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Synthesis and solution structure of the carbonyl cluster dianion $[OsRh_4(CO)_9(\mu_2\text{-}CO)_6]^{2-}$

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Abstract

The dianion $[OsRh_4(CO)_{15}]^{2-}$ has been obtained by reduction of a mixture of $Rh_4(CO)_{12}$ and $Os_3(CO)_{12}$. Variable temperature ^{13}C NMR spectra in solution indicate that the mixed metal cluster is isostructural with $[FeRh_4(CO)_{15}]^{2-}$ and $[RuRh_4(CO)_{15}]^{2-}$, with the Os atom located in an apical position within the trigonal bipyramidal metal skeleton. The overall ideal symmetry is C_s, with nine carbonyls terminally bound (three each on the apical metals and one each on the equatorial metals) and six bridging (the three Rh_{eq}–Rh_{eq} edges and two Os–Rh_{eq} and one Rh_{ap}–Rh_{eq} edges).

Introduction

In the past few years our interest in the chemistry of pentanuclear carbonyl clusters having a trigonal bipyramidal metal skeleton led us to devise procedures for synthesizing them selectively. In particular the bimetallic species of the general formula $[MRh_4(CO)_x]^{y-}$ were made, where M = Fe [1,2], Ru [3] ($x = 15$, $y = 2$); Rh [4], Ir [5] ($x = 15$, $y = 1$); Ni [6], Pt [7] ($x = 12$, 14, $y = 2$) and $[MIr_4(CO)_x]^{y-}$, with M = Fe [8], Ru [9] ($x = 15$, $y = 2$); Pt [10] ($x = 12$, 14, $y = 2$). In extension of this work we decided to investigate the possible existence of a species such as $[OsRh_4(CO)_{15}]^{2-}$, and succeeded in making it and structurally characterizing it in solution. This completes the isostructural triad $[MRh_4(CO)_{15}]^{2-}$ (M = Fe, Ru, Os).

Results

The $[OsRh_4(CO)_{15}]^{2-}$ anion was synthesized by a modification of the procedure reported for $[RuM_4(CO)_{15}]^{2-}$ (M = Rh, Ir) [3,9]. In those cases we observed that the reduction of the neutral carbonyls $Ru_3(CO)_{12}$ and $M_4(CO)_{12}$, performed at room temperature in methanol containing NaOH under 1 atm of CO gave accepta-

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ble yields only in the presence of a considerable excess of Ru, up to five times the stoicheiometric; this was ascribed to the reluctance of the trimeric Ru species to break apart into mononuclear fragments which could take part in clusterization to give the mixed metal species. This effect was found to be even more marked with Os complexes, and even with an excess of $Os_3(CO)_{12}$ the reaction at room temperature was found to be very slow (requiring several weeks). The difficulties can be overcome by moderate heating, but it is important to keep the temperature below the boiling point of the mixture, say at 55–60 °C, so that there is enough CO present in solution; under these conditions the reduction is complete within 12–24 h. The most relevant advantage of this procedure is that it can be carried out with stoicheiometric amounts of both carbonyls, that is 1/3 mole of $Os_3(CO)_{12}$ per mole of $Rh_4(CO)_{12}$. At the beginning of the reaction the insoluble $Os_3(CO)_{12}$ is treated on its own with an excess of NaOH under CO; within one hour a yellow-orange solution is obtained giving IR bands at 2035m, 2000s, 1870–1860m. The stoicheiometric amount of $Rh_4(CO)_{12}$ is added at this time and the solution turns deep green, owing to reduction to $[Rh_7(CO)_{16}]^{3-}$ [11]. Upon heating, slow condensation to the mixed species $[OsRh_4(CO)_{15}]^{2-}$ is observed, and there is no evidence for intermediate products. The end of the reaction is indicated by the presence in the IR spectrum of essentially the bands of the product. Owing to the presence of even trace amounts of $[Rh_7(CO)_{16}]^{3-}$, the solution sometimes assumes a green tone which masks the yellow of the pure product. The anion $[OsRh_4(CO)_{15}]^{2-}$ is indefinitely stable in the reaction medium, and can be easily isolated by precipitation with a slight excess of a suitable bulky cation in yields up to 70–80%. An initial purification is usually made by extraction with THF, (which leaves behind some impurities, mainly of $[Rh_7(CO)_{16}]^{3-}$) and reprecipitation by addition of 2-propanol. Lemon to amber-yellow crystals of $[PPN_2][OsRh_4(CO)_{15}]$ (PPN denotes the bis(triphenylphosphine)iminium cation) may be obtained by the slow diffusion of 2-propanol into a THF or acetone solution under a CO atmosphere.

The compound is stable for long time under nitrogen or CO, but decomposes upon exposure to air, either in solution or as a finely powdered solid.

The IR spectrum of $[PPN]_2[OsRh_4(CO)_{15}]$ is shown in Fig. 1. The similarity of the pattern of bands to that of $[MRh_4(CO)_{15}]^{2-}$ (M = Fe, Ru) [1–3] and even $[RuIr_4(CO)_{15}]^{2-}$ [9] is very close, as expected for compounds of such similar structures.

^{13}C NMR spectra

The ^{13}C NMR variable temperature spectra (Table 1) of a sample of $(PPN)_2[OsRh_4(CO)_{15}]$ (ca. 25% ^{13}CO enriched) recorded at 50.3 MHz in THF-d_8 under a CO atmosphere are shown in Fig. 2. The results are consistent with an overall idealized symmetry C_s for the anion, as previously found in $[FeRh_4(CO)_{15}]^{2-}$ and $[RuRh_4(CO)_{15}]^{2-}$. As can be seen from Fig. 3, in which the atom labeling is the same as that previously used [3] in order to facilitate comparison of the data in Table 2, of the nine terminally bonded CO groups, there is one on each of the three equatorial Rh_A and Rh_B atoms, and three on each of the apical metals Os and Rh_C. Three of the six edge-bridging carbonyls are located, as is usual in these trigonal bipyramidal structures, on the central triangle edges, while other two bridge between the Os atom and the two equatorial atoms Rh_A, and the sixth connects the third equatorial Rh_B atom to the apical Rh_C.

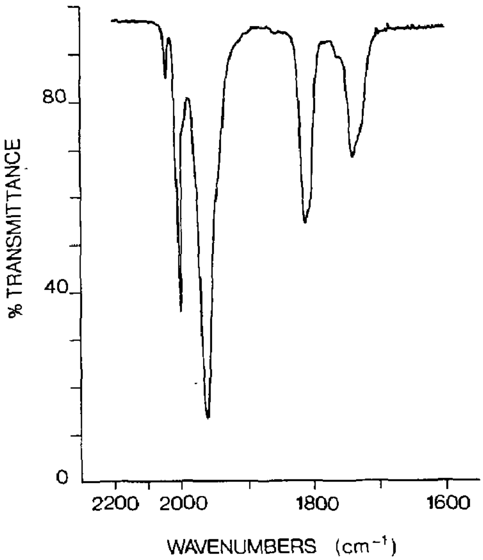

Fig. 1. IR spectrum of $[OsRh_4(CO)_{15}]^{2-}$ as $[PPN]^+$ salt in THF under 1 atm CO; bands (cm^{-1}) at 2042w, 2003s, 1962vs, 1813ms, 1739m (w = weak, s = strong, m = medium).

In the low temperature spectrum (−85 °C) (see Table 1) all the equivalent carbonyls produce a distinct, unequivocally assignable, resonance. The bridging CO region (230–270 ppm) shows four signals which can be easily assigned. One of the two signals of relative integration 2, at 236.7 ppm ($^1J(Rh_A–C_i)$ 30.9 Hz) is unambiguously due to C_i bridging Rh_A and the apical osmium, while the other at 257.5 ppm ($^1J(Rh_{A-B}–C_g)$ 27.7 Hz) is due to the two equivalent C_gO bridging in the equatorial plane Rh_A and Rh_B, with very similar if not coincident J values making it a triplet. The two resonances of intensity 1 are assigned to C_h bridging in the equatorial plane (triplet at 262.6 ppm, $^1J(Rh_A–C_h)$ 34.2 Hz), and C_j bridging the apical Rh_C to the equatorial Rh_B (doublet of doublets at 253.3 ppm, $^1J(Rh_{B,C}–C_j)$ 25.5 and 37.8 Hz). With reference to Table 2, the chemical shifts found for C_g, C_h and C_j agree well with those obtained for $[FeRh_4(CO)_{15}]^{2-}$ and $[RuRh_4(CO)_{15}]^{2-}$,

Table 1

Variable temperature ^{13}C NMR of $[OsRh_4(CO)_{15}]^{2-}$ as $[PPN]^+$ salt in THF-d_8 δ in ppm; ($^1J(Rh–C)$) and [$^2J(C–C)$] ± 2 Hz

	−85 °C	−50 °C	−10 °C	Room temperature
C_a	178.9	178.9	178.9	–
C_b	184.9	184.9 [25.6]	184.9	–
C_c	203.4 (96.8)	203.4 (98.3)	203.3 (98.5)	–
C_d	202.6 (94.5)	202.7 (94.4)		
C_e	198.2 (77.8)	collapsed	ca. 201.6 (ca. 76)	–
C_f	208.4 (56.0)			
C_g	275.5 (27.7)	257.0 (30.6) [20.1]	256.7	257.7 (32.4)
C_h	262.6 (34.2)	262.3 (36.2) [21.4]	ca. 262	
C_i	236.7 (30.9)	236.4 (32.2) [26.4]	ca. 236 (ca. 28)	–
C_j	253.3 (25.5, 37.8)	253.3 (25.5, 37.4)	ca. 253	–

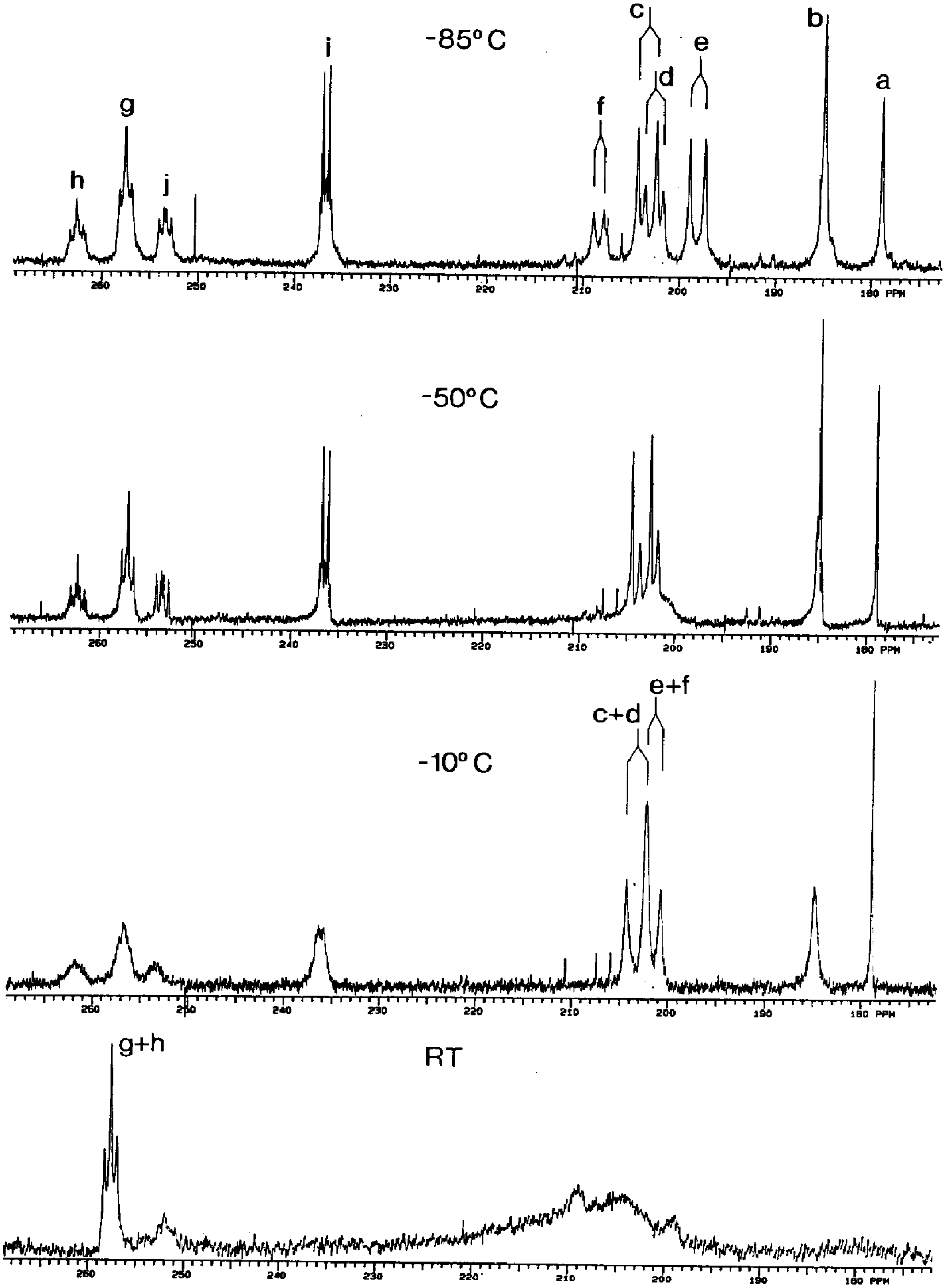

Fig. 2. Variable temperature ^{13}C NMR spectra of $[PPN]_2[OsRh_4(CO)_{15}]$ in THF-d_8 under CO (ca. 25% ^{13}CO).

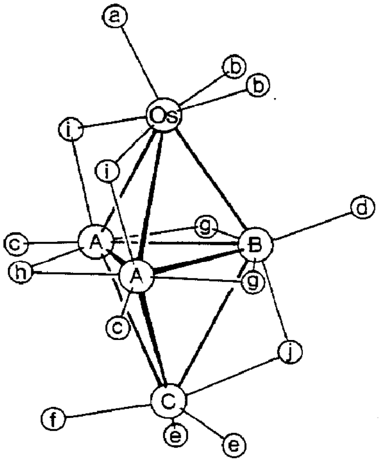

Fig. 3. Schematic representation of the structure of $[\mathrm{OsRh_4(CO)_{15}}]^{2-}$.

while C_i shows a significant shift to low frequencies. This is probably due to the proximity of the Os, and a similar effect can be seen for the two signals liying at the lowest frequencies in the terminal CO region, at 178.9 and 184.9 ppm, with integration ratio 1/2. Because of the absence of coupling to rhodium they are assigned to the three carbonyls bonded to apical Os, C_a, and C_b, respectively. The changes observed for the chemical shifts of these carbonyls on going from the iron to the ruthenium and to the osmium derivative are in good agreement with the average values of 212.9, 199.7, and 176.4 ppm found for $\mathrm{M_3(CO)_{12}}$ (M = Fe, Ru, Os) [12].

This region also shows four doublets that must all be assigned to the carbonyls terminally bonded to the rhodium atoms. These carbonyls which, owing to coincidence, gave only two resonances in $[\mathrm{FeRh_4(CO)_{15}}]^{2-}$, and could not be absolutely assigned in the case of $[\mathrm{RuRh_4(CO)_{15}}]^{2-}$ (Table 2), can be unambiguously assigned in the present case. The two doublets of intensity 2, at 198.2 ppm (*J* 77.8 Hz) and at 203.4 ppm (*J* 96.8 Hz) must be assigned to C_e and C_c, respectively, while the two

Table 2

Comparison of ^{13}C NMR chemical shifts in $[\mathrm{OsRh_4(CO)_{15}}]^{2-}$ at −85 °C, $[\mathrm{RuRh_4(CO)_{15}}]^{2-}$ at −103 °C and $[\mathrm{FeRh_4(CO)_{15}}]^{2-}$ at −86 °C, all as $[\mathrm{PPN}]^+$ salt in THF-d_8. δ in ppm; (^1J(Rh–C)) ± 2 Hz

	$[\mathrm{OsRh_4(CO)_{15}}]^{2-}$	$[\mathrm{RuRh_4(CO)_{15}}]^{2-}$	$[\mathrm{FeRh_4(CO)_{15}}]^{2-}$
C_a	178.9	199.7	216.3
C_b	184.9	208.6	217.3
C_c	203.4 (96.8)	[a] 202.8 (95.0)	200.5 (91.5)
C_e	198.2 (77.8)	[a] 199.8 (77.6)	
C_d	202.6 (94.5)	ca. 204 (ca. 92)	201.3 (91.6)
C_f	208.4 (56.0)	210.8 (60.2)	
C_g	257.5 (27.7)	260.5 (32.5)	259.4 (30.5)
C_h	262.6 (34.2)	264.9 (ca. 35)	263.5 (36.6)
C_i	236.7 (30.9)	252.0 (34.6)	253.5 (33.6)
C_j	253.3 (25.5, 37.8)	255.2 (25.6, ca. 39)	250.4 (25.9, 39.7)

[a] These two assignments were previously reversed [3].

small doublets at 202.6 ppm (J 94.5 Hz) and 208.4 ppm (J 56.0 Hz) are respectively due to C_d and C_f. When the temperature is raised, even at −50 °C the resonances at 198.2 and 208.4 ppm collapse into a broad resonance. This collapse confirms the assignments previously made, because since all the other resonances are unaffected, it must be due to a fluxional process involving only the terminally bound carbonyls C_f and C_e, in a rocking motion on the apical rhodium. At this temperature the two-bond C–C couplings further confirmed the assignments. These interactions can, as previously shown [10], be seen for those carbonyls which lie nearly in a *trans* disposition, as is the case for C_b and C_i (ca. 26 Hz) and for C_g and C_h (ca. 21 Hz). A similar interaction between C_f and C_j can also be seen, though not measured, in the complex resonances observed at −85 °C; at −50 °C when the coupling with C_f is lost the resonance of C_j becomes sharper.

At −10 °C a further fluxional process appears, and the three apical carbonyls are all equivalent and give a doublet at 201.6 ppm (^1J(Rh–C) ca. 76 Hz). Even C_c and C_d become equivalent, and give a single signal, the doublet at 203.3 ppm (^1J(Rh–C) 98.5 Hz). The chemical shifts coincide with the values deduced from weighted mean, 201.6 and 203.2, respectively. The Os-bonded terminal carbonyls still give two resonances, but whereas C_a is always sharp, C_b has considerably broadened. The same effect was previously found for $[FeRh_4(CO)_{15}]^{2-}$ [2], and can be accounted for in terms of the different roles played by C_a and C_b in the fluxional processes involved.

At room temperature the collapse of the terminal carbonyls is almost complete, while in bridging region a triplet (^1J(Rh–C) 32.4 Hz) is visible at 257.7 ppm, rising sharply alongside the still visible C_j resonance. This is due, as previously suggested for the Fe–Rh and Ru–Rh analogoues, to both equatorial C_g and C_h becoming equivalent through migration of the other twelve carbonyls.

Substantially the same results were obtained with a series of spectra at 20.1 MHz.

It is noteworthy that in the light of these results the low temperature spectrum previously reported for $[RuRh_4(CO)_{15}]^{2-}$ [3], in which the two pairs of signals relative to C_c, C_e and C_d, C_f were not unambiguously assigned, can now be correctly assigned, as shown in Table 2. In view of the similarities in the values of both the chemical shift and the coupling constants, interchange of the labels C_c and C_e cannot be ruled out.

Experimental

All operations were carried out under N_2 or CO as specified, in carefully purified solvents. $Rh_4(CO)_{12}$ was prepared by the published method [13], and $Os_3(CO)_{12}$ was obtained commercially. Infrared spectra were recorded on a Perkin–Elmer 781 spectrophotometer using 0.1 mm CaF_2 cells previously purged with CO. The ^{13}CO enriched sample was obtained by direct exchange at room temperature with 90% ^{13}CO, by use of the standard vacuum-line technique. Variable temperature ^{13}C NMR spectra were recorded at 50.3 and 20.1 MHz on Varian and Bruker instruments, respectively.

Synthesis of $[PPN]_2[OsRh_4(CO)_{15}]$

$Os_3(CO)_{12}$ (150.3 mg, 0.166 mmol) was placed in a Schlenk tube, which was then evacuated and filled with CO. A 1.7 *M* solution of NaOH methanol (15 ml, 25.5

mmol) was added and the mixture stirred. After ca. 1 h, when all the osmium carbonyl was dissolved and an orange solution had been formed, $Rh_4(CO)_{12}$ (374.8 mg, 0.501 mmol) was added and the resulting green solution was kept at 55–60 °C, always with stirring and with a slight positive CO pressure maintained by means of a mercury valve. After about 12 h at this temperature, a green-yellow solution was obtained, along with a white precipitate, mainly Na_2CO_3. The IR spectrum showed the characteristic bands of the sodium salt at 2055w, 2017s, 1977vs, 1820m, 1785mw cm^{-1}. The mixture was treated dropwise with a solution of (PPN)Cl (0.86 g, 1.5 mmoles in 7.5 ml MeOH) to give a precipitate of yellow flakes. This precipitate was filtered off under CO, washed with 2-propanol (10 ml), then water (5×10 ml), then 2-propanol (2×5 ml) again, and vacuum dried. Extraction with THF (10 ml) under CO gave a brown-yellow solution with a fairly satisfactory IR spectrum; slow diffusion under CO of 2-propanol (25 ml) cautiously layered on this solution gave crystalline, amber crystals. Yield 811 mg (78%).

If the THF extract contains significant amounts of by-products, further recrystallization from acetone/2-propanol is advisable. This generally yields larger crystals.

Analysis Found: C, 49.47; H, 2.78; N, 1.63. $C_{87}H_{60}N_2O_{15}OsP_4Rh_4$ calcd.: C, 49.78; H, 2.88; N, 1.34%.

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