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Roles of a tetrahydroborate ligand in a facile route to ruthenium(II) ethyl hydride complexes, and a kinetic study of ethane reductive elimination

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The tetrahydroborate ligand in $[Ru(\eta^2\text{-}BH_4)(CO)H(PMe_2Ph)_2]$, **1**, allows conversion under very mild conditions to $[Ru(CO)(Et)H(PMe_2Ph)_3]$, **7**, by way of $[Ru(\eta^2\text{-}BH_4)(CO)Et(PMe_2Ph)_2]$, **4**. Deprotection of the hydride ligand in **7** (by BH_3 abstraction) occurs only in the final step, thus preventing premature ethane elimination. A deviation from the route from **4** to **7** yields $[Ru(\eta^2\text{-}BH_4)(COEt)(PMe_2Ph)_3]$, **6**, but does not prevent ultimate conversion to **7**. Modification of the treatment of **4** yields an isomer of **7**, **10**. Both isomers eliminate ethane at temperatures above 250 K: the immediate product of elimination, thought to be $[Ru(CO)(PMe_2Ph)_3]$, **11**, can be trapped as $[Ru(CO)(PMe_2Ph)_4]$, **12**, $[Ru(CO)H_2(PMe_2Ph)_3]$, **3a**, or $[Ru(CO)(C{\equiv}CCMe_3)H(PMe_2Ph)_3]$, **13**. The elimination is a simple first-order process with negative $\Delta S^{\ddagger}$ and (for **7**) a normal kinetic isotope effect (k_H/k_D = 2.5 at 287.9 K). These results, coupled with labelling studies, rule out a rapid equilibrium with a σ-ethane intermediate prior to ethane loss.

Introduction

For many years chemists have been interested in transition metal complexes which contain both alkyl and hydride ligands. Such complexes are known (or believed) to be involved in catalytic cycles, and the very reaction which usually severely limits their stability (alkane elimination) is itself believed to be the final step in the catalytic hydrogenation of alkenes.[1]

One of the first complexes of this type to be prepared (by Chatt and Hayter[2]) was the ruthenium(II) complex $[Ru(Me)H(Ph_2PCH_2CH_2PPh_2)_2]$, in which the methyl and hydride ligands were conclusively shown to be mutually *cis*. Subsequently Wilkinson and his co-workers reported the preparation of $[Ru(Me)H(OEt_2)_2(PPh_3)_2]$[3] and *cis*-$[Ru(R)H(PMe_3)_4]$ (R = Me[4] and Et[5]), and Bergman obtained *trans*-$[Ru(Me)H(Me_2PCH_2PMe_2)_2]$.[6] With the discovery that simple alkanes may be activated by some transition metal complexes, however, the focus has to some extent shifted away from ruthenium to adjacent metals in the periodic table (for example iridium,[7,8] rhodium,[9,10] osmium,[11] iron[12] and rhenium[13]), for all of which complexes containing both alkyl and hydride ligands have now been obtained from direct reactions with simple alkanes.

We were interested in synthesising and studying the chemistry of ruthenium(II) complexes containing a carbonyl ligand as well as an alkyl and a hydride ligand, because its presence increases the range of reactions which the complexes can potentially undergo. We recognised, however, that the carbonyl ligand was likely also to increase the ease with which the complexes would decompose by alkane elimination, but we hoped to avoid decomposition by generating the complexes under mild conditions. Such an approach was used by Jones and Feher[9] in their studies of alkane activation by rhodium(I) complexes, when they employed an indirect route to generate the rhodium(III) species $[Rh(\eta^5\text{-}C_5Me_5)(Me)H(PMe_3)]$, and were then able to determine its stability with respect to methane elimination. Their synthetic route involved halide abstraction from $[Rh(\eta^5\text{-}C_5Me_5)(Me)Cl(PMe_3)]$ with Ag^+, followed by low-temperature treatment of the resulting cation with a source of hydride ion. We were able to obtain $[Ru(CO)_2(Ph)H(PMe_2Ph)_2]$ by a similar two-stage route from $[Ru(CO)_2(Ph)Cl(PMe_2Ph)_2]$,[14,15] and a second isomer of the same complex from $[Ru(CO)_2Cl(H)(PMe_2Ph)_2]$ and LiPh,[15,16] but our attempts to synthesise similar complexes with an alkyl rather than a phenyl ligand by these methods were unsuccessful. Work which we have recently published,[17] however, suggested an alternative route. We found that the η²-tetrahydroborate complex $[Ru(\eta^2\text{-}BH_4)(CO)H(PMe_2Ph)_2]$, **1**, reacted at low temperatures with nucleophiles L′ {(a), L′ = PMe_2Ph; (b), L′ = CO; (c), L′ = 4-methylpyridine (4-MePy)} by displacement of the bridging hydrogen *trans* to the hydride ligand, giving products $[Ru(\eta^1\text{-}BH_4)(CO)H(L')(PMe_2Ph)_2]$, **2a–2c**. Further treatment with L′ yielded dihydrido-complexes $[Ru(CO)H_2(L')(PMe_2Ph)_2]$, **3a–3c**, by abstraction of BH_3 as the adduct $H_3B{\cdot}L'$. Complex **1** also reacted with C_2H_4, but here initial (and reversible) formation of $[Ru(\eta^1\text{-}BH_4)(CO)(C_2H_4)H(PMe_2Ph)_2]$ was followed by combination of ethene and hydride ligands, allowing a reversion to η²-binding of the tetrahydroborate ligand in the product ethyl complex $[Ru(\eta^2\text{-}BH_4)(CO)Et(PMe_2Ph)_2]$, **4**.

These results demonstrated (i) that the ease with which the tetrahydroborate ligand changes its mode of bonding to ruthenium allows conversion of a hydride ligand into an alkyl ligand under extremely mild conditions, and (ii) that an η²-tetrahydroborate ligand can be regarded as a protected hydride ligand, from which the protection can be removed at an appropriate point, again under very mild conditions, by treatment with two molar equivalents of a nucleophile. In combination, these features seemed to offer a relatively simple route by which complexes containing both an alkyl and a hydride ligand might be prepared without risking premature decomposition by alkane elimination. We therefore studied the reaction of **4** with the nucleophile PMe_2Ph, hoping to generate a complex containing carbonyl, ethyl and hydride ligands. We did, however, envisage the possibility that complications might arise from side-reactions involving combination of the ethyl and carbonyl ligands in **4**.

Apart from the original interest in the mechanism of alkane elimination in the context of catalytic cycles, the fact that the reaction represents the exact reverse of alkane elimination has attracted the attention of theoretical chemists[18,19] and encouraged kinetic studies of the elimination process from well-characterised complexes containing both alkyl and hydride ligands.[20–32] The success of the synthetic approach outlined above, through which we obtained two isomers of $[Ru(CO)(Et)H(PMe_2Ph)_3]$, prompted us not only to determine the conditions under which alkane elimination occurred from the complexes but also to carry out a kinetic study of

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the elimination process. Both synthetic and kinetic work are reported in this paper.

Results and discussion

The NMR data for all new ruthenium complexes are collected in Table 1. All ^{13}C, ^{31}P and ^{11}B data refer to spectra recorded with full proton-decoupling. The ^{1}H spectra were recorded with full ^{31}P-coupling, but $^{1}H\{^{31}P\}$ spectra were also run, with both broad-band and selective decoupling. The NMR data established that all the new ruthenium(II) complexes described below contain either two mutually *trans* PMe_2Ph ligands or a *mer* arrangement of three PMe_2Ph ligands. For complexes containing either an ethyl or a propanoyl ligand, $^{1}H\{^{1}H\}$ decoupling and/or ^{1}H–^{1}H COSY experiments were employed to confirm the coupling between CH_2 and CH_3 protons.

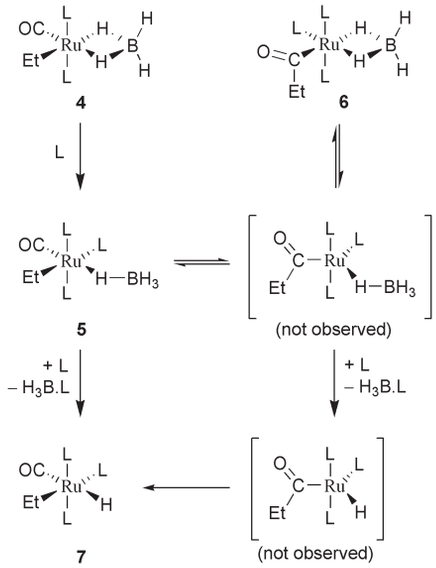
(i) The reaction of [Ru(η²-BH₄)(CO)Et(PMe₂Ph)₂], 4, with PMe₂Ph

At 193 K in CD_3COCD_3 solution, the reaction between equimolar quantities of **4**[17] and PMe_2Ph led to the almost quantitative formation of a single product, [Ru(η¹-BH_4)(CO)Et(PMe_2Ph)$_3$], **5**. Resonances for the ethyl group were found in the ^{1}H NMR spectrum at δ 1.10 (q, CH_3CH_2) and δ 0.98 (m, CH_3CH_2), the latter chemical shift indicating that this group was directly attached to the metal,[17,33] and not part of an acyl ligand.[34] Whereas the methylene protons were coupled to the methyl protons and to all three ^{31}P nuclei, the apparent quartet splitting of the methyl resonance was shown to be due to couplings of roughly equal magnitude to the unique ^{31}P nucleus and the two methylene protons. In **4**, where the ethyl ligand is *cis* to both PMe_2Ph ligands, coupling of the methyl protons in this ligand to the ^{31}P nuclei is too weak to detect.[17] This implied that in **5** the ethyl ligand was *trans* to the unique PMe_2Ph ligand.

The ^{13}C NMR spectrum of **5** recorded in CD_3COCD_3 solution was of rather poor quality. On repeating the reaction in $C_6D_5CD_3$ solution, we concluded from ^{1}H and ^{31}P spectra that **5** was again formed, and obtained a better ^{13}C spectrum. The methylene carbon chemical shift confirmed that the ethyl group was directly attached to the metal[17,33] and not part of an acyl ligand,[34] and the fact that the doublet splitting of the resonance was considerably greater than the triplet splitting provided further evidence that the ethyl group was *trans* to the unique PMe_2Ph ligand.[33] In contrast, the appearance of the resonance for the carbonyl ligand in **5**, at δ 206.5, made it clear that the coupling constants to the three ^{31}P nuclei must all be of similar magnitude, placing this ligand *cis* to all three PMe_2Ph ligands.

A variable temperature ^{1}H NMR study of **5** in CD_3COCD_3 solution revealed that the tetrahydroborate ligand was η¹-bonded to the metal and was undergoing some kind of fluxional motion. At 193 K, a broad resonance integrating for a single proton was observed at δ −12.3, a chemical shift similar to that of δ −11.9 for the bridging hydrogen in [Ru(η¹-BH_4)(CO)H(PMe_2Ph)$_3$], **2a**.[17] We were unable to detect the (presumably extremely broad) resonance for the three terminal protons. When the solution was warmed, the resonance at δ −12.3 rapidly broadened, becoming undetectable at 223 K. Further increase in temperature resulted in the appearance of a very broad resonance at δ −2.3, which sharpened significantly as the temperature was raised to 253 K. Integration showed this resonance to be due to four protons, indicating that the fluxional process was exchanging bridging and terminal tetrahydroborate protons.[35] The corresponding resonance for **2a** was at δ −1.7.[17] Apart from the effects of a further reaction of **5** (see below), the changes in the appearance of the ^{1}H NMR spectrum with temperature were fully reversible, as were those for **2a**. We concluded that the ligand arrangement in **5** was that shown in Scheme 1.

Although **5** was the kinetic product of the reaction between **4** and PMe_2Ph in both CD_3COCD_3 and $C_6D_5CD_3$, it subsequently rearranged (in both solvents) to a new complex, [Ru(η²-BH_4)(COEt)(PMe_2Ph)$_3$], **6**, a process accelerated by raising the temperature to *ca.* 240–250 K. NMR spectra for **6** were similar in both solvents, but those obtained in $C_6D_5CD_3$ (at 240 K) were of rather better quality. The ethyl group was now represented by resonances in the ^{1}H spectrum at δ 1.22 (t, CH_3CH_2) and δ 2.92 (q, CH_3CH_2), and in the ^{13}C spectrum at δ 11.5 (s, CH_3CH_2) and δ 53.6 (s, CH_3CH_2). Comparison with **5** revealed major changes in the methylene chemical shifts and the loss of all splittings due to the ^{31}P nuclei, both indicating the incorporation of the ethyl group into an acyl ligand.[34] This was confirmed by the detection of the acyl resonance at δ 261.8 in the ^{13}C spectrum.[34] The resonances for the protons in the now η²-bonded tetrahydroborate ligand were very reminiscent of those for both **4** and **1**,[17] with a broad resonance at δ 4.79 for the two equivalent terminal protons and separate broad resonances at δ −4.85 and δ −7.41 for the two inequivalent bridging protons. One distinct difference, however, was that the resonance at δ −7.41 showed a large doublet splitting ($|^{2}J_{PH}|$ = 39.6 Hz) by the ^{31}P nucleus in the unique PMe_2Ph ligand. In **1** and **4**, both PMe_2Ph ligands are *cis* to each of the bridging tetrahydroborate hydrogens, whereas in **6** (see Scheme 1) one bridging hydrogen must of necessity lie *trans* to the unique PMe_2Ph ligand. We assume that it is this hydrogen whose resonance shows the doublet splitting. Letts *et al.*[36] have observed the same phenomenon for [Ru(η²-BH_4)H{PhP($CH_2CH_2PPh_2$)$_2$}]. As in the case of **1** and **4**, the resonances for the hydrogens in the tetrahydroborate ligand broadened with increasing temperature (a process which was reversed on cooling), indicating a scrambling of bridging and terminal hydrogens, presumably *via* an η¹-tetrahydroborate intermediate. The onset of broadening occurred at a significantly lower temperature for the bridging hydrogen *trans* to the propanoyl ligand than for that *trans* to PMe_2Ph, implying that the Ru–HB bond *trans* to the acyl ligand breaks more readily than that *trans* to PMe_2Ph. The two steps which connect **5** and **6** in Scheme 1 account both for the conversion of **5** to **6** and for the fluxionality of the η²-tetrahydroborate ligand in **6**.



Scheme 1 The route to isomer **7** of [Ru(CO)(Et)H(PMe_2Ph)$_3$] (L = PMe_2Ph).

In both CD_3COCD_3 and $C_6D_5CD_3$, the initial effect of treating **5** with at least an equimolar amount of PMe_2Ph and then warming the solution to 250 K was to produce a mixture of **6** and a further species **7**. The ratio of **6** to **7** slowly decreased, with eventual quantitative formation of **7**. As **7** appeared, so also did an equimolar quantity of $H_3B{\cdot}PMe_2Ph$.[17] **7** could also be obtained, together with $H_3B{\cdot}PMe_2Ph$, by treating **6** with PMe_2Ph at 243 K. In addition to three PMe_2Ph ligands, it contained a hydride ligand, characterised by a quartet resonance ($|^{2}J_{PH}|$ = 25.0 Hz) at δ −6.52 in the ^{1}H NMR spectrum, and a carbonyl ligand, responsible for a doublet of triplets ($|^{2}J_{PC}|$ = 7.3

Table 1 NMR data for new complexes[a]

Complex	Nucleus, temperature	δ/ppm (multiplicity, area)	Assignment	Coupling constants/Hz	Assignment
5	^{31}P, 213 K[b]	−10.8 (t)	PMe_2Ph	28.5	$\|^2J_{PP}\|$
		5.5 (d)	PMe_2Ph	28.5	$\|^2J_{PP}\|$
	^{1}H, 213 K[b]	−12.3 (br, 1)[c]	$RuHBH_3$		
		0.98 (m, 2)[d]	CH_3CH_2	6.8	$\|^3J_{HH}\|$
		1.10 (q, 3)	CH_3CH_2	6.8	$\|^3J_{HH}\|$
				6.8	*trans*-$\|^4J_{PH}\|$
		1.14 (d, 6)	PMe_2Ph	7.1	$\|^2J_{PH}\|$
		1.56 (t, 6)	PMe_2Ph	6.6	$\|^2J_{PH} + {}^4J_{PH}\|$
		1.63 (t, 6)	PMe_2Ph	6.0	$\|^2J_{PH} + {}^4J_{PH}\|$
	^{13}C, 210 K	5.9 (dt)[d]	CH_3CH_2	49.2	*trans*-$\|^2J_{PC}\|$
		14.8 (t)	PMe_2Ph	28.8	$\|^1J_{PC} + {}^3J_{PC}\|$
		15.9 (t)	PMe_2Ph	29.5	$\|^1J_{PC} + {}^3J_{PC}\|$
		17.9 (d)	PMe_2Ph	21.5	$\|^1J_{PC}\|$
		21.8 (s)	CH_3CH_2		
		206.5 (m)[d]	CO		
6	^{31}P, 240 K	6.9 (d)	PMe_2Ph	35.5	$\|^2J_{PP}\|$
		20.8 (t)	PMe_2Ph	35.5	$\|^2J_{PP}\|$
	^{1}H, 240 K	−7.41 (br d, 1)	RuH_2BH_2[e]	39.6	*trans*-$\|^2J_{PH}\|$
		−4.85 (br, 1)	RuH_2BH_2[f]		
		1.09 (t, 6)	PMe_2Ph	5.6	$\|^2J_{PH} + {}^4J_{PH}\|$
		1.16 (d, 6)	PMe_2Ph	8.7	$\|^2J_{PH}\|$
		1.22 (t, 3)	CH_3CH_2CO	7.2	$\|^3J_{HH}\|$
		1.70 (t, 6)	PMe_2Ph	5.9	$\|^2J_{PH} + {}^4J_{PH}\|$
		2.92 (q, 2)	CH_3CH_2CO	7.2	$\|^3J_{HH}\|$
		4.79 (br, 2)	RuH_2BH_2		
	^{13}C, 240 K	11.5 (s)	CH_3CH_2CO		
		13.9 (t)	PMe_2Ph	29.5	$\|^1J_{PC} + {}^3J_{PC}\|$
		18.7 (d)	PMe_2Ph	28.8	$\|^1J_{PC}\|$
		ca. 20.4[g]	PMe_2Ph		
		53.6 (s)	CH_3CH_2CO		
		261.8 (m)[d]	CH_3CH_2CO		
7	^{31}P, 240 K	2.6 (t)	PMe_2Ph	21.2	$\|^2J_{PP}\|$
		18.4 (d)	PMe_2Ph	21.2	$\|^2J_{PP}\|$
	^{1}H, 240 K	−6.52 (q, 1)	RuH	25.0	$\|^2J_{PH}\|$
		0.92 (d, 6)	PMe_2Ph	6.0	$\|^2J_{PH}\|$
		1.21 (m, 2)[d]	CH_3CH_2	7.5	$\|^3J_{HH}\|$
		1.48 (t, 6)	PMe_2Ph	5.4	$\|^2J_{PH} + {}^4J_{PH}\|$
		1.50 (t, 6)	PMe_2Ph	5.6	$\|^2J_{PH} + {}^4J_{PH}\|$
		1.89 (dt, 3)	CH_3CH_2	5.9	*trans*-$\|^4J_{PH}\|$
				7.5	$\|^3J_{HH}\|$
	^{13}C, 240 K	−3.5 (dt)	CH_3CH_2	48.6	*trans*-$\|^2J_{PC}\|$
				10.4	*cis*-$\|^2J_{PC}\|$
		19.4 (t)	PMe_2Ph	27.7	$\|^1J_{PC} + {}^3J_{PC}\|$
		19.7 (t)	PMe_2Ph	30.5	$\|^1J_{PC} + {}^3J_{PC}\|$
		21.7 (d)	PMe_2Ph	20.8	$\|^1J_{PC}\|$
		25.2 (s)	CH_3CH_2		
		206.0 (dt)	CO	7.3	$\|^2J_{PC}\|$
				10.8	$\|^2J_{PC}\|$
8	^{31}P, 220 K	10.1 (s)	PMe_2Ph		
	^{1}H, 220 K	−9.87 (br, 1)[h]	$RuHBH_3$		
		0.74 (sext, 2)	CH_3CH_2	7.3	$\|^3J_{HH}\|$
				7.3	$\|^3J_{PH}\|$
		1.52 (t, 3)	CH_3CH_2	7.3	$\|^3J_{HH}\|$
		1.56 (t, 6)	PMe_2Ph	6.2	$\|^2J_{PH} + {}^4J_{PH}\|$
		1.60 (s, 3)	4-*Me*Py		
		1.64 (t, 6)	PMe_2Ph	5.7	$\|^2J_{PH} + {}^4J_{PH}\|$
		4.70 (br, 3)[h]	$RuHBH_3$		
		7.34 (d, 2)	4-Me*Py*, $H^{3,5}$	5.1	$\|^3J_{HH}\|$
		8.79 (d, 2)	4-Me*Py*, $H^{2,6}$	5.1	$\|^3J_{HH}\|$
	^{11}B, 200 K	−29.0 (br)	$RuHBH_3$		
9	^{31}P, 250 K	14.9 (s)	PMe_2Ph		
	^{1}H, 250 K	−14.74 (t, 1)	RuH	24.7	$\|^2J_{PH}\|$
		0.50 (tq, 2)	CH_3CH_2	10.8	$\|^3J_{PH}\|$
				7.5	$\|^3J_{HH}\|$
		1.62 (t, 6)	PMe_2Ph	5.9	$\|^2J_{PH} + {}^4J_{PH}\|$
		1.63 (t, 6)	PMe_2Ph	5.7	$\|^2J_{PH} + {}^4J_{PH}\|$
		1.66 (s, 3)	4-*Me*Py		
		1.82 (t, 3)	CH_3CH_2	7.5	$\|^3J_{HH}\|$
		6.00 (d, 2)	4-Me*Py*, $H^{3,5}$	5.9	$\|^3J_{HH}\|$
		7.85 (d, 2)	4-Me*Py*, $H^{2,6}$	5.9	$\|^3J_{HH}\|$
	^{13}C, 250 K	11.2 (t)	CH_3CH_2	11.7	$\|^2J_{PC}\|$
		15.9 (t)	PMe_2Ph	27.6	$\|^1J_{PC} + {}^3J_{PC}\|$
		18.8 (t)	PMe_2Ph	27.6	$\|^1J_{PC} + {}^3J_{PC}\|$
		20.0 (s)	4-*Me*Py		
		23.9 (s)	CH_3CH_2		
		125.5 (s)	4-Me*Py*, $C^{3,5}$		
		150.3 (s)	4-Me*Py*, C^4		
		153.0 (s)	4-Me*Py*, $C^{2,6}$		

Table 1 (*Contd.*)

Complex	Nucleus, temperature	δ/ppm (multiplicity, area)	Assignment	Coupling constants/Hz	Assignment
		200.9 (t)	CO	10.8	$\|^2J_{PC}\|$
10	^{31}P, 245 K	−4.1 (t)	PMe_2Ph	22.3	$\|^2J_{PP}\|$
		11.0 (d)	PMe_2Ph	22.3	$\|^2J_{PP}\|$
	^{1}H, 245 K	−8.05 (dt, 1)	RuH	94.4	*trans*-$\|^2J_{PH}\|$
				28.9	*cis*-$\|^2J_{PH}\|$
		0.51 (tqd, 2)	CH_3CH_2	8.8	$\|^3J_{PH}\|$
				7.5	$\|^3J_{HH}\|$
				7.4	$\|^3J_{PH}\|$
		0.95 (d, 6)	PMe_2Ph	6.2	$\|^2J_{PH}\|$
		1.44 (t, 6)	PMe_2Ph	5.6	$\|^2J_{PH} + {}^4J_{PH}\|$
		1.51 (t, 6)	PMe_2Ph	5.2	$\|^2J_{PH} + {}^4J_{PH}\|$
		1.73 (t, 3)	CH_3CH_2	7.5	$\|^3J_{HH}\|$
	^{13}C, 245 K	0.5 (q)	CH_3CH_2	10.8	$\|^2J_{PC}\|$
		16.2 (d)	PMe_2Ph	19.4	$\|^1J_{PC}\|$
		16.5 (td)[d]	PMe_2Ph	27.7	$\|^1J_{PC} + {}^3J_{PC}\|$
		22.6 (td)[d]	PMe_2Ph	31.2	$\|^1J_{PC} + {}^3J_{PC}\|$
		26.4 (s)	CH_3CH_2		
		202.9 (td)	CO	11.4	$\|^2J_{PC}\|$
				8.0	$\|^2J_{PC}\|$
12	^{31}P, 260 K	3.7 (s)	PMe_2Ph		
	^{1}H, 260 K	1.32 (t)[j]	PMe_2Ph	4.1	$\|^2J_{PH} + {}^4J_{PH}\|$
	^{13}C, 283 K	23.9 (tt)	PMe_2Ph	23.2	$\|^1J_{PC} + {}^3J_{PC}\|$
				3.5	*cis*-$\|^3J_{PC}\|$
		223.9 (quin)	CO	4.5	$\|^2J_{PC}\|$
13	^{31}P, 250 K	−6.0 (t)	PMe_2Ph	21.5	$\|^2J_{PP}\|$
		6.0 (d)	PMe_2Ph	21.5	$\|^2J_{PP}\|$
	^{1}H, 250 K	−7.69 (dt, 1)	RuH	92.5	*trans*-$\|^2J_{PH}\|$
				27.0	*cis*-$\|^2J_{PH}\|$
		1.08 (d, 6)	PMe_2Ph	6.8	$\|^2J_{PH}\|$
		1.54 (s, 9)	CMe_3		
		1.71 (t, 6)	PMe_2Ph	6.0	$\|^2J_{PH} + {}^4J_{PH}\|$
		1.76 (t, 6)	PMe_2Ph	6.7	$\|^2J_{PH} + {}^4J_{PH}\|$
	^{13}C, 250 K	16.8 (d)	PMe_2Ph	20.8	$\|^1J_{PC}\|$
		20.5[j]	PMe_2Ph		
		22.1 (t)	PMe_2Ph	31.7	$\|^1J_{PC} + {}^3J_{PC}\|$
		29.8 (s)	CMe_3		
		32.9 (s)	CMe_3		
		101.2 (td)	RuC≡C	21.4	$\|^2J_{PC}\|$
				18.8	$\|^2J_{PC}\|$
		116.0 (s)	RuC≡C		
		204.4 (q)	CO	10.9	$\|^2J_{PC}\|$

[a] Except where indicated otherwise, spectra were recorded in $C_6D_5CD_3$ solution. Resonances for phenyl protons and carbon atoms omitted. [b] Recorded in CD_3COCD_3 solution. [c] Recorded at 193 K: see text. [d] One or more splittings not fully resolved. [e] *Trans* to PMe_2Ph. [f] *Trans* to EtCO. [g] Partly masked by solvent resonances. [h] Recorded at 195 K: see text. [i] Central peak of triplet broadened: see text. [j] Obscured by solvent resonances: located by a ^{1}H–^{13}C COSY experiment.

and 10.8 Hz respectively) in the ^{13}C spectrum at δ 206.0. The sizes of the coupling constants indicated that both ligands were *cis* to all three PMe_2Ph ligands.[37] The remaining coordination site in **7** was occupied by an ethyl ligand. The ^{1}H and ^{13}C resonances for this ligand, which were linked by a ^{1}H–^{13}C COSY experiment, showed splitting patterns very similar to those for the ethyl ligand in **5**, confirming that here again the ethyl ligand was *trans* to the unique PMe_2Ph ligand. Thus **7** was our desired product, $[Ru(CO)(Et)H(PMe_2Ph)_3]$, with the ligand arrangement shown in Scheme 1.

The initial reaction between **4** and PMe_2Ph could have involved (a) abstraction of BH_3 by the PMe_2Ph, (b) combination of ethyl and carbonyl ligands, or (c) a switch to η^1-coordination of the tetrahydroborate ligand. Each would have left a vacant site on the metal to be occupied by PMe_2Ph, giving **7**, **6** and **5** respectively. In the event, (c) proved to be the kinetically favoured pathway, although the resulting complex **5** was less stable than **6**. On addition of more PMe_2Ph to **5**, rearrangement to **6** still managed to compete with the abstraction of BH_3 from **5** to give **7**. Nevertheless the ultimate result was (as we had hoped) complete conversion to **7**. Given the evidence for the extreme lability of the Ru–H bonds to the tetrahydroborate ligand in **6**, it seems reasonable that the first step on the route from **6** to **7** should be the formation of the five-coordinate species $[Ru(\eta^1\text{-}BH_4)(COEt)(PMe_2Ph)_3]$ (see Scheme 1). The order of the remaining two steps (breakdown of the acyl ligand and abstraction of BH_3) is uncertain: both possibilities are shown in the scheme.

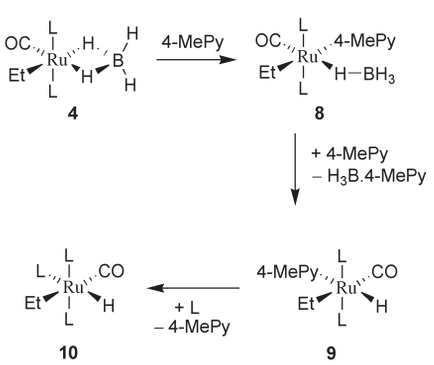
Thus $[Ru(\eta^2\text{-}BH_4)(CO)H(PMe_2Ph)_2]$, **1**, is indeed a convenient starting material from which to make a complex containing carbonyl, alkyl and hydride ligands. As we had anticipated, the stability of **7** proved to be distinctly limited, with ethane elimination occurring at a significant rate at temperatures above 250 K. In addition, none of the intermediates between **1** and **7** was stable at room temperature (although **4** can be stabilised by storage under C_2H_4[17]), but the fact that each step could be carried out at low temperature meant that this was not a handicap. Insurance against ethane elimination occurring earlier in the reaction sequence was provided by the fact that the hydride ligand required for the elimination was "protected" (by being part of a tetrahydroborate ligand) until the BH_3 was removed at the end of the sequence.

(ii) The reaction of 4 with 4-MePy: a route to an isomer of 7

Like PMe_2Ph, 4-MePy proved to be capable of displacing one bridging hydrogen from the metal in **4**, yielding $[Ru(\eta^1\text{-}BH_4)(CO)Et(4\text{-}MePy)(PMe_2Ph)_2]$, **8**. The reaction was carried out in $C_6D_5CD_3$ at 220 K, and **8** was sufficiently stable at this temperature to allow ^{1}H and ^{31}P NMR spectra to be obtained. These established the presence of a single 4-MePy ligand and an ethyl group in **8**. On the basis of the chemical shift for the

methylene protons, δ 0.74, the ethyl group was evidently directly attached to the metal. No resonances for the tetrahydroborate ligand could be detected at 220 K: on cooling to 210 K a very broad resonance integrating for one proton was observed at δ −9.87, and this sharpened considerably on further cooling to 195 K. At this temperature a further, extremely broad, resonance had become visible at δ 4.70. Comparison with the spectra of the η^1-tetrahydroborate complexes **2a**, **2c**[17] and **5** indicated that the resonance at δ −9.87 was due to the bridging hydrogen in an η^1-bonded tetrahydroborate ligand, and it seemed likely that the resonance at δ 4.70 was due to the three non-bridging hydrogens. The collapse of the resonances on restoring the temperature to 220 K was presumably due to increasingly rapid scrambling of the bridging and terminal hydrogens, as observed for **2a**, **2c** and **5**, but the limited stability of **8** thwarted attempts to obtain spectra at high enough temperatures to detect the averaged resonance for all four hydrogens. An ^{11}B spectrum of **8**, recorded at 200 K, contained a broad resonance at δ −29.0, close to the value of δ −28.9 for **2a**.[17] We inferred the presence of the carbonyl ligand in **8** from the fact that **8** was formed from **4** and (see below) reacted with more 4-MePy to form **9**, both of which definitely contained a carbonyl ligand.

The reaction of **8** with more 4-MePy was carried out at 250 K, and it yielded H_3B·4-MePy[17] and a single ruthenium complex [Ru(CO)(Et)H(4-MePy)(PMe_2Ph)$_2$], **9**. Complex **9** was sufficiently stable for good quality NMR spectra to be obtained at 250 K, and these established the presence of all the ligands. We had expected a ligand arrangement analogous to that in **7**, with mutually *trans* carbonyl and hydride ligands, and the ethyl ligand *trans* to 4-MePy. The clearest indication that this was not the case came from the chemical shift for the hydride ligand, δ −14.74, very different from the values (δ −4.46 to δ −7.16) for a hydride *trans* to CO in **2b**, **3a**–**3c**[17] and **7**, but similar to those (δ −15.01, δ −11.43 and δ −11.3) for a hydride *trans* to 4-MePy in **2c**, **3c**[17] and [Ru(CO)H(4-MePy)$_2$(PPh_3)$_2$]BF_4[38] respectively. On this basis we assigned the ligand arrangement shown in Scheme 2 to complex **9**.



Scheme 2 The route to isomer **10** of [Ru(CO)(Et)H(PMe_2Ph)$_3$] (L = PMe_2Ph). The ligand arrangement in **8** is uncertain.

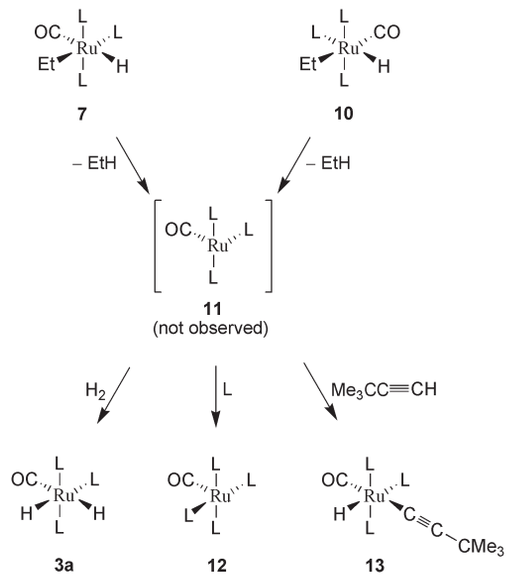
Since we had already decided to study the kinetics of ethane elimination from **7**, the possibility that **9** might exchange its 4-MePy for PMe_2Ph without change in the overall ligand arrangement raised the prospect of obtaining, and studying ethane elimination from, an isomer of **7**. Indeed, treatment of the $C_6D_5CD_3$ solution of **9** with PMe_2Ph at 250 K resulted in the release of 4-MePy and the formation of a single complex **10** whose NMR spectra, recorded at 245 K, confirmed that it was a second isomer of [Ru(CO)(Et)H(PMe_2Ph)$_3$] and clearly indicated the ligand arrangement shown in Scheme 2. The pattern of coupling constants for the resonance for the hydride ligand at δ −8.05 (dt, $|^2J_{PH}|$ = 94.4 and 28.9 Hz respectively) placed it *trans* to the unique PMe_2Ph ligand,[37] while those for the carbon atom in the carbonyl ligand and for the methylene carbon in the ethyl ligand indicated that both of these ligands must be *cis* to all three PMe_2Ph ligands. The chemical shift, δ 0.51, for the methylene protons in the ethyl ligand of **10**, while quite different from that (δ 1.21) for its isomer **7**, in which the ethyl ligand is *trans* to PMe_2Ph rather than to CO, was very similar to the corresponding value of δ 0.50 for **9**, as expected since both complexes have CO *trans* to the ethyl ligand.

The route for the conversion of **4** to **10** is shown in Scheme 2, but it should be noted that the ligand arrangement in **8** is uncertain. We suspect that the weakness of the bond between the metal and the 4-MePy ligand, demonstrated by the ease of conversion of **9** into **10**, also facilitates a switch in the positions of the CO and 4-MePy ligands, but cannot be sure whether this occurs during the formation of **8** or (as implied in Scheme 2) in the process of its conversion into **9**.

(iii) Reactions of isomers 7 and 10 of [Ru(CO)(Et)H(PMe_2Ph)$_3$]

In $C_6D_5CD_3$ solution both isomers of [Ru(CO)(Et)H(PMe_2Ph)$_3$] decomposed at a significant rate at temperatures above 250 K. When the decomposition was monitored by ^{1}H and ^{31}P NMR spectroscopy, it was clear from the steady growth of a singlet resonance at δ 0.80 in the ^{1}H NMR spectrum that the process involved the reductive elimination of ethane, but the ^{31}P spectrum and the remainder of the ^{1}H spectrum became increasingly complex. Evidently the initial ruthenium(0) product, tentatively assumed to be the 16-electron species [Ru(CO)(PMe_2Ph)$_3$], **11**, decomposed with the formation of a variety of other products. In order to simplify matters, various reagents were added in the hope that each would trap **11**, converting it into a single, stable 18-electron species.

Since **7** was formed by treating **4** with two molar equivalents of PMe_2Ph, and **10** by addition of PMe_2Ph to **9**, the simplest method of trapping **11** seemed to be to perform each of the decompositions in the presence of excess PMe_2Ph. When solutions of **7** and **10** containing free PMe_2Ph were warmed to 270 K, NMR studies confirmed that ethane elimination was now accompanied by the formation of a single ruthenium complex, and that both isomers gave the same complex, **12**. The complex was labile, with simultaneous broadening of resonances for coordinated and free PMe_2Ph in the ^{31}P and ^{1}H NMR spectra of the solution, and we did not attempt to isolate it. The likeliest formula for **12**, however, was [Ru(CO)(PMe_2Ph)$_4$], since a ^{13}C NMR spectrum recorded at 283 K included a 1 : 4 : 6 : 4 : 1 quintet at δ 223.9, implying the presence of a carbonyl ligand coupled to four apparently equivalent ^{31}P nuclei. At this temperature, the ^{31}P resonance for **12** was a reasonably sharp singlet, and from the ^{1}H and ^{13}C spectra it appeared that all the methyl substituents in the PMe_2Ph ligands were equivalent. A ligand arrangement consistent with these findings would be a square-based pyramid (see Scheme 3), with CO at the apex and with the four PMe_2Ph ligands forming the base of the pyramid. The methyl proton resonance was not well resolved (although it became a sharp singlet on decoupling at the frequency of the ^{31}P resonance for **12**), but the methyl carbon resonance was a clear triplet of triplets, implying that *trans*-$|^2J_{PP}|$ was large enough to result in "virtual coupling" ($|^1J_{PC} + {}^3J_{PC}|$ = 23.2 Hz) between a given methyl carbon and both its "own" ^{31}P nucleus and the one *trans* to it,[39] and that the resulting triplet was further split by a weaker coupling (*cis*-$|^3J_{PC}|$ = 3.5 Hz) to the two ^{31}P nuclei *cis* to it. It should be noted that the related Ru(0) complex [Ru(PMe_3)($Me_2PCH_2CH_2PMe_2$)$_2$] is known to have a square-pyramidal ligand arrangement.[40] In contrast, however, [Ru(CO)($Me_2PCH_2CH_2PMe_2$)$_2$] is trigonal bipyramidal, and Jones[40] has suggested that this difference in geometry could be linked to the preference of a strongly π-accepting ligand for an equatorial position in the trigonal bipyramidal structure. If **12**, which also contains a carbonyl ligand, is trigonal bipyramidal, it must be fluxional in solution, with pairs of axial and equatorial PMe_2Ph ligands rapidly exchanging positions at 283 K by the Berry[41] mechanism. NMR spectra of **12** recorded at 213 K did show some broadening of the resonances for the ^{31}P nuclei and



Scheme 3 Trapping reactions following ethane elimination from $[Ru(CO)(Et)H(PMe_2Ph)_3]$ (L = PMe_2Ph).

the methyl protons, perhaps as a result of the decreased rate of such a fluxional process.

A $C_6D_5CD_3$ solution of **7** was also treated with H_2 at 250 K. The temperature of the solution was raised to 270 K, and at this temperature the weakening of the resonance for dissolved H_2 at δ 4.50 was accompanied by the steady growth of the singlet resonance for ethane at δ 0.80. The other product of the reaction was shown by NMR studies to be the known complex $[Ru(CO)H_2(PMe_2Ph)_3]$, **3a**.[37] The affinity of $[Ru(CO)(PMe_2Ph)_3]$, **11**, for H_2, and the lability of **12** were both illustrated by the fact that **12** was found to react with H_2 at 260 K to give complete conversion to **3a** and PMe_2Ph.

The third trapping agent tried was $HC{\equiv}CCMe_3$. Both **7** and **10** reacted with $HC{\equiv}CCMe_3$ in $C_6D_5CD_3$ to give slow but complete conversion to ethane and the same ruthenium(II) species, $[Ru(CO)(C{\equiv}CCMe_3)H(PMe_2Ph)_3]$, **13**. Attempts to obtain a solid sample of **13** were unsuccessful, but NMR characterisation confirmed the presence and arrangement of all the ligands. The ^1H NMR spectrum contained a resonance at δ −7.69 (dt, $|^2J_{PH}|$ = 92.5 and 27.0 Hz respectively), indicating that the hydride ligand was *trans* to the unique PMe_2Ph ligand,[37] and there was a singlet at δ 1.54 for the CMe_3 protons. A quartet at δ 204.4 in the ^{13}C spectrum showed that the carbonyl ligand was *cis* to all three PMe_2Ph ligands, and the sizes of the coupling constants for the metal-bound carbon atom in the alkynyl ligand (δ 101.2, td, $|^2J_{PC}|$ = 21.4 and 18.8 Hz, respectively) confirmed that the same was true for the alkynyl ligand. Thus the ligand arrangement was that shown in Scheme 3. In many respects, the NMR spectra of **13** closely resembled those of the known complex $[Ru(CO)_2(C{\equiv}CCMe_3)H(PMe_2Ph)_2]$.[42]

Scheme 3 summarises the reactions of **7** and **10** with the trapping agents. The mechanism of the initial step will be discussed later in the light of the kinetic results. The stereochemistry shown for **11** in the scheme is based on the structure of $[Ru(CO)_2\{PMe(CMe_3)_2\}_2]$,[43] which is a somewhat distorted trigonal bipyramid in which one equatorial site is vacant. It should, however, be noted that $[Ru(Me_2PCH_2CH_2PMe_2)_2]$[44] is believed to be planar, and that the C–Ru–C angle in $[Ru(CO)_2(PMe_3)_2]$[45] must be close enough to 180° to account for the failure to observe an IR band for the symmetric stretching mode of the two carbonyl ligands.

(iv) The preparation and study of $[Ru(CO)(C_2H_4D)D(PMe_2Ph)_3]$, d_2-7

In order to study the effect on the rate of ethane elimination from **7** of replacing the hydride ligand by deuteride, we prepared $[Ru(\eta^2\text{-}BD_4)(CO)D(PMe_2Ph)_2]$, d_5-**1**, by the method used to obtain **1**,[17] but using deuterated reagents. The chemical shift of the resonance for the ^{31}P nuclei in d_5-**1** was virtually identical with that for **1**, and the same applied to the resonances for the PMe_2Ph ligands in the ^1H NMR spectrum of d_5-**1**. Very small resonances were observed at the chemical shifts for the hydride ligand and the tetrahydroborate hydrogens in **1**, indicating that deuteration was almost, but not quite, complete. Conversion of d_5-**1** to $[Ru(\eta^2\text{-}BD_4)(CO)(CH_2CH_2D)(PMe_2Ph)_2]$, d_5-**4**, was then attempted by treatment with C_2H_4 in $C_6D_5CD_3$ at 250 K. Over a period of some 44 h, the ^{31}P resonance for d_5-**1** was completely replaced by a new resonance with almost exactly the same chemical shift as that for **4**,[17] and the new resonances for the protons in the PMe_2Ph ligands also matched those for **4**. In the early stages of the reaction, the growing resonances for the α- and β-protons in the ethyl ligand, at δ 1.30 and δ 0.99 respectively (very close to the values for **4**), were approximately equal in area. The α-proton resonance was a quintet (due to roughly equal splittings by the two ^{31}P nuclei and by two β-protons), and the β-proton resonance was a triplet (the only detectable splittings being by the two α-protons), exactly as expected for $[Ru(\eta^2\text{-}BD_4)(CO)(CH_2CH_2D)(PMe_2Ph)_2]$. As the reaction progressed, however, these resonances became rather poorly resolved and unsymmetrical in shape, and integration indicated that the final distribution of deuterium between α- and β-positions was roughly statistical. Clearly the reversibility of the reaction between **1** and ethene[17] was allowing the $[Ru(\eta^2\text{-}BD_4)(CO)(CH_2CH_2D)(PMe_2Ph)_2]$ to equilibrate with $[Ru(\eta^2\text{-}BD_4)(CO)(CHDCH_3)(PMe_2Ph)_2]$, and probably also with some $[Ru(\eta^2\text{-}BD_4)(CO)(CH_2CH_3)(PMe_2Ph)_2]$ and small amounts of species containing two or more deuterium atoms in the ethyl ligand. We did not anticipate (see later) that the rate of elimination from **7** would be significantly affected by either the presence or the position of deuterium atoms in the ethyl ligand, so this mixture (which, for simplicity, we will call d_5-**4**) was used in the preparation of d_2-**7**. This was undertaken in the same way as the conversion of **4** to **7**. NMR spectra of d_2-**7** were very similar to those of **7**, with the exception of the α- and β-proton resonances in the ethyl ligand which (although at the expected chemical shifts) were rather complex and poorly resolved, and similar in their relative areas to those for the samples of d_5-**4**.

Integration of the small hydride resonance in the ^1H NMR spectrum of the sample of d_2-**7** used in the kinetic studies, relative to those for the methyl protons in the mutually *trans* pair of PMe_2Ph ligands, indicated that the deuteration in this position was about 94% complete. This integration was also used to help determine the mechanism of ethane elimination from **7**. There is substantial evidence for the existence of σ-alkane complexes of several transition metals, in which the alkane is attached to the metal without cleavage of a C–H bond.[46–48] Computational studies support the view that such species must also act either as intermediates or as transition states both in the activation of alkanes by transition metals and in the process of alkane elimination from complexes containing alkyl and hydride ligands.[49–52] In the event that a σ-alkane complex is an intermediate in alkane reductive elimination, and is formed reversibly and relatively rapidly from the original complex, prior to a slower step involving detachment of the alkane from the metal, this will allow hydrogen exchange to occur between alkyl and hydride ligands, provided that the metal can switch its point of attachment from one C–H bond to another. There is evidence to show that this intramolecular switching process between C–H bonds can occur with a very low activation energy, particularly when both bonds involve the same carbon atom, and many cases of intramolecular hydrogen exchange of this type have been reported.[21,23,25,27,29–31,48,53] In order to discover whether such an exchange occurred between ethyl and hydride ligands in **7**, a sample of d_2-**7** (*ca.* 94% deuterated in the hydride position) was stored in $C_6D_5CD_3$ solution at 253 K, a temperature at which the elimination of ethane was very slow. After three days,

integration of the hydride resonance relative to those for the methyl protons in the mutually *trans* pair of PMe_2Ph ligands in the d_2-**7** remaining in the solution indicated no significant drop in the level of deuteration in the hydride position. We concluded that, if an alkane complex $[Ru(CO)(\sigma\text{-}C_2H_6)(PMe_2Ph)_3]$ was indeed an intermediate in the process of ethane elimination from **7**, its rate of reconversion to **7** must be very low relative to the rate of ethane loss to form **11**.

(v) Kinetic studies of ethane elimination from isomers 7 and 10 of $[Ru(CO)(Et)H(PMe_2Ph)_3]$

Solutions of **7** required for the kinetic studies were obtained by treating $C_6D_5CD_3$ solutions of **4** with the required quantity of PMe_2Ph (*i.e.* a molar ratio of 1 : 2). At 250 K this resulted in rapid and complete conversion to **7**. Similar treatment of **4** with 4-MePy at 250 K yielded **9**, which was then converted to **10** by adding an equivalent amount of PMe_2Ph, still at 250 K. Where PMe_2Ph was the chosen trapping agent, this was allowed for by increasing the initial addition of PMe_2Ph to the solution of **4** or **9**. Otherwise, the appropriate trapping agent was added prior to the transfer of the solution of **7** or **10** to the NMR probe. The progress of ethane elimination was normally monitored by integrating the hydride resonance in the ^1H NMR spectrum of **7** or **10**. This resonance was chosen because it was well enough separated from other reactant or product resonances to make accurate integration straightforward.

In the initial kinetic run with **7**, carried out at 282.6 K, no trapping agent was added. Despite the range of ruthenium decomposition products formed, the plot for the first-order disappearance of **7** was essentially linear for over 2.5 half-lives, giving a rate constant of $1.53(4) \times 10^{-4}$ s^{-1}. This simple kinetic behaviour was, in itself, a strong indication that ethane reductive elimination occurred directly from **7**, and did not require the prior loss of some other ligand, or attack by an external species. A second run, also at 282.6 K, was carried out using a similar concentration of **7** (0.06 mol dm^{-3}) but with a substantial concentration of free PMe_2Ph (0.23 mol dm^{-3}), so that complete conversion to **12** occurred during the run. Again the first-order plot was essentially linear for over 2.5 half-lives, despite the fact that the concentration of free PMe_2Ph in the solution fell by around 25% during the run. This fact, and the good agreement between the rate constant obtained, $1.47(5) \times 10^{-4}$ s^{-1}, and that obtained in the absence of free PMe_2Ph indicated that the PMe_2Ph was not involved in the rate-determining step. We concluded that this step was indeed the elimination of ethane, and that it was not preceded or accompanied by PMe_2Ph dissociation from (or addition to) **7**.

A further check was made by determining the rate constant at 282.6 K for the disappearance of **7** in the presence of $HC{\equiv}CCMe_3$. For this run, initial concentrations of **7** and $HC{\equiv}CCMe_3$ were 0.06 and 0.08 mol dm^{-3}, respectively. Complete conversion to **13** was observed, and values for the rate constant were derived both by monitoring the disappearance of the hydride resonance for **7** and by following the appearance of that for **13**. Despite the large variation in the concentration of free $HC{\equiv}CCMe_3$ during the run, both plots were essentially linear for nearly 2.5 half-lives, ruling out any involvement of $HC{\equiv}CCMe_3$ in the rate-determining step. The rate constants obtained, $1.42(3) \times 10^{-4}$ s^{-1} and $1.55(8) \times 10^{-4}$ s^{-1} respectively, were in reasonable agreement with one another and with the values obtained with no trapping agent and with PMe_2Ph as trap.

For isomer **10** of $[Ru(CO)(Et)H(PMe_2Ph)_3]$, kinetic studies were carried out only for the reaction with PMe_2Ph to give ethane and **12**. Three runs were carried out at 277.2 K, the initial concentrations of **10** being 0.07, 0.04 and 0.04 mol dm^{-3}, and those of free PMe_2Ph 0.14, 0.17 and 0.05 mol dm^{-3}, respectively. Each first-order plot was essentially linear for at least 2.5 half-lives, despite the substantial variation in PMe_2Ph concentration during the runs (particularly the last of the three). The rate constants obtained were $2.53(5) \times 10^{-4}$, $2.55(9) \times 10^{-4}$ and $2.39(13) \times 10^{-4}$ s^{-1}, respectively. As with **7**, it appeared that ethane elimination from **10** was a simple first-order process, and that the only role of the PMe_2Ph was to capture $[Ru(CO)(PMe_2Ph)_3]$, **11**, the immediate ruthenium product of the elimination.

Table 2 Kinetic data used to obtain activation parameters for ethane elimination from isomers **7** and **10** of $[Ru(CO)(Et)H(PMe_2Ph)_3]$[a]

Complex	T/K	$10^4\,k$/s^{-1}
7	277.2	0.660(30)
		0.747(22)
		0.838(25)
	282.6	1.37(4)
		1.53(4)
		1.47(5)
	287.9	3.18(8)
		3.35(4)
		3.27(5)
	293.3	5.23(17)
		5.33(16)
		4.94(20)
10	266.3	0.599(12)
		0.784(12)
		0.638(14)
	271.9	1.46(6)
		1.19(6)
		1.07(3)
	277.2	2.53(5)
		2.39(13)
		2.55(9)
	282.6	4.30(7)
		4.81(16)
		4.59(7)

[a] For all these kinetic runs, the solvent was $C_6D_5CD_3$ and the trapping agent PMe_2Ph.

Further runs were then carried out, all with PMe_2Ph as the trapping agent, to obtain values for the activation parameters for ethane elimination from **7** and **10**. The highest temperatures at which we managed to obtain a satisfactory amount of data within two or three half-lives were 293.3 K for **7** and 282.6 K for **10**. At lower temperatures we were increasingly hampered by the amount of instrument time required and by poorer reproducibility of the values obtained for the rate constants. Despite this, the data listed in Table 2 gave reasonably satisfactory Eyring plots. From these, values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 80(6) kJ mol^{-1} and −37(21) J K^{-1} mol^{-1}, respectively, were obtained for **7**, whereas for **10** the values were 71(7) kJ mol^{-1} and −59(25) J K^{-1} mol^{-1}.

In order to determine the effect on the rate of ethane elimination from **7** of replacing the hydride ligand by a deuteride ligand, we studied elimination from d_2-**7**, $[Ru(CO)(C_2H_4D)D(PMe_2Ph)_3]$. Our assumption (see earlier) that the rate of elimination from **7** would not be significantly affected by the presence of deuterium in the *ethyl* ligand was supported by the work of Parkin and Bercaw,[30] who found that, whilst the rate of CH_4 elimination from $[W(\eta^5\text{-}C_5Me_5)_2(Me)H]$ differed markedly from the rate of CH_3D elimination from $[W(\eta^5\text{-}C_5Me_5)_2(Me)D]$, the rates of elimination of CH_3D and CD_4 from $[W(\eta^5\text{-}C_5Me_5)_2(Me)D]$ and $[W(\eta^5\text{-}C_5Me_5)_2(CD_3)D]$, respectively, were virtually identical.

Since the kinetic studies of ethane elimination from **7** and **10** had been performed by monitoring the disappearance from the ^1H NMR spectrum of the resonance due to the hydride ligand, a change in procedure was necessary for d_2-**7**. We chose to follow the disappearance of the resonances due to the methyl protons in the mutually *trans* PMe_2Ph ligands. In order to check that this would be a satisfactory procedure, a further kinetic run was carried out on **7** itself, at a temperature of 287.9 K, and using initial concentrations of **7** and the trapping agent PMe_2Ph of 0.07 and 0.21 mol dm^{-3}, respectively. Rate constants were obtained using both the hydride resonance for **7** and the methyl proton resonances mentioned above. The two plots, both

essentially linear for at least 2.5 half-lives, gave rate constants of $3.27(5) \times 10^{-4}$ s^{-1} and $3.10(7) \times 10^{-4}$ s^{-1}, respectively. Since the two figures were in reasonable agreement, a run was then carried out with d_2-**7** and PMe_2Ph, using the same concentrations and the same temperature as those for **7**. Again the plot was linear for over 2.5 half-lives, and the rate constant, $1.22(2) \times 10^{-4}$ s^{-1}, was significantly lower than those for **7**. Comparison of this value with the one obtained for **7** by the same technique, $3.10(7) \times 10^{-4}$ s^{-1}, gave a figure of 2.5 for the ratio k_H/k_D at 287.9 K.

(vi) The mechanism of ethane elimination from 7 and 10

The results of the reactions described in Section (iii) had suggested that both **7** and **10** decomposed by ethane elimination to give $[Ru(CO)(PMe_2Ph)_3]$, **11**, which could then be trapped as a stable ruthenium(0) or ruthenium(II) species. In the case of **7**, the fact that ethane elimination occurred from **7** itself, and did not require prior loss of some other ligand or attack by some external species, was clearly shown by the simple first-order behaviour of the reaction, whose rate was not significantly affected by the presence or absence of a reagent to trap **11**, by variation in the initial concentration of such a reagent, variation in its concentration during a given run, or even a change in the reagent used. The more limited study of **10** led to similar conclusions.

This simple behaviour mirrors that exhibited by a variety of other complexes, containing metals such as rhodium,[23,25] iridium,[32] platinum,[20,28] rhenium[21] and tungsten.[29–31] There are, however, exceptions: for example, Flood[11] has presented evidence to show that one pathway for CMe_4 elimination from $[Os(CH_2CMe_3)H(PMe_3)_4]$ involves prior loss of PMe_3, and Bercaw[24] has proposed that ligand loss (either chloride or a solvent molecule) precedes alkane elimination from some platinum(IV) complexes.

It should be appreciated that the difference between the rate constants for ethane elimination from **7** and **10** at each of the two temperatures common to both studies was only a factor of about 3, corresponding to a very small difference in $\Delta G^{\ddagger}$ values. Even the rather larger differences between the pairs of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were not statistically significant, so the conclusion must be that the mechanism of the elimination is probably similar for the two isomers.

There has been much interest in the fact that the reductive elimination of alkanes from some transition metal complexes is associated with an inverse kinetic isotope effect (*i.e.* elimination from a particular hydride complex is slower than that from the corresponding deuteride complex). In a recent paper on methane elimination from $[W\{(\eta^5\text{-}C_5Me_4)_2SiMe_2\}(Me)H]$, Parkin and co-workers[31] have emphasised that the key to this effect lies in the existence of an intermediate alkane σ-complex {see eqn. (1)}:

$$[M](R)(H) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [M](\sigma - HR) \xrightarrow{k_3} [M] + RH \qquad (1)$$

where [M] represents the metal together with ligands not directly involved in the reductive elimination. In cases where $k_2 \gg k_3$, the rate constant for the overall reductive elimination is given by k_1k_3/k_2, and Parkin argues that it is the shift of the equilibrium between starting material and intermediate σ-complex on replacing hydrogen by deuterium which causes the inverse kinetic isotope effect (*i.e.* $k_{1D}/k_{2D} > k_{1H}/k_{2H}$). This type of kinetic behaviour should therefore be associated with deuterium scrambling between alkyl and hydride ligands, and Parkin has shown that such scrambling does indeed occur in $[W\{(\eta^5\text{-}C_5Me_4)_2SiMe_2\}(Me)D]$.[31] Bergman and his co-workers have established a similar link between an inverse kinetic isotope effect and deuterium scrambling for $[Rh(\eta^5\text{-}C_5Me_5)(Et)H(PMe_3)]$[25] and $[Ir(\eta^5\text{-}C_5Me_5)(C_6H_{11})H(PMe_3)]$,[27] as have Flood *et al.*[23] for $[Rh(Cn)(Me)H(PMe_3)]^+$ {Cn = $(MeNCH_2CH_2)_3$} and Jones *et al.*[22,54] for a range of complexes $[Rh(Tp')(CNCH_2CMe_3)(R)H]$ {Tp′ = *tris*-(3,5-dimethylpyrazolyl)borate, R = alkyl}. In contrast, where $k_2 \ll k_3$, the rate constant for the overall reductive elimination is simply k_1, and in such cases Parkin[31] argues that a normal kinetic isotope effect should be observed.

Our study of d_2-**7** {see Section (iv)} had clearly shown that, if a σ-ethane complex $[Ru(CO)(\sigma\text{-}C_2H_6)(PMe_2Ph)_3]$ is an intermediate in the process of reductive elimination from **7**, its rate of conversion to **7** must be very low relative to the rate of ethane loss to give **11** {*i.e.* $k_2 \ll k_3$ in eqn. (1)}. On this basis the rate constant for the reductive elimination would simply be k_1, and our observation of a normal kinetic isotope effect ($k_H/k_D = 2.5$) would be in accordance with Parkin's proposals. The negative entropies of activation we observed for ethane elimination from both **7** and **10** could presumably be attributed to the development of some degree of interaction between methyl and hydride ligands *en route* to the transition state in the k_1 step. It should be noted, though, that our results are equally compatible with a simpler mechanism in which there is no intermediate, and only one transition state.

Normal kinetic isotope effects have been observed for alkane reductive elimination from a number of other complexes, including several of platinum(II).[20,26,28] For these complexes, there was no suggestion that an equilibrium between the platinum(II) starting material and an intermediate platinum(0) σ-alkane complex might precede the loss of the alkane. An interesting case is that of $[Ir(CO)(Et)H_2(Ph_2PCH_2CH_2PPh_2)]$, studied by Deutsch and Eisenberg.[32] As in the case of the two isomers, **7** and **10**, of $[Ru(CO)(Et)H(PMe_2Ph)_3]$, but in sharp contrast to $[Ir(\eta^5\text{-}C_5Me_5)(C_6H_{11})H(PMe_3)]$,[27] alkane elimination shows a normal kinetic isotope effect (and also a negative entropy of activation). Given that $[Ir(CO)(Et)H_2(Ph_2PCH_2CH_2PPh_2)]$ contains a very similar ligand set to those in **7** and **10**, it may well be that the nature of the ligands in a complex can be as important as the choice of metal in affecting the mechanism of alkane elimination.[55]

In summary, our results show that reductive elimination of ethane from **7** and **10** is a simple first-order process, requiring neither prior or simultaneous loss of another ligand nor attack by some external species. They do not eliminate the possibility that a σ-ethane complex acts as an intermediate (rather than simply as a transition state) in the process, but unequivocally rule our a rapid pre-equilibrium with such an intermediate prior to ethane loss.

Experimental

All experimental work (except the preparations of **4** and d_5-**4**) was carried out under an atmosphere of N_2. The NMR spectra (including those used to obtain kinetic data) were recorded on a Bruker AMX 500 spectrometer. The preparation of complex **1** and its conversion to **4** have been described in the literature:[17] the conversion was carried out at 273 K. The same methods were used to obtain d_5-**1** and d_5-**4**: for the former, $NaBD_4$ and EtOD were used instead of $NaBH_4$ and EtOH, and for the latter (see previous section) the conversion was carried out at 250 K. When **4** or d_5-**4** was stored in $C_6D_5CD_3$ solution, this was performed at 253 K under an atmosphere of ethene. Before the solution was used, the ethene was removed by purging the solution with N_2.

The routes from 4 to 7 and from 4 to 10

The reactions were carried out in NMR tubes, typically using 17 mg (0.04 mmol) of **4** in 1 cm^3 of $C_6D_5CD_3$ or CD_3COCD_3. Details of the other reactants, molar ratios of reactants and temperatures employed have been given earlier in the text. Because of the sensitivity of **7** and **10** to ethane elimination, no attempt was made to isolate them from solution in a pure state.

Trapping reactions of 7 and 10

Solutions of **7** required for these reactions could be straightforwardly prepared in an NMR tube by treating **4** {typically between 16 mg (0.04 mmol) and 36 mg (0.09 mmol)} in $C_6D_5CD_3$ solution (1 cm^3) with two molar equivalents of

PMe_2Ph at 250 K, using NMR spectroscopy to check that conversion to **7** was complete. Similar treatment of **4** with two molar equivalents of 4-MePy at 250 K yielded **9**: after checking that conversion to **9** was complete, one molar equivalent of PMe_2Ph was added, also at 250 K, to convert **9** into **10**.

(i) Trapping with PMe_2Ph. For these reactions only, the preparations of **7** from **4** and of **10** from **9** were carried out using more PMe_2Ph than the amounts given above, so that *ca.* two molar equivalents of PMe_2Ph remained in the solutions of **7** and **10**. When the temperature of the NMR probe was raised to 270 K, both **7** and **10** were slowly converted to **12** with elimination of ethane. Because of its lability (see earlier), **12** was characterised only by NMR spectroscopy.

(ii) Trapping with H_2. A solution of **7**, in an NMR tube fitted with a Young's tap, was connected to the vacuum manifold of a Schlenk line and subjected to three freeze–pump–thaw cycles in order to achieve complete degassing. The solution was refrozen, and H_2 was introduced into the NMR tube by opening the tap to the gas manifold of the Schlenk line, which had been filled with H_2 at 1 atm. pressure. After closing the tap, the solution was allowed to warm up to 250 K and shaken to ensure thorough mixing. The tube was then placed in the NMR probe, pre-cooled to 250 K. When the probe temperature was raised to 270 K, ethane elimination occurred over a period of hours, with formation of **3a**, identified by comparison of its NMR spectra with those of an authentic sample of the complex.[37] Complex **3a** was also formed even when the solution of **7** used contained free PMe_2Ph, and when a solution of **12** (obtained as described above) was allowed to react with H_2 at 260 K.

(iii) Trapping with $HC{\equiv}CCMe_3$. Solutions of **7** and **10** were treated with an equimolar quantity of $HC{\equiv}CCMe_3$ at 250 K, and then placed in the probe of the spectrometer at 250 K. As in the case of the reactions with PMe_2Ph, the effect of raising the probe temperature to 270 K was to cause ethane elimination. Both **7** and **10** yielded the same product, **13**. Attempts to obtain a solid sample of **13** by column chromatography and crystallisation were unsuccessful, but the complex was characterised by NMR spectroscopy.

Kinetic studies

Solutions of **7** or **10**, typically containing between 0.04 and 0.07 mmol of the complex, were prepared from **4** as described under "Trapping reactions of **7** and **10**". The procedure to obtain a solution of d_2-**7** from d_5-**4** was the same as that for obtaining **7** from **4**. For kinetic runs with PMe_2Ph as the trapping agent, the amount of PMe_2Ph added was in excess of that required to produce **7**, d_2-**7** or **10**, and the concentration of PMe_2Ph actually present in the solution at the start of the kinetic run was calculated by allowing for the amount consumed in the production of **7**, d_2-**7** or **10**. For the run in which $HC{\equiv}CCMe_3$ was used as the trapping reagent, a solution of **4** was treated with exactly the amount of PMe_2Ph required to convert it to **7**. The appropriate amount of $HC{\equiv}CCMe_3$ was then added to the solution of **7**.

The NMR tube was then transferred to the probe of the spectrometer, which had been pre-cooled to the desired temperature. For each setting of the variable temperature unit of the NMR spectrometer used in kinetic runs, the true probe temperature was determined by calibration using a methanol capillary held in an NMR tube containing $C_6D_5CD_3$.[56]

After allowing a few minutes for the sample to reach probe temperature, spectra were recorded at appropriate intervals. For each point on a given kinetic plot, eight scans were accumulated: the total time required represented only a very small fraction of the overall reaction time, even at the highest temperature used. The resonances used to monitor the reactions have been identified in the Results section. As a safeguard against any variations in instrument performance during a kinetic run, in each spectrum the area of the resonance monitored was divided by the area of the resonance for the small amount of $CD_2HC_6D_5$ present in the solution. Attempts were also made to obtain rate constants by monitoring the resonance for free ethane. Unfortunately the growth of this resonance tailed off as kinetic runs progressed, and the resonance actually decreased somewhat in area towards the end of the reaction. Presumably this was due to some loss of ethane into the gas phase above the solution.

It should be noted that the solutions used for the kinetic runs also contained the adducts $H_3B{\cdot}PMe_2Ph$ or $H_3B{\cdot}$4-MePy. Two runs carried out at 277.2 K with similar PMe_2Ph concentrations, but with markedly different concentrations (0.07 and 0.04 mol dm^{-3}) of **10** (and therefore also of $H_3B{\cdot}$4-MePy) gave rate constants of $2.53(5) \times 10^{-4}$ s^{-1} and $2.55(9) \times 10^{-4}$ s^{-1}, respectively, suggesting that the adduct had no significant effect on reaction rate (and also that reaction rate did not depend on the *initial* concentration of the ruthenium complex used).

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