Formation of $H_2Ru_6(CO)_{17}$ from $H_2Ru_6(CO)_{18}$ an improved synthesis of $HRu_6(CO)_{17}$ B [1]

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Abstract

Spontaneous decarbonylation of the octahedral cluster $H_2Ru_6(CO)_{18}$ produces the bicapped tetrahedral cluster $H_2Ru_6(CO)_{17}$. The clusters $H_2Ru_6(CO)_{18}$ and $H_2R_6(CO)_{17}$ have strikingly similar IR and ^1H NMR spectra. In appearance they are indistinguishable; both are deep purple in color. The decarbonylation reaction is partially reversible under low pressures of CO. Reaction of $H_2Ru_6(CO)_{17}$ with $BH_3S(CH_3)_2$ provides an improved synthesis of $HRu_6(CO)_{17}B$, an octahedral cluster with a boron atom at the center of the Ru_6 core. $HRu_6(CO)_{17}B$ reacts with excess CO at high pressures to produce $HRu_4(CO)_{12}BH_2$ and ruthenaboride clusters with pentanuclear metal cores that are proposed to be $HRu_5(CO)_{15}B$ and $HRu_5(CO)_{16}B$. © 1998 Elsevier Science S.A.

Keywords: Ruthenium clusters; Hexanuclear and pentanuclear ruthenaborides

1. Introduction

The compound $H_2Ru_6(CO)_{17}$, a six vertex 84 valence electron cluster, contains a metal core in the shape of a bicapped tetrahedron (Fig. 1) [1]. From electron counting rules [2,3] it contains six skeletal electron pairs. The analogous cluster $H_2Os_6(CO)_{17}$ has also been prepared [4]. The existence of $H_2Ru_6(CO)_{17}$ was first revealed by an X-ray analysis of a single crystal obtained from a sample of $H_2Ru_6(CO)_{18}$ [5–9] that had been stored for ca. 3 months at room temperature in air. However, the source of $H_2Ru_6(CO)_{17}$ was not immediately apparent. The answer to this question was obscured because $H_2Ru_6(CO)_{18}$ and $H_2Ru_6(CO)_{17}$ are both deep purple solids and their ^1H NMR and IR

spectra are almost identical. In a preliminary account we reported the preparation and structure of $H_2Ru_6(CO)_{17}$ [1]. Described here are details of our study of the formation of $H_2Ru_6(CO)_{17}$ from $H_2Ru_6(CO)_{18}$ and its reactions.
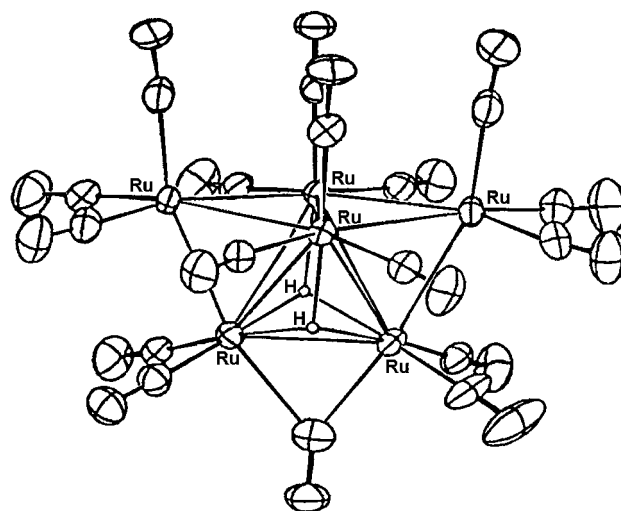

Fig. 1. Molecular structure of (μ-H)$_2$Ru$_6$(CO)$_{17}$. Ortep.

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[1] Dedicated to Professor Kenneth Wade on the occasion of his 65th birthday in recognition of his seminal contributions to the correlation of structural relationships in main group and metal cluster systems.

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2. Results and discussion

2.1. Formation and characterization of $H_2Ru_6(CO)_{17}$

Because $H_2Ru_6(CO)_{18}$ and $H_2Ru_6(CO)_{17}$ have very similar physical characteristics, it was not clear when $H_2Ru_6(CO)_{17}$ was first discovered whether it was prepared in parallel with the synthesis of $H_2Ru_6(CO)_{18}$ or whether it was formed in a subsequent reaction of $H_2Ru_6(CO)_{18}$. Therefore, as a starting point to determine the source of $H_2Ru_6(CO)_{17}$, an authentic sample of $H_2Ru_6(CO)_{18}$ was prepared that was identified from X-ray analyses of single crystals which were shown to have the same structural parameters as previously reported [5,6] in the structure determination of this cluster. The highest mass envelope (M^+) in the FAB mass spectrum of the bulk samples of freshly prepared $H_2Ru_6(CO)_{18}$ appeared at $m/e = 1114$, consistent with the formula $H_2C_{18}O_{18}Ru_6$. The ^1H NMR chemical shift obtained from single crystals dissolved in CD_2Cl_2 solutions [3] were sharp singlets at -15.60 ppm (Fig. 2a). After several months at room temperature, a solid sample of $H_2Ru_6(CO)_{18}$ produced a very broad ^1H NMR signal at ca. -15.5 ppm when it was dissolved in $CDCl_3$ solution (Fig. 2b). Previously, the assignment of the ^1H NMR chemical shift of $H_2Ru_6(CO)_{17}$ had been positively established by observation of a sharp singlet at -15.58 ppm in the CD_2Cl_2 solution of the single crystal used to determine the structure of $H_2Ru_6(CO)_{17}$ (Fig. 2c). The broad peak in the spectrum of the sample that had been stored indicated to us the that the once pure sample now contained both $H_2Ru_6(CO)_{17}$ and $H_2Ru_6(CO)_{18}$. From these observations we concluded that at room temperature freshly prepared $H_2Ru_6(CO)_{18}$,
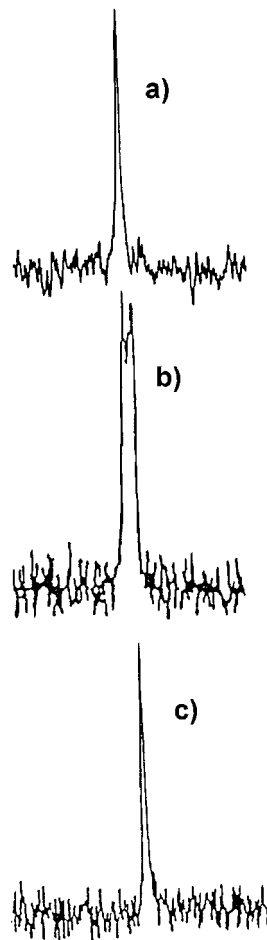

Fig. 2. ^1H NMR spectra of: (a) $H_2Ru_6(CO)_{18}$; (b) mixture of $H_2Ru_6(CO)_{18}$ and $H_2Ru_6(CO)_{17}$; (c) $H_2Ru_{6j}(CO)_{17}$.

undergoes slow, spontaneous decarbonylation to give $H_2Ru_6(CO)_{17}$ (95% yield) (Eq. (1)).

$$H_2Ru_6(CO)_{18} \rightarrow H_2Ru_6(CO)_{17} + CO \qquad (1)$$

This conclusion was verified by subjecting solid samples of freshly prepared $H_2Ru_6(CO)_{18}$ to dynamic vacuum for several weeks. Resulting gases were collected and identified as CO, principally and a minor amount of H_2 by gas mass spectral analysis. Following extraction by hexane of the minor cluster products, the solid purple product was analyzed by ^1H NMR spectroscopy. The purple product was identified as $H_2Ru_6(CO)_{17}$ by the presence of a sharp singlet at -15.58 ppm in the ^1H NMR spectrum. Thirty one single crystals from a bulk sample, prepared under dynamic vacuum and assigned to the $H_2Ru_6(CO)_{17}$ on the basis of the proton NMR spectrum, were examined by X-ray diffraction and found to have the same lattice parameters and space group as the crystal from which the structure of $H_2Ru_6(CO)_{17}$ was determined. The reverse of Reaction (1) occurs in ca. 10% yield when CO at low pressure (< 100 Torr) is added to the

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[3] Because the difference in ^1H NMR spectral signals for $H_2Ru_6(CO)_{17}$ and $H_2Ru_6(CO)_{18}$ is only 0.02 ppm (well within experimental error) each reaction required careful analysis of the products to confirm the presence of pure compounds. Each time $H_2Ru_6(CO)_{17}$ and $H_2Ru_6(CO)_{18}$ were prepared both a ^1H NMR spectrum and a FAB mass spectrum of the products were obtained. When the $H_2Ru_6(CO)_{18}$ was freshly prepared it always exhibited a sharp singlet in the ^1H NMR spectrum and a highest mass peak envelope at $m/e = 1114$ in the FAB mass spectrum. Subsequent preparation of $H_2Ru(CO)_{17}$ was confirmed by the presence of a sharp singlet in the ^1H NMR spectrum and, consistently, a highest mass peak envelope at $m/e = 1086$ in the FAB mass spectrum. These results were obtained repeatedly over the course of one full year of studying the reactions. Samples which contained mixtures of the two clusters were always found to produce a broad peak centered around -15.5 ppm in the ^1H NMR spectrum and they also produced a highest mass peak envelope at $m/e = 1114$ in the FAB mass spectrum. The mass spectrum of mixed samples and those of freshly prepared $H_2Ru_6(CO)_{18}$ differed in the relative intensities of the highest and second highest mass envelopes at $m/e = 1114$ and 1086.

product. At high CO pressure (> 6.5 atm) $H_2Ru_6(CO)_{17}$ is converted to $Ru_3(CO)_{12}$.

Mass spectral analyses are useful in differentiating pure samples of $H_2Ru_6(CO)_{17}$ from $H_2Ru_6(CO)_{18}$. The highest mass peak in the FAB mass spectra of samples of freshly prepared $H_2Ru_6(CO)_{17}$ is consistently found at $m/e = 1086$. Samples of pure $H_2Ru_6(CO)_{17}$ for further studies were identified by this highest mass peak in the FAB mass spectrum.

Other analyses attempting to differentiate between $H_2Ru_6(CO)_{18}$ and $H_2Ru_6(CO)_{17}$ were non-definitive. The solution IR spectra of $H_2Ru_6(CO)_{18}$ and $H_2Ru_6(CO)_{17}$ are virtually identical and do not reveal a band that can be assigned to the bridge carbonyl in the solid state structure of $H_2Ru_6(CO)_{17}$ [1]. The diffuse reflectance solid state IR spectrum of $H_2Ru_6(CO)_{17}$ contains a very weak band at 1950 cm^{-1} consistent with the presence of a bridge carbonyl. Carbon-13 NMR chemical shifts for freshly prepared samples of $H_2Ru_6(CO)_{18}$ and $H_2Ru_6(CO)_{17}$ in CDCl$_3$ are within experimental error, 194 and 195 ppm respectively. Limited solubilities precluded investigation of low temperature ^{13}C NMR spectra.

Though they are only moderately soluble in CH_2Cl_2 and $CHCl_3$, both $H_2Ru_6(CO)_{18}$ and $H_2Ru_6(CO)_{17}$ form deep purple solutions. They are insoluble in nonpolar hydrocarbons and rapidly fragment to smaller clusters in oxygen containing solvents such as THF, acetone, alcohols, or diethyl ether. CH_2Cl_2 solutions of $H_2Ru_6(CO)_{18}$ stored from 1 week to 3 months under O_2, N_2, CO_2, contained mostly $H_4Ru_4(CO)_{12}$ or $Ru_3(CO)_{12}$ with small amounts of $H_2Ru_4(CO)_{13}$. Compositions of the mixtures varied with temperature and length of storage. Reaction of $H_2Ru_6(CO)_{17}$ with H_2 produced $H_4Ru_4(CO)_{12}$.
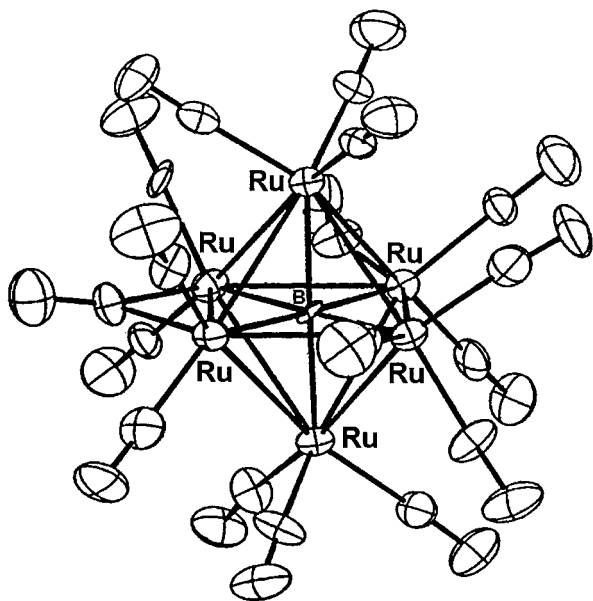
2.2. Conversion of $H_2Ru_6(CO)_{17}$ to $HRu_6(CO)_{17}B$.

The ruthenaboride $HRu_6(CO)_{17}B$ was isolated in 21% yield from the reaction of $H_2Ru_6(CO)_{17}$ with excess $BH_3S(CH_3)_2$. This is a significantly larger yield of $HRu_6(CO)_{17}B$ than that obtained from our previously reported synthesis [1]. Additionally, isolation of this product is more easily achieved.

We previously reported the molecular structure of $HRu_6(CO)_{17}B$ from a single crystal X-ray analysis (Fig. 3) [10]. It consists of an octahedral metal core with an interstitial boron atom, 16 terminal carbonyls, one bridging carbonyl and a hydrogen that was not located. The structure of this boride is very similar to that of the interstitial carbide $Ru_6(CO)_{17}C$ [11]. Therefore it was of interest to demonstrate that the single crystal from which we determined the molecular structure of $HRu_6(CO)_{17}B$ was indeed this compound rather than the carbide. First of all the two compounds crystallize in different space groups ($P2_1/n$ and $P2/c$ or Pc, respectively) which are not interconvertible. Second we obtained proton (-17.78 ppm) and boron-11 (194 ppm) NMR spectra from the crystal from which the structure was determined (Fig. 4). These spectra are consistent with spectra of the bulk material and of other single crystals from the same reaction. Draper et al. have also reported a compound of formula $HRu_6(CO)_{17}B$ [12]. It has a slightly different molecular structure which crystallizes in a different space group has slightly different chemical shifts in the ^{11}B NMR and ^{1}H NMR spectra than the boride we reported [10].

While the number of ruthenaboride clusters reported in the literature is growing, until recently none have been identified having a pentaruthenium metal core [13]. The pentaruthenium carbide cluster $Ru_5(CO)_{15}C$ [14], is readily produced by reaction of CO with $Ru_6(CO)_{17}C$. We investigated a similar route to the pentanuclear ruthenaboranes by reaction of CO with $HRu_6(CO)_{17}B$. Reaction of $HRu_6(CO)_{17}B$ with CO at high pressures (> 6 atm) and elevated temperatures, produced the known clusters $Ru_3(CO)_{12}$ and $HRu_4(CO)_{12}BH_2$ [15] and two previously unidentified ruthenaborides. We were unable to completely separate these ruthenaborides through a combination of fractional crystallization and TLC. But this mixture is believed to be pentanuclear ruthenaborides. The highest mass envelope (M^+) in the FAB mass spectrum of the bulk sample at $m/e = 967$ is consistent with the highest mass component of the mixture being $HRu_6(CO)_{16}B$. We believe that the second runthenaboride component is $HRu_5(CO)_{15}B$.

The ^{11}B NMR spectrum of the mixture contains two low field signals that fall between the ^{11}B NMR signals of $HRu_6(CO)_{17}B$ (198 ppm) and $HRu_4(CO)_{12}BH_2$ (109 ppm). Assignments of these resonances were made consistent with the trend of ^{11}B NMR signals to lower field

Fig. 3. Molecular structure of $HRu_6(CO)_{17}B$, Ortep.

as the boron atom is bound to increasing numbers of metal atoms [16] and are based upon comparison with analogues of pentaruthenaboride clusters. The ^{11}B NMR signal at 180.9 ppm may be assigned to a cluster with formula $HRu_5(CO)_{16}B$, by comparison with the isovalent osmaborane, $HOs_5(CO)_{16}B$ [24] that produces a singlet at 184.4 ppm. It is indicative of a boron atom that resides at an interstitial position. This is also consistent with the observation that, in general, the boron NMR signals of ruthenaboranes are found slightly upfield from those of the analogous osmaboranes [17,18]. In the case of $HRu_5(CO)_{15}B$, comparison with the gold phosphine derivative, allows assignment of its [11]B resonance. The broad, singlet ^{11}B NMR signal at 172.4 ppm in the spectrum of the proposed pentanuclear ruthanaboride mixture compares well with that of $Ru_5(CO)_{15}B(AuPPh_3)$ [13], a broad singlet at 172.5 ppm. The broadness of the signal could be due to some coupling of the hydride to the boron atom which is probably located in or slightly below a basal plane of four ruthenium atoms analogous to the position of the 'pseudo proton' $Au(PPh_3)$ in $Ru_5(CO)_{15}B(AuPPh_3)$ [13].
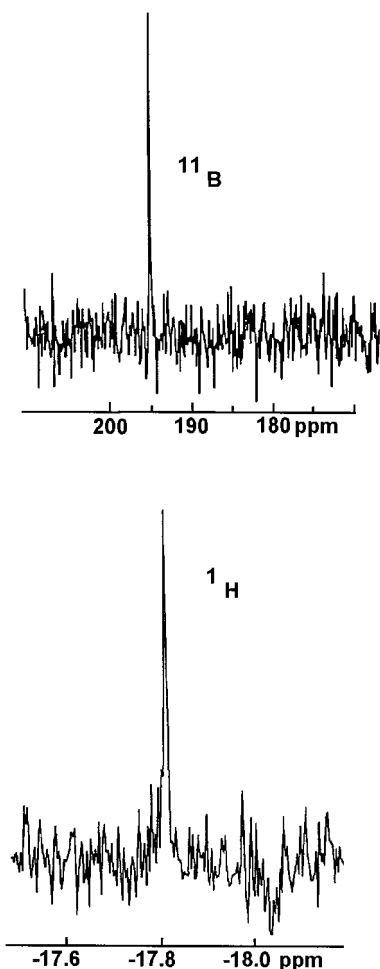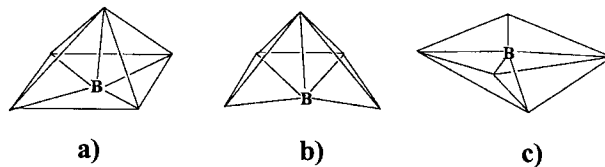
Fig. 5. Possible core structures of: (a) $HRu_5(CO)_{15}B$; (b) and (c) $HRu_5(CO)_{16}B$.

The ^{1}H NMR spectrum of the proposed pentanuclear ruthenaboride mixture contains two sharp singlet signals at −17.48 and −19.94 ppm. It is clear that two compounds are present as the relative ratio of the signals varied with changing conditions employed in the attempted separation of components. Assignment of ^{1}H signals was made by comparing changes in the ratio of ^{1}H signals with [1]B signals as conditions for separation of clusters were changed. The singlet signal at −17.48 ppm is assigned to $HRu_5(CO)_{16}B$ and the singlet signal at −19.94 ppm is assigned to $HRu_5(CO)_{15}B$. The proton chemical shifts are consistent with the presence of bridging hydrides in these compounds.

The geometric arrangements of the metal cores and main group atoms in ruthenium carbonyl clusters containing an interstitial carbon, nitrogen or boron atom have been found to be almost identical between isoelectronic clusters. Thus the tetranuclear 62 electron clusters have dihedral metal cores with the wingtip metals bridged by the main group atom [15,16,19–23] and the 86 electron, hexanuclear clusters are often octahedral with interstitial main group atoms [1,24,25]. On this basis possible locations of the boron atom in the pentanuclear ruthenaboride clusters are proposed. In $HRu_5(CO)_{15}B$ (Fig. 5a) it is likely that the boron would be located in the base of a square pyramid of ruthenium atoms, the position in which the carbon is found in $Ru_5(CO)_{15}C$ [14] an isoelectronic cluster. For the structure of $HRu_5(CO)_{16}B$, two possibilities are to be considered. From the electron count, structures derived by removing two vertices from a pentagonal bipyramid are to be considered. One structure would have a metal core like that of the B_5 core in B_5H_{11} (Fig. 5b) the other example would be like the osmaborane, $HOs_5(CO)_{16}B$ [24]. An Os_5 core based upon the prentagonal bipyramid, but with two nonadjacent vertices removed (Fig. 5c). The boron atom in $HOs_5(CO)_{16}B$ is found in the interstitial position of a metal osmium core.

3. Experimental

All manipulations involving air and moisture sensitive compounds were carried out using standard vacuum line techniques or in a controlled atmosphere box under prepurified nitrogen. Separations using thin-layer chromatography were performed in a dry box on 2-mm

Fig. 4. ^{11}B NMR and ^{1}H NMR spectra of a single crystal of $(\mu$-H$)Ru_6(CO)_{17}B$.

silica gel plates with 1:1 CH_2Cl_2:hexane as eluent. Reactions with CO were done in a Parr Autoclave Reactor Model T316.

3.1. NMR, infrared, and mass spectra

NMR spectra were obtained in the FT mode on the following instruments: Brüker-250 [^{1}H (250.13 MHz), ^{11}B (80.25 MHz)], Brüker-200 [^{1}H (200.13 MHz)]. Chemical shifts are referenced to the following standards: ^{1}H NMR $(CH_3)_4Si$ $\delta = 0.00$ ppm; and ^{11}B NMR BF_3OEt_2 $\delta = 0.00$ ppm.

Infrared spectra were collected with a Mattson Polaris spectrophotometer. Solution spectra were obtained in Perkin–Eimer cells consisting of KBr or KCl windows with 0.1-mm Teflon spacers.

Mass spectra of gases were obtained at the Chemical Instrumentation Center of the Ohio State University using a BaIzer Residual Gas Analyzer and FAB mass spectra were obtained by use of a VG-70-250S mass spectrometer.

3.2. Solvents and chemicals

Tetrahydrofuran (J.T. Baker) and toluene (Mallinckrodt) were refluxed over sodium benzophenone ketyl and stored in sealed flasks containing sodium benzophenone ketyl. $CHCl_3$ (Mallinckrodt), CH_2Cl_2 (Mallinckrodt) and CH_3CN (Mallinckrodt) were refluxed over P_2O_5 for several days under reduced pressure, distilled and stored in sealed flasks. Hexanes (J.T. Baker) were stirred over concentrated H_2SO_4 for several days, refluxed over CaH_2 under reduced pressure, distilled, and stored in sealed flasks. Deuterated solvents were treated by methods identical to their protiated equivalents.

CO_2 and HCl were purified by passing the respective gas through traps held at $-78°C$ and $-111°C$ and were stored at $-78°C$. Prepurified H_2 (Union Carbide), O_2 (Air Products), N_2 (Matheson), and CO (Matheson) were used without further purification. KH (Aldrich, oil dispersion) was washed with pentane in a dry box and stored in sealed flasks. $BH_3S(CH_3)_2$ (Aldrich, 1.0 M in CH_2Cl_2) was used without further purification. $Ru_3(CO)_{12}$ [8] and $K_2Ru_6(CO)_{18}$ [26] were prepared by published methods.

3.3. Preparation of $H_2Ru_6(CO)_{18}$

A modified published procedure [8] was employed to prepare $H_2Ru_6(CO)_{18}$. In a typical reaction, 1 mmol of anhydrous HCl was condensed at $-196°C$ into a suspension of $K_2Ru_6(CO)_{18}$ (212.0 mg, 0.179 mmol) in CH_2Cl_2 (20 ml). The solution was warmed to room temperature, and stirred. After 6 h the resulting purple solid was filtered in air, washed with hexanes, washed with distilled H_2O, dissolved in CH_2Cl_2, and the resulting purple solution was dried by stirring for 2 h in $MgSO_4$ (1–2 g). The solution was filtered and solvent was removed by rotary evaporation. The products were characterized by IR, ^{1}H NMR, and mass spectrometry. Yield: 40.5 mg of $(\mu\text{-H})_2Ru_6(CO)_{18}$, 20% yield based on $K_2Ru_6(CO)_{18}$. The other products were identified by ^{1}H NMR spectroscopy as a mixture of $H_2Ru_4(CO)_{13}$, $H_4Ru_4(CO)_{12}$, $K[H_3Ru_4(CO)_{12}]$, and $K[HRu_4(CO)_{13}]$.

3.4. Preparation of $H_2Ru_6(CO)_{17}$

Freshly prepared $H_2Ru_6(CO)_{18}$ (41 mg, 37 mmol) was placed in a 25-ml flask and the flask was subjected to dynamic vacuum for 3–6 weeks. Evolved gases were collected by a Toeppler Pump on a vacuum line and identified as CO as the principal component and a minor amount of H_2 by gas mass spectroscopy. The solid products were washed with hexanes yielding an orange solution of $H_2Ru_4(CO)_{13}$ and $H_4Ru_4(CO)_{12}$ based on ^{1}H NMR and IR spectroscopic analysis) and purple, solid $H_2Ru_6(CO)_{17}$ which was filtered in an extractor (37.5 mg, 95% yield based on $H_2Ru_6(CO)_{18}$). ^{1}H NMR spectrum [$(CDCl_3$, 30°C) -15.58 ppm (s)]. FAB mass spectrum [(3-NBA matrix) M^+ peak maximum intensity in the parent ion envelope $m/e = 1086$].

3.5. Preparation of $HRu_6(CO)_{17}B$

CH_2Cl_2 (20 ml) was condensed at $-196°C$ into a 50-ml flask containing $H_2Ru_6(CO)_{17}$ (505.6 mg, 0.4662 mmol). In a dry box, $BH_3S(CH_3)_2$ (0.47 ml, 0.47 mmol) in CH_2Cl_2 was syringed into the flask, transferred to a vacuum line, evacuated at $-196°C$, warmed to room temperature, and stirred. After 6 h the purple solution had turned red orange. Solvent was removed in vacuo and the resulting red-brown solid was washed with hexanes 5–6 times in an extractor. (The hexane solution contained $H_4Ru_4(CO)_{12}$, $H_2Ru_4(CO)_{13}$, and $HRu_4(CO)_{12}BH_2$ identified by their respective ^{1}H and ^{11}B NMR spectra). Small portions of CH_2Cl_2 were then added to the red-brown solid (precipitating unreacted $H_2Ru_6(CO)_{17}$ which was filtered off). The purple-red solution was purified by successive recrystallizations in CH_2Cl_2. The final product was washed with hexanes yielding $HRu_6(CO)_{17}B$ (107.9 mg, 0.0986 mmol, 21% based on $H_2Ru_6(CO)_{17}$) as a red solid.

3.6. Studies of solid samples of $H_2Ru_6(CO)_{18}$

Solid samples of freshly prepared $H_2Ru_6(CO)_{18}$ were stored for 3 months and the products analyzed. The storage and identification were as follows. (a) A foil-wrapped sample, stored at $-10°C$ in an evacuated 25-ml flask contained $H_4Ru_4(CO)_{12}$, $H_2Ru_4(CO)_{13}$, $H_2Ru_6(CO)_{18}$. (b) A sample stored in an open flask on

a bench top contained $H_2Ru_6(CO)_{18}$, $H_2Ru_6(CO)_{17}$, and $H_4Ru_4(CO)_{12}$. (c) A sample stored under N_2 in a dry box in a screw top vial contained $H_2Ru_6(CO)_{18}$ and $H_2Ru_6(CO)_{17}$. (d) A sample stored in a vial on a bench top for one year was found to contain an insoluble solid and $H_2Ru_6(CO)_{17}$.

3.7. Reactions of $H_2Ru_6(CO)_{18}$ in solution

$H_2Ru_6(CO)_{18}$ in methanol, Et_2O, acetone, and toluene in air or under N_2 changed from purple to red to yellow over periods ranging from minutes to a few days. IR and NMR spectroscopic analysis indicated the presence of $H_2Ru_4(CO)_{13}$, $H_4Ru_4(CO)_{12}$, or $Ru_3(CO)_{12}$ as final products.

3.8. $H_2Ru_6(CO)_{17}$ with excess CO

A CH_2Cl_2 solution (25 ml) of $H_2Ru_6(CO)_{17}$ (20 mg, 0.0184 mmol) was added to a high pressure reactor and was flushed with CO (100 psi) seven times then pressurized to 1 atm and stirred at room temperature. After 12 h the purple solution had become yellow and an IR spectrum identified the product as $Ru_3(CO)_{12}$.

3.9. $H_2Ru_6(CO)_{17}$ with two equivalents of CO

CH_2Cl_2 (25 ml) was condensed at $-196°C$ into a 50-ml flask containing $H_2Ru_6(CO)_{17}$ (50.3 mg, 0.0462 mmol). CO (0.08 mmol) was expanded into the flask which was warmed to room temperature and stirred for 12 h. Removal of solvent in vacuo from the red-tinged solution gave a red-purple solid which was washed with hexanes in an extractor yielding an orange solution [$H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ by ^{1}H NMR spectroscopy] and a purple solid [$H_2Ru_6(CO)_{18}$ and $H_2Ru_6(CO)_{17}$ by ^{1}H NMR and FAB mass spectral analysis].

3.10. Reaction of $HRu_6(CO)_{17}B$ with CO

In a dry box $HRu_6(CO)_{17}B$ (161.1 mg, 0.1477 mmol) was placed in Parr Reactor and 60 ml of toluene (or heptane) was added. The reactor was flushed 12 times with CO, pressurized to 950 psi with CO, heated to 80°C, and stirred. After 12 h the reactor was cooled to room temperature and vented. In a dry box the resulting red solution was transferred to a 100-ml vacuum flask equipped with an extractor. Solvent was removed in vacuo leaving a red-brown solid in the flask, which was washed with hexanes yielding an orange-yellow solution and red-orange solid ($HRu_6(CO)_{17}B$ by analysis). Successive recrystallization of the hexane solution removed residual $HRu_6(CO)_{17}B$. The final products were analyzed and identified as a mixture of $HRu_5(CO)_{15}B$ and $HRu_5(CO)_{16}B$. ^{11}B NMR spectrum [(CDCl$_3$, 30°C)

180.9 (s) 173.2 (s, br) ppm]. ^{1}H NMR spectrum [(CDCl$_3$, 30°C) -17.48(s), -17.79(s), -19.94(s)) ppm]. FAB mass spectrum [(3 NBA Matrix) highest intensity peak, M^+ envelope $m/e = 967$ followed by successive loss of CO's]. Changes in the relative peak intensities in the ^{11}B NMR and ^{1}H NMR spectra occurred under different separation methods.

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