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Synthesis of some Heterobinuclear Compounds Containing Os–Re Bonds and the Crystal Structure of the Heterobimetallic Anionic Complex $[HOsRe(CO)_8Br]PPN$

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Abstract

The reaction of $[HOs(CO)_4]PPN$ with $[Re(CO)_5Br]$ gives the new heterobimetallic complex anion $[HOsRe(CO)_8Br]PPN$ in high yield and the neutral complex $[HOsRe(CO)_9]$ as a minor product (PPN is the bis(triphenylphosphine)iminium cation). The molecular structure of $[HOsRe(CO)_8Br]PPN$ has been determined by X-ray crystallography. The crystals are triclinic, space group $P\bar{1}$ with $a = 11.762(2)$, $b = 14.206(2)$, $c = 14.333(2)$ Å, $\alpha = 117.75(1)$, $\beta = 92.68(1)$, $\gamma = 95.55(1)°$ and $Z = 2$. The structure was solved by conventional heavy atom methods and least-squares refinement gave R of 0.043 ($R_w = 0.039$, $w = (\sigma^2 F)^{-1}$) for 3072 observed reflections. The structure of the anion $[HOsRe(CO)_8Br]^-$ shows an $HOs(CO)_4$ group bonded to an $Re(CO)_4Br$ group by a single Os–Re bond of length 2.995(1) Å. The hydride and bromide ligands are in equatorial positions on osmium and rhenium respectively. The two parts of the molecule are staggered and there are no bridging ligands. Some reactions of $[HOsRe(CO)_9]$ and $[HOsRe(CO)_8Br]PPN$ are also described. The reaction of $[Os(CO)_4]^{2-}$ with $Re(CO)_5Br$ gave $[OsRe(CO)_9]^-$ as the major product and $[Re_2Os(CO)_{14}]$ as a minor product.

Introduction

There is currently much interest in heterobimetallic complexes [1–3]. This is in part due to the discovery that such complexes may be efficient catalysts or catalyst precursors for a variety of reactions and that the heterobimetallic system is a better catalyst than its constituents individually [4, 5]. It is also of interest to investigate reaction pathways for heterobimetallic complexes since they cannot necessarily be predicted from a knowledge of their monometallic fragments [6].

We were interested in trying to find a rational route to the synthesis of compounds containing Os–Re and Os–Mn bonds and now report our results.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 180 grating spectrophotometer. Mass spectra were recorded using a VG Micromass 16F spectrometer operating at an ionizing voltage of 70 eV; samples were introduced into the instrument using a direct probe. NMR spectra were obtained using a Bruker WH 90 spectrometer and chemical shifts are relative to tetramethylsilane (δ 0.00 ppm). Melting points were determined on a hot-stage microscope (Reichert Thermovar) and are uncorrected. Reactions were routinely carried out in a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled from the following drying agents under nitrogen before use: hexane from sodium wire, tetrahydrofuran (THF) from $LiAlH_4$, acetonitrile from P_2O_5 and methanol was purified by a standard procedure [7]. Microanalyses were performed by F. and E. Pascher, Bonn, F.R.G. The following compounds were prepared by literature procedures: $Na_2[Os(CO)_4]$ [8], $[HOs(CO)_4]PPN$ [9], $[Re(CO)_5Br]$ [10], $[Re(CO)_5I]$ [11] and $[Mn(CO)_5Br]$ [12].

Reaction of $Na_2[Os(CO)_4]$ with $[Re(CO)_5Br]$

A suspension of $Na_2[Os(CO)_4]$ (0.35 g, 0.99 mmol) in THF (20 ml) was stirred with $[Re(CO)_5Br]$ (0.40 g, 0.99 mmol) at room temperature for 20 h. The solvent was removed under reduced pressure and the resulting yellow residue, which we believe to be mainly $Na[OsRe(CO)_9]$, was washed with hexane to remove traces of $[Re_2(CO)_{10}]$ and $[HOsRe(CO)_9]$. This residue was dissolved in methanol (5 ml) and a solution of PPNCl (0.57 g, 0.99 mmol) in methanol (4 ml) was added. Concentrating this solution and addition of water gave yellow–orange $[HOsRe(CO)_8Br]PPN$ (0.07 g, 6%) (see later) which was filtered off; further addition of water gave a yellow solid, $[OsRe(CO)_9]PPN$ (0.35 g, 31%) melting point (m.p.)

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110–120 °C. *Anal.* Found: C, 46.2; H, 3.3; N, 1.5%. Calc. for $C_{45}H_{30}NO_9OsP_2Re$: C, 46.3, H, 2.6, N, 1.2%. IR (THF): ν(CO) 2089(sh), 2077(w), 2040(w), 2004(sh), 1995(s), 1970(w), 1909(sh), 1877(vs) cm^{-1}; ^1H NMR (CD_3CN): δ2.54 (C_6H_5).

In a separate experiment, the yellow Na[OsRe(CO)$_9$] was stirred with acetic acid (2 ml) in THF (5 ml) for 2 h. The solvent was removed under reduced pressure and the residue extracted with hexane to yield a pale yellow solution of [HOsRe(CO)$_9$] which was identified (see later) by its IR and ^1H NMR spectra [13, 14].

When the reaction of $Na_2[Os(CO)_4]$ with [Re(CO)$_5$Br] was carried out in a 1:2 molar ratio, then in addition to the other products, a low yield of yellow microcrystalline [$Re_2Os(CO)_{14}$] m.p. 192–202 °C (decomp.) was obtained from the hexane extracts. These microcrystals were identified by IR (cyclohexane): ν(CO) 2092(m), 2019(vs), 1981(s) cm^{-1}, in agreement with literature values [15], and by a parent ion in the mass spectrum at *m/e* 958 with the correct isotope pattern.

Reaction of [HOs(CO)$_4$]PPN with [Re(CO)$_5$Br]

A solution of [Re(CO)$_5$Br] (0.21 g, 0.52 mmol) in THF (5 ml) was added dropwise over 5 min to a solution of [HOs(CO)$_4$]PPN (0.44 g, 0.52 mmol) in THF (20 ml) and the resulting solution stirred for 23 h. The solvent was removed under reduced pressure to give an oily orange residue which was extracted with hexane (5 × 20 ml). The solvent was removed under reduced pressure from the filtered hexane extracts to give [HOsRe(CO)$_9$] as a colourless oil (the compound could be further purified by sublimination) (0.06 g, 18%). IR (hexane): ν(CO) 2091(vw), 2081(s), 2068(w), 2046(s), 2040(m), 2028(vs), 2005(s), 1997(w), 1984(s) cm^{-1}; ^1H NMR (C_6D_6): δ −10.37; the mass spectrum showed a molecular ion at *m/e* 629 with the correct isotope pattern and peaks corresponding to sequential loss of 9 CO groups were observed. The hexane insoluble solid was recrystallized from methanol/ether to give yellow crystals of [HOsRe(CO)$_8$Br]PPN (0.50 g, 79%) m.p. 115–125 °C. *Anal.* Found: C, 43.5; H, 2.7; N, 1.3; Br, 6.3; Os, 18.6; Re, 15.8. Calc. for $C_{44}H_{31}BrNO_8OsP_2Re$: C, 43.3; H, 2.6; N, 1.2; Br, 6.6; Os, 15.6; Re, 15.3%. IR (THF): ν(CO) 2091(w), 2043(s), 2019(m), 1991(vs), 1980(sh), 1956(m), 1946(m), 1895(m) cm^{-1}; far IR (Nujol); ν(Re–Br) 179(s) cm^{-1}; ^1H NMR (CD_3CN); δ −10.50 (Os–H) $^1J(^{187}Os-^1H)$ 40.5 Hz; δ 7.46 (C_6H_5). The IR spectrum of the hexane soluble portion showed it to contain [IOsRe(CO)$_9$], [$Re_2(CO)_{10}$] and [Re(CO)$_5$I].

Reactions of [HOsRe(CO)$_9$]

With CH_3I

A solution of [HOsRe(CO)$_9$] (0.02 g, 0.03 mmol) in THF (5 ml) was treated with CH_3I (0.002 ml, 0.03 mmol) and the solution stirred for 18 h. The solvent was removed under reduced pressure and the residue recrystallized from CH_2Cl_2/petroleum ether (boiling point 30–40 °C) to give [IOsRe(CO)$_9$] (0.02 g, 88%) as a pale yellow solid m.p. 105–110 °C which was identified on the basis of its mass spectrum (which showed a parent ion at *m/e* 758 with the correct isotope pattern and the loss of 9 CO groups) and its IR spectrum (hexane): ν(CO) 2092(m), 2055(m), 2052(sh), 2041(s), 2024(vs), 2015(sh), 2005(m), 1988(s) cm^{-1}.

With CBr_4

Similarly, the reaction of [HOsRe(CO)$_9$] with CBr_4 in hexane gave [BrOsRe(CO)$_9$] (71%) as a white solid m.p. 105–110 °C with a parent ion in the mass spectrum at *m/e* 708; IR (hexane): ν(CO) 2094(m), 2055(m), 2042(s), 2032(sh), 2023(vs), 2015(sh), 2004(m), 1986(s) cm^{-1}.

With CCl_4

Similarly, the reaction of [HOsRe(CO)$_9$] with an excess of CCl_4 gave [ClOsRe(CO)$_9$] (75%) as white needles m.p. 100–105 °C with a parent ion in its mass spectrum at *m/e* 694; IR (hexane): ν(CO) 2095(w), 2081(vw), 2068(vwsh), 2056(m), 2044(s), 2023(vs), 2015(sh), 2004(m), 1986(s) cm^{-1}.

With I_2

A solution of [HOsRe(CO)$_9$] (0.01 g, 0.02 mmol) in hexane (5 ml) was treated with iodine (0.05 g, 0.20 mmol) and the mixture allowed to stand at room temperature for 30 min. The volatiles were removed to yield a yellow solid (0.01 g) which was shown to be a mixture of *cis*-[$Os(CO)_4I_2$] and [Re(CO)$_5$I] on the basis of its IR spectrum in hexane.

Reactions of [HOsRe(CO)$_8$Br]PPN

With CF_3COOH

A solution of [HOsRe(CO)$_8$Br]PPN (0.03 g, 0.03 mmol) in CH_3CN (3 ml) was treated with CF_3COOH (0.2 ml) and the solution allowed to stand for 2 h, after which time the reaction was judged to be complete by IR monitoring. The volatiles were removed under reduced pressure and shown to contain [$H_2Os(CO)_4$] by IR and ^1H NMR spectroscopy; the white solid that remained was shown to be [$Re(CO)_4Br$]$_2$ on the basis of its IR spectrum.

With PPh_3

A solution of [HOsRe(CO)$_8$Br]PPN (0.05 g, 0.04 mmol) in THF (5 ml) was treated with PPh_3 (0.01 g, 0.04 mmol) and the solution heated at 60 °C for 3 days, after which time reaction was judged to be complete by disappearance of ν(CO) bands of the starting material. The solvent was removed under reduced pressure and the residue triturated with hexane to give a pale yellow solid (0.06 g, 91%) of [$HOs(CO)_3(PPh_3)Re(CO)_4Br$]PPN m.p. 65–75 °C. *Anal.* Found: C, 49.9; H, 3.8; N, 0.9. Calc. for $C_{61}H_{46}BrNO_7OsP_3Re$: C, 50.4; H, 3.2; N, 1.0%. IR (THF): ν(CO) 2078(vw), 2043(m), 2018(sh), 2005(s), 1992(vs), 1955(m), 1946(m), 1887(ms) cm^{-1}; ^1H NMR (CD_3OD): δ −8.12 (Os–H) $^2J(^{31}P-^1H)$ 14 Hz, δ 7.46 (C_6H_5).

Crystal and Intensity Data

Yellow crystals of [$HOsRe(CO)_8Br$]PPN suitable for X-ray structural studies were obtained by recrystallization of the compound from methanol/water. Accurate cell parameters were determined by a least-squares analysis of the setting angles of 24 reflections ($14° \leqslant \theta \leqslant 15°$) which were automatically located and centred on an Enraf-Nonius CAD4 diffractometer. The intensities of 3 reference reflections were checked every hour to monitor crystal decay and centering checked every 100 measured reflections. The data were Lp processed and an empirical absorption correction applied [16]. Crystal data and details of the final refinement are listed in Table 1.

Solution and Refinement of the Structure

The atomic coordinates of the osmium and rhenium atoms were obtained from a three-dimensional Patterson map by comparison with the Patterson grid constructed, using the symmetry elements of the centrosymmetric space group, $P\bar{1}$, corresponding to two general positions. Four subsequent difference Fourier syntheses yielded the positions of the bromine, carbon and oxygen atoms of the anion, as well as the two phosphorus, nitrogen and carbon atoms of the PPN cation. The hydride ligand was located at a distance of 1.66 Å from the osmium atom. This hydrogen was inserted and subsequently constrained to ride at a distance of 1.66(1) Å from the osmium atom. The hydrogen atoms on the phenyl rings were placed in calculated positions. Eight least-squares refinements in which the osmium, rhenium, bromine, two phosphorus, nitrogen and eight oxygen atoms were treated anisotropically and the hydrogens and all carbon atoms were treated isotropically, yielded a conventional R factor of 0.043. A weighing scheme $(\sigma^2 F)^{-1}$, gave $R_w = 0.039$. The analyses of variance, computed after the final least-squares refinement, were satisfactory. A final difference Fourier synthesis revealed maximum residual electron density <1 e $Å^{-3}$, near the osmium and rhenium atoms resulting from inadequate modelling of their thermal anisotropy. Table 2 lists the final fractional atomic coordinates and thermal parameters with estimated deviations in parentheses. Scattering factors were taken from Cromer and Mann [18] with dispersion corrections from Cromer and Liberman [19]. All computations were carried out at the Computer Centre of the University of Cape Town on a Sperry 1100/81 computer with SHELX76 [20] (data reduction, structure solution and refinement) and PLUTO [21] (illustrations).

TABLE 1. Crystal data, data collection and refinement parameters for [$HOsRe(CO)_8Br$]PPN

Crystal data	
Molecular formula	$C_{44}BrH_{31}NO_8OsP_2Re$
Molecular weight (g mol^{-1})	1219.99
Space group	$P\bar{1}$
a (Å)	11.762(2)
b (Å)	14.206(2)
c (Å)	14.333(2)
α (°)	117.75(1)
β (°)	92.68(1)
γ (°)	95.55(1)
V ($Å^3$)	2097.9
Z	2
D_c (Mg m^{-3})	1.93
μ(Mo Kα) (mm^{-1})	6.7
F(000)	1164
Data collection	
Crystal dimensions (mm)	0.06 × 0.13 × 0.13
Scan mode	$\omega-2\theta$
Scan width, ω (°)	(0.79 + 0.35 tan θ)
Aperture width (mm)	(1.16 + 1.05 tan θ)
Aperture length (mm)	4
Crystal decay (%)	1.32
Range scanned, θ (°)	1–23
Radiation used, Mo Kα, λ (Å)	0.7107
Refinement	
No. reflections collected	4574
No. reflections observed	3072 (with $I_{rel} > 2\sigma I_{rel}$)
No. of parameters	309
$R = \Sigma \lVert F_o\rvert - \lvert F_c\rVert / \Sigma \lvert F_o \rvert$	0.043
$R_w = \Sigma w^{1/2} \lVert F_o\rvert - \lvert F_c\rVert / \Sigma w^{1/2} \lvert F_o\rvert$	0.039
Weighting scheme, w	$(\sigma^2 F)^{-1}$

Results and Discussion

Reaction of $Na_2[Os(CO)_4]$ with $[Re(CO)_5Br]$

Our initial investigations of this reaction were carried out in an attempt to prepare the trinuclear heterobimetallic complex [$Re_2Os(CO)_{14}$] [15] in high yield by an apparently logical route

$$Na_2[Os(CO)_4] + 2[Re(CO)_5Br] \longrightarrow [Re_2Os(CO)_{14}] + 2NaBr \qquad (1)$$

Although some [$Re_2Os(CO)_{14}$] was isolated from this reaction, the yield was very low and did not represent a significant improvement on the previously reported synthesis from the reaction of [$Re_2(CO)_{10}$] and [$Os_3(CO)_{12}$] [15].

TABLE 2. Fractional atomic coordinates (×10^4) and temperature factors (Å^2 × 10^3) with e.s.d.s in parentheses

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
Os	3710(1)	2888(1)	3397(1)	*
Re	5040(1)	2108(1)	1504(1)	*
Br	6914(2)	3304(2)	2745(2)	*
P1	8752(4)	2665(3)	−2534(3)	*
P2	10787(3)	1699(3)	−2075(3)	*
N	9923(11)	2257(10)	−2420(9)	*
O1	2253(12)	3758(11)	5233(11)	*
O2	2312(11)	642(10)	2170(10)	*
O3	4818(12)	5072(11)	3743(10)	*
O4	5669(10)	2335(10)	4494(11)	*
O5	2873(11)	739(10)	104(9)	*
O6	6387(14)	1276(12)	−464(12)	*
O7	4400(12)	4015(12)	1261(11)	*
O8	5726(11)	340(11)	2019(10)	*
H1	2636(57)	2789(77)	2549(58)	16(30)
C1	2795(18)	3370(16)	4498(17)	69(6)
C2	2868(16)	1432(15)	2619(14)	55(5)
C3	4428(16)	4201(16)	3612(14)	59(5)
C4	4965(16)	2551(14)	4097(14)	55(5)
C5	3719(17)	1273(15)	642(15)	61(6)
C6	5908(17)	1604(16)	282(17)	62(6)
C7	4624(17)	3336(17)	1338(15)	62(6)
C8	5454(15)	973(14)	1813(13)	46(5)
C111	8162(12)	3381(12)	−1313(11)	32(4)
C112	8354(16)	3119(15)	−502(15)	68(6)
H112	8810(16)	2527(15)	−598(15)	92(11)
C113	7893(16)	3722(15)	473(16)	70(6)
H113	8095(16)	3598(15)	1089(16)	92(11)
C114	7190(15)	4439(14)	583(14)	57(5)
H114	6818(15)	4803(14)	1252(14)	92(11)
C115	6965(16)	4686(15)	−200(15)	68(6)
H115	6460(16)	5244(15)	−108(15)	92(11)
C116	7449(15)	4164(14)	−1138(15)	60(6)
H116	7275(15)	4348(14)	−1719(15)	92(11)
C121	7679(13)	1579(11)	−3367(11)	34(4)
C122	7720(13)	1068(12)	−4463(12)	39(4)
H122	8283(13)	1378(12)	−4781(12)	92(11)
C123	6994(14)	141(13)	−5118(14)	52(5)
H123	7049(14)	−228(13)	−5899(14)	92(11)
C124	6202(15)	−293(14)	−4691(14)	57(5)
H124	5641(15)	−940(14)	−5164(14)	92(11)
C125	6175(15)	201(14)	−3597(14)	57(5)
H125	5643(15)	−133(14)	−3278(14)	92(11)
C126	6894(14)	1120(13)	−2957(13)	49(5)
H126	6834(14)	1475(13)	−2176(13)	92(11)
C131	8940(13)	3541(12)	−3109(11)	33(4)
C132	9971(14)	4191(13)	−2887(13)	49(5)
H132	10613(14)	4145(13)	−2433(13)	92(11)
C133	10146(16)	4922(15)	−3300(14)	60(5)
H133	10895(16)	5390(15)	−3145(14)	92(11)
C134	9264(14)	4969(14)	−3916(13)	53(5)
H134	9372(14)	5488(14)	−4203(13)	92(11)
C135	8213(15)	4316(14)	−4162(14)	58(5)
H135	7583(15)	4371(14)	−4621(14)	92(11)
C136	8053(14)	3593(13)	−3762(12)	47(5)
H136	7306(14)	3116(13)	−3941(12)	92(11)
C211	10707(12)	1912(12)	−745(11)	34(4)
C212	11252(14)	2879(13)	86(13)	45(5)
H212	11728(14)	3408(13)	−61(13)	92(11)
C213	11087(15)	3093(15)	1118(14)	58(5)
H213	11471(15)	3781(15)	1723(14)	92(11)
C214	10405(15)	2385(14)	1301(15)	61(5)
H214	10333(15)	2551(14)	2053(15)	92(11)
C215	9848(16)	1446(15)	492(15)	68(6)
H215	9324(16)	956(15)	655(15)	92(11)
C216	10022(14)	1193(14)	−556(13)	50(5)
H216	9640(14)	499(14)	−1155(13)	92(11)
C221	10569(13)	270(12)	−2868(11)	34(4)
C222	11273(14)	−346(13)	−2644(12)	43(4)
H222	11914(14)	−1(13)	−2058(12)	92(11)
C223	11071(15)	−1452(14)	−3242(14)	59(5)
H223	11574(15)	−1898(14)	−3082(14)	92(11)
C224	10228(15)	−1931(15)	−4039(14)	55(5)
H224	10091(15)	−2732(15)	−4450(14)	92(11)
C225	9547(16)	−1332(14)	−4288(14)	59(5)
H225	8913(16)	−1688(14)	−4880(14)	92(11)
C226	9748(14)	−209(13)	−3688(12)	47(5)
H226	9271(14)	231(13)	−3883(12)	92(11)
C231	12213(12)	2163(11)	−2162(11)	32(4)
C232	12393(14)	2654(12)	−2822(12)	40(4)
H232	11719(14)	2749(12)	−3208(12)	92(11)
C233	13494(15)	2988(14)	−2943(14)	58(5)
H233	13616(15)	3315(14)	−3422(14)	92(11)
C234	14424(17)	2891(14)	−2372(14)	68(6)
H234	15219(17)	3168(14)	−2428(14)	92(11)
C235	14257(16)	2380(14)	−1767(14)	60(5)
H235	14932(16)	2271(14)	−1395(14)	92(11)
C236	13189(15)	2063(13)	−1650(13)	51(5)
H236	13091(15)	1718(13)	−1185(13)	92(11)

Anisotropic temperature factors (Å^2 × 10^3) (starred items)

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os	42(1)	45(1)	39(1)	17(1)	1(1)	6(1)
Re	47(1)	44(1)	37(1)	19(1)	4(1)	6(1)
Br	64(2)	88(2)	70(2)	39(1)	1(1)	−3(1)
P1	34(3)	33(3)	37(3)	18(2)	4(2)	6(2)
P2	30(3)	38(3)	35(3)	18(2)	5(2)	8(2)
N	36(8)	57(9)	33(8)	25(7)	9(6)	11(7)
O1	79(10)	72(10)	75(10)	26(9)	20(9)	27(8)
O2	73(10)	69(9)	58(9)	22(7)	5(7)	−25(8)
O3	91(11)	58(9)	68(10)	11(8)	11(8)	−5(8)
O4	49(8)	84(10)	104(11)	54(9)	−24(8)	−10(7)
O5	71(10)	71(9)	55(9)	25(8)	−3(8)	8(8)
O6	107(13)	107(13)	77(11)	34(11)	42(10)	19(11)
O7	104(12)	90(11)	88(11)	60(10)	18(9)	27(10)
O8	73(10)	73(10)	76(10)	41(8)	16(8)	29(8)

The main product of the reaction of $Na_2[Os(CO)_4]$ with $[Re(CO)_5Br]$ was a yellow, hexane insoluble solid which we believe to be $Na[OsRe(CO)_9]$

$$\mathrm{Na_2[Os(CO)_4] + [Re(CO)_5Br] \longrightarrow Na[OsRe(CO)_9] + NaBr} \qquad (2)$$

and which we isolated as the bis(triphenylphosphine)-iminium (PPN) salt (see 'Experimental')

$$\mathrm{Na[OsRe(CO)_9] + PPNCl \longrightarrow [OsRe(CO)_9]PPN + NaCl} \qquad (3)$$

The compound $[OsRe(CO)_9]PPN$ was characterized by elemental analysis and its IR spectrum was consistent with this formulation. In particular, a very strong, low frequency ν(CO) band is observed for $[OsRe(CO)_9]PPN$ at 1877 cm^{-1} (see 'Experimental') which compares well with bands at 1878 cm^{-1} for $[Os_2(CO)_8]^{2-}$ [22], 1882 cm^{-1} for $[HOs_2(CO)_8]^-$ [22] and 1870 cm^{-1} for $[FeMn(CO)_9]^-$ [23]. The compound $Na[OsRe(CO)_9]$ was further characterized by reaction with acetic acid which resulted in the formation of $[HOsRe(CO)_9]$ (eqn. (4)) which was characterized by ^1H NMR, mass spectrometry, IR and some reactions (see later).

$$\mathrm{[HOsRe(CO)_9] + CH_3COOH \longrightarrow [HOsRe(CO)_9] + CH_3COONa} \qquad (4)$$

$Na[OsRe(CO)_9]$, which we believe is formed as the first product in the reaction of $Na_2[Os(CO)_4]$ with $[Re(CO)_5Br]$, is presumably too weak a nucleophile to react with a second molar equivalent of $[Re(CO)_5Br]$ to give the trimer $[Re_2Os(CO)_{14}]$ and hence the low yield of the trimer. Other products isolated in low yields in the reactions of $Na_2[Os(CO)_4]$ with $[Re(CO)_5Br]$ were $[Re_2(CO)_{10}]$, $[HOsRe(CO)_9]$ and $[HOsRe(CO)_8Br]^-$. The latter two products could be formed from some $[HOs(CO)_4]^-$ impurity in $[Os(CO)_4]^{2-}$ (see below).

Reaction of [HOs(CO)$_4$]PPN with [Re(CO)$_5$Br]

The reaction of $[HOs(CO)_4]PPN$ with $[Re(CO)_5Br]$ (1:1 molar ratio) in THF resulted in the formation of two main products. The minor product was the hexane soluble heterobimetallic hydride $[HOsRe(CO)_9]$ which was isolated as a colourless oil (18%)

$$\mathrm{[HOs(CO)_4]PPN + [Re(CO)_5Br] \longrightarrow [HOsRe(CO)_9] + PPNBr} \qquad (5)$$

This compound has previously been reported [13, 14] but not completely characterized and not previously obtained pure (see later). The major product of the reaction (obtained in 80% yield) was the heterobimetallic anion $[HOsRe(CO)_8Br]PPN$ formed by the nucleophile $[HOs(CO)_4]^-$ substituting a CO ligand in $[Re(CO)_5Br]$

$$\mathrm{[HOs(CO)_4]PPN + [Re(CO)_5Br] \longrightarrow [HOsRe(CO)_8Br]PPN + CO} \qquad (6)$$

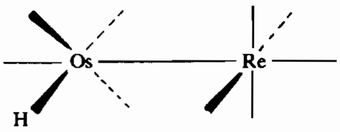
This new heterobimetallic anion was characterized by IR, far IR, ^1H NMR, elemental analysis (see 'Experimental') and X-ray crystal structure determination and some reactions (see later).

In a similar way, the reaction of $[HOs(CO)_4]PPN$ with $[Re(CO)_5I]$ was investigated. It was thought that with I^- as a better leaving group that maybe a higher yield of $[HOsRe(CO)_9]$ might be obtained. This was found not to be the case and the major product, obtained in 81% yield, was the heterobimetallic anion $[HOsRe(CO)_8I]PPN$, which was characterized in a similar way to the bromo-analogue and described in 'Experimental'. The heterobimetallic carbonyl iodide, $[IOsRe(CO)_9]$ was observed as a minor product and presumably formed by iodination of $[HOsRe(CO)_9]$.

$$\mathrm{[HOs(CO)_4]PPN + [Re(CO)_5I] \longrightarrow [HOsRe(CO)_8I]PPN + CO} \qquad (7)$$

Reactions and Characterization of [HOsRe(CO)$_9$]

Although the heterobimetallic carbonyl hydride $[HOsRe(CO)_9]$ has been reported before [13, 14] it has only been obtained impure and only briefly mentioned. We have now isolated pure $[HOsRe(CO)_9]$, albeit in fairly low yields, as the minor product from the reaction of $[HOs(CO)_4]PPN$ with $[Re(CO)_5Br]$ (eqn. (5)). The compound was obtained as a colourless oil and characterized by IR, ^1H NMR and mass spectrometry (see 'Experimental'). The ^1H NMR shows a singlet at δ −10.37, which corresponds well with δ −10.11 for $[H_2Os_2(CO)_8]$ [24] and with that previously reported for impure samples of $[HOsRe(CO)_9]$ [13, 14]. We also observe peaks which we assign as satellites corresponding to $^1J(^{187}Os-^1H)$ of 37.5 Hz (cf. 38 Hz for $[H_2Os_2(CO)_8]$ [25] which is consistent with the hydride ligand bound to Os. This combined with the observation of 9 bands in the ν(CO) region of the IR spectrum suggests a structure with an $Re(CO)_5$ group bonded to an $HOs(CO)_4$ group with the hydride ligand in the equatorial position



Further support for this formulation came from the reaction of the compound with iodine which caused cleavage of the Os–Re bond and gave a mixture of *cis*-$[Os(CO)_4I_2]$ and $[Re(CO)_5I]$ which were identified by their IR spectra

$$\mathrm{[HOsRe(CO)_9] + 2I_2 \longrightarrow \textit{cis}\text{-}[Os(CO)_4I_2] + [Re(CO)_5I] + HI} \qquad (8)$$

The presence of the terminal Os–H bond is also supported by the nearly quantitative conversion to the corresponding carbonyl halides, under mild conditions, on reaction with CH_3I, CBr_4 or CCl_4.

$$[HOsRe(CO)_9] + CY_3X \longrightarrow [XOsRe(CO)_9] + CY_3H \qquad (9)$$

The compound $[ClOsRe(CO)_9]$ has been mentioned previously as the product of the above reaction [13] but only characterized by its mass spectrum. We now give further characterization data for this compound and for the bromo- and iodo-analogues. The three heterobimetallic carbonyl halides were all isolated as air stable pale-yellow to colourless solids and all show similar IR spectra with 8 or 9 bands in the ν(CO) region (see 'Experimental'). In their mass spectra, parent ions were observed at the correct mass, with the correct isotope patterns and all showed fragmentation of 9 CO groups. We believe that these heterobimetallic carbonyl halides have structures analogous to $[HOsRe(CO)_9]$ with the halide ligand on an equatorial site on osmium. Similarly, it is thought that there is no configuration change on reaction of $[H_2Os_2(CO)_8]$ with CX_4 to give $[X_2Os_2(CO)_8]$ and the structure of the compounds $[X_2Os_2(CO)_8]$ (X = Cl [26] or I [27] have been determined crystallographically and indeed show the X groups in the equatorial positions.

Properties, Reactions and Characterization of [HOsRe(CO)$_8$Br]PPN

The heterobimetallic carbonyl anion complex $[HOsRe(CO)_8Br]$PPN, was isolated as a yellow crystalline solid in nearly 80% yield. The ^1H NMR spectrum of this anionic complex shows a singlet at δ −10.50 with satellites due to $^1J(^{187}Os–^1H)$ of 40.5 Hz, thus proving that the hydride ligand is bound to osmium. A band in the far IR of the compound at 179 cm^{-1} could be assigned to ν(Re–Br). This data coupled with the IR spectrum in the ν(CO) region which shows 8 bands, suggests a structure with an $HOs(CO)_4$ group bonded to an $Re(CO)_4Br$ group. The formation of this compound can be rationalized by $[HOs(CO)_4]^-$ acting as a nucleophile and displacing CO from $[Re(CO)_5Br]$ to give a compound with a donor–acceptor metal–metal bond $[H(CO)_4OsRe(CO)_4Br]^-$. Other examples of this type of complex have recently been reported including $[HFeM(CO)_9]^-$ (M = Cr, Mo or W) [28], $[Os_4(CO)_n(PMe_3)]$ (n = 13–15) [29] and $[\eta^5\text{-}C_5H_5(CO)_2RhPt(C_6F_5)_2(CO)]$ [2]. The observation of this donor–acceptor metal–metal bond in heterobimetallic complexes with a variety of different metals and ligand systems suggests that this type of bonding may be quite common.

To further characterize the anion $[HOsRe(CO)_8Br]$PPN we attempted a number of reactions, however the anion appears to be a weak nucleophile. Toward CH_3I for example, it showed very little reaction after 20 h at room temperature. Protonation with CF_3COOH resulted in the cleavage of the Os–Re bond and cis-$[H_2Os(CO)_4]$ and $[Re(CO)_4Br]_2$ were the products detected by IR. Reaction with PPh_3 gave CO substitution only after 3 days at 60 °C and from ^1H NMR data the substitution appeared to take place at osmium.

Description of the Structure of [HOsRe(CO)$_8$Br]PPN

To establish the structure of $[HOsRe(CO)_8Br]$PPN, we carried out an X-ray diffraction study of the compound and the structure of the anion is shown in Fig. 1. This structure confirms that the osmium is

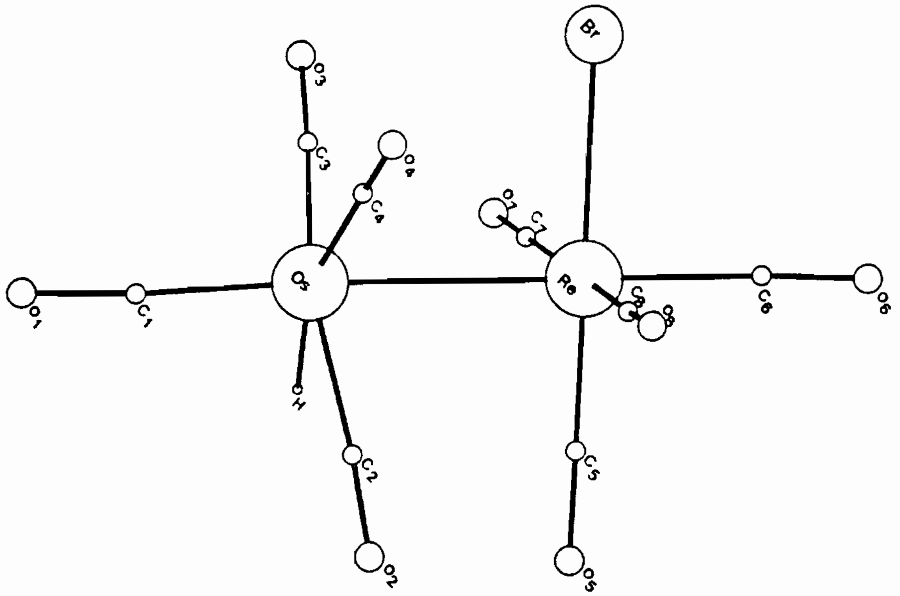


Fig. 1. The structure of the $[HOsRe(CO)_8Br]$ anion showing the atomic labelling.

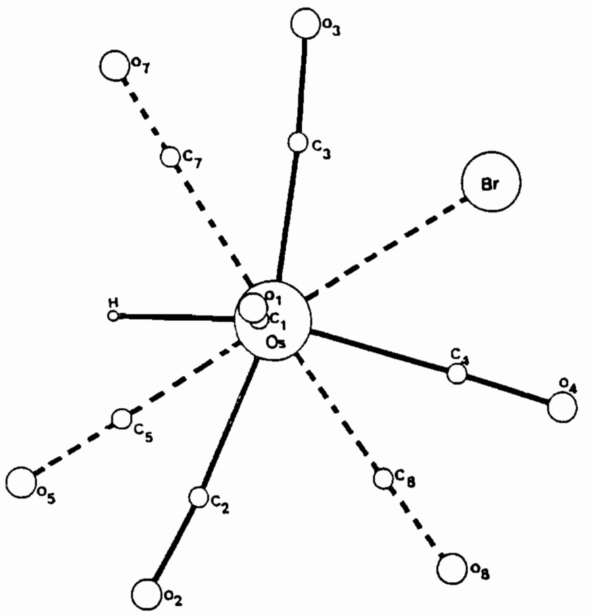


Fig. 2. A view of the [HOsRe(CO)$_8$Br] anion viewed along the Os–Re axis.

TABLE 3. Bond lengths (A) for the [HOsRe(CO)$_8$Br] anion with e.s.d.s in parentheses

Os–Re	2.995(1)
Re–Br	2.646(2)
Os–H1	1.66(8)
Os–C1	1.85(2)
Os–C2	1.96(2)
Os–C3	1.85(2)
Os–C4	1.96(2)
Re–C5	1.86(2)
Re–C6	1.94(2)
Re–C7	1.97(3)
Re–C8	1.96(2)
C1–O1	1.19(3)
C2–O2	1.12(2)
C3–O3	1.20(3)
C4–O4	1.13(3)
C5–O5	1.18(2)
C6–O6	1.15(3)
C7–O7	1.08(3)
C8–O8	1.14(3)

bonded directly to rhenium and that there are no bridging ligands. There are four carbonyl ligands bonded to both metal atoms and the hydride and bromide ligands occupy equatorial positions on osmium and rhenium respectively. The coordination geometry about both metal atoms is irregular octahedral with somewhat greater irregularity at osmium. Figure 2 is a view of [HOsRe(CO)$_8$Br]$^-$ along the Os–Re bond and shows that the equatorial ligands on Os are staggered with respect to the equatorial ligands on Re. This staggering is expected on steric grounds and is usually found in bimetallic compounds where there is no multiple metal–metal bonding, for example in [Os$_2$(CO)$_8$X$_2$] (X = Cl [26], X = I [27]), [Re$_2$(CO)$_{10}$] [30] and [Re$_2$(CO)$_9$I]$^-$ [31].

Selected bond lengths for [HOsRe(CO)$_8$Br]PPN are reported in Table 3 and bond angles in Table 4. The PPN cation shows expected bond lengths and angles. The osmium–rhenium bond distance in the [HOsRe(CO)$_8$Br] anion was found to be 2.995(1) Å. This is longer than the Os–Re distances found in the clusters [HOs$_3$Re(CO)$_{15}$] of 2.957(1) Å [32] and [HOs$_3$Re(CO)$_{15}$(NCCH$_3$)] of 2.959(1) Å [33] but similar to the metal–metal bond distances in the homometallic anions [Os$_2$(CO)$_8$]$^{2-}$ of 2.992(1) Å [34], [Re$_2$(CO)$_9$I]$^-$ of 3.052(4) Å [31] and [Re$_4$(CO)$_{16}$]$^{2-}$ of 2.989 Å [35].

The terminal Os–H distance of 1.66(8) Å in [HOsRe(CO)$_8$Br]$^-$ is shorter than the bridging Os–H 1.845(3) Å found from a neutron diffraction study on [Os$_3$(CO)$_{10}$(μ-H)$_2$] [36] but similar to Os–H of 1.659(3) Å found in [OsH$_4$(PMePh)$_3$] [17]. The Re–Br distance of 2.646(2) Å is similar to that found for [Re(CO)$_5$Br] of 2.62(1) Å [37].

The metal–carbon and carbon–oxygen distances in [HOsRe(CO)$_8$Br]$^-$ are in the ranges 1.85(2)–1.97(2) and 1.08(3)–1.20(2) Å respectively which may be expected from studies on related compounds. The equatorial carbonyl ligands lean towards the centre of the structure with the average M–M^1–C (equatorial) angle of 86.0(5)°; this behaviour is often observed in binuclear metal carbonyl complexes [26, 27, 30, 31]. We also observe that the Re–Os–C (equatorial) angles are more acute than the Os–Re–C (equatorial) angles.

Conclusions

Although the reaction of a carbonylate anion with a metal carbonyl halide is a rational and useful method for the preparation of some heterobimetallic compounds [38], the reactions do not always take the expected course. Thus we find that the main product of the reaction of [HOs(CO)$_4$]PPN with [Re(CO)$_5$Br] is the heterobimetallic anion [HOsRe(CO)$_8$Br]$^-$ and the expected neutral complex [HOsRe(CO)$_9$] was obtained only as a minor product. Also the reaction of [Os(CO)$_4$]$^{2-}$ with [Re(CO)$_5$Br] gave the anion [OsRe(CO)$_9$]$^-$ as the major product and [Re$_2$Os(CO)$_{14}$] as a minor product. Reactions of [HOs(CO)$_4$]$^-$ or [Os(CO)$_4$]$^{2-}$ with [Mn(CO)$_5$Br] were also investigated. These reactions were however found to be more complex and the products less stable than in the case of the reactions with [Re(CO)$_5$Br].

TABLE 4. Bond angles (°) for the [$HOsRe(CO)_8Br$] anion and the PPN cation with e.s.d.s in parentheses

[$HOsRe(CO)_8Br$] anion

H1–Os–Re	84.4(25)
C1–Os–Re	175.5(7)
C1–Os–H1	91.1(26)
C2–Os–Re	82.7(6)
C2–Os–H1	67.2(37)
C2–Os–C1	95.8(8)
C3–Os–Re	81.4(6)
C3–Os–H1	96.0(38)
C3–Os–C1	98.8(9)
C3–Os–C2	157.9(9)
C4–Os–Re	86.4(6)
C4–Os–H1	163.0(32)
C4–Os–C1	98.1(10)
C4–Os–C2	97.5(8)
C4–Os–C3	96.8(9)
Br–Re–Os	89.5(1)
C5–Re–Os	90.1(6)
C5–Re–Br	179.6(5)
C6–Re–Os	179.7(3)
C6–Re–Br	90.2(5)
C6–Re–C5	90.2(8)
C7–Re–Os	86.8(6)
C7–Re–Br	90.3(5)
C7–Re–C5	89.7(9)
C7–Re–C6	93.4(10)
C8–Re–Os	88.7(5)
C8–Re–Br	86.9(4)
C8–Re–C5	93.1(9)
C8–Re–C6	91.2(9)
C8–Re–C7	174.6(7)
O1–C1–Os	174.9(18)
O2–C2–Os	174.3(19)
O3–C3–Os	175.4(18)
O4–C4–Os	178.3(17)
O5–C5–Re	179.2(21)
O6–C6–Re	177.3(15)
O7–C7–Re	179.1(16)
O8–C8–Re	177.5(13)

PPN cation

P1–N–P2		158.3(12)
C111–P1–N		114.1(8)
C121–P1–N		111.4(7)
C121–P1–C111		106.0(7)
C131–P1–N		110.2(8)
C131–P1–C111		107.2(8)
C131–P1–C121		107.7(8)
C211–P2–N		113.7(7)
C221–P2–N		112.9(7)
C221–P2–C211		104.2(8)
C231–P2–N		110.4(9)
C231–P2–C211		107.5(7)
C231–P2–C221		107.7(7)
C_{ring}–C_{ring}–C_{ring}	in the range	116.5(15)–123.4(21)
C_{ring}–C_{ring}–P	in the range	118.1(4)–124.8(15)

Supplementary Material

Structure factors may be obtained from the authors on request.

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