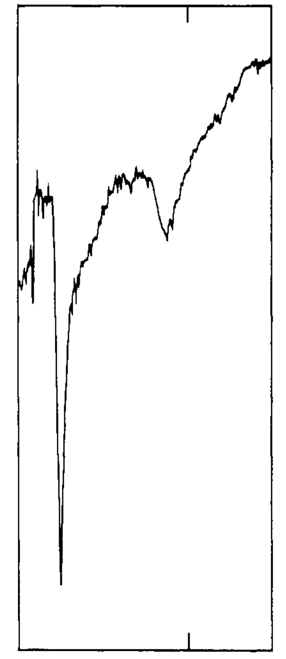

Figure 3. Ruthenium–hydrogen stretching absorptions in the infrared spectrum of $HRu_5C(CO)_{15}Br$ at 90 K.

The Metal–Hydrido Stretching Modes. Two absorptions in the spectrum of each $HRu_5C(CO)_{15}X$ complex which are found to sharpen significantly on cooling to 90 K are assigned to the metal–hydrogen stretching modes of a μ-bridging hydrido ligand. The relevant region of the spectrum of $HRu_5C(CO)_{15}Br$ at 90 K is shown in Figure 3; the simplicity of these absorptions strongly suggests that only one such H ligand is present in each cluster molecule.

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(12) Vibrational coupling of this type is quite feasible in the Fe analogue where the basal planes of neighboring molecules face each other.[3]

(13) The high-frequency shoulder on the 690-cm^{-1} band is believed to arise from the out-of-plane rocking mode of the hydride ligand; this assignment will be discussed elsewhere.[11]

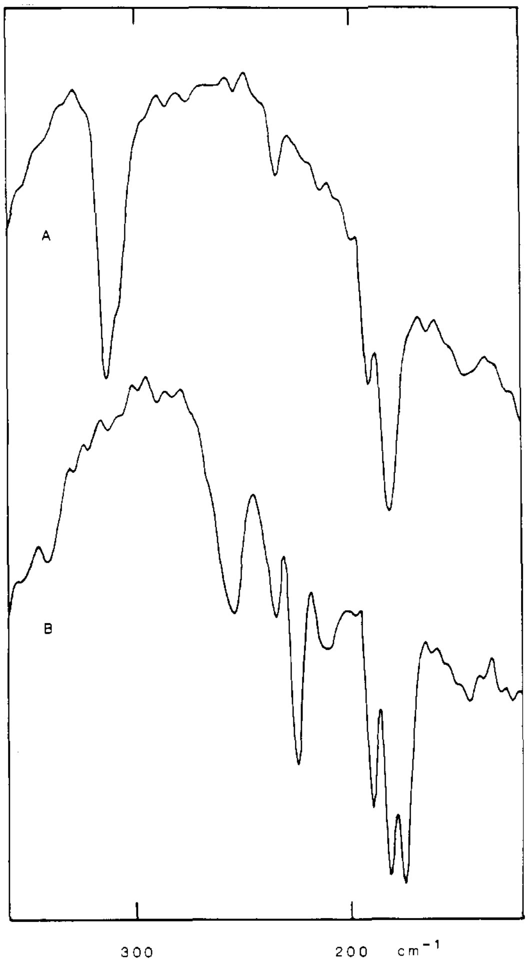

Figure 4. Far-infrared spectra of $HRu_5C(CO)_{15}Cl$ (A) and $HRu_5C(CO)_{15}Br$ (B) at 298 K.

It was demonstrated recently[14] that a simple relationship exists for μ-bridging hydrides between the ratio of the two M–H stretching modes and the MHM angle, α, viz.:

$$\nu_{\text{asym}}(\text{MH})/\nu_{\text{sym}}(\text{MH}) = \tan(\alpha/2) \qquad (1)$$

This expression is adequate where the angle $\alpha \lesssim 120°$ but becomes inaccurate at larger angles due to the influence of the interbond bending force constant, which is neglected in this treatment. In the present case we may use eq 1 to estimate the RuHRu angle. We assign the more intense absorption, mean frequency 1324 cm^{-1}, to the antisymmetric stretching mode[14] and the weaker absorption to the symmetric mode. This assignment yields an estimate of the interbond angle as 93° and implies that the H ligand bridges a fairly short Ru–Ru bond.

It is possible to estimate the angles α corresponding to the various types of metal–metal bond in the analogous $[Os_5C(CO)_{15}I]$ anion. We make the usual assumption that the Os–Os and Ru–Ru bonds will be of approximately equal length and will take a Ru–H bond length of 1.8 Å, as has been determined in a number of structural studies (see, for example, ref 15–17). The three types of metal–metal bond in the $[Os_5C(CO)_{15}I]^-$ cluster[4] would then given rise to angles α of 99 (one), 108 (four), and 109° (two).[18] It would thus appear that the observed Ru–H stretching frequencies are consistent with a $HRu_5C(CO)_{15}X$ structure analogous to that of $[Os_5C(CO)_{15}I]^-$, with the hydride ligand bridging the short hinge bond of the metal–atom "bridged butterfly" arrangement.

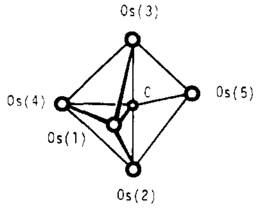

Figure 5. Configuration of the Os_5C skeleton of the $[Os_5C(CO)_{15}I]^-$ anion (ref 4).

The Far-Infrared Spectral Region. Generally, in unsubstituted metal carbonyl cluster complexes, the 350–100-cm^{-1} region is clear of absorptions due to lower frequency carbonyl modes, and it is this region in which we expect to observe absorptions due to metal–halogen and metal–metal stretching modes. The far-infrared spectra of $HRu_5C(CO)_{15}Cl$ and $HRu_5C(CO)_{15}Br$ are shown in Figure 4, where it is seen that the most striking difference between these spectra relates to the asymmetric band at 313 cm^{-1} in the spectrum of the former complex which apparently shifts to 256 cm^{-1} in the spectrum of the latter (Table I). This observation supports the presence of *terminally bonded* halogen in these complexes.[19]

The asymmetry noted in the band assigned to the Ru–Cl stretching mode of $HRu_5C(CO)_{15}Cl$ is almost certainly due to the ^{35}Cl–^{37}Cl isotope splitting; the analogous effect in the Ru–Br stretching absorption (with a very much reduced isotope shift) could be responsible for the slightly increased breadth apparent in this band.

The decrease in frequency in ν(RuX) on going from $HRu_5C(CO)_{15}Cl$ to $HRu_5C(CO)_{15}Br$ is somewhat less than would be expected,[19] apparently as a result of coupling of ν(RuBr) with certain of the Ru–Ru stretching modes. A comparison of the absorptions due to ν(RuRu) in the two spectra reveals a significantly greater complexity in the case of $HRu_5C(CO)_{15}Br$ (Figure 4), with an additional band of appreciable intensity appearing at 225 cm^{-1}, and an apparent splitting of the band observed at 180 cm^{-1} in the spectrum of $HRu_5C(CO)_{15}Cl$. Both these effects are consistent with coupling of ν(RuBr) with Ru–Ru stretching modes of the same symmetry.

General Discussion. The spectra reported here for $HRu_5C(CO)_{15}Cl$ and $HRu_5C(CO)_{15}Br$ are consistent with a close similarity between these species and the $[Os_5C(CO)_{15}I]^-$ anion, whose structure has been determined by X-ray diffraction,[4] and is depicted in Figure 5, without the carbonyl and halogen ligands. The Os_5C polyhedron possesses symmetry very close to C_{2v}, with Os(2),Os(3)–C = 1.986 Å (mean), Os(1),Os(4)–C = 2.108 Å and Os(5)–C = 2.174 Å; the angle Os(4)COs(1) is 81°.[4] Consideration of these bond lengths suggests that the Os–C stretching mode of highest frequency will be that involving the linear arrangement of Os(3)COs(2). Similarly, of the two modes involving the planar Os(1)Os(4)Os(5)C fragment, the symmetric mode would be expected at higher frequency than the antisymmetric mode. It is thus apparent that the more obvious interpretation of the ν(RuC) absorptions, as suggested earlier for the analogous $HRu_5C(CO)_{15}X$ species, must be treated as unlikely, and we must consider the possibility that the lowest frequency band arises from the antisymmetric, in-plane mode (b_1), while the out-of-plane (b_2) and

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(18) This reasoning neglects any effect which the hydride ligand may have upon the length of the metal–metal bond which it bridges, an assumption which will be validated elsewhere.[11]

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Table II. Force Constant Values Associated with the Stretching of Ru–C Bonds in the Ru$_5$C Polyhedron

desig	bonds[a]	FC,[b] N m^{-1}
k_{RuC}	Ru(2)–C, Ru(3)–C	230 (1)[c]
k'_{RuC}	Ru(1)–C, Ru(4)–C, Ru(5)–C	254 (1)
f_{RuC}	Ru(1)–C, Ru(4)–C	−86 (1)

[a] See Figure 5. [b] FC = force constant. [c] The estimated error is given in parentheses.

symmetric, in-plane (a$_1$) modes occur with nearly equal frequency near 830 cm^{-1}.

An approximate normal-coordinate analysis was performed, using the structural model of Figure 5, for the Ru$_5$C polyhedron in order to test the reasonableness of the assignments suggested above. The results of this analysis are described briefly in the Appendix. It must be concluded that despite the approximations necessary in this treatment these assignments are feasible, although the values of the individual force constants must be treated with some caution.

We thus conclude, based on the assignment of vibrational modes associated with ruthenium–carbido and ruthenium–halogen stretching, the cluster complexes HRu$_5$C(CO)$_{15}$X, X = Cl and Br, are likely to be closely related in structure to the [Os$_5$C(CO)$_{15}$I]$^-$ anion. Consideration of the ruthenium–hydrido stretching frequencies in these complexes suggests that the hydrogen ligand occupies a μ-bridging position across the shortest Ru–Ru bond in each cluster molecule.

Appendix

Approximate Normal-Coordinate Analysis of the Ru$_5$C Polyhedron. The geometry of the Ru$_5$C polyhedron was taken to be that of the analogous arrangement in the [Os$_5$C(CO)$_{15}$I]$^-$ anion[4] (Figure 5). Internal coordinates were taken to coincide with the five Ru–C bonds and a total of nine Ru–Ru vectors, including the two nonbonded vectors Ru(1)–Ru(5) and Ru(4)–Ru(5).

The metal–metal bond stretching force constants were assigned reasonable values, depending upon the Ru–Ru distances, and were not refined in the calculation. The values chosen ranged from 80 N m^{-1} (Ru(1)–Ru(4)) to 10 N m^{-1} for the nonbonded "equatorial" vectors. The ruthenium–carbido bonds are of three types (see Discussion), and initially attempts were made to reproduce the three observed Ru–C stretching frequencies by refinement of three independent force constants. This procedure, however, was found to lead to an unsatisfactory estimate of the antisymmetric, in-plane (b$_1$) stretching frequency, and an alternative approach was made in which the "equatorial" Ru–C force constants were constrained to be equal. This permitted the inclusion in the force field of an interaction constant between the stretching of Ru(1)–C and Ru(4)–C. Refinement of these force constants[20] resulted in exact reproduction of the three Ru–C stretching frequencies, as assigned above, with the values of the force constants as given in Table II. Although it would be expected on bond length grounds that $k_{RuC} > k'_{RuC}$, the presence of the interaction constant precludes a direct comparison.

Registry No. HRu$_5$C(CO)$_{15}$Cl, 78891-40-4; HRu$_5$C(CO)$_{15}$Br, 78919-48-9; Ru$_5$C(CO)$_{15}$, 51205-07-3.

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Synthesis, Structure, and Ligand Dynamics of the Organometallic Anion [Ru$_3$(CO)$_9$C$_2$-*t*-Bu]$^-$

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The organometal cluster HRu$_3$(CO)$_9$C$_2$-*t*-Bu (I) can be readily deprotonated by OH$^-$ in carbon monoxide atmosphere to yield the corresponding anion, isolated as [AsPh$_4$]$^+$[Ru$_3$(CO)$_9$C$_2$-*t*-Bu]$^-$ (II). The variable-temperature ^{13}C NMR spectrum of II in the carbonyl region reveals that the barrier to axial–radial exchange at the metal atoms formerly bridged by the hydrogen is lowered by 5 kcal/mol compared with the same process in I. The barrier to intermetallic scrambling is also lower. Crystals of II are monoclinic, space group $P2_1/a$ with $Z = 4$ in a unit cell of dimensions $a = 21.384$ (15) Å, $b = 18.775$ (12) Å, $c = 10.010$ (8) Å, and $\beta = 96.77$ (7)°. The structure has been solved from diffractometer data by Patterson and direct methods and refined by full-matrix least-squares to $R = 0.066$ for 2741 observed reflections. The basic features of the triangular cluster and the organic ligand in II are maintained virtually unchanged from I, but the metal–metal bond formerly bridged by hydrogen is 0.127 Å shorter that in I. In addition, the three carbonyl groups on these metal atoms have undergone a rotation around the metal–metal bond which corresponds to relief of the steric hindrance caused by the hydride ligand.

The structural and stereochemical consequences of bridging ligands in metal cluster complexes are fundamental to our understanding of this class of molecules. In the case of the μ-hydride ligand, it has been suggested that the three-center–two-electron bond can be considered as a protonated metal–metal bond. This model nicely explains the longer metal–metal bond lengths and the larger metal–carbonyl bond angles in μ-hydride-bridged metal–metal bonds. In the case of doubly bridged metal–metal bonds where the other bridging atom(s) is not hydrogen, a shortening of the metal–metal bond is observed.[1] Recently, Adams and Selegue have observed that in the doubly bridged species (μ-H)(μ-S$_2$CH)Os$_3$(CO)$_{10}$ a shortening of the bridged metal–metal bond of about 0.12 Å results when phosphine substitution on the nonbridged osmium atom causes migration of the hydride ligand to give a

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(1) M. R. Churchill in "Transition Metal Hydrides", R. Bau, Ed., American Chemical Society, Washington, D.C., 1975, p 36.

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