

Tertiary Phosphine Aluminohydride Complexes of Ruthenium(II) and Osmium(II)

Andrew R. Barron and Geoffrey Wilkinson*

Chemistry Department, Imperial College of Science and Technology, London SW7 2AY

The interaction of dichloro tertiary phosphine complexes of ruthenium(II) and osmium(II) with LiAlH_4 in ethers has afforded the complexes $\text{L}_3\text{HM}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{MHL}_3$ where $\text{M} = \text{Ru}$, $\text{L} = \text{PMe}_3$, PEtPh_2 , or PPh_3 ; $\text{M} = \text{Os}$, $\text{L} = \text{PMe}_3$ or PPh_3 . Interaction of tetramethylethylenediamine with $[(\text{Me}_3\text{P})_3\text{HRuAlH}_4]_2$ gives the complex $[(\text{Me}_3\text{P})_3\text{HRu}]_2\text{AlH}_5$. Proton, ^{31}P , and ^{27}Al n.m.r. spectra are reported and the fluxional behaviour of the complexes discussed.

There are numerous examples of monomeric transition-metal borohydride complexes^{1,2} that may have M-H-BH_3 , $\text{M}(\mu\text{-H})_2\text{-BH}_2$, or $\text{M}(\mu\text{-H})_3\text{BH}$ groups; the bridging and terminal B-H hydrides commonly undergo rapid intramolecular exchange,^{3,4} but seldom undergo exchange with any transition-metal terminal M-H hydrides that may also be present in the molecules. Exchange has been observed, e.g. in $\text{RuH}(\text{BH}_4)[\text{PhP}(\text{CH}_2\text{CH}_2\text{-CH}_2\text{PPh}_2)_2]$ ^{5a} and $\text{RuH}(\text{BH}_4)(\text{PMe}_3)_3$,^{5b} but only at elevated temperatures. In $\text{OsH}_3(\text{BH}_4)(\text{PR}_3)_2$, $\text{R} = \text{cyclopentyl}$, at 90 °C only the Os-H and $\text{Os}(\mu\text{-H})_2\text{B}$ hydrogens exchange.⁶

By contrast aluminohydride (AlH_4^-) complexes are dimeric, probably due to the tendency of aluminium to become five-coordinate (not possible for boron) with $\text{M}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{M}$ or $\text{M}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{M}$ units in their structures; the same applies to substituted complexes such as those of $\text{AlH}_3(\text{OBu}^n)^-$.^{7,8} In these species the terminal M-H and bridging $\text{M}(\mu\text{-H})_2\text{Al}$ hydrogen atoms undergo exchange at room temperature^{8,9} and this depends on the geometry around the metal;⁹ there is no exchange between $\text{M}(\mu\text{-H})_2\text{Al}$ and terminal Al-H but exchange between $\text{Al}(\mu\text{-H})_2\text{Al}$ and Al-H can occur.^{7,9}

We now report the synthesis and characterisation of octahedral ruthenium(II) and osmium(II) aluminohydrides that exhibit very facile hydride exchanges.

Results and Discussion

Ruthenium Aluminohydrides $[(\text{R}_3\text{P})_3\text{HRuAlH}_4]_2$.—Treatment of $\text{RuCl}_2(\text{PMe}_3)_4$ ¹⁰ with 2 equivalents of LiAlH_4 in diethyl ether affords a high yield of the colourless, hexane-soluble complex *fac*- $(\text{Me}_3\text{P})_3\text{HRu}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{RuH}(\text{PMe}_3)_3$ (1). By contrast with the similar tungsten and rhenium aluminohydrides⁹ this compound does not react with tetrahydrofuran (thf) to yield a *n*-butoxo-bridged species nor is a butoxide formed if the synthesis is carried out in thf, but only a lower (< 30%) yield of compound (1).

The i.r. spectrum of the complex shows a series of broad peaks between 1800 and 1650 cm^{-1} that are due to bridging and terminal hydrides. Nuclear magnetic resonance spectra show that facile intramolecular hydrogen exchanges are occurring. The ^1H n.m.r. spectrum (Table 1) at 298 K has a broad quartet [$\delta -10.76$ p.p.m., $J(\text{P-H}) = 20.4$ Hz] due to terminal Ru-H and bridging $\text{Ru}(\mu\text{-H})_2\text{Al}$ hydrides. The terminal Al-H and bridging $\text{Al}(\mu\text{-H})_2\text{Al}$ hydrides give a broad signal centred at $\delta 4.60$ p.p.m. where the broadness is presumably due to the large quadrupole moment of ^{27}Al . Attempts to decouple the aluminium and proton signals have met with little success. On cooling the sample the signal due to terminal Al-H and bridging $\text{Al}(\mu\text{-H})_2\text{Al}$ hydride broadens, then de-coalesces into two peaks of equal intensity. One peak is due to the bridging $\text{Al}(\mu\text{-H})_2\text{Al}$ hydrides ($\delta 5.52$ p.p.m.), the other to terminal Al-H hydrides ($\delta 4.53$ p.p.m.).

The activation energy for this exchange calculated¹¹ from the n.m.r. data, $\Delta G^\ddagger = 44.0 \pm 1$ kJ mol⁻¹, T_c 238 K, is comparable to those of the manganese,⁷ tungsten,⁹ and rhenium⁹ systems. However, in the ruthenium complex, by contrast with the exchange in these other aluminohydrides, the exchange between the terminal M-H and bridging $\text{M}(\mu\text{-H})_2\text{Al}$ hydrides occurs in solution even at 178 K. Although some broadening does occur at 178 K this may be ascribed to solvent viscosity effects.

The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum (298 K) shows a sharp singlet ($\delta -2.48$ p.p.m.) indicating a *fac* configuration of phosphorus around the ruthenium; the borohydride $\text{RuH}(\text{BH}_4)(\text{PMe}_3)_3$ has *mer* phosphines.^{5b,†} Selective decoupling of the methyl protons results in a non-binomial quartet, $J(\text{P-H}) = 20.4$ Hz and the second-order nature is due to an $\text{AX}_2\text{X}'$ spin system, confirmed by computer simulation.

Recently, Caulton and co-workers¹² have reported rhenium species of the type $\text{L}_2\text{ReH}_6\text{AlMe}_2$ and $\text{L}_2\text{ReH}_4\text{AlMe}_2$ where $\text{L} = \text{PMe}_2\text{Ph}$ or PMePh_2 , and present detailed arguments for a triply bridged $\text{Re}(\mu\text{-H})_3\text{AlMe}_2$ unit in $\text{L}_2\text{ReH}_4\text{AlMe}_2$. A triple bridge would be the only way in which Al could be five-coordinate. In our previous studies⁷⁻⁹ on compounds of Mn, W, and Re both *X*-ray and ^{27}Al n.m.r. data indicate that five-coordinate Al with a $\text{M}(\mu\text{-H})_2\text{Al}$ bridge is preferred. For the present ruthenium complex a triple bridge seems unlikely since Al can be five-coordinate without and the $^{27}\text{Al}\{-^1\text{H}\}$ n.m.r. signal, a single broad resonance $\delta 74$ p.p.m., $w_{1/2} = 4340$ Hz, is in the region characteristic for five-coordinate $\text{Al}^{7,9,13}$ and is similar to that found for $[(\text{dmpe})_2\text{MnAlH}_4]_2$ [*dmpe* = 1,2-bis(dimethylphosphino)ethane] where there is no possibility of a $(\mu\text{-H})_3$ bridge and Al has a distorted trigonal bipyramidal configuration.

The very labile Ru-H and $\text{Ru}(\mu\text{-H})_2\text{Al}$ exchange may be a consequence of the *fac* octahedral configuration about ruthenium which allows exchange without the rearrangement about the transition metal that will be required in the compounds of W and Re (where the metals have co-ordination numbers of eight and seven, respectively) and possibly closer proximity of the hydrogen on ruthenium to the vacant co-ordination position on Al. Additional support for this view comes from the fact that the exchange process appears equally rapid in the complexes with bulkier phosphines, $(\text{L}_3\text{HRuAlH}_4)_2$, where $\text{L} = \text{PEtPh}_2$ (2) or PPh_3 (3).

We have been unable to obtain *X*-ray quality crystals of these compounds due to twinning or other problems.

The Complex $[(\text{Me}_3\text{P})_3\text{HRu}]_2\text{AlH}_5$.—The interaction of compound (1) with tetramethylethylenediamine (tmen) results

† Note that in ref. 5b interaction of *cis*- $\text{RuCl}(\text{PMe}_3)_4$ and LiAlH_4 in refluxing thf gave *cis*- $\text{RuH}_2(\text{PMe}_3)_4$ for which see also V. V. Mainz and R. A. Andersen, *Organometallics*, 1984, 3, 675.

Table 1. Proton, $^{31}\text{P}\{-^1\text{H}\}$ and $^{27}\text{Al}\{-^1\text{H}\}$ n.m.r. data (298 K)* for aluminohydrides of ruthenium and osmium

Compound	^1H	Assignment	$^{31}\text{P}\{-^1\text{H}\}$	$^{27}\text{Al}\{-^1\text{H}\}$
(1) $[(\text{Me}_3\text{P})_3\text{HRuAlH}_4]_2$	4.60(s)	4 H Al-H, Al($\mu\text{-H}$) $_2$ Al	-2.48(s)	+74(br s)
	1.20(d), $J(\text{P-H}) = 7.2$	54 H P-CH $_3$		
(2) $[(\text{Ph}_2\text{EtP})_3\text{HRuAlH}_4]_2$	-10.76(br q), $J(\text{P-H}) = 20.4$	6 H Ru-H, Ru($\mu\text{-H}$) $_2$ Al	+46.7(s)	+71(br s)
	7.00(m)	60 H P-C $_6$ H $_5$		
	4.51(s)	4 H Al-H, Al($\mu\text{-H}$) $_2$ Al		
	1.23(m)	12 H P-CH $_2$		
	0.82(m)	18 H P-CH $_2$ CH $_3$		
(3) $[(\text{Ph}_3\text{P})_3\text{HRuAlH}_4]_2$	-10.90(br q), $J(\text{P-H}) = 20.0$	6 H Ru-H, Ru($\mu\text{-H}$) $_2$ Al	+47.2(s)	+68(br s)
	7.02(m)	70 H P-C $_6$ H $_5$		
	4.50(br s)	4 H Al-H, Al($\mu\text{-H}$) $_2$ Al		
(4) $[(\text{Me}_3\text{P})_3\text{HRu}_2\text{AlH}_5]$	-10.90(br q), $J(\text{P-H}) = 20.0$	6 H Ru-H, Ru($\mu\text{-H}$) $_2$ Al	-9.57(s)	+78(br s)
	4.50(vbr)	1 H Al-H		
	1.25(d), $J(\text{P-H}) = 5.89$	54 H P-CH $_3$		
(5) $[(\text{Ph}_3\text{P})_3\text{HOsAlH}_4]_2$	-9.57(br q), $J(\text{P-H}) = 18.3$	6 H Ru-H, Ru($\mu\text{-H}$) $_2$ Al	-27.60(s)	+66(br s)
	7.0(m)	70 H P-C $_6$ H $_5$		
	4.35(br s)	4 H Al-H, Al($\mu\text{-H}$) $_2$ Al		
	-12.58(br q), $J(\text{P-H}) = 14.9$	6 H Os-H, Os($\mu\text{-H}$) $_2$ Al		
(6) $[(\text{Me}_3\text{P})_3\text{HOsAlH}_4]_2$	4.50(br s)	4 H Al-H, Al($\mu\text{-H}$) $_2$ Al	-48.11(s)	+68(br s)
	1.31(d), $J(\text{P-H}) = 6.9$	54 H P-CH $_3$		
	-12.60(br q), $J(\text{P-H}) = 15.0$	6 H Os-H, Os($\mu\text{-H}$) $_2$ Al		

* δ in p.p.m. relative to SiMe_4 (^1H), external 85% H_3PO_4 (^{31}P), and external $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ (^{27}Al), J values in Hz.

in the removal of AlH_3 giving insoluble $\text{AlH}_3(\text{tmen})$ and $(\text{Me}_3\text{P})_3\text{HRu}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2\text{RuH}(\text{PMe}_3)_3$ (4). The first complex of this type has been structurally characterised for tungsten.^{8,9} As in compound (1), the terminal Ru-H and Ru($\mu\text{-H}$) $_2$ Al hydride-exchange process is very rapid and proceeds well below 180 K.

Osmium Aluminohydrides.—The osmium complex *fac*-(Ph_3P) $_3$ HOs($\mu\text{-H}$) $_2$ AlH($\mu\text{-H}$) $_2$ AlH($\mu\text{-H}$) $_2$ OsH(PPh_3) $_3$ (5) can be synthesised from $\text{OsCl}_2(\text{PPh}_3)_3$ ¹⁴ and LiAlH_4 in diethyl ether. However, interaction with $\text{OsCl}_2(\text{PMe}_3)_4$ ¹⁵ to obtain the PMe_3 analogue (6) requires tetrahydrofuran as solvent. Spectroscopically these osmium complexes are similar to their ruthenium analogues (see Experimental section and Table 1).

Experimental

Microanalyses were by Pascher, Bonn, and the University of Kent, Canterbury. Melting points were determined in sealed capillaries and are uncorrected. Infrared spectra were recorded in the region 4 000–200 cm^{-1} on a Perkin-Elmer 683 grating spectrometer using Nujol mulls. N.m.r. spectra (in [$^2\text{H}_8$]-toluene) were recorded on JEOL FX90Q or Bruker WM-250 spectrometers; data are given in Table 1. All manipulations were carried out under argon and solvents were dried, distilled, and degassed before use.

All of the compounds are very air sensitive and are readily hydrolysed by protic solvents to hydrido-species (*cf.* ref. 9); although the latter have not been isolated they were shown to be present by their high-field ^1H n.m.r. spectra. The ruthenium complexes slowly decompose at room temperature even under argon or in vacuum but can be stored at -20°C .

Analyses are given in Table 2.

1,2;1,2;2,3;2,3;3,4;3,4-Hexa- μ -hydrido-1,2,3,4-tetrahydrido-1,1,1,4,4,4-hexakis(trimethylphosphine)-1,4-diruthenium(II)-2,3-dialuminium, (1).—To stirred suspension of LiAlH_4 (0.17 g, 4.48 mmol) in Et_2O (100 cm^3) at -78°C was added $\text{RuCl}_2(\text{PMe}_3)_4$ ¹⁰ (0.77 g, 1.62 mmol). After stirring for 10 min the solution was warmed to room temperature and stirred until it was colourless and effervescence had ceased. After removal of the solvent and drying under vacuum the white solid was extracted with hexane

Table 2. Analytical data* for aluminohydrides

Compound	C	H	P	Al
(1) $[(\text{Me}_3\text{P})_3\text{HRuAlH}_4]_2$	30.3	8.9	25.1	7.4
	(29.9)	(8.9)	(25.8)	(7.5)
(2) $[(\text{Ph}_2\text{EtP})_3\text{HRuAlH}_4]_2$	65.0	6.6	12.0	4.0
	(65.0)	(6.5)	(12.0)	(3.5)
(3) $[(\text{Ph}_3\text{P})_3\text{HRuAlH}_4]_2$	70.8	5.7	10.2	2.9
	(70.5)	(5.4)	(10.1)	(2.9)
(4) $[(\text{Me}_3\text{P})_3\text{HRu}_2\text{AlH}_5]$	31.0	8.8	27.0	3.7
	(31.2)	(8.8)	(26.9)	(3.9)
(5) $[(\text{Ph}_3\text{P})_3\text{HOsAlH}_4]_2$	64.2	4.9	9.0	2.7
	(64.3)	(5.0)	(9.2)	(2.7)
(6) $[(\text{Me}_3\text{P})_3\text{HOsAlH}_4]_2$	24.0	7.5	20.6	6.0
	(24.0)	(7.1)	(20.7)	(6.0)

* Required values in parentheses.

(4 \times 100 cm^3); the colourless extract was evaporated and re-extracted into toluene (2 \times 30 cm^3). The extracts were reduced in volume to ca. 10 cm^3 and cooled to -20°C affording white crystals, m.p. 178–180 $^\circ\text{C}$ (decomp.). Yield: 0.53 g, 90%. I.r.: 1 800m, 1 740s, 1 700s, 1 655m, 1 425m, 1 340m, 1 300m, 1 280s, 1 131m, 960m, 940s, 860m, 850m, 820m, 760w, 725m, 680m, 670m, 600w, 580m, and 370w cm^{-1} .

1,1,1,4,4,4-Hexakis(ethylidiphenylphosphine)-1,2;1,2;2,3;2,3;-3,4;3,4-hexa- μ -hydrido-1,2,3,4-tetrahydrido-1,4-diruthenium(II)-2,3-dialuminium, (2).—This complex was prepared as for (1) but using $\text{RuCl}_2(\text{PEtPh}_2)_3$ ¹⁶ to give white crystals, m.p. 188 $^\circ\text{C}$ (decomp.). Yield: 74%. I.r.: 1 790m, 1 750s, 1 685m, 1 610m, 1 310m, 1 265s, 1 155m, 1 095s, 1 030m, 950vw, 865w, 800m, 745m, 730w, 700s, and 530s cm^{-1} .

1,2;1,2;2,3;2,3;3,4;3,4-Hexa- μ -hydrido-1,2,3,4-tetrahydrido-1,1,1,4,4,4-hexakis(triphenylphosphine)-1,4-diruthenium(II)-2,3-dialuminium, (3).—This complex was prepared as for (1) but using $\text{RuCl}_2(\text{PPh}_3)_3$ ¹⁷ Extraction of the reaction mixture with toluene (2 \times 50 cm^3), reduction in volume, and cooling to -78°C gave a white microcrystalline solid, m.p. 193–196 $^\circ\text{C}$. Yield: 82%. I.r.: 1 845m, 1 760s, 1 650m, 1 600w, 1 430s, 1 310w, 1 260m, 1 180m, 1 155m, 1 095s, 1 030m, 870m, 800m, 745s, 735m, 700s, 580w, 530s, 520s, 470w, and 420w cm^{-1} .

1,2;1,2;2,3;2,3;3,4;3,4-Hexa- μ -hydrido-1,2,3-trihydrido-1,1,1,3,3,3-hexakis(trimethylphosphine)-1,3-diruthenium(II)aluminium, (4).—Tetramethylethylenediamine (0.2 cm³, 1.33 mmol) was added to a toluene solution of [(Me₃P)₃HRuAlH₄]₂ (0.52 g, 0.72 mmol). After stirring for 5 h, the solvent was removed, the residue extracted with hexane, and the extract reduced in volume and cooled to -80 °C to afford white crystals, m.p. 125–134 °C (decomp.). Yield: 0.29 g, 58%. I.r.: 1 800m, 1 740s, 1 650m, 1 340m, 1 285s, 960m, 940s, 860m, 845m, 730m, 680m, and 590m cm⁻¹.

1,2;1,2;2,3;2,3;3,4;3,4-Hexa- μ -hydrido-1,2,3,4-tetrahydrido-1,1,1,4,4,4-hexakis(triphenylphosphine)-1,4-diosmium(II)-2,3-dialuminium, (5).—To a suspension of LiAlH₄ (0.21 g, 5.53 mmol) in diethyl ether (60 cm³) at -78 °C was added OsCl₂(PPh₃)₃¹⁴ (1.33 g, 2.35 mmol). The mixture was stirred for 10 min, then allowed to warm to room temperature. After stirring for 16 h the solvent was removed and the yellow residue extracted with toluene (2 × 40 cm³); reduction in volume and cooling to -20 °C produced a white microcrystalline solid, m.p. 107–114 °C (decomp.). Yield: 0.41 g, 35%. I.r.: 1 950w, 1 875m, 1 770s, 1 670w, 1 430m, 1 300m, 1 175m, 1 150m, 1 090s, 1 025m, 1 000m, 870br, m, 745s, 690s, 565m, 520s, and 410m cm⁻¹.

1,2;1,2;2,3;2,3;3,4;3,4-Hexa- μ -hydrido-1,2,3,4-tetrahydrido-1,1,1,4,4,4-hexakis(trimethylphosphine)-1,4-diosmium(II)-2,3-dialuminium, (6).—To a stirred solution of LiAlH₄ (0.2 g, 5.53 mmol) in thf (100 cm³) was added OsCl₂(PMe₃)₄¹⁵ (1.00 g, 1.72 mmol) and the solution refluxed until colourless (ca. 3 h). After cooling, the solvent was removed and the oil dried under vacuum for 48 h. Extraction with hexane (2 × 30 cm³) and reduction of the extract to 10 cm³ gave, on cooling, a white crystalline solid, m.p. 89–97 °C (decomp.). Yield: 0.32 g, 40%. I.r.: 1 795m, 1 730s, 1 700s, 1 655m, 1 420w, 1 325m, 1 300m, 1 280s, 1 140m, 960m, 940m, 870w, 850m, 815m, 675m, 670m, 600w, and 570m cm⁻¹.

Acknowledgements

We thank the S.E.R.C. for a studentship (to A. R. B.), Miss Sue

Johnson for assistance with ²⁷Al n.m.r. spectra, and Johnson Matthey PLC for loan of ruthenium and osmium.

References

- 1 T. J. Marks and J. R. Kolb, *Chem. Rev.*, 1977, **77**, 263.
- 2 A. Hajos, 'Complex Hydrides,' Elsevier, New York, 1979.
- 3 M. V. Baker and L. D. Field, *J. Chem. Soc., Chem. Commun.*, 1984, 996.
- 4 T. J. Marks and W. J. Kennelly, *J. Am. Chem. Soc.*, 1975, **97**, 1439.
- 5 (a) J. B. Letts, T. J. Mazanec, and D. W. Meek, *J. Am. Chem. Soc.*, 1982, **104**, 3898; (b) J. A. Statler, G. Wilkinson, M. Thornton-Pett, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1984, 1731.
- 6 P. W. Frost, J. A. K. Howard, and J. L. Spencer, *J. Chem. Soc., Chem. Commun.*, 1984, 1362.
- 7 G. S. Girolami, G. Wilkinson, M. Thornton-Pett, and M. B. Hursthouse, *J. Am. Chem. Soc.*, 1983, **105**, 6752; C. G. Howard, G. S. Girolami, G. Wilkinson, M. Thornton-Pett, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1985, 921.
- 8 A. R. Barron, M. Motevalli, M. B. Hursthouse, and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1985, 664.
- 9 A. R. Barron, D. Lyons, G. Wilkinson, M. Motevalli, A. J. Howes, and M. B. Hursthouse, preceding paper.
- 10 R. A. Jones, F. Mayor Real, G. Wilkinson, A. M. Galas, M. B. Hursthouse, and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 551.
- 11 J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High-Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959, p. 223.
- 12 W. A. Skupinski, J. C. Huffman, J. W. Bruno, and K. G. Caulton, *J. Am. Chem. Soc.*, 1984, **106**, 8128.
- 13 R. K. Harris and B. E. Mann, 'N.m.r. and the Periodic Table,' Academic Press, London, 1978.
- 14 A. Oudeman, F. van Rantwijk, and H. Van Bekkum, *J. Coord. Chem.*, 1974, **4**, 1.
- 15 A. S. Alves, D. S. Moore, R. A. Andersen, and G. Wilkinson, *Polyhedron*, 1982, **1**, 83.
- 16 T. A. Stephenson, P. W. Armit, and A. S. F. Boyd, *J. Chem. Soc., Dalton Trans.*, 1975, 1663.
- 17 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 945.

Received 23rd April 1985; Paper 5/567