# A General Route for the Synthesis of Tetranuclear Clusters containing Closed Triruthenium and Triosmium Triangles

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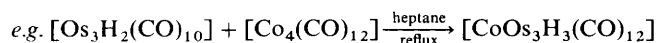*University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW*

The cluster compounds $[N(PPh_3)_2][M_3M'(CO)_{13}]$ (M = Ru or Os, M' = Co) and $[N(PPh_3)_2]$-$[M_3M'H(CO)_{13}]$ (M = Ru or Os; M' = Fe, Ru, or Os) have been prepared in good yield by the reaction of an appropriate tetracarbonylmetalate with the bis(acetonitrile) complexes, $[M_3(CO)_{10}$-$(NCMe)_2]$ (M = Ru or Os). The anionic clusters have been protonated, where possible, to give the corresponding neutral hydride clusters. In addition to known tetranuclear clusters synthesised by this method, we report the new cluster compounds $[N(PPh_3)_2][Os_3RuH(CO)_{13}]$, $[N(PPh_3)_2]$-$[Ru_3OsH(CO)_{13}]$, and $[Ru_3OsH_2(CO)_{13}]$.

Although a large number of tetranuclear metal clusters containing the M_3M' metal framework (M = Ru or Os; M' = Co, Fe, Ru, or Os) have been synthesised,[1] no one general method has been used, and yields have varied considerably from greater than 95% to trace amounts. Some of the more general methods employed to date are given below (thf = tetrahydrofuran, bpho = benzophenone).
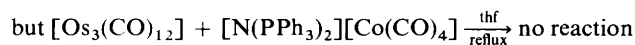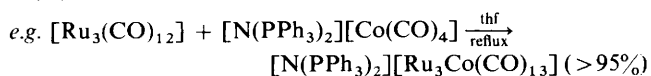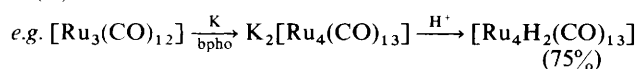
(i) Pyrolysis[1,2]

$e.g.$ $[N(PPh_3)_2][Os_3H(CO)_{11}] \xrightarrow[\text{(18 h)}]{\text{thf}}_{\text{reflux}} N[(PPh_3)_2][Os_4H(CO)_{13}]$
(< 6%)
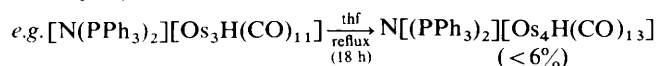
(ii) Addition of co-ordinatively unsaturated species[1,3—5]

$e.g.$ $[Os_3H_2(CO)_{10}] + [Co_4(CO)_{12}] \xrightarrow[\text{reflux}]{\text{heptane}} [CoOs_3H_3(CO)_{12}]$

(iii) Redox condensations[1,6—9]

$e.g.$ $[Ru_3(CO)_{12}] + [N(PPh_3)_2][Co(CO)_4] \xrightarrow[\text{reflux}]{\text{thf}}$
$[N(PPh_3)_2][Ru_3Co(CO)_{13}]$ (> 95%)

but $[Os_3(CO)_{12}] + [N(PPh_3)_2][Co(CO)_4] \xrightarrow[\text{reflux}]{\text{thf}}$ no reaction

(iv) Reduction reactions[10]

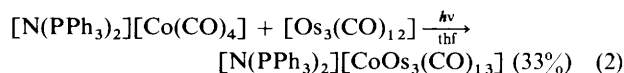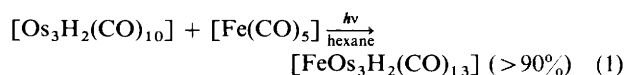$e.g.$ $[Ru_3(CO)_{12}] \xrightarrow[\text{bpho}]{\text{K}} K_2[Ru_4(CO)_{13}] \xrightarrow{\text{H}^+} [Ru_4H_2(CO)_{13}]$
(75%)

In most cases, fairly harsh conditions are required to activate the stable Ru–CO and, in particular, Os–CO bonds. It is probably a lack of activation, or the susceptibility of the product to the aggressive conditions, that results in poor yields or lack of formation of certain clusters.

Geoffroy and co-workers[11,12] have shown that reactions of type (ii) and (iii) can be photoassisted, resulting in better yields and in the generation of some new clusters, $e.g.$ reactions (1) and (2).

$[Os_3H_2(CO)_{10}] + [Fe(CO)_5] \xrightarrow[\text{hexane}]{hv}$
$[FeOs_3H_2(CO)_{13}]$ (> 90%) (1)

$[N(PPh_3)_2][Co(CO)_4] + [Os_3(CO)_{12}] \xrightarrow[\text{thf}]{hv}$
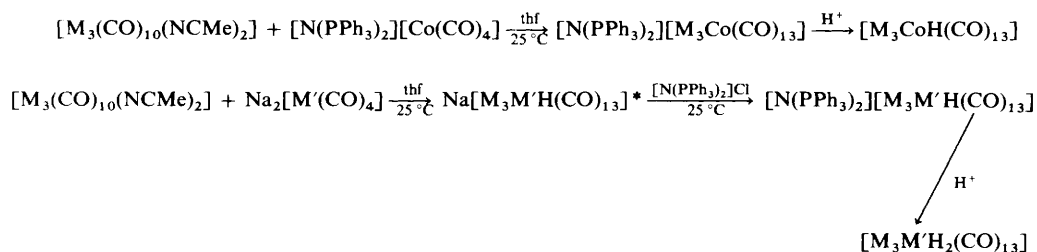$[N(PPh_3)_2][CoOs_3(CO)_{13}]$ (33%) (2)

In this paper we present a general method for the synthesis of tetranuclear clusters containing closed triruthenium and triosmium triangles, which involves the addition of an appropriate tetracarbonylmetalate to the highly reactive bis(acetonitrile) complexes, $[Ru_3(CO)_{10}(NCMe)_2]$ and $[Os_3(CO)_{10}(NCMe)_2]$ respectively. Owing to the reactive nature of the bis(acetonitrile) complexes most reactions were carried out at room temperature, and resulted in good yields. In addition to a large number of known tetranuclear clusters, the synthetic approach described in this paper allows us to report the new cluster compounds $[N(PPh_3)_2][Os_3RuH(CO)_{13}]$, $[N(PPh_3)_2][Ru_3-OsH(CO)_{13}]$, and $[Ru_3OsH_2(CO)_{13}]$.

Results and Discussion

The reaction approach employed in this study of the synthesis of tetranuclear clusters containing closed triruthenium and triosmium triangles is the addition of a carbonylmetalate to $[Ru_3(CO)_{10}(NCMe)_2]$ (1) and $[Os_3(CO)_{10}(NCMe)_2]$ (2), respectively. The reactions studied and the resultant products are summarised in the Scheme.

In all cases the anionic form of the tetranuclear cluster was isolated as the $[N(PPh_3)_2]^+$ salt, since this salt is generally less

$[M_3(CO)_{10}(NCMe)_2] + [N(PPh_3)_2][Co(CO)_4] \xrightarrow[\text{25 °C}]{\text{thf}} [N(PPh_3)_2][M_3Co(CO)_{13}] \xrightarrow{\text{H}^+} [M_3CoH(CO)_{13}]$

$[M_3(CO)_{10}(NCMe)_2] + Na_2[M'(CO)_4] \xrightarrow[\text{25 °C}]{\text{thf}} Na[M_3M'H(CO)_{13}] * \xrightarrow[\text{25 °C}]{[N(PPh_3)_2]Cl} [N(PPh_3)_2][M_3M'H(CO)_{13}]$

$\diagonal\ \text{H}^+$

$[M_3M'H_2(CO)_{13}]$

Scheme. * Not isolated. M = Ru or Os; M' = Fe, Ru, or Os

Table. Spectroscopic properties

Compound	I.r.ᵃ (ν_{CO}/cm^{-1})	¹H N.m.r.ᵇ (τ)		Mass spectrumᶜ (m/e)
[N(PPh$_3$)$_2$][Ru$_3$Co(CO)$_{13}$]	2 069w, 2 020vs, 1 898s, 1 823w (sh), 1 795m, br	2.50 (m)	[N(PPh$_3$)$_2$]$^+$	
[N(PPh$_3$)$_2$][Os$_3$Co(CO)$_{13}$]	2 074w, 2 020vs, 1 970s, 1 796w, br, 1 715w	2.50 (m)	[N(PPh$_3$)$_2$]$^+$	
[N(PPh$_3$)$_2$][Ru$_3$OsH(CO)$_{13}$]	2 064w (sh), 2 035m (sh), 2 024s, 2 006vs (sh), 2 001vs, 1 971m, 1 940w (sh)	2.50 (m) 26.68 (s)	[N(PPh$_3$)$_2$]$^+$ Ru–H	
[N(PPh$_3$)$_2$][Os$_4$H(CO)$_{13}$]	2 072vw, 2 028vs, 2 014vs, 2 002vs, 1 969m (sh), 1 940w (sh)	2.50 (m) 30.10 (s)	[N(PPh$_3$)$_2$]$^+$ Os–H	
[N(PPh$_3$)$_2$][Ru$_3$FeH(CO)$_{13}$]	2 070w, 2 029vs, 2 011vs, 1 995vs, 1 970s, 1 942m (sh)	2.50 (m) 22.60 (s)	[N(PPh$_3$)$_2$]$^+$ Ru–H	
[N(PPh$_3$)$_2$][Os$_3$FeH(CO)$_{13}$]	2 076w, 2 035vs, 2 012vs, 1 996vs, 1 964m (sh), 1 940w (sh)	2.50 (m) 29.49 (s)	[N(PPh$_3$)$_2$]$^+$ Os–H	
[N(PPh$_3$)$_2$][Ru$_4$H(CO)$_{13}$]	2 076w, 2 022vs, 2 003vs, 1 949s, 1 940w (sh), 1 847w, br	2.50 (m) 25.83 (s)	[N(PPh$_3$)$_2$]$^+$ Ru–H	
[N(PPh$_3$)$_2$][Os$_3$RuH(CO)$_{13}$]	2 069w (sh), 2 028vs, 2 014vs, 2 003vs, 1 971ms (sh), 1 940w (sh), 1 836w, br	2.50 (m) 29.30 (s)	[N(PPh$_3$)$_2$]$^+$ Os–H	
[Ru$_3$CoH(CO)$_{13}$]	ᵈ 2 107w, 2 085w, 2 074s, 2 060vs, 2 053vs, 2 036m, 2 026m, 2 021m, 2 016m (sh), 1 906w, 1 862m	27.71 (s)	Ru–H	727
[Os$_3$CoH(CO)$_{13}$]	ᵈ 2 113w, 2 080s, 2 057vs, 2 035m (sh), 2 020m (sh), 1 893w, br, 1 848w, br	30.14 (s)	Os–H	1 000
[Ru$_3$OsH$_2$(CO)$_{13}$]	ᵈ 2 083m (sh), 2 077vs, 2 065vs, 2 053vs, 2 023s, 2 016m, 1 992w (sh)	28.66 (s)	Ru–H	860
[Os$_4$H$_2$(CO)$_{13}$]	ᵈ 2 081vs, 2 064vs, 2 056vs, 2 019s, br	31.40 (s)	Os–H	1 134
[Ru$_4$H$_2$(CO)$_{13}$]	ᵈ 2 077vs, 2 066vs, 2 053vs, 2 034m, 2 022s, 2 006w, 1 968w, br, 1 883w	28.67 (s)	Ru–H	770
[Os$_3$RuH$_2$(CO)$_{13}$]	ᵈ 2 081vs, 2 066vs, 2 055vs, 2 017m, br, 1 852w, br	31.05 (s, br)	Os–H	1 043

ᵃ In CH$_2$Cl$_2$. ᵇ In CDCl$_3$. ᶜ Based on ^{101}Ru, ^{59}Co, and ^{192}Os. ᵈ In cyclohexane.

sensitive to moisture than the Na$^+$ salt, and to facilitate purification of the anionic clusters by thin-layer chromatography (t.l.c.). Most reactions were performed at ambient temperature and yields of greater than 50% were generally obtained if a stoicheiometric amount of the carbonylmetalate was added (yields were found to be poorer if an excess of carbonylmetalate was added). The good yields and mild conditions used emphasise the advantage of using the highly reactive bis(acetonitrile) complexes (1) and (2).

The anionic tetranuclear clusters were protonated, where possible, with concentrated H$_2$SO$_4$, to give the neutral hydrido tetranuclear clusters. In most cases the protonation reaction proceeded almost quantitatively, with the associated shift in ν_{CO} to higher wavenumber being observed.

The spectral data for the complexes are listed in the Table, while the chemical analyses for the new compounds are listed in the Experimental section.

Preparation of [N(PPh$_3$)$_2$][M$_3$Co(CO)$_{13}$] *and* [M$_3$CoH(CO)$_{13}$] (M = Ru *or* Os).—Reaction of (1) with [N(PPh$_3$)$_2$]-[Co(CO)$_4$] gives the known compound [N(PPh$_3$)$_2$][Ru$_3$-Co(CO)$_{13}$][6,12] in virtually quantitative yield (95%), while reaction of (2) with [N(PPh$_3$)$_2$][Co(CO)$_4$] results in the formation of [N(PPh$_3$)$_2$][Os$_3$Co(CO)$_{13}$][11] in ca. 60% yield. Previous methods of preparing [N(PPh$_3$)$_2$][Ru$_3$Co(CO)$_{13}$],[6,12] although giving similar yields, have required more severe conditions involving heating to reflux, while a previous method of preparing [N(PPh$_3$)$_2$][Os$_3$Co(CO)$_{13}$],[11] involving irradiation of [N(PPh$_3$)$_2$][Co(CO)$_4$] and [Os$_3$(CO)$_{12}$] for 48 h, resulted in a yield of 33%.

Protonation of [N(PPh$_3$)$_2$][Ru$_3$Co(CO)$_{13}$] and [N(PPh$_3$)$_2$]-[Os$_3$Co(CO)$_{13}$] with H$_2$SO$_4$ results in the formation of [Ru$_3$CoH(CO)$_{13}$] and [Os$_3$CoH(CO)$_{13}$] respectively, both of which are easily identified by the presence of a hydride signal in the ¹H n.m.r. spectrum. The yield in both cases is virtually quantitative which is an improvement on previous methods[6] where a 63% yield of [Ru$_3$CoH(CO)$_{13}$] and only trace amounts of [Os$_3$CoH(CO)$_{13}$] were obtained.

Preparation of [N(PPh$_3$)$_2$][M$_4$H(CO)$_{13}$] *and* [M$_4$H$_2$-(CO)$_{13}$] (M = Ru *or* Os).—The homonuclear clusters [N-(PPh$_3$)$_2$][Ru$_4$H(CO)$_{13}$] and [N(PPh$_3$)$_2$][Os$_4$H(CO)$_{13}$] were prepared by reacting (1) and (2) with Na$_2$[Ru(CO)$_4$] and Na$_2$[Os(CO)$_4$] to form Na[Ru$_4$H(CO)$_{13}$] and Na[Os$_4$H-(CO)$_{13}$] respectively, after which Na$^+$ was replaced by [N(PPh$_3$)$_2$]$^+$ in a metathesis reaction with [N(PPh$_3$)$_2$]Cl. The proton incorporated in the cluster is assumed to be abstracted from the thf solvent and is observed as a singlet in the ¹H n.m.r. spectrum. [N(PPh$_3$)$_2$][Ru$_4$H(CO)$_{13}$] was isolated in 65% yield, which compares favourably with the method used by Shore and co-workers,[10] involving reduction of [Ru$_3$(CO)$_{12}$] with potassium and benzophenone followed by a metathesis reaction with [N(PPh$_3$)$_2$]Cl. [N(PPh$_3$)$_2$][Os$_4$H(CO)$_{13}$] is obtained in 60% yield which is an improvement on previous attempts[2] that resulted in yields of 26% or less.

Protonation of [N(PPh$_3$)$_2$][Ru$_4$H(CO)$_{13}$], using H$_2$SO$_4$, affords the α-isomer of [Ru$_4$H$_2$(CO)$_{13}$], characterised by its ¹H n.m.r. spectrum,[13] in quantitative yield. This compound has been synthesised previously in 75% yield, by direct protonation of K$_2$[Ru$_4$(CO)$_{13}$].[10] Protonation of [N-(PPh$_3$)$_2$][Os$_4$H(CO)$_{13}$] yields the analogous osmium compound, [Os$_4$H$_2$(CO)$_{13}$], in nearly quantitative yield. Lewis and co-workers[14] have prepared this cluster previously in 80% yield by omitting the metathetic displacement of Na$^+$ by [N(PPh$_3$)$_2$]$^+$.

Preparation of [N(PPh$_3$)$_2$][M$_3$M'H(CO)$_{13}$] *and* [M$_3$M'H$_2$-(CO)$_{13}$] (M = Ru *or* Os; M' = Fe, Ru, *or* Os).—Complexes (1)

and (2) react with $Na_2[Fe(CO)_4]$ to yield $Na[Ru_3FeH(CO)_{13}]$ and $Na[Os_3FeH(CO)_{13}]$, which when further reacted with $[N(PPh_3)_2]Cl$ produce $[N(PPh_3)_2][Ru_3FeH(CO)_{13}]$ and $[N-(PPh_3)_2][Os_3FeH(CO)_{13}]$ with the respective yields being 55 and 60%. Previous attempts to synthesise these compounds have involved refluxing a solution of $[Ru_3(CO)_{12}]$ and $[N(PPh_3)_2][FeH(CO)_4]$ for 4 h to give a 47% yield in the case of $[N(PPh_3)_2][Ru_3FeH(CO)_{13}]$,[12] while $[N(PPh_3)_2][Os_3-FeH(CO)_{13}]$ was prepared by refluxing $[N(PPh_3)_2]_2[Fe_3-(CO)_{11}]$ with $[Os_3(CO)_{12}]$ for 7 h followed by addition of $FeCl_3$ and Co.[15]

Attempts to prepare $[Ru_3FeH_2(CO)_{13}]$ and $[Os_3FeH_2-(CO)_{13}]$ by direct protonation of the appropriate anionic clusters with H_2SO_4 failed, resulting in decomposition. However, both these compounds have been prepared previously. $[Ru_3FeH_2(CO)_{13}]$ was prepared by direct protonation of $Na_2[Ru_3Fe(CO)_{13}]$ using 20% aqueous H_3PO_4, with yields of up to 56% being recorded.[1,2] On the other hand, $[Os_3FeH_2-(CO)_{13}]$ may be synthesised directly in yields greater than 90% using the photoassisted addition of $[Os_3H_2(CO)_{10}]$ and $[Fe(CO)_5]$ described by Burkhardt and Geoffroy.[11]

The reaction of (2) with $Na_2[Ru(CO)_4]$ results in the formation of $Na[Os_3RuH(CO)_{13}]$, which was further reacted with $[N(PPh_3)_2]Cl$ to produce a 40% yield of the new cluster $[N(PPh_3)_2][Os_3RuH(CO)_{13}]$. The structure of this cluster appears, on the basis of spectral comparison, to be similar to $[N(PPh_3)_2][Os_3FeH(CO)_{13}]$, the crystal structure of which has been determined.[15]

Protonation of $[N(PPh_3)_2][Os_3RuH(CO)_{13}]$ with H_2SO_4 produces the known compound $[Os_3RuH_2(CO)_{13}]$ in ca. 90% yield. Previous attempts to produce this cluster have involved irradiating a hexane solution of $[Ru_3(CO)_{12}]$ and $[Os_3H_2-(CO)_{10}]$ for 70 h, with yields varying from 23 to 53%.[11]

The reaction of (1) with $Na_2[Os(CO)_4]$ gave $Na[Ru_3-OsH(CO)_{13}]$ which was further reacted with $[N(PPh_3)_2]Cl$ to form the new cluster $[N(PPh_3)_2][Ru_3OsH(CO)_{13}]$ in ca. 60% yield. This cluster, on the basis of its spectroscopic data, appears to have a structure similar to $[N(PPh_3)_2][Ru_3FeH(CO)_{13}]$.[1]

Direct protonation of $[N(PPh_3)_2][Ru_3OsH(CO)_{13}]$ with H_2SO_4 yields a new hydrido cluster, $[Ru_3OsH_2(CO)_{13}]$, which was characterised by means of its spectroscopic properties and, in particular, its mass spectrum, which shows the sequential loss of 13 carbonyl groups. On the basis of this data it is suggested that the structure of $[Ru_3OsH_2(CO)_{13}]$ is similar to $[Ru_3FeH_2(CO)_{13}]$, the crystal structure of which has been determined.[1]

In conclusion, we have shown that the reaction of the bis(acetonitrile) complexes (1) and (2) with an appropriate carbonylmetalate provides a general route for the synthesis of tetranuclear clusters incorporating the Ru_3M' and Os_3M' ($M = Co$, Fe, Ru, or Os) framework. Apart from providing good yields of known compounds, it facilitates the synthesis of the new clusters $[N(PPh_3)_2][Ru_3OsH(CO)_{13}]$, $[N(PPh_3)_2]-[Os_3RuH(CO)_{13}]$, and $[Ru_3OsH_2(CO)_{13}]$, which could not be synthesised using previously reported methods.

Experimental

All reactions were performed using standard Schlenk equipment under dry nitrogen. Tetrahydrofuran (thf) was freshly distilled over sodium–bpho before use, while dichloromethane and cyclohexane were dried over calcium hydride and sodium respectively. The starting materials $[Ru_3(CO)_{10}(NCMe)_2]$[16] (1), $[Os_3(CO)_{10}(NCMe)_2]$[17] (2), $[N(PPh_3)_2][Co(CO)_4]$,[18] $Na_2[Fe(CO)_4]$,[19] $Na_2[Ru(CO)_4]$,[20] and $Na_2[Os(CO)_4]$[21] were prepared using methods described in the literature. ^1H N.m.r. spectra were obtained using a Bruker WM 250 spectrometer,

while solution i.r. spectra were recorded using KBr cells on a Perkin-Elmer 983 spectrometer.

(a) Preparation of $[N(PPh_3)_2][Ru_3Co(CO)_{13}]$.—Tetrahydrofuran (10 cm³) was added to a sealed vessel containing (1) (50 mg, 0.075 mmol) and $[N(PPh_3)_2][Co(CO)_4]$ (55 mg, 0.077 mmol) with constant stirring. Reaction was fast, with the colour of the solution changing from yellow to dark red. After 1 h the reaction mixture was chromatographed. T.l.c., using dichloromethane–acetone–cyclohexane (40:20:40) as eluant, yielded $[N(PPh_3)_2][Ru_3Co(CO)_{13}]$ isolated as a dark red solid, in virtually quantitative yield (90 mg, 95%).

(b) Preparation of $[N(PPh_3)_2][Os_3Co(CO)_{13}]$.— The reaction of (2) (50 mg, 0.054 mmol) with $[N(PPh_3)_2][Co(CO)_4]$ (38 mg, 0.053 mmol) was similar to that described in (a), thf (10 cm³) being added with constant stirring. During 1 h the solution changed from orange to red. T.l.c., using dichloromethane–acetone–cyclohexane (50:10:40) as eluant, yielded $[N(PPh_3)_2]-[Os_3Co(CO)_{13}]$ as an orange oil. The product was precipitated as an orange powder from dichloromethane-hexane solution (50 mg, 60%).

(c) Preparation of $[N(PPh_3)_2][Ru_3OsH(CO)_{13}]$.—Tetrahydrofuran (25 cm³) was added to a sealed vessel containing (1) (50 mg, 0.075 mmol) and $Na_2[Os(CO)_4]$ (27 mg, 0.077 mmol) with constant stirring. Overnight the solution changed from yellow to dark red-brown; the solvent was removed in vacuo and a solution of $[N(PPh_3)_2]Cl$ (43 mg, 0.075 mmol) in dichloromethane (20 cm³) added to the residue. The solution was stirred for 1 h, before being chromatographed. T.l.c., using dichloromethane–acetone–cyclohexane (40:20:40) as eluant, yielded $[N(PPh_3)_2][Ru_3OsH(CO)_{13}]$ as the major product (63 mg, 60%), isolated as a dark red-brown solid, with $[Ru_3(CO)_{12}]$ and decomposition products constituting the remainder (Found: C, 42.1; H, 2.2; N, 1.1. $C_{49}H_{31}NO_{13}OsP_2Ru_3$ requires C, 42.1; H, 2.2; N, 1.1%).

(d) Preparation of $[N(PPh_3)_2][Os_4H(CO)_{13}]$.—Tetrahydrofuran (25 cm³) was added to a sealed vessel containing (2) (50 mg, 0.0054 mmol) and $Na_2[Os(CO)_4]$ (19 mg, 0.054 mmol). The solution was refluxed for 1 h, during which time the colour changed from yellow to deep red. The solvent was removed in vacuo and a solution of $[N(PPh_3)_2]Cl$ (30 mg, 0.053 mmol) in dichloromethane (20 cm³) was added. The solution was stirred for 1 h before being chromatographed. T.l.c., using dichloromethane–acetone–cyclohexane (50:10:40) as eluant, yielded $[N(PPh_3)_2][Os_4H(CO)_{13}]$ as a red oil. The product was precipitated as a red solid (53 mg, 60%) from a dichloromethane–hexane mixture.

(e) Preparation of $[N(PPh_3)_2][Ru_3FeH(CO)_{13}]$.—The reaction procedure was similar to that described in (c), $Na_2[Fe(CO)_4]$ (16 mg, 0.075 mmol) reacting with (1) (50 mg, 0.075 mmol). T.l.c., using the same conditions as described in (c), yielded $[N(PPh_3)_2][Ru_3FeH(CO)_{13}]$ as the major product (52 mg, 55%), isolated as a black solid, with $[Ru_3(CO)_{12}]$ (12 mg, 25%) and decomposition products (20%) constituting the remainder.

(f) Preparation of $[N(PPh_3)_2][Os_3FeH(CO)_{13}]$.—Tetrahydrofuran (25 cm³) was added to (2) (50 mg, 0.054 mmol) and $Na_2[Fe(CO)_4]$ (12 mg, 0.056 mmol) in a sealed vessel, with constant stirring. The reaction mixture was stirred for 3 h during which time the colour of the solution changed from yellow to deep red. The solvent was removed in vacuo and a solution of $[N(PPh_3)_2]Cl$ in dichloromethane (20 cm³) added. The solution was stirred for 1 h before being chromatographed. T.l.c., using dichloromethane–acetone–cyclohexane (50:10:40)

as eluant, yielded $[N(PPh_3)_2][Os_3FeH(CO)_{13}]$ as a red oil. The product was precipitated as a red-brown solid (50 mg, 60%) from a dichloromethane–hexane solution.

(g) *Preparation of* $[N(PPh_3)_2][Ru_4H(CO)_{13}]$.—The reaction procedure was similar to that described in (c), $Na_2[Ru(CO)_4]$ (20 mg, 0.077 mmol) reacting with (1) (50 mg, 0.075 mmol), followed by the addition of $[N(PPh_3)_2]Cl$ (45 mg, 0.078 mmol) as before. T.l.c., using the same conditions as described in (c), yields $[N(PPh_3)_2][Ru_4H(CO)_{13}]$ as the major product (60 mg, 65%) isolated as a dark red solid, with $[Ru_3(CO)_{12}]$ and decomposition products constituting the remainder.

(h) *Preparation of* $[N(PPh_3)_2][Os_3RuH(CO)_{13}]$.—The reaction procedure was similar to that described in (f), (2) (50 mg, 0.054 mmol) reacting with $Na_2[Ru(CO)_4]$ (14 mg, 0.054 mmol), followed by the addition of $[N(PPh_3)_2]Cl$ (34 mg, 0.054 mmol) as before. T.l.c., using the same conditions as described in (f), yielded $[N(PPh_3)_2][Os_3RuH(CO)_{13}]$ as a red oil. The product was precipitated as a red-brown solid (34 mg, 40%) from a dichloromethane–hexane solution (Found: C, 37.4; H, 2.0; N, 0.9. $C_{49}H_{31}NO_{13}Os_3P_2Ru$ requires C, 37.4; H, 2.0; N, 0.9%).

(i) *Protonation of* $[N(PPh_3)_2][Ru_3Co(CO)_{13}]$.—The complex (30 mg, 0.24 mmol) was dissolved in CH_2Cl_2 (5 cm³). An excess (1 drop) of concentrated H_2SO_4 was added with constant stirring. Reaction was instantaneous, the colour of the solution changing from dark red to red. The solution was then filtered through a silica frit to remove excess acid and the volume reduced. T.l.c., using dichloromethane–cyclohexane (20:80) as eluant, yielded $[Ru_3CoH(CO)_{13}]$, isolated as a red solid (16 mg, 93%).

(j) *Protonation of* $[N(PPh_3)_2][Os_3Co(CO)_{13}]$.—The complex (30 mg, 0.02 mmol) was protonated with concentrated H_2SO_4 as described in (i). Reaction was instantaneous, the colour of the solution changing from dark red to orange. T.l.c., using the conditions described in (i), yielded $[Os_3CoH(CO)_{13}]$, isolated as red-orange crystals, in quantitative yield (ca. 95%) (Found: C, 15.7; H, 0.1. $C_{13}HCoO_{13}Os_3$ requires C, 15.7; H, 0.1%).

(k) *Protonation of* $[N(PPh_3)_2][Ru_3OsH(CO)_{13}]$.—The complex (30 mg, 0.02 mmol) was protonated as described in (i). The reaction was instantaneous, the colour of the solution changing from dark red-brown to red. T.l.c., using the conditions described in (i), yielded a quantitative amount of $[Ru_3OsH_2(CO)_{13}]$, isolated as a bright red solid (Found: C, 18.4; H, 0.3. $C_{13}H_2O_{13}OsRu_3$ requires C, 18.2; H, 0.2%).

(l) *Protonation of* $[N(PPh_3)_2][Os_4H(CO)_{13}]$.—The complex (30 mg, 0.018 mmol) was protonated as described in (i). Reaction was instantaneous as indicated by the change in colour of the solution from deep red to orange. T.l.c., using the conditions described in (i), yielded $[Os_4H_2(CO)_{13}]$ as an orange powder (19 mg, 95%).

(m) *Attempted Protonation of* $[N(PPh_3)_2][Ru_3FeH(CO)_{13}]$.—Attempts to prepare $[Ru_3FeH_2(CO)_{13}]$ from $[N(PPh_3)_2][Ru_3FeH(CO)_{13}]$ by direct protonation using concentrated H_2SO_4 failed. On addition of the acid, reaction was instantaneous, the colour of the solution changing from black to yellow-orange. T.l.c., using the conditions described in (i), yielded $[Ru_3(CO)_{12}]$ and $[Ru_4H_2(CO)_{13}]$, with decomposition products constituting the remainder.

(n) *Attempted Protonation of* $[N(PPh_3)_2][Os_3FeH(CO)_{13}]$.—Attempts to prepare $[Os_3FeH_2(CO)_{13}]$ from $[N(PPh_3)_2]$-

$[Os_3FeH(CO)_{13}]$ by direct protonation using concentrated H_2SO_4 failed. On addition of the acid, the colour of the solution lightened, but t.l.c., using the conditions described in (i), yielded mainly decomposition products.

(o) *Protonation of* $[N(PPh_3)_2][Ru_3H(CO)_{13}]$.—$[Ru_4H_2-(CO)_{13}]$ was prepared from $[N(PPh_3)_2][Ru_4H(CO)_{13}]$ using the method described in (i). On addition of H_2SO_4, the colour of the solution lightened from dark red, indicating that reaction had taken place. T.l.c., using the same conditions as described in (i), gave a quantitative yield of $[Ru_4H_2(CO)_{13}]$, isolated as a red-orange solid.

(p) *Protonation of* $[N(PPh_3)_2][Os_3RuH(CO)_{13}]$.—The complex (30 mg, 0.019 mmol) was protonated using the method described in (i). Reaction was instantaneous, the colour of the solution changing from deep red to orange. T.l.c., using the conditions described in (i), yielded $[Os_3RuH_2(CO)_{13}]$ (18 mg, 90%), isolated as an orange solid.

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