Synthesis of Hydrido- and Deuterio-Carbonyl Cluster Complexes of Ruthenium, Iron-Ruthenium, and Osmium from Metal Carbonyls and Hydrogen at Atmospheric Pressure[1]

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Abstract: $Ru_4H_4(CO)_{12}$ and $Os_3H_2(CO)_{10}$ are obtained in high yield and purity by reaction of H_2 at atmospheric pressure at 120° in hydrocarbon solutions of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, respectively. Further treatment of $Os_3H_2(CO)_{10}$ with H_2 leads to $Os_4H_4(CO)_{12}$. $Ru_4D_4(CO)_{12}$ is obtained from $Ru_3(CO)_{12}$ and D_2 in hydrocarbon solvent; however, extensive hydrogen exchange with solvent is observed in the osmium system. $Ru_4H_2D_2(CO)_{12}$ is obtained in the reaction of D_2 with $Ru_4H_2(CO)_{13}$ and the new mixed metal complex $FeRu_3H_4(CO)_{12}$ is obtained from $FeRu_3H_2(CO)_{13}$ and H_2. Substances are characterized by ir, NMR, Raman, and mass spectrometry.

We report here our studies of the treatment of metal carbonyls with H_2 (or D_2) at atmospheric pressure and elevated temperature giving a convenient synthesis[2] of a number of hydrido (or deuterio) carbonyl metal clusters. We were led to this reaction through earlier observations in the chemistry of $Re_4H_4(CO)_{12}$.[3] This complex is readily transformed into higher carbonyls in contact with CO at atmospheric pressure as indicated in reaction sequence (1); at

$$\begin{tikzcd}
Re_4H_4(CO)_{12} + 5CO \arrow[r, "25^\circ"'] & Re_3H_3(CO)_{12} + ReH(CO)_5 \arrow[d, "60^\circ"] \\
& \frac{1}{2}H_2 + \frac{1}{2}Re_2(CO)_{10}
\end{tikzcd} \qquad (1)$$

slightly elevated temperatures, H_2 evolution was observed. This suggested to us that the reverse of this transformation might be possible and indeed when H_2 at atmospheric pressure is bubbled through a hydrocarbon solution of $Re_2(CO)_{10}$ at 150°, the lower carbonyl cluster compounds are obtained, first $Re_3H_3(CO)_{12}$ subsequently replaced by $Re_4H_4(CO)_{12}$.[2] We subjected a number of other carbonyls to this treatment and found several hydrido-metal carbonyl cluster complexes of ruthenium, osmium, and a mixed iron-ruthenium cluster can be obtained through this route.

Ruthenium

Treatment of $Ru_3(CO)_{12}$ with H_2 gives $Ru_4H_4(CO)_{12}$ conveniently in high yield and purity. Excellent analytical data were obtained for our product which displays five maxima in the carbonyl stretching region of the ir (see Table I) consistent with that independently obtained by Piacenti and coworkers[4] in an autoclave reaction of $Ru_3(CO)_{12}$ with H_2 at 110° and 150 atm, but in contrast to earlier reports[5] of two isomers α and β of the same formulation each with different and more complex carbonyl ir absorptions. Both we and the Italian group have shown that the spectrum reported for the "α isomer" is derived from a mixture of $Ru_4H_4(CO)_{12}$ and $Ru_3(CO)_{12}$ which can easily be separated by column chromatography. Indeed single crystals suitable for structure determination of $Ru_3(CO)_{12}$[6] were obtained from a solution containing "α-$Ru_4H_4(CO)_{12}$". Regarding the "β isomer", we have not been able to observe any evidence for its existence either in the direct reaction of $Ru_3(CO)_{12}$ with H_2 or in attempts to repeat the earlier preparations.

As previously noted,[5] considerable hydrogen loss accompanies ionization and fragmentation in the mass spectrum of $Ru_4H_4(CO)_{12}$; the observed and calculated intensities for the parent ion multiplet are given in the upper part of Figure 1 and Table A.[7] We find a conventional R factor,

$$R = \Sigma\{|I_{\text{obsd}} - I_{\text{calcd}}|/I_{\text{calcd}}\}$$

to be a convenient index of the match between the average observed and calculated data; for the parent ion multiplet of $Ru_4H_4(CO)_{12}$, $R = 17.1\%$. By adjusting the composition of the parent ion $Ru_4H_n(CO)_{12}$ over the range $n = 4, 3, 2, 1, 0$, a best least-squares fit ($R = 6.5\%$) is obtained for the values: $n = 4$, 65%; $n = 3$, 19%; $n = 2$, 0%; $n = 1$, 0%; and $n = 0$, 16%. The data are presented in Table B.[7] Further details regarding the measurements and computations for mass spectra are given in the experimental section. The principal fragments in the spectrum of $Ru_4H_4(CO)_{12}$ are given in Table C.[7] Fragments corresponding to successive loss of 12 CO groups with concomitant hydrogen loss and a fragment corresponding to Ru_4C^+ are observed.

$Ru_4D_4(CO)_{12}$ was prepared by the reaction of $Ru_3(CO)_{12}$ and D_2. By contrast with $Ru_4H_4(CO)_{12}$, its mass spectrum shows a very close fit between the observed and calculated peaks in the parent ion multiplet; see lower trace of Figure 1 and Table D,[7] R factor = 5.4%. There also is correspondingly higher retention of deuterium in the lower mass fragments (see Table E[7]) which are closely analogous to those of $Ru_4H_4(CO)_{12}$. The carbonyl stretching absorptions for $Ru_4D_4(CO)_{12}$ show either very small or no shifts in the maxima from those observed for $Ru_4H_4(CO)_{12}$; however, differences in the relative intensities are quite pronounced; these are shown in Figure 2, upper trace, to compare with that published for $Ru_4H_4(CO)_{12}$ (Figure 1 of ref 4).

Only weak features in the ir may be observed for the modes of bridging hydrogen; see the review by Kaesz and Saillant[8] and references cited therein. For $Ru_4H_4(CO)_{12}$ Johnson, Lewis, and Williams[5b] report a broad band centered around 1284 ($\Delta\nu_{1/2} \sim 40$)cm^{-1} which was observed to shift to 902 ($\Delta\nu_{1/2} \sim 20$)cm^{-1} in the deuterated derivative. The hydrogen modes are somewhat more prominent in the Raman. The spectra for $Ru_4H_4(CO)_{12}$ and $Ru_4D_4(CO)_{12}$ have been published in the above-mentioned review;[8] the data are presented in Table II. Two weak and broad but perfectly discernible bands are observed at 1585 and 1290 cm^{-1} in the former which shift to 1153 and 909 cm^{-1} in the latter. Both shifts conform very well to the expected isotope ratio (see Table II) with the bands for the deuterated derivative displaying narrowing in the bandwidth typical of such

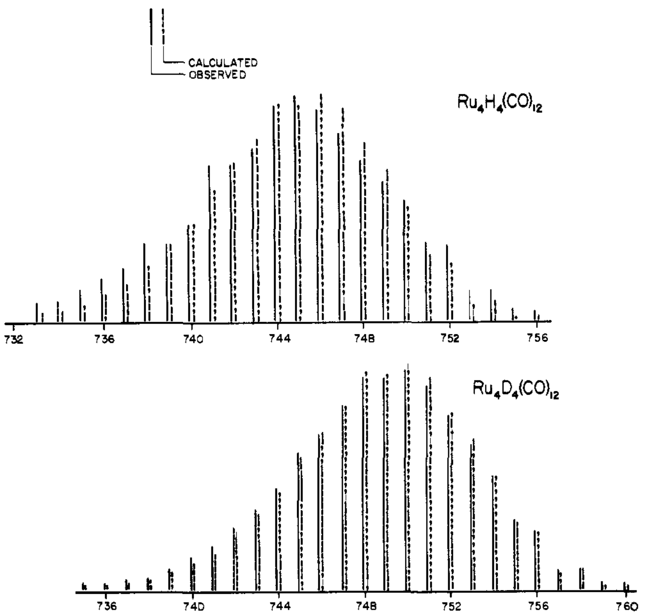


Figure 1. Calculated and average observed peaks in the parent ion multiplet: $Ru_4H_4(CO)_{12}$, cf. Table A;[7] $Ru_4D_4(CO)_{12}$, cf. Table D.[7]

Table I. Infrared Absorptions in the Carbonyl Region and ^1H NMR Data

Compound	Maxima (cm^{-1})[a]	Chemical shift (τ)[b]
$Ru_4H_4(CO)_{12}$[c]	2081 (s), 2067 (vs), 2030 (m), 2024 (s), 2009 (w)	27.98 ($CDCl_3$)
$Ru_4H_2D_2(CO)_{12}$	2080 (s), 2067 (s), 2029 (m), 2023 (s), 2008 (w)	28.07 ($CDCl_3$)
$Ru_4D_4(CO)_{12}$	2079 (s), 2067 (s), 2029 (m), 2023 (s), 2008 (w)	
$FeRu_3H_4(CO)_{12}$	2085 (s), 2070 (s), 2054 (s), 2044 (vw), 2031 (m br), 2012 (w), 1998 (w), 1990 (w)	29.35 (CH_2Cl_2)
$Os_3H_2(CO)_{10}$[d]	2112 (vw), 2076 (s), 2063 (m), 2026 (s), 2011 (s), 1989 (w), 1973 (vw), 1957 (vw)	21.73 ($CDCl_3$)
$Os_4H_4(CO)_{12}$[e]	2086 (m), 2069 (s), 2022 (s), 2000 (m)	

[a] Cyclohexane solution. [b] In ppm, relative to tetramethylsilane τ 10; solvent is indicated in parentheses. [c] Maxima agree within 1 cm^{-1} and chemical shift within 0.08 ppm with those reported by Piacenti et al.,[4] which also contains a reproduction of the ir spectrum in the carbonyl region. [d] Maxima agree within 1 or 2 cm^{-1} with those reported by Johnson, Lewis, and Kilty.[13a] [e] Maxima agree within 1 cm^{-1} with those reported by Moss and Graham.[15]

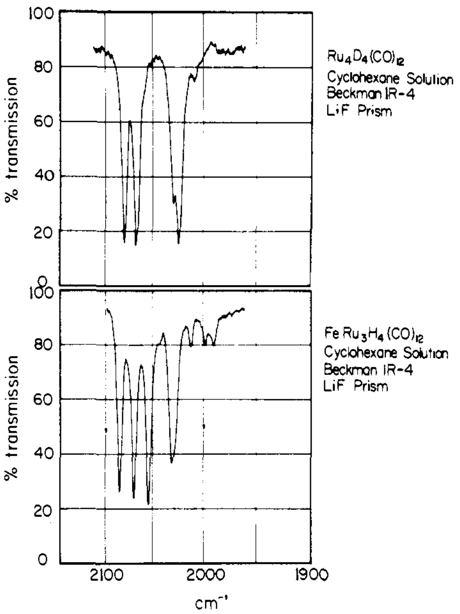


Figure 2. Infrared absorption in the carbonyl stretching region $Ru_4D_4(CO)_{12}$ and $FeRu_3H_4(CO)_{12}$ (see data, Table I): cyclohexane solution, Beckman IR 4/L*i*F prism.

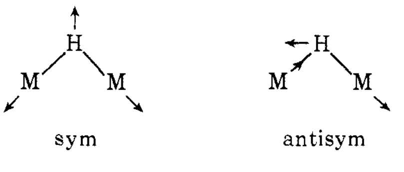
Table II. Raman Data (cm^{-1})

$Ru_4H_4(CO)_{12}$[a]	$Ru_4H_2D_2(CO)_{12}$[b]	$Ru_4D_4(CO)_{12}$[a]
2109 s	2109 s	2109 s
2078 w		2075 w
2061 w		2061 w
2030 m	2029 sh	2029 m
2021 s	2019 sh	2020 m
2014 s	2015 s, br	2014 s
2010 s	2010 sh	2010 s
2002 m	1998 sh	2001 m
1990 m	1993 m	1991 m
1585 w, br[c]	1587 w, br[c]	
1290 w–m, br[d]	1291 w, br[d]	
	1156 w, br[e]	1153 w–m, br[e]
	909 w, br[f]	909 w–m, br[f]
617 w	613 w, br	595 w
592 w	580 w–m	578 w
577 w		
472 vs	469 vs	470 vs
444 m	444 m	443 w
432 m		420 w–m
420 m, br	422 m	354 w
365 w		
353 w	357 w	

[a] Spectra of these derivatives are displayed as Figure 3 in the review by Kaesz and Saillant.[8] [b] See Figure 2. [c] $\Delta\nu_{1/2}$ = 32 cm^{-1}. [d] $\Delta\nu_{1/2}$ = 14 cm^{-1}. [e] $\Delta\nu_{1/2}$ = 18 cm^{-1}; $\Delta\nu_H/\nu_D$ = 1.375. [f] $\Delta\nu_{1/2}$ = 9 cm^{-1}; $\Delta\nu_H/\nu_D$ = 1.420.

bridging modes.[9] Because of the broadness of the peaks, a rather shallow potential well for hydrogen or deuterium may be surmised. A retrospective investigation of the ir spectra (KBr pellets) reveals broad and very weak features at 1605 and 1272 cm^{-1} for $Ru_4H_4(CO)_{12}$ and 1095 and 895 cm^{-1} for $Ru_4D_4(CO)_{12}$.

The mixed isotope derivative $Ru_4H_2D_2(CO)_{12}$ was prepared by reaction of D_2 with $Ru_4H_2(CO)_{13}$; as in the treatment of this cluster with H_2 (to give $Ru_4H_4(CO)_{12}$) the reaction is complete *within 2 min at 70°*. Under these conditions, exchange with H_2 (or D_2) with product may be assumed to be negligible as shown by independent treatment of $Ru_4H_4(CO)_{12}$ with D_2 (approximate half-life for exchange at 70° ~3hr). The mass spectrum of this material displayed a parent ion whose match of observed to calculated peak intensities resulted in an *R* factor of 8.6% (see Figure A and Table F)[7] somewhere between those obtained for $Ru_4H_4(CO)_{12}$ and $Ru_4D_4(CO)_{12}$; the principal fragments in the mass spectrum of $Ru_4H_2D_2(CO)_{12}$ are given in Table G.[7] The Raman spectrum, Table II and Figure 3, displayed two pairs of broad bands corresponding to each of the pairs separately observed for the pure hydrido and pure deuterio species. The additivity of these spectral features indicates to us that the absorptions must arise from isolated M-H-M or M-D-M oscillators. *Two* absorptions, a symmetrical and an antisymmetrical mode, are expected if the bridging system is bent.[10] The displacement vectors (not scaled to exact atomic motions) are illustrated below.



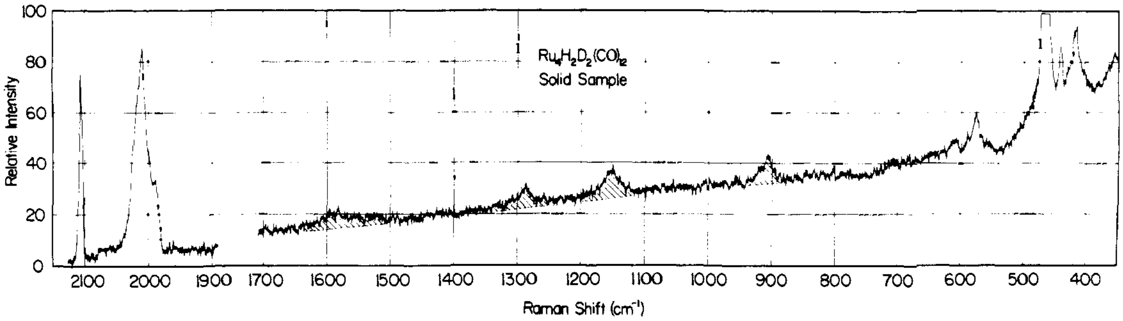


Figure 3. Raman spectrum of $Ru_4H_2D_2(CO)_{12}$; see Table II.

Due to lack of information of the stretching and the interaction force constants the M–H–M bond angle cannot be calculated at this time.

Iron-Ruthenium

The facile reaction of H_2 with $Ru_4H_2(CO)_{13}$ prompted us to subject the corresponding mixed metal derivative $FeRu_3H_2(CO)_{13}$[11] to this same treatment. Under relatively mild conditions, we have been able to make the new species $FeRu_3H_4(CO)_{12}$. The asymmetry introduced by the heterometal system is manifested by additional complexity in the carbonyl stretching absorptions, see Figure 2, lower trace. Because it was possible that the reduced symmetry either in $FeRu_3H_2(CO)_{13}$ or $FeRu_3H_4(CO)_{12}$ could lead to two types of hydrogens, low temperature NMR spectra of these two compounds were attempted. Resonances of both remained singlets, down to −120° for dimethyl ether solution of $FeRu_3H_2(CO)_{13}$ and −130° for THF solution of $FeRu_3H_4(CO)_{12}$. After 2 days in an NMR tube, the latter displayed two new signals in the region τ 27 with no signal for $FeRu_3H_4(CO)_{12}$ remaining. Chromatography on silica gel yielded $FeRu_3H_2(CO)_{13}$ and a mixture of $Ru_4H_4(CO)_{12}$ and another unidentified substance. Attempted crystallization from CH_2Cl_2-hexane yielded a mixture of $Ru_4H_4(CO)_{12}$ and a compound having a parent ion in the mass spectrum at *m/e* 910. The latter appeared to be unstable to chromatography, decomposing to $Ru_4H_4(CO)_{12}$ upon further attempts at purification. One must conclude that $FeRu_3H_4(CO)_{12}$ and one of its decomposition products are extremely unstable species. Similar thermal instability leading to disproportionation to $Ru_4H_4(CO)_{12}$ and other unidentified species was observed in the mass spectrum.

Other attempts to arrive at a mixed metal derivative were made starting with $FeRu_2(CO)_{12}$.[11] The conditions required for reaction of this starting cluster led only to decomposition and disproportionation resulting in formation of $Ru_4H_4(CO)_{12}$ as the only isolatable product. Similarly, $[Me_3SiRu(CO)_4]_2$,[12] upon treatment with H_2, gave the tetrahydrido-tetrametal derivative which apparently is the thermodynamically preferred product under these conditions.

Osmium

By contrast with the ruthenium system, the direct reaction of H_2 with $Os_3(CO)_{12}$ at atmospheric pressure leads predominantly to the trinuclear derivative $Os_3H_2(CO)_{10}$. This is obtained in considerable improvement both in convenience and yield (73%) over earlier preparations[13] involving the treatment of $Os_3(CO)_{12}$ with base or sodium amalgam followed by acidification; in these preparations, the dihydro-trimetal cluster is obtained in yields ranging from 2.8 to 22%. Our infrared data (Table I) agree well with previous reports for this compound whose structure has also now been determined.[14] By contrast with the previous report, however, we found good agreement between observed and calculated peak heights in the parent ion multiplet in the mass spectrum, R = 4.6%, see Figure 4 and Table H.[7] A least-squares fit allowing for hydrogen loss in the parent ion $Os_3H_n(CO)_{10}$ showed improvement to R = 3.1% for the composition: n = 2, 93%; n = 1, 3%; n = 0, 4%. The data are shown in Table I;[7] further details regarding the computations are given in the experimental section. The principal peaks in the mass spectrum for $Os_3H_2(CO)_{10}$ are given in Table J;[7] fragments corresponding to loss of ten CO groups with accompanying hydrogen loss were observed together with fragments calculated for $Os_3(CO)_2C^+$, $Os_3(CO)C^+$, and Os_3C^+.

Attempts to obtain a deuterated derivative by bubbling D_2 through $Os_3(CO)_{12}$ led to a product whose parent ion in the mass spectrum showed considerable departure toward lower *m/e* peaks and R = 40.7% from that calculated for $Os_3D_2(CO)_{10}$. In view of the good fit obtained in the parent ion multiplet for $Os_3H_2(CO)_{10}$ if anything, a better fit was expected for the deuterated derivative; we therefore concluded that extensive hydrogen exchange with hydrocarbon solvent had occurred. Assuming that the parent ion multiplets for $Os_3HD(CO)_{10}$ and $Os_3D_2(CO)_{10}$ would give at least as good a fit as observed for $Os_3H_2(CO)_{10}$ and that the efficiency for ionization of the three clusters was comparable, we obtained a least-squares fit (R = 2.9%) to the observed multiplet for a product mixture containing approximately 9% $Os_3D_2(CO)_{10}$, 42% $Os_3HD(CO)_{10}$, and 49% $Os_3H_2(CO)_{10}$; the data are presented in Figure B and Table K.[7] This result contrasts markedly with the ruthenium system in which, under comparable conditions, essentially pure $Ru_4D_4(CO)_{12}$ could be obtained from $Ru_3(CO)_{12}$ and D_2.

Continued treatment of $Os_3H_2(CO)_{10}$ with H_2 leads to $Os_4H_4(CO)_{12}$ in somewhat reduced yield (29% based on initial $Os_3(CO)_{12}$). This still represents improvement over earlier reports. A four-band pattern is observed for our product, see Table I and Figure 4. This is different from each of two previous spectra reported by Lewis and coworkers,[13] which differ from each other, but in agreement with the maxima reported by Moss and Graham[15] for this derivative. The product obtained here must be analogous in structure to that of $Ru_4H_4(CO)_{12}$; the medium intensity band corresponding to that at 2030 cm^{-1} in the latter could easily have shifted and become buried under the 2022-cm^{-1} band in $Os_4H_4(CO)_{12}$.

The mass spectrum of $Os_4H_4(CO)_{12}$, like that for $Os_3H_2(CO)_{10}$, shows good agreement between the calculated and observed peak heights in the parent ion multiplet, R = 4.6%; see Figure 4 and Table L.[7] A least-squares fit allowing for hydrogen loss in the parent ion multiplet $Os_4H_n(CO)_{12}$ showed improvement to R = 2.5% for the composition: n = 4, 94%; n = 3, 0%; n = 2, 0%; n = 1, 3%; n = 0, 3%. The data are shown in Table M;[7] further details regarding the computations are given in the experimental section. The principal fragments in the mass spectrum of

$Os_4H_4(CO)_{12}$ are given in Table N;[7] these correspond to successive loss of 12 CO groups concurrent with hydrogen loss and other fragments with masses calculated for $Os_4(CO)_3C^+$, $Os_4(CO)_2C^+$, $Os_4(CO)C^+$, and Os_4C^+.

Conclusions

The syntheses presented above have greatly facilitated further studies on the hydrido-metal clusters such as the preparation and investigation of hydrogen tautomerism in $[(C_6H_5)_4As][Ru_4H_3(CO)_{12}]$[16] and in the substituted clusters $Ru_4H_4(CO)_{12-x}L_y$, L = $P(OMe)_3$, x = 1-4,[17] or investigation of olefin complexes.[18]

With the exception of $Re_2(CO)_{10}$, which results have been reported in preliminary fashion[2] and are to be included in a separate paper elsewhere, other carbonyl derivatives we have treated with H_2 at atmospheric pressure have not yielded useful results; these are summarized in the experimental section below. The high temperatures required to initiate the reaction in most cases prove to be a drawback as demonstrated for the reaction of H_2 with $FeRu_2(CO)_{12}$ from which no mixed metal derivative was isolated in contrast to the milder conditions used in the reaction of H_2 with $FeRu_3H_2(CO)_{12}$ to give $FeRu_3H_4(CO)_{12}$. We are presently attempting to extend the range of usefulness of this reaction by combining the treatment of carbonyl derivatives with H_2 at atmospheric pressure using photochemical excitation to permit lower reaction temperatures. In addition, investigations are also under way with starting materials containing other than carbonyl groups which may prove to be more reactive to elemental hydrogen.

Experimental Section

All manipulations were performed initally under an atmosphere of nitrogen; however, except for those products specifically identified below as unstable in air, the compounds for the most part can be handled in solution and subjected to chromatographic separation without undue precautions. Solvents were dried and freed from dissolved oxygen where compatible by distillation from calcium hydride or by treatment with molecular sieves accompanied by the bubbling of dry nitrogen through a glass frit for 15-20 min.

Reagents. Commonly available carbonyl derivatives and $Ru_3(CO)_{12}$ were purchased either from Pressure Chemical Co. of Pittsburgh, Pa., or Alfa Inorganics, Danvers, Mass. $Ru_4H_2(CO)_{13}$ was prepared by either of two methods: reduction of $Ru_3(CO)_{12}$ with sodium amalgam[5a] or reflux of $Ru_3(CO)_{12}$ in octane.[5b] $FeRu_2(CO)_{12}$ and $FeRu_3H_2(CO)_{13}$ were prepared by the reaction of $Fe(CO)_5$ with $Ru_3(CO)_{12}$ as described by Yawney and Stone.[11] $[Me_3SiRu(CO)_4]_2$ was prepared as described by Knox and Stone.[12] OsO_4 was purchased from Alfa Inorganics. $Os_3(CO)_{12}$ was prepared by the high pressure reaction of OsO_4 and CO.[13a]

Ir Spectra. All carbonyl region ir spectra were obtained on a Beckman IR-4 spectrophotometer equipped with LiF prism. Solution spectra were obtained in cells equipped with CaF_2 windows using cyclohexane as solvent. The absorption frequencies were calibrated against a sharp cyclohexane absorption at 2138.5 cm^{-1}. Absorption maxima for solution spectra are presented in Table I and selected spectra in Figure 2.

Mass Spectra were obtained by Ms. B. Irwin on an AEI-MS9 spectrometer with a direct inlet probe at temperatures of 100-120° for the compounds of ruthenium and up to 200° for the compounds of osmium. The ionizing voltage was 70 eV. Both pressure variations and arcing were observed during ionization of metal cluster compounds causing random fluctuations in beam intensity; these would affect relative peak heights for various fragments and even peaks within the multiplet of a given fragment. Analysis of the parent ion multiplets was therefore based on the average of several measured spectra each scaled to a total intensity of 100; the average normalized spectra are given in the third column in Tables A, D, F, H, K, and L.[7] The last column in each of these tables, headed "Average deviation" gives an indication of the variation obtained for each peak in the observed spectra. A least-squares fit allowing for hydrogen loss in the parent ion multiplets was also carried out, see Tables B, I, and M.[7] Initially, the composition is varied by increments of 5% for all but the lowest mass species whose composition is determined by difference (total composition is normalized to 100%). Further refinement is then carried out at 1% increments around the composition yielding the lowest residual in the first computation. A conventional R factor, mentioned in the discussion section above, was calculated to give a measure of the fit between the observed and calculated spectra. A column showing the difference between the calculated and observed peaks in the parent ion multiplets is also given in the tables which in some cases together with the corresponding figures provide a rapid visual impression to be formed about the quality of the fit between the two spectra. These calculations were carried out on the UCLA IBM 360/91 computer using MASPAN, a program written in Fortran IV by M.A.A.; copies and instructions are available on request.

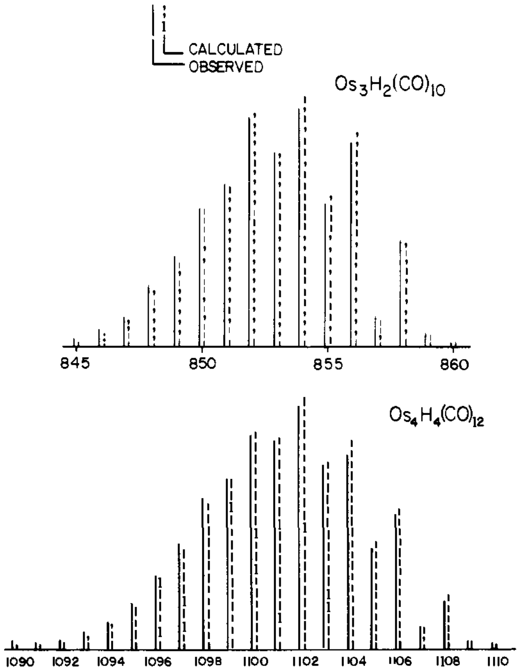


Figure 4. Calculated and average observed peaks in the parent ion multiplets: $Os_3H_2(CO)_{12}$, see Table H;[7] $Os_4H_4(CO)_{13}$, see Table L.[7]

NMR spectra were obtained at ambient temperature on a Varian A-60D, and at low temperature on a Varian HA-100 spectrometer, equipped with variable temperature probe. The data are presented in Table I.

Raman spectra were obtained on a Cary-81 spectrophotometer equipped with a Spectra-Physics 125 He/Ne laser with an exciting line at 15803 cm^{-1}; the data were obtained on finely ground solid samples held in a parabolic solid sample holder. The data for $Ru_4H_4(CO)_{12}$, $Ru_4D_4(CO)_{12}$, and $Ru_4H_2D_2(CO)_{12}$ are presented in Table II while the spectrum for the latter is shown in Figure 3.

Reaction of H_2 and D_2 with $Ru_3(CO)_{12}$; Preparation of $Ru_4H_4(CO)_{12}$ and $Ru_4D_4(CO)_{12}$. Hydrogen was bubbled through an octane solution (80 ml) of $Ru_3(CO)_{12}$ (257 mg, 0.364 mmol) at reflux for 1 hr during which time the mixture turned yellow and the ir spectrum indicated that all the starting material had been consumed. The solution was concentrated and filtered through a short silica gel column and recrystallized from CH_2Cl_2-hexane as a yellow powder, identified as $Ru_4H_4(CO)_{12}$ by ir and ^1H NMR (see Table I), Raman (see Table II), MS (Figure 1, Tables A, B[7]), and elemental analysis. Yield was 179 mg (0.241 mmol), 88%; when the reaction was carried out on a more concentrated sample, the solution turned dark and the yields were reduced.

Anal. Calcd for $C_{12}H_4O_{12}Ru_4$: C, 19.36; H, 0.54; O, 25.79; Ru, 54.53. Found:[19a] C, 19.33; H, 0.54; O, 25.62; Ru, 54.53.

$Ru_4D_4(CO)_{12}$ was prepared analogously by bubbling deuterium gas through an octane solution of $Ru_3(CO)_{12}$. This material was characterized by its ir (Table I, Figure 2), Raman (Table II), and mass spectrum (Figure 1 and Tables D, E[7]).

Reaction of H_2 and D_2 with $Ru_4H_2(CO)_{13}$; Preparation of $Ru_4H_2D_2(CO)_{12}$. $Ru_4H_2(CO)_{13}$ (100 mg, 0.13 mmol) in refluxing hexane (35 ml) was treated with hydrogen gas bubbling through

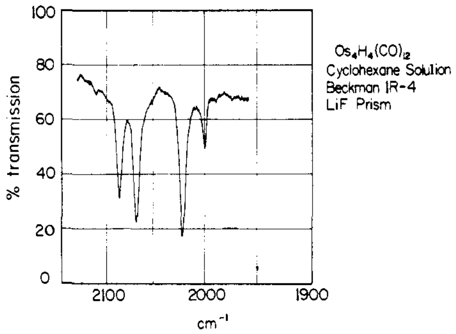


Figure 5. Infrared absorptions in the carbonyl stretching region for $Os_4H_4(CO)_{12}$; see data, Table I: cyclohexane solution, Beckman IR 4/LiF prism.

slowly at atmospheric pressure. Within *2 min* the deep red solution of the dihydride had become bright yellow. The solution was filtered hot and concentrated, affording essentially quantitatively a bright yellow powder on cooling, identified as $Ru_4H_4(CO)_{12}$ by spectroscopic means.

In a similar fashion use of D_2 gas generates a product identified as $Ru_4H_2D_2(CO)_{12}$; see Table I, Figure A[7] and Tables E, F.[7] The Raman spectrum of $Ru_4H_2D_2(CO)_{12}$, Figure 3, contains the characteristic broad absorptions due both to bridging hydrogen, observed in $Ru_4H_4(CO)_{12}$, and bridging deuterium, observed in $Ru_4D_4(CO)_{12}$.

Reaction of $Ru_4H_4(CO)_{12}$ with Deuterium; Hydrogen-Deuterium Exchange. (i) A refluxing hexane (25 ml) solution of $Ru_4H_4(CO)_{12}$ (~25 mg) was treated with D_2 gas for 3 hr at atmospheric pressure. Concentration and crystallization of the solution afforded a yellow powder with the characteristic ir of an $Ru_4H_{4-n}D_n(CO)_{12}$ species. The shift to higher mass for the parent ion of the material in the mass spectrum compared with $Ru_4H_4(CO)_{12}$ was consistent with deuteration of the order of 55%; because of the unknown degree of H (or D) loss from the parent ions of intermediate species $n = 1, 2, 3$, this estimation is necessarily approximate.

(ii) $Ru_4H_4(CO)_{12}$ (~700 mg) was sealed in a Carius tube (~150-ml volume) with deuterium gas (~700 mm) at 25° in the absence of solvent. After heating at 130-140° for 3 hr some decomposition occurred, with deposition of a ruthenium metallic mirror, but crystallization of the residue from dichloromethane-hexane gave a yellow powder, indicated by mass spectra of the molecular ion to be deuterated $Ru_4H_4(CO)_{12}$. The shift of intensity to higher mass compared with $Ru_4H_4(CO)_{12}$—the pattern was centered on *m/e* 746—was indicative of approximately 25% deuteration.

Reaction of H_2 with $FeRu_3H_2(CO)_{13}$; Preparation of $FeRu_3H_4(CO)_{12}$. Hydrogen was bubbled through a solution of $FeRu_3H_2(CO)_{13}$ (232 mg, 0.320 mmol) in 75 ml of refluxing hexane. After 6 hr the solution was orange, and the ir showed mainly a new product, with some starting material remaining. The solution was concentrated and chromatographed on silica gel with hexane, eluting an orange band followed by a slow-moving red band identified by ir as starting material. The first band was collected and solvent removed yielding dark red powder recrystallized from CH_2Cl_2-hexane and identified as $FeRu_3H_4(CO)_{12}$ by ir (see Figure 2 and Table I), ^1H NMR (Table I), and elemental analysis; yield 152 mg (0.218 mmol), 83.5% based on $FeRu_3H_3(CO)_{13}$ consumed.

Anal. Calcd for $C_{12}H_4FeO_{12}Ru_4$: C, 20.61; H, 0.58. Found:[19b] C, 21.02; H, 0.95.

The product of the reaction of H_2 with $FeRu_3H_2(CO)_{13}$ has a mass spectrum with a parent peak at *m/e* 701, with fragments corresponding to successive loss of 12 CO groups with concomitant hydrogen loss. The compound is not thermally stable at probe temperatures of 100-120° needed to see any signal and rearrangement to $Ru_4H_4(CO)_{12}$ occurred to an extent of about 25%. Because the $P - n$CO ($n = 1, 2$) multiplets of $Ru_4H_4(CO)_{12}$ overlap with both the high and low mass regions of the parent ion multiplet of $FeRu_3H_4(CO)_{12}$, the comparison of calculated and observed peak components for the parent ion of this molecule was not attempted.

Action of Hydrogen on $FeRu_2(CO)_{12}$. Passage of hydrogen at atmospheric pressure through a refluxing heptane solution (50 ml) of $FeRu_2(CO)_{12}$ (0.05 g, 0.084 mmol) for 0.5 hr produced a cloudy yellow solution. After filtering off the solids, concentration and cooling of the filtrate induced the crystallization of $Ru_4H_4(CO)_{12}$ (0.015 g, 48%). The remaining solution showed, in addition to bands due to $Ru_4H_4(CO)_{12}$, weak bands due to $FeRu_3H_4(CO)_{12}$.

Action of Hydrogen on $[Ru(Me_3Si)(CO)_4]_2$. After dispersing H_2 through an octane solution (50 ml) of $[Ru(Me_3Si)(CO)_4]_2$ (0.30 g, 0.52 mmol) at 65° for 1 hr, the solution had become deeper yellow and ir indicated the formation of $Ru_4H_4(CO)_{12}$. On increasing the temperature to 90° the reaction was completed within a further hour to give a clear yellow solution of spectroscopically pure $Ru_4H_4(CO)_{12}$. Evaporation yielded 0.178 g (92%) of the product.

Action of H_2 on $Os_3(CO)_{12}$; Syntheses of $Os_3H_2(CO)_{10}$ and $Os_4H_4(CO)_{12}$. Hydrogen was bubbled through a solution of $Os_3(CO)_{12}$ (200 mg, 0.221 mmol) in octane (40 ml) at 120°. After 1.5 hr the solution had become deep red, and the ir indicated little starting material remaining. The reaction was stopped at this point, concentrated, and chromatographed on silica gel with hexane as eluant. A deep purple band was obtained, identified as $Os_3H_2(CO)_{12}$ as indicated below, with a small amount of $Os_3(CO)_{12}$ following. Yield of $Os_3H_2(CO)_{10}$ was 130 mg (0.153 mmol), 73% based on $Os_3(CO)_{12}$ consumed.

When deuterium gas is bubbled through a solution of $Os_3(CO)_{12}$ for 2 hr, product obtained after chromatography indicated extensive exchange with hydrogen of hydrocarbon solvent, as mentioned in the discussion above. Analysis of product mass spectrum was carried out with the aid of MASPAN, described above; the relative intensities for all possible combinations of $Os_3H_2(CO)_{12}$, $Os_3HD(CO)_{10}$, and $Os_3D_2(CO)_{10}$ were calculated at 5% increments, and the sum of the squares of the deviations between each calculated set of intensities was compared with the experimental. Further refinement at 1% increments were then carried out to a further minimum around the lowest value for the sum of least squares obtained in the first set. The results have been presented in the discussion section and are also shown in Figure B and Table K.[7] The analysis must be regarded as approximate at this time as no provisions were made for either hydrogen or deuterium loss in the parent ion multiplets or the relative sensitivity of hydrogen and deuterium derivatives for lack of the totally deuterated material. These omissions, however, are not likely to affect the final results to a significant extent.

When hydrogen is bubbled through the above mentioned solution of $Os_3(CO)_{12}$ past the previous point, the ir after 41 hr showed only one product. The yellow solution was concentrated and chromatographed on silica gel with hexane as eluant. A colorless compound was eluted followed by green and brown bands which were not characterized because of their small quantities. The first substance was identified as $Os_4H_4(CO)_{12}$; see Table I, Figure 5 and mass spectrum, Figure 4, and Tables L, M, and N;[7] yield 65 mg (0.059 mmol), 29% based on $Os_3(CO)_{12}$.

Treatment of Miscellaneous Carbonyl and Cyclopentadienyl-Carbonyl Derivatives with H_2. The following derivatives were treated with H_2 in solution and at the temperatures and times given below. Known substances identified by their carbonyl absorptions are reported; in each case where unidentified bands were observed, reaction mixtures were subjected to chromatography. No new products were isolated in these attempts.

$Mn_2(CO)_{10}$ gave only brown decomposition at all temperatures up to and including refluxing decane 150°. Ir showed no new carbonyl containing products.

$[(\eta\text{-}C_5H_5)Mo(CO)_3]_2$ in refluxing decane for 24 hr gave some broad CO bands at 1800-1900 cm^{-1} accompanied by much decomposition; no products could be isolated. $Mo(CO)_5{\cdot}THF$[20] was converted to $Mo(CO)_6$. $Fe_3(CO)_{12}$ was converted to $Fe(CO)_5$ in refluxing octane in 2 hr. An acidified solution of $[Na]_2[Fe_4(CO)_{13}]$[21] was extracted with hydrocarbon giving unstable $Fe_4H_2(CO)_{13}$; this converted at room temperature to $Fe_3(CO)_{12}$ under bubbling H_2, a mode of decomposition also observed in absence of external supply of H_2. $Co_2(CO)_8$ gave $Co_4(CO)_{12}$ at room temperature; the latter gave evidence only of decomposition upon further treatment at elevated temperature. $MnRe(CO)_{10}$[22] forms an equilibrium mixture of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ and no other reaction other than subsequent decomposition of $Mn_2(CO)_{10}$ along with formation of $Re_3H_3(CO)_{12}$.[2] $Mn_3H_3(CO)_{12}$ in decane at 75° gave only $Mn_2(CO)_{10}$ after 2 hr.

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Supplementary Material Available. Fourteen tables and two figures relating to the mass spectral data and its analysis will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-3942.

References and Notes

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Synthesis and Characterization of Tetraphenylarsonium Tri-μ-hydrido-dodecacarbonyltetraruthenate. Observation of Structural Isomers and Their Rapid Interconversion in a Hydrido–Metal Cluster Anion[1]

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Abstract: The title compound is synthesized by treatment of $Ru_4H_4(CO)_{12}$ with alcoholic KOH for a short period followed by precipitation with $(C_6H_5)_4AsCl$. Raman spectrum indicates bridging hydrogen through a broad absorption centered at 1442 cm^{-1}, $\Delta\nu_{1/2} \sim 55$ cm^{-1}. Proton magnetic resonance spectra at low temperature reveal the presence in nearly equal concentrations of two isomers one of C_2 or C_{2v} and one of C_{3v} symmetry which are rapidly interconverting. Equilibrium constants and thermodynamic parameters have been obtained in dimethyl ether, tetrahydrofuran, and acetone-d_6 solutions. For the equilibrium: C_2 (or C_{2v}) isomer $\rightleftarrows$ C_{3v} isomer, $K = 1.21$ at $-100°$ in acetone-d_6; $\Delta H = -8.4 \times 10^2$ cal/mol and $\Delta S = -4.5$ cal/(mol deg). Line shape analysis yields activation parameters $\Delta H^{\ddagger} \sim 11$ kcal/mol and $\Delta S^{\ddagger} \sim 0.2$-8 eu for the interchange of hydrogen environments; spin saturation transfer studies indicate this occurs through a combination of intramolecular tautomerism and isomerization pathways.

Whereas substitution of CO predominates in the treatment of hydrido-metal carbonyl cluster complexes with phosphines or phosphites,[2,3] reagents of higher basicity and lower nucleophilicity can lead to deprotonation.[3] In derivatives where the hydrogen atoms are located in positions bridging the metal-metal bonds,[3] they are shielded by the groups bonded to the metals from contact with external reagents. Accordingly, we found the reaction of $Ru_4H_4(CO)_{12}$ with alcoholic KOH to be slow at room temperature. After stirring overnight, however, the hydrido-metal cluster is eventually consumed but only an intractable brown solid showing a broad and featureless absorption in the carbonyl stretching region of the ir is obtained. Further investigations revealed that treatment of the original mixture at 55° for 0.5 hr, followed immediately by the addition of tetraphenylarsonium chloride, gives a red crystalline compound in high yield identified as $[(C_6H_5)_4As][Ru_4H_3(CO)_{12}]$ (**1**).

Infrared spectra for the carbonyl stretching region of **1** in two different solvents and in KBr pellet are given in Table I; the spectrum in acetone solution is shown in Figure 1. These indicate only terminal carbonyl groups, and from the complexity of the pattern one may assume either that a species of low symmetry or that more than one species is present.

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