Table IX. Electronic Spectroscopy Data for Selected Complexes

complex	concn, M[a]	peak position, nm	extinction coeff
(t-BuDMP)$_2$(PPh$_3$)RuCl$_2$ [b]	1.0×10^{-3}	517, 714	770, 360
(PPh$_3$)$_3$RuCl$_2$ [c]	1×10^{-3}	480, 750	1350, 515
trans-(BzlDMP)$_4$RuCl$_2$	1×10^{-3}	508	250
	1×10^{-4}	488	750

[a] All solvents were CH$_2$Cl$_2$ except for (PPh$_3$)$_3$RuCl$_2$, in which benzene was the solvent. [b] Obeys the Beer–Lambert law only for freshly prepared solutions. [c] Agrees with the data in ref 52.

which rapidly dissociates in solution. The complex *trans*-(BzlDMP)$_4$RuCl$_2$ does not obey the Beer–Lambert law, suggesting that at low concentration it also dissociates.

The unusual behavior of the ruthenium phosphole complexes could indicate great potential for catalysis. It has been shown, qualitatively, that these complexes are in fact hydrogenation catalysts. Four complexes were qualitatively tested for catalytic activity as described in the Experimental Section (viz. (PPh$_3$)$_3$RuCl$_2$, (CH$_3$DMP)$_4$RuCl$_2$, (t-BuDMP)$_2$(PPh$_3$)RuCl$_2$, and *cis*-(Bzl$_3$P)$_2$Ru(CO)$_2$Cl$_2$) and all exhibited the ability to catalyze the hydrogenation of 1-heptene to heptane at roughly comparable rates. It remains to be seen just how effective or selective these complexes will be as catalysts, and further study is in progress.

Acknowledgment. The financial assistance of the University of Nevada at Reno Research Advisory Board is gratefully acknowledged. J.H.N. is grateful to the National Science Foundation (Grant No. CHE 77-08937) for providing funds to purchase the Fourier transform NMR spectrometer. K.S. is indebted to the University of Hawaii Computing Center. L.B.M. was supported by a department fellowship (University of Hawaii). We are grateful to Prof. M. P. Simonnin for the ^{1}H{^{31}P} NMR spectra.

Registry No. *trans*-(PhDBP)$_2$Ru(CO)$_2$Cl$_2$, 86495-08-1; *cis*-(PhDBP)$_2$Ru(CO)$_2$Cl$_2$, 86421-44-5; *cis*-(PhDMP)$_2$Ru(CO)$_2$Cl$_2$, 86495-69-4; *trans*-(BzlDMP)$_2$Ru(CO)$_2$Cl$_2$, 86421-45-6; *cis*-(BzlDMP)$_2$Ru(CO)$_2$Cl$_2$, 86470-38-4; *cis*-(n-BuDMP)$_2$Ru(CO)$_2$Cl$_2$, 86421-46-7; *trans*-(t-BuDMP)$_2$Ru(CO)$_2$Cl$_2$, 86421-47-8; *cis*-(t-BuDMP)$_2$Ru(CO)$_2$Cl$_2$, 86470-39-5; *cis*-(BzlDMP)$_4$RuCl$_2$, 86421-48-9; *trans*-(BzlDMP)$_4$RuCl$_2$, 86470-40-8; *trans*-(PhDMP)$_4$RuCl$_2$, 86421-49-0; *cis*-(PhDMP)$_4$RuCl$_2$, 86470-41-9; *cis*-(CH$_3$DMP)$_4$RuCl$_2$, 86421-50-3; *trans*-(CH$_3$DMP)$_4$RuCl$_2$, 86470-42-0; *trans*-(n-BuDMP)$_4$RuCl$_2$, 86436-03-5; (t-BuDMP)$_2$(PPh$_3$)RuCl$_2$, 86421-51-4; *trans*-(t-BuDMP)$_4$RuCl$_2$, 86421-52-5; *trans*-(PPh$_3$)$_4$RuCl$_2$, 86470-43-1; *trans*-(PPh$_3$)$_3$RuCl$_2$, 41756-81-4; *trans*-(n-BuDMP)$_2$Ru(CO)$_2$Cl$_2$, 86495-09-2; *trans*-(CH$_3$DMP)$_2$Ru(CO)$_2$Cl$_2$, 86421-53-6; *trans*-(PhDMP)$_2$Ru(CO)$_2$Cl$_2$, 86421-54-7; (PhDMP)$_3$Ru(CO)Cl$_2$, 86436-04-6; 1-heptene, 592-76-7.

Supplementary Material Available: Stereoviews of the (PhDMP)$_3$Ru(CO)Cl$_2$ molecule and the unit cell and listings of the changes in cell constants, thermal parameters, coefficients of least-squares planes, and observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

---

(52) James, B. R.; Markham, L. D. *Inorg. Chem.* **1974**, *13*, 97.

Contribution from the Laboratoire de Chimie de Coordination du CNRS
associé à l'Université Paul Sabatier, 31400 Toulouse, France

Synthesis and Spectroscopic Characterization of Trihydrido Mixed-Metal Tetranuclear Clusters (μ-H)$_3$M$_3$Ni(η^5-C$_5$H$_5$)(CO)$_9$ (M = Ru, Os). Low-Temperature X-ray Diffraction Study of the Osmium Derivative

GUY LAVIGNE, FOUNE PAPAGEORGIOU, CHRISTIAN BERGOUNHOU, and JEAN-JACQUES BONNET*

Received June 1, 1982

Simple synthetic reactions to produce hydrido mixed-metal clusters through a hydrogen-assisted condensation of triruthenium or triosmium carbonyl clusters with a cyclopentadienyl nickel dimer [(η^5-C$_5$H$_5$)Ni(CO)]$_2$ are reported. The resulting tetranuclear cluster complexes (μ-H)$_3$M$_3$Ni(η^5-C$_5$H$_5$)(CO)$_9$ (M = Ru, Os) have been obtained in ca. 70% yield (based on M$_3$(CO)$_{12}$) and characterized by microanalysis, mass spectrometry (including a detailed analysis of the parent ion multiplet), and IR and ^{1}H NMR spectra. The osmium derivative has been characterized by a low-temperature X-ray diffraction experiment. X-ray data (−165 °C): orthorhombic, space group *Ccmm*, $a = 10.274$ (2) Å, $b = 14.735$ (8) Å, $c = 35.488$ (5) Å, $V = 5372$ Å^3; $R(F) = 0.046$, $R_w(F) = 0.041$ for 1316 reflections with $F_o^2 > 3\sigma(F_o)^2$. The tetranuclear mixed-metal cluster crystallizes with $^1/_2$ mol of (μ-H)$_2$Os$_3$(CO)$_{10}$. It possesses a tetrahedral closo arrangement for the Os$_3$Ni core (crystallographic symmetry C_s). Bond distances of interest are Os–Os = 2.869 (2) and 2.866 (2) Å and Os–Ni = 2.564 (5) and 2.563 (5) Å. The three hydride ligands are expected to bridge osmium–osmium vectors. Variable-temperature ^{1}H NMR experiments for both ruthenium and osmium derivatives show an invariant hydride signal within the range +20 to −90 °C.

Introduction

We are evaluating the scope of a simple synthetic approach of new mixed-metal clusters through a hydrogen-assisted condensation of pure polynuclear carbonyl complexes of the second- and third-row transition metals with first-row transition-metal complexes.

At moderate temperature, condensations induced by molecular hydrogen at atmospheric pressure have been observed, leading to some remarkable syntheses of homonuclear hydrido transition-metal cluster complexes in high yield and purity.[1,2] More recently, direct conversion of a metallo-ligated cluster to a closed polyhedron was obtained in the presence of molecular hydrogen, yielding the pentahydrido mixed-metal derivative (μ-H)$_5$Os$_3$Re(CO)$_{12}$.[3] In keeping with this, we attempted the synthesis of hydrido mixed-metal Ru–Ni and Os–Ni cluster complexes, which are rare in comparison with other series.[4]

---

(1) Kaesz, H. D. *Chem. Br.* **1973**, *9*, 344.

(2) Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942.

(3) Churchill, M. R.; Hollander, F. J.; Lashewycz, R. A.; Pearson, G. A.; Shapley, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 2430.

(4) Chini, P.; Heaton, B. T. *Top. Curr. Chem.* **1977**, *71*.

Earlier reports by Sappa and co-workers[5] showed that the preparation of such mixed-metal clusters often requires the use of bridging alkyne ligands. In the absence of such ligands, the authors noted that an unsaturated cluster, tentatively formulated as "$(Cp)NiRu_3(CO)_9$", could be isolated with low yield from the reaction of $Ru_3(CO)_{12}$ with cyclopentadienyl nickel derivatives.[5] In contrast, the same reaction performed with $Os_3(CO)_{12}$[6] led to the hexanuclear mixed-metal cluster $(\eta^5\text{-}C_5H_5)_3Ni_3Os_3(CO)_9$.

The present paper shows that $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ behave similarly when they are allowed to react with $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$ in the presence of molecular hydrogen at atmospheric pressure, yielding the trihydrido mixed-metal clusters $(\mu\text{-}H)_3M_3Ni(\eta^5\text{-}C_5H_5)(CO)_9$ (M = Os, Ru). Such condensations may be relevant to the existence of reactive trinuclear hydrido ruthenium and osmium intermediates being generated "in situ".

The X-ray structure of $(\mu\text{-}H)_3Os_3Ni(\eta^5\text{-}C_5H_5)(CO)_9$ is discussed in comparison with that of $(\mu\text{-}H)_2Os_3Ni(\mu\text{-}CO)_2(CO)_8(PPh_3)_2$, the only precedent within the tetranuclear osmium–nickel series.[7]

Experimental Section

General Comments. The compounds reported in this study do not exhibit particular sensitivity to air at room temperature so that they can be handled in solution without undue precautions. However, as a matter of routine in this laboratory, the reactions were performed under an atmosphere of prepurified nitrogen with use of Schlenk tubes and vacuum lines. All organic solvents were reagent grade; they were degassed prior to use.

$Ru_3(CO)_{12}$ was prepared by a published procedure.[8] $Os_3(CO)_{12}$ was purchased from Johnson Matthey Chemicals; $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$ was purchased from Pressure Chemicals. $H_2Os_3(CO)_{10}$ was prepared as described by Kaesz and co-workers.[2]

Analytical data were obtained from the "Service Central de Microanalyse du CNRS".

Spectroscopic Data. IR Spectra. Solution spectra in the ν(CO) region were recorded on a Perkin-Elmer 225 spectrophotometer, with cyclohexane as a solvent. These spectra were calibrated on saturated water vapor lines.

^{1}H NMR Spectra. Variable-temperature ^{1}H NMR spectra were recorded on Bruker WH 90 and Bruker WM 250 spectrometers. Chemical shifts (δ) given in this paper are relative to internal Me_4Si reference.

Mass Spectra. High-resolution mass spectra were obtained on a Varian MAT 311A with direct inlet probe (EI) at 65 °C. Analysis of the parent ion multiplets was made by averaging four scans of the same multiplet. The average normalized spectra were compared with theoretical spectra by using the MASPAN program.[9] A quantitative estimate of the goodness of fit between the calculated and observed spectra is given by an R factor defined as

$$R = \sum_{i=0}^{N} |I_i^o - I_i^c| / \sum I_i^c$$

where N is the number of peaks in the multiplet and I_i^o and I_i^c are the observed and calculated intensities of the ith peak, respectively.

Syntheses. $(\mu\text{-}H)_3Os_3Ni(\eta^5\text{-}C_5H_5)(CO)_9$ (1). In our initial experiment, hydrogen was bubbled through an octane solution (50 mL) containing $Os_3(CO)_{12}$ (194 mg) and $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$ (130 mg) at reflux for 2 h. A metallic nickel mirror was deposited on the glass vessel.

Slow evaporation of the solution gave three kinds of crystals: (i) unreacted $Os_3(CO)_{12}$, (ii) violet crystals which were easily identified as the well-known cluster complex $(\mu\text{-}H)_2Os_3(CO)_{10}$, and (iii) black, prismatic lozenge-shaped crystals which were subsequently formulated as the trihydrido mixed-metal cluster $(\mu\text{-}H)_3NiOs_3(CO)_9(\eta^5\text{-}C_5H_5)$ (**1**) crystallizing with $^1/_2$ mol of the dihydrido osmium cluster $(\mu\text{-}H)_2Os_3(CO)_{10}$ (crystals of type I). Evidence for the presence of both clusters within a single crystal was obtained from the X-ray diffraction study (vide infra). Accordingly, a C_6D_6 solution obtained by dissolution of type I crystals displayed the high-field ^{1}H NMR resonances of both these hydrido cluster complexes (δ = −12.2 for $(\mu\text{-}H)_2Os_3(CO)_{10}$ and δ = −17.80 for **1**).

Chromatographic workup allowed the separation of the pure mixed-metal cluster compound according to the following procedure. The octane solution containing the reaction mixture was reduced in volume under vacuum. Silica gel was added, and the solution was evaporated to dryness. The solid residue was added at the top of a 3 × 40 cm column packed with silica gel 60 (Merck, 230–400 mesh). Elution with pentane gave two violet bands. The first one was identified as $(\mu\text{-}H)_2Os_3(CO)_{10}$ (yield ca. 10%); the second one was shown to contain the pure trihydrido mixed-metal cluster compound **1**. Further elution with acetone gave unidentified products. Brown, intractable material was also retained on the top of the column. The pure mixed-metal cluster **1** was recrystallized from acetone as black prismatic needles (type II) directly suitable for X-ray analysis[9] (145 mg, 71.4% yield based on osmium). This experimental procedure is the simplest route to the mixed-metal cluster **1** since it does not require isolation of $(\mu\text{-}H)_2Os_3(CO)_{10}$, which is generated "in situ". Attempts to prepare **1** from preformed $(\mu\text{-}H)_2Os_3(CO)_{10}$ were indeed successful, but in the absence of hydrogen, the yields were found to be considerably lower, and hence hydrogen proved to be necessary. In a typical experiment, $(\mu\text{-}H)_2Os_3(CO)_{10}$ (210 mg) and $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$ (74 mg) were refluxed in 50 mL of octane for 2 h while hydrogen was bubbled into the solution. After cooling, the reaction mixture was evaporated to dryness and chromatographed. Elution with pentane gave only one band. Recrystallization from acetone–pentane gave 165 mg of crystals (type II) (70% yield). Anal. Calcd for $Os_3NiC_{14}O_9H_8$: Ni, 6.18; C, 17.71; H, 0.85. Found: Ni, 5.95; C, 17.85; H, see below.

While the purity of our crystalline sample could be determined by mass spectrometry and ^{1}H NMR, we found an intriguing systematic high percentage of hydrogen: average 3.13%. A careful control of the analysis routines allowed us to understand this discrepancy. Indeed, in the usual procedure, elemental hydrogen is converted into H_2O by oxidation at 1050 °C; metallic oxides are also generated and generally retained on a filter. H_2O is condensed at −40 °C and then passed over carbon at 1000 °C, giving carbon monoxide, which is then oxidized over CuO and titrated as CO_2. However, we have found that the highly volatile osmium tetroxide generated in the initial pyrolysis cannot be retained on the filter and is condensed along with water. When passed over carbon, each mole of OsO_4 then generates 4 mol of CO, which is erroneously accounted for as 8 H. Assuming the total amount of OsO_4 to be condensed with H_2O, we find that the amount of hydrogen should be overestimated by 2.55, which is consistent with our observation. (We have checked the analysis of a sample of commercial $Os_3(CO)_{12}$ to lead to a "dummy" hydrogen weight of 2.45%, indicating that at least 90% of the osmium tetroxide passes through the filter.) Investigators should then be aware that the analytical procedure described above is not suitable for osmium-containing products.

IR (ν(CO), cyclohexane): 2090 (w), 2062 (s), 2004 (s), 1990 (w) cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6, room temperature): δ 5.73 (s, 5 H, cyclopentadienyl), −17.80 (s, 3 H, hydride). Variable-temperature spectra (deuterated acetone as solvent) in the range +20 to −50 °C showed no modification.

Although the complex proved to crystallize under several crystalline forms,[10] all of the kinds of crystals gave the same mass spectrum showing the parent ion at m/e 950. The fragmentation pattern indicated two prevailing fragmentation routes: (i) successive loss of nine CO groups, followed by loss of cyclopentadienyl and loss of nickel; (ii) successive loss of two CO groups, loss of cyclopentadienyl, loss of seven CO groups, and loss of nickel. A detailed analysis of the parent ion multiplets was made by using the MASPAN program.[9] A

---

(5) Sappa, E.; Manotti Lanfredi, A. M.; Tiripicchio, A. *J. Organomet. Chem.* **1981**, *221*, 93 and references therein.

(6) Sappa, E.; Lanfrachi, M.; Tiripicchio, A.; Tiripicchio Camellini, M. *J. Chem. Soc., Chem. Commun.* **1981**, 995.

(7) Farrugia, L. J.; Howard, J. A. K.; Mitrprachachon, P.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981**, 171.

(8) We have found that the amounts of starting materials and solvents for this synthesis can be favorably tripled without any decrease of the yield of the reaction: Mantovani, A.; Cenini, S. *Inorg. Synth.* **1976**, *16*, 47.

(9) MASPAN computer program, version 6, written by Art Cabral at UCLA in 1978 and kindly supplied by H. D. Kaesz.

(10) The complex crystallizes in several crystalline forms, one of which is isomorphous with that of the ruthenium complex.[12]

comparison of average observed multiplets with the theoretical isotopic multiplet pattern is given in Table IX. The goodness of fit was given by a satisfactory value of $R = 3.36\%$.[11]

$(\mu\text{-H})_3Ru_3Ni(\eta^5\text{-}C_5H_5)(CO)_9$ (2). Under the experimental conditions reported for the osmium derivative (octane solution, 120 °C, continuous hydrogen stream), low yields of the mixed-metal cluster were prepared, and the most abundant species generated was $H_4Ru_4(CO)_{12}$. Optimum yields of the mixed cluster were obtained at lower temperature (80–90 °C). The low solubility of $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$ in octane at these temperatures led us to prefer ethoxyethanol as solvent for this synthesis.

In a typical experiment, hydrogen was bubbled through a mixture of $Ru_3(CO)_{12}$ (780 mg) and $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$ (370 mg) in 50 mL of ethoxyethanol at 80–85 °C for 90 min. After cooling and solvent removal under reduced pressure, chromatographic workup on silica gel (pentane as eluent) afforded two bands: (i) a yellow broad band, which was identified as the known complex $H_4Ru_4(CO)_{12}$ (traces); (ii) a green-black band, which proved to contain the pure mixed-metal cluster complex $(\mu\text{-H})_3Ru_3Ni(\eta^5\text{-}C_5H_5)(CO)_9$ (**2**) (330 mg, yield 39%). Traces of other unidentified products could also be eluted with toluene. In all cases, black, intractable material was retained at the top of the column. If the latter reaction is carried out for 8 h, the yield is improved to 74%.

The compound **2** can be recrystallized from various solvents. Crystals directly suitable for X-ray analysis[12] were grown by slow evaporation of acetone solutions as black, prismatic needles. Anal. Calcd for $Ru_3NiC_{14}O_9H_8$: Ni, 8.61; C, 24.65; H, 1.18. Found: Ni, 8.38; C, 24.75; H, 1.19. IR (ν(CO), cyclohexane): 2088 (w), 2060 (s), 2015 (s), 2000 (m) cm^{-1}. ^1H NMR (250 MHz, CD_2Cl_2, room temperature): δ 5.71 (s, 5 H, cyclopentadienyl), −16.07 (s, 3 H, hydride). Variable-temperature experiments in the range +20 to −90 °C showed no temperature dependence for this spectrum.

The mass spectrum clearly showed the parent ion multiplet at m/e 683. The fragmentation pattern proved to be the same as for the osmium derivative. A detailed analysis of the parent ion multiplet was made by using the MASPAN program.[9] The results are displayed in Table X. The R value is 3.35%.[13]

X-ray Structure Analysis of Type I Crystals. $(\mu\text{-H})_3Os_3Ni(\eta^5\text{-}C_5H_5)(CO)_9\cdot{}^1/_2(\mu\text{-H})_2Os_3(CO)_{10}$. Collection and Reduction of X-ray Data. Preliminary Laue and precession photographs showed complex **1** to crystallize in an orthorhombic cell. Systematic absences were consistent with space groups *Cmcm* (No. 63), *Cmc*2_1 (No. 36), and *Ama*2 (No. 40). The structure was successfully solved in the space group *Ccmm*, a nonstandard setting of *CmCm*. The crystal selected for intensity data collection was glued on a glass fiber with Apiezon N grease and transferred to an Enraf-Nonius CAD4 diffractometer equipped with a low-temperature device. All intensity measurements were made at −165 ± 1 °C. The setting angles of 25 reflections within the range $24° < 2\theta(\text{Mo}) < 26°$ were refined by least-squares procedures, leading to the cell constants that are reported in Table I along with pertinent crystal and intensity data. A total of 2504 reflections were recorded up to $2\theta(\text{Mo}) = 46°$. These intensities were corrected for Lorentz, polarization, and absorption effects[14] and reduced to observed structure factor amplitudes, with use of a p value of 0.03.[15]

Table I. Experimental Data for the X-ray Diffraction Study

Crystal Data

formula: $(\mu\text{-H})_3Os_3Ni(CO)_9(\eta\text{-}C_5H_5)\cdot{}^1/_2(\mu\text{-H})_2Os_3(CO)_{10}$
cryst syst: orthorhombic
space group: *Ccmm*
cell parameters (at −165 ± 1 °C)
$a = 10.274$ (2) Å
$b = 14.735$ (3) Å
$c = 35.488$ (5) Å
$V = 5372$ Å^3
cryst shape: lozenge-based parallelepiped
boundary faces: {001}, {110}, {1$\bar{1}$0}
dist from these faces to arbitrary origin: 0.014 mm, 0.055 mm, 0.055 mm
cryst vol: 0.34×10^{-3} mm^3
density (calcd): 3.40 g cm^{-3}
$\mu = 232$ cm^{-1}
min and max transmission factors: 0.187, 0.513

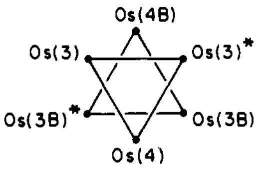
Intensity Data

radiation: Mo Kα ($\lambda = 0.709\,30$ Å) from monochromator
takeoff angle: 3°
data collection procedure: intensities recorded with the flat mode available on Enraf-Nonius CAD4, procedure allows recording at min abs
θ limits: 1.40–23°
scan mode: ω scan
scan range: 0.5° below Kα_1 to 0.5° above Kα_2
scan speed: 2° min^{-1} (θ)
std reflecns: {262}, {407}, {080}; no signif dev
reflecns collected: 2504
unique data used: 1316, $F_o^2 > 3\sigma(F_o)^2$
final R values: $R = 0.046$, $R_w = 0.041$
std error in an observn of unit wt: 1.38 e

After processing, only those 1316 unique reflections with $F_o^2 > 3\sigma(F_o)^2$ were used in subsequent calculations.

Solution and Refinement of the Structure. The direct method approach[14] based on 303 normalized structure factors yielded the correct osmium and nickel atom coordinates. Subsequent refinements and difference Fourier calculations led to the location of all nonhydrogen atoms.

Atomic scattering factors for all atoms were taken from Cromer and Waber's tabulation.[16] Anomalous dispersion terms for Os and Ni atoms were included in F_c.[17] The structure solution revealed the existence of two different cluster units within the unit cell: (i) a triangular cluster unit based on Os(1), Os(2), Os(1)* (crystallographic symmetry C_{2v}; starred atoms are related to equivalent positions obtained through the mirror plane); (ii) a tetranuclear cluster unit based on Os(3), Os(3)*, Os(4), Ni (crystallographic symmetry C_s). Refinement of such metal atoms with isotropic temperature factors showed abnormal discrepancies between the B values of Os(1) and Os(2) and those of Os(3) and Os(4). The larger B values associated with the latter atoms might be indicative of partial occupancy of these sites. Indeed, a careful observation of a Fourier map showed additional peaks, labeled as Os(3B) and Os(4B), which strongly suggested the occurrence of two orientations for the osmium triangle as shown schematically:



(Such a disorder also implied a slight splitting of the apical nickel atom.)

A statistical distribution between two sites was thus to be considered. Approximate values of occupancy factors were first assigned on the

---

(11) Attempts to estimate hydrogen loss were made since the observed multiplet might result from the overlap of the parent ion $H_3Os_3Ni(C_5H_5)(CO)_9^+$ with the fragmentation ions $H_2Os_3Ni(C_5H_5)(CO)_9^+$, $HOs_3Ni(C_5H_5)(CO)_9^+$, and $Os_3Ni(C_5H_5)(CO)_9^+$. The deconvolution of these overlapped ions gave a nonsignificant improvement of the R factor, $R = 2.8\%$, for a fitted percent contribution of 98.7% $H_3Os_3Ni(C_5H_5)(CO)_9^+$, 0% $H_2Os_3Ni(C_5H_5)(CO)_9^+$, 0% $HOs_3Ni(C_5H_5)(CO)_9^+$, and 1.3% $Os_3Ni(C_5H_5)(CO)_9^+$.

(12) Crystal data: tetragonal, $a = b = 30.004$ (5) Å, $c = 10.476$ (5) Å. This structure raises an intricate problem of disorder, which we have not yet been able to solve.

(13) Attempts to estimate hydrogen loss were made by assembling four formulas differing by the number of hydride ligands. The deconvolution routine gave a nonsignificant decrease of the R value: $R = 2.16\%$ for 97.3% H_3, 0% H_2, 0% H_1, and 2.7% H_0.

(14) The main programs used were the following: the Northwestern absorption program, AGNOST, which includes the Coppens–Leiserowitz–Rabinovitch logic for Gaussian integration and the Tompa De Meulenaur analytical method; Germain's MULTAN; Zalkin's FORDAP Fourier summation program; Johnson's ORTEP; Busing and Levy's ORFFE error function program; Ibers' NUCLS full-matrix least-squares program, which in its nongroup form closely resembles the Busing–Levy ORFLS program.

(15) Mosset, A.; Bonnet, J.-J.; Galy, J. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2639.

(16) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(17) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography", Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

Table II. Positional and Thermal Parameters for the Nongroup Atoms of $H_3Os_3Ni(C_5H_5)(CO)_9$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Os(1)	0.4388 (1)	0.09059 (9)	$^1/_4$	13.2 (6)	10.0 (6)	16.1 (8)	−1.7 (6)	0	0
Os(2)	0.1987 (2)	0	$^1/_4$	11.2 (9)	11.3 (9)	24 (1)	0	0	0
Os(3)	0.2824 (1)	0.40265 (8)	0.05370 (4)	23.0 (6)	25.5 (6)	18.5 (7)	−1.4 (6)	1.2 (5)	−2.9 (7)
Os(4)	0.4796 (1)	$^1/_2$	0.09404 (6)	19.6 (8)	25.4 (9)	22 (1)	0	0.8 (8)	0
Ni	0.2382 (5)	$^1/_2$	0.1122 (2)	19 (3)	35 (3)	15 (3)	0	4 (2)	0

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O(1)	0.221 (2)	0.340 (1)	$^1/_4$	2.2 (5)	O(8)	0.525 (2)	0.349 (1)	0.1517 (7)	3.5 (5)
O(2)	0.345 (1)	0.218 (1)	0.1892 (5)	2.6 (4)	O(9)	0.758 (3)	$^1/_2$	0.0663 (9)	3.0 (6)
O(3)	0.007 (2)	0.161 (2)	$^1/_4$	3.0 (5)	O(5)	0.288 (3)	0.295 (2)	0.0844 (9)	2.8 (6)
O(4)	0.245 (2)	0	0.1650 (7)	2.4 (5)	C(6)	0.102 (3)	0.392 (2)	0.048 (1)	4.0 (8)
C(1)	0.116 (3)	0.369 (2)	$^1/_4$	0.7 (6)	C(7)	0.323 (3)	0.348 (2)	0.008 (1)	3.6 (7)
C(2)	0.381 (2)	0.172 (1)	0.2119 (7)	1.7 (4)	C(8)	0.507 (2)	0.407 (2)	0.1298 (8)	2.0 (5)
C(3)	0.078 (3)	0.099 (3)	$^1/_4$	2.8 (8)	C(9)	0.654 (4)	$^1/_2$	0.077 (1)	1.8 (8)
C(4)	0.226 (3)	0	0.1971 (9)	0.7 (5)	C(10)	0.242 (4)	$^1/_2$	0.173 (1)	3.2 (10)
O(5)	0.295 (2)	0.231 (1)	0.1028 (6)	2.8 (4)	C(11)	0.169 (3)	0.421 (2)	0.1573 (10)	3.1 (7)
O(6)	−0.013 (2)	0.380 (1)	0.0442 (6)	2.8 (4)	C(12)	0.060 (3)	0.452 (2)	0.136 (1)	3.6 (7)
O(7)	0.353 (2)	0.310 (1)	−0.0193 (6)	2.5 (4)					

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. The form of the anisotropic thermal ellipsoid is $\exp[-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. The quantities given in the table are the thermal coefficients $\times 10^3$.

basis of respective peak heights in a three-dimensional Fourier synthesis which clearly showed the predominance of the orientation based on Os(3), Os(3)*, Os(4). These occupancy factors were then correlated and refined satisfactorily by least-squares procedures to final values of 0.845 and 0.155, which were then fixed. It is worth noting that refinement of such a disordered model restored acceptable values for isotropic thermal parameters of osmium atoms. Subsequent three-dimensional difference Fourier maps clearly showed (i) all carbon and oxygen atoms associated with the trinuclear cluster unit based on Os(1)–Os(1)*–Os(2) and (ii) all carbon and oxygen atoms associated with the privileged orientation of the tetranuclear cluster unit based on Os(3)–Os(3)*–Os(4)–Ni(1). However, the corresponding atoms associated with the alternative orientation of the latter unit were poorly discernible, owing to their low occupancy factors. Consequently, such atoms were not included in the initial model, which was refined with isotropic temperature factors.

The observed geometry of the tetranuclear cluster unit in its predominant orientation was then assumed to be retained in the alternative orientation based on Os(3B), Os(3B*), Os(4B). Accordingly, the latter molecular site was entered and refined as a rigid group duplicating the geometry of the main orientation. Final cycles of full-matrix least-squares refinement included anisotropic thermal parameters for independent osmium and nickel atoms, and isotropic thermal parameters for all other atoms. On the basis of 1316 reflections with $F_o^2 > 3\sigma(F_o)^2$ for 110 variables, final conventional R values are $R(F) = 0.046$ and $R_w(F) = 0.041$.

Final positional and thermal parameters of all independent atoms are listed in Table II while those of the rigid-group atoms appear in Table III, which is available as supplementary material. A complete listing of observed and calculated structure factor amplitudes is also available as supplementary material.

Results and Discussion

Earlier reports on the chemistry of $Ru_3(CO)_{12}$[2] provided a simple high-yield route to $H_4Ru_4(CO)_{12}$. Nevertheless, the mechanism of this hydrogen-assisted synthesis is rather complex. If it does follow the pattern set for osmium[18]

$$Os_3(CO)_{12} \xrightarrow{H_2} H_2Os_3(CO)_{11} \xrightarrow{-CO} H_2Os_3(CO)_{10} \rightarrow H_4Os_4(CO)_{12}$$

then triruthenium hydrido intermediates should be generated prior to cluster growth. Although evidence for such complexes has not yet been obtained in ruthenium chemistry, valuable indications about their existence as intermediates might be obtained if the chemistry of $Ru_3(CO)_{12}$ in the presence of hydrogen could duplicate the chemistry of $H_2Os_3(CO)_{10}$. The rich chemistry of the latter complex has been attributed to the presence of a dihydrido-bridged Os–Os double bond which may be reduced on addition.[18] Extensive exploitation of this property provided new routes to mixed-metal clusters.[7,19–22] Our synthesis of $(\mu\text{-H})_3Os_3Ni(\eta^5\text{-}C_5H_5)(CO)_9$ from $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$ and $H_2Os_3(CO)_{10}$ is relevant to the unsaturation of the osmium cluster.

A prerequisite for the observed condensation could be a cleavage of the binuclear nickel dimer, providing unsaturated nickel fragments are added next onto the hydrido triosmium cluster.

It should be noted that the reported synthesis is mechanistically more complex than a simple addition to $H_2Os_3(CO)_{10}$: the unpaired number of hydride ligands found in the mixed complex shows that intermolecular hydride transfer has occurred, allowing the cluster to adjust the required number of bonding electrons.

Regarding now the similar synthesis of $(\mu\text{-H})_3Ru_3Ni(\eta^5\text{-}C_5H_5)(CO)_9$ from $Ru_3(CO)_{12}$ in the presence of hydrogen, we suggest that this condensation may be relevant to the existence of trinuclear hydrido ruthenium intermediates being generated "in situ". This is consistent with the fact that the mixed complex is neither synthesized from $Ru_3(CO)_{12}$ in the absence of hydrogen[23] nor available from $H_4Ru_4(CO)_{12}$.

Crystal Structure of $(\mu\text{-H})_3Os_3Ni(CO)_9(\eta\text{-}C_5H_5)$. The complex $(\mu\text{-H})_3Os_3Ni(\eta\text{-}C_5H_5)(CO)_9$ has been obtained in two crystalline forms. Crystals of types I and II respectively have been obtained before and after chromatographic workup (vide supra). The structure of a type I crystal is described here.

The crystal consists of the packing of eight molecular units of the tetranuclear mixed-metal cluster $(\mu\text{-H})_3Os_3Ni(\eta^5\text{-}C_5H_5)(CO)_9$ and four molecular units of the known trinuclear cluster complex $H_2Os_3(CO)_{10}$ as shown in Figure 1 (supplementary material). Layers of $H_2Os_3(CO)_{10}$ units are found in crystallographic planes $z = 0.25$, $z = 0.75$ and are mutually separated by two layers of tetranuclear units.

---

(18) Deeming, A. J. "Transition Metal Clusters"; Johnson, B. F. G.; Ed.; Wiley: New York, 1980; p 391 and references therein.

(19) Farrugia, L. J.; Howard, J. A. K.; Mitrprachachon, P.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1978**, 260. See also: Farrugia, L. J.; Howard, J. A. K.; Mitrprachachon, P.; Spencer, J. L.; Stone, F. G. A.; Woodwrad, P. *Ibid.* **1981**, 155.

(20) Bhaduri, S.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Watson, D. J. *J. Chem. Soc., Chem. Commun.* **1978**, 343.

(21) Plotkins, J. S.; Alway, D. G.; Weisenberger, C. R.; Shore, S. G. *J. Am. Chem. Soc.* **1980**, *102*, 6156.

(22) Shapley, J. R.; Park, J. T.; Churchill, M. R.; Bueno, C.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 7385.

(23) Hsieh, A. T. T.; Knight, J. K. *J. Organomet. Chem.* **1971**, *26*, 125.

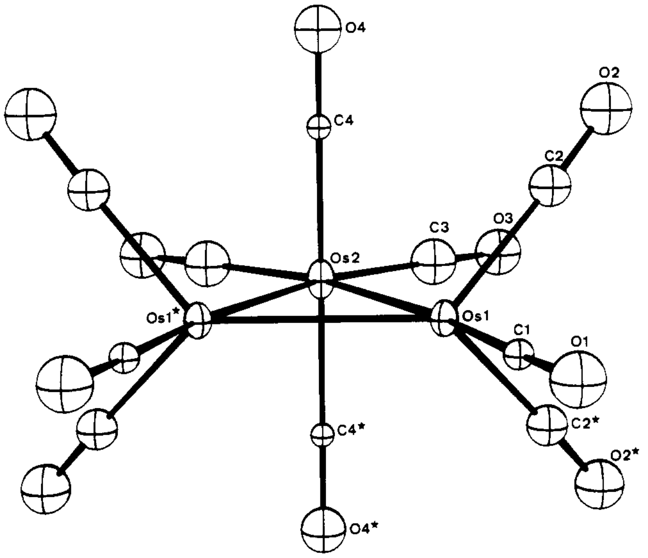


Figure 2. Perspective view of the $(\mu\text{-H})_2Os_3(CO)_{10}$ unit crystallizing with complex **1**. Thermal ellipsoids are given at the 50% probability level.

Table IV. Interatomic Distances (Å) with Esd's for $(\mu\text{-H})_2Os_3(CO)_{10}$[a]

	Osmium-Osmium		
Os(1)-Os(1)*	2.670 (2)	Os(1)-Os(2)	2.804 (2)
	Osmium-Carbon		
Os(1)-C(1)	1.91 (3)	Os(2)-C(3)	1.91 (4)
Os(1)-C(2)	1.91 (2)	Os(2)-C(4)	1.90 (3)
	Carbon-Oxygen		
C(1)-O(1)	1.16 (3)	C(3)-O(3)	1.17 (4)
C(2)-O(2)	1.11 (3)	C(4)-O(4)	1.16 (4)

[a] Atoms marked with an asterisk are related to equivalent positions through the mirror plane.

Table V. Bond Angles (deg) with Esd's for $(\mu\text{-H})_2Os_3(CO)_{10}$

	Os_3 Triangle		
Os(1)*-Os(1)-Os(2)	61.58 (3)	Os(1)*-Os(2)-Os(1)	56.84 (6)
	Os-Os-CO		
Os(1)*-Os(1)-C(1)	108.2 (8)	Os(2)-Os(1)-C(2)	91.6 (6)
Os(2)-Os(1)-C(1)	169.7 (8)	Os(1)-Os(2)-C(3)	102 (1)
Os(1)*-Os(1)-C(2)	129.2 (7)	Os(1)-Os(2)-C(4)	82.6 (7)
	C-Os-C		
C(1)-Os(1)-C(2)	95.6 (8)	C(3)-Os(2)-C(4)	95.4 (5)
C(2)-Os(1)-C(2)*	90 (1)	C(4)-Os(2)-C(4)*	163 (2)
C(3)-Os(2)-C(3)*	99 (2)		
	Os-C-O		
Os(1)-C(1)-O(1)	177 (2)	Os(2)-C(3)-O(3)	178 (3)
Os(1)-C(2)-O(2)	177 (2)	Os(2)-C(4)-O(4)	178 (3)

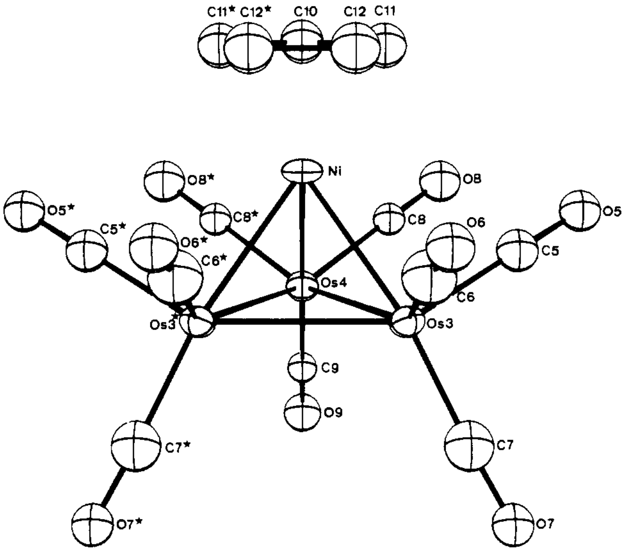


Figure 3. Perspective view of the tetranuclear cluster complex $(\mu\text{-H})_3Os_3Ni(\eta^5\text{-}C_5H_5)(CO)_9$ (**1**). Thermal ellipsoids are given at the 50% probability level.

Table VI. Interatomic Distances (Å) with Esd's for $(\mu\text{-H})_3Os_3Ni(CO)_9(\eta\text{-}C_5H_5)$[a]

	Metal-Metal		
Os(3)-Os(3)*	2.869 (2)	Os(3)-Ni	2.564 (5)
Os(3)-Os(4)	2.866 (2)	Os(4)-Ni	2.563 (5)
	Metal-Carbon		
Os(3)-C(5)	1.92 (3)	Os(4)-C(9)	1.90 (4)
Os(3)-C(6)	1.87 (3)	Ni-C(10)	2.15 (5)
Os(3)-C(7)	1.85 (3)	Ni-C(11)	2.10 (3)
Os(4)-C(8)	1.89 (3)	Ni-C(12)	2.14 (3)
	Carbon-Oxygen		
C(5)-O(5)	1.15 (3)	C(8)-O(8)	1.16 (3)
C(6)-O(6)	1.20 (3)	C(9)-O(9)	1.13 (4)
C(7)-O(7)	1.17 (3)		
	Carbon-Carbon		
C(10)-C(11)	1.49 (4)	C(12)-C(12)*	1.42 (5)
C(11)-C(12)	1.43 (4)		

[a] Atoms marked with an asterisk are related to equivalent positions through the mirror plane.

$(\mu\text{-H})_2Os_3(CO)_{10}$. The structure of this molecule has been reported in three independent publications,[24-26] including a neutron diffraction experiment.[26] When crystallized alone, $(\mu\text{-H})_2Os_3(CO)_{10}$ adopts an approximate C_{2v} symmetry, while a crystallographic symmetry is observed here. An ORTEP diagram of this complex, including the labeling scheme, is given in Figure 2. Interatomic distances and bond angles are listed in Tables IV and V, respectively.

It should be noted that metal-metal bond distances (Å) derived from our low-temperature diffraction data are shorter than those derived from previous X-ray and neutron measurements:

	present work (108 K)	ref 24 (room temp)	ref 26 (neutron data, 110 K)
bis(μ-hydrido) bridged			
double-bond Os-Os	2.670 (2)	2.681 (1)	2.683 (1)
single-bond Os-Os	2.804 (2)	2.817 (1)	2.815 (1)
		2.812 (1)	2.814 (1)

Other geometric features are in full agreement with those previously discussed for this molecule, the only differences being related to the crystallographic C_{2v} symmetry in the present work.

$(\mu\text{-H})_3NiOs_3(\eta^5\text{-}C_5H_5)(CO)_9$. A perspective view of the mixed-metal tetranuclear cluster complex is shown in Figure 3, which includes the labeling scheme. Interatomic distances and bond angles are listed in Tables VI and VII, respectively. The disorder described in the Experimental Section is shown in Figure 4 (supplementary material). It thus appears that the polyhedron defined by terminal oxygen atoms is not dramatically modified, whatever the orientation of the metal tetramer.

The tetranuclear cluster $(\mu\text{-H})_3Os_3Ni(\eta\text{-}C_5H_5)(CO)_9$ possesses a tetrahedral "closo" arrangement for the Os_3Ni core.

---

(24) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2697.

(25) Allen, V. F.; Mason, R.; Hitchcock, P. B. *J. Organomet. Chem.* **1977**, *140*, 297.

(26) Broach, R. W.; Williams, J. M. *Inorg. Chem.* **1979**, *18*, 314.

Table VII. Bond Angles (deg) with Esd's for $(\mu\text{-H})_3Os_3Ni(CO)_9(\eta\text{-}C_5H_5)$

	Metal-Metal-Metal		
Os(3)-Os(4)-Os(3)*	60.08 (6)	Os(3)-Os(4)-Ni	56.0 (1)
Os(3)*-Os(3)-Os(4)	59.96 (3)	Os(3)-Ni-Os(3)*	68.1 (1)
Os(3)*-Os(3)-Ni	55.97 (7)	Os(3)-Ni-Os(4)	68.0 (1)
Os(4)-Os(3)-Ni	56.0 (1)		
	Metal-Metal-Carbon		
Os(3)*-Os(3)-C(6)	95 (1)	Ni-Os(4)-C(8)	88.6 (7)
Os(4)-Os(3)-C(5)	96.3 (9)	Os(4)-Ni-C(10)	103 (1)
Os(3)-Os(4)-C(8)	94.5 (8)	Os(3)-Ni-C(10)	143.7 (4)
Os(3)*-Os(3)-C(7)	115.7 (9)	Os(4)-Ni-C(11)	121.2 (8)
Os(4)-Os(3)-C(7)	119.6 (9)	Os(3)-Ni-C(11)	111.5 (9)
Os(3)-Os(4)-C(9)	121 (1)	Os(4)-Ni-C(12)	158.3 (8)
Ni-Os(3)-C(5)	90.5 (9)	Os(3)-Ni-C(12)	106.6 (9)
Ni-Os(3)-C(6)	87 (1)	Os(3)-Ni-C(12)*	131.0 (9)
	Carbon-Metal-Carbon		
C(5)-Os(3)-C(6)	91 (1)	C(8)-Os(3)-C(8)*	93 (2)
C(5)-Os(3)-C(7)	97 (1)	C(8)-Os(3)-C(9)	94 (1)
C(6)-Os(3)-C(7)	96 (1)		
	Metal-Carbon-Oxygen		
Os(3)-C(5)-O(5)	178 (3)	Os(4)-C(8)-O(8)	179 (3)
Os(3)-C(6)-O(6)	177 (3)	Os(4)-C(9)-O(9)	179 (4)
Os(3)-C(7)-O(7)	176 (3)		

As previously noted,[7] nickel does not follow the pattern set for platinum, since 60-electron Os_3Pt clusters exhibit a "butterfly" arrangement of metal atoms. In the present case, the cluster consists of an equilateral triangle of osmium atoms capped in a symmetric way with a bridging nickel atom. The osmium–osmium bonds (Os(3)–Os(3)* 2.869 (2) Å; Os(3)–Os(4) = 2.866 (2) Å) are perfectly equivalent within experimental error. Likewise, nickel–osmium bonds are equivalent (Os(3)–Ni = 2.564 (5) Å; Os(4)–Ni = 2.563 (5) Å).

The nine terminal carbonyl groups bound to osmium exhibit osmium–carbon bond distances (from 1.85 (3) to 1.92 (3) Å) within the range currently observed in osmium cluster complexes.[27] The symmetric distribution of these carbonyl groups about osmium atoms is such that the molecule can be idealized as C_{3v}, excluding the cyclopentadienyl ligand.

The three hydride ligands were not located in this structure. Nevertheless, all structural features bear evidence that they are bridging the three osmium–osmium vectors.

(i) The criterion of metal–metal bond length variations[28] can be considered in this case since no other bridging ligands than hydrides are involved. It should be noted that valuable comparison with other M–M and M–H–M bond distances are restricted to tetrahedral clusters. As previously noted,[27] such bond lengths in tetrahedral species tend to be 0.1 Å shorter than in triangular species. A series of typical values of M–M and M–H–M bond lengths in tetranuclear clusters are listed in Table VIII, clearly showing that osmium–osmium distances in the present cluster fall into the range of Os–H–Os bonds. With regard to Os–Ni distances, both values (2.564 (5), 2.563 (5) Å) in this complex are significantly shorter than that of the hydrido-bridged bond Os–Ni = 2.733 (1) Å in $NiOs_3(\mu\text{-}H)_2(\mu\text{-}CO)_2(CO)_8(PPh_3)_2$;[7] clearly, hydride ligands are not bridging Os–Ni vectors in the present complex.

(ii) The position of hydride ligands can be inferred from the distribution of carbonyl groups. Table VIII shows that nickel–osmium–carbon angles (average 88.7°) are significantly smaller than osmium–osmium–carbon angles (average 107.0°) in such a way that carbonyl ligands appear to be pushed back from Os–Os edges. This trend is markedly observed for carbonyl ligands trans to the nickel atom (average Os–Os–C 118.8°), each of these CO groups being adjacent to two hydride ligands. Such geometric features have been already discussed for closely related trihydrido cluster complexes.[29,32–34] Accordingly, idealized positions for the three hydride ligands are respectively trans to C(5)O(5), C(5)*O(5)* for H(1), C(6)O(6), C(8)*O(8)* for H(2), and C(8)O(8), C(6)*O(6) for H(2)*. The assumption of face-bridging hydrido ligands is not to be considered in this case since it would require a

Table VIII. Some Examples of Os–Os and Os–H–Os Bond Lengths (Å) in Tetranuclear Clusters Involving Hydridges as the Only Bridging Ligands

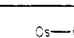
	Os–Os		ref
$H_3CoOs_3(CO)_{12}$		2.909 (1) 2.893 (1) 2.901 (1)	29
$Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR)$	2.777 (1) 2.741 (1)	2.789 (1)	19
$(\mu\text{-}H)Os_3W(CO)_{12}(\eta^5\text{-}C_5H_5)$	2.783 (2) 2.798 (3)	2.933 (3)	30
$(\mu\text{-}H)_3Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)$	2.825 (2) 2.827 (2)	2.941 (2)	30
$(\mu\text{-}H)_5Os_3Re(CO)_{12}$		2.838 (3) 2.838 (3) 2.964 (2)	3
$(\mu\text{-}H)_3Os_4(CO)_{12}^-$	2.811 (2) 2.785 (2)	2.977 (2) 2.920 (2)	31
$(\mu\text{-}H)_2Os_3Co(CO)_{10}(\eta^5\text{-}C_5H_5)$	2.778 (1)	2.940 (1) 2.870 (1)	44
$(\mu\text{-}H)_3Os_3Ni(CO)_9(\eta^5\text{-}C_5H_5)$		2.869 (2) 2.866 (2)	this work

Table IX. Comparison of Average Observed Multiplets with Theoretical Isotopic Multiplet Patterns for $H_3Os_3Ni(C_5H_5)(CO)_9$ (MASPAN Program Output)[a]

mass	calcd	av obsd	av norm	diff	av dev
938	0.0067	0.0000	0.0000	0.0067	0.0000
939	0.0203	0.0275	0.2041	−0.0071	0.0275
940	0.0855	0.1242	0.9225	−0.0388	0.0210
941	0.2175	0.2346	1.7422	−0.0171	0.0212
942	0.6101	0.6486	4.8159	−0.0385	0.0213
943	1.1974	1.2834	9.5299	−0.0860	0.0429
944	2.5356	2.7737	20.5957	−0.2382	0.1196
945	3.8458	4.0704	30.2239	−0.2245	0.0673
946	6.4309	6.5824	48.8768	−0.1516	0.1230
947	7.8145	7.9209	58.8151	−0.1063	0.1138
948	11.5747	11.3976	84.6309	0.1772	0.0994
949	10.6817	10.4874	77.8724	0.1943	0.1204
950	14.0001	13.4674	100.0000	0.5327	0.1533
951	9.8484	9.6591	71.7221	0.1893	0.0647
952	13.1711	12.5573	93.2418	0.6138	0.2634
953	4.4981	4.6503	34.5303	−0.1522	0.0324
954	8.2784	8.3339	61.8823	−0.0556	0.1391
955	1.8052	1.8901	14.0348	−0.0849	0.0972
956	2.3781	2.5939	19.2605	−0.2158	0.1078
957	0.5148	0.5657	4.2007	−0.0509	0.0420
958	0.4216	0.5106	3.7916	−0.0891	0.0218
959	0.0652	0.1104	0.8197	−0.0452	0.0004
960	0.0737	0.1104	0.8197	−0.0367	0.0004
961	0.0113	0.0000	0.0000	0.0113	0.0000
total	100.0868	100.0000		−0.0868	

[a] *R* factor is 3.361% out of a possible 200%. σ^2 is 0.0100.

---

(27) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1980**, *19*, 306.

(28) Bau, R.; Koetzle, T. F. *Pure Appl. Chem.* **1978**, *50*, 55. See also: Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1.

(29) Bhaduri, S.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Watson, D. J. *J. Chem. Soc., Chem. Commun.* **1978**, 343.

(30) Churchill, M. R.; Hollander, F. J.; Shapley, J. R.; Foose, D. S. *J. Chem. Soc., Chem. Commun.* **1978**, 535.

(31) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Zuccaro, C. *Acta Crystallogr., Sect. B* **1978**, *B34*, 3765.

(32) Sheldrick, G. M.; Yesinowski, J. P. *J. Chem. Soc., Dalton Trans.* **1975**, 873.

(33) Ciani, G.; Sironi, A.; Albano, V. G. *J. Chem. Soc., Dalton Trans.* **1977**, 1667.

(34) Gladfelter, W. L.; Geoffroy, G. L.; Calabrese, J. S. *Inorg. Chem.* **1980**, *19*, 2569.

Table X. Comparison of Average Observed Multiplets with the Theoretical Isotopic Multiplet Pattern for $H_3Ru_3Ni(C_5H_5)(CO)_9$ (MASPAN Program Output)[a]

mass	calcd	av obsd	av norm	diff	av dev
666	0.0095	0.0000	0.0000	0.0095	0.0000
667	0.0015	0.0000	0.0000	0.0015	0.0000
668	0.0136	0.0000	0.0000	0.0136	0.0000
669	0.0681	0.1279	1.1928	−0.0598	0.0228
670	0.0838	0.1639	1.5290	−0.0801	0.0293
671	0.1723	0.2048	1.9108	−0.0326	0.0248
672	0.4162	0.4750	4.4309	−0.0588	0.0398
673	0.4924	0.4882	4.5537	0.0042	0.0266
674	1.0491	1.1173	10.4216	−0.0681	0.0180
675	1.7153	1.8236	17.0098	−0.1082	0.0813
676	2.2676	2.3738	22.1422	−0.1062	0.0620
677	3.6083	3.7108	34.6140	−0.1025	0.0318
678	4.9506	5.0314	46.9317	−0.0808	0.0664
679	5.8594	5.9319	55.3317	−0.0725	0.0516
680	8.4217	8.3341	77.7385	0.0876	0.0724
681	9.0965	8.9474	83.4600	0.1491	0.0750
682	10.3550	9.9368	92.6889	0.4181	0.1067
683	11.1716	10.7206	100.0000	0.4510	0.0332
684	10.0875	9.6178	89.7129	0.4697	0.0674
685	8.9427	9.0415	84.3376	−0.0988	0.1743
686	7.9849	7.9600	74.2490	0.0249	0.0854
687	4.4723	4.6470	43.3459	−0.1747	0.0473
688	4.5665	4.7380	44.1949	−0.1714	0.0489
689	1.5267	1.5668	14.6145	−0.0400	0.0347
690	1.6534	1.8477	17.2349	−0.1943	0.0744
691	0.4160	0.5000	4.6643	−0.0840	0.0272
692	0.3746	0.4369	4.0750	−0.0622	0.0275
693	0.0810	0.1541	1.4379	−0.0731	0.0035
694	0.0632	0.1028	0.9586	−0.0396	0.0023
695	0.0098	0.0000	0.000	0.0098	0.0000
696	0.0075	0.0000	0.0000	0.0075	0.0000
total	99.9387	100.0000		−0.0613	

[a] *R* factor is 3.357% out of a possible 200%. σ^2 is 0.0100.

particular arrangement of CO ligands[35,36] that is not found here.

Molecular Structure of $(\mu\text{-H})_3M_3Ni(\eta^5\text{-}C_5H_5)(CO)_9$ (M = Ru, Os). The above structural data reported for the osmium derivative are in full agreement with spectral data of both complexes in solution. The precise number of three hydrido ligands could be determined in both cases from the ^1H NMR spectrum by integration of cyclopentadienyl and hydride signals. Moreover, detailed analysis of mass spectra (see Experimental Section and Tables IX and X) provides an unambiguous formulation as a trihydrido cluster complex. Two hydrides were previously found in the related compound[7] $NiOs_3(\mu\text{-H})_2(\mu\text{-CO})_2(CO)_8(PPh_3)_2$. This discrepancy is indeed related to the presence of a cyclopentadienyl group, which accounts for five electrons in the total numbering of bonding electrons. Complexes **1** and **2** are thus respectively isoelectronic with $H_3CoOs_3(CO)_{12}$[29] and $H_3CoRu_3(CO)_{12}$.[34] However, unlike these complexes, which were found to have several isomers, the occurrence of a temperature-invariant hydride signal in the range +20 to −90 °C is reasonably relevant to the existence of a single structure in solution. Chemical shifts found for this hydride signal in both Ru and Os derivatives are consistent with their assignment as Ru–H–Ru[34,37,38] and Os–H–Os[7,19] signals. Such features are in agreement with the current tendency[39] of hydrides to coordinate to the heavier atoms in mixed clusters. Exceptions[7] may reflect the requirement for individual atoms to attain their own 18e configuration.

As a concluding remark, let us mention that cyclopentadienyl derivatives are particularly interesting candidates in view of the synthesis of new mixed-metal clusters. The cyclopentadienyl group allows the metal to contribute for a number of bonding electrons necessarily different than in carbonyl analogues, thus yielding different structures. This can be illustrated by recent examples in the literature.[4,6,30,40–44]

When our paper was reviewed, a preliminary communication[45] and a paper[46] appeared concerning closely related syntheses of the trihydrido osmium nickel cluster.

Acknowledgment. Financial assistance from the CNRS (ATP "Chimie fine") is gratefully acknowledged. We are grateful to Prof. H. D. Kaesz and Dr. A. Cabral for providing us with the MASPAN program and to J. Roussel for careful recording of high-resolution mass spectra.

Registry No. **1**, 82678-96-4; **1**·$^1/_2(\mu\text{-H})_2Os_3(CO)_{10}$, 86307-84-8; **2**, 85191-96-4; $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$, 12170-92-2; $Os_3(CO)_{12}$, 15696-40-9; $Ru_3(CO)_{12}$, 15243-33-1; $(\mu\text{-H})_2Os_3(CO)_{10}$, 41766-80-7.

Supplementary Material Available: Listings of rigid-group parameters (Table III) and observed and calculated structure factor amplitudes and stereoscopic views showing the molecular packing within the unit cell (Figure 1) and the two alternative orientations for the tetranuclear unit (Figure 4) (10 pages). Ordering information is given on any current masthead page.

---

(35) Wilson, R. D.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 4687.

(36) Teller, R. G.; Wilson, R. D.; McMullan, R. K.; Koetzle, T. F.; Bau, R. *J. Am. Chem. Soc.* **1978**, *100*, 3071.

(37) Koepke, J. W.; Johnson, J. R.; Knox, S. A. R.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3947.

(38) Steinhardt, P. C.; Gladfelter, W. L.; Harley, A. D.; Fox, J. R.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 332.

(39) Takusagawa, F.; Fumagalli, A.; Koetzle, T. F.; Steinmetz, G. R.; Rosen, R. P.; Galdfelter, W. L.; Geoffroy, G. L.; Bruck, M. A.; Bau, R. *Inorg. Chem.* **1981**, *20*, 3823.

(40) Shapley, J. R.; Hardwick, S. J.; Foose, D. S.; Stucky, G. D.; Churchill, M. R.; Bueno, C.; Hutchinson, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 7383.

(41) Braunstein, P.; Tiripicchio, A.; Tiripicchio Camellini, M.; Sappa, E. *Inorg. Chem.* **1981**, *20*, 3586.

(42) Busetto, L.; Green, M.; Howard, J. A. K.; Hessner, B.; Jeffery, J. C.; Mills, R. M.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 1101.

(43) Churchill, M. R.; Bueno, C.; Kennedy, S.; Bricker, J. C.; Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 627.

(44) Churchill, M. R.; Bueno, C.; Kennedy, S.; Bricker, J. C.; Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 627.

(45) Shore, S. G.; Hsu, W. L.; Weisenberger, C. R.; Caste, M. L.; Churchill, M. R.; Bueno, C. *Organometallics* **1982**, *1*, 1405.

(46) Castiglioni, M.; Sappa, E.; Valle, M.; Lanfranchi, M.; Tiripicchio, A. *J. Organomet. Chem.* **1983**, *241*, 99.