A Systematic Synthetic Route to Ruthenium Carbonyl Cluster Anions[1]

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Systematic reduction of $Ru_3(CO)_{12}$ by alkali metal–benzophenone for the preparation of ruthenium carbonyl cluster anions is described. By specifying molar ratios of $Ru_3(CO)_{12}$ to alkali metal–benzophenone (1:3, 1:2, 1:3/2, 1:1), stoichiometric reactions were carried out to prepare $[Ru_4(CO)_{12}]^{4-}$, $[Ru_3(CO)_{11}]^{2-}$, $[Ru_4(CO)_{13}]^{2-}$, and $[Ru_6(CO)_{18}]^{2-}$, respectively, in high yields. The anion $[Ru_4(CO)_{12}]^{4-}$ can also be prepared by the reaction of $[Ru_3(CO)_{11}]^{2-}$ with 1 equiv of alkali metal–benzophenone and by the reaction of $[Ru_4(CO)_{13}]^{2-}$ with 2 equiv of alkali metal–benzophenone. The anion $[Ru_3(CO)_{11}]^{2-}$ reacts with 0.33 equiv of $Ru_3(CO)_{12}$ to give $[Ru_4(CO)_{13}]^{2-}$. This anion can react with 0.67 equiv of $Ru_3(CO)_{12}$ to yield $[Ru_6(CO)_{18}]^{2-}$. The latter can also be prepared directly from $[Ru_3(CO)_{11}]^{2-}$ by reaction with 1 equiv of $Ru_3(CO)_{12}$. Also described are preparations of the conjugate acids of these anions through selective protonation reactions with HCl or HBr, and the new anion $[HRu_4(CO)_{12}]^{3-}$ has been prepared. Properties of the salts prepared and infrared and NMR spectra are described.

Introduction

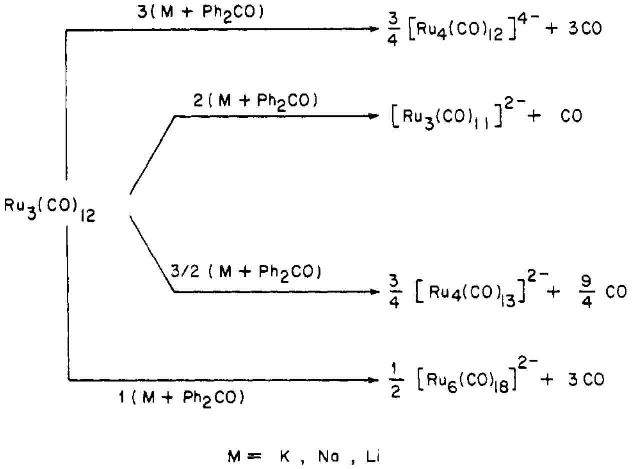
In preliminary communications[4,5] we reported syntheses of the new anions $[Ru_4(CO)_{13}]^{2-}$, $[Ru_4(CO)_{12}]^{4-}$, and $[Ru_3(CO)_{11}]^{2-}$. These preparations represented the first examples of designed stoichiometric reductions of $Ru_3(CO)_{12}$, by a metal, which were specific for the particular anion to be prepared and produced that anion in high yield.

In this presentation we give details on the stoichiometric reduction of $Ru_3(CO)_{12}$ by alkali metal–benzophenone in THF to give alkali-metal salts of $[Ru_3(CO)_{11}]^{2-}$, $[Ru_6(CO)_{18}]^{2-}$, $[Ru_4(CO)_{13}]^{2-}$, and $[Ru_4(CO)_{12}]^{4-}$. We also show through a series of stoichiometric reactions how $[Ru_3(CO)_{11}]^{2-}$ is converted to anions of higher nuclearity. From this work, it is clear that the anions cited above can be prepared by simply choosing molar ratios of reactants which are consistent with the desired stoichiometric reaction. Such well-controlled relationships are also observed in the interconversions of ions through reactions of additional alkali metal or reactions with $Ru_3(CO)_{12}$. Furthermore, we find that through selective protonation reactions the conjugate acids of the anionic species are readily prepared. The new anion $[HRu_4(CO)_{12}]^{3-}$ is reported.

Results and Discussion

A. Stoichiometric Reduction of $Ru_3(CO)_{12}$ and Polynuclear Anions by Alkali Metal–Benzophenone. By specifying molar ratios of $Ru_3(CO)_{12}$ to alkali metal benzophenone (1:3, 1:2, 1:3/2, 1:1), it was possible to carry out stoichiometric reactions according to Scheme I. The anions $[Ru_4(CO)_{12}]^{4-}$, $[Ru_4(CO)_{13}]^{2-}$, and $[Ru_6(CO)_{18}]^{2-}$ can be prepared by using mixtures of appropriate molar ratios of $Ru_3(CO)_{12}$ and alkali metal–benzophenone. However, the anion $[Ru_3(CO)_{11}]^{2-}$ can be prepared quantitatively only if $Ru_3(CO)_{12}$ is added in small increments to a solution of alkali metal–benzophenone in THF until the appropriate molar ratio for $[Ru_3(CO)_{11}]^{2-}$ is achieved. By keeping the alkali metal in excess until the last increment of $Ru_3(CO)_{12}$ is added, this method for preparing $[Ru_3(CO)_{11}]^{2-}$ minimizes the formation of higher nuclearity clusters through reaction of the $[Ru_3(CO)_{11}]^{2-}$ which is generated with unreacted $Ru_3(CO)_{12}$. Preparation of $[Ru_3(CO)_{11}]^{2-}$ under the conditions chosen is relatively rapid (10–15 min/increment added). An appreciably slower secondary reaction (1 day) can occur between excess of alkali metal and $[Ru_3(CO)_{11}]^{2-}$ (eq 1), but the addition of increments of $Ru_3(CO)_{12}$ is sufficiently rapid to avoid this possibility. One further route to the $[Ru_4(CO)_{12}]^{4-}$ ion is the reduction of $[Ru_4(CO)_{13}]^{2-}$ by an alkali metal–benzophenone (eq 2). All of the reactions which used potassium–benzophenone as the reducing agent (Scheme I, reactions 1 and 2) were faster than those in which sodium–benzophenone or lithium–benzophenone was the reductant.

Scheme I



$$M_2[Ru_3(CO)_{11}] + M[(C_6H_5)_2CO] \rightarrow {}^3/_4M_4[Ru_4(CO)_{12}] + 2CO + (C_6H_5)_2CO \quad (1)$$

$$M = K, Na, Li$$

$$M_2[Ru_4(CO)_{13}] + 2M[(C_6H_5)_2CO] \rightarrow M_4[Ru_4(CO)_{12}] + CO + 2(C_6H_5)_2CO \quad (2)$$

$$M = K, Na, Li$$

By specifying molar ratio of reactants and by measuring the amount of CO gas evolved, the course and extent of each of the reactions cited in Scheme I and eq 1 and 2 were

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[1] Deprotonation reactions of $H_4Ru_4(CO)_{12}$ have been employed to prepare $[H_3Ru_4(CO)_{12}]^-$ and $[H_2Ru_4(CO)_{12}]^{2-}$.[2,3]

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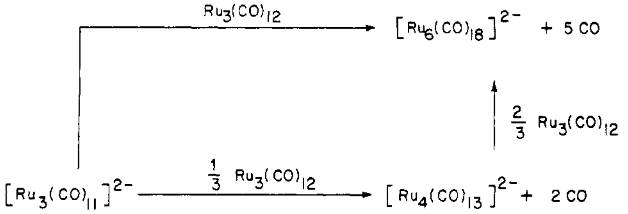
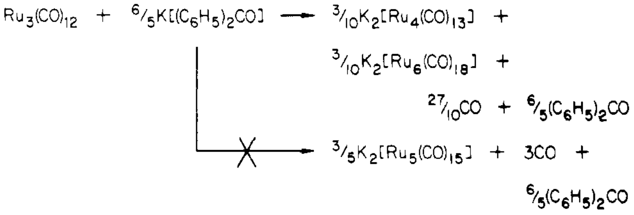
Scheme II



readily determined. Procedures we describe for the preparation of $[Ru_3(CO)_{11}]^{2-}$, $[Ru_4(CO)_{13}]^{2-}$, and $[Ru_4(CO)_{12}]^{4-}$ are the only ones reported to date. The preparation of $[Ru_6(CO)_{18}]^{2-}$ has been achieved in several ways[6] including a recent preparation[7] which is analogous to the one we have reported in Scheme I.

In view of the well-behaved stoichiometric reactions cited in Scheme I, an attempt was made to prepare the unknown pentanuclear cluster anion $[Ru_5(CO)_{15}]^{2-}$ through the reaction of $Ru_3(CO)_{12}$ with $K[(C_6H_5)_2CO]$ in a 1:6/5 molar ratio in THF. This reaction produced $K_2[Ru_4(CO)_{13}]$ and $K_2[Ru_6(CO)_{18}]$ as the only detectable ruthenium cluster anions. The volume of carbon monoxide evolved was consistent with the formation of these products (eq 3). No evidence was obtained for a pentanuclear species. Protonation of the reaction mixture yielded equal amounts of $H_2Ru_4(CO)_{13}$ and $H_2Ru_6(CO)_{18}$.



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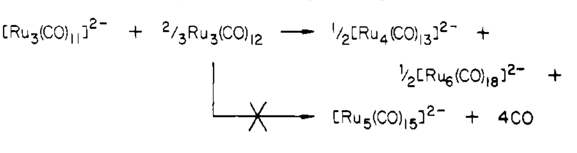
B. Reactions of $Ru_3(CO)_{12}$ with Polynuclear Anions. Triruthenium dodecacarbonyl reacts with several of the anions cited above according to Scheme II. These reactions occur readily and quantitatively. Evolved CO is a measure of the extent of reaction, and the infrared spectrum of the isolated solid reveals a single component.

The hydrido carbonyl cluster anions $[HRu_4(CO)_{13}]^-$ and $[HRu_6(CO)_{18}]^-$ can be prepared through reactions analogous to those reported in Scheme II when $[HRu_3(CO)_{11}]^-$ is used as the starting material instead of $[Ru_3(CO)_{11}]^{2-}$. However, these reactions proceed more slowly and they are not clean reactions.

From the reaction of $[Ru_3(CO)_{11}]^{2-}$ with $Ru_3(CO)_{12}$ in a 1:2/3 molar ratio it was hoped to obtain the unknown pentanuclear species $[Ru_5(CO)_{15}]^{2-}$. The only detectable products were $[Ru_4(CO)_{13}]^{2-}$ and $[Ru_6(CO)_{18}]^{2-}$ as ruthenium cluster anions. Carbon monoxide evolved was consistent with the formation of these products (eq 4). No evidence was obtained for a pentanuclear species. Protonation of the reaction mixture yielded equal amounts of $H_2Ru_4(CO)_{13}$ and $H_2Ru_6(CO)_{18}$.



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C. Protonation Reactions. Alkali-metal salts can be readily protonated in THF at room temperature.

1. Protonation of $[Ru_3(CO)_{11}]^{2-}$. Reaction 5 produces $[HRu_3(CO)_{11}]^-$. This anion has been prepared previously by other methods.[8] The reaction of $K[HB(CH_3)_3]$ with

$$[Ru_3(CO)_{11}]^{2-} + HBr \rightarrow [HRu_3(CO)_{11}]^- + Br^- \quad (5)$$

$Ru_3(CO)_{12}$ is probably the simplest route to $[HRu_3(CO)_{11}]^-$.[9] Protonation of $[Ru_3(CO)_{11}]^{2-}$ by 2 equiv of HCl results in the formation of $H_2Ru_3(CO)_{11}$ which rapidly decomposes at room temperature. This observation is in accord with an eariler study,[10] but we have analyzed the gaseous decomposition product (section E1).

2. Protonation of $[Ru_4(CO)_{13}]^{2-}$. Reaction 6 is the only route currently available to $[HRu_4(CO)_{13}]^-$ in high yield, and reaction 7 is the best method for obtaining $H_2Ru_4(CO)_{13}$. The cluster $H_2Ru_4(CO)_{13}$ was previously obtained as a side product in a variety of reactions.[11]

$$[Ru_4(CO)_{13}]^{2-} + HBr \rightarrow [HRu_4(CO)_{13}]^- + Br^- \quad (6)$$

$$[Ru_4(CO)_{13}]^{2-} + H_2SO_4 \rightarrow H_2Ru_4(CO)_{13} + SO_4^{2-} \quad (7)$$

3. Protonation of $[Ru_4(CO)_{12}]^{4-}$. Since $K_4[Ru_4(CO)_{12}]\cdot THF$ is insoluble in THF, it is not a useful starting material in the mono-, di-, and triprotonation of $[Ru_4(CO)_{12}]^{4-}$. The salt $Na_4[Ru_4(CO)_{12}]$ is, however, soluble in THF and was shown to undergo reactions 8–10. Reaction

$$[Ru_4(CO)_{12}]^{4-} + HBr \rightarrow [HRu_4(CO)_{12}]^{3-} + Br^- \quad (8)$$

$$[Ru_4(CO)_{12}]^{4-} + 2HBr \rightarrow [H_2Ru_4(CO)_{12}]^{2-} + 2Br^- \quad (9)$$

$$[Ru_4(CO)_{12}]^{4-} + 3HBr \rightarrow [H_3Ru_4(CO)_{12}]^- + 3Br^- \quad (10)$$

8 is the only successful route to $[HRu_4(CO)_{12}]^{3-}$ to date. Attempted preparation of $[HRu_4(CO)_{12}]^{3-}$ by deprotonation of $[H_2Ru_4(CO)_{12}]^{2-}$ gives a mixture of products.[2] Reactions 9 and 10 are not favored routes to $[H_2Ru_4(CO)_{12}]^{2-}$ or $[H_3Ru_4(CO)_{12}]^-$ since the total procedure is more demanding than the preparation of these anions through the deprotonation of $H_4Ru_4(CO)_{12}$.[2,3]

Total protonation of $[Ru_4(CO)_{12}]^{4-}$ (reaction 11) is readily achieved with either the sodium or potassium salt of this anion, but the potassium salt is preferred since it is easier to isolate in pure form. Hydrogenation of $Ru_3(CO)_{12}$ is still the simplest method for the preparation of $H_4Ru_4(CO)_{12}$.[12]

$$[Ru_4(CO)_{12}]^{4-} + H_2SO_4(\text{excess}) \rightarrow H_4Ru_4(CO)_{12} + 2SO_4^{2-} \quad (11)$$

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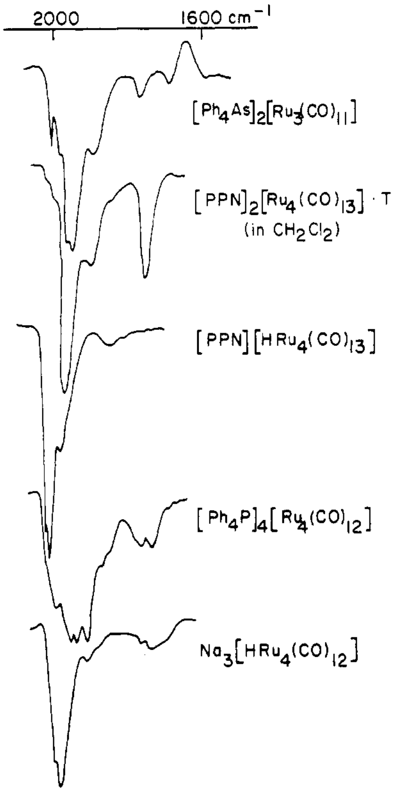

Figure 1. Infrared spectra in the carbonyl stretching region in THF except for $[PPN]_2[Ru_4(CO)_{13}]\cdot THF$ in CH_2Cl_2.

4. Protonation of $[Ru_6(CO)_{18}]^{2-}$. Protonation of this anion to form $[HRu_6(CO)_{18}]^-$ and $H_2Ru_6(CO)_{18}$ has been described previously.[6]

D. Metathesis Reactions. Alkali-metal salts of the carbonyl cluster anions and hydrido carbonyl cluster anions discussed above readily undergo metathesis reactions with the salts [PPN]Cl, $[P(C_6H_5)_4]Cl$, and $[As(C_6H_5)_4]Cl$.

E. Properties. In general, the alkali-metal salts of the ruthenium carbonyl cluster anions are sensitive to moisture. Exceptions are $[HRu_3(CO)_{11}]^-$ and $[HRu_6(CO)_{18}]^-$. The metathesized salts with PPN^+, $[P(C_6H_5)_4]^+$ and $[As(C_6H_5)_4]^+$ are less moisture sensitive than the alkali-metal salts. With one or two exceptions all of the alkali-metal salts which are isolated as solids contain some THF as a solvate. Where THF is shown in a formula in the following sections, it has been identified through infrared spectra and elemental analyses.

1. $[Ru_3(CO)_{11}]^{2-}$ and Its Conjugate Acids. The salts $K_2[Ru_3(CO)_{11}]$, $Na_2[Ru_3(CO)_{11}]$, and $[As(C_6H_5)_4]_2[Ru_3(CO)_{11}]$ have been isolated as crystalline solids. However, only a viscous liquid was obtained during attempts to isolate solid $Li_2[Ru_3(CO)_{11}]$ from THF. Infrared spectra of the carbonyl stretching region of solutions of these salts are given in Table I. For salts of $[Ru_3(CO)_{11}]^{2-}$, bridging carbonyl stretches occur over the range 1600–1755 cm⁻¹. The infrared spectrum of $[(C_6H_5)_4As]_2[Ru_3(CO)_{11}]$ is depicted in Figure 1. A structure containing a single edge-bridging carbonyl has been proposed for $[Os_3(CO)_{11}]^{2-}$ on the basis of infrared and carbon-13 NMR spectra.[5] The $[Ru_3(CO)_{11}]^{2-}$ ion probably has a similar structure. Unfortunately the carbon-13 NMR spectra of $[Ru_3(CO)_{11}]^{2-}$ as the Li^+ and K^+ salts in THF-d_8 (25 to −100 °C) show a single, temperature-independent, averaged signal at 215.5 ppm.

The preparation, structure, and infrared, ^{13}C NMR, and ^1H NMR spectra of $[HRu_3(CO)_{11}]^-$ (the conjugate acid of $[Ru_3(CO)_{11}]^{2-}$) ion have been reported earlier.[8,9] While our

Table I. Infrared Spectra of the Cluster Anions in the Carbonyl Stretching Region

anion	compd	solv	bands,[a] cm⁻¹
$[Ru_3(CO)_{11}]^{2-}$	$K_2[Ru_3(CO)_{11}]$	THF	2012 (m), 1978 (m (sh)), 1955 (s), 1942 (s), 1914 (s (sh)), 1883 (s (sh)), 1715 (w (br)), 1640 (m), 1600 (vw)
	$Na_2[Ru_3(CO)_{11}]$	THF	2012 (m), 1982 (m (sh)), 1957 (s), 1945 (s), 1920 (s (sh)), 1715 (w (br)), 1625 (w (br)), 1600 (vw)
	$Li_2[Ru_3(CO)_{11}]$	THF	2034 (m), 1998 (m (sh)), 1962 (s), 1948 (s), 1920 (m (sh)), 1882 (m), 1610 (m)
	$[Ph_4As]_2[Ru_3(CO)_{11}]$	THF	2012 (m), 1980 (m (sh)), 1972 (m (sh)), 1952 (s), 1935 (s), 1887 (m), 1755 (w), 1675 w (br)
$[Ru_4(CO)_{13}]^{2-}$	$K_2[Ru_4(CO)_{13}]$	THF	1945 (s), 1915 (m (sh)), 1895 m (sh), 1815 (m), 1770 (m), 1738 (m (sh)), 1718 (s)
	$Na_2[Ru_4(CO)_{13}]$	THF	1950 (vs), 1905 (m (sh)), 1815 (w), 1777 (w), 1740 (m (sh)), 1723 (s)
	$Li_2[Ru_4(CO)_{13}]$	THF	1972 (s), 1920 (m (sh)), 1818 (w), 1775 (w), 1708 (w), 1685 (w)
	$[PPN]_2[Ru_4(CO)_{13}]\cdot THF$	CH_2Cl_2	1945 (s), 1895 (m (sh)), 1715 (s)
$[HRu_4(CO)_{13}]^-$	$K[HRu_4(CO)_{13}]$	THF	2022 (s (sh)), 2000 (s), 1949 (m (sh)), 1850 (w (br))
	$Na[HRu_4(CO)_{13}]$	THF	2022 (s (sh)), 2000 (s), 1960 (m (sh)), 1933 (w (sh)), 1850 (w (br))
	$Li[HRu_4(CO)_{13}]$	THF	2022 (s), 2000 s (sh), 1952 (m (sh)), 1850 (w (br))
	$[PPN][HRu_4(CO)_{13}]$	CH_2Cl_2	2018 (s (sh)), 2001 (s), 1973 (m (sh)), 1835 (w (br))
$[Ru_4(CO)_{12}]^{4-}$	$K_4[Ru_4(CO)_{12}]\cdot THF$	Nujol mull	2078 (m), 1938 (m), 1865 (s), 1845 (s), 1790 (s), 1610 (w)
	$Na_4[Ru_4(CO)_{12}]$	THF	1925 (s (sh)), 1918 (s), 1865 (m (sh)), 1670 (m), 1640 (w), 1610 (w)
	$Li_4[Ru_4(CO)_{12}]$	THF	1972 (s), 1945 (s), 1928 (s), 1920 (s), 1885 (m), 1770 (w)
	$[Ph_4P]_4[Ru_4(CO)_{12}]$	CH_3CN	1980 (s (sh)), 1945 (s), 1930 (s), 1898 (s), 1850 (m (sh)), 1745 (m), 1710 (m), 1660 (w)
$[HRu_4(CO)_{12}]^{3-}$	$Na_3[HRu_4(CO)_{12}]$	THF	1965 (m (sh)), 1942 (s), 1880 (w), 1730 (vw (sh)), 1710 (w (br))
$[Ru_6(CO)_{18}]^{2-}$	$K_2[Ru_6(CO)_{18}]$	THF	2010 (s (sh)), 1983 (vs), 1930 (m (sh)), 1801 (w (br)), 1770 (w (br)), 1733 (w (br))
	$Na_2[Ru_6(CO)_{18}]$	THF	2010 (s (sh)), 1980 (vs), 1930 (m (sh)), 1805 (w (br)), 1763 (w (br)), 1740 (w (br))
	$Li_2[Ru_6(CO)_{18}]$	THF	2014 (s (sh)), 1983 (vs), 1930 (m (sh)), 1795 (w (br)), 1765 (w (br)), 1733 (w (br))

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak; br, broad; sh, shoulder.

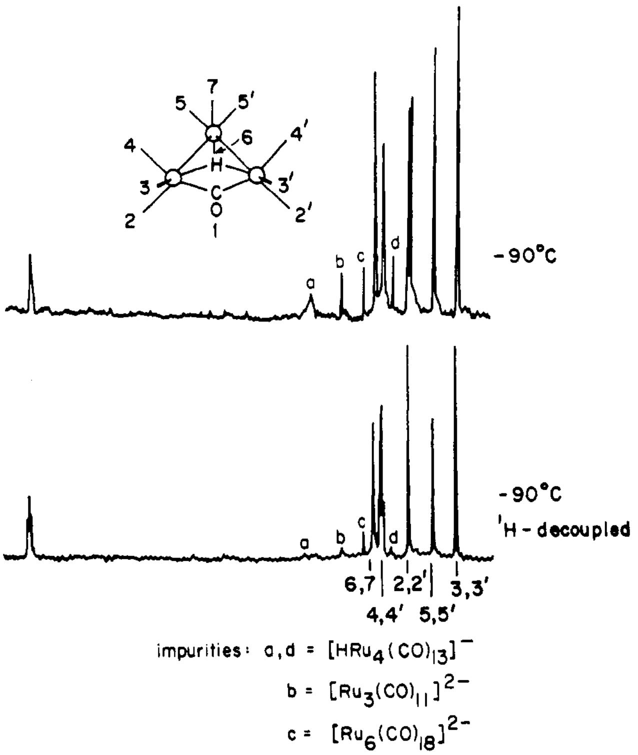

Figure 2. Low-temperature carbon-13 NMR spectra of a 50% ^{13}C-enriched sample of K[HRu$_3$(CO)$_{11}$] in THF-d_8. Calculations on the basis of peak area per carbonyl indicate that total impurity equals 1.6%.

variable-temperature ^{13}C NMR spectra of K[HRu$_3$(CO)$_{11}$] in THF-d_8 are in general agreement with this report,[8b-c] we differ[8b] with respect to spectroscopic assignments. Figure 2 presents carbon-13 NMR spectra of K[HRu$_3$(CO)$_{11}$]at -90 °C (^{1}H coupled and decoupled) under the condition of slow exchange. Our assignments are consistent with assignments of carbon-13 NMR spectra of [HFe$_3$(CO)$_{11}$]$^-$ and HRu$_3$(CO)$_{10}$(COCH$_3$) which are structurally similar to [HRu$_3$(CO)$_{11}$]$^-$.[13,14] The signal at 282 ppm is assigned to carbonyl 1 since bridging carbonyls generally resonate at lower field than terminal carbonyls.[15] On the basis of the known[8b] structure of [HRu$_3$(CO)$_{11}$]$^-$, six resonances (four of relative area 2 and two of relative area 1) are expected under limiting slow-exchange conditions. The presence of five signals, each of area 2, at -90 °C suggests that symmetrically nonequivalent axial carbonyls (6 and 7) on the unique ruthenium atom produce accidentally degenerate signals (210.2 ppm). The resonance at 197.8 ppm is assigned to the equatorial carbonyls 5 and 5′ on the unique ruthenium atom because it is unaffected by proton decoupling and because equatorial carbonyls generally resonate at higher field than axial carbonyls.[16] Since the strongest hydride coupling usually occurs trans to the hydride ligand,[17] the resonance at 202.9 ppm, with $J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$ = 12.8 Hz, is attributed to carbonyls 2 and 2′ which are trans to the hydrogen bridge. When the signal at 208.8 ppm is proton decoupled, $J_{^{13}\mathrm{C}-^{13}\mathrm{C}}$ = 18 Hz is observed. Since the same coupling constant is displayed by the bridging carbonyl, this signal is assigned to 4,4′, the carbonyls trans to the bridging carbonyl. The signal at 193.0 ppm is assigned to 3,3′. Carbonyls cis to a bridging carbonyl generally have resonances at higher field than carbonyls trans to a bridging carbonyl.[18] At room temperature, a single resonance was observed at 200.9 ppm indicating that complete scrambling of the CO groups occurs in [HRu$_3$(CO)$_{11}$]$^-$.

On reaction of K$_2$[Ru$_3$(CO)$_{11}$] with 2 equiv of HBr in THF at -78 °C the solution changes color from red-brown to deep brown and forms a precipitate. The H$_2$Ru$_3$(CO)$_{11}$ formed is apparently stable at -78 °C, but upon warming to room temperature 2 mol of gas/mol of cluster is evolved. This gas consists of 52% CO and 48% H$_2$. Infrared spectra of the nonvolatile decomposition product revealed the presence of Ru$_3$(CO)$_{12}$ as the major component. Work is continuing to determine the order in which the gases are evolved.

2. Ru$_4$(CO)$_{13}$$^{2-}$ and Its Conjugate Acids. The salts K$_2$[Ru$_4$(CO)$_{13}$]·0.5THF, Na$_2$[Ru$_4$(CO)$_{13}$]·0.5THF, and [PPN]$_2$[Ru$_4$(CO)$_{13}$]·THF have been isolated as crystalline solids. However, only a viscous liquid was obtained during attempts to isolate solid Li$_2$[Ru$_4$(CO)$_{13}$] from THF. Infrared spectra of the carbonyl stretching region of solutions of these salts are given in Table I. For salts of [Ru$_4$(CO)$_{13}$]$^{2-}$, the bridging carbonyl stretches occur in the range 1685–1818 cm^{-1}. These spectra are notably different in the bridge stretching region. Four absorptions are observed in the bridge stretching region of all three alkali-metal salts, but only one bridge absorption is observed for [PPN]$_2$[Ru$_4$(CO)$_{13}$]·THF (Figure 1) and [P(C$_6$H$_5$)$_4$]$^+$, [As(C$_6$H$_5$)$_4$]$^+$, and [N(n-C$_4$H$_9$)$_4$]$^+$ salts of this anion. These observations are common for salts of multiply charged anions and have been attributed to ion pairing in the alkali-metal salts.[19] Interaction between the alkali-metal cation and oxygen atom of at least one carbonyl bridge effectively reduces the symmetry of the anion, producing a complex pattern of bridge absorptions. A similar effect occurs in the case of K$_2$[H$_2$Ru$_4$(CO)$_{12}$].[2]

Infrared bands due to THF are observed.[20] K$_2$[Ru$_4$(CO)$_{13}$]·0.5THF (in CH$_3$CN): 2940 (w), 1030–1060 (w (br)), 920 (w), and 910 (w) cm^{-1}. Na$_2$[Ru$_4$(CO)$_{13}$]·0.5THF (in CH$_3$CN): 2820 (m), 1060 (w (br)), 1005 (w (br)), and 900 (w) cm^{-1}. [PPN]$_2$[Ru$_4$(CO)$_{13}$]·THF (in CH$_2$Cl$_2$): 2705 (w), 1030 (m), 1001 (m), and 890 (w) cm^{-1}.

Carbon-13 NMR spectra of [Ru$_4$(CO)$_{13}$]$^{2-}$ show a single sharp signal at 223.5 ppm, at room temperature. This resonance is broadened at -100 °C, and by -138 °C, the lowest temperature attained, the signal has disappeared into the base line.

Potassium, sodium, and [PPN]$^+$ salts of [HRu$_4$(CO)$_{13}$]$^-$ (the conjugate acid of [Ru$_4$(CO)$_{13}$]$^{2-}$) were isolated as crystalline solids. However, only a viscous liquid was obtained during attempts to isolate the lithium salt from THF. Infrared spectra of the carbonyl stretching region of solutions of these salts are given in Table I. For salts of [HRu$_4$(CO)$_{13}$]$^-$, the bridging carbonyl stretches occur in the range (1835–1850 cm^{-1}). Bands due to THF are observed[20] at 880 (w) and 817 (w) cm^{-1} for K[HRu$_4$(CO)$_{13}$]·0.25THF.

Proton NMR spectra of K[HRu$_4$(CO)$_{13}$]·0.25THF reveal a single, temperature-invariant resonance (25 to -80 °C)

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at τ 25.84. This peak falls in the metal hydride region usually assigned to edge-bridging hydrides.[2,3]

Variable-temperature carbon-13 NMR spectra of $[PPN][HRu_4(CO)_{13}]$ were recorded in the range 25 to −138 °C. As was the case in $[Ru_4(CO)_{13}]^{2-}$, the slow-exchange limit was not attained. At room temperature, a single sharp resonance was observed at 205 ppm. Upon cooling, this resonance broadened and a strongly hydrogen coupled satellite signal (J = 11.1 Hz) was observed. At −138 °C a second resonance (197.7 ppm), which also showed hydrogen coupling (J_{C-H} = 8 Hz), was observed and a broad peak centered at 235 ppm began to rise from the base line. This signal showed hydride coupling as seen in height enhancement during proton decoupling. This resonance was intermediate between the normally accepted range of chemical shift for bridging carbonyls (270–298 ppm) and terminal carbonyls (190–215 ppm) and is probably representative of an intermediate fluxional process which equilibrates terminal and bridging carbonyls.

Properties of $H_2Ru_4(CO)_{13}$, the conjugate acid of $[HRu_4(CO)_{13}]^-$, have been reported previously.[4,11]

3. $[Ru_4(CO)_{12}]^{4-}$ and Its Conjugate Acids. The potassium, sodium, and $[(C_6H_5)_4P]^+$ salts of $[Ru_4(CO)_{12}]^{4-}$ were isolated as crystalline solids. However, only a viscous liquid was obtained during attempts to isolate the lithium salt. The salt $K_4[Ru_4(CO)_{12}]\cdot THF$ is insoluble in THF and $(C_2H_5)_2O$.

Infrared spectra of $[Ru_4(CO)_{12}]^{4-}$ salts in the carbonyl stretching region are presented in Table I, and that of $[(C_6H_5)_4P]_4[Ru_4(CO)_{12}]$ is depicted in Figure 1. For salts of this anion, bridging carbonyl stretches occur over the range 1610–1790 cm^{-1}. The infrared spectrum of $K_4[Ru_4(CO)_{12}]\cdot THF$ in Nujol mull shows bands at 2740 (w), 1033 (m, (br)), 972 (w), and 890 (w) cm^{-1} due to the presence of THF.[20] The salt $Na_4[Ru_4(CO)_{12}]$ in THF-d_8 has a single temperature-invariant carbon-13 signal at 227 ppm from 25 to −85 °C. When $K_4[Ru_4(CO)_{12}]$ was prepared in glyme in the presence of crypt-2,2,2, the salt was soluble in DMF and the carbon-13 NMR spectrum (δ 227) from 25 to −65 °C was in complete accord with that of the sodium salt.

The conjugate acid of $[Ru_4(CO)_{12}]^{4-}$ was obtained as $Na_3[HRu_4(CO)_{12}]\cdot 0.5THF$. Its infrared spectrum in the carbonyl stretching region is given in Figure 1 and Table I. Bridging carbonyl stretches occur over the range (1710–1730 cm^{-1}). The infrared spectrum of $Na_3[HRu_4(CO)_{12}]\cdot 0.5THF$ in CH_3CN shows bands at 1025–1060 (w (br)) and 915 (w) cm^{-1} due to the presence of THF.[20] Proton NMR spectra of this anion in THF reveal a single resonance at τ 27.2. This peak falls in the metal hydride region usually assigned to edge-bridging hydrides.[2,3] Carbon-13 NMR spectra of $Na_3[HRu_4(CO)_{12}]\cdot 0.5THF$ in THF-d_8 were recorded at −80 and −90 °C. A slow-exchange limit was not attained. At −80 °C, two resonances are observed at 218.1 and 207.6 ppm which integrate roughly as 5:7 accounting for 12 carbonyl groups. On proton decoupling the signal at 207.6 ppm enhances. At −90 °C, the lowest temperature attained, two additional peaks at 289 and 281 ppm have begun to rise from the base line, possibly due to bridging carbonyls. The signal at 207.6 ppm shows hydride coupling as seen by enhancement during proton decoupling.

4. $[Ru_6(CO)_{18}]^{2-}$ and Its Conjugate Acids. The salts $K_2[Ru_6(CO)_{18}]$ and $Na_2[Ru_6(CO)_{18}]$ were isolated as crystalline solids. However, only a viscous liquid was obtained during attempts to isolate solid $Li_2[Ru_6(CO)_{18}]$ from THF. Infrared spectra of the carbonyl stretching region of solutions of these salts are given in Table I. They are very similar to the previously reported salt $[PPN]_2[Ru_6(CO)_{18}]$.[6,7] The properties of this anion have been described earlier.

Syntheses and structures of the conjugate acids $[HRu_6(CO)_{18}]^-$ and $H_2Ru_6(CO)_{18}$ have been previously reported.[6,21]

Experimental Section

All manipulations were carried out on a standard high vacuum line or in a glovebox under an atmosphere of dry, pure nitrogen.[22] Tetrahydrofuran, diethyl ether, and hexane were dried by stirring with $LiAlH_4$ for 2 days. The dried solvents were vacuum distilled into storage bulbs which contained sodium and benzophenone and were equipped with Teflon stopcocks. Methylene chloride as well as CH_3CN were dried by stirring over P_2O_5 for several days followed by vacuum distillation into storage bulbs. Deuterated solvents were dried and stored in the same manner as their protium-containing analogues. Hexane which was used for chromatography was stirred over concentrated H_2SO_4 for 2 days. It was then decanted and used without further distillation.

Benzophenone (J. T. Baker) and $Ru_3(CO)_{12}$ (Strem Chemicals) were used as received. Carbon monoxide, 90% ^{13}C enriched (Stohler Isotope Chemicals), was used as received for enrichment of $Ru_3(CO)_{12}$.[23] The compound 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (PCR Research Chemicals, Inc., under the trade name Kryptofix 222) was dried under vacuum for 24 h. Hydrogen bromide and HCl (Matheson Gas Products) were passed through a −78 °C trap and stored in a Pyrex tube equipped with Kontes stopcock at −78 °C. In a N_2-filled glovebox sodium and potassium were cut, washed with hexane, and stored. Lithium was freshly cut in air immediately before use.

Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer. Solid samples were run as KBr pellets or as Nujol mulls between KBr plates in an air-tight holder. Solution spectra of anionic and neutral compounds were obtained in liquid cells with 0.1- or 0.5-mm Teflon spacers and KBr windows.

Mass spectra of gaseous samples were obtained on a modified AE1 MS-10 spectrometer. Known mixtures of H_2 and CO were used to calibrate a group of instrument settings replicated for all determinations of relative H_2 and CO concentrations in unknown samples.

NMR spectra were recorded on either a Bruker HX-90 spectrometer operating in the FT mode at 22.6 (^{13}C) and 90 MHz (^1H) or a Bruker WM-300 spectrometer operating in the FT mode at 75.5 (^{13}C) and 300 MHz (^1H). The spectrometers were equipped with variable temperature and heteronuclear spin-decoupling capabilities. Perdeuterated solvents provided both a deuterium lock frequency and internal standard for shift assignments.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

A. Preparation of the Anions. 1. 1:3 Molar Ratio of $Ru_3(CO)_{12}$ to Alkali Metal. Preparation of $K_4[Ru_4(CO)_{12}]\cdot THF$. Potassium metal (0.0747 g, 1.91 mmol), $Ru_3(CO)_{12}$ (0.407 g, 0.636 mmol), and benzophenone (0.348 g, 1.91 mmol) were placed in a 100-mL flask in a N_2-filled glovebox. The vessel was equipped with a Teflon covered stir bar and a stopcock adaptor. At −78 °C about 10 mL of THF was distilled into the evacuated vessel. The vessel was placed in an oil bath and heated, with constant stirring, at 55–60 °C for 48 h or until no blue coloration was evident. After 48 h, a light red precipitate was seen, and the solution was almost colorless. The reaction vessel was immersed in liquid N_2, and the gas evolved in the reaction was collected (100%) and analyzed as 5% H_2 and 95% CO. In a N_2-filled glovebox the reaction vessel was attached to an extractor. After evacuation, the solution was filtered, washed repeatedly with THF, and dried under vacuum; yield 0.400 g (87% based on $Ru_3(CO)_{12}$). The salt was isolated as $K_4[Ru_4(CO)_{12}]\cdot THF$.

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Anal. Calcd for $C_{16}H_8K_4O_{13}Ru_4$: C, 19.83; H, 0.83; K, 16.14; Ru, 41.72. Found: C, 19.60; H, 0.53; K, 16.24; Ru, 41.68.

The sodium salt $Na_4[Ru_4(CO)_{12}]$ was prepared by using appropriate amounts of $Ru_3(CO)_{12}$, sodium, and benzophenone. The procedure was the same as the potassium reduction discussed above with the exception of the following items: (1) The reduction required about 60 h. (2) The product was soluble in THF, and it was precipitated by removing THF and adding hexane.

2. 1:2 Molar Ratio of $Ru_3(CO)_{12}$ to Alkali Metal. Preparation of $K_2[Ru_3(CO)_{11}]$. A two-neck bulb, equipped with a stir-bar and a vacuum line extractor with a collection bulb, was loaded with 0.105 g (0.58 mmol) of benzophenone and 0.024 g (0.61 mmol) of metallic potassium. A tip tube containing 0.1663 g (0.26 mmol) of $Ru_3(CO)_{12}$ was attached to the side arm of the two-neck bulb in a glovebox. The vessel was evacuated, and 3–4 mL of THF was distilled into it at −78 °C. The potassium–benzophenone solution was stirred for several hours until no more chunks of potassium could be seen. Triruthenium dodecacarbonyl was then added portionwise (10–20 mg every 15 min) while the mixture was stirred at room temperature. The mixture was stirred until the last increment of $Ru_3(CO)_{12}$ was added, and no more unreacted $Ru_3(CO)_{12}$ could be seen. At this stage about 100% of theoretical CO had evolved. The solvent THF was then removed, and about 5 mL of CH_2Cl_2 was added to induce precipitation. The precipitate was filtered, washed with CH_2Cl_2, and dried under vacuum; yield 0.160 g (90%). Anal. Calcd for $C_{11}K_2O_{11}Ru_3$: C, 19.16; K, 11.34; Ru, 43.97. Found: C, 19.35; K, 11.09; Ru, 43.75.

The sodium salt $Na_2[Ru_3(CO)_{11}]$ and the lithium salt $Li_2[Ru_3(CO)_{11}]$ (in solution) were prepared by using appropriate amounts of the reactants. The procedures were the same as above with the exception that the sodium salt was precipitated by adding hexane to the concentrated solution in CH_2Cl_2.

3. 1:3/2 Molar Ratio of $Ru_3(CO)_{12}$ to Alkali Metal. Preparation of $K_2[Ru_4(CO)_{13}]\cdot0.5THF$. A reaction vessel, equipped with a stir bar and a vacuum line extractor, was loaded with 0.930 g (1.45 mmol) of $Ru_3(CO)_{12}$, 0.0926 g (2.37 mmol) of potassium metal, and 0.405 g (2.22 mmol) of benzophenone. After evacuation about 10 mL of dry THF was condensed into the vessel. The mixture was stirred for 24 h at room temperature or until at least 95% of the theoretical amount of gas had evolved. Mass spectra of this gas typically showed 5% H_2 and 95% CO. The volume of THF in the reaction vessel was reduced to about 1 mL, and then 5 mL of dry CH_2Cl_2 was condensed into the vessel to induce precipitation of red $K_2[Ru_4(CO)_{13}]\cdot0.5THF$. The mixture was filtered, and the mixed solvent was then removed under vacuum. Fresh CH_2Cl_2 (5 mL) was used to wash the solid. The washings were removed, and the precipitate was dried under vacuum overnight. The compound precipitates as $K_2[Ru_4(CO)_{13}]\cdot0.5THF$; yield 0.84 g (88% based on $Ru_3(CO)_{12}$). Anal. Calcd for $C_{15}H_4O_{13.5}K_2Ru_4$: C, 20.41; H, 0.46; Ru, 45.81. Found: C, 20.18; H, 0.82; Ru, 46.44. The compound was also derivatized by its metatheses reaction with [PPN]Cl to yield $[PPN]_2[Ru_4(CO)_{13}]\cdot THF$, the analysis of which is reported in section D.

The sodium salt $Na_2[Ru_4(CO)_{13}]\cdot0.5THF$ was prepared by using $Ru_3(CO)_{12}$ (0.7713 g, 1.206 mmol), sodium (0.0416 g, 1.809 mmol), and benzophenone (0.3289 g, 1.795 mmol). The procedure was the same as above with the exception of the following items: (1) After the evolved gas was measured, the solvent THF was removed by distillation and 5 mL of $(CH_3)_2O$ was condensed into the vessel. Dry CH_2Cl_2 (5 mL) was added, and the $(CH_3)_2O$ was distilled from the reaction mixture at −78 °C, which induced precipitation of a brick-red solid. Addition of about 2 mL of CH_2Cl_2 to the vessel caused more precipitation. The mixture was filtered and the precipitate was washed with fresh CH_2Cl_2 to remove benzophenone. (2) Yield: 0.520 g (68%, based on $Ru_3(CO)_{12}$). The salt was isolated as $Na_2[Ru_4(CO)_{13}]\cdot0.5$ THF. Anal. Calcd for $C_{15}H_4Na_2O_{13.5}Ru_4$: C, 21.17; H, 0.48; Na, 5.41. Found: C, 20.70; H, 0.98; Na, 5.67.

The lithium salt $Li_2[Ru_4(CO)_{13}]$ was prepared in solution as above.

4. 1:1 Molar Ratio of $Ru_3(CO)_{12}$ to Alkali Metal. Preparation of $K_2[Ru_6(CO)_{18}]$. Potassium metal (0.027 g, 0.69 mmol), $Ru_3(CO)_{12}$ (0.4415 g, 0.69 mmol), and benzophenone (0.1225 g, 0.69 mmol) were placed in a 100-mL flask in a N_2-filled glovebox. The procedure used was the same as that described in section A1 with the exception of the following items: (1) The reaction required about 20 h for completion. (2) The product precipitated from a concentrated THF solution upon addition of CH_2Cl_2. The infrared spectrum (Table I) is in excellent agreement with the literature.[6,7] Yield: 0.350 g, 85% based on $Ru_3(CO)_{12}$.

The sodium and lithium salts $Na_2[Ru_6(CO)_{18}]$ and $Li_2[Ru_6(CO)_{18}]$, respectively, were also prepared by using appropriate amounts of the reactants. The procedures were the same as above with the exception that reductions using sodium and lithium were much slower.

B. Reactions of Polynuclear Anions with Alkali Metal–Benzophenone. 1. Reaction of $[Ru_3(CO)_{11}]^{2-}$ with Alkali Metal–Benzophenone. Preparation of $K_4[Ru_4(CO)_{12}]\cdot THF$. Potassium metal (0.002 g, 0.05 mmol), $K_2[Ru_3(CO)_{11}]$ (0.0352 g, 0.05 mmol), and benzophenone (0.0092 g, 0.05 mmol) were placed in a 50-mL flask in a N_2-filled glovebox. The procedure for the reaction was the same as described in section A.1; yield 0.027 g (80%).

The salts $Na_4[Ru_4(CO)_{12}]$ and $Li_4[Ru_4(CO)_{12}]$ were also prepared by using appropriate amounts of the reactants. The procedures were the same as described above (section A.1)

2. Reaction of $[Ru_4(CO)_{13}]^{2-}$ with Alkali Metal–Benzophenone. Preparation of $K_4[Ru_4(CO)_{12}]\cdot THF$. Potassium metal (0.010 g, 0.26 mmol), benzophenone (0.040 g, 0.21 mmol), and $K_2[Ru_4(CO)_{13}]$ (0.100 g, 0.12 mmol) were placed in a 30-mL flask in a N_2-filled glovebox. The procedure for the reaction was the same as described in section A.1; yield 0.100 g (87%).

Reductions using sodium–benzophenone and lithium–benzophenone were carried out as above.

C. Reactions of Polynuclear Anions with $Ru_3(CO)_{12}$. 1. Reaction of $[Ru_3(CO)_{11}]^{2-}$ with 0.33 Equiv of $Ru_3(CO)_{12}$. Preparation of $K_2[Ru_4(CO)_{13}]\cdot0.5THF$. Triruthenium dodecacarbonyl (0.016 g, 0.025 mmol) and $K_2[Ru_3(CO)_{11}]$ (0.048 g, 0.070 mmol) were placed in a 50-mL reaction vessel. The procedure was the same as described in section A.3; yield 0.052 g (84% based on $K_2[Ru_3(CO)_{11}]$).

The sodium salt $Na_2[Ru_4(CO)_{13}]$ and the lithium salt $Li_2[Ru_4(CO)_{13}]$ (in solution) were prepared as above.

2. Reaction of $[Ru_3(CO)_{11}]^{2-}$ with 1 Equiv of $Ru_3(CO)_{12}$. Preparation of $K_2[Ru_6(CO)_{18}]$. Triruthenium dodecacarbonyl (0.055 g, 0.086 mmol) and $K_2[Ru_3(CO)_{11}]$ (0.060 g, 0.087 mmol) were placed in a 50-mL reaction vessel. The procedure was the same as described in section A.4.

The sodium salt $Na_2[Ru_6(CO)_{18}]$ and the lithium salt $Li_2[Ru_6(CO)_{18}]$ (in solution) were prepared as above.

3. Reaction of $[Ru_4(CO)_{13}]^{2-}$ with 0.67 Equiv of $Ru_3(CO)_{12}$. Preparation of $K_2[Ru_6(CO)_{18}]$. The procedures for the preparation of $K_2[Ru_6(CO)_{18}]$, $Na_2[Ru_6(CO)_{18}]$, and $Li_2[Ru_6(CO)_{18}$ (in solution) by using appropriate amounts of the reactants were the same as above.

D. Metathesis Reactions. Preparation of $[(Ph_3P)_2N]_2[Ru_4(CO)_{13}]\cdot THF$ from $K_2[Ru_4(CO)_{13}]$. The reduction of $Ru_3(CO)_{12}$ was conducted as described in section A.3 above. Following the measurement of CO, a stoichiometric amount of $[(Ph_3P)_2N]Cl$ was added to the reaction mixture. A 10-mL portion of dry CH_2Cl_2 was distilled into the reaction vessel. The reaction was warmed to room temperature and allowed to stir for 1 h. The mixed solvent was removed and fresh CH_2Cl_2 condensed into the reaction bulb, in order to dissolve the $[(Ph_3P)_2N]_2[Ru_4(CO)_{13}]$. The solution was filtered, and the residue on the frit (KCl, identified by X-ray powder diffraction pattern) was washed several times with CH_2Cl_2. Under N_2, the vessel containing the red filtrate was placed on another extractor. Addition of diethyl ether caused the precipitation of $[(Ph_3P)_2N]_2[Ru_4(CO)_{13}]\cdot THF$. The mixture was filtered, washed with fresh Et_2O, and dried overnight under vacuum. For a typical reaction a yield of about 60% is obtained. Anal. Calcd for $C_{89}H_{68}N_2O_{14}P_4Ru_4$: C, 55.72; H, 3.60; P, 6.46; Ru, 21.08. Found: C, 56.07; H, 3.56; P, 6.53; Ru, 20.66.

Metathesis of all the other anions were carried out by the above method with the exception of the following items: (1) The sodium salt $Na_4[Ru_4(CO)_{12}]$ was metathesized in CH_3CN by using $[Ph_4P]Br$. (2) The potassium salt $K_2[Ru_3(CO)_{11}]$ was metathesized in THF by using $[Ph_4As]Br$.

E. Protonation Reactions. 1. Preparation of $K[HRu_4(CO)_{13}]\cdot0.25THF$. A reaction flask containing a Teflon-covered stir bar and an extractor was loaded with 0.4974 g (0.587 mmol) of $K_2[Ru_4(CO)_{13}]$ in a N_2-filled glovebox. The apparatus was evacuated, and 15 mL of dry THF was distilled into the reaction bulb. The solution was then frozen at −196 °C and 0.588 mmol anhydrous HBr was condensed onto it. With continuous stirring the reaction mixture was warmed first to −78 °C and then to room temperature where it was allowed to stir for 1.5 h in order to ensure complete reaction. The reaction mixture was filtered and washed thoroughly to remove KBr (identified by X-ray powder pattern). THF was removed from the filtrate. Under N_2 the reaction vessel was attached to a clean extractor, and 5 mL of CH_2Cl_2 was distilled into it. The mixture was stirred, filtered, washed with CH_2Cl_2, and dried under vacuum. The salt was isolated as $K[HRu_4(CO)_{13}]\cdot 0.25THF$; yield 0.350 g (72% based on $K_2[Ru_4(CO)_{13}]$). Anal. Calcd for $C_{14}H_3KO_{13.25}Ru_4$: C, 20.34; H, 0.37; K, 4.73; Ru, 48.91. Found: C, 20.22; H, 0.25; K, 4.84; Ru, 48.59%.

The salts $Na[HRu_4(CO)_{13}]$ and $Li[HRu_4(CO)_{13}]$ (in solution) were prepared by the above procedure.

2. Preparation of $H_2Ru_4(CO)_{13}$. The reduction of $Ru_3(CO)_{12}$ was conducted as described in section A.3 above in a two neck flask using $Ru_3(CO)_{12}$ (0.337 g, 0.528 mmol), K (0.033 g, 0.844 mmol), and benzophenone (0.152 g, 0.830 mmol). Following the measurement of CO, an acid addition tube containing 10 mL of H_2SO_4 (concentrated) and 8 mL of THF was attached to the reaction flask under N_2. The reaction bulb was maintained at 0 °C, and the acid was allowed to drip into the solution which was vigorously stirred. The color of the solution turned from red to brown. Acid addition was continued until the brown color changed to red. The vessel was opened to the air, and the solution was poured into a 1-L flask containing 200 mL of hexane and 100 mL of ice. The product was extracted with hexane until the extracts were almost colorless. The remainder was extracted with CH_2Cl_2. Both batches of extracts were placed over $MgSO_4$ overnight and filtered. The extract in CH_2Cl_2 was then taken to dryness, dissolved in hexane, and added to the hexane extract. The volume of the combined solutions was then reduced by distillation to give a saturated solution. The solution was placed on a silica column, 7-cm height and 2-cm diameter, and eluted with hexane. The first yellow band contained small amounts of $H_4Ru_4(CO)_{12}$ and $Ru_3(CO)_{12}$. The remaining red band was then eluted with CH_2Cl_2, and solvent was evaporated to obtain pure $H_2Ru_4(CO)_{13}$. It was washed with a small volume of pentane; yield 0.305 g (75% based on $Ru_3(CO)_{12}$).

3. Preparation of $Na_3[HRu_4(CO)_{12}]\cdot 0.5THF$. A reaction bulb with a stir bar and an extractor was loaded with 0.0341 g (1.483 mmol) of Na, 0.2701 g (1.48 mmol) of benzophenone, and 0.3164 g (0.496 mmol) of $Ru_3(CO)_{12}$. The reduction was conducted as described in section A.1. Following the measurement of CO, the solution was frozen at −196 °C and 0.372 mmol of HBr was condensed onto the solution. With continuous stirring the reaction mixture was warmed first to −78 °C and then to room temperature where it was allowed to stir for 1 h. The reaction mixture was filtered and washed thoroughly to remove NaBr (identified by X-ray powder pattern). THF was removed from the filtrate. Under N_2 the reaction vessel was attached to a clean extractor and 4 mL of CH_2Cl_2 was distilled into it. The mixture was stirred, filtered, washed with CH_2Cl_2, and dried under vacuum. The compound precipitates as $Na_3[HRu_4(CO)_{12}]\cdot 0.5THF$, yield 0.200 g. Anal. Calcd. for $C_{14}H_5O_{12.5}Na_3Ru_4$: C, 19.86; H, 0.60; Ru, 47.76. Found: C, 18.60; H, 0.72; Ru, 46.29. The composition of the product $Na_3[HRu_4(CO)_{12}]\cdot 0.5$ THF was confirmed by its reactions with 1, 2, and 3 equiv of HBr as described below to yield the known species $[H_2Ru_4(CO)_{12}]^{2-}$, $[H_3Ru_4(CO)_{12}]^-$, and $H_4Ru_4(CO)_{12}$, respectively.

4. Stepwise Protonation of $Na_3[HRu_4(CO)_{12}]\cdot 0.5THF$. Protonation of $Na_3[HRu_4(CO)_{12}]\cdot 0.5THF$ (0.046 g, 0.054 mmol) was achieved in the same way as described in section E.1 by using 0.056 mmol of HBr. Following the removal of NaBr by filtration, solvent THF was pumped away leaving the sodium salt of the known[2,3] anion $[H_2Ru_4(CO)_{12}]^{2-}$ (identified by its IR spectrum), yield 0.042 g. The entire yield was then protonated as above in THF by using 0.054 mmol of HBr producing NaBr and the known[2,3] (identified by its infrared spectrum) anion $[H_3Ru_4(CO)_{12}]^-$. Sodium bromide was removed by filtration, and the filtrate containing the anion $[H_3Ru_4(CO)_{12}]^-$ was protonated again with 0.054 mmol of HBr to yield the parent acid $H_4Ru_4(CO)_{12}$ and NaBr. Sodium bromide was removed by filtration, and the solvent THF was pumped away from the filtrate leaving the known[1,2] compound $H_4Ru_4(CO)_{12}$ (identified by its infrared spectrum) which was finally washed with a small amount of pentane; yield 0.030 g (88% based on $Na_3[HRu_4(CO)_{12}]\cdot 0.5THF$).

5. Preparation of $H_4Ru_4(CO)_{12}$. The reduction of $Ru_3(CO)_{12}$ was conducted as described in section A.1 above in a two-neck flask using $Ru_3(CO)_{12}$ (0.813 g, 1.272 mmol), Na (0.088 g, 3.814 mmol), and benzophenone (0.694 g, 3.814 mmol). Following the measurement of CO the protonation was carried out by using excess H_2SO_4 as described in section E.2. The hexane extract of the protonated product was placed on a silica column and eluted with about 1000 mL of hexane. The first 10 mL of the solution was discarded since it contained $Ru_3(CO)_{12}$ impurity. Solvent was evaporated from the remaining solution to obtain pure $H_4Ru_4(CO)_{12}$, yield 0.620 g (87%).

6. Preparation of $K[HRu_3(CO)_{11}]$. Protonation of $K_2[Ru_3CO)_{11}]$ (0.111 g, 0.161 mmol) was conducted in THF by using 0.161 mmol of HCl. The procedure was the same as described in E.1. Following the removal of KCl, the solvent THF was removed from the filtrate. The filtrate bulb was attached to a clean extractor, and 2 mL of CH_2Cl_2 was added to it followed by 4 mL of hexane inducing precipitation of red $K[HRu_3(CO)_{11}]$. The precipitate was filtered, washed, and dried; yield 0.075 g. The sodium salt $Na[HRu_3(CO)_{11}]$ and lithium salt $Li[HRu_3(CO)_{11}]$ (in solution) were prepared in the same manner. Infrared and NMR (^1H and ^{13}C) spectra of this anion were in excellent agreement with values in the literature.[8,9]

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Registry No. $K_2[Ru_3(CO)_{11}]$, 85781-74-4; $Na_2[Ru_3(CO)_{11}]$, 85781-75-5; $Li_2[Ru_3(CO)_{11}]$, 85781-76-6; $[Ph_4As]_2[Ru_3(CO)_{11}]$, 85781-78-8; $K_2[Ru_4(CO)_{13}]$, 75215-44-0; $Na_2[Ru_4(CO)_{13}]$, 85781-79-9; $Li_2[Ru_4(CO)_{13}]$, 85781-80-2; $[PPN]_2[Ru_4(CO)_{13}]$, 75215-46-2; $K[HRu_4(CO)_{13}]$, 76917-54-9; $Na[HRu_4(CO)_{13}]$, 85781-81-3; $Li[HRu_4(CO)_{13}]$, 85781-82-4; $[PPN][HRu_4(CO)_{13}]$, 76917-53-8; $K_4[Ru_4(CO)_{12}]$, 75234-73-0; $Na_4[Ru_4(CO)_{12}]$, 85781-83-5; $Li_4[Ru_4(CO)_{12}]$, 85781-84-6; $[Ph_4P]_4[Ru_4(CO)_{12}]$, 85781-86-8; $Na_3[HRu_4(CO)_{12}]$, 85781-87-9; $K_2[Ru_6(CO)_{18}]$, 85781-88-0; $Na_2[Ru_6(CO)_{18}]$, 85781-89-1; $Li_2[Ru_6(CO)_{18}]$, 85781-90-4; $Ru_3(CO)_{12}$, 15243-33-1; $[Ru_4(CO)_{13}]^{2-}$, 75215-45-1; $[Ru_4(CO)_{12}]^{4-}$, 85781-85-7; $Na_2[H_2Ru_4(CO)_{12}]$, 85781-91-5; $[H_3Ru_4(CO)_{12}]^-$, 70073-18-6; $H_4Ru_4(CO)_{12}$, 34438-91-0; $K[HRu_3(CO)_{11}]$, 80662-65-3; $Na[HRu_3(CO)_{11}]$, 71936-71-5; $Li[HRu_3(CO)_{11}]$, 85781-92-6; lithium benzophenone, 16592-10-2; sodium benzophenone, 3463-17-0; potassium benzophenone, 4834-86-0.