High Yield Syntheses of New Tetraruthenium Carbonylates: $[Ru_4(CO)_{13}]^{2-}$, $[HRu_4(CO)_{13}]^-$, and $[Ru_4(CO)_{12}]^{4-}$; a Simple, High Yield Preparation of $H_2Ru_4(CO)_{13}$

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Summary The anions $[Ru_4(CO)_{13}]^{2-}$ and $[Ru_4(CO)_{12}]^{4-}$ are formed in high yield by the controlled reduction of $Ru_3(CO)_{12}$ with potassium–benzophenone and, upon subsequent protonation, lead to $[HRu_4(CO)_{13}]^-$, $H_2Ru_4(CO)_{13}$, and $H_4Ru_4(CO)_{12}$ quantitatively.

THE tetranuclear cluster $H_2Fe_4(CO)_{13}$ and its conjugate bases, $[HFe_4(CO)_{13}]^-$ and $[Fe_4(CO)_{13}]^{2-}$, have been known for over twenty years.[1] While the ruthenium analogue $H_2Ru_4(CO)_{13}$ is also well known, its conjugate bases $[HRu_4(CO)_{13}]^-$ and $[Ru_4(CO)_{13}]^{2-}$ have eluded isolation or identification, although their presence in solution has been suggested.[2,3] Interestingly, $H_2Ru_4(CO)_{13}$ and $[HRu_4(CO)_{13}]^-$ have been implicated as active species in catalytic systems.[2,4] We report here the synthesis, isolation, and spectral properties of the new ions $[HRu_4(CO)_{13}]^-$, $[Ru_4(CO)_{13}]^{2-}$, and $[Ru_4(CO)_{12}]^{4-}$. In addition, we report a high yield synthesis for $H_2Ru_4(CO)_{13}$, which previously has only been obtained as a side product in a variety of reactions.[3,5]

The basis for our syntheses is the controlled reduction of $Ru_3(CO)_{12}$. While such reductions are known to produce anionic species, reactions reported previously were found to yield complex mixtures.[3,6] The preparation of $[Ru_4(CO)_{13}]^{2-}$, reaction (1), and all subsequent reactions were

$$4Ru_3(CO)_{12} + 6KPh_2CO \rightarrow 3K_2[Ru_4(CO)_{13}] + 9CO + 6Ph_2CO \quad (1)$$

performed using vacuum line procedures which allowed careful measurement and identification of evolved gases, permitting determination of reaction stoicheiometry. Dodecacarbonyltriruthenium was treated with 1·6 equiv. of potassium–benzophenone (*ca.* 10% excess), in tetrahydrofuran (THF). Stirring the solution overnight at −78 °C and for 24 h at 25 °C afforded a deep red solution and 85% of the theoretical amount of CO. Consistent with the CO evolution, the red salt $K_2[Ru_4(CO)_{13}]$ was obtained in 80% yield by precipitation with CH_2Cl_2. Alternatively, metathesis of the reduction mixture with $[(Ph_3P)_2N]Cl$ and precipitation from a CH_2Cl_2–Et_2O solution yielded $[(Ph_3P)_2N]_2[Ru_4(CO)_{13}]$ as a light red-brown powder in 70% yield.

TABLE. I.r. spectra (1600—2100 cm^{-1}) of tetraruthenium salts.

Salt	$\nu(CO)/cm^{-1}$	
$K_2[Ru_4(CO)_{13}]$[a]	1945 s	1770 m
	1915 m (sh)	1738 m (sh)
	1895 m (sh)	1718 s
	1815 m	
$[(Ph_3P)_2N]_2[Ru_4(CO)_{13}]$[b]	1950 s	1750 s
	1898 m (sh)	
$K[HRu_4(CO)_{13}]$[a]	2020 s	1970 m (sh)
	2000 s	1850 w (br)
$[(Ph_3P)_2N][HRu_4(CO)_{13}]$[b]	2018 s	1975 m (sh)
	2001 s	1830 w (br)
$K_4[Ru_4(CO)_{12}]$[c]	1978 m	1845 s
	1938 m	1790 s
	1865 s	1610 w

[a] In THF solution. [b] In CH_2Cl_2 solution. [c] Nujol mull.

I.r. spectra (Table) of $[Ru_4(CO)_{13}]^{2-}$ salts indicate the presence of bridging carbonyl groups with absorptions in the range 1718—1815 cm^{-1}. The simpler spectrum displayed by $[(Ph_3P)_2N]_2[Ru_4(CO)_{13}]$ is presumably due to the lack of ion-pairing in this salt, as suggested by studies of $[H_2Ru_4(CO)_{12}]^{2-}$ salts.[7] The ^{13}C n.m.r. spectrum of $[(Ph_3P)_2N]_2[Ru_4(CO)_{13}]$, 35% enriched in ^{13}CO, consists of a single peak at 223·7 p.p.m. in CD_2Cl_2–$CHClF_2$ (1:3, v/v) down to −100 °C. At −130 °C, the lowest temperature attained, this peak disappears into the baseline.

Protonation of $K_2[Ru_4(CO)_{13}]$ with 1 equiv. of HCl in THF proceeded rapidly, without gas evolution, at −78 °C to yield $[HRu_4(CO)_{13}]^-$ [reaction (2)]. Removal of KCl and precipitation with CH_2Cl_2 yielded $K[HRu_4(CO)_{13}]$ as a red-brown powder. An analogous reaction in CH_2Cl_2 was used to produce $[(Ph_3P)_2N][HRu_4(CO)_{13}]$.

$$K_2[Ru_4(CO)_{13}] + HCl \rightarrow K[HRu_4(CO)_{13}] + KCl \qquad (2)$$

Potassium and $[(Ph_3P)_2N]$ salts of $[HRu_4(CO)_{13}]^-$ exhibit similar i.r. spectra (Table) with weak bridging carbonyl absorptions at 1850 and 1830 cm^{-1}, respectively. This spectrum is similar in appearance to that of $[(Ph_3P)_2N][HFeRu_3(CO)_{13}]$, its iso-electronic analogue.[8] The ^1H n.m.r. spectrum of $[(Ph_3P)_2N][HRu_4(CO)_{13}]$ displays a single, temperature-independent, hydride resonance at τ 25·84 down to −80 °C in CD_2Cl_2. The ^{13}C n.m.r. spectrum (35% enrichment) at −58 °C consists of a single sharp peak at 203·7 p.p.m. in CD_2Cl_2–$CHClF_2$. At −138 °C, this peak broadens, another broad peak occurs at 235 p.p.m., and peaks in the terminal carbonyl region appear. Some of the terminal carbonyls are strongly coupled to hydrogen, as evidenced by proton decoupling experiments.

A 75% yield of $H_2Ru_4(CO)_{13}$, based on initial $Ru_3(CO)_{12}$, is obtained by direct acidification of the reduction solution, extraction with hexane, and chromatographic separation on silica gel with hexane as eluent [reaction (3)].

$$K_2[Ru_4(CO)_{13}] + H_2SO_4 \text{ (excess)} \rightarrow H_2Ru_4(CO)_{13} + K_2SO_4 \qquad (3)$$

The anion $[Ru_4(CO)_{12}]^{4-}$ was produced according to reaction (4). 3 equiv. of potassium–benzophenone were treated with $Ru_3(CO)_{12}$ in THF at 50 °C. Stirring for 36 h produced 100% of theoretical CO evolution and $K_4[Ru_4(CO)_{12}]$ as an orange precipitate in >85% yield.

$$4Ru_3(CO)_{12} + 12KPh_2CO \rightarrow 3K_4[Ru_4(CO)_{12}]\text{(solid)} + 12CO + 12Ph_2CO \qquad (4)$$

The salt $K_4[Ru_4(CO)_{12}]$ was also produced by the direct reduction of $K_2[Ru_4(CO)_{13}]$. The reaction is stoicheiometric. Reaction of 2 equiv. of potassium–benzophenone with 1 equiv. of $K_2[Ru_4(CO)_{13}]$ at 50 °C produced a clear, colourless solution, complete precipitation of $K_4[Ru_4(CO)_{12}]$, and 1 equiv. of CO [reaction (5)].

$$K_2[Ru_4(CO)_{13}] + 2KPh_2CO \rightarrow K_4[Ru_4(CO)_{12}] \text{ (solid)} + CO + 2Ph_2CO \qquad (5)$$

The i.r. spectrum of $K_4[Ru_4(CO)_{12}]$ as a Nujol mull exhibits very broad absorptions (Table). Insolubility of this compound has, for the time being, precluded further spectral identification. However, protonation of the salt with sulphuric acid led quantitatively to $H_4Ru_4(CO)_{12}$, [reaction (6)].

$$K_4[Ru_4(CO)_{12}] \text{ (solid)} + H_2SO_4 \text{ (excess)} \rightarrow H_4Ru_4(CO)_{12} + K_2SO_4 \qquad (6)$$

Chemical analyses for all salts were in accord with the formulations presented here. Structural elucidation of the anions reported is in progress.

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[1] W. Hieber and R. Werner, *Chem. Ber.*, 1957, **90**, 286, 1116; W. Hieber and E. Becker, *ibid*, 1950, **63**, 1405; W. Hieber and J. G. Floss, *ibid*, 1957, **90**, 1617; W. Hieber and N. Kahlen, *ibid*, 1958, **91**, 2223; W. Hieber and A. Lipp, *ibid*, 1959, **92**, 2075, 2085.

[2] P. C. Ford, R. G. Rinker, G. Ungermann, R. M. Laine, V. Landis, and S. A. Moya, *J. Am. Chem. Soc.*, 1978, **100**, 4595; C. Ungermann, V. Landis, S. A. Moya, H. Cohen, H. Walker, R. G. Pearson, R. G. Rinker, and P. C. Ford, *ibid.*, 1979, **101**, 5922.

[3] B. F. G. Johnson, R. D. Johnston, J. Lewis, B. H. Robinson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2856.

[4] G. A. Vaglio, D. Osella, and M. Valle, *Transition Met. Chem.*, 1977, **2**, 94.

[5] A. J. Canty, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, 1972, **43**, C35; C. R. Eady, B. F. G. Johnson, J. Lewis, M. C. Malatesta, P. Machin, and M. McPartlin, *J. Chem. Soc., Chem. Commun.*, 1976, 945; J. Knight and M. J. Mays, *J. Chem. Soc., Dalton Trans.* 1972, 1022; C. R. Eady, B. F. G. Johnson, and J. Lewis, *ibid.*, 1975, 2606; D. B. W. Yawney and B. J. Doedens, *Inorg. Chem.*, 1972, **11**, 838 and references cited therein.

[6] H. D. Kaesz, *Chem. Br.*, 1973, **9**, 344, and references cited therein.

[7] K. E. Inkrott and S. G. Shore, *Inorg. Chem.*, 1979, **18**, 2817; K. E. Inkrott and S. G. Shore, *J. Am. Chem. Soc.*, 1978, **100**, 3954.

[8] P. C. Steinhardt, W. L. Gladfelter, A. D. Harley, J. R. Fox, and G. L. Geoffroy, *Inorg. Chem.*, 1980, **19**, 332.